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Novel photoelectrochemical hydrogen peroxide sensor based on hemin sensitized nanoporous NiO based photocathode

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ABSTRACT

In this paper, a novel, facile and self-operating photocathode based on hemin sensitized three-dimensional (3D) nanoporous NiO was developed. Compared with pure NiO nanomaterials, the as prepared hemin sensitized NiO photocathode showed enhanced cathodic photocurrent under visible-light irradiation ($\lambda \geq 400$ nm). The cathodic photocurrent was sensitively and selectively enhanced upon the addition of H_2O_2. The common interferents such as ascorbic acid, dopamine, and glutathione, caused less than 10% of the photocurrent change compared with the photocurrent response of the same concentration (2.0×10^{-5} mol/L) of H_2O_2 on ITO/NiO/hemin electrode, indicating good selectivity of the method. The ITO/NiO/hemin electrode showed a linear range of 0.5–500 μmol/L with a low detection limit of 0.1 μmol/L (S/N = 3) for the detection of H_2O_2. In addition, the method was also successfully applied to the detection of H_2O_2 in real samples.

1. Introduction

As being a very powerful, safe and effective oxidant, hydrogen peroxide (H_2O_2), is also an indispensable intermediate product in most of the environmental and biological circulation processes [1]. As a result, rapid and accurate monitoring of H_2O_2 is of great interest. Until now, various H_2O_2 sensing strategies have been developed, including fluorescent, colorimetric and electrochemical techniques [2–6]. Compared with other techniques, the photoelectrochemical measurement, as a newly developed and promising analytical technique, has drawn growing interest due to its simple equipment and high sensitivity.

Since it was firstly reported by Willner et al. in 2001 [7], photoelectrochemical (PEC) analysis that is based on photoinduced electron transfer processes at electrode/interfaces has been recognized as an efficient detection technique [8,9]. PEC analysis has elegant merits of high sensitivity, easy integration, simple equipment, cost-effectiveness and rapidness for detection. Up to now, PEC sensors have been successfully applied in various analytical fields, such as DNA analysis, immunoassay, and environment monitoring [10–13]. The sensing principles of PEC detection mainly depend on the analytes induced by photocurrent change of the photoelectrochemically active species modified electrode. So, the photoelectrochemically active materials play a crucial role in the performance of the as developed PEC sensors. To the best of our knowledge, most of the photoelectrochemically active materials are mainly concentrated on photoanodes made up of n-type semiconductors or sensitized n-type semiconductors, such as CdS quantum dots (QDs) [14,15], CdSe/ZnS [16], TiO_2 [17], or sensitized TiO_2 [18–21]. However, because of the inherent photoinduced hole oxidation reaction at the photoanode/electrolyte surface, it is still highly demanding and challenging to develop highly selective PEC sensing system with innovative signaling mechanism for the detection of small biomolecules.

Fortunately, besides the widely reported photoanodes, there is another type of photoelectrode—photocathode [22]. Different from the extensively researched photoanode based on the n-type semiconductors, photocathodes are made up of p-type semiconductors which prefer to interact with electron acceptors rather than the electron donors in the electrolyte solution [23,24]. Compared with photoanode sensing, photocathode sensing possesses more appealing traits, for example, less dependence of the electron donor and stronger capability of anti-interference from reductive agents coexisting in biological samples. So, it is fascinating and promising to explore new photocathode in PEC analysis. Unfortunately, up to now, the PEC sensing based on photocathode is still very limited.

Considering the advantages of photocathode, herein, we reported a novel PEC sensor for the determination of H_2O_2 using hemin sensitized p-type NiO with a three-dimensional (3D) nanoporous structure as the self-operating photocathode. Cathodic photocurrent of the hemin sensitized p-type NiO would be observed under visible light irradiation ($\lambda \geq 400$ nm) and the cathodic photocurrent was sensitively enhanced by the addition of H_2O_2, indicating that H_2O_2 acted as an efficient electron acceptor of the photo-generated electrons of the photocathode.

