

Electrogenerated chemiluminescence of CdSe quantum dots dispersed in aqueous solution

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1. ABSTRACT

Electrogenerated chemiluminescence (ECL) of CdSe quantum dots (QDs) dispersed in aqueous solution was studied with bare electrode. The ECL emission was observed at -1.4 V vs. Ag/AgCl and the ECL spectrum peak is similar to that of the defect photoluminescence (PL) spectrum, indicating the surface defects played a critical role in the emission process. The experiment results suggested that dissolved oxygen had a great effect on the ECL intensity. Other influence factors including the electrochemical parameters and QDs concentration were investigated in detail. As an application of the CdSe QDs ECL, the pyrogallol (1, 2, 3-trihydroxybenzene) was detected in aqueous solution. Under the optimal conditions, a linear relationship between ECL intensity and pyrogallol concentration was obtained in the range from 4.0×10^{-7} to 2.0×10^{-5} M with a correlation coefficient of 0.9904 and the limit of detection was 6.6×10^{-8} M (S/N = 3). A possible mechanism about ECL of QDs was also discussed.

2. INTRODUCTION

Quantum dots (QDs) have been extensively studied due to their unique electronic and optical properties (1-3). In comparison with organic dyes and fluorescent proteins, QDs offer several unique advantages, such as size- and composition-tunable emission from visible to infrared wavelengths, large absorption coefficients across a wide spectral range, and high levels of brightness and photostability (4). Owing to their broad excitation profiles and narrow/symmetric emission spectra, QDs have been used in numerous applications, including fluoroimmunoassays, biological imaging and biosensing (3, 5-7).

Electrogenerated chemiluminescence (ECL) based on a light emission phenomenon has already been widely used in both elucidating the mechanism of reaction and bioanalytical detection due to its prominent virtues such as high sensitivity, simplified optical setup and very

low background signal (8-11). Advantages of combining ECL with QDs undoubtedly extend to both fundamental study and bioanalytical application of QDs. In 2002, Bard and his co-workers reported the first ECL phenomenon of liquid phase silicon QDs in nonaqueous solution (N, N'-dimethylformamide and acetonitrile) (12). Subsequently, the same group described ECL of CdSe, CdSe/ZnSe, Ge, CdTe QDs in organic media (13-16) and Weller *et al.* (17) proved that CdSe QDs can act as chemiluminescent emitter. Zou *et al.* (18) investigated ECL of QDs with depositing QDs on a paraffin-impregnated graphite electrode. However, in previous work, the studies about ECL of QDs are mostly in the presence of organic media, or by modifying them to electrodes. Actually, ECL of QDs in aqueous solution has a wider potential as a sensor using in biological analysis.

In this paper, ECL of CdSe QDs dispersed in aqueous solution was investigated with naked electrode. The method is very simple, which avoids complicated modifying electrode or using toxic organic solution. Good reversible ECL and a high reproducibility can be observed in aqueous solution of CdSe QDs under continuous cyclic voltammograms (CVs) for 11 cycles (Figure 1). The results demonstrate that CdSe QDs dispersed in aqueous solution is a promising luminescent material used in ECL system. Influences of some factors on the ECL intensity were investigated. As an application of CdSe QDs ECL, we determined the pyrogallol in aqueous solution. A linear response to pyrogallol was observed in the concentration range between 4.0×10^{-7} and 2.0×10^{-5} M.

3. MATERIALS AND METHODS

3.1. Apparatus

The transmission electron microscopy (TEM) image of the CdSe QDs was acquired on a JEM2010FEF high-resolution transmission electron microscope (Japan). The UV-vis absorption spectra were performed on a Thermo Nicolet Corporation Model evolution 300 spectrophotometer coupled with a 1.00 cm quartz cell. The photoluminescence (PL) spectrum was acquired with Perkin-Elmer model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source. The ECL spectrum was obtained using color filters coupled with photomultiplier tube (PMT) held at -800 V. pH measurements were made with a Model PHS-3C meter (Shanghai Leici Equipment Factory, China).

Cyclic voltammogram and ECL curves were obtained simultaneously using electrochemical workstation coupled with a chemiluminescence detector (Xi'an Remax Science and Technology Co. Ltd., Xi'an, China). A three-electrode system was employed with Pt wire as a counter electrode, Ag/AgCl as a reference electrode, and 300- μ m diameter Pt disk as a working electrode. The solution used in each experiment required only 0.5 ml.

