



An electrochemiluminescent sensor for phenolic compounds based on the inhibition of peroxydisulfate electrochemiluminescence

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ABSTRACT

An electrochemiluminescent sensor for phenolic compounds based on the quenching effects of phenolic compounds on the electrogenerated chemiluminescence (ECL) of peroxydisulfate solution has been developed. Firstly, gold nanoparticles (AuNPs) were electrodeposited on the surface of glassy carbon electrode (GCE) for assembling L-cysteine (L-cys) through strong binding interactions between AuNPs and the functional groups of $-SH$ and $-NH_2$ of L-cys. Then, gold colloidal nanoparticles (nano-Au) and L-cys were assembled to achieve L-cys/nano-Au/L-cys/AuNPs film modified electrode. The ECL behavior of peroxydisulfate solution had been investigated in detail at the L-cys/nano-Au/L-cys/AuNPs/GCE, and phenolic compounds were found to be able to inhibit the ECL of peroxydisulfate solution. Based on this principle, an ECL sensor had been developed for detecting phenolic compounds. Due to the facts that both gold nanomaterials (AuNPs and nano-Au) and L-cys could promote the electron transfer and amplify the ECL signal of peroxydisulfate solution, the combination of them provided a rapid, simple and sensitive method for the detection of a series of phenolic compounds. The resulting sensor showed potential use in the pharmaceutical industry and environmental monitoring.

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1. Introduction

A large variety of phenolic compounds were widely used in the chemical industry and as germicides or pesticides in agronomic practices [1,2]. Some of them are toxic contaminants in medicinal, food and environmental matrices and have harmful effects on human and animal health and food quality [3–5]. Therefore, the sensitive and rapid determination of phenolic compounds is of paramount importance. In recent years, many analytical methods are available for the determination of phenolic compounds, such as capillary electrophoresis [6], high performance liquid chromatography (HPLC) [7], fluorescence detection [8] and chemiluminescence detection (CL) [9]. However, these methods need relatively time-consuming and complex sample pre-treatment procedures, and are unsuitable for on site analyses.

Electrochemiluminescence (ECL), also known as electrogenerated chemiluminescence combines the electrochemical and luminescent techniques [10]. It involves the electrochemical formation of excited states and as such is a sensitive probe of electrochemical, energy and electron transfer at electrified interfaces [11]. As an important and powerful analytical technique, ECL attracts considerable attention due to its advantages, such as high

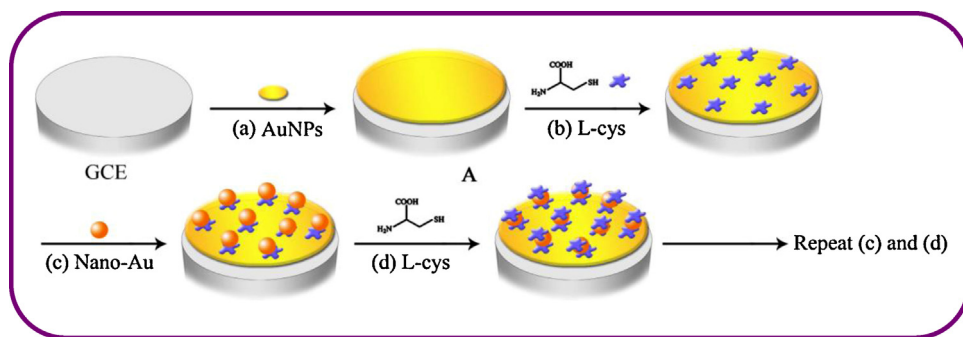
sensitivity, good reproducibility, easy controllability and flexibility [12,13]. However, so far to our knowledge, only few ECL methods have been reported to determine phenolic compounds. McCall et al. developed a $Ru(bpy)_3^{2+}$ ECL system for the determination of phenolic compounds [14,15]. Wen et al. fabricated an ECL sensor based on quantum dots (QDs) to determine phenolic compounds [16]. However, high costs of $Ru(bpy)_3^{2+}$ and inherent toxicity in most of the QDs used in ECL studies would limit the applications of above two kinds of ECL systems in a bioassay [17–19]. Thus it is necessary for developing economy, nontoxic and simple ECL species.

L-Cysteine (L-cys) is an α -amino acid, containing $-NH_2$ and $-SH$ groups, which had been widely used to construct sensors [20,21]. Niu and co-workers found that L-cys could enhance the ECL signal of peroxydisulfate solution greatly [18]. Gold nanomaterials are widely used in many ECL sensors due to the ability to enhance the electrode conductivity, facilitate the electron transfer and enhance the ECL intensity [22,23]. Since the layer-by-layer (LBL) assembly technique represents a promising and environmental preparation method for multilayer films because no complicated instruments or chemical reactions are involved [24,25], in our present work, it was used to fabricate the LBL assembly films of gold nanomaterials (AuNPs and nano-Au) and L-cys to achieve the detection of a series of phenolic compounds.

