



Direct electrochemiluminescence of CdTe quantum dots based on room temperature ionic liquid film and high sensitivity sensing of gossypol

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ABSTRACT

A new method with high sensitivity was developed to determine gossypol content using CdTe quantum dot (QD) electrochemiluminescence (ECL) with a room temperature ionic liquid (RTIL) modified glassy carbon (GC) electrode. It was found that use of RTIL film on the GC electrode can greatly enhance the ECL intensity of CdTe QDs, and the ECL peak potential and ECL onset potential were both shifted positively. Under optimal conditions, the quenching effect of gossypol on the ECL emission of CdTe QDs was observed, and ECL intensity showed a good linear relationship in the gossypol concentration range of 5.0×10^{-7} to 5.0×10^{-9} M with a detection limit of 5.0×10^{-9} M. The proposed method was used to detect gossypol in cottonseed oil with satisfactory results. As a result, the introduction of an RTIL-modified electrode can extend the analytical applications of QD ECL systems.

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1. Introduction

Gossypol ($C_{30}H_{30}O_8$) is a polyphenolic compound that has been associated with a wide range of important applications, including use as a male oral contraceptive [1], an anticancer agent [2,3], and in other biological functions [4,5]. It contains a yellow pigment and is most likely the major toxic ingredient extracted from cottonseeds [6]. Cottonseed and cottonseed meal are widely used as protein supplements in animal feed, and cottonseed oil has been consumed as edible oil. Cottonseed oil soapstock is the principal byproduct of cottonseed oil refinement and is increasingly used in animal feed additives; cottonseed hulls are used as a source of additional fiber in animal feeds and usually contain much lower gossypol concentrations than do whole cottonseeds. Gossypol occurs in these cottonseed products in both protein-bound and free forms; the free form is toxic. Signs of acute gossypol poisoning are breathing difficulty, violent and labored respiration, weakness and death. The food and animal agricultural industries must manage gossypol levels to avoid this toxicity, and cottonseed oil must therefore be carefully refined. An analysis of free gossypol levels may be useful in supporting a diagnosis of gossypol poisoning. However, to date, HPLC [7–9] and UV–vis [10] methods have been used for its quantitatively analytical measurement. Therefore, the development of a more simple and sensitive method for gossypol detection is of great importance.

Electrochemiluminescence (ECL), which is developed from chemiluminescence (CL), not only retains the advantages of CL but also has other fascinating features, such as the use of simple equipment, an electrochemically triggered process with ultra low optical background and excellent temporal and spatial controllability, and this method has been employed in a number of fields [11–16]. Recently, ECL research involving quantum dots (QDs) has received considerable momentum because of optical, electrical, electrochemical and luminescent properties that make QDs an attractive material for application in ECL, beginning when Bard and coworkers [17] first reported ECL of Si QDs in an organic solvent. Subsequently, ECL of other QDs in organic solutions [18–22] and in aqueous [23–37] systems has been quickly developed. The latter research has been of more interest since it can vastly enrich strategies for potential applications and has been subsequently designed for H_2O_2 [24,26], glucose [27], amino acid [28] and proteins [29,30]. Previously, the QD ECL method has not been used for gossypol detection. In these cases, ECL research was carried out with bare electrodes or by modifying QDs with electrodes. Studies using direct ECL of QDs and using chemically modified electrodes are rare. Our previous work has introduced the CNT-modified electrode into ECL of CdTe QDs and found this to be an effective approach to optimization of the ECL of QDs [32]. Further studies regarding the direct ECL of CdTe QDs with RTIL-modified electrodes were therefore conducted and are reported here.

Ionic liquids (ILs) are ionic compounds consisting of large organic cations and various kinds of anions that exist in the liquid state over a wide temperature range [37]. Investigation of ILs has gained increasing attention because of their unique chemical

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and physical properties, such as high chemical and thermal stabilities, negligible vapor pressure, high ionic conductivity, low toxicity, and the ability to dissolve a wide range of organic and inorganic compounds [38]. Recently, as a new kind of chemically modified electrode, IL-modified electrodes have aroused great interest [39–41] due to characteristics such as a simple preparation procedure, wide potential windows, high rates of electron transfer, and good anti-fouling ability. The electrochemical behaviors of different kinds of IL-modified electrodes have been reported previously. For example, Safavi et al. reported the direct electrochemistry of Hb and its electrocatalytic effect based on direct immobilization on a carbon IL electrode [42]. Sun et al. studied the electrochemical behaviors of guanosine on an IL-modified carbon paste electrode, and furthermore used it for guanosine detection [43]. However, to the best of our knowledge, ECL studies with an RTIL-modified electrode have been rarely reported, and there is no previous report on the ECL of QDs using RTIL-modified electrodes.

