Oxygen Containing Functional Groups Dominate the Electrochemiluminescence of Pristine Carbon Dots

Yunlong Qin,†,‡ Naiyun Liu,§ Hao Li,§ Yue Sun,§ Lulu Hu,§ Siqi Zhao,§ Dongxue Han,*,†∥ Yang Liu,*,§ Zhenhui Kang,§ and Li Niu†,∥

†Engineering Laboratory for Modern Analytical Techniques, c/o State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China
‡University of Science and Technology of China, Hefei, Anhui 230029, P. R. China
§Jiangsu Key Laboratory for Carbon-based Functional Materials and Devices, Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123, P. R. China
∥Center for Advanced Research on Analytical Science, School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R. China

*Supporting Information

ABSTRACT: In this study, electrochemiluminescence (ECL) properties of carbon dots (CDs, less than 10 nm) have been investigated. Such CDs were fabricated via electrochemical etching strategy from graphite rods. Subsequently, a series of CDs were prepared through controlled surface engineering technique by a wet chemical method, including the oxidized-CDs (oCDs), partially reduced-CDs (rCDs), and fully reduced-CDs (F-rCDs). In-depth characterizations including UV−vis, FT-IR, Raman, XPS, etc. revealed significant differences in features of these CDs, especially the condition of surface grafted oxygen containing functional groups. ECL results suggested that all of the annihilation ECL of CDs, oCDs, and rCDs demonstrated a stable positively charged luminophore (R+*) and an unstable negatively charged luminophore (R−*) at the surface of GCE and possessed a 365 nm emission peak and consistent emission range from 550 to 850 nm. During further structural mode investigation and ECL properties simulation, the surface construction nature of CDs was speculated and the significant role of oxygen containing groups in ECL behavior of CDs was also verified. According to the ECL behavior from all of these samples, the probable ECL mechanism of CDs was then proposed, which further interpreted the indispensable contributions of oxygen containing functional groups to the ECL property of CDs.

INTRODUCTION

Recently, much attention has been focused on fluorescent carbon quantum dots (CQDs), which have gradually become a rising star due to their benign, abundant, and inexpensive nature. Generally, CQDs should consist of carbon dots (CDs),1,2 graphene quantum dots,3 as well as orderly doped carbon nanostructures (e.g., graphitic phase polymeric C3N4 and its derivatives).4 The outstanding electrochemical properties of CDs as electron donors and acceptors, causing chemiluminescence5,6 and electrochemiluminescence,7,8 endow them with wide potentials in optronics,9 catalysis,10 and sensors.11,12 The rich photoluminescent and photochemical properties of CDs also make them available candidates as efficient catalysts13 and active additives commonly used in energy devices14 for performance improving. In addition, the tailorable surface chemistry of CDs could further facilitate their functionalization and integration with other functional materials.15−17 While, in this field, an in-depth understanding on CDs properties is still a huge challenge, as well as the initial step in widening their applications toward nanocatalysis, sensing, environment, and new energy fields.

Electrochemiluminescence (ECL) strategy is well-known for its excellent sensitivity to surface states and is considered as a powerful tool to probe the surface states of nanoparticles. Zheng et al. reported a simple and effective method for preparing water-soluble CDs with ECL activity by applying a scanning potential to graphite rods and presented observations on the ECL behavior during and after the preparation of CDs.18 In their study, the ECL emission (maximum emission at 535 nm) of CDs was observed when the potential was cycled between +1.8 and −1.5 V. The ECL mechanism of CDs was suggested to involve the formation of excited-state CDs (R*)...
via electron-transfer (ET) annihilation of negatively charged (R\(^{-}\)) and positively charged (R\(^{+}\)) CDs, showing a more stable positively charged CDs thus with stronger cathodic ECL signal and weaker anodic ECL signal. Besides, Zhou et al. reported ECL emission (470 nm) of CDs at Pt electrodes when scanned or pulsed between −2.3 and +2.3 V, where almost no ECL emission was observed at the positive region, concluding that the positively charged CDs were more stable than negatively charged ones.\(^{19}\) Yet, Zhu et al. observed the ECL behavior of CDs from a facial microwave method. When scanned from −2.0 to +2.0 V at an ITO electrode, stronger anodic ECL emission was detected, which indicated that the negatively charged CDs were more stable than the positively charged ones.\(^{20}\) Xu et al. investigated the PL and cathodic coreactant ECL of low oxidative and high oxidative CDs, demonstrating a high oxidative CDs/K\(_2\)S\(_2\)O\(_4\) system was more appropriate for ECL application, such as detecting Cu\(^{2+}\) ions.\(^{21}\) On the whole, the exact mechanism of ECL for CDs remains unsettled, and the ECL properties of CDs still need further systematic study.

