Solvent Effects on Fluorescence Properties of Carbon Dots: Implications for Multicolor Imaging

Xiaomin Huo, Honglie Shen,* Rui Liu, and Jing Shao

ABSTRACT: Carbon dots (CDs) are synthesized by the solvothermal method with four kinds of solvents including water, dimethylformamide (DMF), ethanol, and acetic acid (AA). The aqueous solutions of the above CDs emit multiple colors of blue (470 nm), green (500 nm), yellow (539 nm), and orange (595 nm). The structures, sizes, and chemical composition of the CDs are characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS). The optical properties of multicolored CDs are analyzed by UV−vis absorption and photoluminescence (PL) spectra. It has been revealed that DMF is the key solvent to synthesize CDs for the red shift of fluorescence emission, which could be enhanced by adding an AA solvent. The structures of functional groups such as the contents of graphitic N in carbon cores and oxygen-containing functional groups on the surface of CDs are affected by these four solvents. According to the oxidation and selective reduction of NaBH₄, the implication for multicolor imaging has been discussed based on the COOH, C−O−C, and C≡O functional groups.

1. INTRODUCTION

Carbon dots (CDs) are a new sort of zero-dimensional carbon nanomaterials with particle sizes less than 10 nm. According to their structure, CDs consist of carbon nanodots (CNDs), graphene quantum dots (GQDs), and polymer dots (PDs). CDs are environmentally friendly and low-toxic fluorescent nanomaterials. CDs also possess good biocompatibilities and excellent optical properties, which are applied for sensing and bioimaging. They are expected to replace the traditional semiconductor quantum dots with biological toxicity and environmental hazards, especially CdSe quantum dots owing to a high fluorescence quantum yield.

According to the rule of Kasha, the fluorescence emission wavelength of organic dyes and semiconductor quantum dots remains unchanged with the excitation wavelength since the photons are emitted rapidly from the ground-state energy level to the lowest excited-state energy level. The organic dyes hold a narrow excitation wavelength and instability of emission. However, the fluorescence behaviors of CDs do not conform to this rule, and they depend on the excitation wavelength. CDs have excellent photostability due to the optical emission mechanism of the carbon core and the surface. When exposed to exciting light for a long time, the luminescence intensity hardly decreases and no light flickers. The stable fluorescence behavior of CDs can make up for the shortcomings of organic dyes and semiconductor quantum dots. At present, there are three sorts of fluorescence mechanisms proposed for CDs such as the quantum effect, surface state, and compound radiation of electron−hole pairs. The red shift of the emission spectra that are independent of the excitation wavelength may be caused by their size, the amount of graphitic nitrogen, and emission sites. On the contrary, CDs have a different surface state with inconformity groups because the fluorescence is dependent on the excitation wavelength. Recently, Jiang had observed that the chemical luminescence of NaIO₄ and H₂O₂ would be enhanced by CDs due to their self-trap state. The photoluminescence (PL) of CDs could reflect the characteristics of the quantum-confined effect and the surface trap state. However, the PL mechanism of CDs is still a controversial issue and not an accurate conclusion. Zhang had prepared two different CDs using two kinds of CDs by different methods. The one with high-oxygen-content functional groups showed dependence on the excitation wavelength, while the other did not. The oxidation can also improve the surface defects of CDs, which generate more excited capture centers and present red-shifted
It was found that the extent of red shift was also consistent with the increase of the oxygen content and COOH groups on the surface of CDs.

The CDs with excitation wavelength dependence have been successfully prepared with citric acid (CA) by thermal method. They are mainly spherical carbon nanodots with an sp^3 hybrid structure that is nearly amorphous, or with an sp^2 hybridized core featured with an obvious crystal lattice that is coated by an amorphous shell. To further improve the fluorescence yield of CDs, nitrogen is doped into carbon cores with urea as the nitrogen source. Water and glycol are generally used as synthesized solvents, which may influence the organic groups on the surface of CDs. In our work, CA is used as the carbon source and urea as the nitrogen source to prepare

**Figure 1.** HRTEM images and DLS data of the CDs synthesized by solvothermal treatment in the four solvents: (a) CDs-B, (b) CDs-G, (c) CDs-Y, and (d) CDs-R.

