



# Cathodic electrochemiluminescence from self-designed near-infrared-emitting CdTe/CdS/ZnS quantum dots on bare Au electrode

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## ABSTRACT

Cathodic electrochemiluminescence (ECL) from self-designed near-infrared (NIR)-emitting CdTe/CdS/ZnS quantum dots (QDs) on bare Au electrode in aqueous solution was studied. Strong and stable ECL signals at  $-1.25$  V with an onset potential of  $-0.98$  V produced by the highly effective electron-transfer reactions between electron-injected CdTe/CdS/ZnS QDs and reduced  $S_2O_8^{2-}$  are observed. Passivation of the QD surfaces with ZnS shell increased ECL intensity by 9 times when compared to CdTe/CdS QDs. The good correspondence of the ECL emission peak with the photoluminescence results suggested the surface states of the QDs had been largely passivated by ZnS shell. Furthermore, the effects of pH, buffer solutions, electrode materials and concentrations of  $K_2S_2O_8$  on ECL intensity were investigated, and a possible ECL mechanism was also proposed.

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## 1. Introduction

Electrochemiluminescence (ECL) has been developed as one of the most versatile analytical techniques because of its high sensitivity, simplified optical setup, and excellent controllability in space and time [1]. In ECL, quantum dot (QD)-based systems are extremely important for their strong ECL responses and promising applications in chemical sensing [2,3]. Particularly, near-infrared (NIR)-emitting QDs with emission wavelengths between 650 and 900 nm would play an increasing role in the near future with the development of QD-based ECL sensors in actual biological samples due to their outstanding photostability, longer decay lifetime and special properties in tissue [4]. Currently, there has been a growing interest in ECL studies of NIR-emitting QDs [5,6]. Sun et al. studied the ECL from PbS QDs in  $CH_2Cl_2$  media and demonstrated that ECL was more sensitive than photoluminescence (PL) to surface chemistry [5]. Zhu's group studied the strong ECL from water-soluble CdSeTe/ZnS QDs and proposed a QDs-coreactant ( $S_2O_8^{2-}$ ) ECL mechanism [6]. However, the ECL studies from NIR-emitting QDs have proven to be much more challenging and it is difficult to obtain water-soluble NIR-emitting QDs with indispensable properties as ECL biosensors, such as low applied potential, high ECL activity and stable ECL signals. To achieve such objectives, it is essential to design some simple and effective water-soluble NIR-emitting QDs for ECL study, which might promote the further development of ECL biosensors.

Herein, we present the fabrication of CdTe/CdS/ZnS QDs and the investigation of ECL from the QDs in aqueous solution. The epitaxial

growth of a CdS shell on a soft nanocrystalline core (CdTe) resulted in a bandgap-tunable QDs could tune the PL emission to NIR range [7] and provide a possibility for obtaining low potential ECL emission [8]. On the other hand, the ZnS shell efficiently increased the structural stability and protected the surface properties of the QDs, which could offer an avenue for producing strong and stable ECL signals. During cathodic scanning, the NIR-emitting QDs showed a strong and stable ECL signal at  $-1.25$  V, which was 9 times larger than the intensity of the maximum ECL emission from CdTe/CdS QDs. The observed similar peaks of the ECL and PL spectra demonstrated that a significant reduction of deep surface traps from the QDs passivated with ZnS shell. The goal of studying this system is to fabricate higher efficiency NIR ECL reagent for various ECL applications in biological samples, as well as gain a better understanding of the fundamental properties of the ECL from NIR-emitting QDs.

## 2. Experimental section

### 2.1. Apparatus and reagents

ECL studies were performed using a Model MPI-EII ECL Analyzer Systems, and the details on manipulation could be found in previous report [9]. Data of absorption spectra, PL, X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) were acquired according to the reported methods [10]. Tellurium powder,  $CdCl_2 \cdot 2.5H_2O$ ,  $NaBH_4$ ,  $ZnCl_2$ ,  $Na_2S \cdot 9H_2O$ ,  $K_2S_2O_8$  and mercaptopropionic acid (MPA) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). All chemicals concerned were of analytical grade and all solutions were prepared with ultrapure water obtained from a Millipore water purification system ( $\geq 18$  M $\Omega$ , Milli-Q, Millipore).

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## 2.2. Preparation of samples

The NIR-emitting MPA-CdTe/CdS QDs were synthesized according to the hydrothermal method [11]. A quarter of the obtained crude products were precipitated for three times by ethanol with centrifugation at 8000 rpm for 5 min and the resultant precipitates were re-dissolved in 5 mL ultrapure water and used as CdTe/CdS QDs in subsequent steps.