Here, we investigated the ECL property of CDs, which were produced through an economically superior and easy-fabricating method.\(^{22}\) Such CDs were found to consist of an intact sp\(^2\) carbon core and outer oxygen containing functional groups. Then the surface state of CDs was further controlled by oxidation degrees, including oxidation (oCDs), partial reduction (rCDs), and full reduction (F-rCDs). The annihilation ECL properties of those CDs were subsequently studied thoroughly. ECL emission behaviors from CDs, oCDs, rCDs, and F-rCDs in the UV region (365 nm) as well as broad region (from 350 to 850 nm) were observed. The former ECL emission might come from the defective sp\(^2\) carbon structure corresponding to the \(n \rightarrow \pi^*\) electron transition, while the latter probably originated from the surface grafted oxygen containing groups, which introduced several defect energy levels (i.e., multimission center) to the CDs. Our results also proved that the annihilation ECL of the CDs, oCDs, and rCDs had a stable positively charged luminophore (R\(^{+}\)) and an unstable negatively charged luminophore (R\(^{-}\)) at the surface of GCE. However, the ECL behaviors were found conspicuously varied with different oxidative degrees, where the ECL intensity of rCDs was weaker than that of CDs and oCDs, and furthermore the ECL intensity of F-rCDs was negligible. Such phenomenon should be ascribed to the oxygen containing functional groups of CDs which have significant impact on the ECL properties. Subsequently, further ECL study of structural mode molecules to simulate the ECL behavior of CDs was introduced, which could speculate the surface construction nature of CDs and confirm the critical effect of oxygen containing groups on ECL of CDs.

## EXPERIMENTAL SECTION

**Chemical Reagents.** Na\(_2\)H\(_2\)PO\(_4\), \(2\)H\(_2\)O, \(2\)Na\(_3\)HPO\(_4\), \(1\)H\(_2\)O, Na\(_2\)CO\(_3\), NaOH, KCl, K\(_2\)[Fe(CN)\(_6\)]\(_{3}\), \(0\)% \(\Delta\)\(_2\)H\(_2\)O, \(80\)% hydrazide hydrate, phenol, p-benzoquinone, benzoic acid, and benzyl alcohol were bought from Sinopharm Chemical Reagent Co. Ltd. Ultrapure water was utilized through the whole experiment.

**Fabrication of CDs, oCDs, rCDs, and F-rCDs.** CDs were fabricated through a simple and high output method in our group described before.\(^{22}\) Generally, two graphite rods placed parallel in ultrapure water were applied with 15–60 V with a direct current (DC) power supply; thus, the anode graphite rod was exfoliated into CDs in a black solution. The solution was then filtered using slow-speed filter paper, and subsequently the filtrate was centrifuged at a speed of 10 000 rpm for 30 min to remove the larger particles. Finally, the solution was freeze-dried into powder for further use.

To implement oxidation, \(200\) mL of \(30\)% \(\Delta\)\(_2\)H\(_2\)O\(_2\) solution was mixed with \(200\) mL of original CDs solution, and then the mixture was stirred at \(80\) °C for 4 h. After cooling to room temperature, excess \(\Delta\)\(_2\)H\(_2\)O\(_2\) was removed through dialysis (MWCO 3500 Da) for 3 days. Last, the solution was freeze-dried to get the sample, named as oCDs. To realize partial reduction, taking \(200\) mL of CDs solution, \(5\) g of Na\(_2\)BH\(_4\) was added into \(200\) mL of CDs solution with constant stirring at the room temperature for 10 h. Then the solution was dialyzed (MWCO 3500 Da) to remove the excess salt ions, following with a freeze-drying procedure to get the sample for further use, named as rCDs. To achieve complete reduction, \(20\) mL of \(80\)% hydrazide hydrate was added into \(100\) mL of CDs solution. Then the mixture was stirred at \(80\) °C for 6 h, and substitute dialysis (MWCO 3500 Da) was conducted to remove the excess deities, followed by further freeze-drying to get the sample for further use, denoted as F-rCDs.

