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ORIGINAL PAPER

Electrodeposition of CdSe quantum dots and its application to an electrochemiluminescence immunoassay for α-fetoprotein

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Abstract We report on the first label-free electrochemiluminescence (ECL) immunosensor for α-fetoprotein (AFP). It is based on the use of CdSe quantum dots that were electrodeposited directly on a gold electrode from an electrolyte (containing cadmium sulfate, EDTA and selenium dioxide) by cycling the potential between 0 and -1.2 V (vs. SCE) for 60 s. The electrodeposited dots were characterized by scanning electron microscopy and energy dispersive spectroscopy. Under optimal conditions, the specific immunoreaction between AFP and anti-AFP resulted in a decrease of the ECL signal because of the steric hindrance and the transfer inhibition by peroxodisulfate. The quenching effect of the immunoreaction on the intensity of the ECL was used to establish a calibration plot which is linear in the range from 0.05 to 200 ng mL^{-1}. The detection limit is 2 pg mL^{-1}. The assay is highly sensitive and satisfactorily reproducible. In our opinion it opens new avenues to apply ECL in label-free biological assays.

Keywords Biosensor · CdSe · Electrochemiluminescence · Electrodeposition · Immunoassay

Introduction

Semiconductor nanomaterials have generated tremendous interest due to their unique luminescent properties. With size-tunable emission spectra and broad absorption spectra [1, 2], they have been found potential applications in biological labels and bioimaging [3–5]. Since the electrochemiluminescence (ECL) of Si nanocrystals was first reported by Bard [6], special attention has been paid to the ECL of semiconductor nanomaterials especially II–VI semiconductors containing CdS, CdSe, and CdTe due to the promising advantages of ECL such as simplified optical setup, high sensitivity, low background signal and excellent selectivity [7–11]. Liu et al. used water-soluble CdTe quantum dots (QDs) as biological labels for the detection of AFP [12, 13]. Ju's group have developed a series of QDs based ECL immunosensors for the detection of biomolecules [14, 15], and they have combined QDs with kinds of carbon materials or polymers to enhance the ECL intensity of the QDs. However, in all those assays, water soluble semiconductors were synthesized first with different diameters, and then immobilized on the electrode or the carriers. The process of preparing water soluble semiconductors and fabricating ECL immunosensors is complicated, inconvenient and time-consuming. Thus, it is of great significance to find an effective, simple and one-step method to fabricate semiconductor nanomaterial-based immunosensor which could be directly applied in ECL immunoassay.

Electrodeposition is an attractive method for the synthesis of semiconductor thin films and nanostructures, because it is convenient, inexpensive, quick, simple and parameter controllable [16]. A variety of semiconductors have been investigated with electrodeposition, especially cadmium compounds, and most of the reports concerned about the photoelectrochemical performance and photoluminescence characteristics of the electrodeposited semiconductors. Those study results indicate that cadmium semiconductors can be potential materials in constructing optical devices [17–24]. CdSe as one of the most important II–VI

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semiconductors has been employed for construction of various sensors and cells for its electrical and optical properties [25–28]. There are rarely reports concerning ECL from electrodeposited CdSe and its applications in biosensors although the thin film of CdSe can provide an effective way to construct semiconductor-based ECL biosensors in aqueous solutions.

Nowadays, sensitive detections of antigens are of critical need in biochemical and biomedical research. Studies on fabricating rapid, sensitive, and low-cost immunosensor have gained tremendous attention recently. AFP is a most widely used tumor marker to diagnose hepatocellular cancer [29]. The average concentration of AFP in healthy human serum is about 10 ng mL^{-1} and its level in serum often increases under disease conditions [30], so sensitive detection of AFP is of particular importance for diagnosing and monitoring the treatment of hepatocellular cancer in clinical analysis. A series of immunoassay methods have been developed for the detection of AFP [31–36]. However, ultrasensitive methods for detecting low concentration of AFP are still a challenge.

