Fabrication of a novel nonenzymatic hydrogen peroxide sensor based on Se/Pt nanocomposites

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A novel nonenzymatic hydrogen peroxide sensor was successfully fabricated based on the Se/Pt nanocomposites. The nanocomposites were constructed via a simple solvothermal method, and were confirmed by X-ray diffraction (XRD), energy-dispersive X-ray spectrometry (EDS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Cyclic voltammetry (CV) was used to evaluate the electrochemical performance of the nanocomposites at glassy carbon electrode (GCE). The results indicated that the Se/Pt nanocomposites exhibited excellent electrocatalytic activity to the reduction of H2O2 and could be used to construct a hydrogen peroxide amperometric sensor with a low detection limit and wide responding range.

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1. Introduction

The detection of hydrogen peroxide plays a significant role in many fields including clinic, food, pharmaceutical and environmental analyses [1]. Thus, several analytical methods have been developed for the detection of H2O2, such as fluorescence, chemiluminescence, and electrochemical methods [2–5]. Among these methods, electrochemical detection of H2O2 is distinctive for its low detection limit as well as low costs [6,7]. However, most sensors based on enzymes or proteins may result in limited lifetime, stability problem and complex procedures in the fabrication process. Thus, the development of enzyme-free H2O2 sensors with low detection limit and wide responding range has become a trend. Nowadays, nanomaterials have been investigated extensively in the fabrication of enzyme-free H2O2 sensors [8,9]. However, only a few reports have been found on the nonenzymatic sensors based on nanocomposites [10].

Recently, nanocomposites especially semiconductor and metal nanocomposites have been extensively investigated for their potential applications in catalysis, electronic and optoelectronic devices [11,12]. Platinum with unique catalytic properties has been used in the catalysis of methanol, glucose et al. [13,14]. As an important semiconductor, selenium has many properties such as high photocatalyticity and catalytic activity [15]. Therefore, it is reasonable to expect that Se and Pt nanocomposites have both good electro-conductivity and enhanced catalytic activity. Some references reported the fabrication of hollow Pt nanostructures by using Se as template [16]. However, no reports have been found on the solvothermal synthesis of Se/Pt nanocomposites and the application in electrocatalysis.

In this work, we developed a facile solvothermal method to synthesize Se/Pt nanocomposites. The nanocomposites modified GCE has a larger current to the reduction of H2O2 than the single-component Pt nanotubes and can be used to construct a nonenzymatic H2O2 sensor. To our best knowledge, it is the first time that Se/Pt nanocomposites are used to fabricate a sensor with a low detection limit and a wide responding range.

2. Experimental section

2.1. Materials

H2O2 (30%), ascorbic acid (AA) and sodium selenite (Na2SeO3) were purchased from Sinopharm Chemical Reagent Co., Ltd. Platinum dichloride (PtCl2) was purchased from Shanghai Yiyang Chemical Co. All other chemicals were used without further purification. Phosphate buffer solution (PBS, 0.1 M pH 7.0) was prepared by mixing stock standard solutions of Na2HPO4 and NaH2PO4.

2.2. Synthesis of the Se/Pt nanocomposites

In order to synthesize the Se/Pt nanocomposites, the Se nanowires were first prepared as follows: 1 mmol of Na2SeO3 and 2 mmol of AA were first dissolved in 10 mL aqueous solution, and then stirred for 2 h at 90–95 ℃. The precipitates were washed with water, ethanol,
and then dried in air. The Se/Pt nanocomposites were prepared using a solvothermal method. Briefly, 0.1 mmol of Se nanowires and 0.1 mmol of PtCl₂ were dispersed in 5 mL of ethanol and loaded into Teflon-lined autoclave (15 mL). After the autoclave was sealed and maintained at 70 °C for 1.5 h, the products were rinsed with dilute HCl and hot water (90 °C), then Se/Pt nanocomposites were collected. Pt nanotubes could be further obtained by soaking the Se/Pt nanocomposites in hydrazine monohydrate for 4 h.

2.3. Characterization

XRD patterns were obtained with a Philips X’pert Pro X-ray diffractometer (CuK radiation, λ = 0.15418 nm). EDS analysis was carried out by using a SEM equipped with an energy-dispersive X-ray detector (Shimadzu, SSX-550). SEM and TEM images were taken on a LEO-1530VP field-emission scanning electron microscope and a FEI Tecnai-12 microscope with an accelerating voltage of 120 kV, respectively.

2.4. Electrochemical measurements

Electrochemical measurements were performed on a CHI 630 electrochemical workstation (Chenhua, Shanghai, China) with a conventional three-electrode system. A platinum wire was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was the reference. The nanomaterials were dispersed in water in 1.0 mL of water, then 10 μL of this suspension was dropped onto the electrode and dried in a silica gel desiccator. The working electrode was glassy carbon electrode (GCE, 3 mm in diameter) modified with Se/Pt nanocomposites, Pt nanotubes, Se nanowires or their simple mixture with the same mass respectively. Electrochemical experiments were all carried out in PBS under a high purity nitrogen atmosphere.
3. Result and discussion

3.1. Characteristics of the Se/Pt nanocomposites

XRD was used to characterize the as-prepared products. Firstly, Se nanowires were prepared by a template-free method with AA as a reducing agent. All the reflections of the prepared selenium nanowires could be assigned to trigonal bulk selenium (JCPDS card No. 06-0362) (curve a in Fig. 1A). After the reaction with PtCl₂, the newly-appeared diffraction peaks located at 39.88°, 46.38° and 67.54°, corresponded to the (111), (200) and (220) lattice planes respectively, which was in good agreement with face-centered cubic Pt (JCPDS card No.04-0802) (curve b in Fig. 1A), indicating the reduction of Pt (II). In order to study the coating shell, the template was dissolved to obtain Pt nanotubes (JCPDS card No.04-0802) (curve c in Fig. 1A). The as-prepared nanocomposites were characterized by EDS, indicating that all the samples were of high purity (Fig. 1B).