**ECL Setup.** The electrochemical and electrochemiluminescence measurements were performed in a homemade electrochemical cell (see Scheme S1), including a \(3\) mm diameter glassy carbon electrode (GCE) as the working electrode (WE), a Ag/AgCl electrode as the reference electrode (RE), and a Pt coiled wire as the counter electrode (CE). As for the electrolyte solution, each sample was dissolved in \(0.1\) M phosphate buffered saline (PBS) containing \(0.1\) M KCl at the same concentration of \(0.1\) mg/mL. As for the electrolyte solution of the structural mode molecules, samples were dissolved in \(0.1\) M PBS containing \(0.1\) M KCl, at \(20\), \(20\), \(2\), \(2\), and \(0.2\) mmol/L concentrations respectively for phenol, benzyl alcohol, benzoic acid, p-benzoquinone, and \(3\),\(4\),\(9\),\(10\)-perylenetetracarboxylic acid anhydride, depending on their own solubility. Before each electrochemical measurement the electrolyte solution was bubbled with \(N_2\) to remove the dissolved \(O_2\). The glass tube inserted CE was light tight using aluminum foil to exclude the possible ECL emission interference generated at the CE. Cyclic voltammetry electrochemiluminescence was scanned between −2.5 and +2.5 V at a scan rate of 1 V/s. Chronoamperometry electrochemiluminescence was conducted at a step potential of −2.5 and +2.5 V along with a pulse width of 1 s. All EC and ECL measurements were conducted on the SECML multianalytical system developed by our group (DyneChem Lt. Co., Changchun, China).

**Characterization.** Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected on the FEI/Philips Tecnai F20 (200 kV) transmission electron microscope. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Spectrum One, PerkinElmer). Raman spectra studies were carried out on an HR 800 Raman spectroscope (JY, France) equipped with a synapse CCD detector and a confocal Olympus microscope. UV–vis absorption spectra were obtained with a JASCO J–815 spectropolarimeter. X-ray photoelectron spectra (XPS) were performed with a KRATOS Axis ultra DLD X-ray photoelectron spectrometer with monochromatized Al K\(_\alpha\) X-rays (\(h\nu = 1283.3\) eV).

## RESULTS AND DISCUSSION

**Structure of CDs.** A typical transmission electron microscopy (TEM) image of pristine CDs is shown in Figure
1a, which demonstrates that the CDs were well dispersed and had a narrow size distribution with diameter in the range of about 3−4.2 nm (Figure 1a inset at lower right). The high-resolution TEM (HRTEM) image (Figure 1a inset at upper right) presents a good crystalline property, with a well-defined lattice spacing of 0.21 nm corresponding to the in-plane lattice spacing of graphene (110 facet).23 Since ultraviolet−visible (UV−vis) spectroscopy is a useful tool to probe the electron transition, the corresponding spectrum shows that CDs possessed a clear absorption peak at about 230 nm and a broad absorption at visible spectrum (Figure 1b). It is learned from a previous report that the absorption of graphene oxide (GO) had a similar peak at 230 nm and the peak gradually red-shifted to 270 nm when GO was reduced to reduced graphene oxide (rGO).24 So reasonably the electron transition of CDs might come from the surface of CDs, which probably have a defective sp² structure and a lot of oxygen containing functional groups, a structure similar to GO. Interestingly, it appeared to be an unusual black color observed by the naked eye (Figure 1b inset), which was different from most CDs which show a brown color as we know.25,26 Taking the cases of GO and rGO, a well-recovered sp² structure could obviously increase charge carrier concentration and thus hinder the transmission of incident light.27 It is reasonable to speculate that our CDs had a well-undestroyed sp² conjugate structure in the core, which was also confirmed by the conspicuous lattice spacing in HRTEM.

