Enhanced solid-state electrogenerated chemiluminescence of Au/CdS nanocomposite and its sensing to H$_2$O$_2$

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Abstract

Au nanoparticles (AuNPs) are good quenchers once they closely contact with luminophore. Here we reported a simple approach to obtain enhanced electrogenerated chemiluminescence (ECL) behavior based on Au/CdS nanocomposite films by adjusting the amount of AuNPs in the nanocomposite. The maximum enhancement factor of about 4 was obtained at an indium tin oxide (ITO) electrode in the presence of co-reactant H$_2$O$_2$. The mechanism of this enhancement was discussed in detail. The strong ECL emission from Au/CdS nanocomposites film was exploited to determine H$_2$O$_2$. The resulting ECL biosensors showed a linear response to the concentration of H$_2$O$_2$ ranging from $1.0 \times 10^{-8}$ to $6.6 \times 10^{-4}$ mol L$^{-1}$ with a detection limit of 5 nmol L$^{-1}$ ($S/N = 3$) and good stability and reproducibility.

1. Introduction

CdS semiconductor nanocrystals (NCs) have been widely used in many fields ranging from microelectronics to nonlinear optics, optoelectronics, photoelectrochemistry and catalysis for the past several decades because of their intrinsic properties, such as good chemical stability, easy preparation [1]. As a valuable detection method, electrogenerated chemiluminescence (ECL) is becoming more common for analytical applications due to its promising advantages, such as, simplified set-up, low background signal, high sensitivity, and easy controllability [2].

Since Bard and co-workers first reported on ECL properties of Si NCs in organic solvent and proposed the mechanism and the nature of ECL from NCs [3], many efforts have been made to research the preparation and application of various semiconductor NCs and different morphological nanomaterials with ECL activity, such as CdO NCs, CdS NCs, CdSe NCs, CdTe NCs, CdS nanotubes [4–19]. Particularly when immobilized on electrode surfaces, the electrochemically reduced or oxidized semiconductor NCs could also react with co-reactants to generate ECL in the vicinity of the electrode and the durable ECL biosensors could be developed [13]. Zhu and co-workers observed ECL phenomena of CdS NCs for the first time and developed a novel label-free biosensor based on the ECL of CdS NCs for the detection of H$_2$O$_2$ [6] and low-density lipoprotein [12]. Zou and Ju developed the first ECL sensors based on CdSe NCs for H$_2$O$_2$ detection in aqueous solution [13]. Soon, the analytes detected by CdSe and CdTe NCs were further applied to catechol derivatives [15], human prealbumin [16], glucose [17], tyrosine [18], and methimazole [19].

However, ECL from semiconductor NCs at the electrodes often suffered from several problems, such as poor analytical reproducibility and weak ECL signals. In order to solve these problems, a large number of efforts have been made. Taking into account the cooperative physical and chemical properties of semiconductor NCs nanocomposites to the single-component, carbon nanotube/CdS nanocomposites [8,20] were used to enhance the ECL and further applied to develop signal-on enzymes based sensors [20]. Recently, Au nanoparticles (AuNPs) were successfully used to enhance and quench the ECL from CdS:Mn film by tuning the distance between AuNPs and CdS:Mn film and further applied to the detection of DNA [21]. Zhu and co-workers also used AuNPs as an amplification substrate to improve the detection sensitivity in protein ECL analysis [12]. However, the ECL performance of Au/CdS nanocomposites has not been investigated in detail. In this work, the influence of AuNPs on the ECL of CdS NCs with different fabrication approaches and different amounts of AuNPs were discussed in detail. An enhanced ECL response of the Au/CdS nanocomposite film was observed, and the enhanced mechanism was proposed. At last, the analytical application of the ECL enhancement from the Au/CdS nanocomposite film was exploited to determine H$_2$O$_2$. The results demonstrated here may provide guidance in fabricating sensitive ECL sensing films.

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H$_2$O$_2$
2. Experimental

2.1. Chemicals and reagents

HAuCl₄·4H₂O (48%, w/w), CdCl₂, Na₂S·9H₂O, thioglycolic acid (TGA), and a 30% H₂O₂ solution were purchased from Shanghai Chemical Reagent Company (Shanghai, China). A solution of H₂O₂ was freshly prepared before use. 0.1 mol L⁻¹ phosphate buffer solution (PBS) with different pH values was prepared by mixing the stock solutions of K₂HPO₄ and NaH₂PO₄ and adjusting the pH with 0.1 mol L⁻¹ H₃PO₄ or NaOH solution. All other chemicals were of analytical reagent grade commercially available and used as received. Water for all solutions was purified using a Milli-Q (Millipore, USA) water purification system.

