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Electrodeposition of gold nanoparticles on indium/tin oxide electrode for fabrication of a disposable hydrogen peroxide biosensor

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ABSTRACT

A novel disposable third-generation hydrogen peroxide (H_2O_2) biosensor based on horseradish peroxidase (HRP) immobilized on the gold nanoparticles (AuNPs) electrodeposited indium tin oxide (ITO) electrode is investigated. The AuNPs deposited on ITO electrode were characterized by UV–vis, SEM, and electrochemical methods. The AuNPs attached on the ITO electrode surface with quasi-spherical shape and the average size of diameters was about 25 nm with a quite symmetric distribution. The direct electron chemistry of HRP was realized, and the biosensor exhibited excellent performances for the reduction of H_2O_2. The amperometric response to H_2O_2 shows a linear relation in the range from 8.0 μmol L^{-1} to 3.0 mmol L^{-1} and a detection limit of 2 μmol L^{-1} (S/N = 3). The K_M^{app} value of HRP immobilized on the electrode surface was found to be 0.4 mmol L^{-1}. The biosensor indicates excellent reproducibility, high selectivity and long-term stability.

1. Introduction

Hydrogen peroxide (H_2O_2) is not only a by-product of several highly selective oxidases, but also an essential mediator in food, biology, medicine, industry and environmental analysis [1]. The sensitive and accurate determination of H_2O_2 is becoming of practical importance. Many techniques have been developed for the determination of H_2O_2. Among these procedures, electrochemical technique based on enzyme biosensors has been extensively employed for determination of H_2O_2 with simplicity, intrinsic selectivity and sensitivity [2,3]. As a result of the easy availability in high purity and low cost, horseradish peroxidase (HRP) has been the most widely studied in the development of enzyme-based amperometric biosensors [1,4–6].

However, the utility of an enzyme-based electrode may be limited by the gradual fouling of its surface and/or loss of enzyme activity. Such a problem can be minimized with the use of disposable electrodes. The most commonly amperometric disposable electrodes based on HRP enzyme for the analysis of H_2O_2 were mainly constructed by screen-printed carbon electrodes. Unfortunately, redox enzymes usually exhibit sluggish electron transfer at conventional electrode surfaces due to their three-dimensional structure, the shielding of redox active centers by their insulated protein shells and unfavorable orientation on the electrode surface [7]. The disposable amperometric HRP biosensors were usually based on mediators. Gao et al. [8] constructed the disposable biosensor using multilayer HRP enzymes which covalently immobilized onto the surface of amino groups modified screen-printed carbon electrode. Morrin presented an effective, facile method for biosensor fabrication by drop-coating conducting non-diffusion PANI/DBSA mediator and enzyme simultaneously onto disposable screen-printed carbon electrodes [9]. Such mediated peroxide biosensors could facilitate the electron transfer and provide low-detection limit, but it is inconvenient to add a mediator in the fabrication process and reduce the reaction selectivity due to mediators [10].

Gold nanoparticles (AuNPs) are used increasingly in many electrochemical applications since they have the ability to enhance the electrode conductivity and facilitate the electron transfer, thus, improving the analytical selectivity and sensitivity. Especially the small size and biocompatible ability of AuNPs allows them utilized widely as a base in modification of various biosensors to promote the direct electron transfer (DET) of some proteins, such as HRP [1,11,12], hemoglobin [13], myoglobin [2], glucose oxidase [14,15] and superoxide dismutase [16,17]. AuNPs can assist in constructing an interface for DET of redox-active proteins while retaining their bioactivity, operating simplicity without mediator and low expense of fabrication. The incorporation of the HRP with AuNPs in the matrix produces very satisfying results with enhanced sensitivity, high reproducibility, wide linearity and a low-detection limit.

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However, there is less report of screen-printed electrode design based on HRP and AuNPs. Tangkuaram developed a highly stable H_2O_2 biosensor on screen-printed carbon electrode based on HRP bound with AuNPs in the matrix of chitosan [18].

