



Enhanced electrochemiluminescence of CdTe quantum dots with carbon nanotube film and its sensing of methimazole

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ABSTRACT

A novel analytical method was reported based on electrochemiluminescence (ECL) of CdTe quantum dots (QDs) using carbon nanotube (CNT) modified glass carbon (GC) electrode. It was found that the CNT film on the GC electrode could greatly enhance the ECL intensity of CdTe QDs dispersed in aqueous solution, and the ECL peak potential and ECL onset potential both shifted positively. Influences of some factors on the ECL intensity were investigated using CNT modified GC electrode, and a high sensitive method for the determination of methimazole was developed under the optimal conditions. The ECL intensity decreased linearly in the concentration range of 1.0×10^{-9} to 4.0×10^{-7} M for methimazole with the relative coefficient of 0.995, which showed finer sensitivity than that at bare electrode. Thus, CNT modified electrode would have a great merit to expand the application of QD ECL.

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1. Introduction

As a kind of novel luminescence materials, quantum dots (QDs), have been attracted a considerable attention [1–3]. Since Bard and co-workers first reported the electrochemiluminescence (ECL) of Si QDs [4], which introduced a new type of luminescent reagent to ECL systems and opened a new field of ECL studies. Subsequently, ECL analytical techniques coupled with QDs developed rapidly and were extensively studied in both organic [5–9] and aqueous media [10–22]. Recently, more reports have been focused on ECL of QDs in aqueous solution, which avoids using toxic organic solution and has potential application in biological analysis. Generally, the ordinary electrodes such as bare Pt disk electrode [10], GC electrode [11] and indium tin oxide (ITO) electrode [12] were used to investigate the direct ECL behaviors of QDs dispersed in aqueous solution, which showed the simple operating processes. But the bare electrodes needed to be applied high excited electrochemical potential and showed inferior sensitivity for analytical application of QD ECL. Up to now, much effort has been devoted toward using chemically modified electrodes for the ECL studies of QDs. For example, Zou and Ju [13] investigated ECL of CdSe QDs cast on a paraffin-impregnated graphite electrode (PIGE). Zhu and co-workers fabricated the carbon-paste electrode (CPE) using the mixture of graphite powder and QDs [14], and the ECL of

CdS QDs and CdSe QDs [15] were studied. In these cases, ECL researches were carried out by modifying QDs to electrodes. Our groups have been applied our energies to optimizing the ECL systems of QDs according to various avenues, and found carbon nanotube (CNT) modified electrode could greatly improved the ECL of QDs.

CNT as a new class of nanomaterial has been exploited for an electrode material due to their unique electronic, chemical, and mechanical properties. Thus, CNT modified electrodes exhibit superior ability compared with bare electrodes [23,24] and have been extensively used to studied conventional electrochemistry [25–27] and ECL systems [28–30]. Considering the advantages of both CNT modified electrode and QD ECL, our present work aimed to study the ECL of CdTe QDs dispersed in aqueous solution using CNT modified GC electrode, which might be valuable both for studies of QD ECL and for accelerating the application of QD ECL in analytical field.

In this paper, base on ECL of CdTe QDs, a novel analytical method was reported using CNT modified GC electrode. The results demonstrated that CNT film could greatly enhance the direct ECL intensity of CdTe QDs dispersed in aqueous solution, and decrease its ECL peak potential and onset potential. It means that CNT modified GC electrode could prevent the interferences resulted from high potential in aqueous solution. Such a property would promote the application of QDs in CNT fabricating sensor for chemical analysis. Furthermore, a new method for the determination of methimazole was developed. The proposed method showed better detection performance and simple operating processes, which indicated the ECL of QDs has wider potential application with introducing of CNT film.