To further identify the functional groups of prepared CDs, Fourier transform infrared (FT-IR) spectra as an effective and sensitive strategy was applied to probe the structure of CDs. Figure 1c shows the FT-IR spectrum of CDs, in which a clear broad peak of hydroxyl (−OH) groups is observed centered at 3460 cm⁻¹, a sharp peak of carbonyl (−C==O) groups is peaked at 1725 cm⁻¹, and an adjacent sharp peak of asymmetric stretching vibrational double bond of carbon (−C==C−) groups locate at 1620 cm⁻¹.28,29 The −C==O groups might be attributed to carboxyl groups or ketone groups, ruling out aldehyde groups for the absence of −C−H− stretching vibrational absorption at ~2720 cm⁻¹. Besides, a tiny peak at 2925 cm⁻¹ reveals a few C−H groups at the surface groups, which might ascribe to methylene (−CH₂) groups taking the peak position as reference. Raman spectra were also applied to distinguish the carbon type of CDs, which was presented in Figure 1c. Two well-defined peaks can be found at ~1347 and ~1609 cm⁻¹, which represent D and G bands of carbon, respectively. Generally, the D band represents the vibration of defective sp² carbon, while the G band stands for the vibration of intact sp² carbon, and then the intensity ratio of D and G bands, i.e., Iᵋ/Iᵊ, is usually used to estimate the ordering degree of carbon-based nanomaterials. Here, the Iᵋ/Iᵊ of CDs was calculated to be 1.21, which revealed a considerable amount of defective sp² carbon covering the intact sp² carbon core. X-ray photoelectron spectroscopy (XPS) was also employed to study the structure of CDs. The C 1s high resolution XPS spectrum (see Figure 1d) can be resolved into three peaks with binding energy centered at 284.7, 286.4, and 288.8 eV, corresponding to C==C, C−O, and C==O, respectively.30−33 According to the peak areas of XPS, the semiquantitative content of various groups should be calculated to be 57.20% (C==C), 23.95% (C−O), and 18.85% (C==O).

**ECL Properties of CDs, oCDs, and rCDs.** The annihilation ECL emission of CDs was investigated in detail at a glassy carbon electrode (GCE) in 0.1 M PBS at 0.1 mg/mL concentration. When GCE was applied cyclic voltammetry electrochemiluminescence (CVECL) at a potential between
−2.5 and +2.5 V, ECL emission (see Figure 2a) emerged at the negative scan arising at the onset potential of −1.6 V, while no clear ECL emission appeared at the positive scan. Cyclic voltammetry (not shown) could not get a well-resolved redox peak or electron/hole injection due to the large onset potential out of the potential window of GCE in the PBS solution. Chronoamperometry electrochemiluminescence (Figure 2b) was also conducted to probe the ECL property of CDs. When step potential was applied between −2.5 and +2.5 V at GCE, obvious cathode ECL emission was observed, while no anode ECL signals appeared at +2.5 V, which was consistent with the result of CVECL. Besides, the cathode ECL signal was found to increase gradually with the step potential going on and trended to reach a stable intensity after several steps of voltage. The alike cathode solely ECL emission should be ascribed to the stability of charged CDs (CDs⁺ and CDs⁻). Negatively charged CDs (CDs⁻) and positively charged CDs (CDs⁺) might get several effective collisions, where the electron-transfer annihilation of CDs⁺ and CDs⁻ formed excited CDs (CDs*). Subsequently CDs* came back to ground states of CDs and emitted photons simultaneously, which should be the annihilation ECL generation mechanism of CDs. As speculated in Figure 2d (left side), CDs⁻ were generated in situ within the diffusion region of GCE when at the negative potential. However, if the CDs⁺ produced before were stable enough and remained within the diffusion layer, strong ECL emission occurred with the effective annihilation of CDs⁺ and CDs⁻. Then taking account of Figure 2d (right side), CDs⁺ were generated in situ within the diffusion region of GCE when at the positive potential; however, if the CDs− produced before were not stable that they immediately transformed into normal state CDs within the diffusion region of GCE, then probably no ECL emission occurred with the sole presence of CDs⁺.

Figure 2. (a) Typical CVECL of 0.1 mg/mL CDs in 0.1 M PBS (pH 7) containing 0.1 M KCl (scan rate 1 V/s, from −2.5 to +2.5 V). (b) Typical CAECL of 0.1 mg/mL CDs in 0.1 M PBS (pH 7) containing 0.1 M KCl (pulse width 1 s, high potential +2.5 V, low potential −2.5 V). (c) ECL spectrum of CDs calculated from stable CAECL intensity values with 27 bandpass optical filters. (d) Schematic diagram to explain the relationship between stability of charged CDs and the strength of cathodic or anodic ECL intensity.