2.2. Instruments

A Sirion 200 scanning electron microscopic (SEM) (FEI, USA) was employed to record the images of the nanocomposite films. ECL and electrochemical curves were recorded using a Model MPI-A electrochemiluminescence analyzer system (Xi’an Remax Electronic Science & Technology Co. Ltd., China). The spectral width of the photomultiplier tube (PMT) was 200–800 nm and the voltages of the PMT were set at 800 V in the process of detection. The ECL measurements were performed in 0.1 mol L⁻¹ PBS bubbled with N₂ for at least 20 min and then a N₂ atmosphere was kept over test solution. A conventional three-electrode system was used in the ECL experiments with a saturated calomel electrode (SCE) as the reference electrode, a Pt wire as the counter electrode, and the Au/CdS nanocomposite film modified ITO electrodes as the working electrode.

2.3. Synthesis of AuNPs

All glassware used in the following procedures were cleaned in a bath of freshly prepared 3:1 (v/v) HNO₃ + HCl, rinsed thoroughly with redistilled water, and dried in air. HAuCl₄ and trisodium citrate solutions needed to be filtered through a 0.22 μm microporous membrane filter prior to use. Prepared solutions were stored in brown glass bottles at 4 °C. A solution of AuNPs was synthesized by mixing 2.0 mL of 1% trisodium citrate and 0.75 mL 0.075% NaBH₄/1% trisodium citrate with 500 mL of H2O/5.0 mL of 1% HAuCl₄ solution at room temperature [22]. The resulting AuNPs were characterized by TEM (Tcenai 20, FEI) and UV–vis spectra. The particle diameter of the CdS NCs was ∼4.0 nm.

2.4. Preparation of Au/CdS nanocomposites

The CdS NCs were synthesized according to a method reported in the earlier literature [23]. 4.06 mmol of CdCl₂ was dissolved in 100 mL of water. Then, 9.7 mmol of thioglycolic acid (TGA) as the stabilizer was added to this solution under stirring. The value of pH was adjusted to 10.0 by dropwise addition of a 1 mol L⁻¹ NaOH solution. Then, 4.06 mL of 0.5 mol L⁻¹ Na₂S solution was introduced into the system under stirring. The reaction mixture was refluxed for 12 h. Then ethanol was added with extensive stirring for 10 min, and the yellow precipitate was obtained. The precipitate was collected after centrifuging, subsequently being washed three times with anhydrous ethanol, and being dried in air. 0.1 mg mL⁻¹ CdS stock solutions were obtained via dispersing CdS NCs in water under ultrasonication. The resulting CdS NCs were characterized by TEM (Tcenai 20, FEI) and UV–vis spectra. The particle diameter of the CdS NCs was ∼4.0 nm.

2.5. Fabrication of the modified electrodes

The ITO coated glass plates (Southern Glass Holding Company, China) having sheet resistance of ∼10 Ω with dimensions of 1.5 cm × 1.0 cm were used as electrodes in all experiments. Prior to modification, the ITO electrodes were thoroughly ultrasonicated for 5 min in acetone, ethanol, and water successively, and allowed to dry at room temperature. Then, the above Au/CdS nanocomposite solutions containing an equal amount of CdS NCs and different amount of AuNPs were obtained. For the convenience of discussion, they are denoted by Au₀₀₅/CdS₁, Au₀₁/CdS₁, Au₀₂/CdS₁, Au₀₃/CdS₁, Au₀₄/CdS₁, and Au₀₁/CdS₁, respectively. All of the samples were optically clear solution and no precipitate was observed for 2 months being stored at a temperature of 4 °C.

3. Results and discussion

3.1. Characterizations and ECL behaviors of Au/CdS nanocomposite films

The as-prepared Au/CdS nanocomposite film modified electrode could generate strong and stable ECL when the potential was scanned in the negative direction from 0 to −1.4 V in 0.1 mol L⁻¹ PBS (pH 10.0) containing 1 mmol L⁻¹ H₂O₂ at 100 mV s⁻¹ (Fig. 1).
According to the reports [7,8], upon the potential scan with an initial negative direction, the CdS NCs immobilized on the electrode were reduced to the reduced species (CdS\(^{n-}\)) then CdS\(^{n-}\) could react with \(\text{H}_2\text{O}_2\) to produce the excited states of CdS NCs (CdS\(^*\)), which decayed to the ground state with light emitting. The possible ECL process of the CdS NCs reacted with \(\text{H}_2\text{O}_2\) could be expressed as follows:

\[
\text{CdSNCs} + ne^- \rightarrow n\text{CdS}^{n-} \tag{1}
\]

\[
2\text{CdS}^{n-} + \text{H}_2\text{O}_2 \rightarrow 2\text{CdS}^* + 2\text{OH}^- \tag{2}
\]

\[
n\text{CdS}^* \rightarrow \text{CdSNCs} + h\nu \tag{3}
\]

Therefore, the strong and stable ECL from CdS/Au nanocomposite film was mainly attributed to the highly stable reduced form of CdS NCs as indicated by cyclic voltammograms (inset to Fig. 1). A pair of reduction and oxidation peaks appeared at ca. –1.3 and –0.9V, respectively, which suggested that the reduced form of CdS is stable enough to undergo oxidation on scan reversal [21]. Moreover, there was no ECL signal for bare ITO electrode and AuNPs modified ITO electrode under the same conditions (not shown).