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2. Experiment

2.1. Chemicals and materials

A 5% solution of Nafion in methanol was obtained from Aldrich Chemical Company. Multi-Wall CNTs was purchased from Shenzhen NanotechPort Co., Ltd. (Shenzhen, China). Methimazole (98%) were obtained from Alfa Aesar Chemical Reagent Co., Ltd. Methimazole tablets were purchased from Beijing Dayang Pharmaceutical industry Co., Ltd. (Beijing, China). $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (99.0%), Tellurium powder (99.99%) and NaBH_4 (96%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). Glucose, starch, thioglycolic acid (TGA) and Na_2TeO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd. Alanine, threonine and isoleucine were purchased from Shanghai Boao Biotechnology Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and ultrapure water was used throughout. The 0.1 M phosphate buffer solutions (PBS, pH 8.5), and the buffer pH was adjusted by changing the ratio of Na_2HPO_4 to NaH_2PO_4 . The stock solution of 10 mM methimazole and other common amino acids were prepared and stored in a refrigerator at 4 °C to minimize exposure to light and air. Fresh methimazole solutions were prepared every day.

2.2. Instrumentation

ECL curves were recorded simultaneously using a Model MPI-B from ECL Analyzer Systems (Xi'An Remex Electronic Science & Technology Co. Ltd., Xi'An, China). The voltage of the photo multiplier tube (PMT) was biased at 800 V in the process of detection. A conventional three-electrode system was used for the electrolytic system, a CNT modified GC electrode was used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference electrode. The ultraviolet–visible (UV–vis) spectrophotometry absorption spectrum was acquired with a Thermo Nicolet Evolution 300 Spectrophotometer (America) coupled with a 1.0 cm quartz cell. The photoluminescence (PL) spectrum was measured with a PerkinElmer Model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source. Excitation wavelength was fixed at 390 nm.

2.3. Preparation of CdTe QDs

Thiol-capped CdTe QDs were synthesized according to the method reported previously [31] with some modifications. Briefly, 10 ml of 0.01 M CdCl_2 and 38 ml of ultrapure water were transferred to a small flask. This solution was mixed with 10 μl of TGA at N_2 atmosphere. 1 M NaOH was added to adjust its pH to 11.0, and this mixture became clear. Then 55.5 mg Tri-sodium citrate and 2 ml of 0.01 M Na_2TeO_3 were injected into this mixture, respectively. Finally, 3.0 mg NaBH_4 was added and bubbled with highly pure N_2 for 10 min. After mixing, about 25 ml this mixture was transferred to reaction kettle and kept heating to 180 °C for 60 min, and then thiol-capped CdTe QDs could be obtained. The resulting products were precipitated by acetone, and superfluous TGA and Cd^{2+} were removed with centrifugation at 3000 rpm for 5 min. The resultant precipitate was redispersed in water, reprecipitated by a copious amount of acetone for more than two times, and then kept under dark for further use.

2.4. Fabrication of CNT modified electrode

Prior to modification, the GC electrode was carefully polished mechanically with 1, 0.3 and 0.05 μm Al_2O_3 slurry on the different polishing cloth and then rinsed with ultrapure water, then

sonicated in nitric acid (1:1), NaOH (1 M), anhydrous alcohol and ultrapure water, for about 4 min in turn. The clean electrode was allowed to dry at room temperature.

CNTs were shorted and functionalized as described previously [32]. In brief, 20 mg of CNTs was dispersed in 20 ml of 3:1 (v/v) solution of concentrated sulfuric acid (98%) and concentrated nitric acid (70%) and sonicated for 6 h. The shorted CNTs were filtered and washed with super pure water until the pH was nearly neutral.

About 9 mg of dry shorted CNTs were dispersed in 9 ml of Nafion (0.5%, v/v) to give a 1 mg/ml black suspension. Then 10 μl of this CNT suspension was cast onto the surface of a clean gassy carbon electrode and allowed to dry at room temperature. Finally, 5 μl Nafion was cast and used as a binder to hold the CNTs on the electrode surface stably. The final electrode is taken as a CNT modified GC electrode. If not used immediately, it can be stored at 4 °C in a refrigerator.

2.5. Standard procedures for the ECL detection

ECL measurements were carried out in 0.1 M PBS (pH 8.5) solution containing 5.0×10^{-7} M CdTe QDs with an applied working potential range from 0 to -2.3 V (versus Ag/AgCl) and a cycle scan rate of 0.30 V/s in three-electrode cell mentioned above. A high voltage power supply applied 800 V to the PMT, and ECL signals were recorded by a Model MPI-B ECL analyzer. Each data point was an average of 5 measurements. The different concentrations of methimazole standard solutions or sample solutions were injected in the ECL cell to obtain the calibration curve and sample analysis.