Herein, we introduce a simple and sensitive ECL immunosensor for the detection of AFP based on the ECL of electrodeposited CdSe. CdSe was electrodeposited on the bare Au electrode, and exhibited high ECL intensity and good stability. This method does not require the QDs to be immobilized which is advantageous and more simple. The anti-AFP was directly immobilized onto the Au electrode modified by CdSe, which had enough binding sites after electrodeposited with CdSe. The specific immunoreaction of AFP with anti-AFP resulted in the decrease of ECL intensity, which could be used to detect the AFP. The immunosensor provided a fast, low-cost, and sensitive method for protein detection, which would have a great potential for clinical protein detection.

Experimental

Chemicals

$3CdSO_4 \cdot 8H_2O$, selenium dioxide (SeO_2) and EDTA were purchased from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China, http://gyjthxsj.b2b.hc360.com), N-hydroxysuccinimide (NHS) was from Huifeng Chemical Industry Ltd. (Weinan, China, http://www.sxhfhg.com), 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide hydrochloride (EDC) was from Shanghai Medpep Co. Ltd. (Shanghai, China, http://www.medpep.com/indexe.htm), AFP (Ag), anti-AFP (Ab), human IgG (HIgG) were bought from Shanghai Linc-Bio Science Co. Ltd. (Shanghai, China, http://www.linc-bio.cn), Bovine serum albumin (BSA, 96–99 %) was obtained from Sigma (St. Louis, MO, USA, http://www.sigmaaldrich.com). The human serum samples were provided by the Medical School Hospital of Shandong University (Jinan, China). All other reagents were of analytical reagent grade and used without further purification. 0.1 mol L^{-1} phosphate buffered solution (PBS) with different pH was prepared by mixing the stock solutions of NaH_2PO_4, Na_2HPO_4 and NaCl. 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} $K_2S_2O_8$ and 0.1 mol L^{-1} KCl was used as the electrolyte in the ECL measuring system. Doubly distilled water was used throughout the experiments.

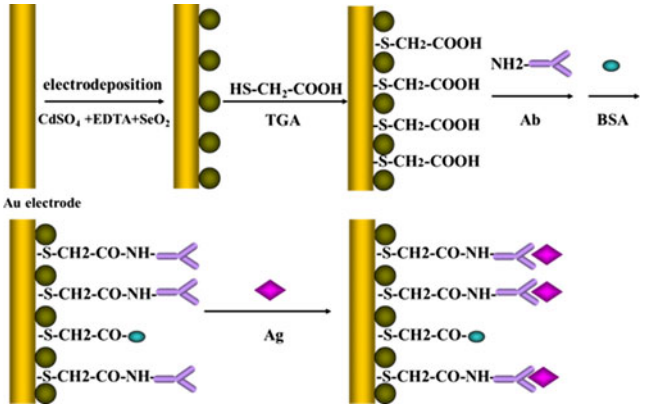
In order to prevent the growth of microorganisms and denature Ag and Ab, all buffers, disposable plastic wares and disposable micro-pipet tips were disinfected under the pressure of 1.4 kg cm^{-2} for 20 min in an autoclave before use.

Instruments

Electrochemical measurements were carried out on a CHI800a electrochemical working station (Shanghai Chenhua, China) and ECL signals were obtained by a PMT (model H9305-04, Hamamatsu Photonics K. K., Japan) with a spectral width of 185–830 nm. A conventional three-electrode system consisted of an Au disk (6-mm-diameter) working electrode, a saturated calomel reference electrode (SCE) and a Pt auxiliary electrode was used in all the electrochemical and ECL measurements. Scanning electron microscope (SEM) image and energy dispersive spectroscopy analysis were recorded by JEOL JSM-6700 F microscope with an EDS system (Japan). Electrochemical impedance spectroscopy (EIS) was carried out with potentiostat galvanostat model 273A (Princeton Applied Research, USA), using the same three-electrode system as that in the ECL detection.