3.2. Reagents

Cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$), mercaptoacetic acid, selenium (Se), Na_2SO_3 , pyrogallol (1, 2, 3-trihydroxybenzene) and NaOH were purchased from

Shanghai Reagent Factory. Sodium dihydrogen phosphate (Beijing Chemicals Company) was used to prepare the electrolyte buffer solution. The pH of the buffer solution was adjusted with 0.1 M NaOH. H_2O_2 was purchased from Shantou Xilong Chemical Factory (Guangdong, China). 0.1 M Na_2SeSO_3 solution was prepared by stirring 0.158 g Se and 0.504 g Na_2SO_3 in 20 ml water and refluxing at approximately 100 C for 1 h. All other reagents were of analytical grade and used without further purification. Double distilled water was used throughout the whole experiments.

3.3. Preparation of CdSe QDs

CdSe QDs used in our experiments were synthesized and purified according to the method reported by Zhu *et al.* (19) with some modifications (20). In a typical synthesis, 0.684 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was dissolved in 50 ml distilled water at a 100 ml 3-neck round-bottom flask and then added to 0.3 ml mercaptoacetic acid. A white colloid was produced immediately in the solution. 1.0 M NaOH solution was used to adjust the pH to 11. Then, the 20 ml 0.1 M Na_2SeSO_3 solution was injected to the 3-neck round-bottom flask at the high-intensity ultrasonic horn (Xinzhì Co., China, Ti-horn, 300W, 40KHz) at 80 C. The whole process was under vigorous stirring at N_2 atmosphere for 0.5 h. After purification by precipitation, centrifugation and decantation, the vacuum-dried CdSe QDs were redispersed in water and kept in dark for further use. The concentrations of CdSe QDs solution were estimated from the absorption spectra using the molar absorptivity at the first absorption maximum for QDs of the size reported by Schmelz *et al.* (21).

4. RESULTS AND DISCUSSION

4.1. Characterization of the CdSe QDs

The particle sizes of the as-prepared CdSe QDs were measured from high resolution transmission electron microscopy image (Figure 2), which shows the average size of CdSe QDs is about 1.6 nm with narrow size distribution.

The UV-vis absorption spectrum indicates quantum confinement peak centered at 373 nm (Figure 3a) and the sharp absorption features demonstrate highly monodisperse samples (22). The band gap from the absorption peak is 3.3 eV (373nm) and is shifted to higher energy from the band gap of bulk CdSe (1.7 eV) (16) due to the well known quantum confinement effect. Figure 3b shows room temperature PL spectrum of CdSe QDs. The broad PL peak centered at 526 nm and 554 nm wavelength is due to defects in the semiconductor QDs crystal structure. These defects are either imperfections in the interior structure or at the surface and the defects may have great effect on ECL of the as-prepared QDs (23). The ECL (Figure 3c) peak at 530 nm is almost identical to the first PL peak at 526 nm. This phenomenon is similar to ECL of CdSe/ZnSe Nanocrystals dispersed in a CH_2Cl_2 solution (14).

4.2. ECL of as-prepared CdSe QDs

Figure 4b shows the CVs and ECL intensity-voltage dependencies of the CdSe QDs aqueous solution at

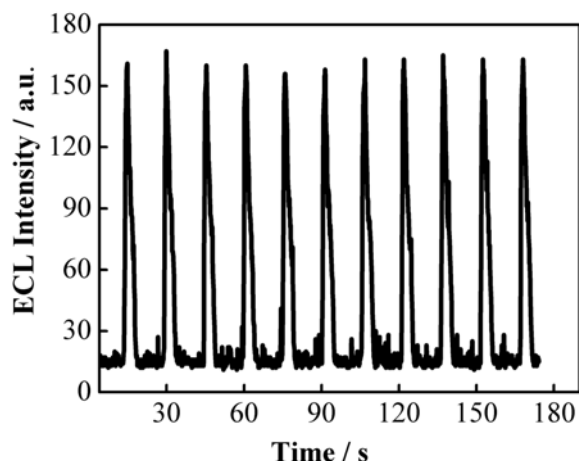


Figure 1. ECL intensity-time curve of 8.2×10^{-4} M CdSe QDs in 0.1 M pH 8.0 PBS buffer solution under continuous CVs for 11 cycles. Scan rate: 0.18 V/s, Scan potential: 0 - -1.4 V vs. Ag/AgCl.