3. Results and discussion

3.1. Characterization of TGA-capped CdTe

Fig. 1 shows the UV–vis absorption spectrum and the PL spectrum of the prepared CdTe QDs. It can be seen that the absorption peak and PL peak of CdTe QDs occurred at 544 nm (band gap of 2.28 eV) and 571 nm, respectively. The particle size of above mentioned CdTe QDs was 3.17 nm, which was calculated in virtue of the empirical equations reported previously [33].

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

In the above equation, λ (nm) is the wavelength of the first excitonic absorption peak of the UV–vis absorption spectrum.

3.2. ECL behaviors of CdTe QDs at CNT modified GC electrode

As shown in Fig. 2, the direct ECL behaviors of CdTe QDs were studied using CNT modified GC electrode and the effect of CNT film

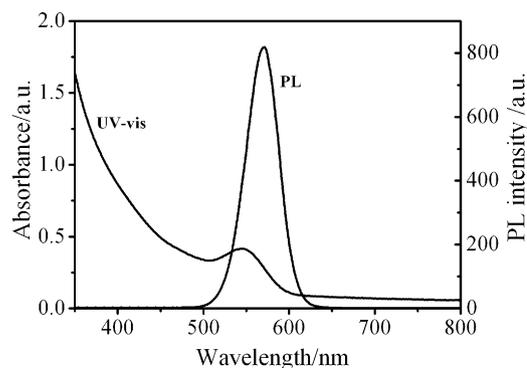


Fig. 1. PL spectrum and UV–vis absorption spectrum of CdTe QDs.

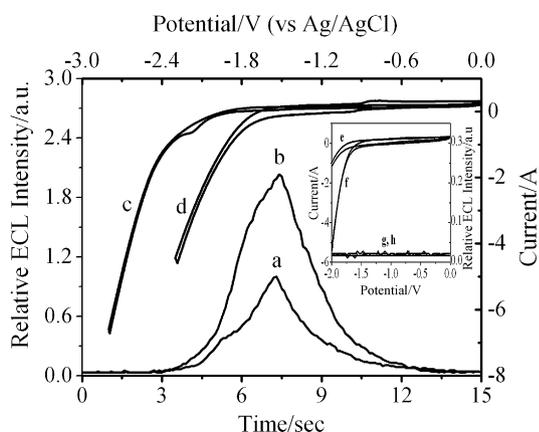


Fig. 2. ECL of CdTe QDs at bare GC electrode and CNT modified GC electrode. (a) ECL curve at bare GC electrode; (b) ECL curve at CNT modified GC electrode; (c) CV curve at bare GC electrode; (d) CV curve at CNT modified GC electrode; inset: ECL curves (g and h) and CV curves (e and f) of CdTe QDs at unused modified (e and g) GC electrode and used modified GC electrode (f and h) (conditions: scan rate, 0.30 V/s; the concentration of CdTe QDs, 5.0×10^{-7} M; 0.1 M PBS pH 8.5; air-saturated solution; PMT voltage, 800 V).

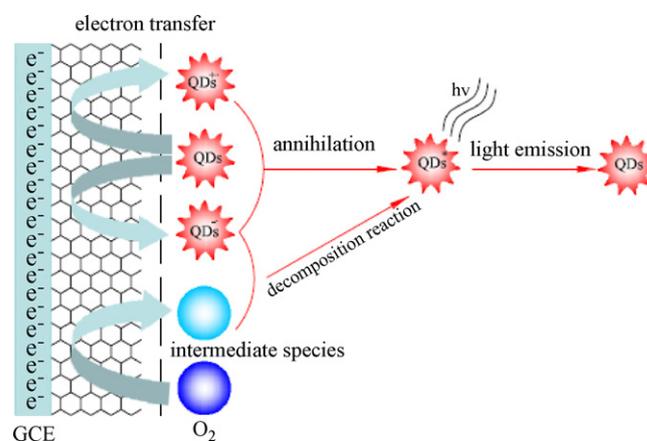
on the ECL properties was investigated. A visible enhancement in the cathodic current was observed using CNT modified GC electrode (curves c and d). CV curves demonstrated that the onset potential of CdTe QDs also shifted positively. These phenomena indicated that the presence of CNTs obviously decreased the potential barriers and efficiently catalyzed the reaction of CdTe QDs [34].

