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Electrogenerated chemiluminescence resonance energy transfer between lucigenin and CdSe quantum dots in the presence of bromide and its sensing application

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ABSTRACT

Electrogenerated chemiluminescence (ECL) of lucignein often suffered from weak signal at positive potential in neutral condition. In the present study, strong anodic ECL was obtained in neutral lucigenin solution at a CdSe quantum dots modified glassy carbon electrode. Electrochemical results suggested that CdSe quantum dots can catalyze the oxidation of lucigenin and bromide, which can generate the anodic ECL. The fluorescence and the ECL spectra revealed that ECL resonance energy transfer (ECL-RET) can occur between lucigenin and CdSe quantum dots. The oxidation product of bromide can promote ECL-RET and increase the anodic ECL signal significantly. The mechanisms of the anodic ECL based on the ECL-RET were proposed. Cytochrome C exhibited apparent inhibiting effect on the anodic ECL emission, based on which a sensitive ECL sensor for the detection of cytochrome C was established.

1. Introduction

During the past few decades, electrogenerated chemiluminescence (ECL) has been paid considerable attention due to its promising advantages, such as simplicity, high sensitivity, and easy controllability [1]. Since chemiluminescence (CL) of lucigenin (N,N′-dimethyl-9,9′-biacridinium dinitrate) was first reported in 1935, the cathodic lucigenin ECL has been widely investigated at different electrodes in alkaline condition [2–8]. However, for bioanalytical applications, it is high desirable to obtain anodic ECL in neutral aqueous media [9]. Only several work studied the anodic lucigenin ECL, which often suffered from weak and unstable signals in neutral solution [10–12]. Previous work found that nanoparticles could greatly enhance lucigenin ECL either by immobilizing on the electrode or dispersing in solution [13,14]. Therefore, it is expected that the intense anodic lucigenin ECL can be obtained by modifying a bare electrode with suitable nanomaterials. Recently, strong and stable cathodic ECL has been obtained at different quantum dots (QDs) modified electrodes in the presence of coreactant [15–17]. Except their excellent ECL behaviors, QDs also exhibited good catalytic effect on CL reactions due to the redox properties of the conduction and valence bands [18]. However, the catalytic application of QDs in ECL investigation is rarely reported.

Luminescence resonance energy transfer (LRET) is a powerful technique for probing changes in the distance between energy donors and acceptors. According to the different types of the donor luminescence, three kinds of LRET, such as fluorescence resonance energy transfer, chemiluminescence resonance energy transfer, and bioluminescence resonance energy transfer, have been reported and widely used in the bioassays [19–21]. Nevertheless, rare attention has been paid to the ECL resonance energy transfer (ECL-RET) as a result of the difficulty in finding a suitable donor/acceptor pair. Up to date, several ECL-RET systems regarding quantum dot, luminol, and $Ru(bpy)_3^{2+}$ have been reported and applied in biosensor [22–25]. These work suggested that ECL-RET can occur between traditional luminescent reagents and quantum dots. However, the exploration of new donor/acceptor pair is still needed and ECL-RET between lucigenin and QDs has never been reported.

Herein, the anodic ECL resulting from ECL-RET between lucigenin (Luc) and CdSe QDs is observed in neutral condition, which can be enhanced greatly in the presence of bromide. Cytochrome C (Cyt C) exhibits inhibiting effect on the anodic ECL signal and can be sensitively detected.

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2. Materials and methods

2.1. Chemicals

Lucigenin and cytochrome C were purchased from Sigma–Aldrich. A lucigenin stock solution (0.01 mol L^{-1}) was prepared by dissolving lucigenin in double distilled water and stored in the refrigerator. All other chemicals were analytical grade and double distilled water was used throughout. 0.1 mol L^{-1} pH 7.4 phosphate buffer solution (PBS) was prepared by mixing the stock solutions of Na_2HPO_4 and NaH_2PO_4, and then adjusting the pH with 0.1 mol L^{-1} NaOH and H_3PO_4.

