Sensors and Actuators B 241 (2017) 1–7

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Layer-by-layer electrodeposited nanowall-like palladium-reduced graphene oxide film as a highly-sensitive electrochemical non-enzymatic sensor

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ARTICLE INFO

Article history:
Received 19 July 2016
Received in revised form 1 October 2016
Accepted 12 October 2016
Available online 12 October 2016

Keyword:
Reduced graphene oxide
Electrochemical deposition
Palladium nanowalls
Hydrogen peroxide
Biosensor

ABSTRACT

Efficient and excellent non-enzymatic electrochemical sensors for H_2O_2 detection, consisting of reduced graphene oxide (rGO) and palladium (Pd) nanowalls with different rGO loadings, were electrochemically deposited in a layer-by-layer fashion onto indium tin oxide (ITO) glass. The structure and morphology of the as-fabricated non-enzymatic sensor electrodes were confirmed by X-ray diffraction, field-emission electron microscopy, and Raman spectroscopy. The effective combination of Pd nanowalls and rGO nanosheets provides many benefits in electrochemical detection, such as charge carriers with rapid transport and a greater number of sensing sites; thus, the Pd-rGO-modified ITO electrode with 0.5 mg ml^{-1} rGO displays the best electrochemical sensitivity with regard to H_2O_2 detection. The responses to H_2O_2 differ linearly with the concentration (from 100 μM to 12 mM). These devices showed a lowest detection limit of 0.24 μM, excellent stability, and high reproducibility. The enhanced sensitivity of the sensor electrode is due to the synergistic effect between the electrocatalytic activity of the Pd nanowalls and the high conductivity and large surface area of rGO.

1. Introduction

The accurate and real-time detection of hydrogen peroxide in vivo, as a biological mediator, can disclose essential associations between biological processes and small molecules and is also beneficial for diagnosis and disease monitoring [1]. Hydrogen peroxide (H_2O_2) is a vital product or intermediate of numerous enzymatic reactions. H_2O_2 is a signaling molecule in a wide array of biological procedures and it is cytotoxic to tissues and cells. Thus, establishing a simple, rapid, and reliable detection technique for H_2O_2 is of significant importance. Furthermore, in comparison to enzymatic detection, electrochemical sensors based on the non-enzymatic technique possess the advantages of low cost, high stability and good reproducibility.

So far, for the determination of H_2O_2, numerous analytical methods have been established. These include electrochemical sensing [2–4], microchip capillary electrophoresis [5], chemiluminescence [6], high-performance liquid chromatography [7], and fluorescence spectrophotometry [8]. Along with the rapid development of nanotechnologies, electrochemical sensors based on numerous electrocatalysts show additional benefits in conjunction with simple operation, real-time analysis, rapid responses, and high sensitivities. Particularly, by simply controlling the potentials, the determination of different substrates can be accomplished. In fact, using electrochemistry to sense H_2O_2 usually yields a low sensitivity and large overpotential at the surfaces of untreated indium tin oxide glass (ITO). Therefore, to improve the electrocatalysis of H_2O_2, highly-efficient electrocatalysts and suitable technologies for surface modification of the electrode are crucial issues [2,9].

Graphene nanosheets, which consist of a layer of two-dimensional sp^2-hybridized carbon atoms, have gathered great interest as an alternative support material because of their high surface area (2630 m^2/g), high conductivity (10^3–10^4 s/m), high electrical mobility (200,000 cm^2 V^{-1} s^{-1}), and high chemical stability [10–12]. These amazing physical and chemical characteristics offer advantages in the fabrication of electrochemical sensors [13], solar cells [10], and catalysis [14]. However, the aggregation of graphene during the reduction process and formation of electro-

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http://dx.doi.org/10.1016/j.snb.2016.10.053
0925-4005/

catalyst composites can dramatically decrease the surface area, thereby causing a significant decrease in the conductivity [11]. Therefore, electrodeposition is used to prepare a thin film of rGO on the surface of the conductive electrode. Electrodeposition produces films of a controllable thickness that demonstrate relatively high stability, due to parameters such as the electrolyte concentration, current density, and scan rate [15].

Recently, graphene has been used as a support material in non-enzymatic biosensors for the fabrication of organic-inorganic composites with noble metal catalysts such as silver, platinum, gold, and palladium (Pd). Pd is an important metal in laboratory and industrial settings due to its good chemical and physical properties, including its wear and corrosion resistance, catalytic ability for various chemical reactions, and high hydrogen absorption capacity [16]. Nevertheless, due to the high cost of Pd, its application in numerous fields on a large industrial scale is prevented. To overcome this challenge, the support materials on which the Pd catalysts are attached have also received much attention; these play a crucial role in enhancing the analytical performance. Up until now, Pd nanostructures with different morphologies (e.g., nanorods [17], nanowires [18], nanocubes [19], nanodendrites [20], and nanopolyhedrons [21]) have been successfully synthesized. It should be pointed out that, due to the complexity of the heterogeneous interface, morphology-controlled growth of Pd nanostructures on solid substrates is more challenging than solution synthesis. Electrodeposition is a convenient approach for the synthesis of Pd nanostructures with a desired morphology on conducting substrates. Many efforts have been made to synthesize Pd on conductive substrates by electrodeposition because the growth rate of the Pd nanostructures can be expediently controlled by the applied potential, which has an effect on the reduction rate of the precursors. Alternatively, poor contact between the Pd nanostructure and the surface of the conductive substrate (e.g., ITO) leads to poor conductivity of the sensor electrode, which causes the sensitivity of the sensor electrode to decrease. Therefore, modification of the sensor electrode by adding the high surface area of graphene increases the conductivity of the electrode and enhances the activity and sensitivity of non-enzymatic H_2O_2 sensors.

