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Extraction of Electrochemiluminescent Oxidized Carbon Quantum Dots from Activated Carbon

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A facile method has been developed to extract oxidized carbon quantum dots (QDs) directly from activated carbon (AC) by chemical oxidation. The method has several advantages including low cost, high yield of QDs (>10%), and large-scale production. The as-prepared oxidized carbon QDs are mainly graphitic structure nanocrystals of 3−4 nm in diameter, have abundant carboxyl groups at their surfaces, and exhibit strong electrochemiluminescent (ECL) activity, suggesting promising applications in ECL biosensing and imaging. The ECL properities, including ECL activities in the absence and presence of coreactants, effects of the size and surface passivation on the oxidized carbon QDs ECL were investigated and discussed in detail.

Introduction

Quantum dots (QDs) have recently attracted much attention for their promising applications, especially those in optoelectronic devices, biology labeling, and biomedicine.[1−4] Compared with conventional semiconductor based QDs, such as CdSe,[5] CdTe,[6] CdSe/ZnSe,[7] PbS,[8] CdS,[9] Si,[10,11] and so on, recently emerging carbon QDs exhibit many advantages, including chemical inertness, low toxicity, easy labeling, and thus attract more and more attention.[12−27] Generally, carbon QDs are nanocrystals (less than 10 nm in diameter[25]) that composed of graphitic carbon (sp2).[18,26] Carbon QDs have been prepared from many carbon sources, such as multiwalled carbon nanotubes (MWCNTs),[14] arc-discharge single-walled carbon nanotubes (SWCNTs),[15,16] candle soot,[17,18] and natural gas soot,[19] nanodiamonds,[20,21] and some organic molecular precursors.[13,22−24] In particular, well carbon QDs have been extensively reported to be extracted directly from graphite.[12,25−28] However, most of the graphitic structures existing in the graphite are relatively big,[29] even in those particles obtained by laser ablation of graphite, tiny particles (less than 10 nm in diameter) are

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still rare,[30] and thus lead to very low yield of carbon QDs. In order to improve yield of carbon QDs in preparation, we have recently tried to extract carbon QDs from a much more common carbon source, namely, activated carbon (AC). As well-known, AC is an amorphous form of carbon, which contains abundant graphite components, most likely tiny fragments of crystalline graphite.[31−33] Therefore, AC should be a more ideal carbon source than pure graphite for the extraction of carbon QDs. Accordingly, we here report a facile method of extracting oxidized carbon QDs from AC by chemical oxidation. This method would show many advantages, including easily obtained carbon source, low cost, high QD yield, simple experimental performance, and thus would be important in large-scale industrial production and extensive application of QDs.

Experimental Section

Materials. Wood based activated carbon powder (200 mesh) and 1−30 kDa molecular weight cut off (MWCO) membranes (Amicon Ultra-4, Millipore) were purchased from local suppliers. Other chemicals were analytically pure and used as received. The phosphate buffer solutions (PBS) of different pH values were prepared by titrating 0.1 mol L^{-1} phosphoric acid solution with a concentrated sodium hydroxide solution to required pH values. The pH 7 PBS for the ECL experiments of the oxidized carbon QDs was added with 0.5 mol L^{-1} Na_2SO_4 to improve the conductibility.

Preparation of Oxidized Carbon QDs. The preparation of oxidized carbon QDs was carried out as follows: (1) 1 g dried AC powder was put into 100 mL 4 mol L^{-1} HNO_3 and refluxed for 24 h. (2) After naturally cooled to room temperature, the AC suspension was neutralized with NaOH and subsequently centrifuged (2770*g*) for 10 min to remove nonfluorescent deposit. (3) The supernatant was further dialyzed against double-distilled water through a dialysis membrane (MWCO of 1 kDa) to remove inorganic salt, that is, $NaNO_3$. (4) The prepared oxidized carbon QDs were separated by ultrafiltering through centrifugal filter devices with four different MWCO membranes, respectively. Five products equivalent to 1−3, 3−5, 5−10, 10−30, and > 30 kDa were obtained. Except for the > 30 kDa fraction, all fractions (1−30 kDa) exhibited fine fluorescent activities. By weighing the nonfluorescent deposit produced in the step 2 and the fraction with molecular weight > 30 kDa produced in the step 4, it can be estimated that the yield of oxidized carbon QDs was higher than 10%. In a control experiment, 1 g of graphite was ground into powder, and used to exact carbon QDs by the same procedures as described above. The yield of oxidized carbon QDs extracted from graphite was estimated to be less than 0.2%. It is evident that AC is a much better carbon source than graphite for the extraction of oxidized carbon QDs (see Figure 1S in the Supporting Information (SI)).