**Figure 2.** (a) XRD and (b) Fourier transform infrared (FTIR) spectra of CDs synthesized by solvothermal treatment in the four solvents.
multicolored CDs of different sizes by the solvothermal method. The four sorts of solvents including water, dimethylformamide (DMF), ethanol, and acetic acid (AA) are used in the synthesis system to adjust the N element or COOH characteristic groups. Their behaviors on the emission wavelength are systematically studied. The complex functional groups on the surface of CDs are also investigated with oxidation and the selective reduction by sodium borohydride (NaBH₄).

2. RESULTS AND DISCUSSION

2.1. Structure of Multicolored CDs. To study the morphology, size and lattice of the four CDs had been tested by high-resolution TEM (HRTEM), as shown in Figure 1. The average sizes of CDs-B, -G, -Y, and -R are about 3.18, 3.25, 3.47, and 3.68 nm, respectively, which are measured by the dynamic light scattering (DLS). From the HRTEM images, it can be seen that all CDs show lattice stripes of graphite carbon. The lattice space of CDs-B synthesized in water is about 0.22 nm, while that of the other three CDs prepared by DMF solvent is 0.21 nm, which is less than CDs-B.

Figure 2a shows the X-ray diffraction (XRD) patterns of the four CDs. It exhibits that the four CDs have a wide diffraction peak near 27.0° corresponding to the (002) crystal face of graphite. Meanwhile, it is observed that the intensity of the diffraction peaks increases and the FWHM of the diffraction peaks decreases from CDs-B, -G, -Y to -R. This indicates that the degree of graphitization increases with the size measured by HRTEM. The chemical stability is also boosted on the same order.

The FTIR spectra of the four CDs are shown in Figure 2b. It reflects the key functional groups on the surface of CDs. CDs-B synthesized in water, which is the most polarization solvent, occupies a large number of polar functional groups such as O−H (3426 cm⁻¹), N−H (3250 cm⁻¹), C=O (1706 cm⁻¹), and C−O (1184 cm⁻¹). However, the vibration intensity of O−H (3426 cm⁻¹), N−H (3250 cm⁻¹), and C=O (1559 cm⁻¹) decreases from CDs-B to -R due to the weak polarization of the four solvents. In addition, C−N (1625 cm⁻¹) and C−
N (1489 cm$^{-1}$) absorption peaks increased slightly, while the intensity of the C$\equiv$H (2700–3000 cm$^{-1}$) and C$\equiv$O$\equiv$C (1097 cm$^{-1}$) absorption peaks increased from CDs-B to -R.

The X-ray photoelectron spectroscopy (XPS) spectra were used to characterize the surface chemical composition of CDs, as shown in Figure 3. The four CDs mainly contain the C, N, and O elements. The C 1s spectrum consists of three peaks at 284.8, 286.8, and 288.6 eV pertaining to the C$\equiv$C/C=C, C$\equiv$N/C=O, and C=O bonds in the four CDs. However, there are peaks corresponding to the COOH component in CDs-G, -Y, and -R at 290.2 eV in the spectra. The content of the COOH group is the highest in CDs-R. The N 1s spectrum had binding energies of 399.5 and 401.1 eV assigned to pyrrole-like N and graphitic N, respectively. The content of the N element increases from 8.4 to 14.6%, attributing to DMF solvent instead of water. However, the contents of graphitic N

Figure 4. UV–vis absorption (insets: photos of the four CD solutions shone under sunlight (left) and UV light (right)): (a) CDs-B, (c) CDs-G, (e) CDs-Y, and (g) CDs-R. PL spectra of the four CD solutions: (b) CDs-B, (d) CDs-G, (f) CDs-Y, and (h) CDs-R.
in the N 1s spectra of CDs-G, -Y, and -R are 6.6, 9.7, and 16.6%, respectively. It is concluded that the DMF solvent blending with ethanol or an AA solvent accelerates the cleavage of the N–H bond and the formation of the C–N–C bond in carbon cores. The O 1s spectrum consists of two components, the C=O and C–O groups, located at 531.0 and 532.3 eV.16,42 The atomic ratio of O decreases from 28.8 to 20.9% in turn. It is observed that the C=O functional groups dominate the surface of CDs-B. However, the C–O–C and COOH groups increase from CDs-G, -Y to -R instead of the C=O groups. It is inferred that the functional groups of CDs such as C=O, C–O–C, COOH, and graphitic N are affected by the DMF solvent mixed with ethanol or the AA solvent according to the FTIR and XPS spectra.