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The method was sensitive and highly selective toward other potential interferents, such as ascorbic acid, dopamine, glutathione, etc..

2. Experimental details

2.1. Chemicals

$Ni(NO_3)_2 \cdot 6H_2O$, hexamethylenetetramine ($C_6H_{12}N_4$), hemin (III), H_2O_2 (30 wt.%), ascorbic acid (AA), tris(hydroxymethyl)aminomethane (Tris), dopamine (DA), glutathione (GSH) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The indium tin oxide (ITO) slices (type N-STN-S1-10) were purchased from Southern Glass Holding Co., Ltd. (Shenzhen, China). The supporting electrolyte for photocurrent measurements was 0.1 mol/L Tris–HCl buffer solution. All solutions were prepared with ultrapure water ($18.2\ M\Omega \cdot cm^{-1}$) obtained from a Heal Force water purification system.

2.2. Instrumentation

PEC measurements were performed with a homemade PEC system. The irradiation source was a 500 W Xe lamp equipped with an ultraviolet cutoff filter ($\lambda \geq 400$ nm). Photocurrent was measured on a CHI 800C electrochemical workstation. A saturated Ag/AgCl, a Pt wire and NiO/hemin modified ITO electrode with an area of 0.25 cm^2 was employed as the reference, counter and working electrode, respectively. The photocurrent measurements were performed at a constant potential of −0.05 V (vs saturated Ag/AgCl). Scanning electron microscopy (SEM) image was obtained on Hitachi S-4800 high resolution scanning electron microscope (Hitachi, Japan). The X-ray powder diffraction (XRD) was acquired using an X'Pert Philips Materials Research Diffractometer using Cu K_α radiation employing a scanning speed of $0.02°\ s^{-1}$ in the 2θ range of 10° to 90°. Electrochemical impedance spectroscopy (EIS) was carried out on a CHI 660D electrochemical workstation in 0.1 M KCl containing 5.0 mmol/L $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture as a redox probe. An applied voltage was 5 mV with a frequency range of 0.1–900 kHz.

2.3. Fabrication of NiO modified ITO (ITO/NiO) electrodes

NiO films were fabricated on conducting ITO glass substrates using the hydrothermal method [25]. The ITO slices were cleaned by immersing in 2.0 mol/L boiling KOH solution dissolved in 2-propanol for 20 min, followed by washing completely with water and dried at 120 °C for 2 h. Deposition of NiO films was achieved by placing the ITO glass in the reaction solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.25 mol/L) and $C_6H_{12}N_4$ (0.25 mol/L). The ITO slices were immersed in a closed bottle with the reaction solution and then heated at 90 °C for 10 min. After that, the ITO electrodes were washed with water for several times, dried and heated to 400 °C for 30 min.

2.4. Fabrication of ITO/NiO/hemin electrode

Hemin (6.5 mg) was added into a mixture of doubly distilled water (8 mL) and ammonia solution (2 mL) to reach a concentration of 1.0×10^{-3} mol/L. To immobilize hemin, the ITO/NiO slices were immersed in 1.0×10^{-4} mol/L hemin (diluted to the desired concentration with doubly distilled water) prepared in alkaline solution for 15 min and then the films were carefully washed with doubly distilled water. The thin film was referred as ITO/NiO/hemin.

2.5. PEC detection of H_2O_2

A series of H_2O_2 solutions with different concentrations were prepared with 0.1 mol/L Tris–HCl (pH 7.0) buffer solution. The ITO/NiO/hemin electrode was put into a sealed PEC cell and immersed in 2 mL of 0.1 mol/L Tris–HCl (pH 7.0). The solution was deaerated by bubbling highly pure nitrogen for 30 min and maintained under nitrogen atmosphere during the photocurrent measurement. The photocurrent of the ITO/NiO/hemin electrode in 0.1 mol/L Tris–HCl (pH 7.0) buffer solution was measured and defined as I_0. After bubbling the supporting electrolyte solution (0.1 mol/L Tris–HCl (pH 7.0)), certain concentration of H_2O_2 was injected rapidly (within 2 s) and the photocurrent was measured after 2 min and defined as I.

