Electrochemistry Communications 11 (2009) 608–611

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Amine-terminated ionic liquid functionalized carbon nanotube-gold nanoparticles for investigating the direct electron transfer of glucose oxidase

Ruifang Gao, Jianbin Zheng *

Institute of Analytical Science, Shaanxi Provincial Key Lab of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, PR China

ARTICLE INFO

Article history:
Received 30 October 2008
Received in revised form 14 December 2008
Accepted 19 December 2008
Available online 27 December 2008

Keywords:
Direct electrochemistry
Electrodeposition
Glucose oxidase
Ionic liquids
Gold nanoparticles
Carbon nanotubes

ABSTRACT

A novel nanocomposite was fabricated by three steps. In the first step, a chemical route was adopted to functionalization single-walled carbon nanotube (SWNT) with a new amine-terminated ionic liquid (NH_2-IL) to form IL-SWNT composite. In the second step, gold nanoparticle (GNP) was electrodeposited onto IL-SWNT to prepare GNP-IL-SWNT nanocomposite. In the last step, IL-GNP-IL-SWNT nanocomposite was obtained by self-assembly NH_2-IL on GNP. Glucose oxidase (GOD) was assembled on this novel composite through ionic interaction and achieved its direct electrochemistry. A pair of well-shaped voltammetric peaks was observed with the formal potentials ($E^{0'}$) at −0.501 V. The GOD modified electrode also exhibited an excellent electrocatalytic activity to the reduction of glucose with a detection limit of 0.8 μmol/L (S/N = 3). The apparent Michaelis–Menten constant (K_m^{app}) was estimated to be 0.022 mM. This protocol had potential application to fabricate the third-generation biosensor.

1. Introduction

Gold nanoparticles (GNPs) has been paid more and more attention because their properties are different from the bulk metal counterparts [1]. GNPs can enhance the bioactivity and electroactivity of some biomolecules except for their nanostructural effects. So GNPs are progressively applied to fabricate various biosensors and modified electrodes in the field of electroanalysis [2,3]. There are various methods to prepare and immobilize GNP for electrocatalytic applications. However, the electrodeposition is commercially attractive because of its performance at room temperature, less experimental setup demanded and the particle size controllable [2].

Carbon nanotubes (CNTs) have attracted considerable attention due to their unique properties since discovered in 1991 [4]. It is reported that CNTs have exhibited their extensive application in the field of strong electrocatalytic response towards many important electroanalysis inorganic compounds or biomolecules [5–8]. Room temperature ionic liquids (RTILs) have been the targets of numerous investigations because of their characteristics such as good chemical and thermal stability, almost negligible volatility, good ionic conductivity and wide electrochemical window. Hence they have been extensively used to prepare modified electrode and biosensors in electroanalysis. For example, several groups have reported that imidazolium ion-based RTILs can form gels with carbon nanotubes by grinding to fabricate several modified electrodes or biosensors [9–12]. Recently, Zhang et al. functionalized single-walled carbon nanotube (SWNT) with a novel ionic liquid 1-propylamine-3-methylimidazolium bromide as bridge to fabricate a novel nanobiocomposite (IL-SWNT) and used to immobilize glucose oxidase (GOD) on it to construct a novel glucose biosensor [13].

In this paper, we present a way for the synthesis of a novel composite comprising of functionalized SWNTs with a new amine-terminated ionic liquid 1-ethylamine-2,3-dimethylimimidazolium bromide (NH_2-IL) followed by electrodeposition of GNP and then self assembled NH_2-IL on GNP to prepare IL-GNP-IL-SWNT nanocomposite. GOD was assembled onto the nanocomposite to investigate its direct electrochemistry and electrocatalysis.

2. Experimental

2.1. Reagents

Single-walled carbon nanotubes (diameter: <10 nm, length: 1–2 μm, purity: ⩾95%) came from Shenzhen Nanotech Port Co. Ltd. The ionic liquid 1-ethylamine-2,3-dimethylimimidazolium bromide (2-EADMIMBr, purity: 98%) was from Shanghai Chengjie Chemistry. Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was from Sinopharm Group Chemical Reagent Co. Ltd. GOD was purchased from Sigma (USA). β-D-glucose was analytical grades. 0.1 mol/L phosphate buffer solution (PBS) was used as the supporting electrolyte. Other reagents were analytical reagent grade and doubly distilled water was used in all the experiments.

* Corresponding author. Tel.: +86 29 88302077; fax: +86 29 88303448.
E-mail address: zhengjb@nwu.edu.cn (J. Zheng).