In this paper, the RTIL of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) was used as a new type of binder to construct a chemically modified glassy carbon (GC) electrode, and the direct ECL of CdTe QDs was studied. The RTIL-modified electrode is capable of improving the electrochemistry reaction in the process of CdTe QD ECL and further increasing the intensity of ECL. Such a property would promote the application of QD ECL with RTIL-fabricated sensors for chemical analysis. The ECL emission of CdTe QDs is quenched by gossypol, and the ECL intensity decreases linearly in the concentration ranges of 5.0×10^{-7} to 5.0×10^{-9} M. Finally, a highly sensitive method for the detection of gossypol was proposed, which shows satisfactory results for detection of the gossypol in cottonseed oil. As a result, the introduction of an RTIL-modified electrode can extend the analytical application of QDs ECL systems.

2. Experiment

2.1. Chemicals and materials

Nafion solution (5.0% in methanol with an equivalent weight of about 1100; Aldrich Chemicals Co.), BMIMPF₆ (99.0%) were purchased from Alfa Aesar Chemical Reagent Co., Ltd. and used without further purification (American). Gossypol was bought from Sigma–Aldrich Chemie (American). CdCl₂·2.5H₂O (99.0%), Tellurium powder (99.9%) and NaBH₄ (96.0%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). Thioglycolic acid (TGA) and Na₂TeO₃ were obtained from Sinopharm Chemical Reagent Co., Ltd. (American). L-Isoleucine (L-Ile), L-threonine (L-Thr), L-alanine (L-Ala), L-proline (L-Pro) and L-glutamic (L-Glu) were purchased from Shanghai Boao Biotechnology Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and ultrapure water was used throughout. A 0.1 M phosphate buffer solution (PBS, pH 7.5) was used, and the buffer pH was adjusted by changing the ratio of Na₂HPO₄ to NaH₂PO₄. The stock solution of 10 mM gossypol was freshly prepared with a 0.5 M NaOH solution from which dissolved oxygen had been removed. Cottonseed oil was obtained from Huazhong Agricultural University.

2.2. Instrumentation

Ultraviolet–visible (UV–vis) absorption and the photoluminescence (PL) spectrum were recorded on a Nicolet Evolution 300UV-Vis spectrophotometer (America) coupled with a 1.0 cm quartz cell and a Perkin-Elmer Model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source, respectively. The excitation wavelength of PL was fixed

at 390 nm. A high-resolution transmission electron microscopy (HRTEM) image of the CdTe QDs was acquired on a JEM2010FEF HRTEM (Japan). ECL emission was detected using a Model MPI-B ECL analytical system (Xi'An Remax Electronic Science & Technology Co. Ltd., Xi'An, China) with an 800 V photomultiplier (PMT) tube voltage. The lab-built electrochemical cell consisted of a Ag/AgCl reference electrode (saturated KCl), a platinum wire counter electrode, and an RTIL-modified electrode as the working electrode.

2.3. Synthesis of thiol-capped CdTe QDs

The CdTe QDs capped with thiols were synthesized according to the literature [44] with little modification. Briefly, 38 ml of ultrapure water and 10 ml of 0.01 M CdCl₂ were transferred to a small flask under N₂ atmosphere and held for about 15 min. Then, 10 μl of TGA was added quickly, followed by adjustment of the pH to 11.0 by dropwise addition of 1 or 0.5 M NaOH, until the mixture became clear. A 55.5 mg quantity of tri-sodium citrate and 2 ml of 0.01 M Na₂TeO₃ were injected into the above mixture solution. Finally, 3.0 mg of NaBH₄ was added, and the solution was de-aerated by highly pure N₂ bubbling for 10 min. After mixing, about 25 ml of this mixture was transferred to a reaction kettle, heated to 180 °C and refluxed for 60 min; thus, thiol-capped CdTe QDs could be obtained. Afterward, the resulting products were precipitated by acetone, and superfluous TGA and Cd²⁺ were removed by centrifugation at 3000 rpm for 5 min. The resultant precipitate was redispersed in water, reprecipitated three times by a copious amount of acetone, and then kept in the dark for further use.

