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Size-dependent electrochemiluminescence behavior of water-soluble CdTe quantum dots and selective sensing of L-cysteine

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ABSTRACT

Water-soluble CdTe quantum dots (QDs) with five sizes (2.25, 2.50, 2.77, 3.12, and 3.26 nm) were synthesized with the hydrothermal method. The electrochemiluminescence (ECL) of CdTe QDs was investigated in detail in air-saturated solution without adding foreign oxidant. It was found that the ECL of CdTe QDs displayed a size-dependent property. With the increasing in the particle size of the CdTe QDs, the ECL intensity was gradually increased, in addition, both ECL peak potentials and ECL onset potentials of CdTe QDs were shifted positively. Influences of some factors on the ECL intensity were investigated. Under the optimal conditions, the ECL intensity had a linear relationship with the concentration of L-cysteine (L-Cys) in the range from 1.3×10^{-6} to 3.5×10^{-5} mol L^{-1} (R^2 0.996) with a detection limit of 8.7×10^{-7} mol L^{-1} (S/N = 3). The proposed method was applied to the determination of L-Cys in real samples with satisfactory results. Compared with previous reports, it has better selectivity for the determination of L-Cys.

1. Introduction

Electrochemiluminescence (ECL) is a special form of chemiluminescence (CL). It has become an important and valuable detection method in analytical chemistry because of its low cost, wide range of analyte, excellent selectivity and high sensitivity [1–3]. Many chemiluminescent reagents were applied in ECL reactions, such as luminol and ruthenium complex, etc. [4–6]. Since they have been extensively studied, it is necessary to look into new luminescent reagents and develop new ECL systems.

Among the miscellaneous functional nanomaterials, quantum dots (QDs) are of considerable interest owing to their variety of superior optical and electrical properties. Recently, some scientists became aware of the potential application of QDs in ECL field. The ECL of Si QDs was first observed by Bard and co-workers in 2002 [7], which introduced a new type of luminescent reagent to ECL systems and opened a new field of ECL studies. Subsequently, the ECL analytical techniques coupled with QDs have been rapidly developed [8–27]. However, these researches were mostly carried out in organic media [7–9,10–12], or by modifying them to electrodes [13–16] in the presence of foreign strong oxidants which are indispensable for the accomplishment of such work. Actually, ECL of QDs in aqueous solution has a wider potential as a sensor in biological analysis.

Our previous works have first reported the ECL of QDs dispersed in aqueous solution with bare electrode [17,27]. It was demonstrated that water-soluble QDs were promising luminescent materials used in ECL system, which avoided complicated modifying electrode or using toxic organic solution. Generally, the foreign strong oxidants are indispensable for the ECL of QDs, but we recently found that the ECL of QDs can be conducted in air-saturated solution without adding any foreign oxidants. Thus, the ECL systems of QDs were simplified, which was undoubtedly of great importance for expanding potential analytical applications of ECL of QDs. Nevertheless, very few reports have been published on size-dependent ECL properties of QDs, though the unique size-dependent properties of QDs have been the subject of considerable interest [28,29]. Therefore, the goal of our present study is to make an in-depth research on the size-dependent ECL behavior of CdTe QDs.

In this paper, the ECL of CdTe QDs with different sizes were conducted in air-saturated solution without adding any additional oxidants at bare glassy carbon (GC) electrode, which simplified the operating processes of our ECL study. Furthermore, the size-dependent ECL properties of CdTe QDs were investigated in detail. Based on the annihilation of ECL emission from CdTe QDs by L-cysteine (L-Cys), a novel method for the high selectivity determination of L-Cys was developed under the optimal conditions. Our

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work would expand the potential applications of QDs in the field of ECL.

2. Experimental

2.1. Apparatus

ECL studies were performed 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 during the whole processes. A conventional three-electrode system was used for the electrolytic system, a glassy carbon 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) absorption spectra were performed on a Thermo Nicolet Corporation Model evolution 300 spectrophotometer coupled with a 1.00 cm quartz cell. The photoluminescence (PL) spectra were acquired with a PerkinElmer Model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source. The Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet Corporation Model avatar 330 spectrometer. The high-resolution transmission electron microscopy (HRTEM) image of the CdTe QDs was acquired on a JEM2010FEF HRTEM (Japan).

