A Facile Preparation of Multicolor Carbon Dots

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Nano Express

Keywords: multicolor carbon dots, solvothermal reaction, tunable photoluminescence

Posted Date: August 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-717592/v1>

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Version of Record: A version of this preprint was published at Nanoscale Research Letters on March 8th, 2022. See the published version at <https://doi.org/10.1186/s11671-022-03661-z>.

Abstract

Carbon dots (CDs) were prepared by classic citric acid and thiourea as precursors, modulating the volume ratio of solvent that is water and DMF under one-pot solvothermal reaction to prepared color-tunable CDs with emissive wavelength from 450 nm to 640 nm. The distinct optical features of these CDs are basis with their differences in the particle size, and the content of the C-N/C-S and $-C\equiv N$, which can be adjusted by controlling the decomposed and carbonization processes during solvothermal reaction. Furthermore, the CDs have significantly potential to be achieved continuous luminescence emitting spectrum by modulating minor distinction which control the ratio of solvent, solvothermal reaction time and temperature. Therefore, the study achieved an efficient approach to tune the color and photoluminescence mechanism of CDs, promote the potential applications in biological and anti-counterfeiting inks.

Introduction

Carbon dots (CDs) are novel fluorescent materials with sizes less than 10 nm¹, which is one of the significant members in the carbon materials. CDs have gradually appeared in a great interest of research since first discovered by Xu et al. in 2004 when they obtained single-walled carbon nanobubbles². And first proposed the concept of CDs till 2006³. They become new star to be promising alternative to rare earth ion and semi-conductor QDs. Thousands of raw materials and “up-bottom” and “bottom-up” approaches have been reported for the synthesis of CDs⁴. CDs have also exhibited a great number of outstanding properties that are excellent biocompatibility, low cost and toxic, aqueous dispersibility, especially photoluminescence compared with traditional organic dyes and metal semiconducting quantum dots in the past decades⁵. It is due to these advantages that have been potentials in many fields with bioimaging⁶, photovoltaics⁷, energy storage⁸ and probe sensing⁹. However, it is difficult to prepare multicolor emissive CDs and this prohibit their development and practical applications¹⁰. There have been previous efforts to form tunable PL of CDs from blue to red spectrum and typically fluorescence^{11,12} tunable with a 100 nm to 150 nm wavelength interval with a strong drop in fluorescence intensity, which are moderately tunable. For example, Miao et al. synthesized of CDs with multicolor emission by thermal pyrolysis of citric acid and urea to control graphitization and surface functionalization¹³. Ding et al. prepared wide range wavelength successfully by changing the solvent in reactions and found the solvent controlling the carbonization processes during the solvothermal reactions¹⁴. Zhu et al. got multi-fluorescence carbon dots via magnetic hyperthermia method in the three different cations¹⁵. Wang et al. obtained multicolor emitting N-doped carbon dots under hydrothermal reaction from ascorbic acid and phenylenediamine precursors¹⁶. Besides, reported CDs can also have multicolor luminescence owing to change the concentration of the precursors and pH in terms of a constant chemical structure¹⁷. Furthermore, in order to obtained clean CDs, purification and separation techniques, such as dialysis and chromatography, are quite time-consuming but necessary^{10,14}. Unfortunately, it is still a challenge to synthesis CDs across the entire visible spectrum.

Here we achieved a series of CDs with the multicolor spectra emitted from 450 nm to 640 nm prepared by conveniently tuning the volume ratio of water to DMF in the same precursors. The prepared CDs presented five colors across from blue to red when excited by 365 nm UV lamp. And hoped to achieve continuous luminescence emitting spectrum under the adjusting the volume ratio of water to DMF. From the results of AFM, Raman spectrum and XPS measurements, the volume ratio of solvents in the reaction process led to the difference in the particle size and the contents of the functional groups of the prepared CDs, resulting the excellent multicolor spectra of CDs. These findings provide an extremely promising for many applications from entire visible spectrum, including photothermal therapy, anti-counterfeiting inks, bioimaging, and sensitive PL sensors^{18–20}.

