Colloids and Surfaces B: Biointerfaces 115 (2014) 295–301

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

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

In situ electrochemical synthesis of highly loaded zirconium nanoparticles decorated reduced graphene oxide for the selective determination of dopamine and paracetamol in presence of ascorbic acid

A.T. Ezhil Vilian, Muniyandi Rajkumar, Shen-Ming Chen *

Electroanalysis and Bioelectrochemistry Laboratory, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC

ARTICLE INFO

Article history:
Received 5 August 2013
Received in revised form
19 November 2013
Accepted 8 December 2013
Available online 17 December 2013

Keywords:
Electrochemical synthesis
Zirconium nanoparticles
Electrochemically reduced graphene
Dopamine
Paracetamol
Selective determination

ABSTRACT

Highly loaded zirconium oxide (ZrO_2) nanoparticles were supported on graphene oxide (ERGO/ZrO_2) via an in situ, simple and clean strategy on the basis of the electrochemical redox reaction between zirconyl chloride and graphene oxide ($ZrOCl_2$ and GO). The electrochemical measurements and surface morphology of the as prepared nanocomposite were studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and field emission scanning electron microscopy (FESEM). This ZrO_2 decorated reduced graphene oxide nanocomposite modified GCE (ERGO/ZrO_2) exhibits a prominent electrocatalytic activity toward the selective detection and determination of dopamine (DA) and paracetamol (PA) in presence of ascorbic acid (AA). The peaks of linear sweep voltammetry (LSV) for DA and PA oxidation at ERGO/ZrO_2 modified electrode surface were clearly separated from each other when they co-existed in the physiological pH (pH 7.0) with a potential value of 140 mV (between AA and DA) and 330 mV (between AA and PA). It was, therefore, possible to simultaneously determine DA and PA in the samples at ERGO/ZrO_2 nanocomposite modified GCE. Linear calibration curves were obtained for 9–237 μM of PA and DA. The ERGO/ZrO_2 nanocomposite electrode has been satisfactorily used for the determination of DA and PA in the presence of AA at pharmaceutical formulations in human urine samples with a linear range of 3–174 μM. The proposed biosensor shows a wide linear range, low detection limit, good reproducibility and acceptable stability, providing a biocompatible platform for bio sensing and bio catalysis.

1. Introduction

The synthesis and investigation of graphene based materials in different fields of science such as physics, chemistry, material science and nanotechnology has been increased, due to its excellent mechanical, electronic and thermal properties [1,2]. It also has an unique electrochemical properties such as fast electron transfer, excellent conductivity and even the wide electrochemical potential window have the ability to enhance the direct electron transfer at the bare electrodes have broadened their applications in the field of electrochemical biosensors [3]. Graphene sheets have tendency to form graphite due to the van der Waals force of attraction [4]. Moreover, due to its hydrophobic nature dispersion of graphene in aqueous media is difficult. Until now, versatile strategies have been employed by several researchers to attain large yield and high quality of graphene [5,6]. Besides, graphene sheets synthesized by much preferred chemical exfoliation method are not virtuous enough for nano electronics applications [7]. Conversely, the electrochemical reduction method is more efficient (without using any toxic solvents), for preparing high quality graphene sheets in large scale with short time to form exfoliated graphene oxide with high sensitive and low cost [8].

On the other hand, studies of nanoparticles and organized low-dimensional nanostructures have their unique capabilities to enhance mass transport, facilitate catalysis, increase surface area, and control an electrode's microenvironment [9]. Also, the nanoparticles provide a high surface-to-volume ratio and enhance the electron transfer kinetics [10]. ZrO_2 nanoparticles are an inorganic oxide, which have been demonstrated as an ideal material for the immobilization of biomolecules with oxygen groups because of its thermal stability, chemical inertness, lack of toxicity, and affinity for the groups containing oxygen [11]. The nanoparticles also

* Corresponding author. Tel.: +886 2 27017147; fax: +886 2 27025238.
E-mail address: smchen78@ms15.hinet.net (S.-M. Chen).

0927-7765/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfb.2013.12.014

provided a three-dimensional stage, and some of the restricted orientations also favored the direct electron transfer between the protein molecules and the conductor surface [12].