2.2. Reagents

$CdCl_2{\cdot}2.5H_2O$ (99.0%), Tellurium powder (99.99%) and $NaBH_4$ (96%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). Thioglycolic acid (TGA) and Na_2TeO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd. A 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 7.1) was used throughout this work. L-Cysteine (L-Cys), L-glycine (L-Gly), L-proline (L-Pro), L-glutamic (L-Glu), L-leucine (L-Leu), L-alanine (L-Ala), L-lysine (L-Lys), L-threnine (L-Thr), L-glutamine (L-Gin), L-aspartic acid (L-Asp), L-isoleucine (L-Ile), L-serine (L-Ser), L-valine (L-Val) and L-asparagine (L-Asn), etc. were purchased from Shanghai Boao Biotechnology Co, Ltd. (Shanghai, China). Fresh L-Cys solutions were prepared every day. Human serum was provided from a healthy volunteer. The stock solutions of 0.1 mol L^{-1} other common amino acids were prepared and stored in a refrigerator. All other reagents were of analytical reagent grade and used as purchased without further purification. Milli-Q (Millipore) water was used throughout.

2.3. Preparation of CdTe QDs

Water-soluble CdTe QDs were synthesized according to the hydrothermal method with slight modifications [30]. Briefly, 10 mL of 0.01 mol L^{-1} $CdCl_2$ and 38 mL of ultrapure water were transferred to a small flask. This solution was mixed with 10 μL of TGA and kept bubbling with highly pure N_2. 1.0 mol L^{-1} NaOH was added to adjust its pH to 11.0, and this mixture became clear. Then 55.5 mg Trisodium citrate and 2.0 mL of 0.01 mol L^{-1} Na_2TeO_3 were injected into this mixture respectively. Finally, 3.0 mg $NaBH_4$ was added at N_2 atmosphere. After mixing, about 25 mL of this mixture was transferred to a reaction kettle and kept heated at 180 °C for 60 min, and then water-soluble CdTe QDs could be obtained. By controlling the heating time, different sizes of CdTe QDs were attained. The resulting products were precipitated by acetone and superfluous TGA and Cd^{2+} were removed with centrifugation at 1086 (×*g*) for 5 min. The resultant precipitate was redispersed in water, reprecipitated by a copious amount of acetone more than two times, and then kept under dark for further use.

2.4. Sample preparation

For preparation of serum, 10 mL of human blood was taken and collected in a sample tube. The serum of blood was separated after putting the sample in an incubator at 37 °C for 30 min for removing red cell. The above serum layer was centrifuged at 1100 (×*g*) for 6 min to precipitate proteins. The resulting human serum solution was then stored at −70 °C until used.

2.5. Standard procedures for the ECL detection

ECL measurements were carried out in a 0.1 mol L^{-1} PBS solution (pH 7.1) in the presence of 4.0×10^{-7} mol L^{-1} CdTe QDs solution using a conventional three electrode cell mentioned above. The applied working potential ranged from 0 to −2.3 V, and a cycle scan rate was 0.34 V s^{-1}. 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 five measurements. The different concentrations of standard L-Cys solutions were injected in the ECL cell to obtain the calibration curve. Similarly, sample solutions were injected in the ECL cell to detect the L-Cys concentrations in sample.

3. Results and discussion

3.1. Characterization of water-soluble CdTe QDs

As shown in Fig. 1(A), the prepared CdTe QDs were characterized by UV–vis and the PL spectra. The particle sizes of CdTe QDs were 2.25, 2.50, 2.77, 3.12, and 3.26 nm, respectively, which were calculated in virtue of the following empirical equation [31]:

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

In the above equation, D (nm) is the diameter of a given QDs, and λ (nm) is the wavelength of the first excitonic absorption peak of the UV–vis absorption spectra. It can be seen that the UV–vis absorption peaks and the PL peaks shifted to longer wavelengths with the increasing QD sizes as a consequence of the well-known quantum size effect. The quantum yield (QY) of the prepared CdTe QDs was obtained in comparison to the PL emission of Rhodamine 6G (QY 95%) [32]. The result supported that the PL QYs of CdTe QDs were 5.5%, 8.5%, 16.0%, 23.6% and 21.4%, respectively.