Methods. High resolution transmission electron microscopy (HRTEM) images of the prepared oxidized carbon QDs (1−30 kDa) were recorded on an electronic microscopy (Tecnai G2 F20S-TWIN 200KV). Elemental analysis for the oxidized carbon QDs was performed on an organic elemental analyzer (Vario MICRO). The infrared spectrum of the carbon QDs solid was obtained on a FT-IR spectrophotometer (Thermo Nicolet 360). X-ray photoelectron spectroscopy spectra of carbon QDs was measured by a ESCAlab 250 XPS system having an Al K source for determining the composition and chemical bonding configurations. UV−vis absorption of the obtained oxidized carbon QDs was characterized by a UV/vis/NIR spectrophotometer (Lambda 750). All fluorescent spectra of prepared carbon QDs were obtained by a fluorescence spectrophotometer (Cary Eclipse Varian). ECL and electrochemcial signals were measured simultaneously by an ECL & EC multifunctional detection system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China) equipped with a three-electrode system (i.e., a Pt wire working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode).

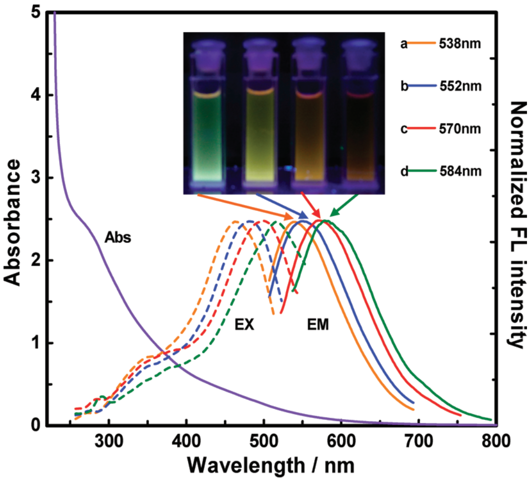

Figure 1. UV−vis absorption for oxidized carbon QDs (1−30 kDa) in aqueous solution and fluorescence spectra for oxidized carbon QDs of different fractions: (a) 1−3 kDa; (b) 3−5 kDa; (c) 5−10 kDa; (d) 10−30 kDa. Inset: Optical photographs of the four fractions obtained under excitation at 365 nm.

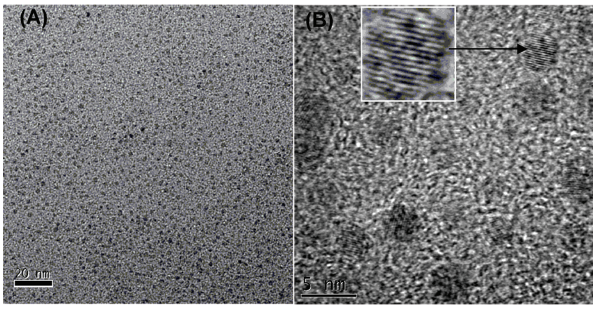

Figure 2. HRTEM images of oxidized carbon QDs (1−30 kDa). (A) the scale bar is 20 nm; (B) the scale bar is 5 nm.