The NIR-emitting MPA-CdTe/CdS/ZnS QDs were prepared by adding the above prepared CdTe/CdS precursor solution to 5 mL  $N_2$ -saturated solution with 0.06 mmol  $ZnCl_2$  and 0.15 mmol MPA (pH 8.5–9.5), and heated to 65 °C. Under vigorous stirring, the prepared 0.05 mmol  $Na_2S$  solution was added slowly to the heated mixture. The prepared precursor solution was refluxed at 65 °C for 60 min. Thus, the NIR-emitting CdTe/CdS/ZnS QDs were successfully obtained.

## 3. Results and discussion

Fig. 1A demonstrates the typical absorption and PL spectra of CdTe/CdS and corresponding CdTe/CdS/ZnS QDs. In PL spectra, a slight red-shift and significantly enhanced PL intensity were observed after ZnS coating, which could be respectively due to the increase in the size of the QDs and the effective passivation of the QD surface with a ZnS shell. In addition, the absorption peak of CdTe/CdS/ZnS QDs was also slightly red-shifted after the formation of a ZnS shell. The obtained QDs were systematically characterized by XRD and HRTEM. XRD patterns (Fig. 1B) of CdTe/CdS QDs and CdTe/CdS/ZnS QDs show the representative diffractive peaks for nanoparticles. With the growth of ZnS shell, the peak positions shifted slightly toward larger angles as compared with the CdTe/CdS QDs, while the pattern of peak widths and shapes almost remained unchanged, which further demonstrated the formation of a ZnS shell on the surface of CdTe/CdS QDs. As shown in Fig. 1(C, D), the

HRTEM images illustrate the nearly spherical and monodispersed QDs and they possessed good crystal structures (inset).

The ECL and cyclic voltammograms (CVs) properties of CdTe/CdS/ZnS QDs at Au electrode were studied in detail. In air-saturated pH 7.0 NaAc–HAc buffer solution, upon cyclic potential scanning the CdTe/CdS/ZnS QDs did not produce any ECL emission (curve a in Fig. 2B), although a cathodic reduction peak of the QDs was observed at  $-0.92$  V (curve a in Fig. 2A), while the reduction of  $K_2S_2O_8$  produced a very weak ECL signal between  $-1.10$  and  $-1.50$  V (curve b in Fig. 2B). After mixing  $K_2S_2O_8$  with CdTe/CdS/ZnS QD solutions, the mixture showed a strong ECL emission peak at  $-1.25$  V with an onset potential of  $-0.98$  V (curve d in Fig. 2B), which was 40 times the intensity of the maximum ECL emission from  $K_2S_2O_8$ . To the best of our knowledge, it was the first time to obtain a potential window from NIR-emitting QDs. Under this potential window, some by-reactions such as the hydrogen evolution for the reduction of  $H_2O$  and interference with the ECL process could be effectively cut down, which may be in favor of the application in biological systems.

Interestingly, we observed two obvious cathodic peaks of CVs from CdTe/CdS/ZnS QDs in pH 7.0 NaAc–HAc buffer solution containing 10 mM  $K_2S_2O_8$  at ca.  $-0.76$  and  $-1.03$  V in Fig. 2A (d), which was respectively corresponding to the reduction of  $S_2O_8^{2-}$  ions (curve b in Fig. 2A) and CdTe/CdS/ZnS phase (curve a in Fig. 2A). This fact indicated that the strong ECL peak at  $-1.25$  V was produced by the reaction of the reduction products from CdTe/CdS/ZnS QDs and  $S_2O_8^{2-}$ . Furthermore, the ECL intensity of this novel ECL reagent was increased more than 9 times over that of CdTe/CdS QDs (curve c in Fig. 2B), which may be due to the decrease of surface traps [12] of the QDs with ZnS shell. Additionally, the ECL intensities collected at  $-1.25$  V remained at a comparatively stable value during consecutive cyclic potential scanning (Fig. 2C), indicating an acceptable stability for ECL detection.