2.4. Fabrication of RTIL-modified electrode

Prior to modification, the GC electrode was carefully polished mechanically with a 1, 0.3, and 0.05 μm Al₂O₃ slurry on different polishing cloths, rinsed with ultrapure water, and then sonicated in nitric acid (1:1), NaOH (1 M), anhydrous alcohol, and doubly distilled water for about 4 min in turn. The clean electrode was allowed to dry at room temperature.

About 0.5 ml of RTILs were transferred to a 5 ml measuring flask, and Nafion (0.5% v/v) was added to constant volume. Then, 8 μl of the RTIL/Nafion was cast onto the surface of a clean GC electrode with a microsyringe and allowed to dry at room temperature to form a stable film. The final electrode produced was an RTIL/GC electrode. If not used immediately, it was stored at 4 °C in a refrigerator.

2.5. Sample preparation

An amount of 5 g of cottonseed oil was collected in a sample tube, and 30 ml of methanol was added. The mixture was shaken for about 7 h at 30 °C. After quiescence, the insoluble substances were filtered from the solution under normal pressure. Then, 5 ml of filtrate was kept bubbling with highly pure N₂, until a yellow powder was finally obtained. The yellow powder was dissolved and diluted with 0.5 M NaOH solution, from which dissolved oxygen had been removed. The diluted samples were spiked with selected amounts of gossypol standard solution and detected with the proposed method.

3. Results and discussion

3.1. Characterization of water-soluble CdTe QDs

From Fig. 1A, the UV–vis absorption spectrum shows that the CdTe QDs solution possesses a well-resolved absorption

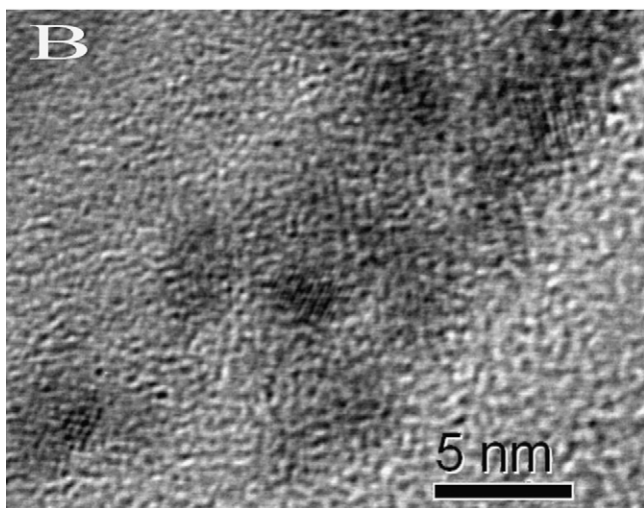
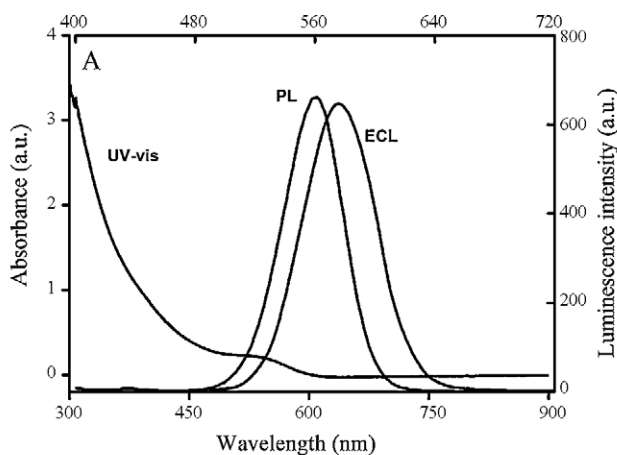


Fig. 1. (A) PL, ECL, and UV-vis absorption spectra of CdTe QD solution (B) HRTEM image of CdTe QDs.

maximum of the first electronic transition, indicating a sufficiently narrow size distribution of the QDs. It can be seen that the absorption peak occurs at 567 nm (band gap of 2.19 eV) of the CdTe QDs. According to literature [45], the particle size can be determined using the following empirical formula:

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + 1.0064\lambda - 194.84$$

In the above equation, D (nm) is the diameter of a given QD, and λ (nm) is the wavelength of the first excitonic absorption peak of the UV-vis absorption spectrum. The results show that the mean diameter of the as-prepared CdTe QDs is 3.06 nm, and the corresponding concentration is 2.15×10^{-6} M.

The ECL and PL spectra of CdTe QDs chosen for investigation of ECL properties are shown in Fig. 1A. The PL peak of CdTe QDs occurs at 559 nm. The ECL spectrum shows a maximum wavelength of around 576 nm, which was markedly red shifted from the PL spectrum. Due to the high surface-to-volume ratio of QDs, surface properties have significant effects on the structural and optical properties.