The ECL curves showed that CNT film on GC electrode greatly facilitated the ECL of CdTe QDs. It can be seen that the ECL intensity of CdTe QDs at CNTs modified electrode was much higher than that observed at bare electrode (curves a and b). The potentials for the onset of an ECL process and ECL peak can provide useful estimates for band edge positions, even when the voltammetric behavior is not very well defined, since electron or hole injection is usually required for emission from the QDs. From Table 1, the ECL peak potential and ECL onset potential both shifted positively at the CNT modified electrode. Thus, such sensor only need lower negative potential to produce ECL of CdTe QDs, which could prevent the interferences that resulted from high potential in aqueous solution.

These results may be due to that the electron transfer reactions in the processes of CdTe QD ECL were greatly promoted. The mechanism of ECL of CdTe QDs on the CNTs modified GC electrode was provided as Scheme 1. It found that the effective surface area of the CNTs modified electrode was much larger than that of the bare GC electrode. What is more, CNTs acted as nanowires connection CdTe QDs or coreactant with electrode surface, which introduced many electrocatalytic sites onto the electrode surface and facilitated the electron transfer through the conducting tunnels of CNTs [35–37]. Finally, the electrochemical performance of the electrode was dramatically improved in present of CNTs film [24–27]. Therefore, the electron transfer reactions in the processes of ECL at CNT modified GC electrode were accelerated compared to bare GC electrode, and the efficiency of producing excited-state QDs was enhanced. All the results mentioned above would not only promote the development

Table 1
Comparison of CdTe QDs the ECL at CNT modified GC electrode and bare GC electrode.

Working electrode	Onset potential (V)	Peak potential (V)	Relative ECL intensity
Bare GC	-1.89	-2.76	1.00
CNT modified GC	-1.09	-2.27	2.04



Scheme 1. The mechanism of ECL of CdTe QDs on the CNTs modified GC electrode.

of QDs ECL system with CNT modified electrode but also accelerate the use of QD ECL in analytical fields.

The ECL and CV curves of the air-saturated blank PBS solution at CNT modified GC electrode also were observed (inset in Fig. 2). No light emission and current peak were detected (curves e, g). Under the same conditions, the obvious light emission of CdTe QDs was observed in the solution (curves a and b), which indicated CdTe QDs was the luminescent reagent. The same experiment was done in the air-saturated blank PBS solution using CNT modified GC electrode which has done continuous CVs for 300 cycles in CdTe QD solution. The similar results were obtained (curves f and h). It means that there nearly was no absorption on the surface of the electrode, or CNT modified GC electrode was not easily contaminated by CdTe QD solution in the process of ECL. Therefore, CdTe QD solution can be studied as an excellent illuminant, and the CNT modified GC electrode was an ideal working electrode using in QD ECL system.

3.3. Optimization of reaction conditions

3.3.1. Effect of CdTe QDs

The concentration of CdTe QDs could affect on the ECL intensity (Fig. 3). With an increasing concentration of CdTe QDs, the formed individual CdTe QD species in the electrochemical scanning process increased, leading to the enhancement in ECL intensity. The strongest ECL intensity was obtained with 5.0×10^{-7} M. When the concentration of the CdTe QDs exceeded 5.0×10^{-7} M, the ECL intensity decreased, indicating that the excessive CdTe QDs could

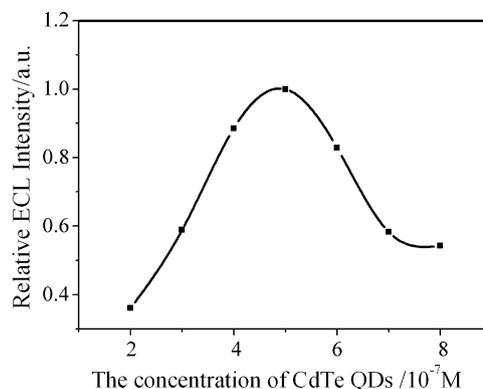


Fig. 3. Effect of concentration of CdTe QDs (conditions: scan rate, 0.30 V/s; 0.1 M pH 8.5 PBS; the potential window, -2.3 to 0 V; CNT modified GC electrode; PMT voltage, 800 V).