2.2. Optical Properties of Multicolored CDs. The colors of the four CD solutions are recorded under daylight (left) and 355 nm laser radiation (right), and the absorption spectra ranging from 200 to 700 nm are shown in Figure 4a,c,e,g. CDs-B solution is yellow and an obvious absorption peak of it is located at 330 and 408 nm, which are assigned to the n–π* transition from the C=O groups in combination with the XPS.16 There is a shoulder peak at 245 nm, shown in Figure 4a,c,e, matching well with the π–π* transition of electrons. According to the FTIR and XPS, it reflects that CDs-B, -G and -Y have the same energy levels provided by the same functional groups assigned to the C≡O/N/C=N domains.35 The quantum yield (QY) of CDs-B was calculated to be approximately 20.1%. CDs-G and -Y solutions are gray, similar to the color of the activated carbon solution. The QY of CDs-G and -Y are 22.1 and 21.9%, respectively. The CDs-R solution is special with a beautiful color of a rose red. The QY of CDs-R is about 24.2%. The obvious absorption peak of CDs-R solution is at 541 nm without an absorption shoulder at 245 nm. Above all, it indicates that there are obvious differences in the absorption spectra in the visible-light region caused by the functional groups of CDs synthesized with different solvents. The DMF solvent is the key to adjust the absorption peaks, and the AA solvent raises the content of these groups.

However, a sharp contrast is observed when a 355 nm laser radiates the four aqueous solutions of CDs. The solutions of CDs-B, CDs-G, and CDs-Y emit bright blue, cyan, and light cyan nearly of white fluorescence, respectively. However, the CDs-R solution exhibits a pretty hot pink. To research the optical properties deeply, the PL spectra of the four CD solutions are determined as shown in Figure 4b,d,f,h. It is obviously observed that the emission wavelength of the four CDs is dependent on the excitation wavelength. The emission peak of CDs-B solution is located at near 410 nm under the excitation wavelength from 280 to 340 nm, which is consistent with the results reported in the literature.35 It gradually shifts toward a longer wavelength along with the excitation wavelength of 440 nm arisen from the complex ligand shell on the surface of CDs, which leads to electron transitions of surface states.43 However, the emissions corresponding to 410 and 567 nm are close to complementary colors. So, the CDs-G and -Y solutions are gray, similar to the color of the activated carbon solution. The QY of CDs-G and -Y are 22.1 and 21.9%, respectively. The CDs-R solution is special with a beautiful color of a rose red. The QY of CDs-R is about 24.2%. The obvious absorption peak of CDs-R solution is at 541 nm without an absorption shoulder at 245 nm. Above all, it indicates that there are obvious differences in the absorption spectra in the visible-light region caused by the functional groups of CDs synthesized with different solvents. The DMF solvent is the key to adjust the absorption peaks, and the AA solvent raises the content of these groups.

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wavelength as shown in Figure 4b. The maximum emission peak is located at the blue light region of 470 nm with its corresponding excitation wavelength of 400 nm. The Stokes shift is 76 nm compared with the excitation spectrum shown in Figure 4a, which represents the heat energies of electron transfer during the excitation and emission processes. However, the emission wavelength is only red-shifted to 535 nm with an even longer excitation wavelength. This indicates that CDs-B solution could not emit orange or red fluorescence.

