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One-pot synthesis of highly dispersed PtAu nanoparticles–CTAB–graphene nanocomposites for nonenzyme hydrogen peroxide sensor

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ABSTRACT

A simple and efficient approach was developed to fabricate an amperometric sensor for hydrogen peroxide (H_2O_2) determination based on one-pot synthesis of highly dispersed PtAu nanoparticles–CTAB–graphene nanocomposites. In this study, graphene oxide was first functionalized with a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB); then PtAu nanoparticles (NPs) were deposited on graphene (GR) via a simple chemical co-reduction method. A large amounts of highly dispersed bimetallic PtAu nanoparticles could be well loaded on the surface of the graphene, as revealed by transmission electron microscopy (TEM). In addition, PtAuNPs–CTAB–GR nanocomposites were also characterized by electrochemical methods including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The experimental results demonstrated that constructed sensor exhibited good catalytic activity toward H_2O_2, and obtained a wide linear range from 5.0×10^{-9} to 4.8×10^{-6} mol/L with a limit of detection (LOD) of 1.7×10^{-9} mol/L (S/N = 3). Moreover, it could also be applied to real samples analysis. The excellent performance of this H_2O_2 sensor could be ascribed to graphene being used as effective load matrix for the deposition of PtAuNPs and synergistic effect of bimetallic PtAuNPs and graphene nanomaterials.

1. Introduction

An accurate and reliable method for the determination of hydrogen peroxide (H_2O_2) is increasing significance to many fields but particularly in electrochemical sensor because H_2O_2 is not only a reactive oxygen species (ROS), but also a by-product of several oxidative metabolic path-ways [1]. Meanwhile, in living organisms, H_2O_2 plays an important role as a signaling molecule in regulating diverse biological processes [2–4]. Up to now, various methods including titrimetry [5], spectrophotometry [6], and chemiluminescence [7]) have been employed to detect H_2O_2. Among these, electrochemical technique has attracted considerable interest due to its inherent advantages of simplicity, high sensitivity, fast response and low-cost [8]. Recently, numerous enzymes modified electrodes were frequently used for detecting relatively low concentrations of H_2O_2 [9–12]. Nevertheless, the relatively of high cost, limited lifetime and the critical operating situation limit enzyme-biosensor applicability. Thus, developing nonenzymatic H_2O_2 sensor with low cost, high sensitivity and good selectivity is of greatly practical importance [13–16].

As well known, Platinum (Pt) nanoparticles (NPs) are excellent substitutes for enzymes to catalyze H_2O_2 in electrochemical sensors because they can decrease its over-potential that occurred at unmodified electrodes [8]. In recent years, Pt-based bimetallic nanocatalysts have been attracted widespread interests, which aim to improve the catalytic activity as well as reduce the cost of catalysts. The study found that the stability of Pt catalyst can be significantly improved after the incorporation of Au [17]. Unfortunately, the probability of nanoparticles aggregation increases owning to high surface energy of particles with diameters in nanometers, decreasing the catalytic activity of the nanoparticles [18]. Therefore, the matrix for the preparation of highly dispersed PtAuNPs is very important.

Graphene nanosheet, a monolayer of carbon atoms closely packed into honeycomb two-dimensional carbon material, has aroused growing interest in many science communities owing to its unique properties such as exceptional thermal and mechanical properties, large surface-to volume ratio and high electrical conductivity [19]. Nevertheless, it is noted that graphene sheets also tend to form irreversible agglomerates through strong stacking and Van der Waals interaction. Thus, both large specific surface

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area and outstanding single-layer electric property of graphene are sacrificed [20], which limit their applications further seriously. Recently, this aggregation could be overcome by covalent and non-covalent functionalized approaches [21,22]. One of these useful methods is the surfactants assist the carbon materials dispersing well in aqueous media, because their charged groups (hydrophilic heads) attract to water and their alkyl chains (hydrophobic tails) adsorb on the surfaces of carbon materials [23]. Thus, despite being a very hydrophobic molecule, graphene is also dispersed well in water using surfactants, such as cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl benzyl sulfate (SDBS) or sodium dodecyl sulfate (SDS) [24]. In addition, researches found that the extent of nanoparticles agglomeration can be effectively reduced by lowering the surface energy by adsorption of stabilizers such as surfactants. Meanwhile, the surfactants-intercalated graphene is a superior substrate for the uniform deposition of metal nanoparticles because it possesses a large surface area, well-dispersion and good electrical conductivity [25]. These unique properties render it a promising candidate for electrochemical sensor application.

Herein, highly dispersed bimetallic PtAuNPs were successfully anchored on CTAB-intercalated graphene by a simple one-pot synthesis method. A nonenzymatic H_2O_2 sensor was fabricated based on PtAuNPs–CTAB–graphene nanocomposites modified glassy carbon electrode (GCE). By combining the advantages of highly dispersed PtAuNPs and graphene, the fabricated sensor exhibits excellent performance toward H_2O_2 with low detection limit, wide linear range, excellent selectivity and reproducibility. Meanwhile, the sensor can be applied to real samples analysis.