Preparation of the electrodeposited CdSe

CdSe were electrodeposited directly onto the bare Au electrode from aqueous electrolytic solution containing 0.2 mol L^{-1} $CdSO_4$, 0.1 mol L^{-1} EDTA and 0.004 mol L^{-1} SeO_2. The pH of the electrolyte was adjusted to 2.75 by adding 1 mol L^{-1} NaOH. Electrodeposition was performed by cycling the potential between 0 and -1.2 V vs. SCE for 60 s at a scan rate of 100 mV s^{-1}. Before electrodeposition, Au electrode was polished carefully with 0.5 and 0.05 μm α-Al_2O_3 powder on fine abrasive paper and washed ultrasonically with water and ethanol, and scanned in 0.5 mol L^{-1} H_2SO_4 between 0 and 1.5 V until a reproducible cyclic voltammogram (CV) was obtained.



Scheme 1 Schematic illustration of the fabrication process of the immunosensor

Fabrication of the ECL immunosensor

Scheme 1 illustrates the fabrication process of the immunosensor. The Au electrode modified with CdSe was firstly immersed in 0.01 mol L^{-1} thioglycolic acid solution for 10 h to introduce the carboxy group onto the electrode surface. After rinsed thoroughly with redistilled water, the electrode was soaked in EDC (100 mg mL^{-1} in H_2O) and NHS (100 mg mL^{-1} in H_2O) for 1 h to activate the carboxy group. And then the electrode was incubated with 20 μL anti-AFP (20 μg mL^{-1}) for 3 h at room temperature and subsequently 20 μL BSA (2 %) for 1 h at 37 °C to block nonspecific sites. After rinsed with 0.1 mol L^{-1} PBS (pH 7.4), the electrode was used as an ECL biosensor.

ECL detection

The ECL biosensor was immersed in 40 μL AFP samples of different concentrations (diluted with pH 7.4 PBS) for 2 h at 37 °C, followed by a thorough washing with 0.1 mol L^{-1} PBS (pH 7.4) to remove unbound AFP. The ECL detection was carried out in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} $K_2S_2O_8$ and 0.1 mol L^{-1} KCl by CV scanning from 0 to -1.7 V. ECL signals related to the AFP concentration could be measured.

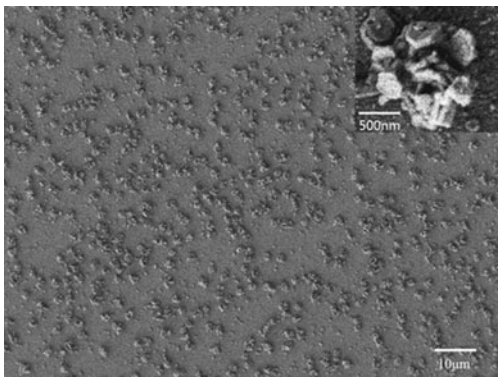


Fig. 1 Representative SEM image of electrodeposited CdSe. Inset: magnification of one aggregate

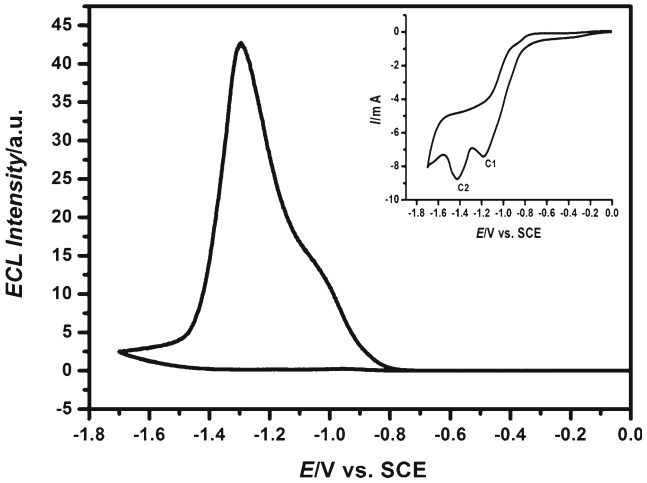


Fig. 2 ECL Intensity-E curves of the CdSe modified Au electrode in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} $K_2S_2O_8$. Inset: cyclic voltammogram of the CdSe modified Au electrode. Scan rate: 50 mV s^{-1}