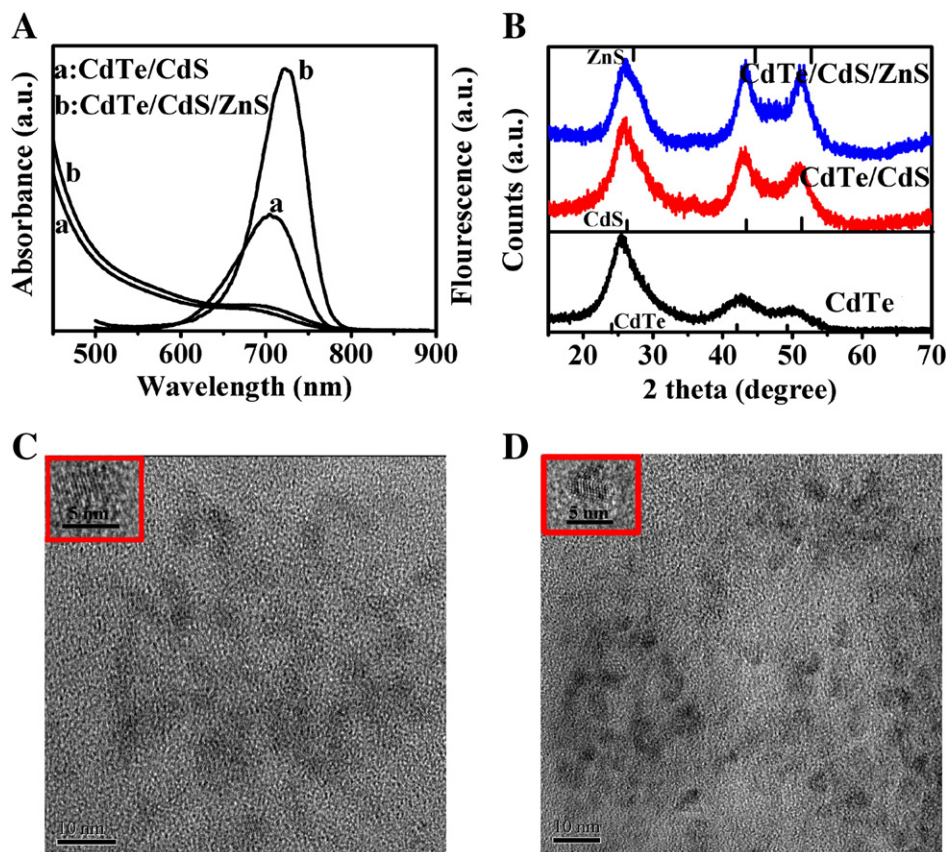
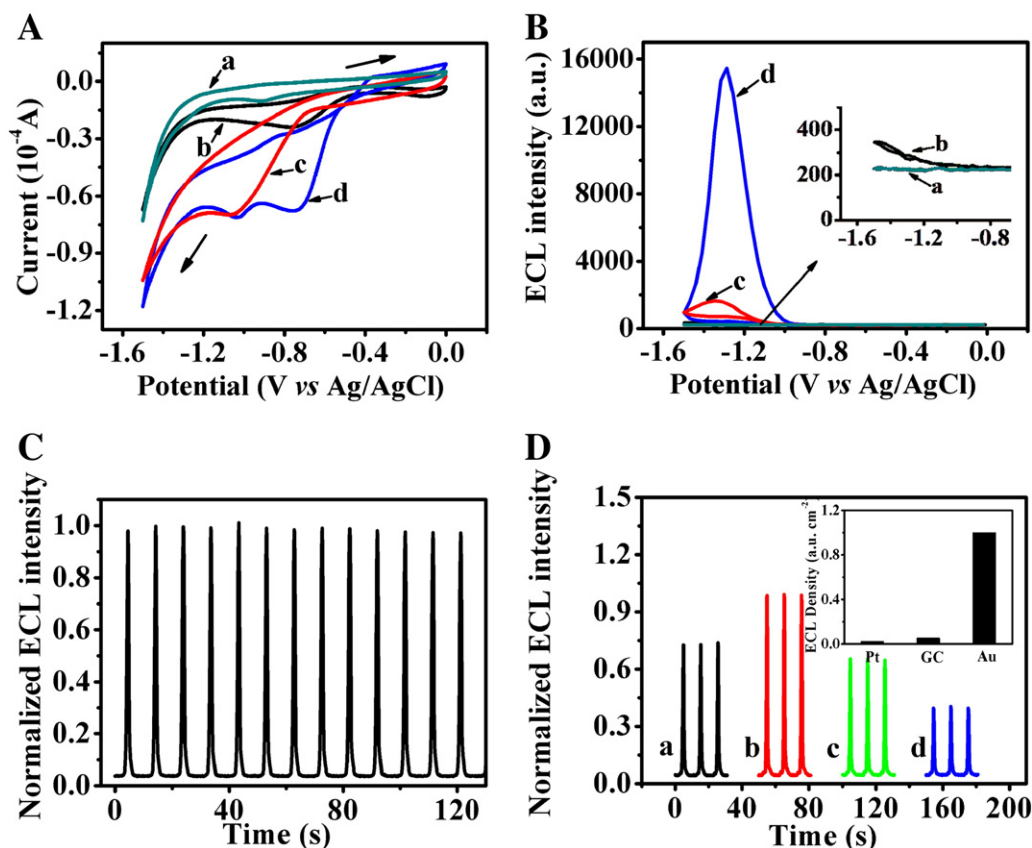