The CdTe QDs were also studied carefully by HRTEM imaging (Fig. 1B). The morphology and size of the CdTe QDs could be observed clearly. The average size of the studied CdTe QDs was about 3.10 nm, and this value was considered close to the predicted value of 3.06 nm resulting from the empirical formula which seems to be convenient for calculation of the size of CdTe QDs.

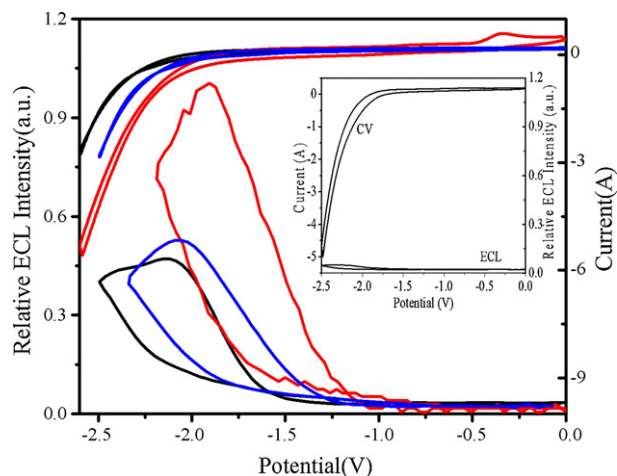


Fig. 2. ECL of CdTe QDs with different electrode. Black line: bare GC electrode; blue line: Nafion-modified GC electrode; red line: RTIL-modified GC electrode. Inset: ECL experiment in blank PBS with the experimental RTIL-modified electrode (conditions: 6.0×10^{-7} M CdTe QD solution; scan rate: 0.34 V/s; 0.1 M pH 7.5 PBS; potential window, -2.2 to 0 V; RTIL-modified GC electrode; PMT voltage, 800 V). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. The ECL of CdTe QDs on an RTIL-modified GC electrode and bare electrode

As shown in Fig. 2, the direct ECL behaviors of CdTe QDs were studied using a bare GC electrode (black line), a Nafion-modified GC electrode (blue line) and RTIL-modified GC electrode (red line); thus, the effect of RTILs was investigated. Compared with the bare electrode and Nafion-modified GC electrode, the peak current was obtained using the RTIL-modified GC electrode, and some enhancement in the cathodic current was also observed. The onset and peak potentials for an ECL process can provide useful estimates for band edge positions, since electron or hole injection is usually required for emission from the QDs. The ECL curves showed that the onset potential of ECL on the RTIL-modified electrode was -1.062 V with the ECL peak potential at -1.905 V, while the onset potential of ECL on the bare electrode was -1.495 V, and the peak potential of the bare was about -2.135 V. This indicates that the ECL onset and peak potential of CdTe QDs both moved in the positive direction. Meanwhile, the ECL intensity of CdTe QDs was nearly twice that observed at the bare electrode, while the ECL intensity increased slightly on Nafion-modified electrode.

The above findings were closely related to the presence of RTILs as the modifier on the GC electrode. The RTILs had large quantities of caves within its molecular structure charges [46,47] and possibly acted as a source of ion carriers to transport charges between the CdTe QDs and electrode. The good conductive performance of RTIL facilitated fast transportation and thus reduced surface diffusion capacitance. On account of these superior qualities, the RTIL-modified GC electrode demonstrated properties such as higher conductivity, fast electron transfer rate, good anti-fouling, inherent catalytic ability, and good adsorptive behaviors [39–41]. Therefore, more CdTe QDs can be accumulated on the surface of the RTIL-modified GC electrode, and the RTIL can act as a very efficient promoter to enhance the kinetics of the electrochemical process. Therefore, electron transfer reactions in the processes of CdTe QD ECL were greatly promoted, the efficiency of producing excited-state QDs was prominently enhanced, and the ECL intensity was augmented.