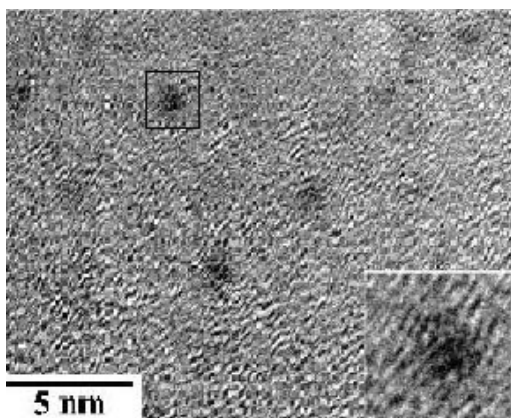


Figure 2. TEM image of CdSe QDs.

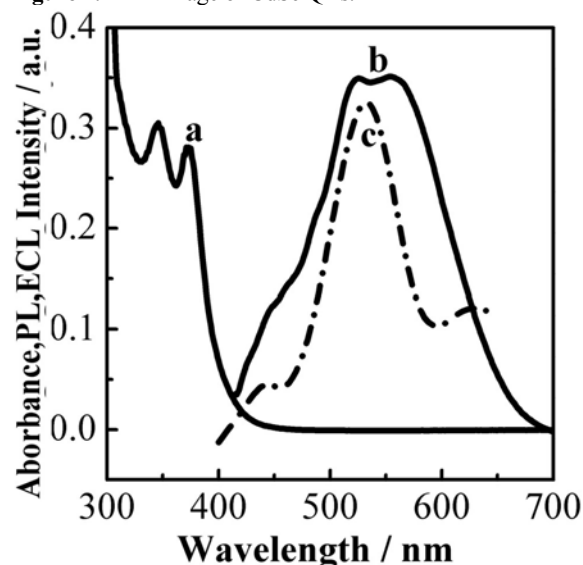


Figure 3. (a) UV-vis absorption spectrum (b) PL spectrum (c) ECL spectrum of CdSe QDs dispersed in aqueous solution.

0.18 V/s. Without CdSe QDs, 0.1 M PBS buffer at pH 8.0 shows very low background current, and no light emission is observed (Figure 4a). At the same conditions, both ECL and the cathodic current are greatly enhanced, and the ECL intensity reaches a maximum value at -1.4 V in the range from 0 V to -1.8 V in the aqueous solution of CdSe QDs (Figure 4b). It indicates CdSe QDs can be reduced to species ($\text{QDs}^{\bullet-}$) (18), which can react with oxidized species or some coreactants to produce excited states QDs^* and to emit light in aqueous system.

4.3. Effect of scan rate on ECL intensity

The effect of scan rate on ECL signal in QDs solution was studied in the range of 0.01~0.20 V/s. As shown in Figure 5, when the scan rate is below 0.08 V/s, ECL intensity is increased clearly with the increase of scan rate. The reason may be attributed to the formation of more reduced CdSe QDs species. The ECL intensity changes slightly along with the scan rate increasing between 0.01 and 0.18 V/s and reaches maximum at 0.18 V/s. So, considering saving time, in the following experiments, a scan rate of 0.18 V/s was recommended.

4.4. Effect of CdSe QDs concentration on ECL intensity

The concentration of CdSe QDs plays an important role for the ECL intensity as QDs can act as chemiluminescent emitter. The effect of CdSe QDs concentration on the ECL intensity was investigated. The result indicates that the ECL intensity increases along with the increasing of CdSe QDs concentration in the range from 0 to 9.0×10^{-4} M. The increasing of emission intensity was due to more reduced CdSe QDs species generated on electrode. When the concentration of CdSe QDs is more than 9.0×10^{-4} M, the ECL intensity decreases with the increasing of CdSe QDs concentration, which is due to an effect called self-absorption in higher concentration (24).

4.5. Effect of dissolved oxygen on ECL intensity

Effect of dissolved oxygen on ECL intensity was also investigated in the following experiments. As shown in Figure 6, when dissolved oxygen was removed from the solution by bubbling high-purity N_2 , light emission intensity of ECL decreased dramatically at the first a few minutes. As bubbling time prolonged, the decreased intensity trend became very slow. After bubbling high-purity N_2 for 50 min, immediately adding H_2O_2 to the solution, the ECL intensity was reversibly enhanced. What's more, the role of dissolved oxygen in the ECL was investigated with the aid of Na_2SO_3 . The result showed ECL intensity decreased greatly upon the addition of Na_2SO_3 (Figure 7). The concentration of oxygen in water can range from 0 to 15 mg/L (25). To acquire stable ECL, double distilled water was used at least 3 days after preparation.

