

Simple Aqueous Solution Route to Luminescent Carbogenic Dots from Carbohydrates

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Over the past two decades quantum dots (QDs) have been the subject of intense research due to a unique combination of properties, particularly their easily tuned optical properties and resistance to photodegradation when compared with organic dyes.^{1,2} QDs may give rise to very promising applications in biosensing³ and bioimaging⁴ if obstacles such as strict synthesis conditions, high prices, and known toxicity (e.g., with CdSe and CdTe QDs) can be addressed.⁴ Thus, significant efforts have been devoted to the synthesis of QDs based on alternative materials with lower toxicity while retaining advantageous optical properties, such as silicon nanoparticles.^{5,6}

Carbon nanoparticles (CNPs) are an alternative type of QDs, isolated from carbon nanotubes (CNTs),⁷ and yield interesting photoluminescence properties.^{8,9} Zhou et al., for example, have devised an electrochemical method to prepare luminescent CNPs from multiwall CNTs,¹⁰ while further studies have shown that CNPs can also be synthesized from other carbonaceous sources. Liu et al. prepared CNPs from candle soot, with a quantum yield of up to 0.02.¹¹ Bourlinos et al. used the thermal decomposition of different ammonium citrate salts to synthesize carbogenic dots, where the citrate unit served as the

source of carbon.^{12,13} Sun et al. achieved an improved quantum yield of 0.10 in their preparation of CNPs by using a two-step synthesis: first, a carbon target was laser ablated, and then the resulting nanoparticles were passivated with diamine-terminated oligomeric poly-(ethylene glycol).¹⁴ More recently, Hu et al. reported a one-step synthesis of luminescent CNPs with a quantum yield of 0.05, through the laser irradiation of carbon powders suspended in an organic solvent.¹⁵

Carbohydrates are widely used to produce carbon materials by hydrothermal treatment because of their sustainability. Different structures of carbon materials such as colloidal spheres¹⁶ and nanofibers¹⁷ were obtained via hydrothermal synthesis between 180 and 220 °C. Here we report a simple aqueous solution route to prepare luminescent carbogenic dots (called carbogenic due to their oxygen content) by using carbohydrates as starting materials, as illustrated in Scheme 1. In short, the carbohydrates were dehydrated using concentrated sulfuric acid, producing carbonaceous materials. The obtained carbonaceous materials were then broken down into individual carbogenic nanoparticles by treatment with nitric acid. Finally, the carbogenic nanoparticles were passivated using amine-terminated compounds, yielding luminescent carbogenic dots.

FT-IR and Raman spectroscopy were used to characterize the carbonaceous materials obtained from the treatment of glucose, sucrose and starch carbohydrates with concentrated sulfuric acid (see Figure S1 in the Supporting Information). In the FT-IR spectra, the carboxyl group was clearly identified, both through the very broad 3300 cm⁻¹ O—H stretching vibration and through the 1705 cm⁻¹ C=O stretching vibration. The existence of sulfonic groups was demonstrated by the characteristic absorption bands at 1074 and 672 cm⁻¹, which were assigned to the symmetric stretching of —SO₃⁻ and C—S stretching vibration. The elemental analysis also showed the existence of sulfur (see Table 2 in Supporting Information). The Raman spectra of these samples to a certain extent feature the characteristic bands of carbon materials—a D-band at 1301 cm⁻¹ and a G-band at 1598 cm⁻¹—superimposed on a broader fluorescence background. From the elemental analysis,

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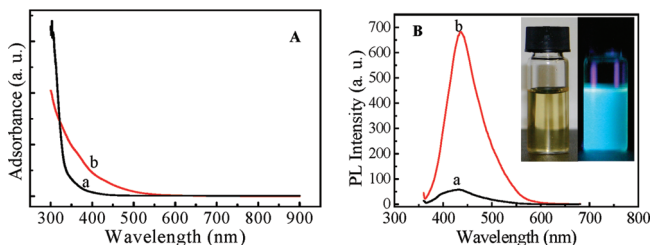
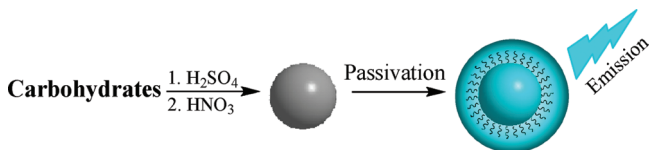


Figure 1. Absorption (A) and emission (B) spectra of carbogenic dots prepared from glucose, before (a) and after (b) TTDDA passivation. Inset: carbogenic dots under ambient light (left) and (B) UV light (365 nm) (right).

Scheme 1. Preparation Procedure of Luminescent Carbogenic Dots



a ratio of carbon, hydrogen, and oxygen of 2.8:2.3:1 was found.