Herein, for the first time, we reported a layer-by-layer electrochemical deposition route for the rapid synthesis of Pd nanowalls, which are assembled as a second layer on reduced graphene oxide (rGO)-modified ITO electrodes. As the primary layer, rGO (with different thickness) was electrodeposited on the surface of ITO and the effect of thickness on the sensitivity of the sensor electrode was investigated. The facile process of electrodeposition allows for accurate control over multiple coated layers without the need for additives and/or organic binders. Moreover, the porous nature of the Pd nanowalls (with large surface areas and active centers) is suitable for enhanced analytical performance. The as-fabricated Pd nanowalls-rGO-modified ITO electrodes with different rGO loadings were utilized as non-enzymatic H_2O_2 sensors in an attempt to gain a better understanding of the effects of rGO thickness on the analytical performance of H_2O_2 detection. The Pd nanowall-rGO-modified ITO with 0.5 mg ml^{-1} rGO exhibited improved properties for H_2O_2 detection over a linear range between 100 μM and 12 mM.

2. Experimental methods

2.1. Chemicals

Analytical grade chemicals (i.e., NaH_2PO_4, Na_2HPO_4, 30 wt% H_2O_2, and $Pd(NO_3)_2$) were procured from Sigma Aldrich and dissolved in double-distilled water (resistance = 18.3 MΩ). Stock solutions of NaH_2PO_4 and Na_2HPO_4 were used to prepare the phosphate-buffered (PBS) solution. The experimental detection was performed with a fresh H_2O_2 solution.

2.2. Electrodeposition of rGO and layer-by-layer electrodeposition of Pd-rGO

For the synthesis of graphene oxide (using a modified Hummers' method), graphite powder was used as a precursor (micron-sized, 1–2 μm, Sigma Aldrich). The electrodeposition of the rGO-modified ITO electrodes with different thicknesses is described in our previous publication [22]. Briefly, the electrodeposition of rGO films with different rGO loadings using a three-electrode electrochemical cell was carried out by a single voltammetric cycle. A platinum wire was utilized as the counter electrode and a clean ITO-deposited glass substrate was used as the working electrode. The solutions contained 15 ml of different concentrations of GO (0.1 mg ml^{-1}, 0.5 mg ml^{-1}, and 1 mg ml^{-1}) and 5 ml of 0.025 M $Mg(NO_3)_2$. The applied potential ranged from 0.0 to −1.5 V (vs. an Ag/AgCl reference electrode) and the scan rate was 2 mV s^{-1}. The as-deposited rGO-modified ITO electrodes with different rGO loadings (i.e., 0.1 mg ml^{-1}, 0.5 mg ml^{-1}, and 1 mg ml^{-1}) are referred to as rGO-1, rGO-2, and rGO-3, respectively.

Fresh rGO-modified ITO thin film electrodes with different rGO loadings were then utilized as working electrodes to grow Pd nanowalls via cyclic voltammetry using two cycles. The solution was made of 3 ml of 0.01 M $Pd(NO_3)_2$ in 112 ml of 0.05 M $Mg(NO_3)_2$ as the supporting electrolyte. The potential scan was from 0.2 to −0.6 V at a scan rate of 10 mV s^{-1}. The as-fabricated Pd nanowalls-rGO-modified ITO thin film electrodes with different rGO loadings (i.e., 0.1 mg ml^{-1}, 0.5 mg ml^{-1}, and 1 mg ml^{-1}) are referred to as PrGO-1, PrGO-2, and PrGO-3, respectively. The electrochemical deposition of pure Pd nanowalls-modified ITO was performed with the same procedures. The electrodes were then rinsed with deionized water and dried in an oven at 50 °C.

2.3. Characterization

An X-ray powder diffractometer (XRD, PANalytical's Empyrean) with monochromatic CuKα radiation (l = 1.54056 Å) was used to characterize the powders. A field emission scanning electron microscope (FESEM-Hitachi SU8000) was utilized to examine the morphology of the electrodes. FTIR analysis was carried out on a Perkin Elmer System 2000 series spectrophotometer (USA) between 4000 and 600 cm^{-1}, while a Renishaw Invia Raman microscope instrument (laser excitation, l = 514 nm) was utilized for the Raman spectroscopy analysis. A potentiostat/galvanostat (Versastat 3) was utilized for the electrochemical experiments.

3. Results and discussions

3.1. Physicochemical characterization

3.1.1. Cyclic voltammograms

Fig. 1 shows the schematic illustration of the overall fabrication procedure for PrGO-modified ITO electrode prepared by the layer-by-layer electrochemical deposition. The cyclic voltammograms (CVs) of the rGO-modified ITO electrode with a 0.5 mg ml^{-1} concentration of GO are illustrated in Fig. 2a. The reduction peak is observed in the negative scan of the graph, which shows the successful reduction of GO. The cathodic peak, which starts at −1.2 V, corresponds to the irreversible electrochemical reduction of GO to rGO. Moreover, Fig. 2b shows the CV profiles for the electrodeposition of Pd nanowalls on the surfaces of rGO-modified ITO electrodes in a potential range from 0.2 to −0.6 V. Two reduction peaks are