The CdTe QDs was also studied carefully by HRTEM image (Fig. 1(B)). The morphology and size of CdTe QDs could be observed clearly. The average size of studied CdTe QDs was about 3.16 nm, and considered close to the value of 3.12 nm resulting from the empirical formula which seems to be convenient to calculate the size of CdTe QDs.

The FT-IR spectra were used to character the structure of the prepared CdTe QDs. From Fig. 1(C), TGA showed a peak at 2566 cm^{-1} for stretch vibration of the S–H bond, which diminished in the spectrum of CdTe QDs. Therefore, it could be concluded that the S–Cd bonds were formatted between TGA and CdTe core. The asymmetric vibration of the carboxyl group in TGA shifted from 1720 to 1551 cm^{-1}, and the symmetric vibration of the carboxyl anion at 1387 cm^{-1} appeared in the spectrum of CdTe QDs, implying that the COOH in TGA turned to its anion. As a result, the structure of the prepared CdTe QDs could be identified as a cadmium-rich CdTe core covered with excess TGA^{2-} anions, which was similar to the structure of CdSe QDs [33].

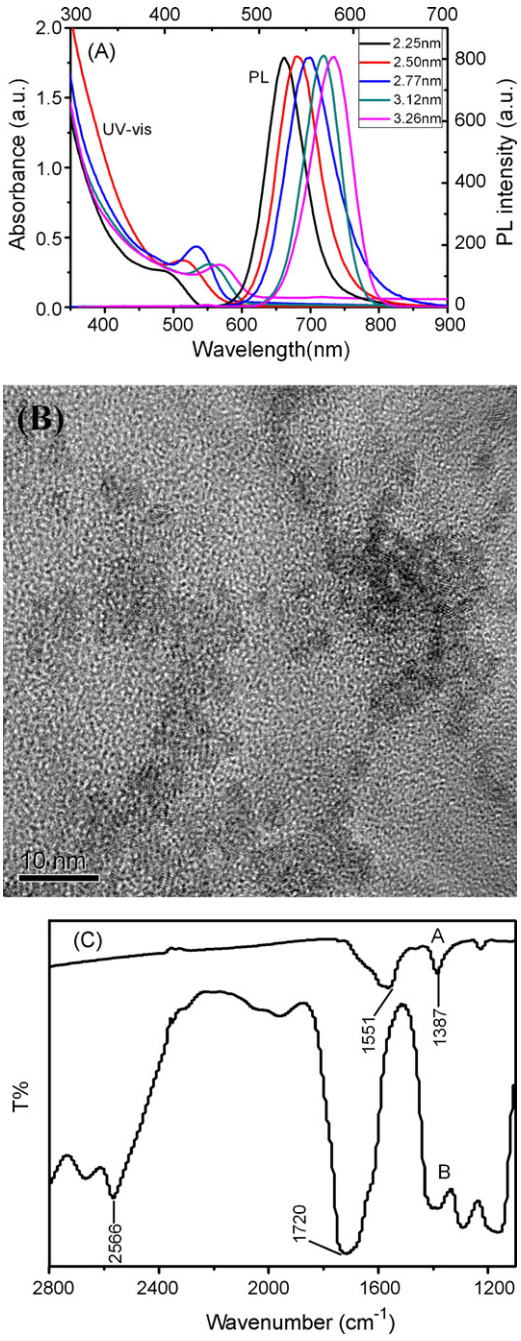

Fig. 1. (A) PL and UV–vis absorption spectra of CdTe QD solution with different sizes of CdTe QDs. (B) The HRTEM image of CdTe QDs, (C) FT-IR spectra of CdTe QDs (a) and TGA (b).

