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ORIGINAL PAPER

An electrochemiluminescence sensor for determination of durabolin based on CdTe QD films by layer-by-layer self-assembly

Fuwei Wan · Jinghua Yu · Ping Yang · Shenguang Ge · Mei Yan

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Abstract This work reported for the first time the use of flow injection electrochemiluminescence (FI-ECL) sensor for the determination of durabolin in an aqueous system based on CdTe quantum dot (QD) films. Aqueous CdTe colloidal solutions were prepared using thioglycolic acid as a capping agent. Zetasizer Nano ZS (Malvern, UK) was employed to characterize the size of CdTe QDs. The UV–vis and photoluminescence spectra of samples were systematically characterized. Indium tin oxide (ITO) slide glass was modified with CdTe QDs by layer-by-layer self-assembly. CdTe QD films were packed into a homemade cell and used as a recognizer of the FI-ECL sensor to determine durabolin. The intensive anodic ECL emission was obtained at a starting potential of +1.3 V (vs. Ag/AgCl) in a carbonate bicarbonate buffer solution with a pH of 9.93 at an ITO electrode. The ECL intensity was correlated linearly with the concentration of durabolin over the range of 1.0×10^{-8}–1.0×10^{-5} g mL^{-1}, and the detection limit was 2.5×10^{-9} g mL^{-1}. The relative standard deviation for the determination of 1.0×10^{-6} g mL^{-1} durabolin was 1.04% (n= 11). This simple and sensitive sensor revealed good reproducibility for ECL analysis. As a result, the new FI-ECL sensor had been successfully applied to the determination of durabolin in food samples. This strategy could be easily realized and opened new avenues for the applications of QDs in ECL biosensing.

Keywords Quantum dots (QDs) · Self-assembly · Flow injection electroluminescence (FI-ECL) · Sensors · Durabolin

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F. Wan · J. Yu (✉) · S. Ge · M. Yan
Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, School of Chemistry and Chemical Engineering, University of Jinan,
Jinan 250022, China
e-mail: wanfw1984@hotmail.com

P. Yang
School of Material Science and Engineering, University of Jinan,
Jinan 250022, China

Introduction

Highly luminescent quantum dots (QDs) have received tremendous attention for their possible luminescent application in aqueous solution [1, 2]. Some bioinorganic conjugations made with CdSe/ZnS core–shell QDs and antibodies have shown potential application in fluoroimmunoassays [3, 4]. Recent work has demonstrated that the layer-by-layer assembly of CdSe QDs in sandwiched polyelectrolyte architecture can improve their photoluminescence (PL) property and be used for the detection of paraoxon [5, 6]. Semiconductor QDs are complementary and in some cases may be superior to the existing fluorophores. Further explorations on their superior emitting properties by different methods were of great importance. In recent years, these QDs provide potential alternatives for developing new electrochemiluminescence (ECL) emitters and preparing new ECL sensors [7, 8].

Electrochemiluminescence technique has been widely used in many fields [9–11]. Compared with chemiluminescence (CL), ECL cannot only retain the advantages of CL, such as the excellent sensitivity and a wide dynamic concentration response range, but can also own some additional advantages over CL [12–14]. First, the application of potential can control the CL reaction and improve its selectivity; second, the generation of light in the vicinity of

the electrode gives improved spatial control for sensitive detection; and third, the target molecules can be electrochemically modified to form a CL-active species and extend its analytical application. Based on these advantages, both $Ru(bpy)_3^{2+}$ and luminol ECL have been widely applied to ECL sensors [15, 16]. However, the analysis based on QD ECL possesses some limitations. Recent research works have indicated QD solution in flow phase which have been used for the detection of several analytes, including nitrite [17], oxidase substrates [18], proteins [19], dopamine [9], and amines [20]. This method has convenient operation, rapid determination, and excellent sensitivity, but a lot of QDs were wasted and are harmful as well to the environment. In this paper, we report on the ECL property of thioglycolic acid (TGA)-capped CdTe QDs in aqueous solution. Indium tin oxide (ITO) slide glass was decorated with CdTe QDs by layer-by-layer (LbL) self-assembly. This decorated slide glass was used as a recognizer of the FI-ECL sensor. To the best of our knowledge, no reports have been found about the application of this FI-ECL sensor to determine analyte up to now.