Fig. 1. (A) PL and absorption spectra of (a) CdTe/CdS and (b) CdTe/CdS/ZnS QDs. (B) XRD patterns of CdTe/CdS and CdTe/CdS/ZnS QDs. (C) HRTEM image of CdTe/CdS QDs. (D) HRTEM image of CdTe/CdS/ZnS QDs.



**Fig. 2.** (A) CVs and (B) ECL-potential curves of (a) CdTe/CdS/ZnS QDs, (b) 10 mM  $K_2S_2O_8$ , (c) CdTe/CdS QDs with 10 mM  $K_2S_2O_8$  and (d) CdTe/CdS/ZnS QDs with 10 mM  $K_2S_2O_8$  in 0.2 M NaAc-HAc buffer solution (pH 7.0). (C) ECL emission from CdTe/CdS/ZnS QDs under continuous CVs for 13 cycles (D) ECL intensity of CdTe/CdS/ZnS QDs in pH (a) 6, (b) 7, (c) 8 and (d) 9 NaAc-HAc buffer solution (0.2 M). Inset of D: Ratio of ECL intensity measured at  $-1.25$  V to electrode area at three electrodes.

The effect of pH on ECL intensity of CdTe/CdS/ZnS QDs had been studied (Fig. 2D). As a result, the ECL signals could be observed in all solutions from pH 6 to 9, and reached the greatest when pH was 7. Subsequently, different buffers including NaAc-HAc, Tris-HCl and phosphate buffer solutions were tested and the results revealed that the QDs could produce the highest ECL response in NaAc-HAc buffer solution. Besides, the ECL intensity also relied on the working electrode material and the maximum value occurred on Au electrode (inset of Fig. 2D). Therefore, pH 7.0 NaAc-HAc buffer solution was selected as the analytical medium and Au electrode was employed as working electrode.

The ECL spectra of the CdTe/CdS and CdTe/CdS/ZnS dispersed in a pH 7.0 NaAc-HAc buffer solution containing 10 mM  $K_2S_2O_8$  were recorded. As shown in Fig. 3A, the ECL spectrum of CdTe/CdS QDs demonstrated a maximum wavelength of around 717 nm, which was red-shifted almost 22 nm from PL spectrum (695 nm). This red-shift between the PL and ECL emission was less than that observed from thiol-capped CdTe in our previous report [9], which indicated that the surface traps of CdTe QDs had been decreased by CdS shell. After coating the ZnS shell, the ECL spectrum of CdTe/CdS/ZnS QDs showed one peak at 702 nm (Fig. 3B), which was almost identical to that in the PL spectrum. It is for the first time to have observed that the peak position of NIR ECL spectrum from aqueous QDs is very similar to that in PL. The fact demonstrated that the strong ECL signals were certainly located in NIR range and resulted from the CdTe/CdS/ZnS QDs whose surfaces had been highly passivated by ZnS shell.

On the basis of the aforementioned experimental results, the mechanism is depicted schematically in Fig. 3C. Briefly, during the cathodic scanning in pH 7.0 NaAc-HAc buffer solution,  $S_2O_8^{2-}$  could be reduced at  $-0.76$  V to produce strong oxidating agents  $SO_4^{\cdot-}$ , which then can inject holes into the highest occupied molecular orbital of reduced

QDs to produce excited state QDs [6,13]. Then the excited QDs emitted ECL. As previously reported [5,13], in the case of PL, the QD core absorbs photons and generates excitons. ECL occurs when two oppositely charged QDs collide, in which case electrons or holes tunnel through the surfaces from one QD to the other, and thus are affected by QD surfaces. So, as shown in Process 2, when the surfaces of CdTe/CdS/ZnS was passivated by ZnS shell, the injected electrons or holes may relax within the core or surface states, and the red-shift between the PL and ECL emission was less than that observed from CdTe/CdS (Process 1). Additionally, we discovered that the cathodic ECL emission intensity was dependent on the concentration of coreactant. With the increase of  $K_2S_2O_8$  concentration, the ECL intensity gradually increased and reached a maximum value at 10 mM (Fig. 3D). When the concentration of  $K_2S_2O_8$  was higher than 10 mM, the ECL signal decreased, which may be due to the quenching reaction [14] between CdTe/CdS/ZnS QDs\* and  $S_2O_8^{2-}$ . The quenching reaction (Eq. (1)) is interesting in that the two strong oxidants generated in the reaction,  $QDs^+$  and  $SO_4^{\cdot-}$ , could be recycled to produce another excited state QDs\*. Such a recycling reaction is probably partly responsible for the strong emission observed in a solution containing such an effective quencher.



