Facile fabrication of Pt-Ag bimetallic nanoparticles decorated reduced graphene oxide for highly sensitive non-enzymatic hydrogen peroxide sensing

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ABSTRACT

A new electrocatalyst, Pt-Ag bimetallic nanoparticles decorated reduced graphene oxide nanocomposite, was successfully synthesized by a facile, eco-friendly and controllable route. The morphological characterization of RGO/Pt-Ag NPs nanocomposite was examined by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) analyzer, X-ray diffraction (XRD) spectrum, and Fourier transform infrared spectrum (FT-IR), respectively. And then, the RGO/Pt-Ag NPs nanocomposite was immobilized on the surface of glassy carbon (GC) electrode to fabricate a novel and highly sensitive non-enzymatic hydrogen peroxide sensor. The electrochemical behaviors of the prepared sensor were investigated by cyclic voltammetry and chronoamperometry. The sensor showed excellent performance toward H_2O_2 with sensitivity as high as 699.6 μA mM^{-1} cm^{-2} and 402.7 μA mM^{-1} cm^{-2}, wide linear range of 0.005–1.5 mM and 1.5–7 mM, and low detection limit of 0.04 μM (S/N=3). Moreover, the prepared hydrogen peroxide sensor was applied to in real samples with satisfactory results. These excellent results indicate that the prepared RGO/Pt-Ag NPs nanocomposite has broad application prospect in the field of sensors.

1. Introduction

Hydrogen peroxide (H_2O_2) is a very important intermediate that plays an important role in environmental monitoring, industrial research, food analysis and medically clinical diagnosis [1–4]. So it is vital significance that H_2O_2 level could be exactly and rapidly detected. Up to now, numerous detection techniques such as high-performance liquid chromatography [5], fluorescence [6], spectrophotometry [7], chemiluminescence [8], and electrochemistry [9–11] have been developed for monitoring H_2O_2. Among these methods, electroanalytical method has been widely used for accurate determination of H_2O_2 owing to its simplicity, low cost, high sensitivity, low detection limit and the possibility for real-time detection. The electrochemical biosensors based on the electrocatalysis of enzyme-modified are frequently used to detect H_2O_2 with satisfactory sensitivity [12,13]. Nevertheless, the enzyme-modified sensors have some inevitable drawbacks such as the complex fabrication procedure, limited lifetime, stability problem and high-cost of the enzymes. So recent many efforts have been devoted to the direct determination of H_2O_2 at the non-enzymatic electrodes. However, the direct electrochemical reduction of H_2O_2 with the conventional electrodes is not effective for analytical application due to slow electrode kinetics [14]. Therefore, it is still highly desirable to develop a high sensitivity and good catalyst for non-enzymatic H_2O_2 detection.

One of the main strategies to improve the non-enzymatic sensor performances is to develop the modified electrode materials with large specific surface area, excellent conductivity, high electrocatalytic activities, etc. Recently, Platinum nanoparticles (Pt NPs) have been attached much attention for their large specific surface area, excellent conductivity and high electrocatalytic activities to H_2O_2. Besides, Pt NPs are also shown to validly lessen the oxidation/reduction overvoltage in H_2O_2 determination, which is important to avoid interference from other co-existing substances [15]. Consequently, there has been growing interests in using Pt nanomaterials to prepare H_2O_2 sensors [16–18]. However, pure Pt catalyst is rather expensive and can be easily poisoned by adsorbed intermediates.

Up to date, it has been proved that alloying Pt with less expensive elements such as Au, Fe, Pd and other transition metals is an effective route to increase the electrocatalytic activity and enhance the long-term catalytic stability [19–22]. Generally, bimetallic nanocatalysts provide not only the access to additional handles for the structures, but also exhibit novel catalytic

properties different from the constituent metals due to the strong electronic coupling [23–25]. The main aimed of our work is to improve electrocatalytic activity to H_2O_2 by investigating more active and lower cost replacements to pure Pt. Silver nanoparticles (Ag NPs), as a typical nobel metal nanoparticles, have aroused growing interest in recent years, because they not only have common characteristics of nobel metal nanoparticles but also have unique properties of biocompatibility, catalysis and low toxicity [26,27]. In this work, we tried to fabricate Pt and Ag bimetallic nanoparticles. Due to the unique catalytic activity and chemical selectivity of the bimetallic nanoparticles, Pt-Ag bimetallic nanoparticles which could play the dual roles of catalyzing redox reactions and also assisting direct electron transfer from the substrate to the electrode surface.

Unfortunately, although the bimetallic nanoparticles have superior performance, the bimetallic nanoparticles with diameters in nanometers may aggregate, which prohibits extensive applications of bimetallic nanoparticles, thus highly dispersed bimetallic nanoparticles is very important in fabricating a highly sensitive sensor. In this respect, hybridizing active components with carbonaceous materials has been proved to be an effective approach to solve this problem [10]. Graphene, a new carbon material composed of single layer of carbon atoms in a closely packed honeycomb two-dimensional lattice, has received much attention in recent years as suitable materials for electrode modification due to its unique characteristics, such as large specific surface area, high electrical conductivity, good biocompatibility and chemical stability, which have made it a promising material for electrochemical sensors [28–31]. So we choose RGO as heterogeneous catalyst supports combined with Pt-Ag bimetallic nanoparticles to fabricate highly sensitive sensors.