Synthesis Of Multicolor Carbon Dots

Multicolor emission CDs were prepared by a one-spot solvothermal process method using a series of volume ratio of water to DMF. As shown in Fig. 1a, 1.26 g (0.2 mol/L) hydrated critic acidic and 1.37 g (0.6 mol/L) thiourea were dissolved in 30 ml mixed solution with a H₂O: DMF volume ratio of 1:0, 1:1, 1:5, 1:9 and 0:1, which were denoted as b-CDs, g-CDs, y-CDs, o-CDs, and r-CDs, respectively. Then, each solution was translated into a Teflon-lined stainless-steel autoclave, followed by heating at 160 °C for 4 h. After that, these CDs solution were filtrated with 0.22 µm membranes to purify. Finally, the prepared CDs were analysed by UV lamp and Photoluminescence (PL) spectra. Interestingly, the five prepared CDs exhibited bright multicolor fluorescence under 365nm UV light, as shown Fig. 1b. The optimal emissive wavelength of the five CDs is 440 nm, 530 nm, 580 nm, 610 nm, and 640 nm, respectively, as shown in the normalized PL spectra in Fig. 1c. Remarkably, the one-step synthesis for multicolor CDs is convenient and efficient method compared with the preparation for multicolor CDs reported²¹.

Results And Discussion

Characterization of the b-, g-and r-CDs

The fluorescence of CDs is related to the particle size, the types and contents of the functional groups, we further performed a series of characterizations, taking b-CDs, g-CDs and r-CDs as examples. The atomic force microscopy (AFM) images in Fig. 2a-c displayed their height distribution of b-CDs, g-CDs and r-CDs. The average height of b-CDs, g-CDs and r-CDs is ~ 3 nm, respectively. While for the lateral particle size, the average diameter is 2 ± 1 nm, 4 ± 1 nm, 6 ± 1 nm for of b-CDs, g-CDs and r-CDs, respectively, as shown in Fig. 2d-f. The results clearly show that the order of the particle sizes from small to large correspond the red-shifted emission of CDs, which is consistent with the previous reported²². It is indicated that more DMF solvents could facilitate the nucleation and growth of CDs²³.

Figure 2g showed the Raman spectra of b-CDs, g-CDs and r-CDs, in which a G band at 1573 cm^{-1} and a D band at 1342 cm^{-1} correspond to graphitic sp² carbon structures and disordered sp³ carbon structures²⁴, respectively. The ratio of I_G/I_D is 1.11, 1.20 and 1.24 for b-CDs, g-CDs and r-CDs, showing the higher

graphitization degree of CDs with increasing the ratio of DMF solvents, consistent with our AFM results of particle size. Therefore, the tunability of the photoluminescence in our work depend on the particle size of CDs²⁵.

Fourier transfer infrared (FT-IR) and X-photoelectron spectroscopy (XPS) characterization were further performed to investigate the types and contents of the functional groups on the b-CDs, g-CDs and r-CDs. The FT-IR spectra of CDs are shown in Fig. 2h. The emerging peaks at $570 \sim 600 \text{ cm}^{-1}$ (C-S bonding)²⁶ and 2050 cm^{-1} (-SCN bonding)²⁷ reveal the nitrogen and sulfur doping in the CDs. The vibration peaks at 3370 cm^{-1} and 3160 cm^{-1} are stretching vibrations of O-H²⁸ and N-H. The peaks at 1710 cm^{-1} , 1610 cm^{-1} and 1410 cm^{-1} are ascribed to the $\nu_{\text{C=O}}$ of the -COOH group⁶, the bending vibration of C = C/N-H and C = C/O-H²⁷, respectively. Obviously, the order of the content of the oxygen-containing groups (especially for O-H) is b-CDs > g-CDs > r-CDs, which is opposite to the order of particle size and wavelength of fluorescence. These results demonstrated that the volume ratio of water to DMF in the chemical reaction process have a significant effect on the particle size and functional groups of CDs.