Results and discussion

Characterization of the CdSe on the Au electrode

During the electrodeposition process, CdSe were synthesized onto the surface of Au electrode by the reaction of Cd^{2+} with Se^{2-} that was formed from the reduction of SeO_3^{2-} in the solution. EDTA was added to form Cd-EDTA complex to avoid the reduction of Cd^{2+}. Typical SEM image of electrode surface with formed CdSe is shown in Fig. 1. As we can see, all the deposited samples presented relatively sphere structures, which were the aggregates of hexagonal CdSe crystalline (inset), and the aggregates distribution was relatively uniform. After the electrodeposition of CdSe,

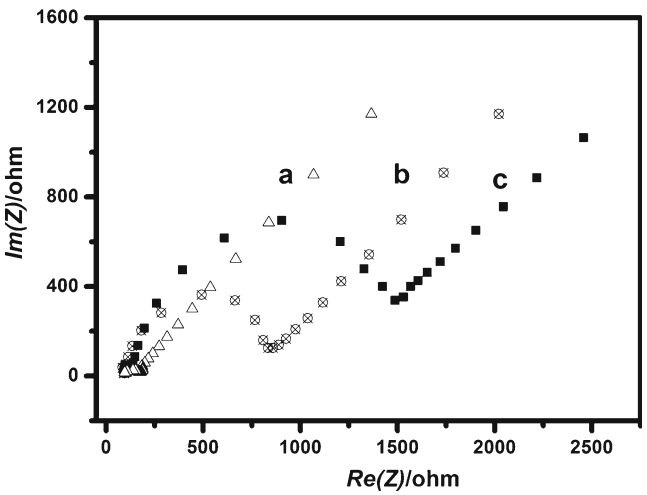


Fig. 3 Electrochemical impedance spectroscopy of **a** bare Au, **b** CdSe/Au, **c** Ab/CdSe/Au in 0.01 mol L^{-1} PBS (2.5 mmol L^{-1} $Fe(CN)_6^{4-/3-}$+ 0.1 mol L^{-1} KCl, pH 7.4). The frequency range is between 0.01 and 100,000 Hz

there were many binding sites left which could be used to immobilize antibody. The energy dispersive spectroscopy analysis further confirmed that the particle is composed of Cd and Se with the atomic ratio almost 1:1 (Cd, 52.70 %; Se, 47.30 %).

