Electrochimica Acta 90 (2013) 35–43

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A novel nonenzymatic hydrogen peroxide sensor based on Ag–MnO_2–MWCNTs nanocomposites

Yang Han, Jianbin Zheng*, Sheying Dong

Institute of Analytical Science, Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, China

ARTICLE INFO

Article history:
Received 19 September 2012
Received in revised form
22 November 2012
Accepted 28 November 2012
Available online 5 December 2012

Keywords:
Nonenzymatic sensor
Multiwall carbon nanotubes
Ag nanoparticles
MnO_2
Hydrogen peroxide

ABSTRACT

A new sandwich structure nanocomposite of Ag nanoparticles supported on MnO_2 modified multiwall carbon nanotubes is synthesized and used for fabricating nonenzymatic H_2O_2 sensor. The morphology and composition of the nanocomposites are characterized by transmission electron microscope, energy-dispersive X-ray spectrum, X-ray diffraction and Fourier transform infrared spectrum. Electrochemical investigation indicates that the nanocomposites possess an excellent performance toward H_2O_2. In deaerated buffer solutions, the sensor could detect H_2O_2 in a linear range of 5.0 μM to 10.4 mM with a correlation coefficient of 0.9993, a sensitivity of 82.5 $\mu A\,mM^{-1}\,cm^{-2}$, a detection limit of 1.7 μM at a signal-to-noise ratio of 3, and a response time of 2 s. Additionally, the sensor exhibits long-term stability, good reproducibility and anti-interference.

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1. Introduction

Accurate determination of hydrogen peroxide (H_2O_2) is extremely important in the field of food industry, pharmaceutical, clinical, industrial and environmental analysis [1–4]. Many techniques have been employed in the determination of H_2O_2, including titrimetry [5], chromatography [6], chemiluminescence [7] and electrochemistry [8]. Among these methods, electrochemistry technique based on enzyme-based biosensors has been developed rapidly due to its low cost and high selectivity [9–12]. However, there are some disadvantages of the enzyme-based biosensors, such as instability, critical operating situation, complicated immobilization procedure and limited lifetime [13]. Therefore, a number of studies have been carried out to improve the nonenzymatic sensors with low detection limit and wide respond range.

Nowadays, with the development of nanotechnology, nanoparticles (NPs) play an important role in improving sensor performance, due to their large specific surface areas and biocompatibilities. The metal nanoparticles, such as Au NPs [14], Pt NPs [15] and Pd NPs [16], were employed to construct H_2O_2 sensor. Silver NPs, as a typical noble metal NPs, have aroused growing interest in recent years, because they not only have common characteristics of noble metal nanoparticles but also have unique properties of biocompatibility, catalysis and low toxicity [17,18]. However, aggregation of nanoparticles prohibits extensive applications, thus highly dispersed metal nanoparticles are very important in fabricating a sensor [19]. Recently, there has been increasing interest in multiwall carbon nanotubes (MWCNTs) as heterogeneous catalyst supports. It is found that MWCNTs have enormous potentials as components of nanoscale electronic devices and sensors, as a result of their properties such as good electrical conductivity, high chemical stability, strong adsorptive ability and high thermal capacity [20,21]. Besides, MWCNTs [22,23] and Ag NPs [24,25] have been employed for detecting H_2O_2 respectively. In order to take full advantage of the two kinds of nanomaterials, Zhao et al. created novel Ag/MWCNTs nanocomposites and disclosed that Ag/MWCNTs nanocomposites could yield high performance toward the detection of H_2O_2, demonstrating the unique properties of each material can be integrated, and the interactions between the two components may bring out novel properties [26]. Thus, Ag/MWCNTs nanohybrids seem to be a promising electrocatalysts in sensor.

