Journal of Electroanalytical Chemistry 727 (2014) 27–33

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Nonenzymatic amperometric determination of hydrogen peroxide by graphene and gold nanorods nanocomposite modified electrode

Pengfei Pang, Zhongming Yang, Shixiu Xiao, Jinling Xie, Yanli Zhang *, Yuntao Gao

Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission & Ministry of Education, Yunnan University of Nationalities, Kunming 650031, PR China
State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China
Department of Chemistry, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:
Received 24 March 2014
Received in revised form 22 May 2014
Accepted 23 May 2014
Available online 2 June 2014

Keywords:
Graphene
Gold nanorods
Nonenzymatic
Hydrogen peroxide

ABSTRACT

Graphene-based electrochemical sensors have recently received much attention due to their outstanding sensing capability and economic viability. In this study, a novel non-enzymatic hydrogen peroxide (H_2O_2) sensor was developed using graphene and gold nanorods (GR-AuNRs) composite modified glassy carbon electrode (GCE). AuNRs were synthesized by seed-mediated growth method, and characterized by ultraviolet–visible spectroscopy (UV–vis) and transmission electron microscope (TEM). The GR-AuNRs composite material is endowed with a large electrochemical surface area and fast electron transfer properties in redox species. A GR-AuNRs composite modified electrode exhibits good performance in terms of the electrocatalytic reduction of H_2O_2; a sensor constructed from such an electrode shows a good linear dependence on H_2O_2 concentration in the range of 30 μM to 5 mM with a sensitivity of 389.2 μA mM^{-1} cm^{-2}. The detection limit is estimated to be 10 μM. Furthermore, the GR-AuNRs modified electrode exhibits freedom of interference from other co-existing electroactive species. This study provides a new kind of nanocomposite modified electrode for electrochemical sensors.

1. Introduction

Hydrogen peroxide (H_2O_2) is a reactive oxygen species and a byproduct of several oxidative metabolic pathways. H_2O_2 has also been recognized as an important regulator of eukaryotic signal transduction, generated in response to various stimuli including cytokines and growth factors [1]. The relationship between H_2O_2 concentration and human health has attracted a great deal of attention, and the determination of H_2O_2 is of practical importance in biochemical, pharmaceutical, clinical, environmental, and industrial research. For this reason, there has been increasing interest in the design of reliable H_2O_2 sensors.

Due to intrinsic simplicity, high sensitivity and selectivity, electrochemical methods have been extensively employed in H_2O_2 sensor designs [2]. A number of sensors have been fabricated based on enzyme and non-enzyme working electrodes, but some of their sensitivity and performance have been hindered by low conductivity, lack of charge carriers, and low active electrode surface area. A useful strategy to overcome these limitations is to incorporate conductive materials. Nanostructured materials are excellent carriers due to their unique chemical and physical properties.

Graphene is a single-atom-thick sheet of sp^2 hybridized carbon atoms that are packed in a hexagonal honeycomb crystalline structure [3–6]. Graphene has attracted increasing interests from the fundamental standpoint as well as for practical applications due to its outstanding electronic, electrochemical, and thermal properties. The unique properties of graphene, such as high surface area-to-volume ratio, fast electron transferring rate and good biocompatibility, suggest that it has the ability to be incorporated in a wide array of applications, including building composites, electronics, and medical therapeutics [7–9]. The good conductivity and macroscopic tunnel effect can make graphene become effective electronic interface between the immobilized enzyme and electrode, can improve the sensitivity of the sensor and the current response and shorten the response time. One of the most promising applications of graphene that has emerged so far is its utilization as a new way of designing novel electrochemical sensors and biosensors [10–13]. As a result, graphene modified electrodes were successfully applied to study and determine some biological and organic molecules, including enzyme [14,15], DNA [16,17], small biomolecules [10,18,19], heavy metal ions [20–22], gas [23–25] etc.

---

* Corresponding author at: Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission & Ministry of Education, Yunnan University of Nationalities, Kunming 650031, PR China. Tel./fax: +86 871 65910017.
E-mail address: yanli.zhang@yahoo.com (Y. Zhang).

http://dx.doi.org/10.1016/j.jelechem.2014.05.028
1572-6657/

Numerous nanomaterials including gold nanoparticles have been widely used for developing of electrochemical sensing platforms [26–29]. Gold nanorods (AuNRs) have versatile applications ranging from biological and chemical sensors to therapeutics, due to their anisotropic shape, unique optical properties and simple surface functionalization [30,31]. AuNRs based platforms can provide more stable biosensing systems due to their rods-like shapes compared to nanoparticles. Thus, gold nanorods and graphene were used to fabricate sensing platforms which were performed under the scope of different techniques such as surface plasmon resonance [32,33], surface enhanced Raman scattering [34], and electrochemical sensor [35,36].

Graphene, whose structure consists of a single layer of sp^2-hybridized carbon atoms, provides an excellent platform for designing composite nanomaterials [37,38]. In this work, a novel non-enzymatic amperometric H_2O_2 sensor was proposed based on GR-AuNRs composite modified glassy carbon electrode (GCE). The AuNRs were prepared using the seed-mediated growth method. The synthesized AuNRs with aspect ratio of 3 were mixed with GR to form a homogeneous solution, which was casting on the surface of electrode to form a GR-AuNRs/GCE. The resulting non-enzymatic sensor exhibits excellent electrocatalytic response to H_2O_2, along with a wide linear range and long-term stability.