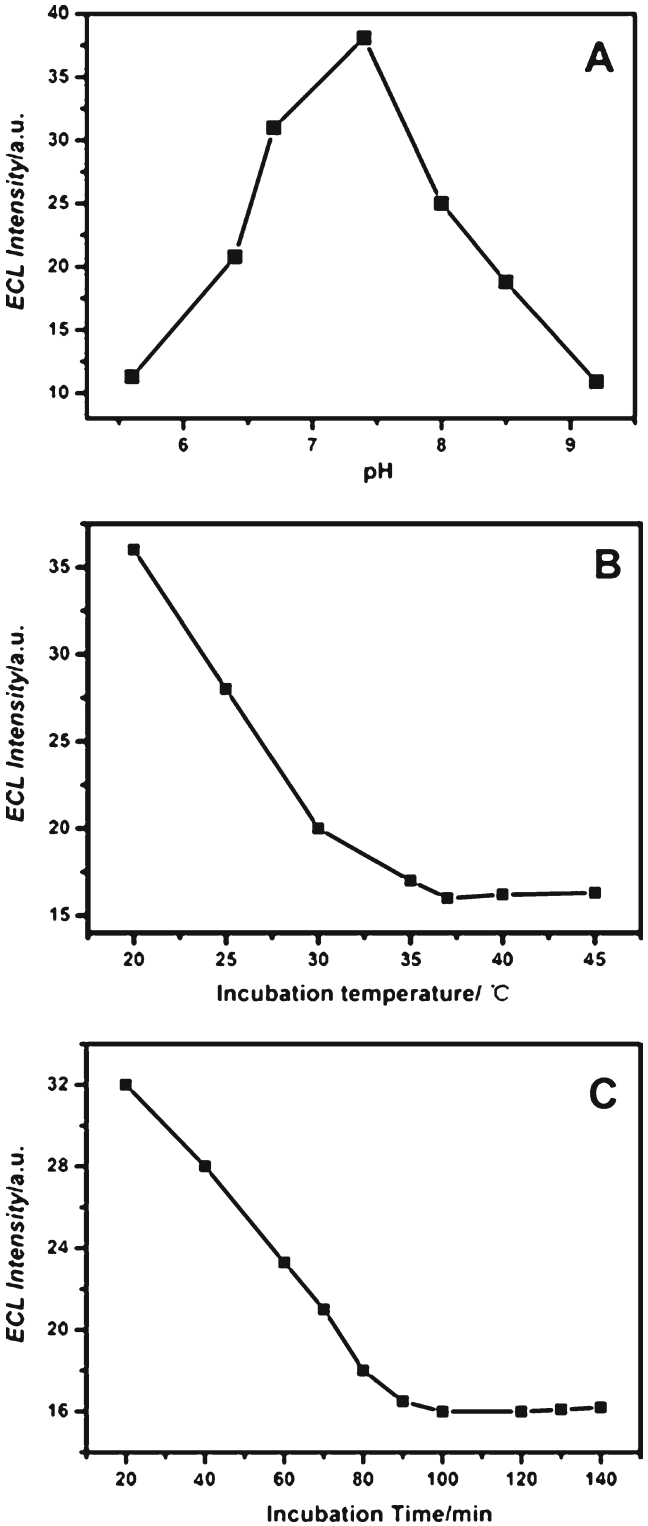


Fig. 4 Effects of pH (**a**), incubation temperature (**b**) and incubation time (**c**) on the performance of the immunosensor in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} $K_2S_2O_8$

Electrochemical and ECL behaviours of the electrodeposited CdSe on the Au electrode

In our work, electrochemical and ECL behavior of the electrodeposited CdSe on the Au electrode were studied with cyclic voltammetry. Figure 2 shows the ECL Intensity-E curve and CVs (inset) of the CdSe deposited on the Au electrode. One ECL peak at -1.30 V was observed which resulted from the reaction of CdSe with $S_2O_8^{2-}$. When the potential was scanned in the negative direction, two cathodic peaks were observed at -1.18 V (C1) and -1.43 V (C2) corresponding to the reduction of $S_2O_8^{2-}$ and CdSe [6], respectively. The CdSe electrodeposited on the Au electrode were reduced to $CdSe^{\bullet-}$, and the reduction of $S_2O_8^{2-}$