Furthermore, the atomic concentrations and oxygen-containing group distribution of b-CDs, g-CDs and r-CDs were characterized by X-photoelectron spectroscopy (XPS), as shown in Fig. 3. The four diagnostic peaks located at 531 eV, 400 eV, 285 eV, and 163 eV correspond to O1s, N1s, C1s, and S2p, respectively. The ratio of O/C was 75%, 25% and 24% for b-CDs, g-CDs and r-CDs, respectively. From the high-resolution spectra in Fig. 3, the C1s spectra were divided into five peaks, namely, C = C/C-C (284.5 eV), C-N/C-S (285.1 eV), C-OH (286.3 eV), C = O (288.3 eV), and O = C-OH (289.0 eV)²⁶. The order of the content of the oxygen-containing groups is b-CDs > g-CDs > r-CDs, consistent with our FT-IR results.

In addition, the N1s high-resolution XPS spectra of b-CDs, g-CDs, and r-CDs were fitted using three components centered at C $\equiv$ N (397.4 eV), pyrrolic N (399.4 eV), and graphite N (401.2 eV), respectively, as shown in Figure S1. The high resolution spectra of the S2p also clearly show the peaks at 164.5 eV and 165.9 eV correspond to S2p^{3/2} and S2p^{3/1} spectra of the C-S-C covalent bond in thiophene-type structure due to the spin-orbit splitting²⁹, which can be agreement with sulfone bridges(-C-SO_x-C)²⁹. From the detailed analyses of the N1s and S2p spectra in Table 1, the content of nitrogen-containing and sulphur-containing groups were increased with the increase the ratio of DMF solvents, compared with the decrease of contents of oxygen-containing groups on CDs.

Optical Properties Of The B-, G-and R- Cds

The UV-Vis absorption spectra of surface states of C = X (X = N, S, O) in the doped CDs showed a well resolved n- π^* transition at 320nm³⁰. However, b-CDs, g-CDs and r-CDs also exhibited energy absorption bands at around 360nm, 420nm and 560nm, respectively, as shown in figure S2. Such energy bands are classically associated with narrowing of the electronic bandgap and results in those red-shift fluorescent CDs³¹. The position of energy absorption bands demonstrated the wavelength region of fluorescent excitation. The optimal emission wavelength of b-CDs and g-CDs is 440 nm and 530 nm, respectively.

While, the dual-emissive wavelength was located at 600 nm and 640 nm for r-CDs. With an increase in excitation wavelength, the PL emission peaks remain nearly shifted, which manifested the excitation-dependent property of b-CDs, g-CDs and r-CDs, implying a possible carbogenic core state emission³². Under solvothermal conditions, decomposition performed between citric acid and thiourea to form N, S-rich CDs with abundant -COOH, -OH, -CSN, -NH₂ on the surface. Obviously, the volume ratio of water to DMF can affect the extents of decomposition and carbonization process in the reaction process²⁹. It can be speculated that the decomposition of precursors and carbonization of solvents gradually increased with the higher volume ratio of water to DMF, resulting in the promoting formation of sp²-domains and red-shifted absorption and emission bands, which corresponding well with their increased particle sizes and Raman spectra. Thus, based on FT-IR, XPS and UV results, we demonstrated a facile preparation of full-color carbon dots by modulating the volume ratio of water and DMF under one-pot solvothermal reaction.

Reaction conditions and Solvent Effects on the PL Emission Properties

We further analysed the effects of reaction conditions (reaction of time and temperature) on the preparation of multicolor CDs, taking the solvent volume ratio 1:1 of water and DMF as an example. As shown in Fig. 5a and b, the maximum emissions of CDs have dramatically red-shifted with reaction time from 2 h to 8 h, and reaction temperature from 120 °C to 180 °C, respectively. When the heated time from 2 h to 8 h at 160 °C, the maximum emission peaks change from blue (460 nm) to red (605 nm). Similarly, when the reaction temperature from 140 °C to 180 °C at 4h, the maximum emission peaks change from blue (450nm) to red (610nm). This shows that the increase of reaction time and reaction temperature lead to the red-shift of CDs emission, which we attributed it due to the carbonization in the materials¹³. As it is known, longer thermal time and higher temperature will promote the carbonization of CDs¹³, Based on these results, we conclude that the emissive wavelength of CDs strongly depends on the carbonization degree of CDs, which is connected well with the particle size and functional groups on CDs.