In this study, electrodeposition was performed firstly in 1% $H AuCl_4$ aqueous solution to construct the gold nanoparticles (AuNPs) layer on the electrode surface. Then, L-cys was adsorbed

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Scheme 1. Schematic diagram of preparation of the ECL sensor.

on the AuNPs film through its functional groups of $-SH$ and $-NH_2$. Subsequently, $\{L\text{-cys}/\text{nano-Au}\}_n$ films were grown on the precursor film by alternately immersing the electrode into the gold colloid solution and L -cys solution to form $\{L\text{-cys}/\text{nano-Au}\}_n/L\text{-cys}/\text{AuNPs}/\text{GCE}$. The assembly process of the modified electrode was characterized with cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). A series of phenolic compounds could inhibit the ECL of peroxydisulfate solution. Based on this fact, the electrochemiluminescent sensors for phenolic compounds were constructed. Due to the combination of gold nanomaterials (AuNPs and nano-Au) and L -cys, the sensor exhibited high sensitivity and long-term stability. The experimental results demonstrated that it had potential use in the pharmaceutical industry and environmental monitoring.

2. Experimental

2.1. Reagents and materials

Gold chloride (HAuCl_4) was obtained from Sigma Chemical Co. (St. Louis, MO, USA). L -Cysteine and $\text{K}_2\text{S}_2\text{O}_8$ were purchased from Kangda Amino Acid Company (Shanghai, China) and Shanghai Chemical Reagent Company (Shanghai, China), respectively. Gold colloidal nanoparticles (nano-Au) with a diameter of 16 nm were produced by reducing gold chloride tetrahydrate with citric acid at 100°C for half an hour [26]. Ferricyanide solutions ($[\text{Fe}(\text{CN})_6]^{4-/3-}$) were obtained by dissolving potassium ferricyanide and potassium ferrocyanide with phosphate buffer (pH 7.0). Phosphate buffer (pH 7.0, 0.1 M) was prepared using 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4 . The supporting electrolyte was 0.1 M KCl. Twice-distilled water was used throughout the experiments.

2.2. Apparatus

Cyclic voltammetric measurements were carried out with a CHI 660D electrochemical workstation (CH Instruments, Chenhua Corp., Shanghai, China). Electrochemical impedance spectroscopy (EIS) measurements were done with a Model IM6e (ZAHNER Elektrick Co., Germany) in the presence of 5.0 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (1:1) mixture as redox probe. All the electrochemical experiments were carried out at room temperature. The ECL emission was monitored with a model MPI-A electrochemiluminescence analyzer (Xi'an Remax Electronic Science & Technology Co. Ltd., Xi'an, China) with the voltage of the photo-multiplier tube (PMT) set at 800 V and the potential scan from 0.0 to -2.0V in the process of detection. All experiments were performed with a conventional three-electrode system. The modified glassy carbon as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) or Ag/AgCl (sat.KCl) as reference electrode.

The topographs of different modified films were investigated with atomic force microscopy (AFM, Veeco, USA).

2.3. Fabrication of the electrochemiluminescence sensor

The glassy carbon electrode (GCE) was polished with 0.3 and $0.05\ \mu\text{m}$ alumina powder successively, followed by washing with distilled water and sonicating in ethanol, distilled water, respectively. After that, electrodeposition was performed in 1% HAuCl_4 aqueous solution to construct the AuNPs layer on the electrode surface with constant potential -0.2V for 30 s. Then, the modified electrode was immersed into L -cys (pH 2.3) solution for 2 h to form the $L\text{-cys}/\text{AuNPs}$ film. Subsequently, $\{L\text{-cys}/\text{nano-Au}\}_n$ films were grown on the precursor film by alternately immersing the electrode into the gold colloid solution and L -cys solution to form $\{L\text{-cys}/\text{nano-Au}\}_n/L\text{-cys}/\text{AuNPs}/\text{GCE}$. The LBL assembly process was shown in Scheme 1.

3. Results and discussion

3.1. Characterization of the electrochemiluminescence sensor

3.1.1. AFM and EIS characterization of the modified films

The surface topographies of different modified films were investigated via AFM and corresponding AFM images were shown in Fig. 1. As presented in Fig. 1A, a large quantity of compact nanoparticles structures were distributed over the entire Au substrate surface with the electrodeposition of AuNPs. After L -cys was assembled onto the AuNPs film through binding interactions between AuNPs and the functional groups of $-SH$ and $-NH_2$ of L -cys, the AFM image of the resulting film obviously changed and exhibited a smoothing effect (Fig. 1B). Fig. 1C was the AFM image of nano-Au/ L -cys/AuNPs modified film. The globular structure was clearly observed due to the adsorption of nano-Au on L -cys layer by covalent bonds. Fig. 1D exhibited the topograph of $L\text{-cys}/\text{nano-Au}/L\text{-cys}/\text{AuNPs}$ modified film. As expected, a smoothing effect was observed again, which was ascribed to the assembly of the dense and compact L -cys layer, indicating that another layer of L -cys was successfully modified on the nano-Au/ L -cys/AuNPs film.

EIS was carried out to study the stepwise assembly of the sensor since it was an effective method to probe the interface properties of modified electrodes. The semicircle portion at higher frequencies in the EIS corresponds to the electron-transfer-limited process and the semicircle diameter equals the electron-transfer resistance, R_{et} . Fig. 2 illustrated the Nyquist plots of the impedance spectroscopy of the different modified electrodes in presence of redox probe $[\text{Fe}(\text{CN})_6]^{4-/3-}$. It can be seen that curve a presented a small semicircle domain with a diameter of $76.42\ \Omega$ (Fig. 2a), implying a fast electron transfer rate between the bare GCE and redox probe $[\text{Fe}(\text{CN})_6]^{4-/3-}$. Curve b-e presented the EIS

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