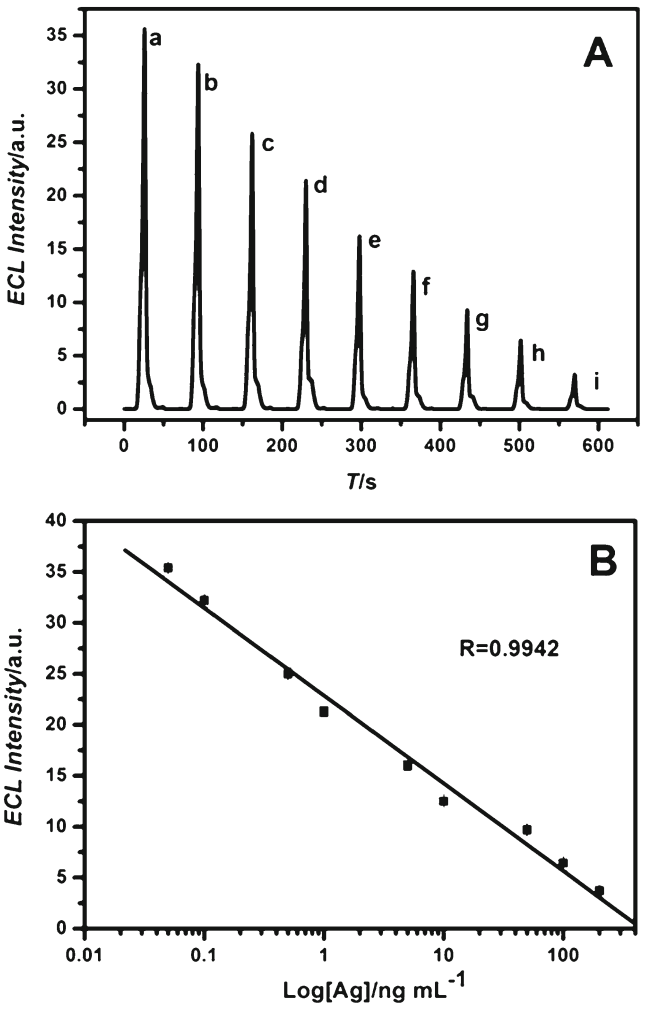


Fig. 5 (**a**) ECL profiles of the immunosensor in the presence of different concentrations of AFP in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} $K_2S_2O_8$: (*a*) 0.05, (*b*) 0.1, (*c*) 0.5, (*d*) 1, (*e*) 5, (*f*) 10, (g) 50, (*h*) 100, (*i*) 200 ng mL^{-1}. (**b**) linear plots of ECL intensity vs. AFP concentrations. Scan rate: 50 mV s^{-1}

produced a strong oxidant $SO_4^{\bullet-}$, which could then react with the negatively charged $CdSe^{\bullet-}$ by electron transfer to produce an excited state ($CdSe^*$) that could emit light [37]. The possible ECL mechanisms are as follows:

$$CdSe + e^- \rightarrow CdSe^{\bullet-} \quad (1)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \quad (2)$$

$$CdSe^{\bullet-} + SO_4^{\bullet-} \rightarrow CdSe^* + SO_4^{2-} \quad (3)$$

$$CdSe^* \rightarrow CdSe + h\nu \quad (4)$$

Electrochemical impedance spectroscopy behaviours

Electrochemical impedance spectroscopy is known as an effective method for probing the features of surface-modified electrodes. Figure 3 shows the typical Nyquist plot of the electrode at different stages. The semicircle diameter at higher frequencies was corresponding to the electron transfer resistance (Ret), It was observed that the EIS of the bare Au electrode displayed an almost straight line (curve a). After the electrode was deposited with CdSe film, the EIS showed an increased electron transfer resistance because the CdSe was semiconductor (curve b). In the final step, the immobilization of antibody significantly increased the electron-transfer resistance (curve c), which was due to the insulating protein layer generated on the assembled surface. The EIS results confirmed that the immunosnesor was sucessfully fabricated.

Optimization of experimental conditions

The effects of pH value and scan rate on the ECL intensity of the immunosensor were investigated as follows. The pH of the solution had great influence on the ECL intensity of the immunosensor (Fig. 4a). ECL intensity increased from 5.5 to 7.4 and then decreased from 7.4 to 9.2. Since the maximum emission intensity was at pH 7.4, the ECL detection was performed in pH 7.4 PBS containing 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} $K_2S_2O_8$.

The incubation temperature and time of the Ag-Ab reaction also affected the analytical results of the immunoassay. The effect of incubation temperature on the immunoreaction was investigated in the range from 20 °C to 45 °C (shown in Fig. 4b), and the ECL intensity reached a minimum value at 37 °C, suggesting that the optimal immunoreaction occurred at this temperature.

We also investigated the effect of incubation time on the immunoreaction (Fig. 4c). As the time increased, the ECL intensity decreased, and reached a constant value after 100 min, indicating that an equilibrium state of immunoreaction was reached. Thus, 37 °C and 100 min were chosen as incubation temperature and time for the detection of AFP in the following experiments.

AFP detection with the ECL immunosensor

After the fabrication of CdSe on the Au electrode, there were enough binding sites left on the surface of the Au electrode for immobilization of antibody. EDC and NHS as the coupling and stabilizing agent could immobilize Ab on the electrode by covalent bonding, and then the AFP was immobilized on the electrode by immunoreaction.