However, the activity of Ag/MWCNTs for H_2O_2 reduction needs to be further enhanced. It is reported that Ag NPs combined with some metal oxides (such as Fe_3O_4 [27], SiO_2 [28], CuO [29], ZnO [30], etc.) display a lot of advantages of prompt response, high sensitivity and low detection limit. Among them, manganese dioxide (MnO_2) is considered as one of the candidates on account of its low cost, high energy density, environmental pollution-free and nature abundance [31,32], and it is also well known as catalysts [33,34]. Besides, MnO_2 could be simply one-step synthesized by reduction of $KMnO_4$ and holds good stability on MWCNTs. Recently,

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* Corresponding author. Tel.: +86 29 88303448; fax: +86 29 88303448.
E-mail address: zhengjb@nwu.edu.cn (J. Zheng).

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http://dx.doi.org/10.1016/j.electacta.2012.11.117

there are also reports on MnO_2/MWCNTs nanocomposites for electrochemical sensor applications [35,36]. Previous approaches to the synthesis of MnO_2/carbon composite include various methods, such as physical mixing [37], electrodeposition [38], sonochemical synthesis [35] and redox reaction [39,40]. In this work, we modify MnO_2 on MWCNTs by employing redox reaction to one-step synthesize MnO_2. Herein, the interaction between MnO_2 and MWCNTs is not simple deposition but covalent attachment [39]. Greater chemical contact and increased contact area between MnO_2 and MWCNTs can improve the electric conductivity of the electrode due to the high electric conductivity of MWCNTs [41].

The aims of the present work are to synthesize Ag–MnO_2–MWCNTs nanocomposites by employing redox reaction and ultrasonic agitation, and to fabricate a novel nonenzymatic sensor of H_2O_2 based on the material by simple cast method, and then to investigate sensor's properties and mechanism.

2. Experimental

2.1. Materials

High purity multiwall carbon nanotubes (MWCNTs, >95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd., of the Chinese Academy of Science. Chitosan (CS, MW $5–6 \times 10^5$, >90% deacetylation) was purchased from Shanghai Yuanju Biotechnology Co., Ltd (Shanghai, China) and was used as fixative. Hydrogen peroxide (30%, v/v aqueous solution) was got from Tianjin Tianli Chemistry Reagent Co., Ltd (Tianjin, China). 0.1 M phosphate buffered saline (PBS, pH 7.2) was used as the supporting electrolyte. All other reagents and chemicals were of analytical reagent grade and doubly distilled water was used in experiments.

2.2. Apparatus and electrochemical measurements

The transmission electron microscope (TEM) image was carried out by Tecnai G^2 F20 S-TWIN (FEI, USA). Surface elemental compositions of the synthesized samples were characterized by an energy-dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) patterns of the samples were observed by D/MAX-3C (Rigaku, Japan). Fourier transform infrared spectrum (FTIR) was recorded with TENSIR 27 (Bruker, German). Electrochemical measurements were carried out in a conventional three-electrode electroanalysis system controlled by EC 550 electrochemical workstation (Gaoss Union Technology Co., Ltd., Wuhan, China) and CHI 660 electrochemical workstation (Shanghai CH Instrument Co., Ltd., China). Glassy carbon electrodes (3 mm in diameter) were used as a working electrode, saturated calomel electrode (SCE) and platinum wire was used as the reference electrode and counter electrode, respectively. All electrochemical experiments were conducted at room temperature (25 ± 2 °C).

2.3. Preparation of the sensor

2.3.1. Functionalization of MWCNTs

Pristine MWCNTs were dissolved in the mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v ratio), and then dispersed in ultrasonic bath for about 4 h. The resulting MWCNTs were separated and washed with doubly distilled water by centrifugation to neutral pH, then washed with acetone and dried in air.

2.3.2. Synthesis of MnO_2–MWCNTs

In a typical procedure, MWCNTs (20 mg) were mixed with $KMnO_4$ (43.6 mg). The mixture was then suspended in 24 mL doubly distilled water and sonicated for 30 min, after which, ethylene glycol was added into the suspension slowly, then sustained magnetic stirred at 50 °C for about 30 min until the color of the $KMnO_4$ was faded, suggesting that MnO_2 were completely deposited on MWCNTs. Finally, the composite products were obtained through centrifuging, water washing, ultrafiltration and drying 10 h at 70 °C.

