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Original Article

Electrochemical Synthesis of Carbon Dots with Full-Color Emission via Oxidation Modulation for Anti-Counterfeiting

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Abstract:
Carbon dots (CDs) have versatile applications in luminescence, whereas identifying the key factors for spectral modulation has been challenging due to numerous synthesis parameters and unmonitorable reaction process. Herein, electrochemical method was employed to obtain CDs with full-color emission (λem=478~625 nm) via modulating volume ratio of ethanol/H_2O in electrolyte, where the real-time monitoring and digital precision control are achieved. All the obtained CDs exhibit excitation independence, acid/alkali resistance and solid-state fluorescence. Structural and optical characterization reveal that oxidation divergence comes from C=O accounts for the adjustable emission. Meanwhile, the potential in anti-counterfeiting been demonstrated by using CDs as fluorescence agents. The proposed simple synthetic strategy is of great significance for finely spectra modulation and efficient synthesis.

Keywords: Carbon dots, Fluorescence mechanism, Electrochemical method, Anti-counterfeiting.

1. Introduction

Fluorescence carbon dots (CDs) have triggered intensive research on many application fields owing to their excellent optical properties[1-4]. Since the desired outcomes of spectrum modulation[5], solid-state fluorescence[6] and diverse applications[7] for CDs has been achieved, current research in the field focuses mainly on the optimization of optical performance, such as ultra-high fluorescence quantum yields[8], narrow emission peaks[9], ultralong room-temperature phosphorescence[10], and so forth. However, there are still two fundamental issues in previous works that have not been properly addressed, which are identifying the key factors for fluorescent modulation and optimizing harsh synthetic for energy efficient, safe, and highly productive synthesis. Until now, many factors such as particle size[11], heteroatom doping[12, 13], surface state [14, 15]and special structures[16, 17] have been found that should be responsible for the optical property regulation toward full-color CDs. Unfortunately, not all luminescence mechanisms can give a clear physical picture, especially the latter two. The main reasons for this situation are unknown intermediate processes and complex reaction systems for CDs synthesis. Therefore, it is necessary to adopt synthetic strategies with parameter controllability and on-line monitorability for deeply elucidating the fluorescence mechanism.

Electrochemistry has been proved a green, practical, and efficient method for the synthesis of high-quality CDs, with the possibility to fine-tune their characteristics by changing operational parameters. And its significant advantage is the capability to selectively modify the surface structure of CDs while preserving their core dimensions and avoiding incorporation of foreign atoms into the carbon lattice, which is valuable for investigating surface-state mechanisms and is often challenging to achieve through alternative techniques[18]. Furthermore, the electron serves as the redox agent in these economical, environmental and controllable processes that aligns with green chemistry principles[19, 20]. Up to now, substantial efforts have been devoted to exploring the structure-properties relationships of CDs. For instance, CDs with the narrowest full width at half maximum of fluorescent spectra in ultraviolet region up to 360 nm using only water as electrolyte was electrochemically was realized via only exfoliated from graphite rods[21]. Luminescence enhancement surface nitrogen and sulfur modification through an electrochemical synthesis method[22]. The size dependence of emission wavelength was also firstly confirmed by electrochemically synthesized full-color CDs[23]. Meanwhile, other factors such as starting material, electrolyte, electrode, electrical conditions and external magnetic field on optical properties of CDs are also studied[24-28]. Recently, blue, green and red luminescence for the CDs modified with amino groups was obtained by electrochemical method, further elucidating the connotation of surface state mechanism[29]. On this basis, the influences of the redox reaction between anode and cathode reactions on CDs formation was systematically investigated, which are firstly employed to construct differentiated strategy for surface-state modulation, so as to obtain multicolor CDs in separated electrodes simultaneously[30]. It seems that recent work has shifted its attention to surface state mechanism, but except for the reported amino groups, there is still huge space for other groups and structures to be explored.