4.6. Sensing application of CdSe QDs dispersed in aqueous solution for detection of pyrogallol

As an active reducing agent, pyrogallol was usually used in studying reaction mechanism. Pyrogallol can react with dioxygen in weakly alkaline solutions to form several intermediate products (26). In our experiments, pyrogallol was also employed to investigate

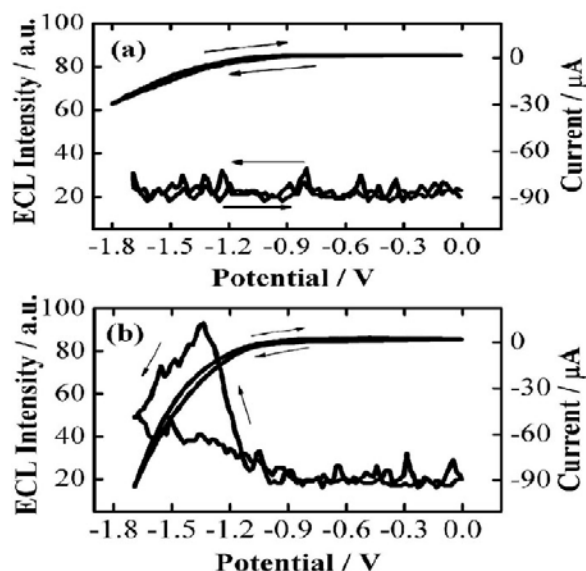


Figure 4. CVs and ECL curves of in the absence of CdSe QDs (a) and in the present of CdSe QDs (b) dispersed in 0.1 M pH 8.0 PBS buffer solution. Scan rate: 0.18 V/s, Scan potential: 0 - -1.8 V vs. Ag/AgCl.

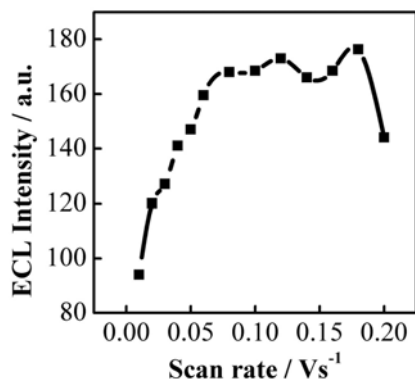


Figure 5. Effect of scan rate on ECL intensity of 8.2×10^{-4} M in 0.1 M pH 8.0 PBS buffer solution. Scan rate: 0.18 V/s, Scan potential: 0 - -1.4 V vs. Ag/AgCl.

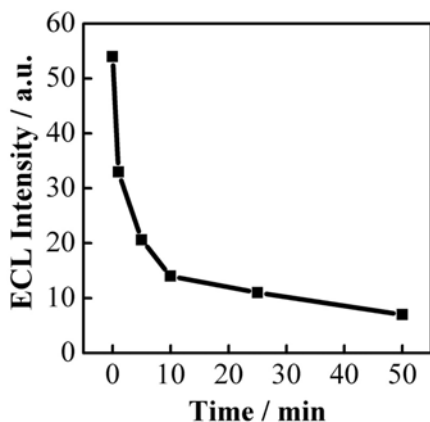


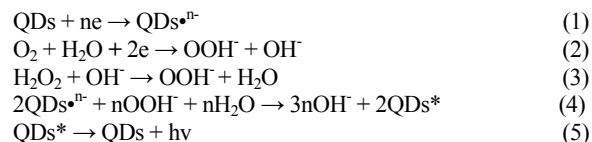
Figure 6. Effect of N₂ bubbling on ECL intensity of 4.5×10^{-4} M CdSe QDs in 0.1 M pH 8.0 PBS buffer solution. Scan rate: 0.18 V/s, Scan potential: 0 - -1.4 V vs. Ag/AgCl.

the mechanism of ECL reaction of CdSe QDs. It was found that pyrogallol appeared to inhibit the ECL intensity of QDs. This may be attributed to dissolved oxygen consumed by pyrogallol.

Furthermore, as a sensing application, we detected pyrogallol in CdSe QDs aqueous solution. A linear relation between the ECL intensity (I) and pyrogallol concentration (c) was obtained from 4.0×10^{-7} to 2.0×10^{-5} M and the corresponding linear regression equation is $I = 130.48 - 10.89 c$ (10^{-6} M) ($r = 0.9904$). The detection limit for pyrogallol was 6.6×10^{-8} M.