Another attractive approach for fabricating the disposable biosensors is to use indium tin oxide (ITO) electrode as the substrate due to their prominent electrochemical and physical characteristics, as well as low cost [19–21]. Zhang has reported the disposable H_2O_2 biosensors based on ITO electrode. One method is to immobilize HRP enzyme in colloidal AuNPs modified chitosan membrane to modify ITO electrode [22]. Another method is based on coentrapment of enzyme and mediator by gold nanoparticles on ITO electrode [23]. Although this served an effective method for fabrication disposable biosensors, the mediators cannot be avoided even though using AuNPs.

As usually, the approaches for AuNPs grown onto ITO coated glass were assembling with polymer [24] and seed-mediated growth method [25]. Electrochemical deposition could provide an easy and rapid alternative for the preparation of gold nanoparticles electrodes in a short time. However, the size of the AuNPs is very large (114–217 nm) [26], which are not very suitable to immobilize enzyme for fabrication biosensors. In the present paper, we develop the method for direct electrochemical deposition of AuNPs on the low-cost ITO substrate to fabricate AuNPs modified ITO electrode. The AuNPs formed on the electrode surface were characterized by UV–vis, SEM, and electrochemical methods. HRP enzyme was chemically adsorbed on the self-assembled monolayers by L-Cysteine (Cys) on the AuNPs/ITO electrode. The optimized conditions for the fabrication and electrochemical behaviors of the enzyme electrode were studied. As far as we know, there is no report about disposable H_2O_2 biosensor based on the DET of HRP on ITO electrode facilitated by AuNPs.

2. Experimental

2.1. Reagents

Potassium aurous cyanide ($KAu(CN)_2$) was obtained from Soochow university special Chemical Reagent Co. Ltd. 2.0 mmol L^{-1} $KAu(CN)_2$ solution was prepared by dissolving 0.0576 g $KAu(CN)_2$ in 100 mL of deionized water. HRP (EC 1.11.1.7, 250 units mg^{-1}) was purchased from Shanghai Chemical Reagent Factory (Shanghai, People's Republic of China). A 3.5 mg mL^{-1} HRP stock solution was stored at 4 °C. 0.05 M phosphate buffer solutions (PBS, pH 6.85), which were prepared from Na_2HPO_4 and KH_2PO_4, were always employed as supporting electrolyte. L-Cysteine was obtained from Guoyao Chemical Regent Co. Ltd. (Shanghai, China). The Cys aqueous solution was freshly prepared and deoxygenated by bubbling pure N_2 gas for about 10 min prior to use. H_2O_2 (30% w/v solution) was purchased from Shanghai Chemical Reagent Company (Shanghai, People's Republic of China), and the fresh solutions of H_2O_2 were prepared daily. All other chemicals employed were of analytical grade and used without further purification. All solutions were made up with doubly distilled deionized water throughout this study.

2.2. Apparatus

Indium tin oxide (ITO) glass (1.1 mm thickness, less than 100 Ω resistance) was purchased from Conduc Optics and Electronics Technology Company. All electrochemical experiments were performed with a CHI830 electrochemical workstation (Shanghai Chenhua Apparatus Inc., China). A homemade three-electrode cell was used with the enzyme electrode (0.6 cm × 0.6 cm) as a working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference. All potentials were reported with respect to the reference electrode. All electrochemical experiments were carried out in 10 mL 0.1 mol L^{-1} phosphate buffer solutions (PBS, pH 6.85) at room temperature. A magnetic stirrer was used to stir the testing solution during the amperometric experiments. All experimental solutions were deaerated by nitrogen gas for at least 15 min, and a nitrogen atmosphere was kept over the solutions in the cell to protect the solution from oxygen during the measurements.

Scanning electron microscopy (SEM) was run with an S-4700 scanning electron microanalyzer (Hitachi, Japan). The samples were coated with thin Au film to well characterize the film. Optical spectra were acquired on a TU-1810 spectrophotometer (Beijing purkinje General Instrument Co. Ltd).

