

Silver nanoparticles/poly(2-(*N*-morpholine) ethane sulfonic acid) modified electrode for electrocatalytic sensing of hydrogen peroxide

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Abstract A sensitive amperometric hydrogen peroxide (HP) sensor was constructed based on silver nanoparticles/poly(2-(*N*-morpholine) ethane sulfonic acid) (PMES) modified glassy carbon electrode. PMES and silver nanoparticles were orderly introduced to the surface of the electrode by electrochemical methods and characterized by cyclic voltammetry, scanning electron microscopy, and X-ray powder diffraction. The fabricated electrode showed a good electrocatalytic activity toward the reduction of HP with a line range from 0.6 μM to 0.54 mM and a detection limit of 0.18 μM . In addition, the sensor exhibited favorable reproducibility and good long-term stability, and was applied to determine HP in real sample with satisfactory result.

Keywords Silver nanoparticles · 2-(*N*-morpholine) ethane sulfonic acid · Hydrogen peroxide · Amperometric sensor

1 Introduction

Hydrogen peroxide (HP) is not only a by-product of several highly selective oxidases, but also an essential mediator in some fields. The rapid, sensitive, and quantitative

determination of HP has become an extremely important research topic. Various techniques including titrimetry [1], chemiluminescence [2, 3], and electrochemistry [4–10] have been employed to determine HP. Among these techniques, more attention has been paid to the electrochemical methods, especially amperometric sensors, due to its quick response, low cost, simple of instrumentation, high sensitivity, and possibility of miniaturization.

In recent years, various amperometric HP sensors based on different materials including enzyme [11], redox proteins [12], complexes of transition metals [13], nanomaterials [14–17], etc. have been reported. Among these materials, nanomaterials, especially metal nanomaterials, play an important role in this area due to their unique properties [18]. Despite these advances, it is still a challenge to explore new sensitive methods for determining HP. Silver nanomaterial, as a typical metal nanomaterial, has attracted growing interest in constructing electrochemical sensors. Recent studies show that silver nanomaterial has excellent characteristic and can exhibit favorable catalytic activity for HP [19–24]. Various electrochemical HP sensors based on silver nanomaterial have been reported [25–29]. Ju et al. [27] prepared silver–DNA hybrid nanoparticles modified electrode for detection of HP and glucose; Hu et al. [28] reported a HP sensor based on myoglobin immobilized on silver nanoparticles-doped carbon nanotubes film. Sun et al. [29] reported a HP sensor based on silver nanoparticles.

Polymer films have received extensive interest in recent years, and have been considered to be an ideal support material for electrochemical sensor due to their good chemical stability, reproducibility, homogeneity, strong adherence to electrode surface, and excellent catalytic activity [30]. Electropolymerization is an effective approach to prepare polymer film modified electrode.

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Various electrochemical sensors [31–35] based on polymer films modified electrode have been successfully constructed. 2-(*N*-morpholino) ethanesulfonic acid (MES) is a biological buffer commonly used in enzymatic studies and protein purification. To the best of our knowledge, the usage of MES as a modifier for the fabrication of HP sensor had never been reported until our recent work. On the other hand, polymers films have been proven to be suitable matrices for dispersing metallic nanomaterial, and the composites of polymer and metal nanomaterial can exhibit some new properties than polymer or metal nanomaterial alone [25, 36–39]. Chen et al. [25] reported a HP sensor based on silver nanograins incorporated poly(3,4-ethylenedioxythiophene) modified electrode. Zhang et al. [39] fabricated an amperometric HP sensor based on the silver nanoparticles/poly(alizarin yellow R) modified electrode.

In this article, the PMES, for first time, was immobilized onto the surface of electrode via electropolymerization by cyclic voltammetry (CV), silver nanoparticles (AgNPs) were then electrodeposited on the surface of the PMES modified electrode to fabricate an electrochemical HP sensor with enhanced electrocatalytical activities. The fabricated sensor exhibited high sensitivity, good selectivity, well reproducibility, and stability, and was applied to determine HP in real sample with satisfactory result.