Durabolin is administered by intramuscular injection in an oily base [21]. The positive effects of the drug include muscle growth, appetite stimulation, increased red blood cell production, and bone density [22, 23]. Clinically, it is used in treating anemia, neoplasia including breast cancer, rebuilding of muscles after a debilitating disease, and treatment of osteoporosis in postmenopausal women [24]. Various methods based on osteryoung square wave voltammetry [21, 25], high-performance liquid chromatography (HPLC) [26], and ultra HPLC combined with time-of-flight mass spectrometry [27] have been developed for the determination of durabolin. Some of them are complex, time-consuming, and require tedious sample pretreatment. Thus, the development of new analytical methods for sensitive and rapid detection of durabolin combining with multifarious techniques is still an attractive subject.

The new FI-ECL system was established by overcoming several drawbacks of conventional ECL systems [28, 29]. The ECL thin-layer flow cells made by different researchers might be quite different in appearance [30]. These types of ECL flow cell had the following drawbacks: (1) Large dead volume, especially when the reference electrode was placed near the inlet, would reduce both the detection sensitivity and separation efficiency of the sample in HPLC; (2) high IR drop, especially when the reference electrode was located at the downstream, caused high overpotential and thus decreased the sensitivity of ECL detention; and (3) high flow resistance made it difficult to remove possible gas bubbles, which would cause significant noise. To overcome these drawbacks, a new type of ECL flow cell (see Fig. 1) was designed and used in our homemade FI-ECL system. Moreover, the cell has other advantages: good emission efficiency and receiving sensitivity, cost effectivity, and high sensitivity. After being established, the new FI-ECL system was adopted to investigate the ECL response of durabolin in the presence of the ECL of QDs and further detect durabolin in biological samples. This method could be easily realized, thus opening new avenues for the application of QDs in ECL biosensor.

Experiments

Reagents

All chemicals used were of analytical grade or the highest purity available. TGA and 3-aminopropyltrimethoxysilane (APS) were purchased from Alfa Aesar China Ltd. Tellurium (Te) powder, sodium borohydride ($NaBH_4$), cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), $Cd(ClO_4)_2$, and rhodamine 6G were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Durabolin was supplied by the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), alcohol, and toluene were purchased from Tian Jin Da Mao Chemical Reagent Factory (Tian Jin, China). Milli-Q water was used throughout. A 0.1 M carbonate bicarbonate buffer solution was used throughout the work, and the pH was adjusted by changing the ratio of Na_2CO_3 to $NaHCO_3$.

Apparatus

ECL was conducted on a CHI 760D electrochemical working station (CHI Co.) with a homemade FI-ECL system comprising a CdTe QD-decorated ITO working electrode, a platinum counter electrode, and a Ag/AgCl (saturated KCl) reference electrode. The ECL emission was detected synchronously with a flow injection luminescence analyzer (IFFM-E, Xi'an Remex Electronic instrument High-Tech Ltd., Xi′an, China) at room temperature. The homemade ECL cell was placed in front of the detection window of the photomultiplier tube (PMT). UV–vis absorption spectra were measured on a UV-3101 spectrophotometer (Shimadzu, Japan). The PL spectra were recorded with a LS-55 spectrofluorometer (P.E. USA). The sizes of CdTe QDs were measured on Zetasizer Nano ZS (Malvern).

Preparation of water-soluble CdTe QDs

CdTe QD solution was prepared according to a previously reported method [2]. Typically, 0.2020 g of $CdCl_2{\cdot}2.5H_2O$ was dissolved in 35 mL of water and 160 μL of TGA was