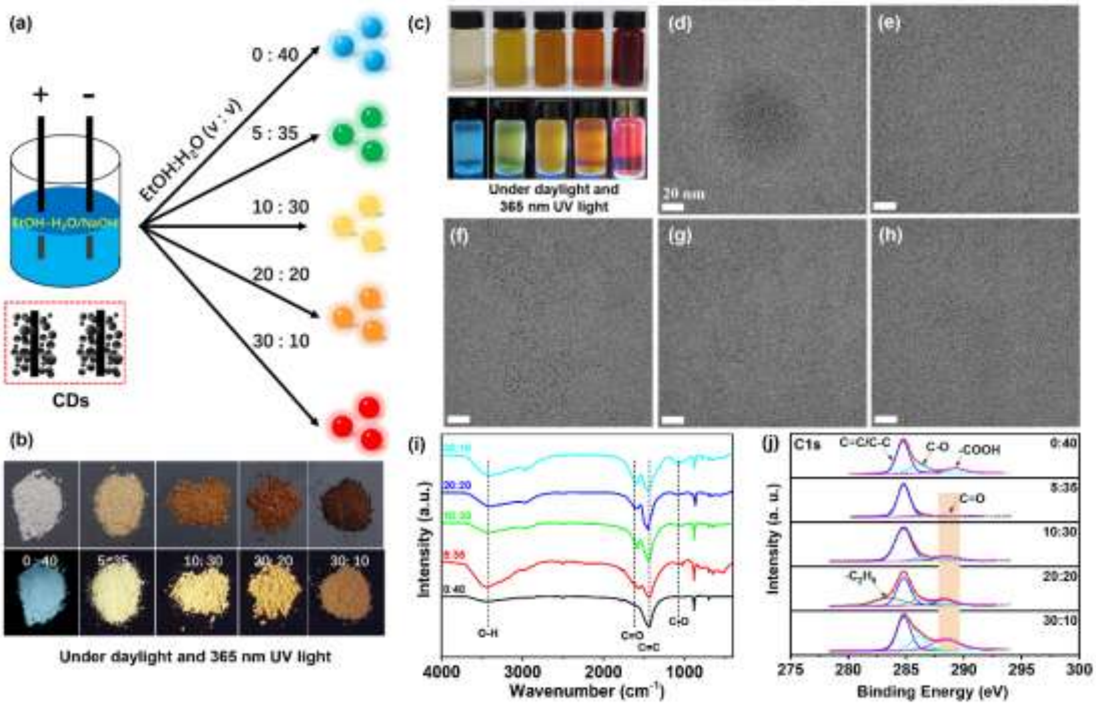

Figure 1 (a) Synthesis of CDs with electrochemical method from graphite electrodes. (b) CDs powder and (c)CDs solution under daylight and 365 UV lamp, respectively. (d-h) TEM images of CDs. (i) FTIR and (b) Raman spectra of CDs.

Herein, full-color CDs with emission from blue (478 nm) to red (625 nm) were electrochemically exfoliated from graphite rods simply by changing the ratio of water and ethanol in the electrolyte without additional modifiers. The obtained CDs exhibit excitation independence, excellent acid and alkali resistance, solid-state fluorescence and similar particle size except for different C=O bond content, making it suitable for anti-counterfeiting. Structural and optical characterization reveal that tunable emission for CDs is mainly originated from the different bombardment effects of the active free radicals generated by different volume ratio of ethanol/H_2O in electrolyte, and ethanol tends to introduce the C=O groups on the CDs surface, thus leading to the emission red shift. The proposed simple synthetic strategy is of great significance for finely spectra modulation with C=O related surface state and efficient synthesis.