4.7. The possible mechanism of ECL of CdSe QDs

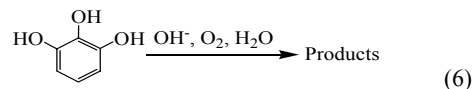
In comparison with previous work, the ECL mechanism of CdSe QDs in present work is investigated in aqueous solution, so it is very important to study the mechanism. Based on above results and some references (15 – 18, 27), a possible mechanism for the ECL of CdSe QDs is suggested as follows:



When electrode potential scanned from 0 V to -1.8 V, QDs can be reduced to $\text{QDs}^{\bullet n-}$ (Eq.(1)). Since ECL occurred in aqueous solution, the coreactants such as dissolved oxygen or its reduced product OOH^- took part in the reaction Eq.(2-4). When excited states QDs^* comes back to ground states, light emission occurs (Eq.(5)).

Concerning ECL of QDs, the surface states and the quantum size effects play an important role on generating chemiluminescence and previous reports have also indicated that ECL of QDs is very sensitive to surface states (17). Unlike the result with CdSe QDs reported previously, the negative window voltage (~ -1.8 V) is substantially less negative potential than the optical band gap estimated from the absorption maximum in Figure 3a, indicating the excitation potential of CdSe QDs is nearer to 0 V and required energy is corresponding lower. It is attributed to extremely small size of the CdSe QDs used in the experiments, resulting in more surface defects generated and these defects can act as temporary “traps” for the electron or hole. Energy required from trap to trap to produce luminescence is less than that from valence band to the conduction band (23). Above results are consistent with the result that ECL behavior of QDs is sensitive to and dependent on their surface defects.

As mentioned above, dissolved oxygen has great influence on ECL intensity due to OOH^- produced from it reacting with $\text{QDs}^{\bullet n-}$ (Eq.(2,3)). If pyrogallol was added to the system, it would react with oxygen (Eq.(6)) (26), which resulted in decrease of ECL intensity, and which meanwhile provided a further confirm to the above results about the role of dissolved oxygen.



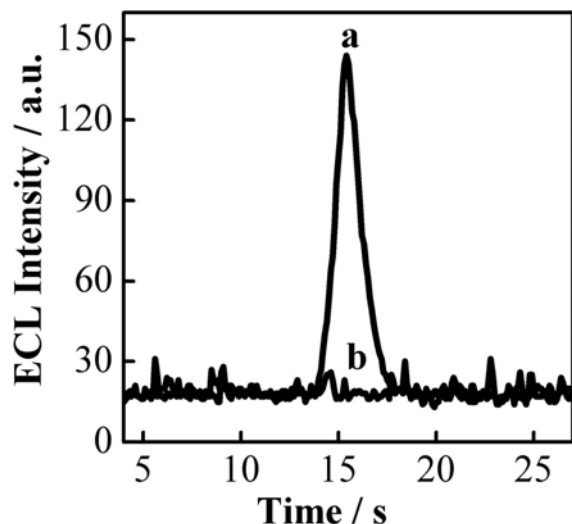


Figure 7. ECL curves of CdSe QDs (a) before and (b) after adding Na_2SO_3 .

5. SUMMARY

In summary, a novel and simple method was developed to obtain ECL from CdSe QDs dispersed in aqueous solution. The ECL of CdSe QDs has been investigated in detail, which can be used as a sensor for the determination of pyrogallol. The proposed method also opens a potential way for QDs ECL application to the bioanalysis in future.

6. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support for this research by Program for New Century Excellent Talents in Chinese Ministry of Education (NCET-05-0668), the Key (Key grant) Project of Chinese Ministry of Education (106120), the Key Program from Hubei Province of China (2005AA201C25), the Nature Science Foundation from Hubei Province of China (2006ABA160) and National Natural Science Foundation of China (20275028). We also thank Associate Professor Dongshan Zhao of Center for Electron Microscopy (Wuhan University), for his help with TEM measurements.

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Abbreviations: ECL: Electrogenerated chemiluminescence; QDs: quantum dots; PL: photoluminescence; CVs: cyclic voltammograms; TEM: transmission electron microscopy; PMT: photomultiplier tube;

Key Words: Electrogenerated chemiluminescence, CdSe, Quantum dots

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