Table 1 Figures of merits of comparable methods for determination of alpha-fetoprotein

Method	Reagent(s) used	Analytical ranges	Detection limit	Interferents	Ref.
electrochemiluminescence immunoasssy	glucose oxidase anchored AuNPs@MWCNTs	0.01–80 ng mL^{-1}	0.03 pg mL^{-1}	BSA, CEA, HCG	31
amperometric enzyme immunosensor	horseradish peroxidase modified platinum nanoparticles	0.25–100 ng mL^{-1}	0.08 ng mL^{-1}	Not mentioned	32
amperometric immunosensor	self-assembly of a redox multi-wall carbon nanotube	0.5–20 ng mL^{-1}	0.26 ng mL^{-1}	BSA, CEA, PSA, dopamine	33
chemiluminescent multiplex immunoassay	horseradish peroxidase label	1.0–80 ng mL^{-1}	0.89 ng mL^{-1}	Not mentioned	34
Sandwich-type electrochemiluminescence immunosensor	Ru-silica@Au composite	0.05–50 ng mL^{-1}	0.03 ng mL^{-1}	Not mentioned	35
chemiluminescence enzyme immunoassay	double-codified gold nanoparticles	0.008–0.3 ng mL^{-1}	5 pg mL^{-1}	Not mentioned	36
electrochemiluminescence immunosensor	electrodeposited CdSe	0.05–200 ng mL^{-1}	2 pg mL^{-1}	HIgG, BSA	This work

AuNPs Au nanoparticles; *MWCNTs* multiwall carbon nanotubes; *CEA* carcinoembryonic antigen; *HCG* human chorionic gonadotropin; *PSA* prostatespecific antigen; *HIgG* human immunoglobulin

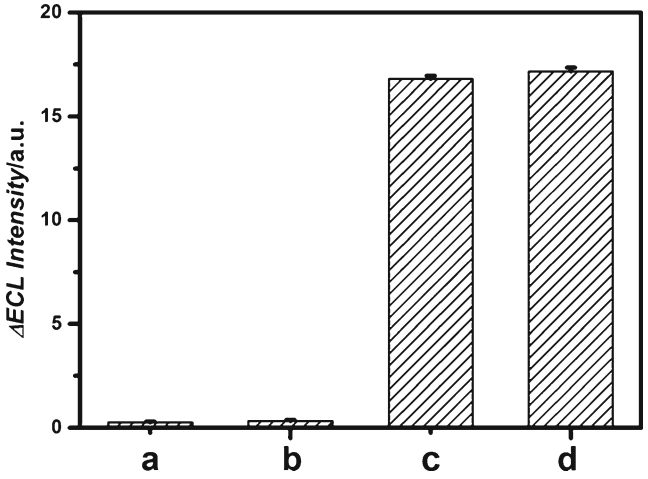


Fig. 6 ECL signal changes of the immunosensor in **a** 100 ng mL^{-1} BSA, **b** 100 ng mL^{-1} human IgG, **c** 1 ng mL^{-1} AFP, **d** mixture of 1 ng mL^{-1} AFP, 100 ng mL^{-1} human IgG, and 100 ng mL^{-1} BSA in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} $K_2S_2O_8$. Scan rate: 50 mV s^{-1}

Figure 5a shows the ECL responses of the immunosensor after incubating in different concentrations of AFP. The ECL intensity decreased gradually with the increasing concentration of AFP. This can be explained by the fact that the specific binding of anti-AFP with AFP increased steric hindrance, which could inhibit the transfer of $K_2S_2O_8$ to the surface of CdSe on the electrode during the ECL reaction. This phenomenon implied that the ECL intensity of the electrodeposited CdSe on the electrode was corresponding to the concentration of AFP, and the ECL immunosensor could be utilized for determination of AFP concentration.

The standard calibration curve for AFP detection is shown in Fig. 5b. The ECL intensity decreased with the AFP concentrations in the range from 0.05 ng mL^{-1} to 200 ng mL^{-1}, and the detection limit was 0.002 ng mL^{-1}.