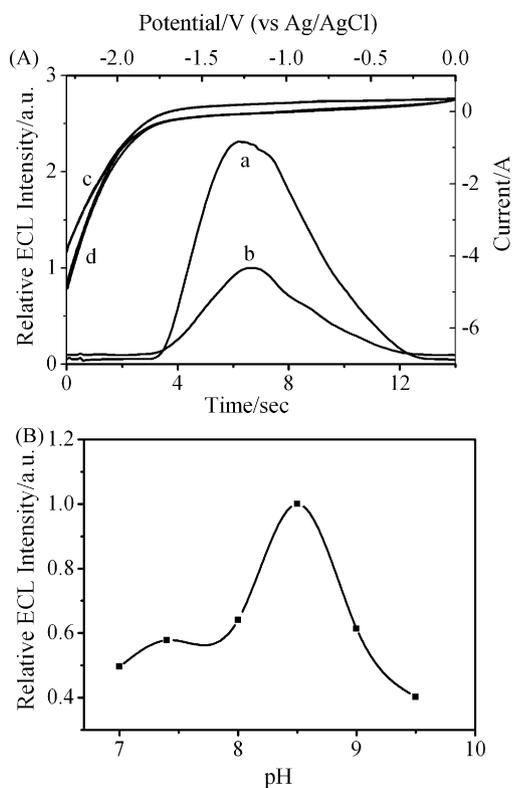


Fig. 4. (A) Effect of dissolved oxygen and (B) effect of pH. (a and d) ECL in air-saturated solution; (b and c) ECL after bubbling high-purity N_2 for 30 min (conditions: the potential window, -2.3 to 0 V; scan rate, 0.30 V/s; the concentration of CdTe QDs, 5.0×10^{-7} M; 0.1 M PBS pH 8.5 ; CNT modified GC electrode; PMT voltage, 800 V).

inhibit the generation of excited-state CdTe QDs, which was due to an effect called self-absorption in higher concentration [38].

3.3.2. Effect of dissolved oxygen

Effect of dissolved oxygen on ECL intensity was also investigated in the following experiments. As shown in Fig. 4A, when dissolved oxygen was removed from the solution by bubbling high-purity N_2 , light emission intensity of ECL decreased dramatically, indicating that dissolved oxygen was an important coreactant for producing ECL of CdTe QDs in the solution. To acquire stable ECL, air-saturated CdTe QD solution was recommended in our experiments.

3.3.3. Effect of PH

The pH of the buffer solution is a crucial factor influencing the ECL reaction of QDs. Thus, the effect of pH on the ECL of CdTe QDs was investigated in a pH range from 7.0 to 9.5 prepared from PBS. As shown in Fig. 4B, at first, the ECL intensity increased gradually with the increasing pH. But when pH became higher than 8.5 , ECL intensity of CdTe QDs began to decrease obviously. Therefore, the pH 8.5 PBS was selected for the following ECL experiment.

3.3.4. Effect of scan rate

The effect of scan rate on the CdTe QDs ECL intensity at CNTs modified GC electrode was also investigated, and the results (see Fig. 5) showed that a higher scan rate of the applied potential would cause a stronger ECL intensity at CNT modified GC electrode in the range of 0.24 – 0.30 V/s. However, along with the increase of the scan rate between 0.30 and 0.36 V/s, the increased scan rate induced decreasing of the ECL intensity. That was because the electrochemical process was irreversible, and high scan rate was unfavorable to the electrochemical reaction of CdTe QDs. When the scan rate

