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RESEARCH PAPER

A Hydrogen Peroxide Sensor Based on Pt@Au Nanoparticles Loading to Polyethyleneimine Functionalized Carbon Nanotubes

WANG Wei-Wei, QIU Yu, ZHANG Shao-Peng, LI Jia-Wei, LU Xiao-Quan, LIU Xiu-Hui*

Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

Abstract: A novel hydrogen peroxide sensor was fabricated by the seed-mediated growth method. Firstly, polyethyleneimine (PEI) functionalized multiwalled carbon nanotubes (MWNTs) were used as growth scaffold on a glass carbon electrode (GCE). Then, Au nanoparticles were uniformly electrodeposited as seeds. Finally, Pt nanoparticles (PtNPs) grew on Au PtNPs to form Pt@Au core-shell structure nanocomposite. A new type of electrochemical sensor based on Pt@Au/PEI-MWNTs nanocomposites for detection of hydrogen peroxide was then developed, and the designed Pt@Au/PEI-MWNTs/GCE was characterized by electrochemical methods and field emission scanning electron microscopy (FESEM). The differential pulse experiment results showed that the modified electrode exhibited excellent electrocatalytic activity towards the reduction of H_2O_2 with the wide linear range from 9.2×10^{-8} to 1.3×10^{-3} M. The correlation coefficient was 0.9994 and the detection limit was down to 3.1×10^{-8} M at the signal-to-noise ratio of 3.

Key Words: Seed-mediated growth; Polythyleneimine; Functionalized carbon nanotubes; Pt@Au nanoparticles; Modified electrode; Hydrogen peroxide

1 Introduction

Hydrogen peroxide (H_2O_2) can accelerate the aging process of human body[1], and has a close relation with many pathological changes. Once the hydrogen peroxide in human body exceeds the limitation, it would cause some of irreversible damages such as cardiac cell necrosis or even death[2]. Therefore, it is essential to develop a rapid, accurate and reliable method to detect H_2O_2. Many techniques were employed in the determination of H_2O_2, such as electrochemical techniques[3,4], spectrophotometry[5], chemiluminescence[6], fluorescence spectrometry[7], chromato-graphy[8] and so on. Among these methods, the electrochemical method was widely used due to its high specificity, sensitivity and wide linearity range, particularly in amperometric biosensors based on peroxidase and hemoglobin. Nevertheless, the inherent instability, limited lifetime and the critical operating situation of emzymes limit the application of enzyme-biosensors. Thus, it is necessary to develop nonenzymatic electrochemical sensors for the determination of H_2O_2. To date, various electrode materials such as metal oxides[14] and conducting polymers[15] have been used for this purpose.

It is reported that metal nanoparticles (NPs), especially precious metals (PtNPs, PdNPs, AgNPs, AuNPs etc.), have large surface areas, special binding sites, and accelerate electron-transfer[16,17] which could decrease the over-potential occurred at unmodified electrodes[18]. Among those metal, PtNPs possessed high catalytic activity and were used to test carbinol[19], formaldehyde[20], glucose[21] and so on. The results found that the catalytic property of PtNPs was closely related to its size, shape and structure[22]. Therefore, the matrix for the preparation of highly dispersed PtNPs is very important.

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* Corresponding author. Email: liuxh@nwnu.edu.cn
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Extensive researches proved that multi-walled carbon nanotubes (MWNTs) can be used as an excellent carrier material because they possess large specific surface area and high conductivity[23]. Moreover, polyethyleneimine (PEI), as a common polyelectrolyte dispersant, not only retained the stability through the polymer chain or its own charge, but also improved the dispersion of MWNTs in aqueous solution after PEI functionalized CNTs[24]. Therefore, the dispersion of MWNTs in aqueous solution was greatly improved after functionalization[25]. Recently, the research to prepare target nanoparticles through seed-mediated growth method aroused widespread attention. This method can not only eliminate distribute unevenly of metallic nanoparticles on MWNTs[26], but also increase the loading amounts of the target nanoparticles.