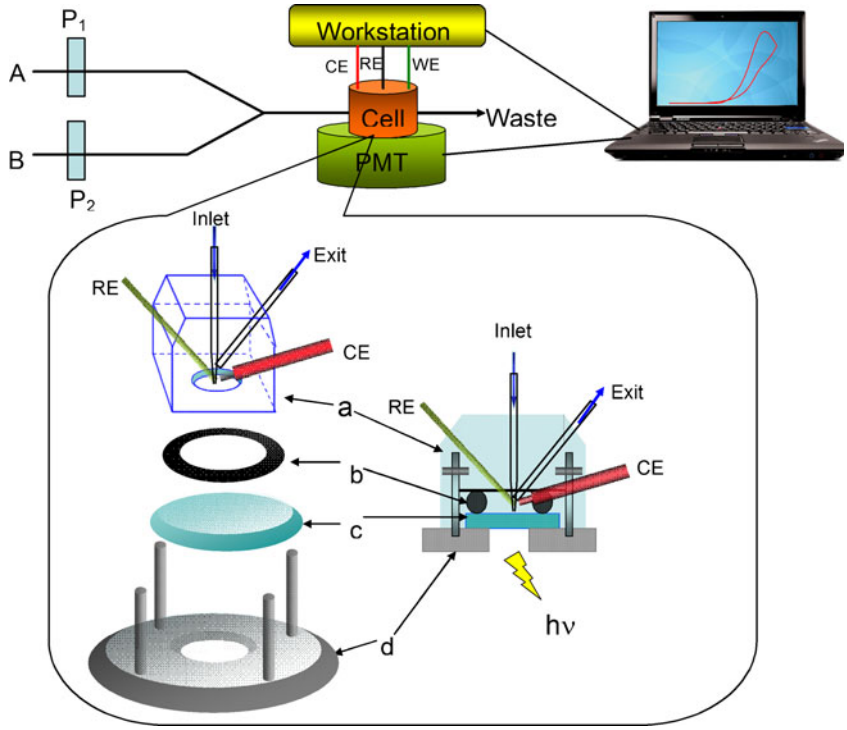

Fig. 1 Schematic diagram of the FI-CL system and the ECL cell. *A* Durabolin standard solution. *B* Carbonate bicarbonate buffer solution. P_1, P_2 peristaltic pump, *Cell* FI-ECL cell, *PMT* photomultiplier tube. *a* Top Perspex block; *b* airtight rubber; *c* ITO slide glass; *d* bottom Perspex block. *RE* reference electrode, *CE* counter electrode, *WE* working electrode

added in the water. Then, the pH values of the solution were adjusted to 11.3 by adding dropwise 1 M NaOH solution. After, the resulting clear solution was bubbled with highly pure N_2 for 20 min and 10.0 mL of the NaHTe solution (produced by reaction of 0.1252 g $NaBH_4$ and 0.0572 g Te powder in oxygen-free water) was then quickly injected into the vigorously stirred solution; CdTe nanocrystals grew gradually by refluxing at 100 °C The diverse colors (particle sizes) of the CdTe QDs were obtained through different refluxing times. The final QD solutions were rather stable for more than 3 months when kept in a refrigerator at 4 °C.

Preparation of CdTe QD films on the ITO surface

ITO slide glass with a surface resistance of 30–60 Ω cm^{-2} was cut into 3.0×1.0-cm slides. The surface treatment of ITO slide glass was performed using the procedure described in detail in a preceding paper [31]. The substrates were cleaned with acetone, ethanol, and water, respectively. They were immersed into 1 M NaOH for 30 min and then rinsed with copious amounts of water and dried at 120 °C for 2 h.

CdTe QD films on the ITO surface were prepared according to the literature [32]. The schematic was shown in Fig. 2. The resultant substrates were first modified by being immersed in a toluene solution of APS for 30 min and were then rinsed with toluene and dried with N_2. In LbL self-assembling processes using APS, the modified substrate was first dipped into an aqueous solution of TGA (0.15 M, pH ~10, containing Cd^{2+} as a form of $Cd(ClO_4)_2$) for 5 min. In this stage, the amino group in APS was linked with the carboxyl group in TGA together with the hydrolysis of APS on the surface. Accordingly, TGA molecules play an important role in preventing the hydrolyzed products of APS from completely dissolving in water. The sample was then immersed in the aqueous QD colloidal solution for 10 min to form a QD layer. Each step was interrupted with doubly distilled water rinsing and N_2 drying. The cycle was repeated until obtaining the desired number of layers.

Analytical procedures

Investigations of ECL behaviors were performed using the system shown schematically in Fig. 1. Flow tubes (A, B) were connected with durabolin standard or sample solution and buffer solution, respectively.