2.2. Instruments

The electrochemical measurements were recorded with CHI 660D electrochemical workstation (CH Instruments Co., China). The ECL emission measurements were conducted on a model MPI-M electrochemiluminescence analyzer (Xi'An Remax Electronic Science & Technology Co., Ltd., China) at room temperature, and the voltage of the photomultiplier tube (PMT) was set at −800 V in the process of detection. All experiments were carried out with a conventional three-electrode system, including a modified GCE as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively. A commercial 5 ml cylindroid glass cell was used as ECL cell and was placed directly in front of the PMT. High resolution transmission electron microscopy (HRTEM) was obtained on a JEOL-2100 transmission electron microscopy (JEOL, Japan). The UV–vis absorption spectra were obtained on a Shimadzu UV-3600 spectrophotometer (Shimadzu, Japan). The fluorescence measurements were carried out on a RF-5301PC FL spectrophotometer (Shimadzu, Japan). The ECL spectrum was obtained by collecting the ECL data during cyclic potential sweep with 8 pieces of filter at 425, 450, 475, 500, 525, 550, 575, and 600 nm, respectively.

2.3. Fabrication of CdSe QDs modified electrode

Mercaptoacetic acid-capped CdSe QD was synthesized following literature procedures and characterized as shown in Figs. S1 and S2 [15]. A glassy carbon electrode was mechanically polished to a mirror with alumina pastes of 1.0, 0.3 and 0.05 μm respectively, and then cleaned thoroughly in an ultrasonic cleaner with alcohol and water sequentially. When it was dried with blowing N_2, 10 μL of CdSe QDs was spread on the working area and dried at the room temperature to fabricate CdSe QDs modified GCE (denoted as QDs/GCE). Electrochemical impedance spectroscopy (EIS) was used to monitor the fabrication process of CdSe QDs on a bare GCE as shown in Fig. S3. Due to the existence of electrostatic repulse force between negatively charged QDs and $[Fe(CN)6]^{3-/4-}$, the diameter of Nyquist circle increases with the amount of QDs modified on the electrode, which can indicate that QDs are successfully modified on the GCE.

3. Results and discussion

3.1. ECL of lucigenin at the QDs/GCE

Previous work revealed that the anodic lucigenin ECL could be obtained at nanomaterial modified electrode but its intensity was weaker than the cathodic counterpart [10]. In the present study, CdSe quantum dots were synthesized and the size of QDs was estimated to be 2.2 nm according to Peng's work [26]. The anodic ECL was comparatively studied at the QDs/GCE in neutral lucigenin solution with and without bromide as shown in Fig. 1. One extremely weak anodic ECL located at ~1.50 V at the QDs/GCE in phosphate buffer solution (PBS) can be assigned to the reaction between the oxidized QDs and $O_2^{\bullet-}$ [17]. In the presence of lucigenin, no anodic ECL is observed at the bare GCE while one anodic ECL is observed at 1.20 V at the QDs/GCE, suggesting that QDs is necessary for the anodic ECL. The intensity of anodic ECL is enhanced 4-times in the presence of bromide, revealing that Br^- can participate in ECL reactions. The similar effect of bromide on $Ru(bpy)_3^{2+}$ ECL was also reported by Bard et al. and they claimed that the oxidation product of Br^- can participate ECL reactions [27]. The mechanism of the anodic ECL and the enhancing effect of bromide on the present ECL system will be discussed in the following.