2.3. Preparation of gold-nanoparticle electrode

A sheet of ITO (3 cm × 0.6 cm) was firstly pretreated according to the method described in our previous work [16]. It was sonicated with dilute ammonia, deionized water, absolute ethanol and deionized water for about 5 min, respectively. Then the certain part of ITO glass sheet was immersed into the solution: 0.3 mL 2.0 mmol L^{-1} $KAu(CN)_2$ solution, 0.5 mL phosphate buffer solutions (PBS, pH 8.0) and deionized water in a total of 5.0 mL. The mixed solution was deaerated by nitrogen gas for about 5 min. The upper part of the ITO electrode was directly connected with electrochemical workstation. The electrodeposition experiment was carried out in the electric-heated thermostatic water bath at 50 °C. The gold-nanoparticle electrode was prepared in the potential range of −0.4 to −1.3 V for 20 circles at a scan rate of 50 mV s^{-1}.

2.4. Fabrication of HRP/Cys/AuNPs/ITO electrode

The prepared AuNPs modified ITO electrode was firstly immersed in a 10 mmol L^{-1} aqueous solution of Cys for 4 h in the fridge at 4 °C to self-assemble a monolayer of thiols on the AuNPs/ITO electrode. A Cys monolayer was chemisorbed onto the AuNPs. Then the electrode was thoroughly rinsed with water to remove physically adsorbed Cys. Finally, the Cys/AuNPs/ITO electrode was incubated in 3.5 mg mL^{-1} HRP for 8 h in the fridge at 4 °C to fabricate the HRP/Cys/AuNPs/ITO electrode. After rinsed clearly with twice-distilled deionized water, the enzyme electrodes were stored at 4 °C in a refrigerator when not in use.

3. Results and discussion

3.1. Characteristics of AuNPs electrodeposited on ITO electrode

SEMs were used to evaluate the physical appearance and surface characteristics of AuNPs on electrode surfaces. Fig. 1 illustrates the typical SEM images of AuNPs/ITO (a) and Cys/AuNPs/ITO (b) electrode surfaces at high magnification. As can be seen, many spherical gold nanoparticles are electrodeposited on the ITO film coated glass surface (Fig. 1a). The AuNPs prepared by this method are similar to that made by seed-mediated growth [2,25]. The average diameter of these spherical nanoparticles is about 25 nm with a quite symmetric distribution. It is much smaller than that of the report [26], which also used the electrodeposition method. The AuNPs size is a very important factor for the performance of enzyme electrode. It is reported that the small size AuNPs (20 and 24 nm, respectively) results in a higher catalytic capability of HRP based biosensors than larger-sized AuNPs [27,28]. The size of AuNPs has not shown marked difference after soaking in Cys aqueous solution (Fig. 1b). These indicate clearly that the moderate size AuNPs can be effectively formed on the ITO electrode surface through electrodeposition.