Results and Discussion

Characterization. The prepared carbon QDs (1−30 kDa) in solution showed an absorption band centered at 280 nm (see Figure 1), which is similar to that of previously reported carbon QDs.[27] HRTEM images showed the prepared carbon QDs (1−30 kDa) were distributed with diameters in the range of 3−4 nm with discernible lattice structures (see Figure 2). It can also be seen that the particles of the 1−3 kDa fraction were generally smaller, compared with the 10−30 kDa fraction (see SI Figure S2). However,

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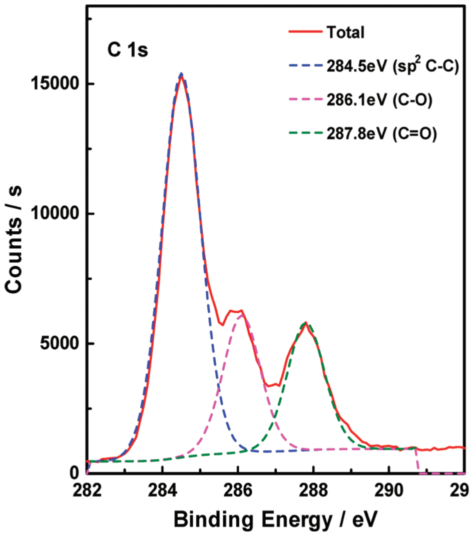

Figure 3. X-ray photoelectron spectroscopy (XPS) spectra of the as-prepared oxidized carbon QDs (1−30 kDa).

some relative bigger particles can also be found in the 1−3 kDa fraction, which means that the MWCO membrane can basically separate the oxidized carbon QDs into different but not very uniform size. The elemental analysis revealed that the purified oxidized carbon QDs (1−30 kDa) contained (in wt %): 50.01% carbon, 1.01% hydrogen, 1.67% nitrogen, and 47.31% oxygen. This result indicated that the carbon QDs had high oxygen content, and thus it is more appropriate to call the chemically prepared carbon QDs as "oxidized carbon QDs" than "carbon QDs". The X-ray photoelectron spectroscopy (XPS) results (see Figure 3) exhibited three main peaks of C atoms in the as-prepared carbon QDs at 284.5 eV (C—C), 286.1 eV (C—O), and 287.8 eV (C═O), respectively. The binding energy peak at 284.5 eV showed graphitic structures (sp^2 C—C) of carbon QDs. The Fourier transform infrared (FTIR) spectrum for the dried carbon QDs (see SI Figure S3) showed an apparent absorption peak of —OH group at about 3430 cm^{-1}, an absorption peak of C═O group at 1650 cm^{-1} and two apparent absorption peaks of $-COO^-$ at 1580 and 1390 cm^{-1} respectively. These data show that the obtained oxidized carbon QDs are mainly composed of graphitic carbon, with abundant —COOH groups at their surfaces.

Fluorescence. As an important property of QDs, fluorescence (FL) of the obtained oxidized carbon QDs was investigated with following results: (1) Both excitation spectra and emission spectra of the obtained oxidized carbon QDs showed red-shift when their molecular weight was increased (see Figure 1), indicating that FL of the obtained oxidized carbon QDs is particle size-dependent. It should be note here that the size-depencence of FL was not interfered by oxidation degree of the carbon QDs, since the degree of oxidation was the same for the particles of different sizes. This was confirmed by the experiment: the as-prepared carbon QDs were further refluxed in 4 mol L^{-1} HNO_3 for 10 h to investigate possible further oxidation of their surfaces, however, FL spectra of all the four fractions (i.e., oxidized carbon QDs with different sizes) showed no observable change. (2) Fluorescent intensities of these oxidized carbon QDs were pH-dependent (see SI Figure S4), that is, their intensities showed optimum in the range of pH 5−9, and decreased when the pH value was either lower than 5 or higher than 9. However, their fluorescence wavelengths were independent of pH value of solution. (3) Emission spectra of these prepared oxidized carbon QDs (without surface modification) were independent of excitation wavelength, which is much different from those carbon QDs with surface passivation.[13,22−24]