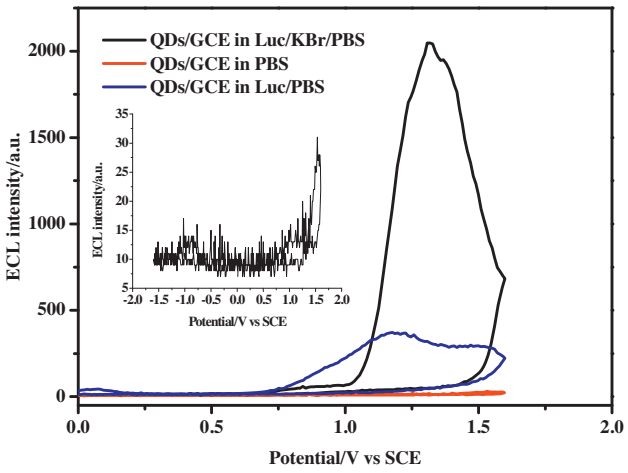

Fig. 1. ECL curves of lucigenin at a QDs/GCE in neutral condition with and without bromide. Lucigenin, 1.0×10^{-4} mol L^{-1}; PBS, 0.1 mol L^{-1}; pH, 7.4; KBr, 0.1 mol L^{-1}; scan rate, 100 mV s^{-1}. The inset is the enlarged ECL curve of the QDs/GCE in PBS.

The effect of pH on the anodic ECL signals was examined in the pH range of 6.0–8.0 as shown in Fig. 2. In the pH range, the ECL intensities increase with the increase of pH value and reach the maximum value at pH 7.4. Further increase of pH value, the ECL signal begins to decrease. These results suggest that OH^- cannot affect the anodic ECL as its influence on lucigenin CL [2].

3.2. Electrochemistry of lucigenin at the bare GCE and the QDs/GCE

Cyclic voltammograms (CVs) of the QDs/GCE and the bare GCE were comparatively studied in Luc/KBr/PBS under air-saturated condition as shown in Fig. 3. In Fig. 3A, the cathodic CV peak (cvp1)

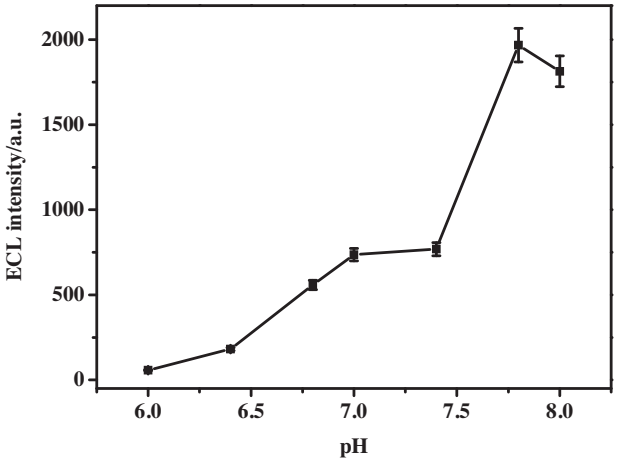

Fig. 2. Effect of pH on ECL signals at a QDs/GCE. Lucigenin, 1.0×10^{-4} mol L^{-1}; PBS, 0.1 mol L^{-1}; KBr, 0.1 mol L^{-1}; scan rate, 100 mV s^{-1}.