2. Materials and methods

2.1. Reagents and apparatus

Graphite powder, chloroauric acid ($HAuCl_4{\cdot}4H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrazine solution was obtained from Fuchen Chemical Reagent Factory (Tianjin China). Cetyltrimethylammonium bromide (CTAB) was purchased from Damao Chemical Reagent Factory (Tianjin, China). All other reagents were of analytical grade and were used as received. Phosphate buffer solution (PBS 0.1 M) with different pH values was used as supporting electrolytes. Double distilled water was used through all experiments.

Cyclic voltammetry (CV) measurements were carried out on a CHI630E electrochemical workstation (CHI Instrument Company, Shanghai, China). A standard three electrode cell was used for all electrochemical experiments with bare and modified GCE ($d = 3$ mm) as working electrode, a platinum (Pt) wire as an auxiliary electrode and an Ag/AgCl as a reference electrode, respectively. Prior to the electrochemical measurements, the solution is purged with N_2 gas for 5 min. All experiments were performed at room temperature.

UV–vis spectra were obtained on Agilent 8453 spectrophotometer. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100 Electron Microscope at an acceleration voltage of 200 kV.

2.2. Synthesis of graphene

Graphene was synthesized from purified natural graphite by the modified Hummers method [39–41]. In a typical synthesis, 2.5 g graphite was slowly added into a stirred concentrated H_2SO_4 (60.0 mL) cooling in an ice-water bath. The mixture of 1.25 g KNO_3 and 7.5 g $KMnO_4$ were added slowly to the suspension more than 30 min under 5 °C and maintained for 2 h. Then the ice bath was removed and the suspension was maintained at 35 °C for 1 h until the suspension become pasty and grey in color. After this, 120 mL H_2O were slowly added into the mixture and the temperature increased 95 °C and maintained for 30 min. The suspension was then diluted with 350 mL warm water and treated with 100 mL 6% H_2O_2 to reduce the residual permanganate and manganese dioxide. The suspension was filtered and washed with 1 M HCl to the filter cake without SO_4^{2-}. The filter cake was dried in the vacuum at 50 °C over night.

After these procedures, the prepared graphite oxide (GO) was reduced to graphene according to the reported method [40,41]. The GO (150 mg) was dispersed in 100 mL H_2O_2 at flask for ultrasonication to a homogeneous dispersion. Hydrazine solution (3 mL) was added in the flask and the solution turn black. The suspension was slowly heated to 95 °C to reflux 24 h and filtered. The filter cake was washed with 5×100 mL deionized water and 5×100 mL methanol and dried to storage.

2.3. Synthesis of AuNRs

The AuNRs were prepared using the seed-mediated growth method as reported previously [42,43]. Briefly, the seed solution was prepared by mixing CTAB (0.1 M, 5 mL) and $HAuCl_4$ (0.5 mM, 5 mL) with freshly prepared ice-cold $NaBH_4$ (10 mM, 0.6 mL), which resulted in the formation of a brownish yellow solution. Vigorous stirring was continued for 2 min, and then, the seed solution was kept at room temperature (25 °C) and used at least 2 h after preparation.

To synthesize the AuNRs, 5 mL of 0.5 mM $HAuCl_4$ and 20 μL of 0.035 M $AgNO_3$ were added to 5 mL of 0.1 M CTAB, followed by addition of 0.1 mL of 1 M HNO_3 and 0.1 mL of 0.1 M ascorbic acid. Ascorbic acid served as a mild reducing agent and changed the solution from dark yellow to colorless. Afterward, 10 μL of the seed solution was added and the color of the solution changed gradually in the first 15 min until finally stabilized over night. The as-prepared AuNRs solution was centrifuged (12,000 rpm for 10 min) and then washed with distilled water once and re-dispersed in water solution. Our experiments yielded AuNRs with aspect ratio 3.

2.4. Preparation of GR-AuNRs modified GCE

Prior to the electrode modification, the GC electrodes were polished with 1 μm and 0.05 μm alumina slurries, and then ultrasonically cleaned by water, ethanol and water for 2 min, respectively. The electrode was allowed to dry in a stream of nitrogen. The modified electrodes were prepared by a simple casting method. Typically, 8 μL of the GR-AuNRs composite suspension (1 mg mL^{-1}, H_2O) was dropped onto the GC electrode and then dried under an infrared heat lamp. The prepared enzyme-free modified electrode is denoted as GR-AuNRs/GCE throughout this paper. For comparative studies we have taken bare GCE and two other electrodes modified in similar fashion which were denoted as: AuNRs/GCE and GR/GCE.

2.5. Electrochemical measurements

Electrochemical measurements were performed with a CHI630E electrochemical system. A standard three electrode cell was used for electrochemical measurements with bare and modified GCE as working electrode, an Ag/AgCl as a reference electrode, a platinum wire as a counter electrode, respectively. Cyclic voltammetric (CV) was recorded from 0 to −1 V at a scan rate of 0.1 V s^{-1} in PBS solution (0.1 M, pH = 9.0). The standard solution or sample solution of H_2O_2 were added into PBS (pH = 9.0). PBS deaerated with high-purity nitrogen is used as supporting electrolyte during the electrochemical experiments towards H_2O_2 reduction.

3. Results and discussion

3.1. Characterization of AuNRs and GR-AuNRs

It is well known that gold nanoparticles exhibit absorption bands in UV–NIR range. Fig. 1 shows the UV–vis spectrum of