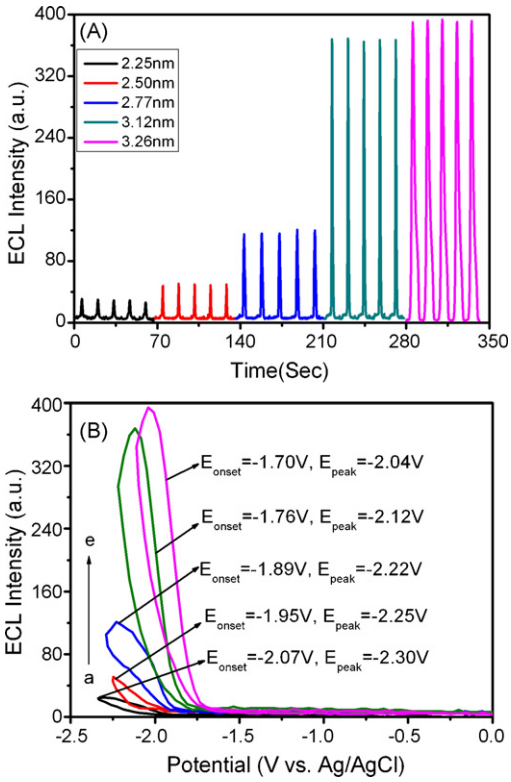

Fig. 2. (A) ECL curves of CdTe QD solution with different sizes. (B) Effects of potential and ECL intensity in CdTe QD solution with different sizes (conditions: 4.0×10^{-7} mol L^{-1} CdTe QD solution with different sizes; scan rate: 0.34 V s^{-1}; 0.1 mol L^{-1} pH 7.1 PBS; PMT voltage: 800 V).

3.2. Size-dependent ECL behavior of CdTe QDs

The size-dependent ECL behavior of CdTe QDs was investigated in air-saturated solution. It was found that the ECL intensity gradually increased while the particle size of CdTe QDs increased, indicating that ECL intensity of CdTe QDs has a size-dependent effect (Fig. 2(A)). Here, the concentrations of CdTe QDs were fixed in all our experiments (4.0×10^{-7} mol L^{-1}). According to ECL energy match theory [34], the ECL intensity depends on both the quantum efficiency of producing excited-state QDs and the luminescent quantum efficiency of excited-state QDs. The quantum efficiency of producing excited-state QDs enhanced with the increasing sizes of QDs, which was probably resulted from the generated energy of ECL reaction matching degree with the chemical energy for formation of excited state of CdTe QDs [28,29]. It is known that energy band gap of QDs decreased with the increment in particle size [31]. In this case, the increment in ECL intensity was possibly acctributed to chemical energy, generated during the ECL reaction of CdTe QDs, more matched the smaller energy band gap of the studied five sizes QDs. The more chemical energy matched the excitation energy need, the stronger the ECL intensity and efficiency. Moreover, the luminescent quantum efficiency of excited-state QDs increased with the increasing QDs sizes, because the confinement energy of excited-state QDs shifted to low energy with the increasing sizes of QDs. In addition, the luminescent quantum efficiency of excited-state QDs was inversely proportional to the confinement energy [35]. As a result, both the quantum efficiency of producing excited-state QDs and the luminescent quantum efficiency of excited-state QDs increased with increment in sizes, which finally resulted in that the ECL intensity of CdTe QDs increased with the particle sizes.

The relationships of ECL peak potentials and ECL onset potentials with the sizes of QDs were illuminated in Fig. 2(B). Both the ECL peak potentials and ECL onset potentials shifted positively with the increasing size or the decreasing band gap of the QDs, indicating that the injection of electrons to the surface of smaller QDs should be more difficult. It has been indicated that the energy band gap of QDs decreased with the increment in particle sizes. The energy levels of QDs move to low energies when the size of QDs increases, since the top of the valence band is shifted toward higher energies and the bottom of the conduction band is moved to lower energies with increasing particle size. This means that the smaller QDs need more energy for injection of electrons to the surface of QDs.

A similar relationship between the band gap of CdTe QDs and their electrochemical behaviors also was observed [28]. Given the fact that the CdTe QDs larger than 4 nm might be unstable, and it was difficult to obtain the large QDs of high quality. Therefore, CdTe QDs of 3.12 nm were chosen to conduct the following experiments. This work possibly provided a promising principle for improving the efficiency of QDs ECL by optimizing the sizes of QDs and the fast preferences of the ECL systems.