Figure 3. (a) Raman spectra of CDs, oCDs, and rCDs. (b) FT-IR transmission spectra of CDs, oCDs, and rCDs.
A stable intensity is essential to get a spectrum of ECL or to carry on some quantitative analysis and detection. Here CAECL was adopted to get a ECL spectrum using a 26 optical bandpass filter, and each data point was extracted from at least nine stable ECL intensity taking average (Table S1). Surprisingly, the ECL spectrum of CDs (see Figure 2c) showed peculiar luminescence position different than other previously reported CDs,18−20 where one sharp peak at 365 nm and another broad and continuous range from 550 to 850 nm were noticed. According to the general energy of the electron transition, the 365 nm luminescence probably comes from the electron transition of $\pi \rightarrow \pi^*$, while the broad luminescence might arise from electron transition of $n \rightarrow \pi^*$ due to the introduction of some defect energy levels.

To further investigate the ECL properties of CDs, surface engineering to CDs was applied and ECL behaviors were observed correspondingly. CDs samples oxidized by H$_2$O$_2$ at 80 °C were denoted as oCDs, while partially reduced ones with NaBH$_4$ at normal temperature were marked as rCDs. After controlled surface modulation, it was found that the TEM images (see Figure S1) showed similar dispersion and dots size, which ensured the efficient surface engineering of CDs meanwhile without disrupting the CDs. UV−vis absorption spectra were further applied to investigate the electron transition of oCDs and rCDs samples. As shown in Figure S2, all three samples showed an absorption peak at about 230 nm and broad absorption at the visible region. The 230 nm peak should correspond to the electron transition of the defective sp$^2$ structure at the periphery of CDs, which demonstrated a similar shell carbon structure of these three samples. Further carbon classification was recorded by Raman spectra (see Figure 3a) as a complement to FT-IR. Two peaks positioned at $\sim$1347 and $\sim$1609 cm$^{-1}$ were observed for all three samples, which should be attributed to defective sp$^2$ carbon and intact sp$^2$ carbon, respectively. The ratio values for $I_D/I_G$ were calculated to be 1.21, 1.27, and 1.19 for CDs, oCDs, and rCDs, respectively, by peak intensity. The unconspicuous difference in $I_D/I_G$ reveals that surface engineering should have little impact on the carbon skeleton of CDs, and thus core and periphery sp$^2$ carbon structure may remain negligible changes. FT-IR characteristic absorption (see Figure 3b) casts light on the process of surface engineering. Three main peaks were marked with the dashed line: the broad 3460 cm$^{-1}$ peak attributed to $-$OH, the sharp $\sim$1725 cm$^{-1}$ peak due to $-C=\ldots$
O, and the 1620 cm\(^{-1}\) peak ascribed to \(-\text{C}=\text{C}\). It was observed that after oxidation the peak centered at 3460 cm\(^{-1}\) became stronger, while the peak at 1725 cm\(^{-1}\) weakened slightly, which indicated that more hydroxyl might occur due to oxidation and less carbonyl existed probably attributing to high temperature processing of CDs. Then after reduction with NaBH\(_4\), the peak positioned at 1725 cm\(^{-1}\) almost disappeared, indicating an efficient and selective reduction of \(-\text{C}=\text{O}\) at normal temperature.

The corresponding annihilation ECL properties were further investigated through CVECL, CAECL, and corresponding ECL spectra (see Figure 4). The CVECL of oCDs and rCDs (see Figure 4a,b) showed a similar behavior as that of CDs, owning a strong cathode ECL intensity but imperceptible anode ECL intensity, which indicated that the three samples had similar stabilities of charged nanoparticles (R\(^{+}\) and R\(^{-}\)). Besides, a slight difference considering the ECL intensity of these three samples was noticed: the ECL strength of rCDs was somewhat weaker than that of CDs and oCDs samples in the same concentration condition, which was probably attributed to the certain decrease of oxygen containing groups. Taking account of the CAECL properties (see Figure 4c,d), the same phenomenon could be observed that all samples exhibited strong cathode ECL intensity and unconspicuous anode ECL intensity, which further proved the similar stability of charged nanoparticles (R\(^{+}\) and R\(^{-}\)), i.e., R\(^{+}\) was stable enough while R\(^{-}\) was not stable for all samples. Also once again, the ECL intensity of CAECL demonstrated that the strength of rCDs ECL annihilation was weaker than that of CDs and oCDs at the same concentration condition, which obviously correlated the ECL of CDs to the oxygen containing groups of CDs. As shown in Figure 4e,f, stable CAECL were applied to get the ECL spectra of oCDs and rCDs. Surprisingly, the spectra of all of the samples showed similar trends, in which a strong emission at 365 nm as well as a broad and consistent emission from 550 to 850 nm occurred. All of the above circumstances demonstrated the existence of multiemission ECL centers for all these CDs, which was a very common phenomenon in the PL of CDs, endowing excitation-dependent PL properties of CDs.