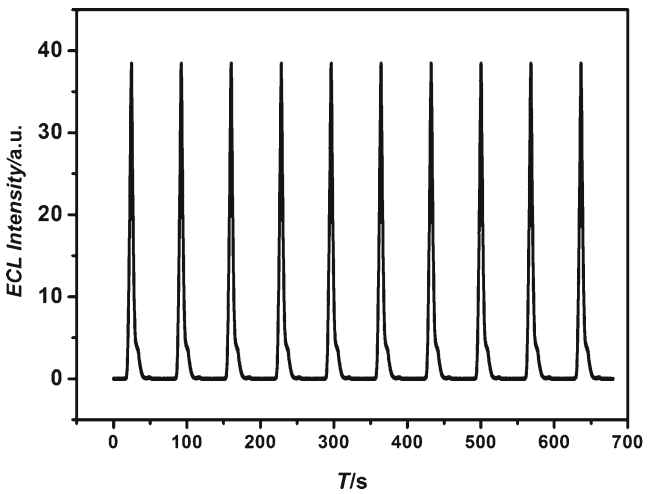


Fig. 7 ECL emission from the immunosensor under continuous cyclic voltammetry for 9 cycles at a scan rate of 50 mV s^{-1} in 0.1 mol L^{-1} PBS (pH 7.4) containing 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} $K_2S_2O_8$

Table 2 Comparison of AFP determination on human serum samples by the ECL immunosensor and ELISA

Serum samples	Our method (ng mL^{-1})[a]	ELISA (ng mL^{-1})	Relative deviation (%)
1	0.032	0.030	6.7
2	2.10	1.97	1.5
3	20.76	19.52	8.2

[a] the average value of three successive detections

The linear equation indicated that the AFP concentration can be quantitatively determined. A comparison of the advantages and disadvantages with other electrochemical methods for the determination of AFP was listed in Table 1.

Specificity, stability and reproducibility of the immunosensor

To investigate the specificity of the immunosensor, we mixed 1 ng mL^{-1} AFP, 100 ng mL^{-1} human IgG, and 100 ng mL^{-1} BSA, and then measured the ECL response of the mixture (Fig. 6). Compared with the ECL response of the immunosensor in the 1 ng mL^{-1} pure AFP, there is no significant difference, and we also investigated the ECL responses of 100 ng mL^{-1} human IgG, and 100 ng mL^{-1} BSA, the results indicate that the human IgG and BSA do not cause observable interference. Thus the immunosensor displays good selectivity for AFP detection.

The ECL emission from the immunosensor under continuous potential scanning from 0 to -1.7 V for 9 cycles is shown in Fig. 7. It can be seen that the ECL signals were high and stable, indicating the good stability of this immunosensor.

The reproducibility of the immunosensor for the detection of AFP was evaluated from the ECL response of the immunosensor to 5 ng mL^{-1} AFP with four different immunosenors made at the same Au electrode. Four measurements resulted in a relative standard derivation of 2.3 %, indicating good reproducibility of the fabrication protocol.

Application of the ECL immunosensor in human AFP levels

Our results demonstrate that the immunosensor exhibits high sensitivity and a low detection limit. The feasibility of the immunoassay system for clinical applications was

Table 3 Recovery test for AFP in spiked human serum samples

Sample number	Recommended (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
1	6.1	10	17.0	109
2	16.3	10	26.5	102

further investigated by analyzing several real human serum samples in comparison with the enzyme-linked immunosorbent assay (ELISA) method. Table 2 shows the correlation between the results obtained by the ECL immunosensor and the ELISA method. The data indicated that there was no significant difference between the two methods, and the recovery test shown in Table 3 indicating satisfactory recoveries, thus the developed ECL immunosensor could be applied to the clinical determination of AFP levels in human serum.

Conclusion

In the present work, a novel semiconductor thin film consist of CdSe has been designed to construct a label-free ECL immunosensor for rapid and sensitive detection of α-fetoprotein (AFP). The electrodeposited CdSe showed high ECL intensity and good biocompatibility which made it a promising candidate to develop ECL immunosensor. As far as we know, this is the first report that the ECL properties of electrodeposited CdSe were investigated and applied in ECL immunosensors. The developed immunosensor combined the advantages of sensitive ECL detection and specific immunoreaction and has been successfully applied in the detection of AFP. Moreover, this method did not require the CdSe to be immobilized which was advantageous and more simple. The developed immunosensor showed high sensitivity and good stability, which may find potential applications for protein detection in clinical analysis.

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