The ECL and cyclic voltammetry (CV) curves of the air-saturated blank PBS solution were also observed (not shown). No light emission and current peak were detected. Under the same conditions, the obvious light emission was observed in the CdTe QDs solution. The same experiment was done in the air-saturated blank PBS solution using the GC electrode which has done continuous CVs for 300 cycles in CdTe QDs solution. Similar results were obtained. It means that there nearly was no absorption on the surface of the electrode, or the working electrode was not easily contaminated by CdTe QDs solution in the process of ECL. Therefore, CdTe QDs can be studied as an excellent illuminant in the field of ECL.

3.3. Conditions optimization

The ECL of CdTe QDs was conducted in air-saturated solution without adding any additional oxidants. Therefore, the effect of dissolved oxygen on ECL intensity was investigated. As shown in Fig. 3(A), when dissolved oxygen was removed from the solution by bubbling high-purity N_2, the light emission intensity of ECL decreased dramatically, indicating that dissolved oxygen was an important coreactant for producing ECL of CdTe in the QDs solution. It was very interesting for producing the ECL emission without adding any foreign oxidants, and the operating processes of ECL were simplified. To acquire both simple process and high ECL intensity, air-saturated CdTe QDs solution was recommended in our experiments.

The contrast experiments were also conducted to examine the influence of coexisting substances (e.g., free $CdCl_2$ and TGA) on ECL of CdTe QDs (Fig. 3(B)). The concentrations of $CdCl_2$ and TGA solution were in agreement with their concentrations in un-pured CdTe QDs solution. With the same electrochemical parameters, the ECL behaviors of $CdCl_2$ and TGA solution were studied. Fig. 3(B) (curves d and g) depicted the ECL behaviors of pure TGA in PBS solution, and showed that no ECL signals and current peaks were observed. However, a pair of peak current appeared in pure $CdCl_2$ solution (curve c), and the ECL signal (curve f) was also quite weak. When TGA solution was added into the $CdCl_2$ solution, reduction peak current was decreased evidently (curve e), and the ECL signal was not observed. Therefore, the free $CdCl_2$ and TGA only affected electrochemical behaviors of CdTe QDs (CV curves), but effect on ECL emission was not obvious.

The effect of concentrations of CdTe QDs was studied (Fig. 4(A)). When the concentrations of CdTe QDs were augmented, the formed individual CdTe QDs species were increased in the scanning process, which resulted in the enhancement of the ECL intensity. When the concentration of the CdTe QDs solution exceeded 4.0×10^{-7} mol L^{-1}, the ECL intensity decreased, indicating that the excessive CdTe QDs could inhibit the generation of excited-state CdTe QDs, which was due to an effect called self-absorption in higher concentration [36].

The CdTe QDs was added to the PBS solution and incubated about 5, 10, 15, 20, 25 and 30 min. Then the effect of incubation time on the ECL of CdTe QDs was investigated (Fig. 4(B)). It was found that there was no obvious effect of incubation time on the ECL of