Based on the grafted oxygen functional groups differences in structure of the three samples and their respective ECL behaviors, an ECL mechanism derived from the surface of CDs could be proposed. The defective sp\(^2\) carbon structure provides a high-energy electron transition (\(\pi \rightarrow \pi^*\)) which might form an excited state of CDs with higher energy. The unstable excited CDs come back to the ground state of CDs, emitting a photon that corresponds to 365 nm. Meanwhile, the oxygen containing functional groups connected to the defective sp\(^2\) carbon structure may introduce several available defect energy levels within the \(\pi \rightarrow \pi^*\) energy gap of the defective sp\(^2\) carbon structure. Thus, parts of the unstable excited CDs at the lower energy level may return back to the ground state of CDs along with broad and consistent emission from 550 to 850 nm. With controlled surface engineering, the ECL spectra almost retain the same trends with that of pristine CDs despite some insignificant difference, which may be attributed to the solid and unchanged carbon skeleton (confirmed by Raman \(I_D/I_G\)), similar electron transition behavior (confirmed by UV-vis), or any other factors. Although the sophisticated mechanism and reason are still not clear, the CDs herein provide a unique ECL luminophor. There is still a big challenge to design an ECL luminophor with UV emission with respect to ruthenium or iridium complexes, and we provide another method to produce UV region emission from the \(\pi \rightarrow \pi^*\) transition of CDs. Also, the multiemission ECL behavior of CDs may become a potential candidate in light-emitting electrochemical cells (LECs) providing a mixing color to make the device simpler.

To further verify the contribution of oxygen containing groups to ECL of CDs, a kind of almost fully reduced CDs was successfully fabricated by hydrazine hydrate, denoted as F-rCDs. The produced F-rCDs possess a weak water-solubility. With strong ultrasonic, the TEM image (Figure S3) of F-rCDs was obtained to characterize the microscopic morphology of the sample, demonstrating the quantum dots state of F-rCDs. Then, FT-IR measurements were conducted to characterize the transform of the reducing process. As seen in Figure 5a, after reduction with hydrazine hydrate, the clear broad peak of hydroxyl (−OH) groups centered at 3460 cm\(^{-1}\) decreased significantly, and the sharp peaks of carbonyl (−C=O) groups and asymmetric stretching vibrational double bond of carbon (−C=C−) groups located at 1725 and 1620 cm\(^{-1}\) separately almost disappeared, which demonstrated the effective reduction of CDs. Besides, a significant broad peak positioned at 3140 cm\(^{-1}\) belonging to −N−H groups and a sharp peak positioned at 1400 cm\(^{-1}\) ascribed to −C−N groups emerged, presenting certain nitrogen doping. Although hard to dissolve, 0.1 mg/mL F-rCDs in 0.1 M PBS (7) containing 0.1 M KCl was prepared through controlled surface engineering, the ECL spectra almost retain the same trends with that of pristine CDs despite some insignificant difference, which may be attributed to the solid and unchanged carbon skeleton (confirmed by Raman \(I_D/I_G\)), similar electron transition behavior (confirmed by UV-vis), or any other factors. Although the sophisticated mechanism and reason are still not clear, the CDs herein provide a unique ECL luminophor. There is still a big challenge to design an ECL luminophor with UV emission with respect to ruthenium or iridium complexes, and we provide another method to produce UV region emission from the \(\pi \rightarrow \pi^*\) transition of CDs. Also, the multiemission ECL behavior of CDs may become a potential candidate in light-emitting electrochemical cells (LECs) providing a mixing color to make the device simpler.37
the same as before. CVECL was adopted to observe the ECL annihilation behavior of F-CDs, and negligible ECL emission was detected. The phenomenon probably attributes to a wide range loss of oxygen containing functional groups, which further confirmed the contribution of oxygen containing groups to ECL annihilation of CDs.