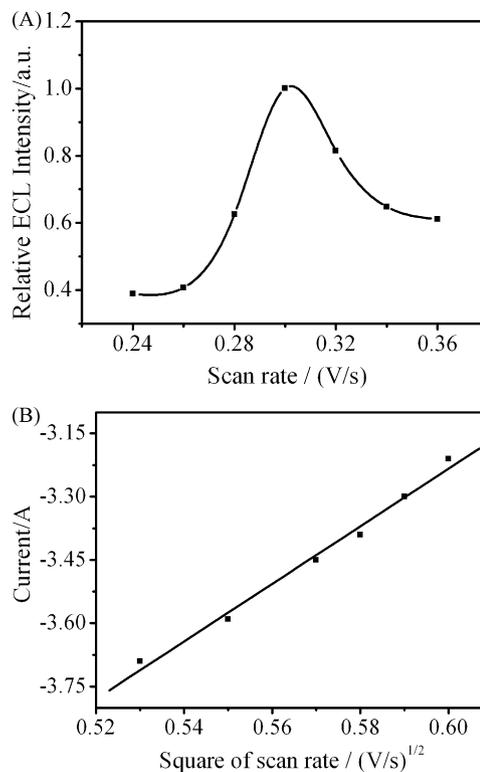


Fig. 5. (A) Effect of scan rate on ECL intensity and (B) plot of current versus square root of scan rate ($v^{1/2}$) (conditions: potential window, -2.3 to 0 V, the concentration of CdTe QDs, 5.0×10^{-7} M; 0.1 M PBS pH 8.5 ; air-saturated solution; CNT modified GC electrode; PMT voltage, 800 V).

reached 0.30 V/s, the ECL intensity attained its maximum. For the reasons showed above, 0.30 V/s was selected as the scanning rate in subsequent work. Further, the cathode peak currents were linearly proportional to the square roots of scan rate at CNT modified GC electrode (Fig. 5B), suggesting that the reaction at CNT modified GC electrode belonged to a surface diffusion-controlled electrochemical process.

3.3.5. Effect of applied potential window

Fig. 6 shows the effect of applied potential windows on the ECL of CdTe QDs at CNT modified GC electrode. The ECL intensity were enhanced with more negative scan potential windows, and reached a maximum at a potential window of -2.3 to 0 V, then decreased. That might be due to the fact that the CdTe QDs in the ECL pro-

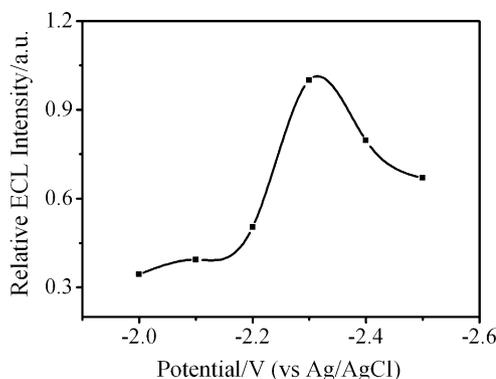


Fig. 6. Effect of the potential window on ECL intensity (conditions: scan rate, 0.30 V/s; the concentration of CdTe QDs, 5.0×10^{-7} M; 0.1 M PBS pH 8.5 ; air-saturated solution; CNT modified GC electrode; PMT voltage, 800 V).

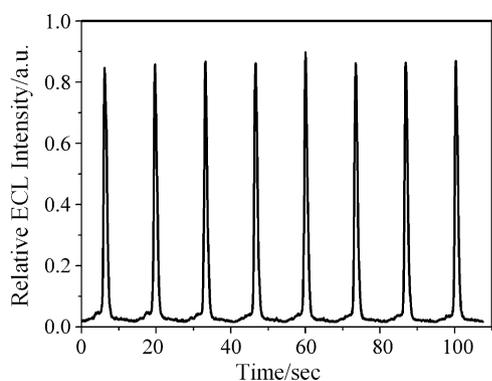


Fig. 7. Stability of CNT modified GC electrode (conditions: the potential window: -2.3 to 0 V; scan rate: 0.30 V/s; the concentration of CdTe QDs: 5.0×10^{-7} M; 0.1 M PBS pH 8.5 ; CNT modified GC electrode; PMT voltage, 800 V).

cesses with a high excited electrochemical potential window were unstable. Thus, the whole ECL experiments were conducted with a potential window of -2.3 to 0 .