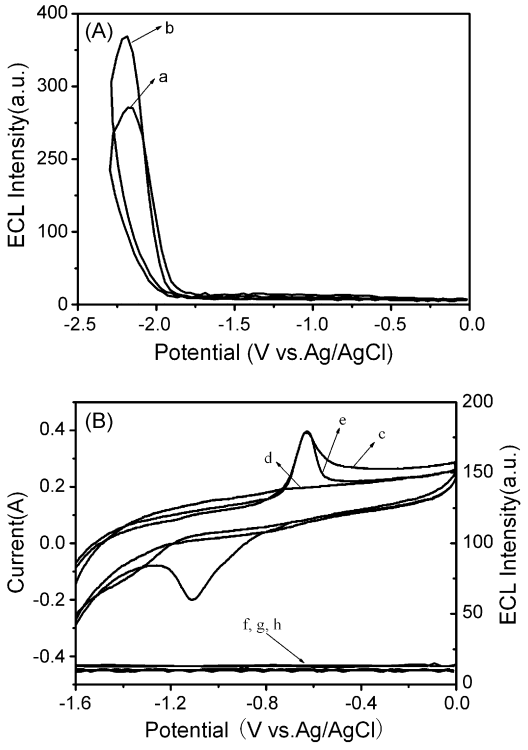

Fig. 3. (A) Effects of dissolved oxygen (a) N_2-saturated CdTe QD solution (4.0×10^{-7} mol L^{-1}); (b) air-saturated CdTe QD solution (4.0×10^{-7} mol L^{-1}) and (B) other coreactants (c) $CdCl_2$; (d) TGA; (e) TGA + $CdCl_2$ (f–h) ECL curves. (Conditions: scan rate: 0.34 V s^{-1}; 0.1 mol L^{-1} pH 7.1 PBS; PMT voltage: 800 V.)

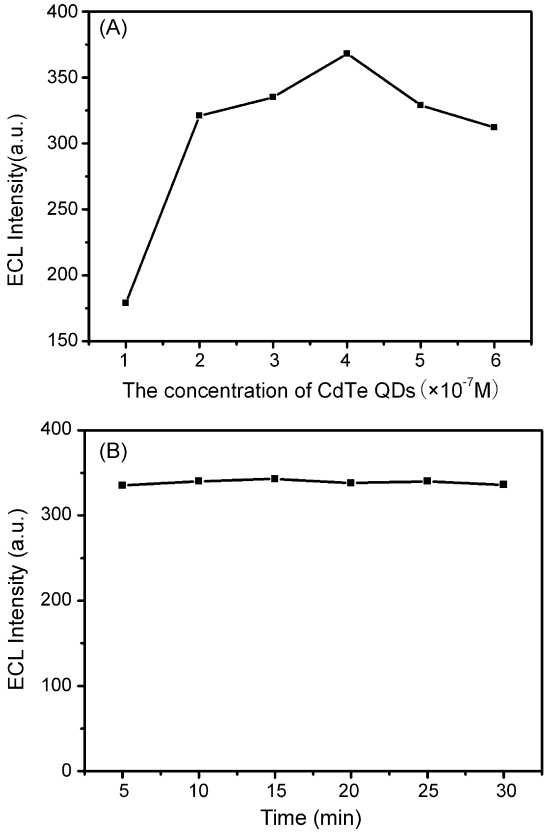

Fig. 4. (A) Effects of concentration of CdTe QDs (conditions: scan rate: 0.34 V s^{-1}; 0.1 mol L^{-1} pH 7.1 PBS; PMT voltage: 800 V) and (B) incubation time. (conditions: 4.0×10^{-7} mol L^{-1} CdTe QD solution; 0.1 mol L^{-1} pH 7.1 PBS; PMT voltage: 800 V).

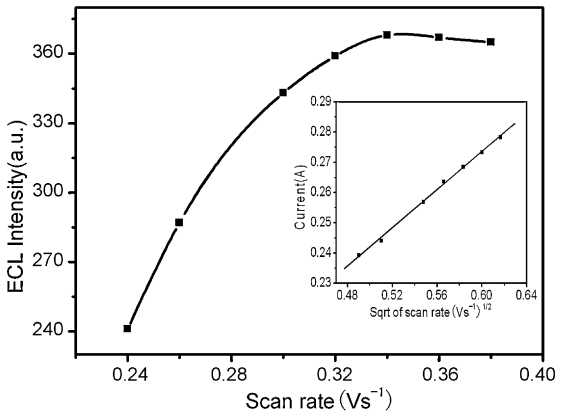

Fig. 5. Effect of scan rate on ECL intensity of CdTe QDs. Inset: Plot of current versus square root of scan rate ($v^{1/2}$) (conditions: 4.0×10^{-7} mol L^{-1} CdTe QD solution; 0.1 mol L^{-1} pH 7.1 PBS; PMT voltage: 800 V).

CdTe QDs in a certain time range, indicating the better stability of ECL.

The scan rate could also affect on the ECL intensity (Fig. 5). With the increasing scan rate, the ECL intensity increased and tended to a constant value at the scan rate of 0.34 V s^{-1}, indicating the ECL intensity reached the saturation point. Therefore, the scan rate of 0.34 V s^{-1} was chosen for the following studies. We also found that the cathode peak current was linear with the square root of the scan rate during CV as shown in Fig. 5 (inset), which indicated that this electrochemical reaction was an irreversible diffusion-controlled electrode process.