2 Experimental

2.1 Reagents and apparatus

All electrochemical measurements were performed on a CHI660A electrochemical workstation (Shanghai Chenhua Instruments Co, China.). The three-electrode system was used in the experiment with bare glassy carbon electrode (GCE) or modified electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a platinum wire as counter electrode. HP detection were performed in phosphate buffer solution bubbled with nitrogen for more than 30 min to exclude the oxygen interference and a blanket of nitrogen was maintained over the solution during the measurements. All potentials given in this article were referred to SCE. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 (Japan); X-ray powder diffraction (XRD) patterns of the products were carried out on a Shimadzu XRD-6000, X-ray diffractometer at a scanning rate of 0.05°/s with 2θ range from 30° to 90°, with high-intensity CuK α radiation ($\lambda = 0.154178$ nm).

AgNO₃ was purchased from Aldrich. MES was obtained from the Jiangsu Chemical Company. Dopamine (DA), ascorbic acid (AA), and uric acid (UA) were obtained from Sigma. HP and other chemicals were of analytical grade

and were obtained from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China), and used without further purification. The phosphate buffer solution (PBS, 0.1 M) was prepared by NaH₂PO₄ and Na₂HPO₄, and adjusted the pH with 0.1 M H₃PO₄ and 0.1 M NaOH solutions. All solutions were prepared with doubly distilled water.

2.2 Fabrication of the modified electrode

Prior to modification, the bare GCE was orderly polished to a mirror-like surface with 1.0, 0.3, and 0.05 μm a-Al₂O₃. Then, the electrode was successively ultrasonically washed with anhydrous ethanol and doubly distilled water, each for 1 min. After being cleaned, the electrode was immersed in 0.1 M PBS (pH 7.0) containing 2.0×10^{-4} M MES and the potential of working electrode was cycled between +0.2 and +2.0 V (vs. SCE) at 100 mV s⁻¹ for 20 scans to form PMES modified electrode. The fabricated electrode was donated as PMES/GCE. The AgNPs/PMES/GCE was prepared by immersing the PMES/GCE into 3.5 mM AgNO₃/0.1 M NaNO₃ solution and electrodeposition for 50 s at 0.181 V (vs. SCE).

3 Results and discussion

3.1 Electropolymerization of the MES on GCE

Figure 1 displayed the continuous CVs for the electropolymerization of MES on GCE in 0.1 M PBS (pH 7.0) at the potential range of +0.2 to +2.0 V (vs. SCE) with the scan rate of 100 mVs⁻¹. As can be seen from the Fig. 1, an anodic peak at about +1.43 V (vs. SCE) was observed at the first cyclic scan, then the anodic peak disappeared at the second cyclic scan, after that an oxidation peak at about +1.06 V (vs. SCE) appeared at the third cyclic scan, and larger peaks were observed on continuous scanning,

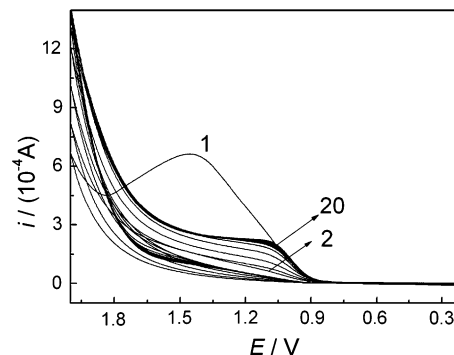


Fig. 1 The CVs for the electropolymerization of MES (2.0×10^{-4} M) in 0.1 M PBS (pH 7.0) on the bare GCE in the potential range from +0.2 to +2.0 V (vs. SCE) at a scan rate of 100 mVs⁻¹

reflecting the continuous growth of the film. These facts indicated that PMES film was successfully electropolymerized on the surface of electrode. When the cyclic scan was scanned up to 20 cycles, the peak currents hardly grew. Therefore, the cyclic scan of 20 was chose to fabricate PMES modified electrode.