The ECL experiment was also conducted in an air-saturated blank PBS solution using an RTIL-modified GC electrode that had undergone continuous CVs for several hundred cycles in CdTe QD

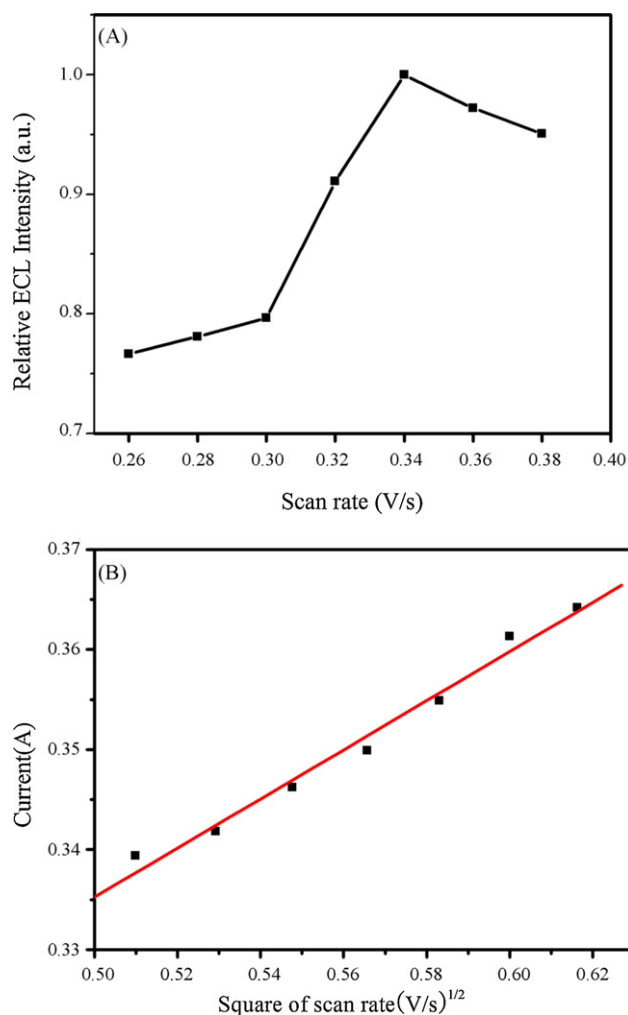


Fig. 3. (A) Influence of scan rate on ECL intensity of CdTe QDs. (B) Plot of current versus square root of scan rate ($v^{1/2}$) (conditions: 6.0×10^{-7} M CdTe QD solution; 0.1 M pH 7.5 PBS; potential window, -2.2 to 0 V; RTIL-modified GC electrode; PMT voltage: 800 V).

solution. The illumination is shown in the inset of Fig. 2 and no obvious ECL emission or current peak was detected. This means that there was nearly zero absorption on the surface of the electrode, or that the RTIL-modified GC electrode was not easily contaminated by the CdTe QD solution in the process of ECL, showing good antifouling behavior. Therefore, the RTIL-modified GC electrode may be considered as an ideal working electrode for use in QD ECL systems.

3.3. Optimization of conditions

3.3.1. Influence of scan rate

The influence of potential scan rate on the ECL responses of the CdTe QD solution were further studied by cyclic voltammetry and the results are shown in Fig. 3. It can be seen that the ECL intensity of CdTe QDs on an RTIL-modified electrode was fortified with increasing scan rate and reached a maximum value at 0.34 V/s, which was due to the formation of more excited-state CdTe QDs in a short time span, thus leading to the enhanced ECL intensity. When the scan rate was higher than 0.34 V/s, the ECL intensity tended to decrease, because the electrochemical process was irreversible, and a high scan rate was unfavorable to the electrochemical reaction of CdTe QDs. In the following experiments, a scan rate of 0.34 V/s was chosen to obtain the maximum emission intensity. Moreover, as illustrated in Fig. 3B, with an increase in the scan rate, an approxi-

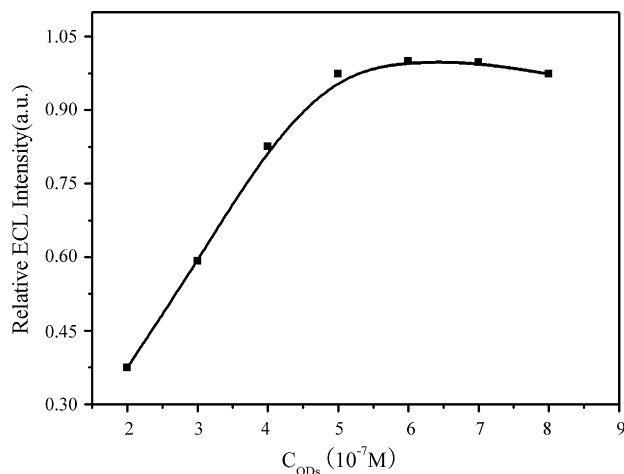


Fig. 4. Influence of concentration of CdTe QDs (conditions: scan rate: 0.34 V/s; 0.1 M pH 7.5 PBS; potential window, -2.2 to 0 V; RTIL-modified GC electrode; PMT voltage: 800 V).

mately linear relationship of peak currents versus the square root of the scan rate ($v^{1/2}$) was obtained, which revealed a typical diffusion-controlled irreversible electrode process.