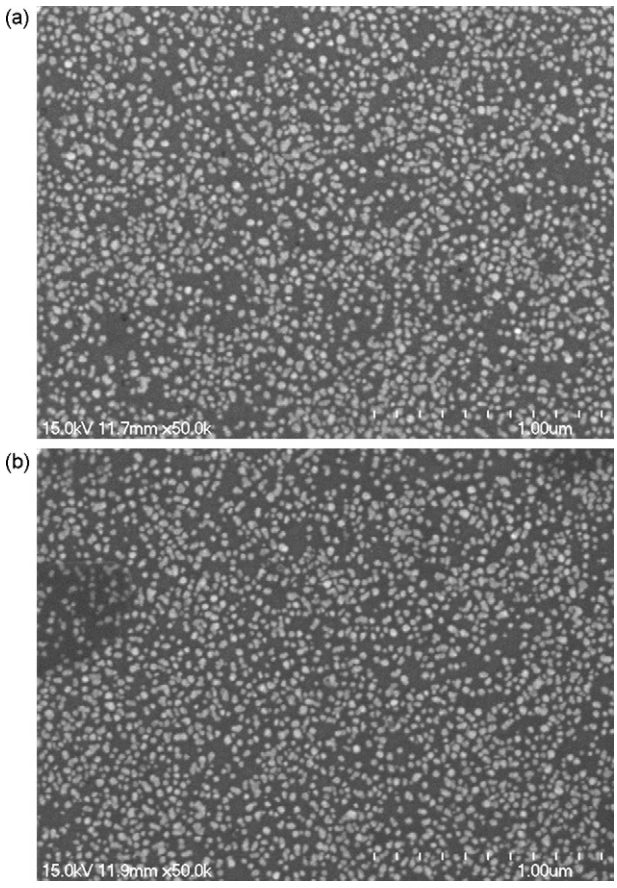

Fig. 1. SEM images of AuNPs/ITO (a) and Cys/AuNPs/ITO (b) electrodes.

UV–vis spectra of the electrodeposited AuNPs are shown in Fig. 2. The AuNPs on the ITO coated glass shows a strong surface plasmon band at 540 nm (Fig. 2a). The absorbance maximum was a little red shift compared with that of the similar size AuNPs made by colloidal methods [29–31]. This was consistent with Zhao's result [32] that the plasmon resonance was shifting to the red for 8 nm when AuNPs immobilized onto glass slide surfaces. The optical properties of metal nanoparticles have much to do with the nanoparticle size, shape, and dielectric environment [33]. After self-assembled with Cys monolayer (Fig. 2b), the strong surface plasmon

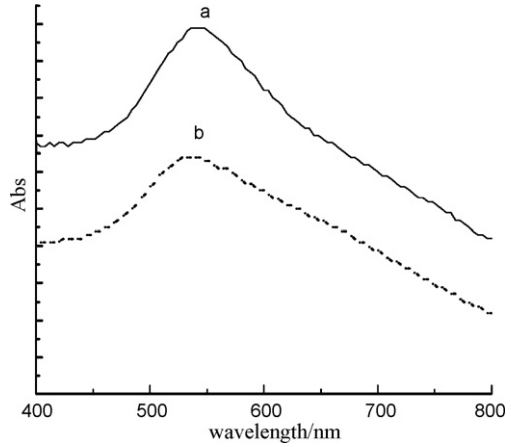

Fig. 2. UV–vis absorption spectra corresponding to: AuNPs/ITO (a) and Cys/AuNPs/ITO (b) electrodes.

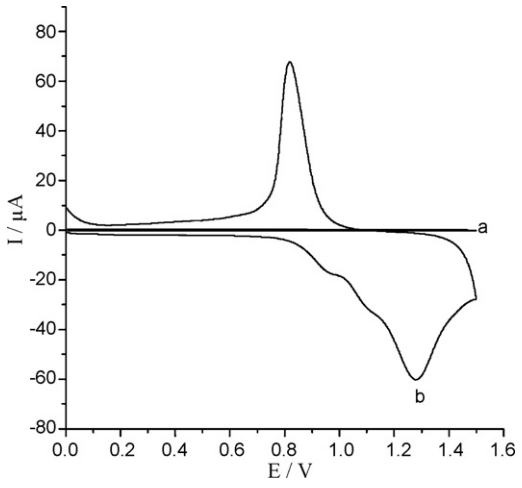

Fig. 3. Cyclic voltammograms of bare ITO (a) and AuNP/ITO (b) electrodes in N_2-saturated 0.05 mol L^{-1} H_2SO_4 solution. Scan rate: 20 mV s^{-1}.

band was located at 533 nm, which shifted to the purple for 7 nm. Considering the results of the SEM images, this may attribute to the interaction between AuNPs and its ligands, which produce changes in the nanoparticle's local dielectric environment [34]. The stability of the AuNPs modified ITO electrode was also investigated through the comparison of the spectra. After sonicated for 3 min, the UV–vis spectrum of the AuNPs electrodeposited on the ITO electrode has nearly no change. It is obvious that the AuNPs can be electrodeposited onto the ITO electrode in high stability.