As the schematic illustration shown in Figure 1a, the electrolyte of the electrochemical process was prepared by mixing ethanol/H_2O (40 mL; volume ratio = 0:40, 3:35, 10:30, 30:10) with 0.4 g of NaOH. By using graphite rods (10 cm in length and 0.6 cm in diameter) as both anode and cathode, the CDs was obtained with static potentials at 60 V (current range of 20–200 mA) for 2 h constant agitation. Accordingly, full-color CDs with blue (B-CDs), green (G-CDs), yellow (Y-CDs) orange (O-CDs) and red (R-CDs) emisson can be obtained by varying volume ratio of ethanol/H_2O under 365 nm UV lamp (Figure 1c). Meanwhile, solid-state emission CDs can be obtained by simple solution drying since the steric hindrance provided by NaOH as shown in Figure 1b, and the colors of them are inconsistent with CDs solution, which should be attributed to the concentration dependence of emission wavelength[31]. The morphology of CDs in Figure 1d-h indicates that all CDs have similar diameter about 2 nm, demonstrating that the emission red shift is not be derived from quantum size effect but the surface states[11]. Fourie transform infrared (FTIR) and X-ray photoelectron spectra (XPS) analyses were performed to investigate the surface functional groups of CDs. From the FTIR shown in Figure 1i, the same four types of chemical bonds in the CDs are identified as C=C, C=O, C-O and O-H[21, 23, 24], suggesting that the main reason for tunable emission is the amounts of chemical bonds. The Fine scan XPS spectra of C 1s for the CDs in Figure 1j can be well-fitted into four curves centered at 284.8 eV, 286.1 eV and 288.4 eV, 289.4 eV, which corresponded to C–C/C=C, C–O, C=O and -COOH bonds, respectively[14, 21, 24]. Except for the B-CDs, the emission wavelengths of other CDs red shift with increasing C=O bond content, consistent with the introduction of more oxygen-containing functional groups with increasing ethanol. This trend declares that C=O related surface states dominate the CD emission behavior, while also the emission mechanism of B-CDs is distinct from the others and may be carbon-core-dominated.

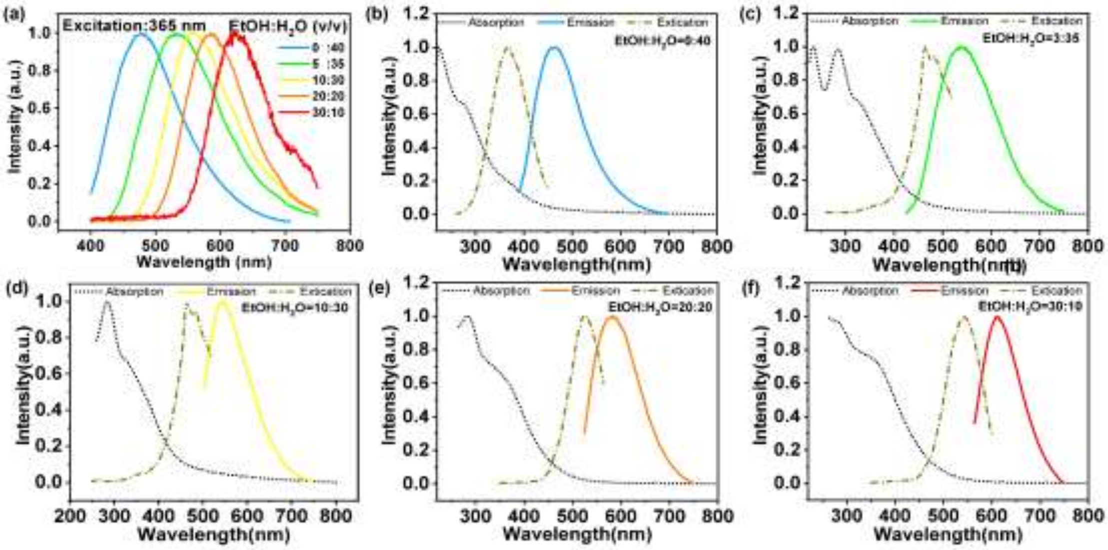

Figure 2 Optical properties of full-color fluorescent CDs. (a)Normalized PL of CDs under 365 nm excitation wavelength. (b)~(f) The absorption, emission and excitation spectra of the CDs for B-CDs, G-CDs, Y-CDs, O-CDs and R-CDs, respectively.

