Biosensors and Bioelectronics 41 (2013) 417–423

Contents lists available at SciVerse ScienceDirect

Biosensors and Bioelectronics

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

Growth of coral-like PtAu–MnO_2 binary nanocomposites on free-standing graphene paper for flexible nonenzymatic glucose sensors

Fei Xiao [a], Yuanqing Li [a], Hongcai Gao [a], Shuibing Ge [b,*], Hongwei Duan [a,*]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, Singapore 637457, Singapore
[b] Department of Physics, Soochow University, Suzhou 215006, China

ARTICLE INFO

Article history:
Received 18 March 2012
Received in revised form
13 June 2012
Accepted 31 August 2012
Available online 15 September 2012

Keywords:
Flexible sensor
Graphene paper
Binary nanocomposites
Electrodeposition
Electrocatalysis
Nonenzymatic glucose detection

ABSTRACT

The growing demand for compact point-of-care medical devices and portable instruments for on-site environmental sampling has stimulated intense research on flexible sensors that can be miniaturized and function under considerable physical deformation. We report a new type of flexible electrochemical biosensors based on free-standing graphene paper carrying binary nanocomposites of PtAu alloy and MnO_2. The coral-like PtAu–MnO_2 nanocomposites are grown on the substrate through one-step template-free electrodeposition, leading to an intimate contact between the PtAu alloy and MnO_2 matrix. The flexible electrode exhibits a unique set of structural and electrochemical properties such as better uniformity, larger active surface areas, and faster electron transfer in comparison with the control electrode prepared by tandem growth of MnO_2 network and PtAu alloy in two steps. In nonenzymatic amperometric glucose detection, the PtAu–MnO_2 binary nanostructure-decorated graphene paper has shown greatly enhanced sensing performance such as wide liner range (0.1 mM to 30.0 mM), high sensitivity (58.54 $\mu A\,cm^{-2}\,mM^{-1}$), low detection limit (0.02 mM, $S/N=3$), satisfactory selectivity, excellent reproducibility and stability, and tolerability to mechanical stress. The strategy of co-growth of metal and metal oxides on freestanding carbon substrates opens new possibility to develop high-performance flexible electrochemical sensors.

1. Introduction

Electrochemical biosensors play pivotal roles in current clinical diagnostics and environmental monitoring because of their high sensitivity and selectivity, excellent reproducibility, and fast response. Recently, growing demand for compact point-of-care medical devices and portable instruments for on-site environmental sampling has stimulated intense research on flexible sensors that can be processed into miniaturized forms and function under considerable physical deformation (Chuang et al., 2010; Wu et al., 2010). Conducting polymers and carbon materials have been commonly used to fabricate free-standing electrodes (Li et al., 2007; Nguyen et al., 2007). The electronic and mechanical properties of these conductive substrates have been tailored through chemical and biological methods (Jiang et al., 2006; Cheung et al., 2009). Particularly, loading of electrocatalytic nanoparticles on the substrates has led to enhanced electrochemically active surface areas and improved sensing performance (Campbell and Compton, 2010).

In this article, we report a new type of flexible electrochemical biosensors based on free-standing graphene paper carrying coral-like binary nanocomposites of PtAu alloy and MnO_2, which are grown on the substrate through one-step co-electrodeposition. Research activities on graphene were originally motivated by the remarkable electronic, thermal and mechanical properties of this single-atom-thick two-dimensional (2D) carbon material such as high charge carrier mobility (200,000 $cm^2\,V^{-1}\,s^{-1}$), excellent thermal conductivity (5000 $W\,m^{-1}\,K^{-1}$), mechanical robustness (fracture strength of 125 GPa), and large specific surface area (theoretical value of 2630 $m^2\,g^{-1}$) (Stankovich et al., 2006; Li et al., 2007; Park et al., 2008). Recent studies have shown that directed self-assembly of individual graphene nanosheets can yield free-standing paper-like materials with typical thickness ranging from 1 μm to 30 μm (Dikin et al. 2007; Li et al., 2008). The graphene paper (GP) features a unique set of structural and electronic properties such as mechanical robustness, structural uniformity, excellent electrical conductivity, and stability in electrochemical environment, making it intriguing carbon substrates for flexible electronics and sensors (Chen et al.,2008; Wang et al., 2009a; Choi et al., 2010; Pei et al., 2010; Xiao et al., 2012).