There is full width at half maxima (FWHM) in PL spectra of CDs-B solution due to the nonuniform size and a variety of surface functional groups of CDs. Figure 4d shows the PL spectra of CDs-G solution. The emission peak of CDs-G solution red-shifts along with the excitation wavelength increasing from 360 to 500 nm as shown in Figure 4c. In PL spectra of CDs-G solution, the shoulder peak appears, which may be attributed to emission from the \( \pi^* \) to surface states. The maximum emission peak is located at the green light region of 500 nm exciting under the wavelength of 420 nm and the Stokes shift is 80 nm. Therefore, there is no change in the UV−vis absorption at 245 nm matching with the \( \pi^* \to \pi^* \) transition originating from the C=C/C=N groups in carbon cores. Figure 5a shows the UV−vis absorption spectra of CDs-B solution after oxidation and reduction. The absorption peaks of CDs-B and -B-br at 330 nm are assigned to the \( n \to \pi^* \) transition from the C=O groups, which is reduced and exhibits a red shift of about 5 nm for CDs-B-r. As shown in Figure 5b, the absorption peaks of CDs-G-br that generate peaks at 312, 488, and 551 nm are more distinct from CDs-G solution.

2.3. Oxidation and Selective Reduction Groups on the Surface of CDs. The UV−vis absorption of the as-prepared, oxidized and selectively reduced CD solutions is shown in Figure 5. It has been investigated that the multicolored CDs are oxidized by oxygen in the air and are selectively reduced by NaBH4. Moreover, NaBH4 is a selective reducing reagent that acts on the C−O−C and C=O groups. Therefore, there is no change in the UV−vis absorption at 245 nm matching with the \( \pi^* \to \pi^* \) transition originating from the C=C/C=N groups in carbon cores.
has more complex surface states and chemical structures after reduction. CDs-Y has great similarities as CDs-G in these aspects as shown in Figure 5c. As shown in Figure 5d, the absorption peaks of CDs-R-br decrease because functional groups of CDs-R are easily oxidized in air. Instead, two new absorption peaks of CDs-R-r appear near 330 and 507 nm. Above all, the content of functional groups on the surface of the CDs is affected by oxygen.

Figure 6a–d shows the PL spectra of the four CDs-r after reduction. The absorption spectra of CDs-G-r, -Y-r, and -R-r solutions obviously shift due to the C−O−C bond, which is selectively reduced by NaBH₄. Compared with PL spectra of CDs-G, -Y and -R solutions, it should be emphasized that the new emission peaks of CDs-G-r, -Y-r, and -R-r appear near 390 nm, though the maximum emission wavelengths remain in the green, yellow, and orange light regions, respectively. The electrons from the C−O−C and C≡O groups need higher energy to excite than those from the COOH groups. Therefore, the contributions of the C−O−C and C≡O groups for fluorescence properties of CDs may be abated by the COOH groups.

Above all, CDs-B (blue, 470 nm), CDs-G (green, 500 nm), CDs-Y (yellow, 539 nm), and CDs-R (orange, 595 nm) with different colors and fluorescence emission wavelengths are gained. It is an immediate result that CDs synthesized by DMF solvent or mixed with ethanol and AA solvents can emit red fluorescence. However, CDs-G synthesized by DMF solvent emits red light weakly. It is similar to CDs-Y, which uses DMF and ethanol solvent simultaneously during the synthesis process. The red-light emission intensity and the corresponding absorption can be greatly enhanced by DMF solvent blending with AA solvents. According to the FTIR and XPS spectra, it is inferred that the contents of graphitic N in carbon cores and COOH functional groups on the surface of CDs are the key to the red shift of emission peaks. The contents of functional groups on the surface of CDs are affected by oxygen. The selective reduction study by sodium borohydride (NaBH₄) demonstrates that the contributions of the C−O−C and C≡O groups for emission of fluorescence relying on the excitation wavelength are abated gradually by the COOH groups. The electrons from the C−O−C and C≡O functional groups need higher energy to excite than those from the COOH groups. It is depicted that the DMF solvent is the key solvent for emitting red fluorescence and its emission intensity could be enhanced by the AA solvent.