The optical properties of full-color fluorescent CDs are studied. It can be observed that the emission spectrum of B-CDs exhibits excitation dependence while the others exhibit excitation independence under different excitation wavelengths (Figure S1). As shown in Figure 2a, the emission of CDs red-shifts from blue to red range (up to 146 nm) with the increase of ethanol under 365 nm excitation light. Meanwhile, emission and excitation spectra in Figure 2b-f indicates that the main emission peaks are center at 478 nm with excitation wavelength at 367 nm for B-CDs, 533 nmwith excitation wavelength at 465 nm for G-CDs , 558 nm with excitation wavelength at 466 nm for Y-CDs , 585 nm with excitation wavelength at 528 nm for O-CDs and 624 nm with excitation wavelength at 545 nm for R-CDs, respectively. The UV-Vis absorption spectra of CDs display two main absorption peaks and exhibit red shift within 271–285 nm and 320–360 nm, which are assigned to the π-π* transition of the aromatic C=C bonds and the n-π* transition of the C=O bonds, indicating that the tunable emission of CDs originates from the absorption red shift caused by C=O[14, 32]. The inconsistency of B-CD is attributed to the mechanism competition between carbon core and surface state, while the B-CDs is mainly dominated by the carbon core since its weak C=O absorption. The surface states mechanism is further confirmed by the polarity dependence of emission for Y-CDs (Figure S2a)[33]. It is worth noting that the emission of CDs shows obvious concentration dependence. As shown in the Figure 2b, the emission of R-CD gradually blue-shifts from 621 nm to 525 nm with the increase of dilution factor, which essentially depends on the degree of non-radiative transitions between surface energy levels on different CDs[34-36]. Moreover, the optical properties of CDs, whose emission dominated by C=O, fortunately possess excellent acid-base resistance because C=O does not react easily with H^+ and OH^- as shown in Figure 2c-d. Therefore, it can be safely said that the C=O surface state dominates most of the optical properties of CDs mentioned above.

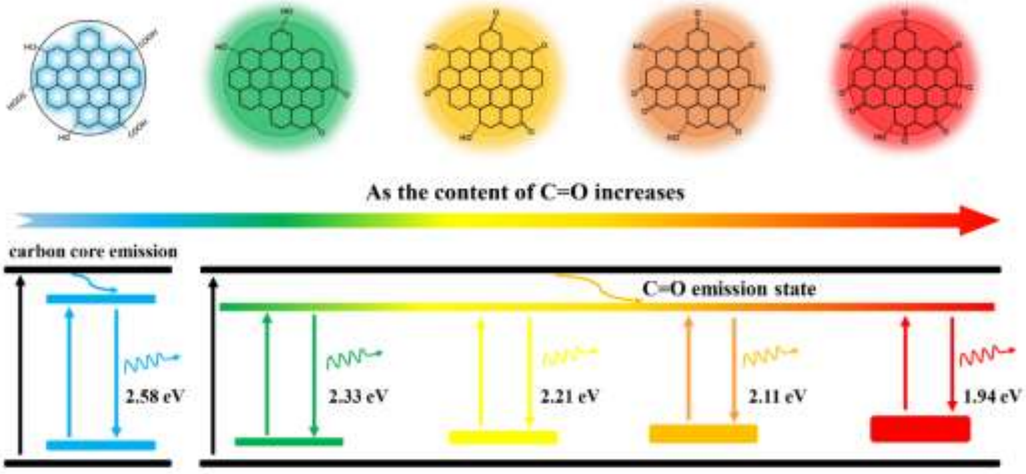

Figure 3 The schematic structure of prepared CDs with multiple emissions and energy level diagram of oxygen-related surface states for CDs.