The cyclic voltammetric (CV) curves and the ECL intensity–potential curves (Fig. 1) showed the effect of AuNPs on the ECL. Fig. 1 shows that the ECL intensity of Au\(_{0.01}/\text{CdS}_1\) nanocomposite film was 4-fold higher than that of the pure CdS NCs film, while the corresponding CV curves of Au\(_{0.01}/\text{CdS}_1\) and CdS NCs modified ITO electrodes showed very close current responses (inset to Fig. 1). To investigate the effect of AuNPs in ECL process, the ECL properties of CdS\(_1–\text{Au}_{0.01}\) (CdS was coated on AuNPs) and Au\(_{0.01}–\text{CdS}_1\) (AuNPs were coated on CdS) films were also studied. As shown in Fig. 1, the ECL responses from both Au\(_{0.01}–\text{CdS}_1\) and CdS\(_1–\text{Au}_{0.01}\) films were slightly lower than that from pure CdS film. It should be mentioned that the quantities of CdS NCs were equal in all films. The above phenomena indicated that the enhancement or quenching of ECL from the CdS film by AuNPs was dependent on the fabrication methods. It could also be explained by the distance-dependent energy transfer [21]. For both films of Au\(_{0.01}–\text{CdS}_1\) and CdS\(_1–\text{Au}_{0.01}\), only close contact occurred between AuNPs and CdS NCs, thus ECL quenching of CdS NCs by AuNPs occurred as a result of Förster energy transfer. For Au\(_{0.01}/\text{CdS}_1\) nanocomposite film, AuNPs were uniformly dispersed in CdS NCs film, thus besides the close contacted CdS NCs, there exist a large amount of remote CdS NCs. There was a balance between quenching by proximal AuNPs via Förster energy transfer and enhancement by remote AuNPs due to the energy transfer from surface plasmon resonances in AuNPs to the ECL of CdS NCs. In this case, the enhancement by remote AuNPs predominated.

In order to confirm this view, ECL spectrum of the Au\(_{0.01}/\text{CdS}_1\) film and the UV–vis absorption spectrum of AuNPs were obtained. As shown in Fig. 2, the ECL emission of Au\(_{0.01}/\text{CdS}_1\) films at 500 nm showed a considerable spectral overlap with surface plasmon absorption of AuNPs. Based on such overlap, it is necessary for efficient energy transfer in photoluminescence or chemiluminescence system [24], the successful ECL energy transfer between CdS NCs and AuNPs could be achieved.

We further investigated the influence of the amount of AuNPs in the nanocomposites on the ECL responses, because the amount of AuNPs in the nanocomposites determined the number ratio of the remote CdS NCs to the proximal AuNPs. As shown in Fig. 3, the ECL intensity increased as the amount of AuNPs increased. The highest ECL intensity was obtained at Au\(_{0.01}/\text{CdS}_1\) modified ITO electrodes. However, as the amount of AuNPs further increased, the amount of proximal CdS NCs increased, as a consequence, the ECL response decreased. According to the experimental results, Au\(_{0.01}/\text{CdS}_1\) as an optimum amount of AuNPs was used in all the subsequent experiments.

In order to further detect the effect of AuNPs in the nanocomposites, SEM was used to assess the morphology of the Au/CdS nanocomposite films. Fig. 4 shows the SEM images of Au\(_{0.01}/\text{CdS}_1\) and Au\(_{0.04}/\text{CdS}_1\) films on glassy carbon patches with constant amount of CdS NCs. The top view of Au\(_{0.01}/\text{CdS}_1\) film displayed relatively homogeneous and close-packed structures (Fig. 4a), which indicated that CdS NCs were incompletely capped on AuNPs at large amounts of AuNPs. These evidences revealed the large effect of AuNPs on the CdS properties in the nanocomposites.