Results and discussion

Characterization of TGA-modified CdTe QDs

UV–vis spectra and PL spectra were recorded (in Electronic supplementary material (ESM) Fig. S1) as in the procedure described in detail in a preceding paper [33, 34]. As shown in ESM Fig. S1a, all UV–vis spectra showed a well-resolved maximum absorption of the first electronic transition, indicating a sufficiently narrow partical size distribution of

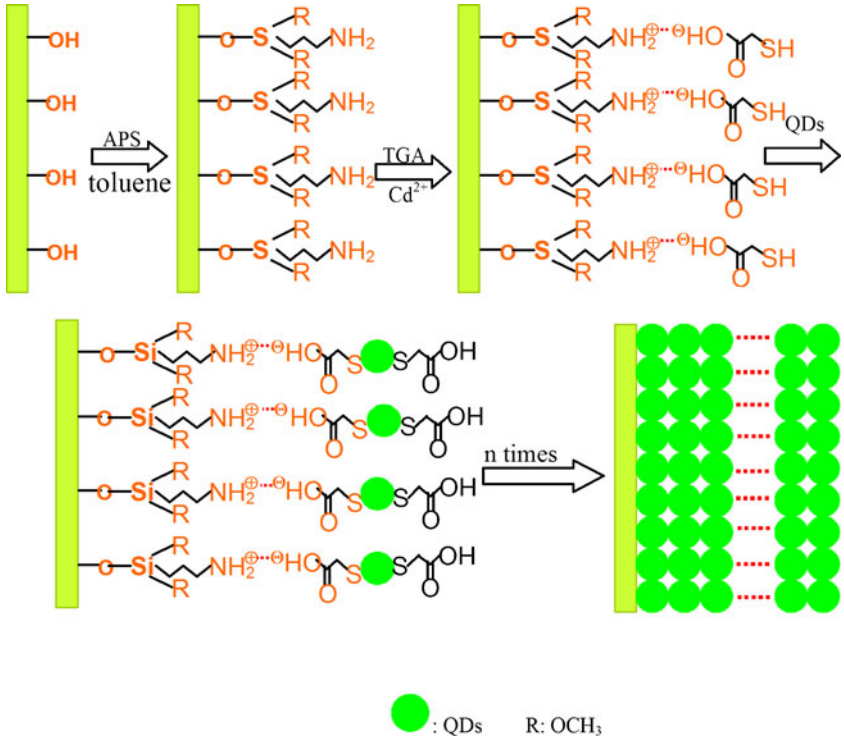

Fig. 2 Schematic diagram of LbL slf-assembled processes of multilayer QD films

the QDs. The results were also confirmed from the PL spectra with full width at half-maximum <40 nm.

The emitting color under UV irradiation (365 nm) of CdTe QDs was from cyan to green, yellow, and, finally, orange with increasing refluxing time (inset in ESM Fig. S1). The red shifts of the color, the absorption edge, and the maximum PL emission wavelength indicated the growth of the CdTe QDs during the refluxing time. This indicated that the size of the QDs could be tuned simply by varying the refluxing time in the bath. The PL intensity also depended on the refluxing time (ESM Fig. S1b).

The sizes of CdTe QDs were measured on Zetasizer Nano ZS (Malvern). The results showed that the CdTe QDs have a monodisperse characteristic and centralized distribution and that the partical sizes were augmented with the increase of refluxing time.

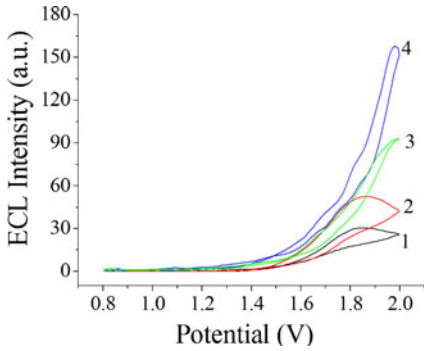

Fig. 3 ECL behaviors of the CdTe QD film. *1* pH 9.93 carbonate bicarbonate buffer solution. *2* pH 9.93 carbonate bicarbonate buffer solution+1.0×10^{-7} g mL^{-1} durabolin. *3* pH 9.93 carbonate bicarbonate buffer solution+5.0×10^{-7} g mL^{-1} durabolin. *4* pH 9.93 carbonate bicarbonate buffer solution+1.0×10^{-6} g mL^{-1} durabolin

Photoluminescence quantum yields (QYs) were investigated according to the literature [35]. Rhodamine 6G was used as the reference material. QY is defined as:

$$Y_u = Y_s \cdot \frac{F_u}{F_s} \cdot \frac{A_s}{A_u}$$

where Y_u and Y_s are the QY of CdTe QDs and rhodamine 6G, F_u and F_s are the integral area of fluorescence of CdTe QDs and rhodamine 6G, and A_u and A_s are the absorption of CdTe QDs and rhodamine 6G, respectively.