3.3.2. Influence of CdTe QD concentration

Fig. 4 shows the effect of CdTe QD concentrations on the ECL intensity. The ECL intensity increases with increasing concentrations of CdTe QDs up to 6×10^{-7} M, because the number of individual CdTe QD species that formed during the electrochemical scanning process increased. The ECL intensity levels off at concentrations around 6×10^{-7} M, and there is a slight decrease at higher concentrations, indicating that excessive CdTe QDs could inhibit the generation of excited-state CdTe QDs, which is due to an effect called self-absorption in higher concentration [48]. To achieve good reproducibility and sensitivity, a concentration of 6×10^{-7} M was used for the following experiment.

3.3.3. Influence of buffer pH

A pH study was carried out to investigate the effect of PBS buffer pH on the CdTe QD system of ECL with the RTIL-modified electrode. As in Fig. 5, the ECL response for the CdTe QD solution obtained with the RTIL film electrode increases from pH 6.5 to 7.5 (prepared from

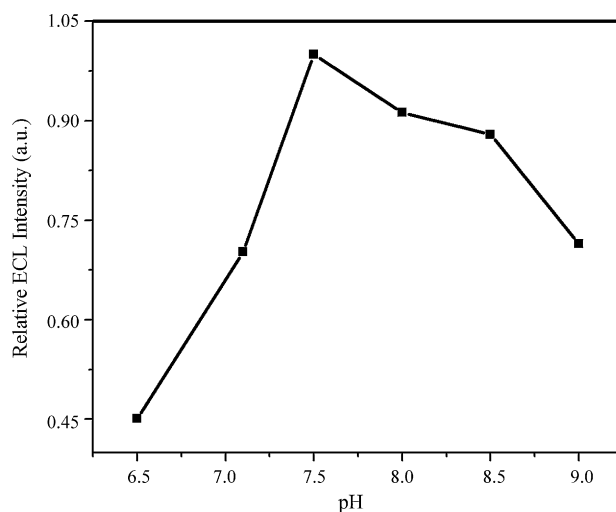


Fig. 5. Influence of pH on the ECL (conditions: scan rate, 0.34 V/s; potential window, -2.2 to 0 V; RTIL-modified GC electrode; concentration of CdTe QDs: 6.0×10^{-7} M; PMT voltage, 800 V).

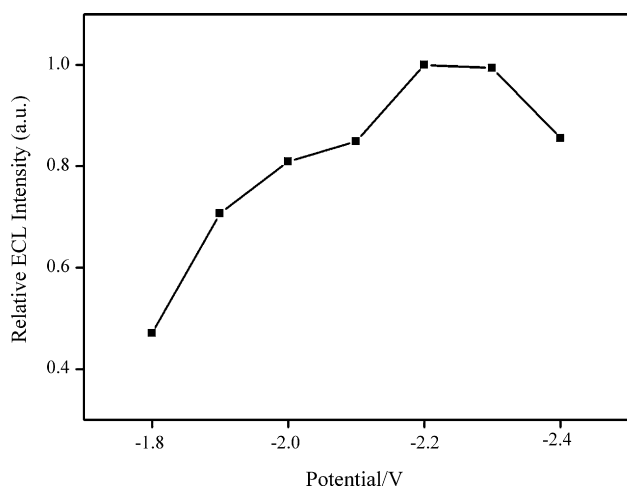


Fig. 6. Influence of applied potential on the ECL. *x*-axis shows the switching potential; *y*-axis shows the maximum ECL of the peak (conditions: 6.0×10^{-7} M CdTe QD solution; scan rate: 0.34 V/s; 0.1 M pH 7.5 PBS; RTIL-modified GC electrode; PMT voltage, 800 V).

PBS) and then obviously decreases at higher pH. Therefore, a PBS pH 7.5 was selected for the following ECL experiment.

3.3.4. Influence of applied potential

The effect of the applied potential was studied, as shown in Fig. 6. The switching potential was selected between -1.80 and -2.40 V. The ECL intensity could be observed in CVs using the RTIL-modified electrode when the switching potential was selected at -1.80 , -1.90 , -2.00 , -2.1 , -2.20 , -2.30 and -2.40 V. It was confirmed that the ECL of the CdTe QDs first increased with an increase in potential scan range, reached a maximum, and then decreased. The maximum ECL intensity was obtained when the switching potential was -2.2 V, which was more positive than our previous studies with the bare electrode. Therefore, the applied potential between 0 and -2.2 V was used to excite the ECL of the CdTe QDs in all experiments.