To analysed the effect of solvents on our prepared CDs, we dissolved CDs separately in to mixed solutions with a H₂O: DMF volume ratio of 1:0, 1:1, 1:5, 1:9, and 0:1, using g-CDs as an example. As shown in Fig. 5c, the emission wavelength of the prepared g-CDs remained unchanged in mixed solutions with varies of H₂O: DMF volume ratio. While the photoluminescence intensity of the emission increased with the volume of DMF. The results indicated that the multicolor CDs come from the differences in physical and chemical properties of CDs them-selves. After the preparation, the solvent has an effect on the photoluminescence intensity, however has no obvious effect on the wavelength or color of the prepared CDs, consistent with early reports³³.

Conclusions

In summary, we have developed a facile and feasible way to synthesis multicolor CDs which is range from entire visible spectrum. We find the selected of solvents of the DMF solvent which is the most

significant for this method under the solvothermal reactions because the solvents were decomposed in carbonization processes as one of the precursors. The photoluminescence mechanism is determined by the particle size and functional groups on CDs, including sp^2/sp^3 domains, oxygen-containing groups, nitrogen-containing and sulphur-containing groups. Our present work performed a facile route to prepare CDs with excellent optical properties for well applications and controlling the formation processes of CDs. Especially adjusting the ratio of different solvents paves the way for the preparation of multicolor and continuous luminescence emitting spectrum CDs. Moreover, the prepared CDs have potential in the bioimaging, anti-counterfeiting inks, photocatalysis and solid-state lighting based good compatibility, low toxic and photostability.

Abbreviations

CDs: Carbon dots; FT-IR: Fourier transform infrared; XPS: X-ray photoelectron spectroscopy; AFM: Atomic Force Microscopy. DMF: N,N-Dimethylformamide; UV/Vis: Ultraviolet and Visible spectrophotometry; H₂O: Deionized water.

Declarations

Acknowledgements

This work was supported by the National Natural Science Foundation of China (12074341, U1832150, 11875236), the Fundamental Research Funds for the Provincial Universities of Zhejiang (2020TD001). We thank the staffs from BL01B beamline of National Facility for Protein Science in Shanghai (NFPS) at Shanghai Synchrotron Radiation Facility.

Authors' Contributions

RSY carried out the experiments, supported the analysis of all data and wrote this manuscript. SL and YR carried out the experiments. ZKW and JLC guided the experiments. LL guided the characterization. LC guided all research steps and approved the final manuscript. All authors read and approved the final manuscript.

Funding

This work was supported by the National Natural Science Foundation of China (12074341, U1832150, 11875236), the Fundamental Research Funds for the Provincial Universities of Zhejiang (2020TD001).

Availability of Data and Materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

There are no conflicts to declare.

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Figures

Figure 1

(a) One-pot hydrothermal synthesis route for CDs with distinct fluorescence characteristics. (b) Five CD samples under Day light and 365 nm UV light. (c) Corresponding PL emission spectra of the five samples, with maximum at 440 nm, 530 nm, 580 nm, 610 nm, and 640 nm, respectively.

Figure 2

AFM images the corresponding height (a) of b-CDs, (b) of g-CDs, (c) of r-CDs and size images distribution (d) of b-CDs, (e) of g-CDs, (f) of r-CDs. Raman spectroscopy (g) and FT-TR spectroscopy (h) of three selected CDs.

Figure 3

XPS full-scan survey analysis (a) of b-CDs, (b) of g-CDs, (c) of r-CDs and C 1s high-resolution level spectra (d) of b-CDs, (e) of g-CDs, (f) of r-CDs.

Image not available with this version

Figure 4

Figure 5

Normalized PL emission spectra of g-CDs with (a) different heated times, (b) different heated temperature. (c) PL emission spectra of g-CDs with different volume ratio of water to DMF, excited at 420 nm.

Supplementary Files

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