Neither the carbonaceous materials nor their aqueous suspension exhibited any detectable photoluminescence. After refluxing the carbonaceous materials in a nitric acid solution for 12 h, the resulting solution exhibited a weak photoluminescence. In addition to the emergence of photoluminescence, the prolonged nitric acid treatment also blue-shifted the maximum emission wavelength, possibly due to the decrease of particle sizes (see Figure S2 in Supporting Information), similar to the phenomenon observed during the photoetching process of CdTe QDs.^{18,19} After nitric acid treatment, the FT-IR spectrum of the obtained carbogenic dots was obviously different from that of the carbonaceous material (see Figure S3 in Supporting Information) which was presumably composed of furan rings cross-linked by domains containing short keto-aliphatic chains, according to the recent description by Baccile et al.²⁰ The bands at 1572 and 1375 cm⁻¹ were ascribed to C=C double-bond stretching vibrations and C—H vibrations, respectively. This result clearly shows that the nitric acid treatment not only broke the carbonaceous materials down into individual carbogenic nanoparticles but also led to a different composition of carbogenic nanoparticles. The elemental analysis revealed an increase in oxygen content (see Table 2 in Supporting Information).

Bright photoluminescence was observed after the carbogenic nanoparticles' surface was further passivated by treatment with 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) at 120 °C for 72 h under nitrogen. The effect of surface passivation on the absorption and emission spectra of glucose-derived carbon dots is shown in Figure 1. The

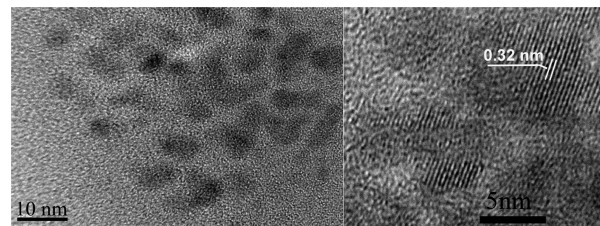


Figure 2. TEM images of TTDDA passivated carbogenic dots prepared from glucose.

absorbance increased in the range of 350 to 550 nm upon surface passivation. The maximum emission wavelength was not significantly changed, but the full width at half-maximum value changed from 81 to 76 nm. Furthermore, the passivation greatly enhanced the photoluminescence intensity, with the quantum yield improving dramatically from 0.01 to 0.13. The inset of Figure 1B shows the carbogenic dots in aqueous solution under ambient light and UV light (365 nm). As shown in FT-IR spectra (see Figure S4, curve c, in Supporting Information), the broadened peak with an increased intensity at 1744 cm⁻¹ and a shoulder at 1648 cm⁻¹ indicates the existence of $\nu_{\text{C=ONR}}$ and $\delta_{\text{CON—HR}}$ vibrations, suggesting carboxylic groups on the surface of carbogenic nanoparticles have been converted into amide groups during the passivation process. The results of zeta potential measurements also support this suggestion. The zeta potential of carbogenic nanoparticles was -37.3 mV, suggesting carbogenic nanoparticles are negatively charged due to carboxylic groups. After passivation, the zeta potential of carbogenic dots was 3.46 mV, indicating the surface was slightly positively charged, due to the conversion of carboxylic acid groups to amide groups. Transmission electron microscopy (TEM) showed that the carbogenic dots have a crystalline structure consisting of parallel crystal planes with a lattice spacing of 3.2 Å (Figure 2) that is close to the (002) lattice spacing of carbon-based materials with turbostratic disorder.^{12,21} This value agrees well with XRD pattern of carbogenic nanoparticles, which shows a diffraction peak centered at $d_{002} = 3.4 \text{ \AA}$ (see Figure S4 in Supporting Information). The diameter of these carbon dots, as estimated from the TEM images, is approximately 5 nm. The elemental analysis reveals the composition of carbogenic dots is C 57.03 wt %, H 7.51 wt %, N 8.51 wt %, and O (calculated) 26.95 wt %.

Our surface passivation strategy used the carboxyl groups on the carbogenic nanoparticles surface, as produced by nitric acid treatment, for attachment to amino-terminated reagents, leading to the formation of amide linkages.^{12,22} Besides TTDDA, three other amino-terminated surface passivation reagents were also investigated: ethylenediamine, oleylamine, and bis(3-aminopropyl) terminated poly(ethylene glycol) (PEG_{1500N}). It was found that the TTDDA passivated carbon dots had the highest quantum yield when excited at 360 nm.

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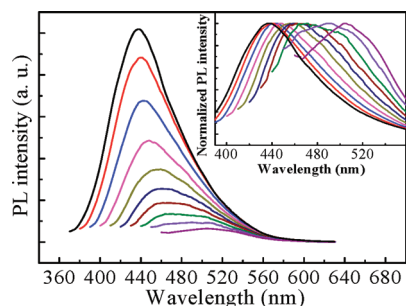


Figure 3. Emission spectra of TTDDA passivated carbogenic dots at different excitation wavelengths progressively increased from 360 nm (on the left) with a 10 nm increment. Carbogenic dots were prepared from glucose-derived carbogenic nanoparticles after 12 h of nitric acid (2.0 M) treatment. Inset: normalized emission spectra.