3.4. The stability of CNT modified GC electrode in studied ECL system

The stability and reproducibility of a CNT modified GC electrode were studied in ECL system of CdTe QDs, as shown in Fig. 7. It was found that the electrode was very stable and had an excellent reproducibility for ECL of CdTe QDs when the sensors had been used and then stored in the PBS buffer solution for 2 weeks at 4°C , which could avoid the serious electrode fouling. The CNT modified GC electrode could be used for ECL studies of CdTe QDs at least 2 weeks without significant changes. Therefore, the CNT modified GC electrode was an ideal working electrode for the studies of CdTe QD ECL.

3.5. Determination of methimazole using CNTs modified GC electrode

Methimazole is an important member of thiol compound, has been widely used in the therapy of hyperthyreosis as an orally active drugs. Its action is to slow iodide integration into tyrosine and thus inhibits the production of thyroid hormones. However, the uncontrolled introduction of this and other thyreostats into the human food chain could have serious health implications. Thus, the development of an ideal method for the detection of methimazole is obviously of significance. Thiol compounds have been of continuing interest because of their quenching effects on the ECL of QDs. Therefore, we investigated the application of CdTe QDs ECL with CNT modified electrode using methimazole as an analyte.

The quenching effect of methimazole on the ECL intensity of CdTe QDs at CNT modified GC electrode was studied and shown

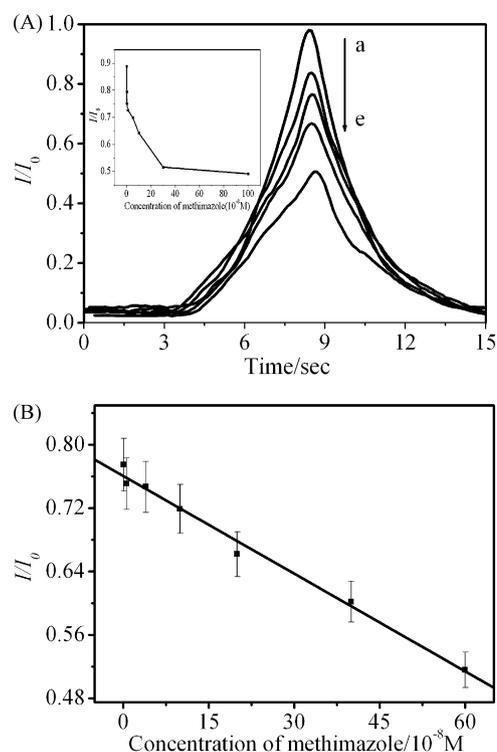
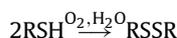


Fig. 8. (A) The quenching effect of methimazole at 0 (a), 0.05 (b), 0.1 (c), 1.0 (d) and 3.0×10^{-7} M (e) on the ECL intensity of CdTe QDs. (B) Linear calibration plot for methimazole (conditions: the potential window, -2.3 to 0 V; scan rate, 0.30 V/s; the concentration of CdTe QDs, 5.0×10^{-7} M; 0.1 M PBS pH 8.5 ; CNT modified GC electrode; PMT voltage, 800 V).

in Fig. 8A. Upon addition of methimazole to the PBS containing 5.0×10^{-7} M CdTe QDs, the ECL intensity decreased greatly, indicating that the methimazole was responsible for the quenching effect. According to the quenching mechanism of some thiol compound on the ECL intensity [18,39], which have been fully illuminated, the possible reason for quenching effect of methimazole could be concluded using the following reaction:



Here, methimazole, as a kind of thiol compound, would react with the dissolved oxygen or its intermediate species produced in the processes of QD ECL and finally resulted in decreasing the ECL intensity. The proposed mechanism was in good agreement with some references. Therefore, the methimazole concentration dependence of the ECL intensity of CdTe QDs could be used for methimazole detection.