Electrochemiluminescence. ECL is a useful technique for both fundamental electrochemistry study and analytical applications.[7,10,34,35] More and more attention has been recently focused on the ECL of QDs. Especially, many QDs have been used in sensors basing on their strong ECL emission and easy labeling.[36−41] However, up to now, most QDs used as ECL luminophore are Cd-based semiconductors, which contain the highly toxic heavy metal, Cd, and thus has raised serious healthy and environmental concerns. Apparently, this would limit extensive applications of this kind of QDs in ECL sensors. The use of recently reported carbon QDs in sensing may be an alternative choice, since they are evidently "green" and exhibit good ECL activity.[24,27,28] Therefore, it is of considerable interest to study the ECL properties of the as-prepared oxidized carbon QDs with high yield in production for extensive applications of QDs in sensing. As have been reported that the surface passivation is helpful for the fluorescence of QDs,[7,36] however, might be unfavorable for their ECL reactions, because ECL reactions of QDs were mostly attributed to their surface state emission.[7,10,34,35] This means our obtained oxidized carbon QDs without any surface passivation might be excellent ECL luminophores. Accordingly, the ECL behaviors of the prepared oxidized carbon QDs were studied in detail in pH 7 phosphate buffer solution (PBS) at a ring-shaped Pt wire working electrode. In experiment, the counter electrode was photic isolated by inserting a Pt wire into a black plastic tube containing 1 mol L^{-1} Na_2SO_4 solution and separating it from testing solutions by a porous ceramic sinter during the ECL observation, to avoid the interference from the counter electrode. As shown in Figure 4, when the potential was cycled between −1.5 and +1.8 V, ECL signals of oxidized carbon QDs (curve (a)) were detected at both negative and positive potential regions whereas no ECL was found in the absence of oxidized carbon QDs (curve (b)). Unlike the ECL responses, no obvious difference in electrochemical response was observed between presence (curve (c)) and absence (curve (d)) of carbon QDs. ECL transients of obtained oxidized carbon QDs were measured

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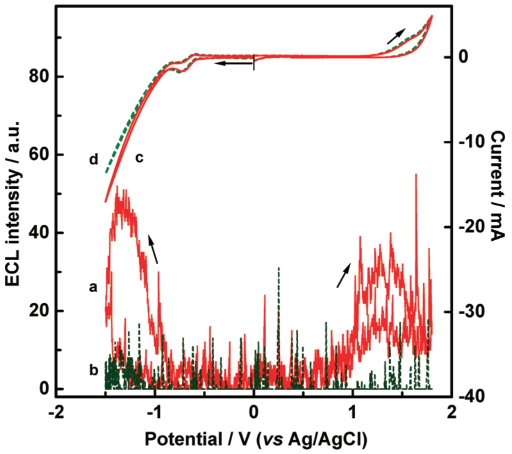

Figure 4. ECL and electrochemical responses obtained for oxidized carbon QDs in PBS (0.1 mol L^{-1} phosphate +0.5 mol L^{-1} Na_2SO_4): (a) ECL for PBS containing oxidized carbon QDs (1−30 kDa); (b) ECL for PBS only; (c) CV for PBS containing oxidized carbon QDs (1−30 kDa); (d) CV for PBS only. The working electrode was a Pt wire (0.5 mm in diameter and 10 mm in length). The potential (vs Ag/AgCl (3 mol L^{-1} KCl)) scan rate was 0.1 V/s.

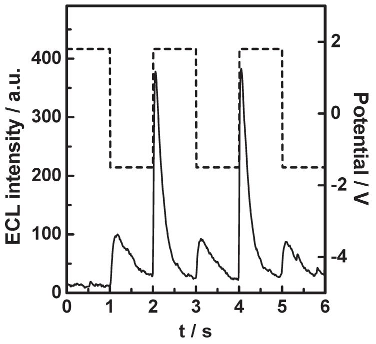

Figure 5. ECL transients (lower curves) of the obtained oxidized carbon QDs (1−30 kDa) by stepping potential (upper curves) between +1.8 and −1.5 V in pH 7 PBS (0.1 mol L^{-1} phosphate +0.5 mol L^{-1} Na_2SO_4) at a Pt wire (ϕ0.5 mm ×10 mm) electrode. The potential was applied versus a Ag/AgCl (3 mol L^{-1} KCl) reference electrode.