With increasing refluxing time, the PL QYs increased markedly. The QY of CdTe QDs increased from 20.2% to 69.4% as the refluxing time was prolonged from 1 to 90 min and then reached a maximum value of 75.3% at 180 min. The remarkable QY is much higher than that of CdTe QDs with other aqueous synthesis [36, 37]. The luminescence efficiency was stable for more than 3 months when kept in a refrigerator at 4 °C. When the refluxing time was 90 min, the QY was high (69.4%), and CdTe QDs have a better dispersion characteristic, centralized distribution, and the average size was 4 nm. The CdTe QDs with refluxing for 90 min was used in this paper.

Fabrication of the FI-ECL cell

The FI-ECL cell (Fig. 1) was fabricated by a cuboid PMMA. The modified ITO slide glass was cut into 1.0-cm

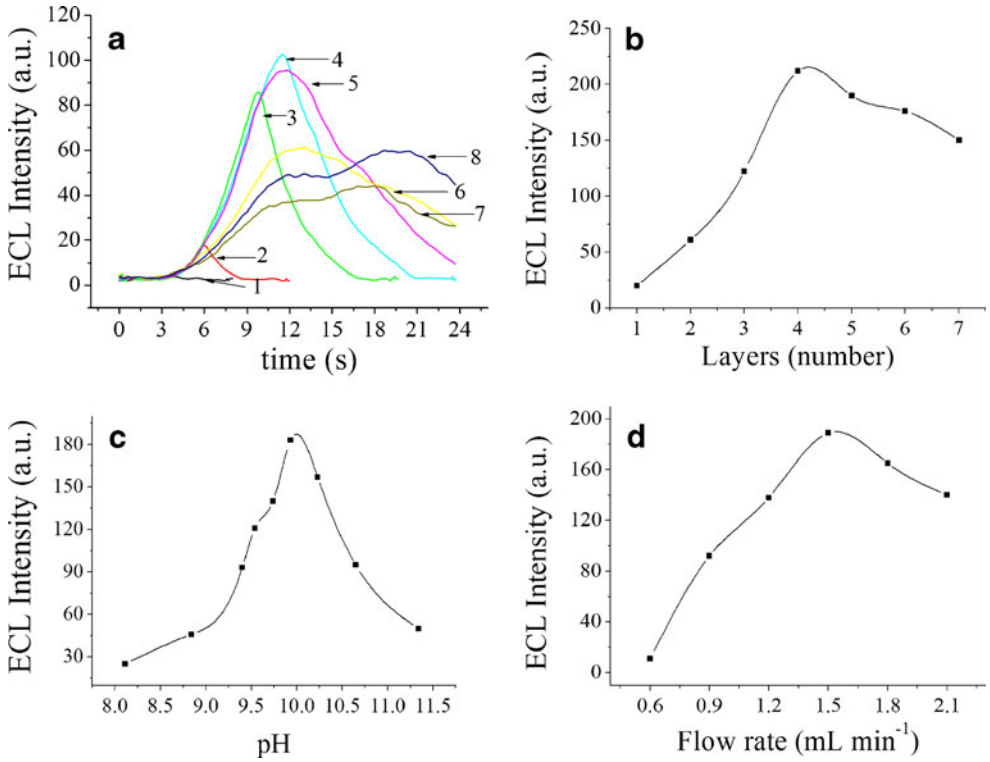

Fig. 4 Effect of experimental conditions. **a**–**d** Effects of voltage range, layers of CdTe QD films, pH, and flow rate, respectively

i.d. and used as working electrode. The FI-ECL cell mainly consisted of an ITO working electrode (WE), two flow tubes, platinum counterelectrode (CE), and Ag/AgCl reference electrode (RE). The WE, two flow tubes, CE, and RE slide together by screws to form the airtight FI-ECL cell (Fig. 1). On top of the cell was an inlet and outlet with tubes, and at the bottom of the cell, a round optical window was made where the ECL signal passed from the ITO to the detection system.

This is the first report that the ITO slide glass decorated with CdTe QDs was applied for ECL analysis. This ECL detection system has some apparent advantages.