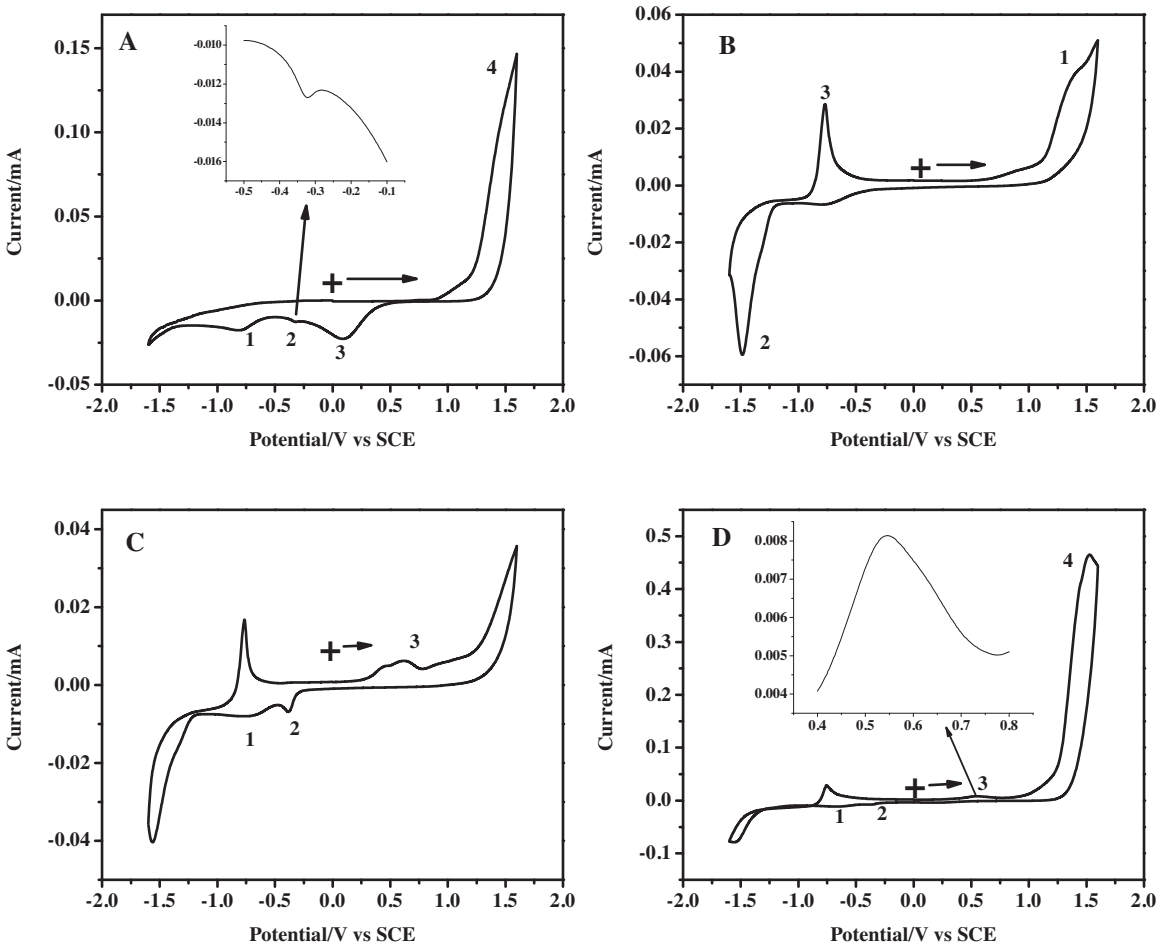

Fig. 3. Cyclic voltammograms of a bare GCE in Luc/KBr/PBS (A), a QDs/GCE in PBS (B), Luc/PBS (C), and Luc/KBr/PBS (D). Lucigenin, 1.0×10^{-4} mol L^{-1}; PBS, 0.1 mol L^{-1}; pH, 7.4; scan rate, 100 mV s^{-1}; KBr, 0.1 mol L^{-1}. The insets in A and D are the enlarged CV of the reduction of lucigenin and the oxidation of DBA.