Calibration curve for methimazole has been constructed using the present ECL sensor of CdTe QDs based on the CNT film. As shown in Fig. 8B, the ratio of the ECL intensity (I) at a given concentration

Table 2

Comparison of characteristics of the proposed method with some published previously for methimazole determination.

Methods	Liner range (M)	Detection limits (M)	R	R.S.D. (%)	Reference
HPLC	2.2×10^{-5} – 1.1×10^{-4}	–	0.9975	2.00	[40]
Fl-spectrophotometric	1.0×10^{-5} – 5.0×10^{-4}	3.0×10^{-6}	0.9989	0.35	[41]
Fl-chemiluminescence	1.8×10^{-5} – 8.8×10^{-4}	–	–	1.90	[42]
RLS	0 – 1.1×10^{-6}	2.0×10^9	–	1.86	[43]
Electrophoresis	1.0×10^{-6} – 5.0×10^{-4}	8.0×10^{-7}	0.9999	–	[44]
SWV	1.0×10^{-5} – 7.0×10^{-3}	0.5×10^{-5}	0.9993	2.89	[45]
Potentiometric titration	1.0×10^{-4} – 5.0×10^{-3}	–	–	0.81	[45]
QDs-ECL-CNT/GCE	1.0×10^{-9} – 4.0×10^{-7}	1.0×10^{-9}	0.9950	3.50	This work

HPLC, high performance liquid chromatography; Fl, flow injection; RLS, resonance light scattering; SWV, square wave voltammetry.

Table 3
Detection Results according to proposed method.

Number	Theory concentration (10^{-8} M)	Detected concentration (10^{-8} M)	Detected content (mg/tablet)	Labeled content (mg/tablet)	R.D. ^a (%)
1	18	17	4.85	5	-3.0
2	1.8	1.81	5.17	5	3.4
3	0.18	0.187	5.35	5	7.0

^a Relative deviation.

of quencher to the initial ECL intensity (I_0), I/I_0 , was proportional to the concentration of methimazole (C). It could be seen that I/I_0 had good linearity with the methimazole concentration and the linear range was wide, extending from 1.0×10^{-9} to 4.0×10^{-7} M. The linear response can be fitted to the equation $I/I_0 = 0.76072 - 0.00411C$ (10^{-8} M) with a remarkable detection limit of 1.0×10^{-9} M, indicating finer sensitivity. The performance of proposed method has been found to be superior to other analytical techniques (Table 2) for the methimazole determination, which means that ECL of QDs would be developed to use as an ideal method to detect thiol compounds in present of CNT film.

The influence of commonly used excipients and common constituents in pharmaceutical dosage forms of methimazole were tested as potential interferents. There was no interference from Ca_2CO_3 , starch, lactose or glucose in the amounts commonly used in pharmaceutical preparations. 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, even when they were present in a 1000-fold weight excess. Furthermore, the possible saline ions in reaction system (Na^+ , K^+ , Mg^{2+} , and Cl^-) did not affect the ECL intensity at their concentrations lower than 0.1 M. Therefore, the proposed method could be practical for the determination of methimazole and showed the ideal selectivity.

3.6. Sample analysis

The active ingredient in the methimazole tablet was tested according to the procedure described above. The content of methimazole in the tablet could be analyzed and the assay result was listed in Table 3. The relative deviations of less than 8% showed the fine accuracy. At the same time, this result also agreed quite well with the labeled amount. It was clear that this method could be applied to the determination of the drug purity as an effective approach.

4. Conclusion

In conclusion, we found that the CNT film could greatly enhance ECL intensity of CdTe QDs in aqueous solution, decrease their ECL onset potential and ECL peak potential, which demonstrated the ECL of QDs could be produced at relatively low negative potential with the CNT modified electrode. It avoided the interferences resulted from high potential in solution of CdTe QDs and provided some new ideas to optimize the QD ECL system. Furthermore, a novel method for determination of methimazole was developed basing on its quenching effect on the ECL intensity of CdTe QDs. It demonstrated that the introducing of CNTs could greatly facilitate the QD ECL analysis systems. Our studies would promote the further studies of QD ECL combined with CNT sensor and its potential analytical applications.

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