by applying 1 Hz potential steps between +1.8 and −1.5 V (see Figure 5). No ECL signal was detected at the first positive (or negative) potential step, however, both evident anodic and cathodic ECL signals were found at the subsequent potential steps. Apparently, both cationic QD radical ($R^{\bullet +}$) and anionic QD radical ($R^{\bullet -}$) are essential for the ECL of oxidized QDs in the absence of coreactants. In other words, the ECL of oxidized carbon QDs was produced via the annihilation between $R^{\bullet +}$ and $R^{\bullet -}$. At the first positive (or negative) potential step, only $R^{\bullet +}$ (or $R^{\bullet -}$) is produced, therefore, no ECL can be generated via the annihilation in this case. However, at the subsequent potential steps, both $R^{\bullet +}$ and $R^{\bullet -}$ can be produced and exist at the vicinity of the working electrode, thus the anihilation between $R^{\bullet +}$ and $R^{\bullet -}$ may happen, and eventually lead to the ECL emission. In addition, the observation of subsequent cathodic and anionic ECL signals implies that both $R^{\bullet -}$ and $R^{\bullet +}$ radicals are stable enough to transfer charge upon colliding and produce the exicited stated QD, R*, in solution. Herein, it should be noted that the applied potential range, that is, +1.8 to −1.5 V (see Figures 4 and 5), is quite large for an aqueous solution.

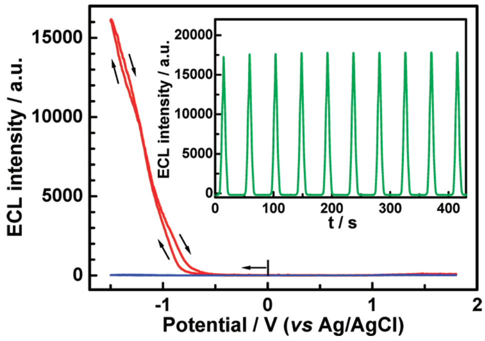

Figure 6. ECL responses of the as-prepared oxidized carbon QDs (1−30 kDa) in the absence (blue line) and presence (red line) of 1 mmol L^{-1} $K_2S_2O_8$; Inset: ECL responses of oxidized carbon QDs-$S_2O_8^{2-}$ system obtained during a continuous potential scan between −1.5 and +0.75 V.

Under the potential condition, partial electrolysis of the solvent (i.e., water) into O_2 and H_2 may occur, and result in large anodic and cathodic current densities (see Figure 4). Generally, high current densities may lead to obvious uncompensated iR_u drop and pH change of solution. Therefore, in present study, 0.5 mol L^{-1} Na_2SO_4 was added into the 0.1 mol L^{-1} phosphate buffer for increasing the conductivity of solution, however, the uncompensated iR_u drop was still significant (more than 100 mV). In contrast, effect of high current denisty on pH value could be neglected by using 0.1 mol L^{-1} phosphate buffer solution (see Figure S5 and relative discussion in SI). The good stability of QD radicals makes these as-prepared carbon QDs possible to form an excellent ECL system with $S_2O_8^{2-}$, a common oxidative coreactant (or hole donor) used in ECL systems. As shown in Figure 6, when 1 mmol L^{-1} $S_2O_8^{2-}$ was added into the oxidized carbon QDs (1−30 kDa) solution as coreactant, the cationic ECL was increased obviously, which was caused by the electron-transfer annihilation between $R^{\bullet -}$ and the electrogenerated $SO_4^{\bullet -}$[27]. Moreover, the strong cationic ECL signal was very stable when the potential was cycled between −1.5 and +0.75 V (see the inset of Figure 6). The maximum ECL emission wavelength of oxidized carbon QDs-$S_2O_8^{2-}$ system was about 600 nm (see Figure 7), indicating an evident red shift from their fluorescence maximum (see Figure 1). Furthermore, the ECL spectrum of the obtained carbon QDs showed size-independent, that is, the maximum ECL wavelengths of oxidized carbon QDs of different sizes (1−3, 3−5, 5−10, 10−30 kDa) were all 600 nm, implying that complicated size-separation of oxidized carbon QDs is unnecessary when they are used as ECL luminophores. These results indicate that the ECL of oxidized carbon QDs is dependent on surface chemistry and the presence of surface states rather than size of particle, like other QDs.[7,10,34,35]