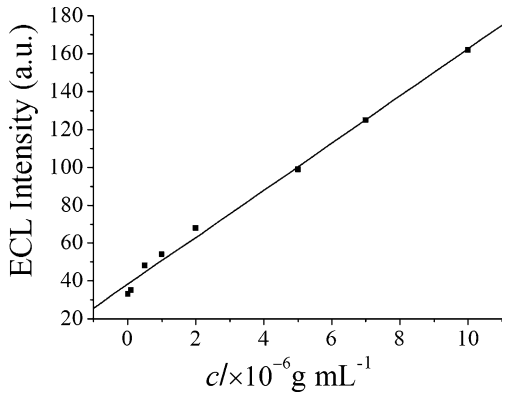

Fig. 5 Relationship between ECL intensity and durabolin concentration

1. The inlet was located on top of the cell; the samples were injected on the ITO WE surface directly, which was the transparent window, so that this kind of ECL detector has a very small dead volume. The WE, CE, and RE were placed so close that the IR drop was decreased easily. The outlet was placed on top of the cell; hence, the gas bubbles cannot produce and the flow resistance is reduced greatly.
2. The surface of the ITO working electrode (as transparent window) was placed opposite the transparent window, resulting in nearly 100% of the ECL emission generated at the surface of the working electrode being able to be detected by PMT. It overcomes the drawback of the ECL emission scattered in all directions, but could only be detected in a very limited angle.
3. The ITO working electrode was located at the bottom of the cell by screws. The modified ITO slide glass was cut into 1.0-cm i.d. and was located to be the transparent window, when, beyond its service life, another modified ITO slide glass can be used to replace the dead one by handling the screws to realize this easy pack. Compared with the glassy carbon electrode and gold electrode, the ITO slide glass was cost-effective and was used for high-quantity production.
4. The working electrode can be located as closely as possible to the PMT; the thickness of the solution thin layer between the surface of the working electrode and the inlet tube is estimated to be only of a few

Table 1 Determination of durabolin in foodstuff samples

Sample no.	Found[a] (μg g^{-1})	Added (μg g^{-1})	Recovered[a] (μg g^{-1})	Recovery (%)
1	7.5	100	16.8	96.0
		30.0	38.7	103.2
2	0.47	10.0	10.9	104.1
		30.0	29.8	97.8

[a] Average of six measurements

micrometers. Moreover, the area of ITO working electrode was larger than that of the glassy carbon electrode or gold electrode. This kind of ECL detector has high sensitivity.

Electrochemical and ECL behaviors of CdTe QD films

The feasibility of the method could be forecasted through the electrochemical and ECL behaviors of CdTe QD films, and the relative ECL intensity is directly related to the sensitivity of the method. The results were shown in Fig. 3. In air-saturated pH 9.93 sodium carbonate buffer solution, the cyclic voltammogram of CdTe QD films showed a weak ECL emission peak at +1.8 V (peak 1). When 1.0×10^{-7} g mL^{-1} durabolin was injected into the cell, the ECL signal enhanced (peak 2). With the increasing concentration of durabolin, the ECL signal enhanced further (peak 3, peak 4). The concentration of durabolin was quantified via the peak height (ECL signal), which was obtained by subtracting the ECL intensity (without durabolin) from that of the sample of durabolin standard solution.

Optimization of experimental conditions

A series of experiments were conducted to select optimum analytical conditions using a 1.0×10^{-6} g mL^{-1} durabolin solution; the results were shown in Fig. 4. The optimal conditions included the voltage range of cyclic voltammetry, the layers of CdTe QDs on ITO slide glass, pH, and the flow rate (Fig. 4a–d, respectively). The low potential was fixed at +0.8 V, the effect of high potential was examined from +1.2 to +3.0 V, the ECL intensity increased with raising the high potential up to +2.0 V, and above +2.0 V, the ECL intensity has a tailing peak. Therefore, the +0.8- to 2.0-V voltage range was used for the further work. The layers of CdTe QD films on ITO slide glass were examined over 1–7 ranges, and the ECL intensity reached up to the maximum value when the ITO slide glass was modified by four layers. The ECL intensity depended on the concentration of the coreactant and pH value of carbonate bicarbonate buffer solution. The maximum intensity occurred at pH 9.93 buffer solution, which was used in the following work. The effect of the flow rate on ECL intensity was examined in the range of 0.6–2.1 mL min^{-1}, and the results showed that the optimum flow rate was 1.5 mL min^{-1}.

As a result, the optimal concentration for the voltage range of cyclic voltammetry, the layers of CdTe QD films, pH, and the flow rate were from +0.8 to +2.0 V, four layers, pH 9.93 and 1.5 mL min^{-1}, respectively.