In the present study, we had tried to design a facile, eco-friendly and controllable route to prepare RGO/Pt-Ag NPs nanocomposite. And a novel and highly sensitive electrochemical sensor for direct analytical detection of H_2O_2 was successfully fabricated. It was found that the prepared H_2O_2 sensor exhibited excellent electrocatalytic activity to H_2O_2 with high sensitivity, low detection limit and wide linear range. With simple synthetic method, using of low cost materials, and excellent electrocatalytic activity, there is no doubt that RGO/Pt-Ag NPs nanocomposite has broad prospect in fabricating high performance sensors.

2. Experimental

2.1. Reagents and materials

Graphene oxide (GO) was obtained from Nanjing XFNANO Materials Tech Co. Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Sigma Aldrich Co. Silver nitrate ($AgNO_3$) and ethylene glycol (EG > 99%) were purchased from Tianjin Chemical Factory (China). Na_2HPO_4 and NaH_2PO_4 were purchased from Tianjin Damao Chemical Reagent Co.(China). Freshly Prepared 0.1 M phosphate buffer solution, consisting of Na_2HPO_4 and NaH_2PO_4 was used as the supporting electrolyte. All aqueous solutions were prepared with doubly distilled water.

2.2. Apparatus

Transmission electron microscopy (TEM) image analysis was performed on Tecnai G^2 F 20 instrument (Philips Holland). The EDX analysis was carried out on an energy-dispersive X-ray spectroscopy (EDX) analyzer which was equipped on the Tecnai G^2 F 20 instrument. The X-ray diffraction (XRD) analysis was performed with a Rigaku D/max-rA with Cu Kα radiation ($\lambda = 1.5418$ Å) (Rigaku, Japan). Fourier transform infrared spectrum

(FT-IR) was recorded with TENSOR 37 (Bruker, German).

Electrochemical experiments were carried out on a 283 Potentiostat-Galvanostat electrochemical workstation (EG&G PARC with M 270 software) with a conventional three-electrode system, including the modified GC electrode as the working electrode, a platinum wire (1 mm diameter) as the counter electrode and an Ag/AgCl electrode (saturated with KCl) as the reference electrode.

2.3. Preparation of RGO/Pt-Ag NPs

In this study, 20 mg of GO was added into 20 mL of doubly distilled water with sonication for 2 h form a stable dispersion. 60 mg of $H_2PtCl_6 \cdot 6H_2O$, and 20 mg of $AgNO_3$ were dissolved into 20 mL of doubly distilled water, and then the mixture was added into the suspension solution of GO and ultrasonically treated for 1 h. Subsequently, 40 mL of ethylene glycol (EG) solution (EG > 99%) was added drop by drop under magnetic stirring. After that, the mixture was transferred to a 100 mL Teflon lined autoclave and kept at 210 °C for 20 h. Finally, the product was obtained through centrifugation and washed with doubly distilled water and ethyl alcohol. Then the product was dried in vacuum oven at 80 °C. RGO, RGO/Pt NPs and RGO/Ag NPs were prepared with the similar method, respectively (The details were presented in Supplementary material).

2.4. Preparation of modified electrodes

Prior to modification, the GC electrode was polished with 0.3 and 0.05 μm α-alumina powder sequentially, and then ultrasonically cleaned in doubly distilled water and ethanol for 5 min, respectively. To prepare 1 mg/mL RGO/Pt-Ag NPs suspension, 10 mg RGO/Pt-Ag NPs was first dispersed in 10 mL water, then 1 mL Nafion alcohol solution (5 wt%) was added with sonication for 2 h. After that, 6 μL of RGO/Pt-Ag NPs suspension solution was immobilized on the surface of the GC electrode and dried naturally. The modified GC electrode was directly used as a non-enzymatic H_2O_2 sensor for the determination of H_2O_2.

3. Results and discussion

3.1. Characterization of RGO/Pt-Ag NPs

The morphologies of the RGO and RGO/Pt-Ag NPs were characterized by TEM. A typical wrinkled reduced graphene oxide sheet was shown in Fig. 1A. As shown in Fig. 1B, it can be seen that the RGO sheet was well decorated by the uniform Pt-Ag bimetallic nanoparticles with very few aggregation, indicating that during the process of loading Pt-Ag bimetallic nanoparticles, RGO made a significant contribution to promoting the homogenous dispersion of Pt-Ag bimetallic nanoparticles and avoiding formation of aggregation. Highly dispersed Pt-Ag bimetallic NPs on RGO supports with larger surface areas has many advantages in catalytic activity and sensor sensitivity [32]. The size of Pt-Ag bimetallic nanoparticles was about 5 nm (Fig. 1C). Furthermore, as shown in Fig. 1D, the EDX analysis revealed that the nanocomposite was consisted of C, O, Pt and Ag elements, and the Cu element in the spectrum should be from the substrate. This result indicating that RGO/Pt-Ag NPs nanocomposite had been synthesized successfully. Additionally, It has an elemental composition of 50.8% Pt and 49.2% Ag, which is consistent with the Pt: Ag ratio in the precursor (with platinum to silver mole ratio of 1:1).

Fig. 2A shows the XRD patterns of the GO (a), RGO (b), RGO/Pt-Ag NPs (c), and Pt-Ag NPs (d). A strong and sharp diffraction peak at 11.9° is assigned to the (001) plane of GO (curve a) [33]. As seen from Fig. 2A (b), the peak at 23.99° (002) is the typical diffraction