The characteristic CV responses were measured in N_2-saturated 0.05 M H_2SO_4 at the scan rate of 100 mV s^{-1} for getting the real surface information of the AuNPs electrodeposited on the ITO electrode. Fig. 3 shows the corresponding CV curves of the bare ITO (a) and AuNPs/ITO (b) electrodes. There is no observable Faradaic current on the bare ITO electrode. The CV of an AuNPs/ITO electrode (Fig. 3b) shows a single oxidation peak at +1.3 V along with the reduction peak at +0.80 V, which attributes to the reduction of gold surface oxide. The AuNPs/ITO electrode exhibits the typical characteristic cyclic voltammetric curves of the bulk Au. This is similar to other gold nanoparticles modified ITO electrodes [11,19,35]. This gives another confirmation that the AuNPs are formed on ITO electrode surfaces.

$Fe(CN)_6^{3-}$ which undergoes a reversible electrochemical reaction at various electrode, is widely used as an electrochemical probe to investigate the characteristics of films on electrode surfaces [36,37]. Fig. 4 shows the CVs of different electrodes in 5 mmol L^{-1} $K_3Fe(CN)_6$ aqueous solution containing 0.1 M KCl at a scan rate of 20 mV s^{-1}. At bare ITO electrode, a reversible electrochemical response for $Fe(CN)_6^{4-/3-}$ with a biggish peak potential separation was observed (Fig. 4a). However, there is a drastic decrease in the peak potential separation when AuNPs electrodeposited on the ITO electrode (Fig. 4b). The peak potential separation, which is inversely proportional to the electron transfer rate [38], is used for electrochemical evaluation of the conductivity of the electrode. Obviously, the AuNPs electrodeposited on the ITO surface largely enhanced the conductivity of the electrode.

3.2. Direct electrochemistry of HRP at HRP/Cys/AuNPs/ITO electrode

The typical CVs of bare ITO, AuNPs/ITO and HRP/Cys/AuNPs/ITO electrode in 0.05 mol L^{-1} PBS solution (pH 6.85) at 100 mV s^{-1} are shown in Fig. 5. A pair of well-behaved and nearly symmetric redox peaks was observed at the HRP/Cys/AuNPs/ITO electrode (Fig. 5c).

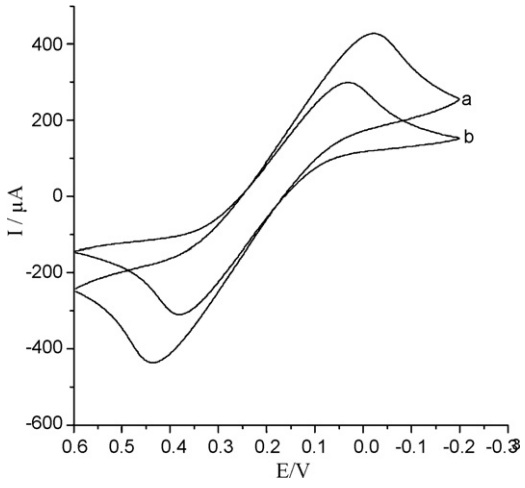

Fig. 4. CVs of 5 mmol L^{-1} $K_3Fe(CN)_6$ in 0.1 mol L^{-1} KCl at bare ITO (a) and AuNP/ITO (b) electrodes. Scan rate: 20 mV s^{-1}.

In contrast, there was no cathodic or anodic peak on both bare ITO (Fig. 5a) and AuNPs modified ITO (Fig. 5b) electrodes. In addition the presence of AuNPs resulted in an obvious increase in the background current due to the increased active electrode area. It confirms clearly that the redox peaks of the HRP/Cys/AuNPs/ITO electrode are attributed to the direct electron transfer of HRP. The formal potential $E^{o\prime}$ of the enzyme electrode, estimated as $(E_{pa} + E_{pc})/2$, is 0.080 V versus SCE. The peak-to-peak separation is 0.167 V at a scan rate of 100 mV s^{-1}. After successive scanning, no noticeable change in CVs of this enzyme electrode was observed. It indicates that AuNPs in biosensors can provide a biocompatibility environment for enzyme and the smaller particles can benefit the electron transfer between HRP and the electrode surface. Furthermore the special nano-structure of AuNPs may acts as "molecular wire", which leads electrons to the redox centers of HRP.