2.3.3. Synthesis of Ag–MnO_2–MWCNTs

MnO_2–MWCNTs powder (10 mg) was dispersed in 50 mL ethanol–water (1:1, v/v ratio) solution, ultrasonically mixed with 1.9 mL of 0.1 mM $AgNO_3$ solution, and subsequently added excess $NaBH_4$ solution in a dropwise manner under stirring condition. The reductive reaction was performed under room temperature for 2 h with continuous magnetic stirring, after which, the composite products were separated from the solution in a centrifuge, ultrafiltration and thoroughly washed with doubly distilled water. The obtained black powder was dried in a vacuum oven at 70 °C for 12 h. For comparison, Ag–MWCNTs and MnO_2–MWCNTs were prepared by the same process.

2.3.4. Electrode modification

The glass carbon electrode (GCE) was prepared by a simple casting method. Prior to use, the GCE was polished with 1.0 and 0.3 μm alumina powder to obtain mirror like surface, respectively, and rinsed with doubly distilled water, followed by sonication in ethanol solution and doubly distilled water successively. Then, the GCE was allowed to dry in a stream of nitrogen. The composites (5 mg) were dispersed into chitosan (5 mL, 0.5%) and sonicated for 10 min; suspension (5 μL) was cast onto the GCE and then dried in air at room temperature.

3. Results and discussion

3.1. Characterization of Ag–MnO_2–MWCNTs nanocomposites

The morphologies and structures of the MnO_2–MWCNTs and Ag–MnO_2–MWCNTs were characterized by TEM as shown in Fig. 1. As seen from Fig. 1A, a thin and relative uniform layer of MnO_2 was grown in the form of nano-rods on MWCNTs. MnO_2–MWCNTs were twisted and intersectant with rough surfaces. Their length ranges were from several to tens of micrometers and the external diameter was about 40–60 nm (Fig. 1B), indicating that the MWCNTs acted as a substrate for the heterogeneous precipitation of a very thin layer of MnO_2. Moreover, the adsorption of MnO_2 onto MWCNTs was found to be very stable, the synthetic MnO_2–MWNTs even could be subjected to sonication in ethanol for 30 min without observable loss of MnO_2 from MWCNTs. Fig. 1C shows that the fine and spherical Ag NPs were deposited on the MnO_2 surfaces, and no Ag NPs aggregation was observed, probably because of the large number of nucleation centers available on the surface of the MnO_2–MWCNTs. The external diameter of Ag–MnO_2–MWCNTs increased to approximately 50–70 nm (Fig. 1D). Furthermore, the EDS patterns revealed that the nanocomposites were composed of C, O, Mn and Ag elements (Fig. 1E and F), suggesting that MnO_2–MWCNTs and Ag–MnO_2–MWCNTs nanocomposites had been synthesized successfully.

Fig. 2A shows the XRD patterns of MWCNTs, MnO_2–MWCNTs and Ag–MnO_2–MWCNTs, as well as the XRD peaks of graphite (JCPDS 41-1487), birnessite-type MnO_2 (JCPDS 42-1317) and cubic phase of Ag (JCPDS 04-0783). As seen from Fig. 2A(a), due to their intrinsic nature, the main features of XRD pattern of MWCNTs were close to those of graphite. Fig. 2A(b) shows the XRD pattern of MnO_2–MWCNTs, in addition to those of the MWCNTs, there were four broad peaks at 2θ around 12°, 25°, 37° and 66°, indexing (0 0 1), (0 0 2), (1 1 0) and (3 1 2) planes, respectively. These peaks can be indexed to birnessite-type MnO_2 including an amorphous phase [42]. Hence, the MnO_2 on MWCNTs should be attributed to the potassium manganese oxide hydrate (birnessite $\delta\text{-}MnO_2 \cdot nH_2O$) with 2D layered structure, which incorporated K^+ ions and H_2O

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