3.2 Characterization of the different electrodes

CV, XRD, and SEM were used to characterize the modified electrode. Figure 2A compared the CVs of the bare GCE and the AgNPs/PMES/GCE (with 50 s silver deposition time) in 0.1 M PBS (pH 7.0). Compared with the bare GCE, one pair of the obvious redox peaks of was observed at +0.426 and +0.181 V (vs. SCE) for the AgNPs/PMES/

GCE (b), which was ascribed to the redox of silver. Figure 2B exhibited the XRD profiles taken from the AgNPs obtained with 50 s electrodeposition time. In the range of $30^\circ < 2\theta < 90^\circ$, the five typical peaks, (111), (200), (220), (311), and (222) can be indexed as the AgNPs, which agree well with the reported data. This indicated that the AgNPs product was well crystallized. Figure 2C showed the SEM images of the AgNPs/PMES/GCE (with 50 s silver deposition time). It could be seen that the surface of electrode had a mass of the AgNPs with uniform size, high density, and good shape. Based on above results, the AgNPs/PMES/GCE could be successfully constructed.

3.3 Electrocatalytic reduction of HP

The electrocatalytic activity of the sensor for the reduction of HP was investigated by CV in 0.1 PBS (pH 7.0). Figure 3 compared CV responses of 2.0 mM HP at the bare GCE (a), the PMES/GCE (b), the AgNPs/GCE (c), and the AgNPs/PMES/GCE (d). The response of HP for the bare GCE and PMES/GCE was not observable and weak (Fig. 3a, b), respectively. Importantly, a more obviously catalytic current appeared for the AgNPs/PMES/GCE (with 50 s silver deposition time) (Fig. 3d) compared with that of the AgNPs/GCE (with 50 s silver deposition time)

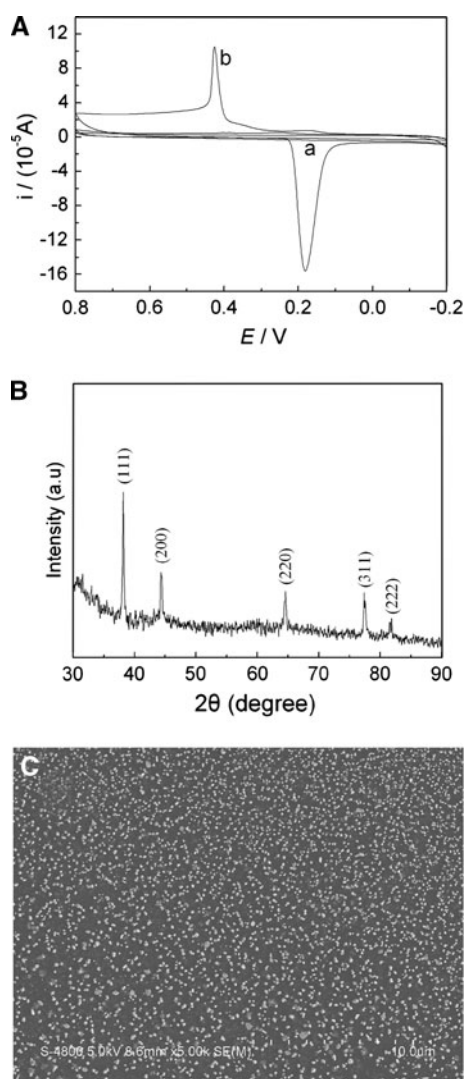


Fig. 2 **A** The CVs of the bare GCE (a) and the AgNPs/PMES/GCE (b) in 0.1 M PBS (pH 7.0) at a scan rate of 100 mVs^{-1} ; **B** The XRD pattern of the AgNPs obtained with 50 s silver electrodeposition time; **C** The SEM images of the AgNPs/PMES/GCE