To get a deeper understanding into the ECL of CDs, several small molecules which have a similar structure with the CDs were selected to conduct the CVECL experiment using the same technology parameter (see Figure 6). The samples were prepared at various concentrations depending on their solubility. The results showed that phenol had a clear cathode ECL emission with an onset potential beyond $-2$ V and no anode ECL emission when scanned between $-2.5$ and $+2.5$ V (Figure 6a). However, benzyl alcohol possessed weaker cathode ECL emission and stronger anode ECL emission (Figure 6b). Concerning benzoic acid, a similarly weak ECL emission appeared at both the cathode and anode scan (Figure 6c). $p$-Benzoquinone had a clear cathode ECL emission and negligible anode ECL emission similar to that of phenol (Figure 6d). 3,4,9,10-Perylenetetracarboxylic acid anhydride, a polycyclic aromatic hydrocarbon with carboxylic acid anhydride functional groups, showed strong cathode ECL emission and negligible anode ECL emission (Figure 6e). While graphite electrode that have a good sp² carbon structure showed no ECL emission when scanned from $-2.5$ to $+2.5$ V in a blank PBS solution (Figure 6f).

The CVECL of the above small molecules may provide us with some insight and speculation into the structure and ECL of CDs: (i) similarity could be easily ruled out between benzoic acid and CDs, as benzoic acid might be somewhat ECL quenching, while CDs possess strong ECL emission; (ii) the graphite electrode produces no ECL emission, that is to say, the charged intact sp² carbon structure is not effective to generate an excited state, which might further confirm the significant contribution of oxygen containing functional groups to ECL emission of CDs; (iii) taking account of benzyl alcohol as an example, the different intensity of the cathode or anode ECL emission should be originated from the stability of charged luminophor ($R^+$ and $R^-$) varying with different functional groups. However, the intrinsic reason for affecting the stability of charged luminophor ($R^+$ and $R^-$), electronegativity or any other factors, remains unclear and needs further investigations.

Figure 6. (a–f) CVECL of phenol, benzyl alcohol, benzoic acid, $p$-benzoquinone, 3,4,9,10-perylenetetracarboxylic acid anhydride, and graphite electrode, respectively.
To further verify the speculated CDs structure, $^1$H nuclear magnetic resonance (NMR) spectroscopy (see Figure 7) was recorded to recognize the hydrogen type and thus cast light on the structure of CDs. Clearly, $^1$H NMR of CDs possessed three main peaks during the whole range of chemical shift, one relatively broad single peak at 3.4 ppm, one sharp quintet peak at 2.5 ppm ascribed to DMSO solvents, and one small sharp peak at 0 ppm belonging to standard TMS. Based on the knowledge of chemical shifts, the 3.4 ppm peak should be assigned to hydroxyl groups. Besides, the small peak distributed at 0.5–1.5 ppm probably claimed the presence of a small number of hydrocarbon chain (C–H) at saturated carbon, which was also confirmed by FT-IR. Furthermore, the absence of downfield $^1$H NMR ruled out the existence of carboxyl groups, which was consistent with the deduction from structural mode molecule ECL behavior.

**CONCLUSION**

In this work, we investigated the ECL property of the pristine CDs, oxidized CDs (oCDs), and partially reduced CDs (rCDs). The annihilation ECL of CDs, oCDs, and rCDs performed stable positively charged luminophore (R$^\ast$) and unstable negatively charged luminophore (R$^-\ast$) at the surface of GCE and possessed a 365 nm emission peak and consistent emission range from 550 to 850 nm, which was unusual for ECL of CDs previously reported. The 365 nm luminescence probably comes from $\pi \rightarrow \pi^\ast$ electron transition of the defective sp$^2$ structure at the periphery, while the 550–850 nm multiemission might originate from the defect energy level at the periphery introduced by oxygen containing groups. The weaker ECL emission of rCDs and the negligible ECL emission of F-rCDs further confirmed the indispensable contribution of oxygen containing groups to ECL of CDs. The multiemission ECL property might provide potential and novel application in light-emitting electrochemical cells (LECs). We also applied structural mode molecules to investigate and simulate the ECL properties of CDs, further confirming the contribution of oxygen containing groups to ECL of CDs and deducing the functional groups on the periphery of CDs.

**REFERENCES**