2. Experimental section

2.1. Apparatus

Transmission Electron Microscope (TEM) image was taken with a JEM-3010 transmission electron microscope (JEOL Co. Ltd., Japan). FT-IR spectra of KBr powder-pressed pellets were recorded on a Fourier Transform-Infrared (FT-IR) spectrophotometer (USA). 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 and a saturated calomel electrode (SCE) were served as the auxiliary and reference electrode. All potentials given in this paper were referred to the SCE. Electrochemical impedance spectroscopy (EIS) experiments were performed on Multi-potentiostat (VMP2, Princeton Applied Research, USA). Before each electrochemical measurement, solutions were thoroughly deoxygenated by bubbling nitrogen through the solution for at least 20 min to remove dissolved oxygen.

2.2. Reagents

Graphite (99.99% SP-1, Bay carbon) with average particle size of 45 μm was obtained from Shanghai Chemical Reagent (Shanghai, China). Hydrogen peroxide solution (30 wt%) was purchased from Beijing Chemical Reagent (Beijing, China), hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) and chloroauric acid ($HAuCl_4{\cdot}3H_2O$) were purchased from Aladdin. Cetyl trimethyl ammonium bromide (CTAB, $C_{16}H_{33}(CH_3)_3NBr$), $NaNO_3$, $KMnO_4$, H_2SO_4 (98%), $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KCl, NaH_2PO_4 and Na_2HPO_4 were bought from Tianjin Chemical Reagent (Tianjin, China). PBS (pH 7.0) was prepared by mixing suitable amounts of 0.2 M NaH_2PO_4/Na_2HPO_4. All chemicals were all of analytical grade, and the solutions were prepared by doubly distilled water.

2.3. Preparation of graphene oxide (GO)

GO was prepared by oxidizing natural graphite powder based on a modified Hummers method [26]. In this method, graphite powder (2 g) was stirred in 46 mL of concentrated H_2SO_4 for 2 h. $NaNO_3$ (1 g) and $KMnO_4$ (6 g) were gradually added to the above solution while keeping the temperature less than 20 °C. The resulting solution was diluted by adding 92 mL of water under vigorous stirring and a dark brown color suspension was obtained. After 15 min, the above mixture was diluted by adding 280 mL of warm water. Following this, 30% H_2O_2 was added until the solution turned bright yellow. The mixture was washed by repeated centrifugation and filtration using 5% HCl aqueous solution in order to remove the residual metal ions. Further, the centrifugation process was repeated with distilled water until the pH of the solution becomes neutral. Finally, the suspension was filtered and the filter cake was redispersed in water to yield a yellow–brown dispersion by ultrasonication. The graphene oxide was obtained by filtration and was allowed to dry under vacuum.

2.4. Preparation of PtAuNPs–CTAB–GR

The PtAuNPs–CTAB–GR nanocomposites were carried out by a facile and versatile hydrothermal synthetic strategy. The details were as follows: as-prepared graphene oxide (0.1 g) was dispersed into 50 mL water under ultrasonic for 1 h, and CTAB (0.25 g) was dissolved into 25 mL water. Next, CTAB solution was added into graphene oxide aqueous dispersion with ultrasonication for 4 h to achieve a well-dispersed suspension, obtaining the CTAB–GO. After that, the CTAB–GO was mixed with $H_2PtCl_6{\cdot}6H_2O$ (3.25 mL, 19.3 mM) and $HAuCl_4{\cdot}3H_2O$ (2.58 mL, 24.28 mM) under ultrasonication for 25 min in N_2 atmosphere. After continuous stirring for 30 min, the pH of the solution was adjusted to 11 with NaOH solution (1.0 M). Following this, 75 mL of $NaBH_4$ (40 mM) solution was added into the above mixture at a stirring rate of 600 rpm for 12 h at 70 °C. The solution was filtered by nylon membrane with 0.22 μm pores, thoroughly washed with water to remove the free materials in the solution, followed by drying in a vacuum overnight at 60 °C for 24 h. So, PtAuNPs–CTAB–GR nanocomposites were obtained. The AuNPs–CTAB–GR, PtNPs–CTAB–GR and PtAuNPs–GR used in the comparable experiments were prepared by similarly procedure.

2.5. Preparation of the H_2O_2 sensor

A glassy carbon electrode (GCE) was polished with 1.0, 0.3 and 0.05 μm alumina slurry to a mirror-like, respectively, followed by rinsing thoroughly with doubly distilled water. Then 10 μL of PtAuNPs–CTAB–GR aqueous solution (0.2 mg/mL) was dropped on the surface of a GCE and dried in air, and then the PtAuNPs–CTAB–GR/GCE was obtained. The CTAB–GO/GCE, AuNPs–CTAB–GR/GCE, PtNPs–CTAB–GR/GCE, PtAuNPs–GR/GCE used in the comparable experiments were prepared by dropping 10 μL of CTAB–GO, AuNPs–CTAB–GR, PtNPs–CTAB–GR and PtAuNPs–GR dispersion of the same concentration onto the GCE, respectively.

3. Results and discussion

3.1. Morphological characterization of PtAuNPs–CTAB–GR nanocomposites

Transmission Electron Microscope (TEM) and Energy Dispersive X-ray Spectroscopy (EDX) were used to observe the morphological characteristics, intrinsic crystal structures and to assay their