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A novel strategy for constructing electrochemiluminescence sensor based on CdS-polyamidoamine incorporating electrodeposited gold nanoparticle film and its application

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ABSTRACT

In this study, a novel strategy for the construction of CdS quantum dots (QDs)-based electrochemiluminescence (ECL) sensor was developed. The stable nanocomposite film was obtained by using self-assembly CdS QDs capped with polyamidoamine (short for CdS-PAMAM) incorporating electrodeposited gold nanoparticles onto the surface of Au electrode. The water soluble CdS-PAMAM QDs were successfully synthesized by using PAMAM as a template and stabilizer. Based on the numerous reactive groups on the dendrimers, the high uniform and well-dispersed CdS-PAMAM QDs were assembled onto the surface of electrodeposited gold nanoparticles film. The feasibility of this manner was confirmed by photoluminescence, absorption spectra, scanning electron microscopy and electrochemical measurements. In addition, the ECL performance of the constructed CdS-PAMAM/GNPs film was investigated. With the synergistic effect of the CdS-PAMAM QDs and electrodeposited gold nanoparticles, the ECL response was dramatically enhanced. The fabricated nanocomposite film demonstrated rather high stability and sensitivity to dopamine detection. Under optimal experimental conditions, the fabricated sensor responded linearly to dopamine concentration in the range of 0.05–10 μmol L^{-1} with a detection limit of 0.012 μmol L^{-1}. Moreover, the sensor exhibited good specificity, stability and reproducibility. The present work shows promising potential for developing new efficient ECL sensor.

1. Introduction

Electrochemiluminescence (ECL) combined the electrochemical and luminescent techniques has the remarkable features such as versatility, simplified optical setup, low background signal, good temporal and spatial control. ECL sensor as a powerful device has been used extensively for the sensitive detection of a wide variety of analytes [1–4]. Compared with the conventional luminescent systems, semiconductor quantum dots (QDs)-based ECL sensor recently has received tremendous attention for the unique size dependently electrochemical and optical properties of the nanomaterials. The QDs-based ECL has been demonstrated to be more sensitive to the surface chemistry and the surface states of QDs, which provide potential alternatives for developing ECL emitters and preparing new ECL sensors [5–8]. However, there are two significant barriers to the application of the QDs-based ECL sensor: first, the ECL intensity of semiconductor QDs still could not come to those of conventional luminescent reagents such as luminal or $Ru(bpy)_3^{2+}$; second, the ECL stability of QDs is also a pending problem to overcome for the configuration of QDs-based ECL sensors [9]. Therefore, efficient methods taken to enhance and stable ECL signal for the QDs-based ECL sensor are crucial.

Recently, much effort has been directed to improve the performance of QDs-based ECL sensors, such as the use of self-assembled monolayer, gold nanoparticle amplification technique and electrostatic entrapment into related polymers. Jie et al. [10] using self-assembly and gold nanoparticle amplification technique developed a label free CdS nanocrystals ECL immunosensor, which provided a high ECL intensity and good sensitivity for the detection of low-density lipoprotein. Wang [11] utilized gold nanoparticle to enhance ECL of CdS thin film for ultrasensitive detection of thrombin.

It is known that dendrimers are perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture. As a kind of familiar dendrimer, polyamidoamine (PAMAM) has been widely applied in many fields, such as catalysts and fabrication of nanoparticles [12]. There have been already many groups reported to synthesize the stable and quality gold nanoparticles and semiconductor QDs with PAMAM as a template, stabilizer and reservoir [13,14]. The advantages of synthesis of semiconductor QDs-PAMAM composites lie in two aspects. For one thing, the prepare conditions are not so extreme as others; for another the

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numerous reactive groups on the surface of dendrimers can be used to render the composites soluble in essentially any solvent and as synthetic handles for attachment of legends to direct binding of the composites to the surfaces [15]. So we can take the advantage of the dendrimer to improve the performance of the nanoparticles modified electrode. For example, Lu [16] had successfully prepared CdS-PAMAM nano-composite membranes on electrode surfaces by an in situ induction precipitation approach via electrochemical reduction, which much enhanced the ECL intensity and the stability.

Gold nanoparticles are used increasingly in many electrochemical applications due to the ability to enhance the electrode conductivity and facilitate the electron transfer [17]. Several approaches have been employed to immobilize the gold nanoparticles onto the substrate surface, such as self-assembly, sol-gel and seed-mediated growth method [9,18,19]. Electrodeposition is a powerful technique for the growth of gold nanoparticles on the surface of electrode. We have found by varying the deposition potential and time one can availably control the size and distribution of gold nanoparticles and obtain a good performance gold nanoparticles modified electrode [20,21].

In present work, we report an efficient method to fabricate a QDs-based ECL sensor by combining the advantages of synthesis of QDs-PAMAM composite and electrodeposition gold nanoparticles technique. The gold nanoparticles were first direct electrodeposited onto the surface of electrode. Then, the water soluble CdS-PAMAM QDs synthesized by PAMAM template technique were assembled onto the surface of gold nanoparticles film. With the synergistic effect of the CdS-PAMAM and gold nanoparticles, the resulting nanocomposite film electrode exhibited enhancement of ECL response in the presence of coreactant $S_2O_8^{2-}$ and good stability. A further application of the sensor was investigated. The results indicated that the QDs-based ECL sensor could be used for the sensitive detection of dopamine.