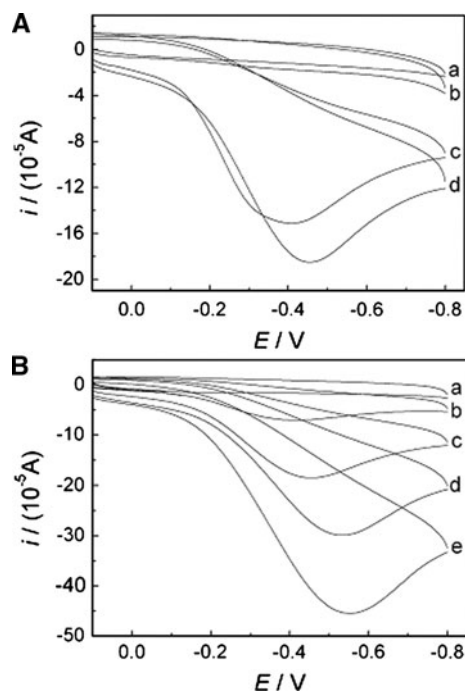


Fig. 3 **A** The CVs of 2.0 mM HP in 0.1 M PBS (pH 7.0) at different electrode: The bare GCE (a), the PMES/GCE (b), the AgNPs/GCE (c), the AgNPs/PMES/GCE (d). **B** The CVs of different concentrations of HP in 0.1 M PBS (pH 7.0) at the AgNPs/PMES/GCE: 0.0 M (a), 1.0 mM (b), 2.0 mM (c), 4.0 mM (d), 8.0 mM (e)

(Fig. 3c) and the cathodic current increased with the concentration of HP increasing (Fig. 3B). These results indicated that the AgNPs/PMES/GCE possessed relatively remarkable catalytic ability for HP reduction.

The silver electrodeposition time has an important effect on the catalytic ability of the sensor. Here, the silver electrodeposition time was optimized by investigating the cathodic current of 2.0 mM HP at the AgNPs/PMES/GCE with various silver deposition time by CV in 0.1 M PBS (pH 7.0). The result was shown in Fig. 4. With the increasing deposition time, the cathodic current of HP increased and obtained a maximum value after a deposition time of 50 s. Thus, 50 s was chosen as optimum deposition time for fabricating the AgNPs/PMES/GCE.

3.4 Sensitivity and selectivity of the HP sensor

Amperometric current–time curve is the most used method to evaluate the electrocatalytic activity of electrochemical HP sensor. Figure 5 showed the typical amperometric response of the AgNPs/PMES/GCE to the successive addition of HP with different concentrations at the applied potential of -400 mV (vs. SCE) in 0.1 M PBS (pH 7.0). As can be seen from the Fig. 5, the sensor exhibited a fast response and well-defined steady-state current responses to HP, and the amperometric response to HP displayed a linear range from $0.6 \mu\text{M}$ to 0.54 mM, the linear regression equation was $i (\mu\text{A}) = 0.8178 + 33.9503 C_{\text{HP}} (\text{mM})$ ($r^2 = 0.9996$) with a detection limit of $0.18 \mu\text{M}$ ($S/N = 3$) (Fig. 5A). The selectivity of the HP sensor was evaluated by using amperometry with three kinds of possible electroactive substances including dopamine (DA), ascorbic acid (AA), uric acid (UA) (whose concentrations were 10 times that of HP) injecting into 0.1 M PBS (pH 7.0) containing $5.0 \mu\text{M}$ HP. In the experiments, no obvious interference was observed (Fig. 5B). Compared with the previous reported electrochemical HP sensors [15, 25, 27,

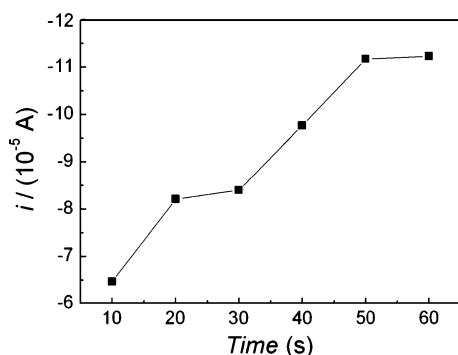


Fig. 4 The effect of silver deposition time on the cathodic current of 2.0 mM HP in 0.1 M PBS (pH 7.0)