Fig. 6 depicts the typical CVs of the enzyme electrode in 0.05 mol L^{-1} PBS (pH 6.85) at different scan rates. With the increasing potential scan rate, the separation of the anodic and cathodic peak potential increased. The anodic (I_{pa}) and cathodic (I_{pc}) peak currents are both linearly proportional to the scan rate (ν) from 10 to 800 mV s^{-1}, as displayed in the inset of Fig. 6. The peak-to-peak separation of HRP also increased with the increase of scan rate

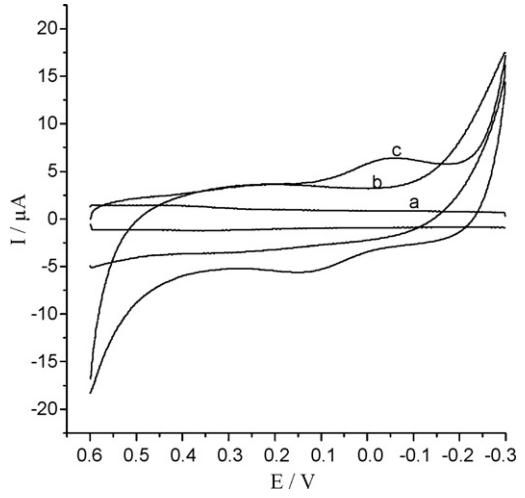

Fig. 5. CVs of bare ITO (a), AuNPs/ITO (b) and HRP/Cys/AuNPs/ITO (c) electrodes in 0.05 mol L^{-1} PBS solution (pH 6.85) at 100 mV s^{-1}.

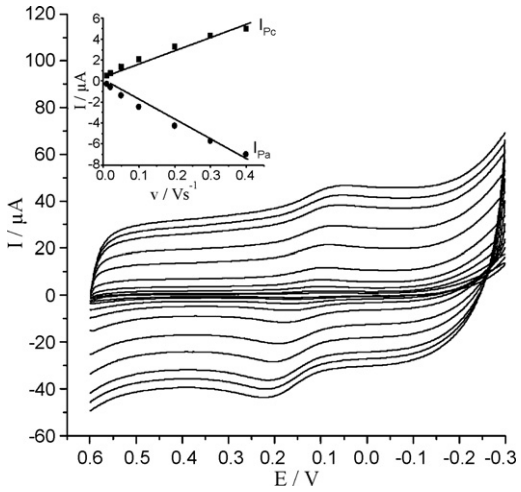

Fig. 6. CVs of the biosensor in 0.05 mol L^{-1} PBS (pH 6.85) at various scan rates. The scan rate (from inner to outer) is 10, 20, 50, 100, 200, 400, 600, 800 mV s^{-1}, respectively. (Inset) Plot of currents vs. scan rate.

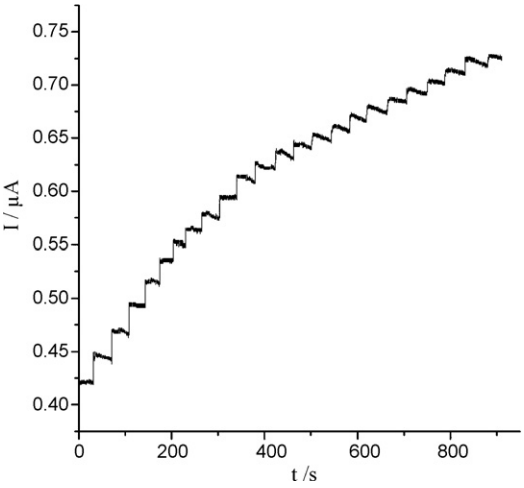

Fig. 7. Typical steady-state response of HRP/Cys/AuNP/ITO electrode on successive injection of aliquot H_2O_2 into 10 mL of stirring PBS (pH 6.85).