The studied potential windows were selected as −1.9 to 0, −2.0 to 0, −2.1 to 0, −2.3 to 0 and −2.5 to 0 V, respectively. It was found that the ECL intensities were enhanced, but the ECL signals reached a maximum at a potential window of −2.3 to 0 V. That might be due to the fact that the CdTe QDs in the ECL processes with a high excited electrochemical potential window were unstable. Thus, to achieve the optimum intensity and stability, a potential window of −2.3 to 0 V was selected for the following ECL experiment.

3.4. The quenching effects of L-Cys on the ECL intensity

The quenching effects of L-Cys on the ECL intensity was studied and shown in Fig. 6. Upon addition of L-Cys to the PBS containing 4.0×10^{-7} mol L^{-1} CdTe QDs, the ECL intensity decreased greatly with an increase in the concentration of L-Cys. The L-Cys was responsible for the quenching effect according to the following reaction:

$$2\,RSH \xrightarrow{O_2, H_2O} RSSR$$

According to the above reaction, if L-Cys was added to the system, it would react with the dissolved oxygen or its intermediate species produced in the processes of QD ECL, which resulted in decreasing the ECL intensity. Meanwhile, it confirms the above results about the role of dissolved oxygen. Here, although the stabilizer TGA was also a thiol compound, FT-IR spectrum (Fig. 1(C)) indicated that the ECL emission was quenched by the L-Cys. The structure of CdTe QDs indicated only S–Cd bond without an SH group present in the QDs. Thus, it did not quench the ECL emission and interfere with the detection of L-Cys. Therefore, our present study aims to develop a finer method for the detection of L-Cys based on our above discussion.

3.5. Application to detection of L-Cys

L-Cys is a naturally occurring amino acid with a thiol group, which plays an important role in several biological processes. L-Cys is involved in a variety of key cellular functions including protein synthesis, detoxicfication, and metabolism, and its insufficiency may cause many diseases. Due to the structural similarity of amino acids and their spectroscopic inertness, most of analytical methods usually involve complicated chromatography separation [37]. Thus, the development of a simple and highly selective method [38] for the detection of L-Cys is obviously of significance.

From the inset of Fig. 6, the ECL intensity decreased linearly with the concentrations of L-Cys. The calibration range for determination of L-Cys was from 1.3×10^{-6} to 3.5×10^{-5} mol L^{-1} with the correlation coefficient of 0.996. The detection limit (S/N = 3) was found to be 8.7×10^{-7} mol L^{-1}. The relative standard deviation (R.S.D.) at the L-Cys concentration of 1.3×10^{-5} mol L^{-1} was 2.0% ($n = 5$), indicating an acceptable reproduction.

To study the selectivity for L-Cys determination with the proposed method in amino acid detection, various amino acids were investigated according to the proposed procedure by increasing amounts of them. As shown in Fig. 7, no interference was observed in the presence of L-Pro, L-Glu, L-Ala, L-Gly, L-Leu, L-Val, L-Thr and L-Ile, even when they were present in a 1000-fold concentration. Furthermore, the ECL intensity decreases were all less than 5% relative to L-Cys in the presence of some other common amino acids

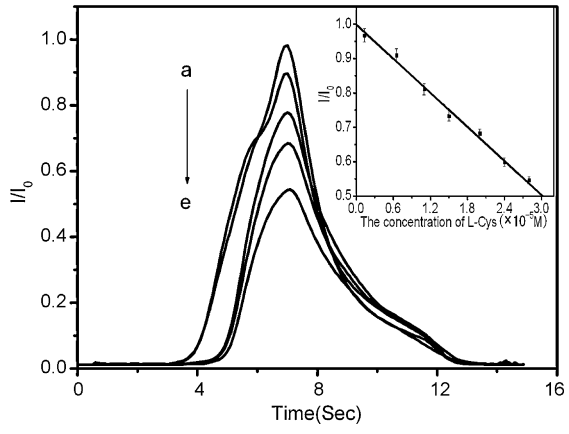

Fig. 6. The quenching effect of L-Cys at 0 (a), 0.65 (b), 1.3 (c), 2.0 (d), and 2.8×10^{-5} mol L^{-1} (e) on the ECL intensity of CdTe QDs. Inset: linear calibration plot for L-Cys (conditions: 4.0×10^{-7} mol L^{-1} CdTe QD solution, scan rate: 0.34 V s^{-1}; 0.1 mol L^{-1} pH 7.1 PBS, PMT voltage: 800 V).