Based on the above analysis, there are several points for the luminescence mechanism. The elemental composition of CDs consists only of carbon, hydrogen and oxygen, without any additional doping elements. The similar size distribution of CDs in TEM image revealed that fluorescence spectra should not be induced by the quantum size effect. Since CDs are usually composed of a carbon core and surface groups, tunable emission may originate from surface states generated by surface groups/structures of CDs and further confirm by its polarity and concentration dependence of emission. XPS finally found that this continuously changing structure was a C=O bond, which could cause the red shift of absorption. Therefore, the CDs formation as well as schematic structure and energy level diagram of the five CDs are given to explain the luminescence mechanism, as shown in Figure 3. Generally, cations and anions collide with the graphite rods under applied electric field, cutting off the original bond-valent structure of graphite and generating new broken or suspended bonds. Then reactive free radicals tend to combine with the broken or suspended bonds to generate stabilized bonds, such as C-OH and C-O. The generated surface groups insert or wedge into the original bulk graphite structure to obtain tiny carbon nanoparticles for CDs. Furthermore, these groups also correspond to different surface state energy levels and determine the fluorescence of the CDs. Specifically, the increase in C=O content comes from the introduction of more oxygen free radicals by ethanol, such change is reflected by the absorption red shift triggered by C=O[14], ultimately enabling tunable energy gap of emission (from 2.33 eV to1.94 eV) through manipulation of the C=O surface states. The emission mechanism of B-CD can be attributed to carbon core emission due to the absence of carbonyl related surface state.

The prepared CDs with multicolor fluorescence and excellent stability make them show great application potential, and Y-CDs was selected to dispersed in PVA (polyvinyl alcohol) solution for anti-counterfeiting applications. As show in Figure 4, PVA film made from Y-CDs exhibits extremely similar PL with Y-CDs in ethanol/H_2O except for blue shift due to different polarity between ethanol/H_2O and PVA solution. The PVA solution with Y-CDs was painted on papers, and it can be seen yellow-green pattern under 365 nm excitation.

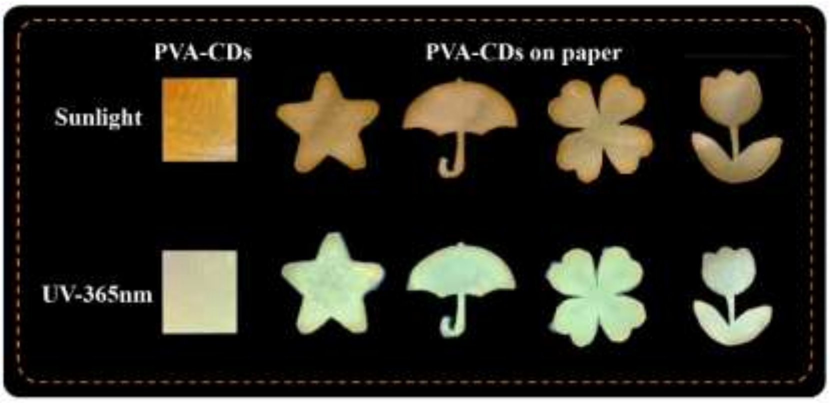

Figure 4 CDs-formed fluorescent characters on commercially available filter paper captured under daylight and 365 UV lamp

In summary, full-color CDs covers blue to red emission (λ_{em}=478~625 nm) were obtained by electrochemical method via modulation of oxygen related surface state. All the CDs exhibit excitation independence, excellent acid and alkali resistance, solid-state fluorescence. The luminescence mechanism fluorescent CDs is explored based on structural and optical characterization. It is the increase of C=O content comes from the introduction of more oxygen free radicals by ethanol arouses the absorption red shift, ultimately enabling tunable energy gap of emission (from 2.33 eV to1.94 eV) through manipulation of the C=O surface states. Furthermore, the application of CDs in the field of anti-counterfeiting has also been verified by Y-CDs.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Supplementary Information

The Supplementary Information are available at: https://www.xxxxxxxxx.

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