### Sensing application of Au/CdS nanocomposite films

At the Au\(_{0.01}/\text{CdS}_1\) modified ITO electrode, the ECL intensity in air saturated 0.1 mol L\(^{-1}\) PBS (pH 10.0) was obtained. When dissolved oxygen was removed from the solution by bubbling N\(_2\) for 20 min, ECL intensity decreased dramatically. Thus, dissolved oxygen participated in the ECL light emission process. In order to improve the sensitivity, N\(_2\) atmosphere was used in all ECL process. The amount of Au\(_{0.01}/\text{CdS}_1\) nanocomposite used in fabrication process of the modified electrodes strongly affected the ECL.
behaviors which were very sensitive to the surface properties and dependence on the surface state. The effect of volume of Au$_{0.01}$/CdS$_1$ colloidal solution for nanocomposite film modified ITO electrode on ECL intensity was also examined (not shown). It was found that the ECL intensity, which was related to the production of CdS$^{•−}$, increased with the volume of Au$_{0.01}$/CdS$_1$ colloidal solution for deposition increased up to 60 µL. The further increase in the volume of nanocomposite for modified electrodes might be leading to the increase of the impedance of the electrode and the change of the surface state of the films. Therefore, the optimum volume of 60 µL of composite was used in all experiments.

According to the literature [8], H$_2$O$_2$ could obviously enhance the ECL intensity of CdS NCs. Thus, the Au$_{0.01}$/CdS$_1$ modified ITO electrode could be used to develop an ECL sensor for H$_2$O$_2$ in aqueous solution. Under optimized fabrication conditions, the effect of pH value of the electrolyte solution on the ECL behaviors was examined. With an increasing of solution pH from 5.2 to 11.0, the ECL intensity of the Au$_{0.01}$/CdS$_1$ in the presence of 1.0 mmol L$^{-1}$ H$_2$O$_2$ increased greatly and then trended to a constant value at pH 10.0 (Fig. 5). The enhancement in ECL emission in the presence of H$_2$O$_2$ was mainly due to the adsorption of Lewis bases, which changed the surface states of the film [25]. Considering the analytical performance of the ECL sensor, pH 10.0 was chosen for determination procedure.

It was well known that the detection of H$_2$O$_2$ plays an important role in many fields, including modern medicine, environmental control, and industrial diagnosis. Thus, a rapid and accurate determination of H$_2$O$_2$ is of great importance. Fig. 6 shows the sensing response of the Au$_{0.01}$/CdS$_1$ modified ITO electrode to H$_2$O$_2$ under the optimum conditions. A linear relationship between the ECL intensity and H$_2$O$_2$ concentration was obtained from 1.0 × 10$^{-8}$ to 6.6 × 10$^{-4}$ mol L$^{-1}$ with a correlation coefficient of 0.9991 ($n$ = 9). The detection limit was 5 nmol L$^{-1}$ at a signal-to-noise ratio of 3. As summarized in Table 1, the present ECL H$_2$O$_2$ sensors based on the Au$_{0.01}$/CdS$_1$ nanocomposite films exhibited wider linear dynamic range and lower detection limit than those of the other ECL H$_2$O$_2$ sensors based on CdSe film [13], CdS hollow spheres thin film [26], and CdS nanotubes [10]. And, the detection performance of ECL sensor for H$_2$O$_2$ based on Au$_{0.01}$/CdS$_1$ film at the present stage was efficient as that of the luminol-enzyme based ECL system [27]. Furthermore, for amperometric biosensors, the detection signal based on the H$_2$O$_2$ oxidation at higher positive potential could lead the sensors susceptible to interference from electroactive species, such as ascorbic acid (AA), and so on. For the present assay, the negative potential detection mode can completely eliminate the interference from the commonly co-existed electroactive species such as AA and uric acid as the previous reports [13,20], and the present ECL sensors showed good anti-interference ability.

The present ECL sensor showed good reproducibility. The fabrication of three sensors showed an acceptable reproducibility.
with the relative standard deviation of 3.6% in 1.0 mmol L\(^{-1}\) \(\text{H}_2\text{O}_2\) solution. Fig. 7 shows the ECL emission from the \(\text{Au}_{0.01}/\text{CdS}_1\) nanocomposite films under continuous potential scanning for 20 cycles. Stable and high ECL signal were observed, which suggested that the sensor was suitable for ECL detection. After this electrode was stored under dark conditions for 1 month, the ECL response did not show an obvious decline, demonstrating good stability.

4. Conclusions

In summary, ECL enhancement of Au/CdS nanocomposite thin film deposited on ITO electrode surface in aqueous solutions was obtained by tuning the amount of AuNPs in the nanocomposite. Under optimal conditions, the ECL intensity of \(\text{Au}_{0.01}/\text{CdS}_1\) nanocomposite films was ca. 4-fold higher than that of pure CdS NCs films. This enhancement would be useful for ECL analysis and detection based on Au/CdS nanocomposite. This work provides an alternative way for designing stable and high-efficient biosensors.

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