Interference investigation

The influence of foreign species was studied by analyzing a standard solution of 1.0×10^{-6} g mL^{-1} durabolin to which increasing amounts of foreign species were added. A substance was considered without interference if the variation of the ECL intensity was within ±5%. The influence of some inorganic ions and organic compounds was studied; all of the foreign species were possible substances with possible concentration in the target sample. The tolerable concentration ratios of foreign species to 1.0×10^{-6} g mL^{-1} of durabolin were over 500-fold protein, Fe, Ca, vitamin A, and vitamin D, 100-fold cyclodextrin, L-leucine, L-proline, L-phenylalamine, L-methionine, K^+, V_{B1}, and bovine serum albumin and 10-fold for diethylstilbestrol, L-tryptophan, L-lysine, L-cysteine, Al^{3+}, Bi^{3+}, V_{B6}, starch, and ascorbic acid. From the above interference investigation, it can be seen that the main substances (such as protein, vitamin A, vitamin D, Fe, and Ca) in the target sample could not interfere in the determination by the present method. Some inorganic ions (Al^{3+}, Bi^{3+}), amino acids (L-tryptophan, L-lysine, L-cysteine), diethylstilbestrol, V_{B6}, starch, and ascorbic acid have a little interference.

Application and analytical performance

Under the optimum conditions, the analytical performance of the proposed method was obtained. The relative ECL intensity (I_{ECL}) was linear to the concentration (c) of durabolin from 1.0×10^{-8} to 1.0×10^{-5} g mL^{-1}. The relationship between ECL intensity and durabolin concentration was shown in Fig. 5. The regression equation was $I_{ECL}=38.17+1.24\times10^{8}c$ (g mL^{-1}, $R=0.9967$). The detection limit was 2.5×10^{-9} g mL^{-1}. The relative standard deviation was 1.04% by 11 replicate determinations of 1.0×10^{-6} g mL^{-1} durabolin; no obvious change was observed.

In order to evaluate the applicability and reliability of the proposed method, durabolin in two samples including egg and chicken was determined. They were all purchased from the supermarket.

First, 5.0-g samples were taken into a 50-mL centrifuge tube with 25 mL *tert*-butyl methyl, respectively. After centrifuging the samples at 9,000 rpm for 3 min, these were oscillated for 10 min and the samples centrifuged again at 6,000 rpm and 4 °C for 10 min. The supernatant and clear solution were taken into a 100-mL pear-shaped bottle and then the aforementioned process was repeated again about the residual to achieve another clear solution. The obtained two clear solutions were taken into rotary evaporators and were evaporated to dryness at room temperature. Then, 2.0 mL doubly distilled water was added into the container and the sample dissolved in water with ultraphonic as well as centrifuged at 6,000 rpm, then the clear solution was filtered with the 0.22-μm filter paper. Lastly, the supernatant was transfered into a 50-mL flask and diluted with doubly distilled water. The results of the determinations and the recovery tests were shown in Table 1. As can be seen from Table 1, the recoveries of added durabolin can be quantitative, and the *t* test assumed that there is no significant difference between recovery efficiency and 100% at a confidence level of 95%.

Stability and reproducibility of FI-ECL sensor

The stability and reproducibility of ECL intensity of the FI-ECL sensor was shown in ESM Fig. S2. ESM Fig. S2a showed the ECL intensity–time curve of 0.1 M, pH 9.93, carbonate bicarbonate buffer solution containing 1.0×10^{-6} g mL^{-1} durabolin under continuous potential scanning for five cycles. The relative standard deviation was 1.80%. It indicated that there was no obvious change in ECL intensity and the sensor had good stability. ESM Figs. S2b and S2c show the ECL intensity–time curves of the FI-ECL sensor under the same conditions after 1 and 2 weeks, respectively. They reflected the good reproducibility of the sensor. In the 2 weeks, the sensor was used in more than 300 cycles, so we can see that the sensor can keep the function and efficiency with 300 cycles in 2 weeks.

Conclusions

A low-cost and sensitive method for the determination of durabolin was developed using QDs as the ECL probe. ITO slide glass was decorated by CdTe QDs via LbL self-assembly. The modified ITO slide glass was packed into a homemade cell and used as a recognizer of the FI-ECL sensor, which can be installed easily. The FI-ECL sensor exhibited a low detection limit, wide linear range, high sensitivity, and good reproducibility for the determination of durabolin. The analysis procedures were simplified and the analysis time was shortened. This strategy could be easily realized and opened new avenues for the applications of QDs in ECL biosensing.

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