3.3.5. Stability and reproducibility of the modified electrode

The stability of the RTIL-modified electrode was further evaluated (Fig. 7). After the modified electrode was stored for several

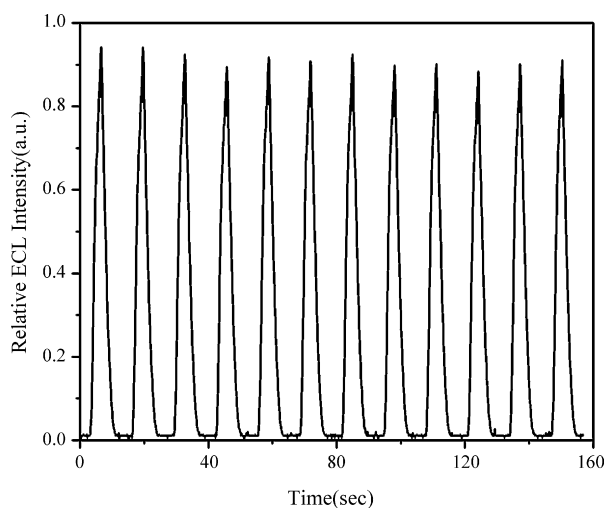


Fig. 7. Stability of RTIL-modified GC electrode (conditions: 6.0×10^{-7} M CdTe QD solution; scan rate: 0.34 V/s; 0.1 M pH 7.5 PBS; potential window, -2.2 to 0 V; RTIL-modified GC electrode; PMT voltage, 800 V).

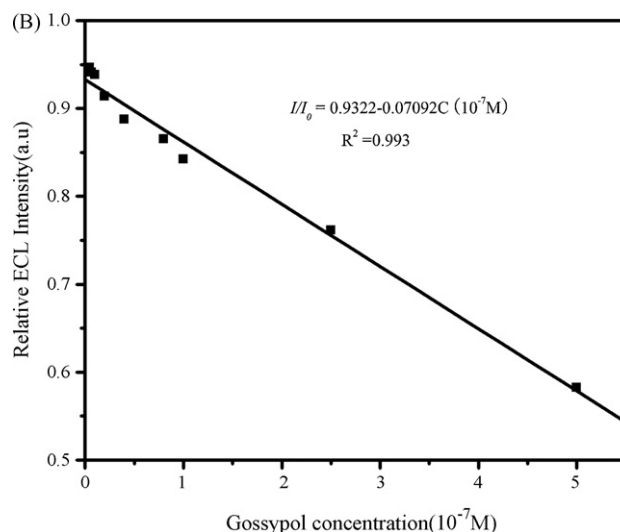
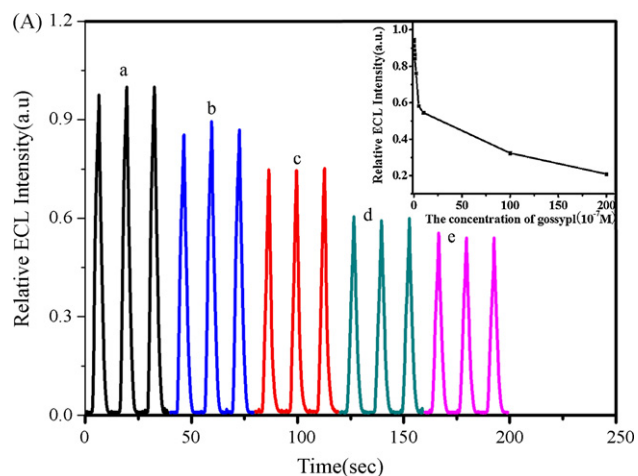


Fig. 8. (A) Quenching effect of gossypol at 0 (a), 0.55 (b), 2.5 (c), 4.5 (d), and 5.5×10^{-7} M (e) on the ECL intensity of CdTe QDs. Inset: Relationship between concentration of gossypol and ECL intensity; (B) linear calibration plot for gossypol (conditions: 6.0×10^{-7} M CdTe QD solution; scan rate: 0.34 V/s; 0.1 M pH 7.5 PBS; potential window, -2.2 to 0 V; RTIL-modified GC electrode; PMT voltage, 800 V).

days, only a small decrease of ECL intensity with fine stability and reproducibility was observed, which could be attributed to the excellent stability of the RTILs film on the modified electrode.