2. Experimental

2.1. Materials

$CdCl_2{\cdot}2.5H_2O$, $HAuCl_4{\cdot}4H_2O$, $K_2S_2O_8$, KCl were purchased from national pharmaceutical group chemical reagent Co. Ltd. (China). H_3PO_4, $Na_2HPO_4{\cdot}12H_2O$, $NaH_2PO_4{\cdot}2H_2O$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ were obtained from shanghai reagent company (Shanghai, China). $Na_2S{\cdot}9H_2O$ were from shanghai chemical technology development Co. Ltd. Asia-system (Shanghai, China). PAMAM (G1-NH_2, 20 wt % in methanol) and dopamine were purchased from Sigma-Aldrich. All other reagents were of analytical reagent grade. Doubly distilled water was used throughout the experiments.

2.2. Apparatus

The electrochemical measurements were carried out on a CHI 660C electrochemical workstation (Shanghai Chenhua Apparatus Inc., China). All electrochemical experiments were carried out with a conventional three-electrode system. The electrodes were a 4-mm-diameter modified Au disk working electrode, a saturated calomel reference electrode (SCE) or Ag reference electrode, and a Pt counter electrode. The ECL emission was detected with a model MPI-A electrochemiluminescence analyzer (Xi'An Remax Electronic Science &Technology Co. Ltd., Xi'An, China) at room temperature. The spectral width of the photomultiplier tube (PMT) was 200–800 nm and the voltage of the PMT was 500–800 V in the detection process. Absorption spectra were acquired on a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Photoluminescence spectra were obtained on an F-4500 spectrophotometer (Hitachi, Japan). Transmission electron microscopy was run with a Tecnai G^2 F20 S-TWIN transmission electronmicroanalyzer (FEI, USA). Scanning electron microscopy was run with an S-4700 scanning electronmicroanalyzer (Hitachi, Japan).

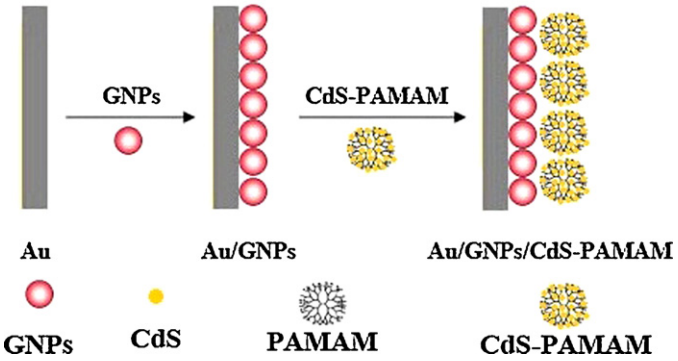

Fig. 1. Schematic diagram for the fabricating procedures of the CdS-PAMAM/GNPs film.

2.3. Preparation of the CdS-PAMAM QDs

CdS-PAMAM QDs were synthesized by a reported method [15]. Firstly, cadmium chloride methanol solution was added into PAMAM dendrimers methanol solution with Cd^{2+}/dendrimers mole ratio of 2, stirred for about 12 h at room temperature in order to make Cd^{2+} coordinate completely with PAMAM dendrimers. Then equimolar sodium sulfide was added to the above methanol solutions, keeping the temperature at 10 °C, after stirred for thirty minutes, CdS-PAMAM QDs were obtained. The product was kept at −10 °C for further use.

2.4. Construction of CdS-PAMAM/gold nanoparticles film electrode

Electrodeposition gold nanoparticles film: A Au disk electrode with 4 mm diameter was polished carefully with 0.05 μm Al_2O_3 powder on fine abrasive paper and washed ultrasonically with ethanol and water. Then, the bare electrode was scanned in 0.5 M H_2SO_4 between −0.2 and 1.5 V until a reproducible cyclic voltammogram was obtained. After rinsed thoroughly with doubly distilled water and allowed to dry at room temperature, the Au electrode was immersed in a relatively optimized solution containing 0.5 mL 1.0 mM $HAuCl_4$, 4.5 mL pH 2.0 (0.13 M H_3PO_4–0.10 M $H_2PO_4^-$) phosphate buffer solution (PBS) for electrochemical deposition with a cycle sweep potential between 300 mV and −520 mV vs. SCE for 80 cycles at 30 °C. A well-dispersed gold nanoparticles film was formed [22].

CdS-PAMAM Assembly: 15 μL CdS-PAMAM QDs solution was dropped on the surface of the electrodeposition gold nanoparticles (GNPs) film and dried in the air. A CdS-PAMAM/GNPs film electrode was obtained. The fabricating procedures of the CdS-PAMAM/GNPs film were shown as Fig. 1 outlines.

2.5. ECL experiments and analytical procedures

ECL experiments were performed in 0.1 M PBS (pH 7.4) containing 0.1 M $K_2S_2O_8$ and 0. 1 M KCl. The linear sweep potential scanned from 0 to −1.7 V. ECL signals were related to the dopamine concentrations, accordingly dopamine could be measured.