Here the sensing performance of our GP-based freestanding nanocomposites is evaluated for the amperometric detection of glucose. Glucose biosensors have attracted a great deal of attention due to the practical medical needs for diabetes diagnosis. Varieties of non-enzymatic glucose biosensors, with

* Corresponding authors. Tel.: +65 65141019; fax: +65 67911761.
E-mail addresses: sbge@suda.edu.cn (S. Ge), hduan@ntu.edu.sg (H. Duan).

0956-5663/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.bios.2012.08.062

particular focus on Pt-based amperometric sensors, have been designed to overcome the intrinsic problems associated with enzymatic biosensors such as the limited long-term stability of the immobilized enzymes and the poor selectivity arising from high overpotentials (Park et al., 2006, Wang et al., 2008; Xiao et al., 2009; Gao et al., 2011; Park et al., 2012). Development of Pt electrocatalysts with well-defined nanostructures and Pt-based alloys has become two effective strategies to improve the electrocatalytic activities and reduce the overall costs (Wang et al., 2009b; Mostafa et al., 2010; Chen and Holt-Hindle, 2010; Kim et al., 2010; Wang, Yamauchi, 2011). On the other hand, accumulating evidence has shown that the structural integration of the nanocatalysts and the carbon supports is also of great impact on the performance of the fabricated sensors (Kou et al., 2011).

In this study, we have developed one electrodeposition protocol for growing structurally integrated PtAu alloy and MnO_2 on freestanding graphene paper (PtAu–MnO_2/GP) from the solution of mixed metal ion precursors (i.e., $PtCl_6^{2-}$, $AuCl_4^-$ and Mn^{2+}). Our results demonstrated that the one-step co-deposition of PtAu alloy and MnO_2 led to coral-like nanocatalysts with large active surface areas in comparison with the control electrode prepared by tandem growth of MnO_2 network and PtAu alloy in two steps. The PtAu–MnO_2/GP had shown superior catalytic performance in glucose oxidation. This new type of binary nanocomposites loaded on the free-standing GP substrate exhibited greatly enhanced sensing performance in terms of sensitivity, selectivity, durability, and tolerability to mechanical stress. The co-growth of metal and metal oxides on freestanding carbon substrates provides a convenient and scalable approach to develop high-performance flexible electrochemical sensors.

2. Experimental

2.1. Chemicals and apparatus

Potassium hexachloroplatinate(IV) hydrate (K_2PtCl_6, purity: 99.9%), potassium tetrachloroaurate(III) hydrate ($KAuCl_4$, purity: 99.9%), manganese sulfate ($MnSO_4$, purity: 99%), graphite powder (<150 μm, 99.99% trace metals basis), hydroiodic acid (HI, 55% in water) and D-glucose (purity: ≥99.5%) were obtained from Aldrich. The working solutions were prepared by diluting the stock solution with phosphate buffer solution (PBS) and water. All other chemicals used were of analytical reagent grade.

Atomic force microscopy (AFM) observation was carried out using a MFP3D microscope (Asylum Research) with a silicon cantilever operating in tapping mode. Scanning electron microscope (SEM) images were obtained using JEOL field-emission scanning electron microscope (JSM-6700 F), equipped to perform elemental analysis by energy dispersive X-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) measurement was performed on a Kratos-Axis spectrometer with monochromatic Al K_α (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer. Electrodeposition, electrochemical impedance spectroscopy (EIS), cyclic voltammetric (CV) and chronoamperometric experiments were performed with a CHI 660 D electrochemical workstation (CH Instrument Company). A conventional three-electrode system was adopted. The working electrode was a GP with the dimension of 10 mm × 10 mm, and the auxiliary and reference electrodes were Pt wire and Ag/AgCl, respectively. Current densities were calculated based on active surface areas, which were determined according to the Randles–Sevcik equation using $[Fe(CN)_6]^{3-/4-}$ as the probe.