The optical properties of these carbogenic dots synthesized via the aqueous solution pathway are either comparable or superior (in terms of quantum yield) to previously reported functionalized carbon dots.^{10,12,14} As shown in Figure 3, their emission is highly dependent on excitation energy: as the excitation wavelength is increased, the emission peak position shifts to longer wavelengths and the intensity decreases. These carbogenic dots also show considerable photostability, with the emission intensity decreasing by only 17% after 19 h of continuous excitation at 360 nm (see Figure S5 in Supporting Information).

The luminescence mechanism of carbogenic dots and carbon dots is still not clearly understood, although the radiative recombination of excitons has been proposed as a possible mechanism.¹⁴ Since our results suggest that surface passivation plays a key role in the strong photoluminescence of carbogenic dots, a control experiment was performed to study the role of the surface passivation reagents which have not been undertaken in previous work.^{14,22} We have found that although TTDDA contains no visible or near-UV chromophore and is not photoluminescent at any visible wavelength, it does luminesce after heating at 120 °C for 72 h under N₂ (the same results obtained for other passivation reagents, such as PEG_{1500N} and ethylenediamine). Interestingly, its emission also depends on the excitation energy (see Figure S6 in Supporting Information) in a similar way as for carbogenic dots. However, the quantum yield for heated TTDDA alone was only 0.020 ± 0.002 (as obtained from three individual experiments), a yield six times lower than that of carbogenic dots. The question then arises whether the photoluminescence of carbogenic dots is completely due to the treatment of passivation reagent. We believe this is not the case, for two reasons. First, the quantum yield of TTDDA-passivated carbogenic dots is much higher than that of heated TTDDA alone, as detailed in the aforementioned control experiment. Second, different responses to excitation wavelength were observed, when the carbogenic dots were prepared by using the same passivation procedure, but different carbogenic nanoparticles were obtained by different synthesis conditions. For the carbogenic nanoparticles obtained by 12 h of nitric acid treatment, after passivation the intensity maximum was found at 440 nm (as shown in Figure 3) and the carbogenic dots prepared

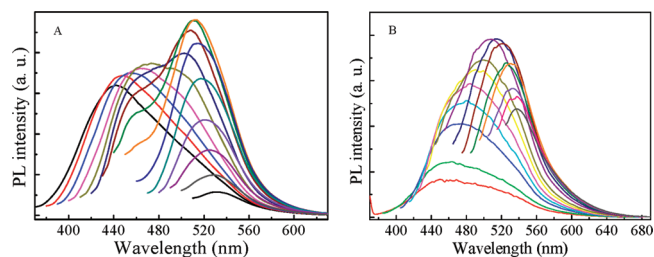


Figure 4. Emission spectra of TTDDA passivated carbogenic dots at different excitation wavelengths progressively increased from 360 nm (on the left) with a 10 nm increment. Carbogenic dots were prepared from glucose-derived carbogenic nanoparticles after 4 h of nitric acid (2.0 M) treatment (A) and starch-derived carbogenic nanoparticles after 12 h of nitric acid (2.0 M) treatment (B).

from those obtained by 4 h of nitric acid treatment had the highest intensity at 512 nm, as shown in Figure 4A (glucose was again used as the starting material). Similar results were obtained for carbogenic dots prepared using starch as the starting material, treated again with nitric acid for 12 h, yielding an emission intensity maximum at 518 nm (Figure 4B). Together, these results suggest that the enhanced luminescence in carbogenic dots was due to the passivation that stabilized the surface energy traps of carbogenic nanoparticles and made them emissive. Different starting materials and nitric acid treatment resulted in the carbogenic nanoparticles with different sizes and distributions of the surface energy trap, which accounts for not only the multicolor photoluminescence of carbogenic dots but also for different responses to excitation wavelengths mentioned above. Besides the mechanism of radiative recombination of excitons, the luminescence from the charge transfer from N to carbon which was found in luminescent carbon nanotubes²³ cannot be ruled out. The role of the passivation agent on the nature of these emissive trap sites will be further investigated, and it is the subject of ongoing studies in our laboratory.

In summary, we have developed a simple aqueous solution route for the preparation of luminescent carbogenic dots, using carbohydrates as the starting materials. The emission wavelength of these carbogenic dots can be tuned by differing the starting material and the duration of the nitric acid treatment. The multicolor emission capabilities and nontoxic nature of these carbogenic dots should enable them to find wide-ranging applications in life science research, such as our ongoing work on applications of carbogenic dots in cell imaging and the preparation of biotinylated carbogenic dots for specific cell tagging.

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Supporting Information Available: Synthesis procedure and characterization data of carbogenic dots (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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