3. Results and discussion

3.1. Structure and composition characterization

The scanning electron microscopy (SEM) image was used to investigate the morphology of the NiO on the ITO electrode (Fig. 1A). It showed that the NiO modified ITO electrode demonstrated a porous architecture, which was highly random interconnected. This structure of NiO may offer great surface area for adsorbing a large quantity of sensitizer along with an efficient transport of the injected holes of the sensitizer to the back conductive ITO electrode. The characteristic peaks of the NiO at 2θ = 37.26°, 43.28°, 62.76°, 75.28° (Fig. 1B) corresponding to the (111), (200), (220) and (311) crystal planes of cubic NiO (JCPDS: 78-0643), can be observed in the XRD patterns.

Hemin sensitized nickel oxide photoelectrode was constructed based on the fact that hemin assembled on nickel oxide through the conjugation of carboxyl group [26]. The self-assembling of hemin on the NiO electrode was confirmed by FT-IR analysis, cyclic voltammogram (CV), photocurrent responses and electrochemical impedance spectroscopy (EIS). The FT-IR of hemin (Fig. 2, curve a) had a peak at 1703 cm^{-1} due to ν(C=O) stretching peak and another peak at 1382 cm^{-1} attributed to the B_{3u} vibration of porphyrin [27]. The absorption peak of NiO at 1633 cm^{-1} was connected with the bending mode (H–O–H) of the water molecules [28]. By comparing the FT-IR spectra of NiO/hemin with NiO, the spectrum of NiO/hemin showed new bands in 1045 and 1382 cm^{-1} (Fig. 2, curve c) ascribed to C–O stretching vibration [29] and B_{3u} vibration of porphyrin [27]. Moreover, by comparing the FT-IR spectra of hemin with NiO/hemin, carboxylic group of hemin at 1703 cm^{-1} was transformed to typical carboxylate species with a broad band at 1644 cm^{-1} (Fig. 2, curve c). These results confirmed the successful binding of hemin molecule to NiO through the conjugation of carboxyl group.

Cyclic voltammetry (CV) was also adopted to characterize the assembly process of the ITO/NiO/hemin electrode. As shown in the cyclic voltammetry (Fig. 3), for ITO/NiO electrode, a couple of redox peaks with the anodic and cathodic peaks potential of 0.313 and 0.27 V vs Ag/AgCl (saturated KCl) was observed (curve a). The anodic peak was due to the transformation of Ni(II) into Ni(III) in the oxide, and the cathodic peak was for the reverse process. While for the ITO/NiO/hemin electrode, besides the redox peaks at 0.313 and 0.27 V, the other redox peaks at −0.265 and −0.416 V vs Ag/AgCl (saturated KCl) were obtained too (curve b), which were close to the redox potential of hemin [30], the results of cyclic voltammetry indicated that hemin was immobilized on ITO/NiO.

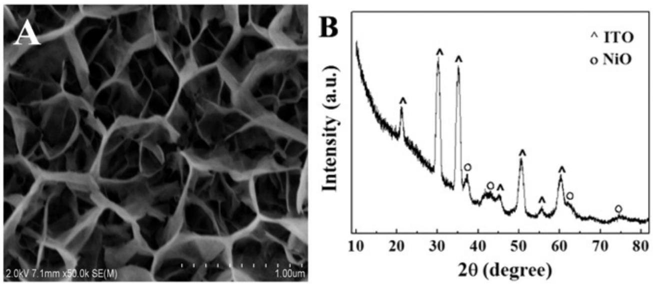

Fig. 1. SEM image (A) and XRD pattern (B) of NiO modified ITO electrode.