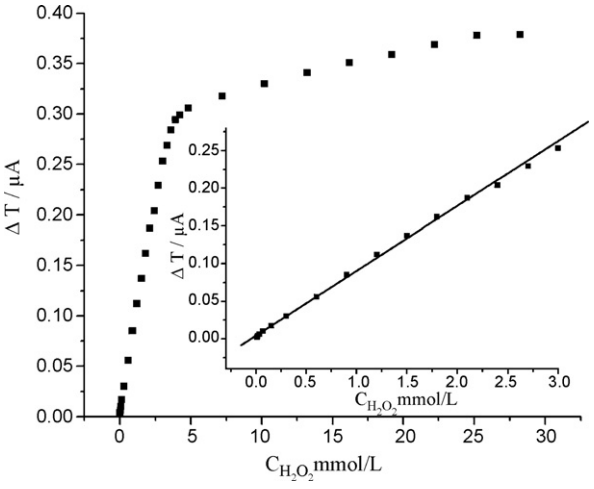

Fig. 8. Calibration curve of the response of the biosensor to concentration. (Inset) The linear part of the calibration curve.

Table 1
Determination of H_2O_2 in plant leaves ($n = 3$).

Samples	Found (mmol L^{-1})	Added (mmol L^{-1})	Total found (mmol L^{-1})	Recovery (%)	Spectrophotometry [44] (mmol L^{-1})
1	0.0532 ± 0.0024	0.050	0.101 ± 0.003	95.6	0.0514
		0.100	0.147 ± 0.007	93.8	
2	0.0613 ± 0.0031	0.050	0.109 ± 0.004	95.4	0.0573
		0.100	0.158 ± 0.005	96.7	

higher than 1.0 V s^{-1}. All these results are in accordance with the typical surface-controlled or thin-layer electrochemical behavior, as expected for immobilized systems.

3.3. Steady-state amperometric response to H_2O_2 and calibration

The dependence of the enzyme electrode on the applied potential for amperometric signal to 0.1 mmol H_2O_2 was investigated initially. In the range between 0.1 and −0.25 V, the response increased first and then reached a pseudo-plateau for lower than −0.15 V. Thus −0.15 V was selected as applied potential in subsequent experiments. Under the optimized experimental conditions, the typical current–time plot of the enzyme electrode resulted from successive injections of H_2O_2 was observed in the stirred buffer solution as shown in Fig. 7. When an aliquot of H_2O_2 was added into the stirring buffer solution, the reduction current rose sharply to reach a steady-state value. The response time (reaching 90% of the maximum response) was less than 5 s, which indicates a fast process and the immobilized HRP could well catalyze the reduction of H_2O_2. It is faster than the reported results of HRP that immobilized on gold colloid/cysteine/nafion-modified platinum disk electrode (10 s) [39] and similar to that of HRP in silica sol–gel network on gold modified electrode [11]. The faster response was mainly attributed to the follows: first, H_2O_2 can freely diffuse to the HRP molecules which are exposed to the surface of AuNPs. Second, the AuNPs are favorable to the orientation of the HRP molecule and provide a necessary conductive pathway to transfer electrons.

Fig. 8 corresponded to the calibration plot of the biosensor. The currents had a good linear relationship with the concentration of H_2O_2 in the range of 8.0 μmol L^{-1} to 3.0 mmol L^{-1} with a correlation coefficient of 0.999. The biosensor has a detection limit of 2.0 μmol L^{-1} estimated at a signal to noise ratio of 3. Tangkuaram reported the H_2O_2 biosensors fabricated by modified HRP on disposable screen-printed carbon electrodes with AuNPs and the linear range of concentration was 10 μmol L^{-1} to 11.3 mmol L^{-1} [18]. By comparison this result, the proposed biosensor shows similar low limit and narrow wide of the linear range. This maybe attribute to lower load of enzyme in the proposed biosensor than that in the screen-printed carbon electrode.