As mentioned above, the as-prepared oxidized carbon QDs exhibited excellent ECL activities, probably due to lack of surface passivation. To further verify this viewpoint, a control ECL experiment was carried out using a kind of surface-passivated carbon QDs, which was prepared by thermal oxidation from citric acid and passivated with $HOCH_2CH_2OCH_2CH_2NH_2$.[22] ECL behaviors of

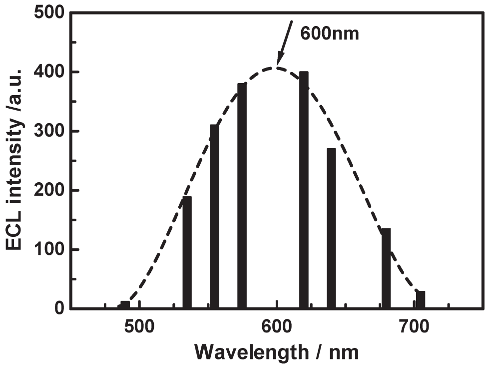

Figure 7. ECL spectrum for the obtained oxidized carbon QDs (1−30 kDa)- $K_2S_2O_8$ coreactant ECL system.

these surface-passivated carbon QDs showed three obvious differences from those of our presently reported carbon QDs (see SI Figure S5): First, much larger ECL signals (especially, anodic ECL signals) were observed when the potential was cycled between −1.5 and +1.8 V. The ECL signals were still observed even when the potential was cycled both in the potential range of 0 to +1.8 V and in the potential range of 0 to −1.5 V. This indicates that the enhanced ECL signals might result from the electron-transfer between the electrogenerated $R^{\bullet+}$ (or $R^{\bullet-}$) and some radical species, most likely from the reduction (or oxidation) of organic capping agents. Second, When 1 mmol L^{-1} $K_2S_2O_8$ was added into the solution, the coreactant ECL intensity observed in the negative potential range was much smaller (<20%) than that of our prepared oxidized carbon QDs, furthermore, the ECL responses seem much worse in stability. Third, a strong background signal, most likely chemiluminescence, was detected during observing the ECL. The much stronger anodic ECL and the background ECL signals indicated that the organic capping agents may severely interfere with the ECL reactions of the carbon QDs. The maximum emission wavelength of the coreactant ECL signal was measured to be about 600 nm (see SI Figure S6), which consistent with that of our unpassivated carbon QDs. That means that some surface states might be still present due to incomplete passivation, and thus participate in the ECL reactions. Summarily, these results indicate that our prepared oxidized carbon QDs without any surface passivation should be more suitable to be ECL luminophores.

Conclusion

A high yield of oxidized carbon QDs (>10%) with graphitic structures was obtained from AC by a facile chemical oxidation method. The high yield of graphitic carbon QDs prepared from AC rather than pure graphite not only verifies that AC as a well-known amorphous form of carbon contains abundant tiny fragments of crystalline graphite, but also suggests that AC is an ideal carbon source for preparing carbon QDs, with the advantages such as low cost, high yield, facile preparation, and potential large-scale industrial production. The as-prepared oxidized carbon QDs were of narrow particle size distribution (3−4 nm), have abundant carboxy groups at their surface, exhibited fine fluorescent activities, excellent photostability, and strong ECL activities, which indicates promising applications in ECL biosensing and imaging.

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Supporting Information Available: Figure S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.