In this study, the PEI functionalized MWNTs were used as growth scaffold on the glass carbon electrode (GCE). Subsequently, Au nanoparticles were electrodeposited uniformly as seeds. Finally, PtNPs grew on AuNPs to form Pt@Au core-shell structure nanocomposites. A novel H_2O_2 electrochemical sensor was successfully prepared. The sensor exhibited excellent performance toward H_2O_2 with high sensitivity, low detection limit, wide linear range, good selectivity and reproducibility.

2 Experimental

2.1 Apparatus

The surface morphology of Pt@Au/PEI-MWNTs composites was characterized by JSM-6701F scanning electron microscopy (SEM, Japan). Electrochemical measurements were performed on a CHI660C electrochemical workstation (Austin, TX, USA) with conventional three-electrode system. A bare or modified glassy carbon electrode (GCE, d = 3.0 mm) was employed as working electrode. A platinum electrode (10 mm × 1 mm) and a saturated calomel electrode (SCE) were respectively served as the auxiliary and reference electrode. All potentials in this paper were referred to the SCE. Before each electro-chemical measurement, solutions were thoroughly deoxygenated by bubbling nitrogen through the solution for at least 20 min.

2.2 Reagents

The multi-walled carbon nanotubes (MWNTs) (diameter: 20–40 nm, length: 1–2 μm, purity: ≥ 95%) were purchased from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). Hydrogen peroxide solution (30%), $K_3[Fe(CN)_6]$, H_2SO_4 (98%) and HNO_3 (68%) were purchased from Beijing Chemical Reagent (Beijing, China); Na_2SO_4 was bought from Shanghai Chemical Reagent (Shanghai, China). Hexachloroplatinic acid ($H_2PtCl_6·6H_2O$), chloroauric acid ($AuCl_3·HCl·4H_2O$) and polyethyleneimine (PEI : M = 10000) were bought from Aladdin. PBS (pH 7.0) was prepared by mixing suitable amounts of 0.2 M NaH_2PO_4/Na_2HPO_4. Other chemicals were all of analytical grade, and the solutions were prepared by doubly distilled water.

2.3 Functionalization of MWNTs

MWNTs-COOH were prepared by reflux the as-received MWNTs in H_2SO_4 and HNO_3 mixed solution (3:1, V/V) at 120 °C for 4 h. PEI-MWNTs were prepared by ultrasonicating a solution of the MWNTs-COOH (2.0 mg) and polyethyleneimine (PEI, 0.1 g mL^{-1}, 6 mL) in water for 1 h, and then unreacted MWNTs were removed by centrifuging. After that, PEI-MWNTs were dried in air. So, PEI functionalized MWNTs were obtained.

2.4 Preparation of H_2O_2 sensor

The bare GC electrode was polished with 0.3 and 0.05 μm aluminum oxide slurries to remove the physically adsorbed substances. The PEI-MWNTs composite film modified electrode was prepared by casting 6.0 μL of the PEI-MWNTs solution on the surface of GC electrode and drying under room temperature. Then, the PEI-MWNTs modified GC electrode was immersed in the deposition solution (0.5 mM $HAuCl_4$ containing 0.2 M Na_2SO_4) and applied a constant potential at −0.2 V for 100 s to obtain the Au/PEI-MWNTs modified GC electrode. After that, the Au/PEI-MWNTs modified GC electrode was immersed in the deposition solution (0.5 mM H_2PtCl_6 containing 0.2 M Na_2SO_4) and applied the same constant potential for 300 s to obtain the Pt@Au/PEI-MWNTs modified GC electrode[27]. The schematic diagram of preparation of Pt@Au/PEI-MWNTs/GC modified electrode is shown in Fig.1.

3 Results and discussion

3.1 SEM characterization of Pt@Au/PEI- MWNTs/GC electrode

Scanning electron microscopy (SEM) was used to characterize the surface morphologies of the modified electrodes. As shown in Fig.2A, the PEI-MWNTs composites formed a network-like structure. The PEI prevented the aggregation of MWNTs effectively, resulting in a high dispersion and a long-term stability in water. After AuNPs electrodeposited on PEI-MWNTs composites, it is clearly that small-sized AuNPs (white dots in Fig.2B, roughly spherical in shape with an average diameter of about 30 nm) presented at moderately high density, non-ordered distribution along the walls of nanotubes, demonstrating that AuNPs were successfully decorated on the PEI-MWNTs by electrodepositing.