at −0.80 V which cannot be found under N_2-saturated condition is the reduction of dissolved O_2. The weak cvp2 at −0.34 V (The inset of Fig. 3A) is the reduction of lucigenin because it can only be observed in the presence of lucigenin. Cvp2 is partially overlapped by cvp3, which make the peak shape not obvious. The cathodic cvp3 at 0.10 V can be assigned to the reduction of Br• because this peak can only be obtained when the switching potential is higher than the oxidation potential of Br^- and disappears when $NaNO_3$ was used as an electrolyte instead. The oxidation peak around ~1.50 V (cvp4) is the oxidation of Br^- to Br• [28,29]. Fig. 3B depicts the CV of the QDs/GCE in PBS. The cvp1 at 1.10 V corresponds to the oxidation of CdSe QDs. The cvp2 at −1.50 V and the cvp3 at −0.75 V are the reduction of cadmium ion and the anodic stripping of cadmium, respectively [17]. Fig. 3C depicts the CV of the QDs/GCE in Luc/PBS. Cvp1 and cvp2 correspond to the reduction of dissolved oxygen and lucigenin as these at the bare GCE. Compared with the reduction of lucigenin at the bare GCE (Fig. 3A), the peak potential of cvp2 (−0.37 V) is negatively shifted while the peak current is slightly increased which should be due to the increase of active surface area of the QDs/GCE [30]. Since no bromide is added in the solution, the peak shape of cvp2 is more obvious compared with that at the bare GCE. One broad oxidation peak (cvp3) is observed at ~0.50 V, which cannot be observed at the QDs/GCE without lucigenin (Fig. 3B), and can be observed only after lucigenin was reduced. It was reported that the reduction product of lucigenin (dimethylbiacridine, DBA) can be re-oxidized at 0.45 V in nonaqueous condition [31]. Therefore, it is reasonable to speculate that this peak corresponds to the oxidation of DBA catalyzed by QDs because this peak cannot be obtained in lucigenin solution at the bare GCE (Fig. 3A). In Fig. 3D, cvp1-3 can be obtained at the same potentials as those of Fig. 3C. The similar CV peaks of DBA in the absence and presence of bromide, suggesting that bromide cannot influence the oxidation of DBA at the QDs/GCE (the inset of Fig. 3D). The oxidation current of bromide (cvp4) at the QDs/GCE increases 3-times compared with the bare GCE (cvp4 in Fig. 3A), suggesting that QDs can catalyze the oxidation of Br^- to Br•. Subsequently, Br• can react with the oxidation product of DBA because the reduction peak of Br• at 0.10 V (cvp3 in Fig. 3A) cannot be observed in the presence of lucigenin.

3.3. ECL-RET between lucigenin and QDs

ECL spectrum, UV–vis absorption spectra and FL spectra of lucigenin and QDs in the presence of KBr were recorded as shown in Fig. 4. In Fig. 4A, the ECL spectrum includes two peaks at 490 nm and 560 nm, corresponding to the ECL emission of lucigenin and QDs respectively [8,15]. It can be found from Fig. 4B that lucigenin solution exhibits two strong and broad absorption bands at ca. 365 nm and 430 nm. QDs solution exhibits a broad absorption band in a range of 300–550 nm, which is consistent with the previous report [15]. Luc/QDs solution shows apparent decreased absorption peaks, although its absorption feature is similar to that of lucigenin solution. The observed difference is that positively charged lucigenin can be spontaneously adsorbed on the surface of negatively charged QDs due to the electrostatic interaction [32]. The UV–vis absorption spectra reveal that there has no chemical interaction between lucigenin and QDs (Fig. 4B).