3.4. Determination of gossypol using the RTIL-modified GC electrode

As shown in Fig. 8A, gossypol can quench the ECL of CdTe QDs when using an RTIL film on a modified electrode. When a certain concentration of gossypol solution was added into the PBS solution containing 6.0×10^{-7} M CdTe QDs, the ECL decreased. As in our previous studies, we demonstrated that the thiol group [31,32] and pyrogallol [23] can both quench the ECL of QDs in aqueous solution. Here, gossypol is a polyphenolic compound, which also can react with dissolved oxygen or its intermediate species produced in the processes of QD ECL and eventually could result in a decrease of the ECL intensity. Meanwhile, this experiment provides further confirmation for our former research. Therefore, the gossypol concentration dependence on the ECL intensity of CdTe QDs could be used for gossypol detection.

Table 1
Determination of gossypol in cottonseed oil.

Sample	Gossypol added (μM)	Gossypol found ^a (μM)	Recovery (%)	Wb of gossypol (%)
1	0	0.08		0.012
2	0.04	0.123	107.5 \pm 4.7	
3	0.08	0.15	92.5 \pm 5.4	
4	0.16	0.247	104.8 \pm 3.3	

Wb: mass fraction.

^a Mean result of five measurements.

3.5. Calibration curve

A calibration curve has been obtained for determination of gossypol in aqueous solution using the RTIL-modified electrode under optimal conditions. As shown in Fig. 8B, the ratio of the ECL intensity (I) at a given concentration of quencher to the initial ECL intensity (I_0), I/I_0 , was proportional to the concentration of gossypol (C). The linear regression equations were $I/I_0 = 0.76072 - 0.00411C$ (10^{-7} M) in the wide range of 5.0×10^{-9} to 5.0×10^{-7} M. The detection limit of gossypol with the RTIL film was estimated to be 5.0×10^{-9} M ($S/N = 3$), and the regression coefficient (R^2) was found to be 0.993. The performance of the proposed method shows superior sensitivity, which means that the ECL of QDs could be useful as an ideal method to detect gossypol.

3.6. Analytical applications

Cottonseed oil is the main edible oil used in northwestern of China. Although almost all gossypol is removed during refining to prevent the risk of toxicity, a certain amount remains to affect the storage quality of the oil. The gossypol content of cottonseed oil is an important health indicator. Therefore, a practical analytical application of the proposed method was further established by the sensitivity measurements of gossypol in cottonseed oil. The cottonseed oil sample obtained from the laboratory was preliminarily treated before the experiment. A standard addition method was adopted to assess the reliability, and the samples were directly spiked with certain amounts of gossypol standard solution. The results of the determination are listed in Table 1. The gossypol content in the studied cottonseed oil was 0.012% ($n = 5$), which is lower than the national health standards (0.02%). Recovery of the spiked gossypol was determined and the results ranged from 92.5 to 107.4%, demonstrating the accuracy of the proposed method.

3.7. Interference study

Other main constituents in cottonseed oil were tested as potential interferents. We found that fatty acid, oleic acid, vitamin C and selected other components in cottonseed oil could affect the ECL intensity of CdTe QDs. Therefore, the cottonseed oil needed to be pretreated before detection. The gossypol was obtained by extraction from cottonseed oil in our experiment. Furthermore, the effect of possible saline ions in cottonseed oil (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) was studied, and the results showed that interferences from these saline ions could be neglected even at high concentration. Similarly, no interference at the 5% level was observed from the presence of some common amino acids such as L-Ile, L-Thr or L-Ala, L-Pro and L-Glu, even when they were present in a 1000-fold weight excess. Therefore, the proposed method may be practical for the determination of gossypol in cottonseed oil and showed acceptable selectivity in tests.

4. Conclusions

In summary, an RTIL-modified glassy carbon electrode can remarkably improve the CdTe QD ECL. As a result, the ECL onset

potential and ECL peak potential decrease with enhancement of ECL intensity, which demonstrated that the ECL of QDs could be produced a relatively low negative potential with the RTILs modified electrode. The interferences resulting from high potential in a solution of CdTe QDs were avoided. Furthermore, the quenching effect of gossypol on the CdTe QD ECL emission was discussed, and a novel method for determination of gossypol was developed, which provided some new ideas for quick and sensitive detection of gossypol. The results indicate that the introduction of RTILs could greatly facilitate the QD ECL analysis systems. This work will promote the further studies of QD ECL combined with the RTIL sensor and extend its potential analytical applications.

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