The plot shows a Michaelis–Menten type response when the concentration of H_2O_2 is at a higher level. The apparent Michaelis–Menten constant (K_M^{app}), a reflection of both the enzymatic affinity and the ratio of microscopic kinetic constants, can be obtained from electrochemical version of the Line weaver–Burk equation [40]. The K_M^{app} was determined by analysis of the slope and intercept for the plot of the reciprocals of the steady-state current versus H_2O_2 concentration. The K_M^{app} value for the HRP/Cys/AuNPs/ITO electrode was found to be 0.4 mmol L^{-1}, which is smaller than those of 4.51 mmol L^{-1} for HRP bound with AuNPs in the matrix of chitosan on screen-printed carbon electrodes [18], 2.3 mmol L^{-1} for HRP/Au colloid self-assembly monolayer electrode [41] and 2.2 mmol L^{-1} for HRP on TMB/AuNPs modified ITO electrode [22], and close to 0.57 mmol L^{-1} of HRP based on chitosan-gold nanoparticle nanocomposite [7]. These results further show that the biosensor exhibits higher biological affinity to H_2O_2 and the HRP enzyme on the electrode kept its activity with a low-diffusion barrier.

3.4. Reproducibility and stability

The repeatability of the biosensor was valued at a H_2O_2 concentration of 0.05 mmol L^{-1} in 50 mmol L^{-1} PBS with the same enzyme electrode. The relative standard deviation (R.S.D.) was 3.2% for nine successive assays. The electrode-to-electrode reproducibility was determined in the presence of the same concentration H_2O_2 with six different enzyme electrodes, prepared independently. It shows an acceptable reproducibility with a R.S.D. of 4.6%.

The stability of the enzyme electrode was also examined during storage in a drying state at 4 °C. It was found that the current response remained nearly 83% of its initial value over 12 weeks. The stability of the biosensor is much better than HRP bound with AuNPs in the matrix of chitosan on screen-printed carbon electrodes [18] or immobilized on AuNPs modified ITO electrode with mediator [22]. The long-term stability can be attributed to good biocompatibility of AuNPs and strongly interaction between enzyme and AuNPs.

3.5. Selectivity and real sample analysis

The effect of substances that might interfere with the response of the biosensor was studied. The selectivity of the biosensor was examined in the presence of 0.2 mmol L^{-1} H_2O_2. The addition of the same concentration uric acid, acetaminophen and glucose did not cause observable interference. While in the presence of 0.2 mmol L^{-1} ascorbic acid the response of the biosensor increased about 8%, which interfered slightly. Only 0.05 mmol L^{-1} sulfide decreased the response 21% and has a significant interference. This result was similar to previous report [42].

In order to illustrate feasibility of the composite modified electrode in practical analysis, the HRP/Cys/AuNPs/ITO electrode was used to detect the H_2O_2 concentration in the extraction solution of the plant leaves. The extraction solution of the plant leaves was prepared as follows [43], the fresh plant leaves were first clear, then triturated the clear leaves, and finally centrifuged. The determination was developed by standard addition method. Table 1 shows the determined values and the recovery values. The results obtained by proposed HRP biosensor were also compared to those determined by spectrophotometric method [44]. The aliquot of sample solution was added in the mixture solution which contained 3,3′,5,5′-tetramethybenzidine and HRP in acetate buffer (pH 5.0). The absorbance of the resulting solution at 652 nm was recorded by spectrophotometer. Analytical recoveries were in the range 93–97% and the results are satisfactory by comparison with the reference method.

4. Conclusions

The method for direct electrochemical deposition of AuNPs onto ITO electrode surface has been developed. The average size of the deposited AuNPs is about 25 nm with a quite symmetric distribution. A disposable electrochemical H_2O_2 biosensor was fabricated

by immobilizing HRP on AuNPs/ITO electrode surface in the presence of Cys. AuNPs is very efficient for retaining the enzyme activity and promoting the electron transfer. The direct electron transfer of HRP in the enzyme electrode was realized and the biosensor could catalyze the direct reduction of H_2O_2. The enzyme electrode exhibits several good electrochemical characteristics such as short response time, high sensitivity, selectively and long-term stability. Based on the AuNPs and low-cost ITO substrate, this proposed method presented here is rapid, easy, and simple. Practically, the promising platform presented here not only can be used for fabrication of disposable biosensors based on HRP, but also can be extended to other proteins.

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