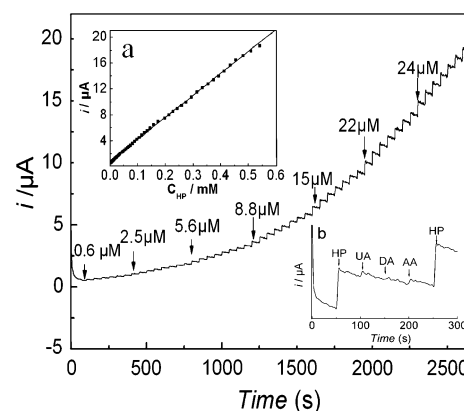


Fig. 5 Amperometric current–time curve for HP reduction at AgNPs/PMES/GCE in stirring 0.1 M PBS (pH 7.0) for the successively increasing the concentration of HP at the range of $0.6 \mu\text{M}$ to 0.54 mM at -400 mV (vs. SCE). The inset: (a) The corresponding linear fit plots of current versus concentration of HP; (b) The amperometric responses of UA, DA, AA, and HP at -400 mV (vs. SCE) under stirring condition

28, 40], the sensor possessed a lower detection limit and a wider linear range. The data were shown in Table 1, indicating the proposed sensor had high sensitivity and good selectivity.

3.5 Reproducibility and stability

The reproducibility and stability of the proposed sensor were investigated. Under the optimum conditions, three modified electrodes were fabricated independently used to detect 0.4 mM HP by CV in 0.1 M PBS (pH 7.0), the peak current were 2.602×10^{-5} A, 2.323×10^{-5} A, and 2.515×10^{-5} A, respectively, with an acceptable RSD of 5.7%. The stability was investigated by CV in 0.1 M PBS (pH 7.0). When the electrode was successively scanned for 30 cycles, and the sensor was then stored in 0.1 M PBS (pH 7.0) for 7 days at 4°C , the CV response of the proposed sensor to the same concentration of HP decreased less than 3.6%. Indicating the sensor has good reproducibility and excellent stability, it could be used for repetitive detection.

3.6 Real sample analysis

To evaluate the feasibility of the method for routine analysis, the sensor was applied to detect HP in three different water sources. Under optimized conditions, amperometric detection of HP in real sample was carried out by the standard addition method. The experiment results were shown in Table 2 (each value was an average of three measurements), which indicated that the sensor had an excellent performances for real sample of HP. It would be applied foreground for routine analysis.

Table 1 Comparison of the analytical data obtained by the different electrodes for determination of HP

Modified electrode	pH	Linear range (μM)	Detection limit (μM)	References
Silver microspheres/GCE	7.0	–	1.2	[15]
Silver nanograins/PEDOT/ITO	7.0	–	7.0	[25]
Ag–DNA/GCE	7.0	2.0–2,500	0.6	[27]
Mb/AgNGs/CNTs/GCE	7.0	2.0–1,200	0.36	[28]
Mb–Chi–ZnO/GCE	7.0	2.0–490	0.21	[40]
AgNPs/PMES/GCE	7.0	0.6–540	0.18	This article

Table 2 Results for determination of HP from different water sources injected with known quantity of HP

Sample	HP Added (μM)	HP Found (μM)	Recovery (%)
Distilled water	40.00	39.82	99.55
Drinking water	40.00	40.18	100.45
River water	40.00	39.78	99.45

4 Conclusion

In summary, we have successfully fabricated a sensitive HP sensor by combining the electrocatalytic activities of AgNPs with PMES film based on simple electrochemical method. The AgNPs/MES/GCE exhibited a relatively remarkable catalytic ability for HP reduction, which was the first application to detect HP. In addition, the sensor exhibited a variety of good electrochemical characteristics including high sensitivity, good selectivity, favorable reproducibility, and good long-term stability, and could be applied to determine HP in real sample with satisfactory result.

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