1388-2481/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2008.12.060

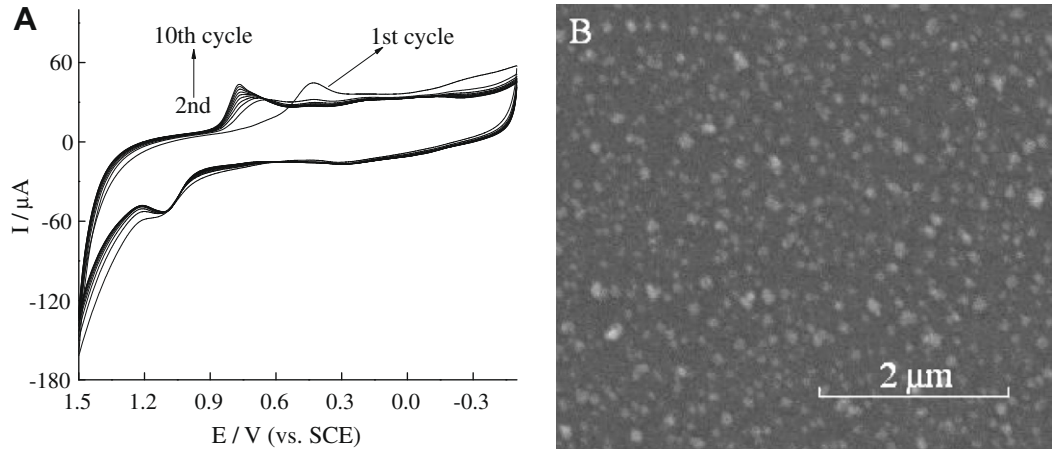

Fig. 1. A: Cyclic voltammograms recorded at IL-SWNT/GCE immersed in the 0.01 M Na_2SO_4 containing 0.01 M H_2SO_4 and 0.5 mM $HAuCl_4$ solution at scan rate of 100 mV/s. B: SEM image of GNP-IL-SWNT with 10-cycle deposition.

2.2. Apparatus

Electrochemical measurements were performed on a CHI660A electrochemical workstation (Shanghai CH Instrument Co. Ltd., China) with conventional three-electrode system. The working electrode was made by the following procedure. A saturated calomel electrode (SCE) and a platinum electrode were served as reference and counter electrode, respectively. All the electrochemical experiments were conducted at room temperature (25 ± 2 °C).

2.3. Fabrication of composite film modified electrode

The SWNT was purified according to literature [14]. IL-SWNT nanocomposite was synthesized according to literature [13]. After obtaining the purified IL-SWNT nanocomposite, 5 μL of IL-SWNT aqueous solution (0.08 mg/mL) was dropped on the surface of a glassy carbon electrode (GCE) and dried in air, and then the IL-SWNT/GCE was obtained. The electrochemical deposition of GNP was performed in 0.01 mol/L Na_2SO_4 aqueous solution containing 0.01 mol/L H_2SO_4 and 0.5 mmol/L $HAuCl_4 \cdot 4H_2O$ [15]. The obtained GNP-IL-SWNT/GCE was then dipped into 15 mg/mL NH_2-IL aqueous solution (N_2-saturated) for 5 h according to the affinity of $-NH_2$ in IL towards the GNPs to prepare IL-GNP-IL-SWNT/GCE. GOD is net negatively charged at pH 7.0 and could be exchange Br^- anion in IL [13]. So, GOD-IL-GNP-IL-SWNT/GCE was obtained by incubating IL-GNP-IL-SWNT/GCE modified electrode in 6 mg/mL GOD for 24 h.

3. Results and discussion

3.1. Electrodeposition of GNP on IL-SWNT composition film

Fig. 1A shows the continuous cyclic voltammograms recorded at an IL- SWNT/CPE in the electrolytic cell of gold electrodeposition under the N_2 atmosphere. The applied potential at the electrode is initially scanned from +1.50 V to negative direction at a scan rate of 100 mV/s. The reduction peak of Au(III) occurred at more negative potentials in the first cycle, and then shifted to more positive potentials in the subsequent nine cycles. The peaks grow with cyclic voltammetric number increasing, indicating that gold particle deposits on the composite film [15]. The SEM (Fig. 1B) also shows that GNPs have been successfully deposited onto the IL-SWNT surface and the average diameter of GNP was about 70–80 nm.

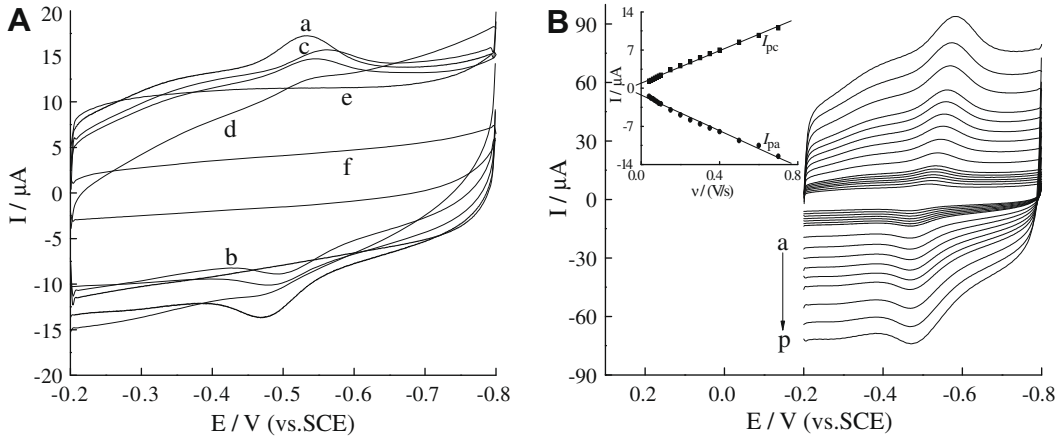

Fig. 2. A Cyclic voltammograms of different modified electrodes: (a) GOD-IL-GNP-IL-SWNT/GCE, (b) GOD-GNP-IL-SWNT/GCE, (c) GOD-IL-SWNT/GCE, (d) GOD-SWNT/GCE, (e) IL-GNP-IL-SWNT/GCE, (f) bare GCE in pH 7.0 PBS at scan rate of 100 mV/s under N_2 atmosphere. B: Cyclic voltammograms of GOD-IL-GNP-IL-SWNT/GCE in pH 7.0 PBS with different scan rates (from a to p: 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 500, 600, 700 mV/s). Inset: the relationship between cathodic and anodic peak current with scan rate *v*.