Dopamine (DA), uric acid (UA) and ascorbic acid (AA) are the important biomolecules which usually coexist together and considered as important molecules for physiological processes in human metabolism. UA and DA deficiencies result in several diseases and disorders [13–16]. The first species plays an important role in human brain and a loss of DA-containing neurons may result in some serious diseases such as Parkinson. The main difficulty with the electrochemical detection of DA in brain fluids is the coexistence of many interfering compounds. Acetaminophenol or paracetamol (PA) has been used comprehensively all over the world as a pharmaceutical pain reliever for patients for the relief of moderate pain for headache, backache and also used for reduction of fevers [17,18]. PA relives pain in the central nervous system and the concentration of it is high. In antagonistic, the physiological levels of DA are below 200 μmol L^{-1} [19], thus, researchers are keen on developing biosensor for the selective detection of dopamine (DA) and paracetamol (PA). But, determination of DA and PA on solid electrodes is challenging one due to the overlapping oxidation peak potentials. There are only few previously reported modified electrodes for the determination of these compounds, such as sodium dodecyl sulfate micelles as masking agent for electrochemical determination of DA in the presence of ascorbic acid [20], Pt–Au hybrid film modified electrode [21], Nafion/carbon coated iron nanoparticles chitosan composite film modified electrode [22] and for PA carbon coated nickel magnetic nanoparticles modified electrodes [23], electrochemically reduced graphene oxide/neodymium hexacyanoferrate modified electrodes[24], and simultaneous electrochemical determination of dopamine and acetaminophenol using multiwalled carbon nanotubes modified glassy carbon electrode [25]. These above reported electrochemical sensors satisfied many of the requirements such as specificity, speed of response, sensitivity and simplicity of preparation. However, the utility of solid-electrode-based sensors is often hampered by not having sufficient selectivity. In particular, complexity of real biological systems may result in overlapping voltammetric signals.

Herein, we report a simple co-electrodeposition method to prepare ERGO/ZrO_2 nanocomposite modified electrode. By taking advantage of the well-defined redox behavior of the ERGO/ZrO_2 nanocomposite, it was successfully employed for the selective electrocatalytic determination of PA and DA. This composite was prepared on GCE and ITO electrodes by simple two steps process by drop casting of GO followed by electrochemical reduction in the zirconyl chloride solution in PBS pH 5. As prepared nanocomposite electrode was characterized using surface analysis technique field emission scanning electron microscopy (FESEM) along with electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). ERGO/ZrO_2 modified electrode successfully separated PA and DA without AA interference and quantified in both lab and real samples, respectively.

2. Experimental

2.1. Apparatus

Electrochemical measurements like cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed by a CHI 1205A electrochemical analyzer. A conventional three-electrode cell was used at room temperature with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the film was studied by FESEM (Hitachi, Japan). EIS were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co. KG, Germany).

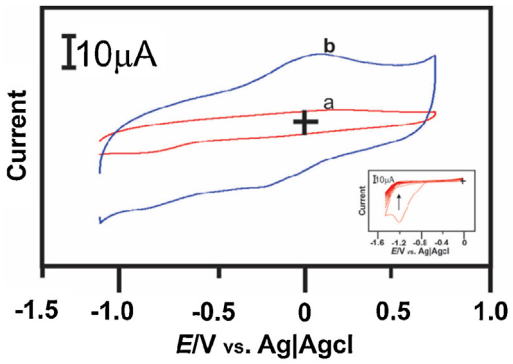

Fig. 1. Cyclic voltammograms obtained at (a) ZrO_2 (b) ERGO/ZrO_2 film modified GCEs in N_2 saturated 0.1 M PBS (pH 7) at Scan rate of 0.1 mV s^{-1}. Inset shows 30 consecutive cyclic voltammograms recorded at a GO-modified GCE in containing N_2 saturated 0.1 M PBS (pH 5) at scan rate of 50 mV s^{-1}.

2.2. Materials

Zirconyl chloride octahydrate ($ZrOCl_2$), graphite powder, ascorbic acid, dopamine and paracetamol were purchased from Sigma–Aldrich. AA, DA and PA solutions were prepared every day. The other chemicals (Merck) that are used in this investigation were of analytical grade (99%). All the solutions are prepared using double distilled water. Electrocatalytic studies were carried out in 0.05 M pH 7 PBS. Pure nitrogen gas was passed through all the experimental solutions for removing dissolved oxygen.

2.3. Electrochemical fabrication of ERGO/ZrO_2 nanocomposite modified electrode

Graphite oxide was synthesized from graphite by the modified Hummer's method [26–28]. The as-obtained graphite oxide was dispersed in water (0.5 mg/mL) and exfoliated by ultrasonication for 2 h to produce graphene oxide (GO). Prior to electrode modification, GCE was polished with 0.05 mm alumina slurry and Buehler polishing cloth. It was then washed with deionized water and ultrasonicated for 3 min each in water and ethanol to remove any adsorbed alumina particles or dirt from the electrode surface and finally dried. ERGO/ZrO_2 nanocomposite was fabricated on the GCE surface by a one-step process. 5 μl of GO dispersion was drop casted on the pre-cleaned GCE and dried in air oven at 30 °C. Then the GO modified GCE was shifted to an electrochemical cell with 4 ml of 0.05 M pH 7 PBS containing 5.0 mM $ZrOCl_2$. 10 consecutive cyclic voltammogram were recorded in the potential range between 0.7 and −1.1 V vs. Ag/AgCl reference electrode at the scan rate of 20 mV s^{-1} to obtain stable voltammogram [29]. The resulting ERGO/ZrO_2 film modified GCE was then rinsed with double distilled water and used for further electrochemical studies.

3. Results and discussion

3.1. Electrochemical characterization of ERGO/ZrO_2 nanocomposite film modified GCE

Fig. 1 represents the cyclic voltammograms of ZrO_2 nanoparticles and ERGO/ZrO_2 nanocomposite modified GCEs. The cyclic voltammogram of the reduction process of GO on GCE in 0.05 M pH