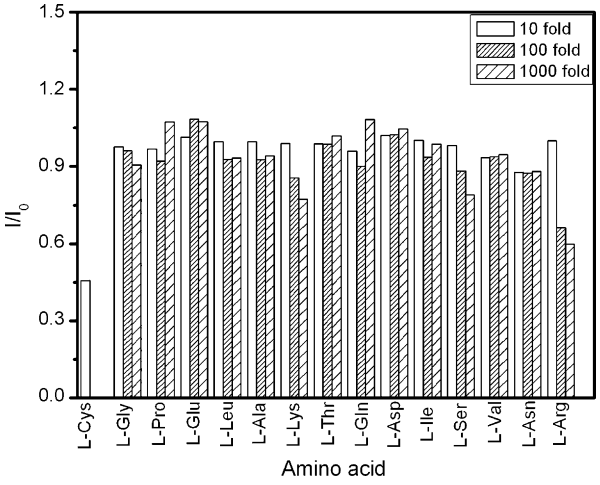

Fig. 7. Interferences of same common amino acid (conditions: 4.0×10^{-7} mol L^{-1} CdTe QD solution; scan rate: 0.34 V s^{-1}; 0.1 mol L^{-1} pH 7.1 PBS, PMT voltage: 800 V).

Table 1
Determination of L-Cys in real samples.

Sample	L-Cys added (μ mol L^{-1})	L-Cys found[a] (μ mol L^{-1})	Recovery (%)	R.S.D.[a] (%)
Synthetic amino acids mixtures				
1	39.0	38.6 ± 2.6	99.0	6.6
2	126.0	126.0 ± 2.0	96.9	1.6
3	210.0	204.4 ± 1.0	97.3	5.5
Human serum				
1	0	364.3 ± 7.6	4.7	
2	100.0	462.1 ± 8.4	98.0	2.6
3	200.0	565.7 ± 10.5	101.0	1.8
4	400.0	735.4 ± 6.5	92.8	1.0

[a] Mean result of five measurements.

with a 100-fold concentration, which also could be neglectable. Therefore, the proposed method is practical for the determination of L-Cys and showed the ideal selectivity.

As a practical use, the proposed method was used to detect L-Cys in synthetic amino acids mixtures and human serum. The recoveries of L-Cys are determined by the standard addition method. The results shown in Table 1. It indicated that the proposed method was suitable for the determination of L-Cys in the presence of other amino acids. Moreover, this method could be also used to successfully detect L-Cys in human serum, and the total concentration were found to be 364.3 ± 7.6 μmol L^{-1}. This value fell in the normal range of total L-Cys (174.0–378.0 μmol L^{-1}) in human serum detected by Stabler et al. [39]. Meanwhile, the method had good recoveries, as given in Table 1. These data suggested the fine accuracy and acceptable practicability of the proposed method.

Our following work also extensively studied the quenching effects of other thiol compounds on the ECL intensity, and the similar results could be demonstrated (not shown). Thus, the proposed method could be developed and applied for thiol compounds detection.

4. Conclusions

In summary, we demonstrated that the ECL behavior of CdTe QDs was size dependent. It gives a new path to further improve the efficiency of QD ECL by optimizing the sizes of QDs, and provides a promising strategy for the fast preferences of the ECL system. Furthermore, it was found that the relative high ECL intensity was also observed in air-saturated solution without adding foreign oxidant, and the operating processes of ECL were simplified. A novel method for the high selectivity determination of L-Cys was developed. In contrast to other ECL sensor methods, this proposed method showed simple operating processes and ideal selectivity. Our studies would promote the further studies of QD ECL sensor and has found potential analytical applications.

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