#### 4. Conclusion

In summary, we have successfully studied the ECL from self-designed NIR-emitting MPA-CdTe/CdS/ZnS QDs. The as-prepared QDs showed strong and stable ECL signals at ca.  $-1.25$  V. The good correspondence of the ECL emission peak with the PL results suggested the surface states of the QDs had been largely passivated by ZnS shell and the negligible

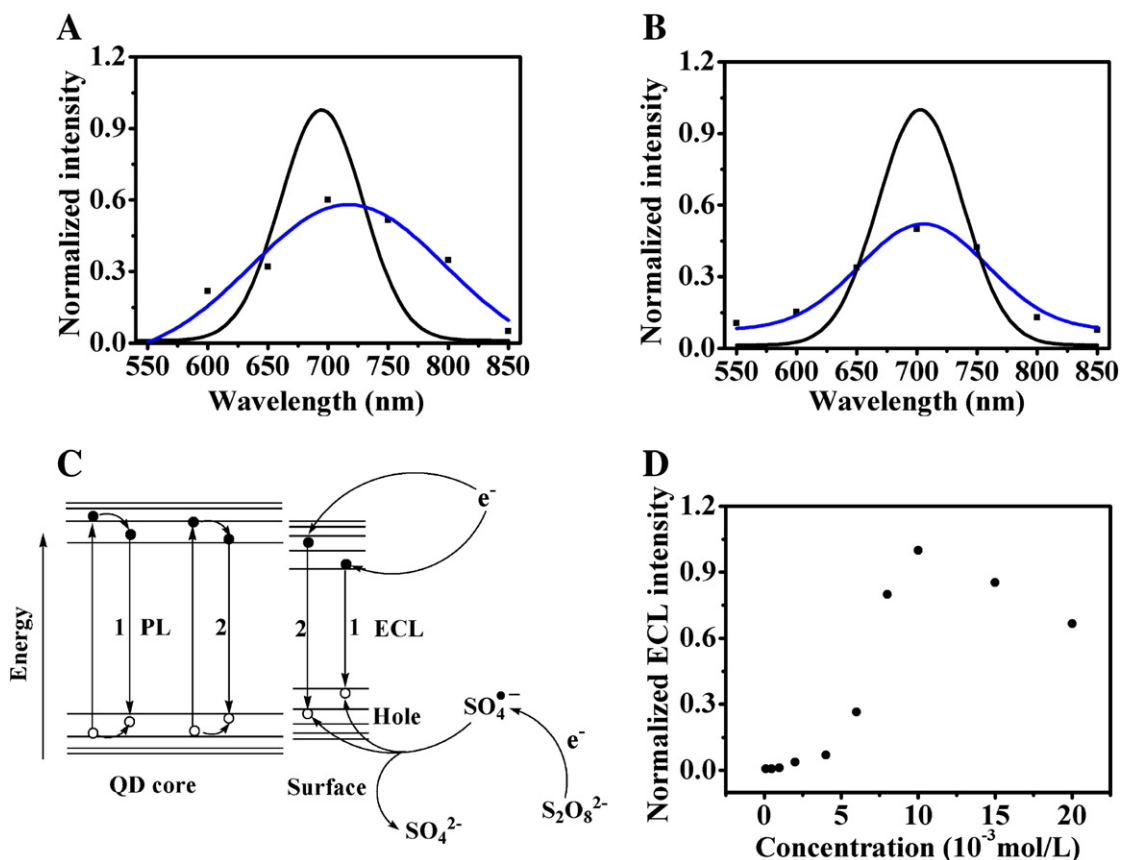


Fig. 3. (A) ECL (square) and PL (line) spectra of CdTe/CdS QDs. (B) ECL (square) and PL (line) spectra of CdTe/CdS/ZnS QDs. (C) Schematic mechanism for PL and ECL. (D) Dependence of the ECL intensities on  $K_2S_2O_8$  concentration.

participation of surface states in the ECL emission. We believe that this work would promote further study on ECL from NIR-emitting QDs and impact actively on the development of ECL biosensors.

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