The structures of the products could be verified by the TEM and SEM images. Selenium nanowires with an average size of 80±10 nm in diameter (Fig. 2A and D) could serve as both template and the reducing agent. The core–shell nanostructures, as shown in Fig. 2B and E, have a larger diameter of about 100 nm than the template, which proves that Pt has covered the surface of Se nanowires, also in agreement with the XRD result. In order to investigate the thickness of the shell, the templates were removed, and Pt nanotubes could be obtained. From curve c in Figs. 1A and 2C, F, the average thickness of the shell is about 20–40 nm, which further proves that the template is t-Se according to the trigonal tips of the nanotubes [16].

3.2. The electrochemical performance of Se/Pt nanocomposites

The Se/Pt nanocomposites exhibited excellent electrocatalytic properties to H₂O₂. Compared to the CV of GCE in PBS with H₂O₂ (curve a in Fig. 3A), the reduction current and oxidation current of Se/Pt nanocomposites modified GCE increased with the increasing concentration of H₂O₂ (curve b, c, d in Fig. 3A), indicating the electroactive property of Se/Pt nanocomposites. In contrast, the behavior of Se nanowires, Pt nanotubes and their simple mixture (1:1) was also studied. The electrochemical behavior of the Se/Pt nanocomposites modified GCE was similar to that of the Pt disk electrode and that of the Pt nanotube modified GCE. As Fig. 3B showed, a much weaker electrocatalytic response was found to H₂O₂ (curve a and inset figure) on the Se nanowires modified electrode, while a larger current signal could be observed on the Se/Pt modified GCE (curve d) compared with Pt nanotubes (curve b) and the simple mixture (curve c). In addition, the electrochemical performances of different modified GCEs in PBS containing 2 mM [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ were also studied (Fig. 3C). A larger amperometric response could be observed at the Se/Pt modified GCE than that of the Pt and simple mixture (Se:Pt = 1:1) modified GCE, indicating that Se/Pt had a larger electroactive surface area. Therefore, the larger current at the Se/Pt modified GCE could be mainly attributed to the enlarged electroactive surface areas of Se/Pt nanocomposites.

3.3. Amperometric responses to the oxidation of H₂O₂

For amperometric sensing application, the prepared electrodes are generally evaluated by measuring current response at a fixed potential with the addition of the H₂O₂. In order to choose the suitable electrode potential, the amperometric responses of the modified GCE at the potentials of −0.3, 0.0 and +0.3 V were investigated as shown in Fig. 4A. Considering both the signal-to-noise ratio and the linear range, 0.0 V was chosen as the working potential for the detection of H₂O₂.

Fig. 4B displays the amperometric response at the Se/Pt nanocomposites and the Pt nanotube modified GCE to the successive addition of H₂O₂ in PBS. As expected from Fig. 4B, the Pt modified GCE exhibited a weaker response to the addition of H₂O₂, while the Se/Pt nanocomposites modified GCE showed a larger catalytic current to the changes of H₂O₂ concentration (curve a in Fig. 4B). Based on the excellent electrocatalytic activity of Se/Pt nanocomposites to H₂O₂, a nonenzymatic sensor was constructed for the detection
of H$_2$O$_2$. Upon addition of H$_2$O$_2$, the sensor responded rapidly to the substrates and could achieve 90% of the steady-state current within 4 s, indicating a fast amperometric response to the reduction of H$_2$O$_2$.

The sensor had a linear relationship with the concentration of H$_2$O$_2$ from 10 μM up to 15 mM with a correlation coefficient of 0.9991 (Fig. 4B (inset)), which was wider than the previous H$_2$O$_2$ sensors [7,10,17,18]. The regression equation was $I (\mu A) = 2.82c + 0.59$ (Where the $c$ is the concentration of H$_2$O$_2$ in mM) with a detection limit of about 3.1 μM (S/N = 3). The sensor showed lower detection limit and wider responding range, indicating that the fabricated sensor could be potentially used for monitoring the concentration of H$_2$O$_2$.

The sensor exhibited good reproducibility in the detection of H$_2$O$_2$ with a relative standard deviation (RSD) of about 5% at 0.1 mM hydrogen peroxide for more than 10 times measurements. The RSD for six sensors prepared at the same conditions was less than 5%. The long-term stability of the prepared sensor was also investigated by amperometric measurements and the current response of sensor retained about 90% of its original response after 3 month’s storing.

4. Conclusion

Se/Pt nanostructures have been prepared via a facile solvothermal method and could be used to fabricate a novel nonenzymatic amperometric sensor for the detection of H$_2$O$_2$. The electrochemical results showed that the nanocomposites modified GCE had a larger current to the reduction of H$_2$O$_2$ than the single-component nanomaterials with wide responding range and low detection limit which might be attributed to the enlarged surface areas. Therefore the Se/Pt nanocomposites provide a promising platform for the study of the application of semiconductor/metal nanocomposites in electrocatalysis and the construction of attractive nonenzymatic amperometric sensor in the future.

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