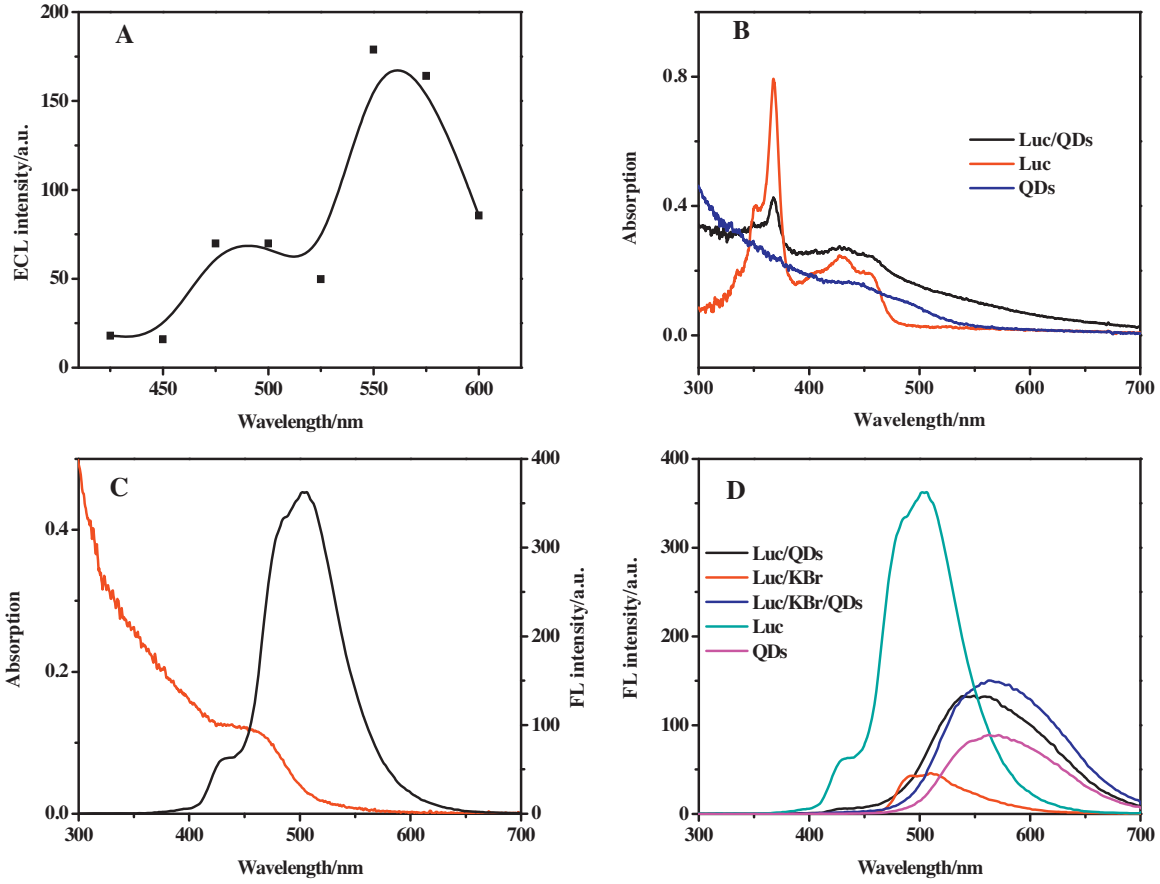

Fig. 4. (A) ECL spectra of lucigenin ECL at the QDs/GCE. (B) UV–vis absorption spectra of Luc, QDs, and Luc/QDs. (C) UV–vis absorption spectra of QDs and FL spectra of lucigenin. (D) Fluorescence spectra of lucigenin, QDs, Luc/QDs, and Luc/QDs/KBr.

It can be found from Fig. 4C that the absorption peak of QDs (465 nm) overlaps with the emission peak of lucigenin (490 nm), suggesting that ECL-RET can occur between them. In Fig. 4D, the maximum FL emissions of lucigenin and QDs are at 500 nm and 565 nm respectively. When KBr was added into lucigenin solution, the FL of lucigenin decreased significantly due to the heavier halide ions quenching effect [33]. When QDs were mixed with lucigenin, the FL of lucigenin almost disappeared while the FL of QDs increased, suggesting that energy transfer occurs between lucigenin and QDs. Br^- is helpful for the energy transfer because the FL of Luc/QDs mixture is further increased in the presence of bromide. The effect of bromide concentration on FL of QDs and Luc/QDs as well as ECL signal was studied as shown in Fig. 5. The FL of lucigenin decreased with the increase of bromide concentration. However, the FL of the Luc/QDs mixture increases with the increase of bromide concentration at low concentration and decreases when bromide concentration is higher than 0.05 mol L^{-1}. The effects of bromide concentrations on the ECL signals exhibited similar behavior while the maximum value appeared at 0.1 mol L^{-1}. The different effects of bromide on FL and ECL also support ECL-RET.