2.2. Preparation of graphene paper

Graphene oxide (GO) was synthesized from synthetic graphite powder based on a modified Hummers method (Supplementary information) (Hummers and Offeman, 1958). Free-standing GO paper was fabricated through a simple and scalable mold-casting method (Xiao et al., 2012). Briefly, aqueous dispersion of GO nanosheets was placed in a casting mold made of polytetrafluoroethylene (PTFE). After water was completely evaporated under room temperature, an integral layer of GO paper with smooth surfaces can be easily peeled off from the PTFE mold. The size of the as-prepared GO paper can be freely adjusted by choosing different sized casting molds, and the thickness of the paper can also be tailored in the range of 1–30 μm by using different volume of GO dispersion. GP was prepared by chemical reduction of GO paper (Pei et al., 2010). In a typical reaction, GO paper was directly immersed into aqueous 55% HI solution in a sealed cuvette at room temperature for 1 h. The HI-reduced GO paper was washed with DI water for several times and dried at room temperature for 10 h to obtain GP.

2.3. Preparation of PtAu–MnO_2/GP electrode

Before electrodeposition, the GP was rinsed with ethanol, acetone and distilled water. Free-standing GP carrying PtAu–MnO_2 integrated nanostructures (denoted as PtAu–MnO_2/GP) electrode was prepared by one-step co-deposition of PtAu and MnO_2 onto the GP from 0.1 M Na_2SO_4 containing 1 mM K_2PtCl_6, 1 mM $KAuCl_4$ and 50 mM $MnSO_4$ using a CV technique in the potential range from 1.4 V to −1.5 V at the scan rate of 250 mV s^{-1}. Pt–MnO_2/GP and Au–MnO_2/GP were fabricated under the same condition. The control electrode was prepared by the tandem growth of MnO_2 and PtAu alloy on GP. Typically, MnO_2 nanowires were firstly electrodeposited on GP from 0.1 M Na_2SO_4 solution containing 50 mM $MnSO_4$ using a CV technique ranging from 1.4 V to −1.5 V at 250 mV s^{-1}. Then PtAu nanoparticles were grown on the surface of MnO_2 nanowires film from 0.1 M Na_2SO_4 solution containing 1 mM K_2PtCl_6 and 1 mM $KAuCl_4$ through CV scanning from 1.0 V to −0.2 V at 250 mV s^{-1}. The as-prepared electrode was denoted as PtAu/MnO_2/GP. PtAu/GP was also prepared by electrodeposited PtAu alloy on bare GP following the similar procedure. After electrodeposition, the modified GP was removed from the precursor solution, carefully washed with DI water to remove excessive electrolyte, and further dried at 50 °C in oven to remove the residual water.

2.4. Collection and preparation of human blood and urine sample

Human blood and urine samples were obtained from a clinical laboratory. Blood sample with anti-coagulant was centrifuged and the blood plasma obtained was used to determine glucose level. Urine samples were used directly without any special treatment. Before analysis, the samples were diluted for 10 times with PBS (pH 7.4) and spiked with certain amount of glucose.

3. Results and discussion

3.1. Physicochemical characterization

The morphology of GO nanosheets prepared by ultrasonication-assisted exfoliation of graphite oxide has been characterized by AFM, showing that GO nanosheets are mostly single-layered graphene with a thickness of about 1.0 nm, and their sizes are in the order of several square micrometers (Fig. 1A). Free-standing GP was fabricated by evaporation-induced self-assembly of GO