3. CONCLUSIONS

The four sorts of CDs are synthesized by the solvothermal method in four solvents, water, dimethylformamide (DMF), ethanol, and acetic acid (AA), leading to CDs-B (blue, 470 nm), CDs-G (green, 500 nm), CDs-Y (yellow, 539 nm), and CDs-R (red, 595 nm) with different colors and fluorescence emission wavelengths. It is obvious that CDs synthesized in DMF solvent or DMF mixed with ethanol or AA solvents instead of water can emit red light. The emission intensity of red light and the corresponding absorption can be greatly enhanced by DMF solvent blending with AA solvents. According to the FTIR and XPS spectra, it is inferred that the contents of graphitic N in carbon cores and COOH functional groups on the surface of CDs are the key to the red shift of emission peaks. The contents of functional groups on the surface of CDs are affected by oxygen. The selective reduction study by sodium borohydride (NaBH₄) demonstrates that the contributions of the C−O−C and C≡O groups for emission of fluorescence relying on the excitation wavelength are abated gradually by the COOH groups. The electrons from the C−O−C and C≡O functional groups need higher energy to excite than those from the COOH groups. It is depicted that the DMF solvent is the key solvent for emitting red fluorescence and its emission intensity could be enhanced by the AA solvent.
4. EXPERIMENTAL SECTION

4.1. Materials. The citric acid (CA), urea, dimethylformamide (DMF), acetic acid (AA), ethanol, sodium borohydride (NaBH₄), sodium hydroxide, and hydrochloric acid were purchased from Nanjing Chemical Reagent Co., Ltd. The dialysis bag (MD44-1000D) and the microporous membrane (0.22 μm) were obtained from Beijing Solarbio Science & Technology Co., Ltd. (China). The ultrapure water was prepared by a laboratory pure water machine (Unique-R20, RSJ Technology Co., Ltd.). All of the above materials were used directly without further purification.

4.2. Synthesis of Multicolored CDs. The CDs were synthesized by the solvothermal method using CA as the carbon source and urea as the nitrogen source in different solvents. CA (2.882 g) and urea (1.201 g) were dissolved in 20.0 mL of ultrapure water, 20.0 mL of DMF, 10.0 mL of DMF and 10.0 mL of ethanol, 10.0 mL of DMF and 10.0 mL of AA, which were named CDs-B, -G, -Y, and -R, respectively. The mixed solutions were stirred evenly at 200 °C for 6 h in an ultrasound bath. Then, the mixture was cooled to room temperature and dialyzed against ultrapure water with a dialysis bag (1000D) by ultrasound treatment for 72 h. The supernatant fluid was collected using the high-speed centrifuge at 12 000 rpm for 30 min and filtered using a microporous membrane (0.22 μm). The powders of CDs were obtained by drying the solutions in a vacuum at 40 °C overnight. It should be noted that CDs need to be stored in a vacuum and in the dark to prevent oxidation. A schematic illustration of the typical experimental measures for the synthesis of CDs is shown in Figure 8.

4.2.1. Functional Groups Oxidized and Selectively Reduced on the Surface of CDs. CDs-B, -G, -Y, and -R were dispersed in ultrapure water to prepare 100 μg/mL solutions. CD solutions (20.0 mL) with different luminescent colors were oxidized in the air for 2 weeks and were named CDs-B-br, -G-br, -Y-br, and -R-br, respectively. Then, CDs-br solutions mixed with 1.0 g NaBH₄ were stirred for 12 h and were denoted as CDs-B-r, -G-r, -Y-r, and -R-r.

4.3. Characterization Techniques. HR transmission electron microscopy (HRTEM, JEM 2100F, JEOL) was conducted to analyze the morphology of CDs. X-ray diffraction (XRD, D8 Advance, Bruker), X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher), dynamic light scattering (DLS, Zetasizer NANO ZS, Malvern) and Fourier transform infrared (FTIR, Nicolet iS 10, Thermo Fisher) were conducted to analyze the structure and composition of CDs. The optical properties of CDs were determined by UV−vis spectrum (D7, Rungee Instrument Technology Co., Ltd.) and photoluminescence spectroscopy (PL, QM40-NIR, PTI). All tests were carried out at room temperature. The quantum yield (QY) of CDs was determined according to quinine sulfate (QY = 54%). The QY of CDs can be calculated from the following equation:

\[ QY = \frac{QY_R \times \frac{m}{m_R} \times \frac{n^2}{n_R}}{100} \]

where QY is the quantum yield in %, m is the slope of the plot of integrated emitting fluorescence intensity vs absorbance, and n is the refractive index in 1.33.

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