3.4. ECL mechanisms

It was reported that the oxidation of DBA could occur via one-electron oxidation to yield $Luc^{\bullet+}$ at the positive potential in nonaqueous solution [31,34]. However, the oxidation of DBA is difficult at the bare GCE in aqueous condition. In the present study, DBA can be oxidized at the QDs/GCE in aqueous solution due to the catalytic effect of QDs. The oxidation product of DBA ($Luc^{\bullet+}$) can react with the dissolved oxygen to generate CL [11]. During CL process, the excited state of N-methylacridone (NMA) can be generated firstly. The excited NMA can transfer its energy to lucigenin forming the excited lucigenin which will emit light at ~490 nm [2,8]. ECL emission was tested under different atmosphere. It was found that ECL signal can be enhanced greatly under O_2 atmosphere and can be inhibited under N_2 atmosphere. Therefore, the ECL peak at 490 nm can be generated as follows:

$$DBA - e \rightarrow Luc^{\bullet+} \quad (1)$$

$$Luc^{\bullet+} + O_2 \rightarrow Luc^{2+} + O_2^{\bullet-} \quad (2)$$

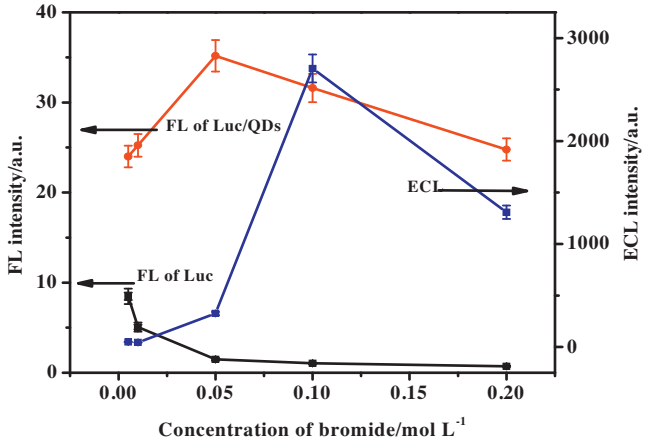

Fig. 5. Effect of KBr concentration on the FL of Luc and Luc/QDs and the ECL signal of lucigenin at the QDs/GCE.

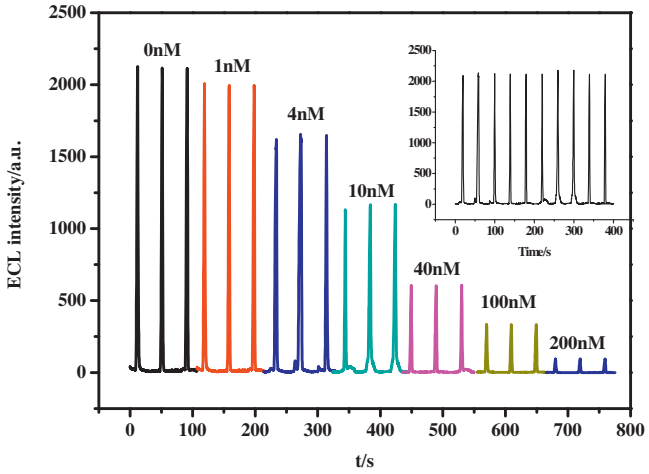

Fig. 6. ECL profiles of different concentrations of Cyt C. The inset is continuously cyclic potential scanning of the sensor for 10 cycles.

$$Luc^{\bullet+} + O_2^{\bullet-} \rightarrow NMA* \quad (3)$$

$$NMA* + Luc \rightarrow NMA + Luc* \quad (4)$$

$$Luc* \rightarrow Luc + h\nu(490\,nm) \quad (5)$$

The excited state of lucigenin can transfer its energy to QDs due to the overlap of the absorption spectra of QDs and the emission spectra of lucigenin. The mechanism for the anodic ECL at ~560 nm should be as follows:

$$Luc* + QDs \rightarrow Luc + QDs* \quad (6)$$

$$QDs* \rightarrow QDs + h\nu(560\,nm) \quad (7)$$

Jiang et al. reported that bromide ($E^0(Br^{\bullet}/Br^-) = 1.92$ V vs. SHE) can enhance lucigenin ECL at low concentration because $Br^{\bullet}$ is capable of participating in CL pathways more efficiently than hydroxyl radicals [4]. In the present study, no anodic ECL was obtained at the bare GCE in the presence of bromide, revealing that the oxidation product of Br^- cannot generate anodic ECL with lucigenin. Weak anodic ECL was obtained at the QDs/GCE in lucigenin without KBr, revealing that QDs is necessary for the anodic ECL. The anodic ECL at the QDs/GCE increases greatly in the presence of KBr, suggesting that both KBr and QDs are needed for the strong anodic ECL. The electrochemical results revealed that QDs can catalyze the oxidation of Br^- and DBA. The oxidation product of DBA ($Luc^{\bullet+}$) can react with the oxidation product of Br^- ($Br^{\bullet}$) to generate anodic lucigenin ECL, which can then transfer its energy to QDs to generate stronger anodic ECL. Further increase in bromide concentration, Br_3^- can be formed ($E^0(Br_2/Br_2^{\bullet-}) = 0.58$ V vs. SHE), which cannot participate in luminescent process and result in the decreased ECL signal. The mechanism of bromide participated ECL should be as follows:

$$Br^- - e \rightarrow Br^{\bullet} \quad (8)$$

$$Br^{\bullet} + Luc^{\bullet+} \rightarrow NMA* \quad (9)$$

3.5. Analytical performance of the ECL sensor

The proposed ECL-RET system is used to detect Cyt C as shown in Fig. 6. The ECL intensity decreased in the presence of Cyt C because Cyt c can react with $O_2^{\bullet-}$, which will compete with ECL reactions [35]. The ECL intensity decreases linearly with the Cyt C concentrations ranging from 1 nM to 200 nM ($R = 0.993$) with a detection limit of 0.8 nM ($S/N = 3$). Compared with other analytical method for the detection Cyt C, the fabricated ECL sensor displays higher sensitivity [36,37]. The selectivity is an important factor for biosensor. To evaluate the specificity of the ECL sensor, the ECL signals were recorded by adding some potential interfering substances in the working solution instead of Cyt C, including dopamine, catechol, cysteine, ascorbic acid, hydroquinone, glucose, thrombin, lysozyme, bovine serum albumin (Fig. S4). Comparing with the quenching effect of Cyt C, the effect of these interferences exhibited negligible inhibiting effects on ECL. According to Eq. (3) in ECL mechanism, superoxide radicals are necessary for the generation of the excited state of NMA. It is well-known that Cyt C has the scavenging ability to superoxide radicals [38]. Therefore, the decreased ECL signal and the good selectivity of ECL sensor should be result from the reaction between Cyt C and superoxide radicals. In order to support this speculation, superoxide dismutase (SOD) was added in the working solution and the decreased ECL signal was obtained. As a result, the present ECL sensor has good selectivity for the determination of Cyt C due to its scavenging ability to superoxide radicals.

The stability is an important factor to the capability of the sensor and it was evaluated by one electrode to monitor the ECL responses as shown in the inset of Fig. 6. There was no obvious change of ECL intensity when the biosensor was studied under continuously cyclic potential scanning for 10 cycles indicating the good stability of the present sensor. The repeatability of the sensor was estimated by assaying 5 nM Cyt C for six replicate measurements. No significant difference was found. The electrode-to-electrode reproducibility was also estimated by detecting 5 nM Cyt C with five different ECL sensors. It was found that five electrodes exhibited similar ECL response and relative standard deviation was 5.7%. The above experimental results indicate that the ECL sensor has good performance.

4. Conclusion

In summary, electrogenerated chemiluminescence resonance energy transfer between lucigenin and CdSe QDs was reported. Anodic lucigenin ECL at the QDs/GCE can transfer its energy to QDs to generate stronger anodic ECL. The oxidation of Br^- can be catalyzed at the QDs/GCE, which can participate in anodic ECL process and enhance ECL signal. The as-prepared ECL sensor can be used in the sensitive detection of Cyt C. Furthermore, ECL-RET between lucigenin and QDs will be a promising option for the development of various lucigenin involved ECL sensors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2015.09.020.

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