Materials Science and Engineering C 45 (2014) 21–28

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Electrochemical behavior and voltammetric determination of acetaminophen based on glassy carbon electrodes modified with poly(4-aminobenzoic acid)/electrochemically reduced graphene oxide composite films

Wencai Zhu [a,b], Hui Huang [a], Xiaochun Gao [a], Houyi Ma [a,*]

[a] Key Laboratory for Colloid and Interface Chemistry of State Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China
[b] School of Chemistry and Chemical Engineering, Qilu Normal University, Jinan 250013, China

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form 4 August 2014
Accepted 29 August 2014
Available online 6 September 2014

Keywords:
Graphene
Poly(4-aminobenzoic acid)
Acetaminophen
Electroanalysis
Voltammetric determination

ABSTRACT

Poly(4-aminobenzoic acid)/electrochemically reduced graphene oxide composite film modified glassy carbon electrodes (4-ABA/ERGO/GCEs) were fabricated by a two-step electrochemical method. The electrochemical behavior of acetaminophen at the modified electrode was investigated by means of cyclic voltammetry. The results indicated that 4-ABA/ERGO composite films possessed excellent electrocatalytic activity towards the oxidation of acetaminophen. The electrochemical reaction of acetaminophen at 4-ABA/ERGO/GCE is proved to be a surface-controlled process involving the same number of protons and electrons. The voltammetric determination of acetaminophen performed with the 4-ABA/ERGO modified electrode presents a good linearity in the range of 0.1–65 μM with a low detection limit of 0.01 μM (S/N = 3). In the case of using the 4-ABA/ERGO/GCE, acetaminophen and dopamine can be simultaneously determined without mutual interference. Furthermore, the 4-ABA/ERGO/GCE has good reproducibility and stability, and can be used to determine acetaminophen in tablets.

1. Introduction

Acetaminophen (Paracetamol or N-acetyl-p-aminophenol) is widely used as an over-the-counter antipyretic (fever reducer) and analgesic (pain reliever). It is an effective and well-tolerated agent employed to reduce fever and alleviate mild-to-moderate pain associated with headache, toothache, backache, muscular aches, arthritis and postoperative pain [1,2]. Generally, the limited use of acetaminophen is safe and has no harmful side effect. However, overdose or long-term use of acetaminophen may cause adverse effects on health because of the accumulation of toxic metabolites, which can lead to severe and sometimes fatal hepatotoxicity and nephrotoxicity [3,4]. Therefore, it is vitally important to develop simple, fast, sensitive, and accurate analytical methods for the determination of acetaminophen in pharmaceutical preparations and biological fluids. To date, many different methods have been employed for determining acetaminophen, such as titrimetry [5], spectrophotometry [6], capillary electrophoresis [7], chemiluminescence [8], liquid chromatography [9] and electrochemical methods [10]. Among them, electrochemical methods have attracted more attention due to its many advantages, e.g., good selectivity, high sensitivity, fast response, simple operation, and low cost. However, acetaminophen only shows sluggish voltammetric response at commonly used electrode surfaces. In order to enhance the voltammetric response and analytical performance for acetaminophen detection, various new sensing materials have been developed to fabricate novel modified electrodes, such as nanogold [11], carbon nanotubes [12], ZrO_2 nanoparticles [13] and nano-TiO_2 [14].

Graphene, a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, has attracted widespread attention recently from both theoretical and experimental researchers due to its unique nanostructure and extraordinary properties [15]. It has shown great potential applications in many fields, such as super capacitors [16], nanoelectronics [17], batteries [18] and ultrasensitive sensors [19]. However, how to prepare graphene sheets with desirable properties remains a significant challenge for scientific research and practical applications. So far, several methods have been developed to produce graphene sheets, such as mechanical cleavage, epitaxial growth, and chemical or electrochemical reduction of graphene oxide. Among them, electrochemical reduction of graphene oxide to graphene has recently attracted more interests due to its fast and green nature [20], and several related studies have been reported [21,22].

Polymer modified electrodes have received great interest in recent years, due to their unique physical and chemical properties, such as high stability and selectivity, good reproducibility and homogeneity, and strong adherence to electrode surface. These outstanding characteristics

* Corresponding author. Tel.: +86 531 88364959; fax: +86 531 88564464.
E-mail address: hyma@sdu.edu.cn (H. Ma).

http://dx.doi.org/10.1016/j.msec.2014.08.067
0928-4931/

make them have potential application in the fields of batteries [23], supercapacitors [24] and sensors [25]. Electropolymerization, which can control the film thickness, permeation and charge transport characteristics by applying different electrochemical parameters, is a good choice for the preparation of polymer films. 4-Aminobenzoic acid (4-ABA), a non-protein amino acid, is widely distributed in nature. The poly(4-ABA) film via electrochemically polymerization of 4-ABA has been used for electrochemical analysis [26,27]. For example, Yang and co-workers reported that hydroquinone and catechol can be completely separated and simultaneously determined at the poly(4-ABA) modified glassy carbon electrode at a relatively low potential in a phosphate buffer solution with pH value of 7.0 [26].

In this paper, we have fabricated poly(4-aminobenzoic acid)/electrochemically reduced graphene oxide composite film modified glassy carbon electrodes (4-ABA/ERGO/GCEs) by a two-step electrochemical method. Electrochemical behavior and voltammetric determination of acetaminophen at the 4-ABA/ERGO/GCE were investigated in detail. The results show that the 4-ABA/ERGO/GCE exhibited excellent electrocatalytic activity towards the oxidation of acetaminophen. Meanwhile, the fabricated electrode also exhibited good reproducibility and operational stability, and could be used to detect acetaminophen in real samples with satisfactory results.

2. Experimental

2.1. Reagents and materials

Acetaminophen, dopamine and ascorbic acid were purchased from Aladdin Chemistry Co., Ltd. All chemicals were of analytical grade and used without further purification. All of the aqueous solutions were prepared with ultrapure water (>18 MΩ cm). The phosphate buffer solutions (PBS, 0.1 M) with various pH values were prepared by mixing the stock solutions of 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4.

2.2. Apparatus

All electrochemical measurements were carried out with a CHI 650A electrochemical workstation in a conventional three-electrode cell at room temperature (~25 °C). The modified glassy carbon electrode (GCE, Φ = 5 mm) was used as the working electrode, and a saturated calomel electrode (SCE) and a Pt plate with a surface area of 4 cm^2 served as the reference electrode and the counter electrode, respectively. All the potentials given in this paper were referred to the SCE. The solutions were deoxygenated by bubbling with high-purity N_2 for at least 10 min prior to electrochemical measurements and a blanket of N_2 was maintained throughout each experiment.

The surface morphology of the as-prepared samples was characterized by transmission electron microscope (TEM, JEM-2100) and field emission scanning electron microscope (FESEM, Hitachi S-4800).

2.3. Preparation of 4-ABA/ERGO/GCE

Graphene oxide (GO) sheets were synthesized from natural graphite powder by a modified Hummers method [28]. The graphene oxide suspension (0.5 mg mL^{-1}) was prepared by dispersing as-synthesized graphene oxide sheets in water with the aid of sonication.

4-ABA/ERGO/GCE was prepared by a two-step electrochemical method. Prior to modification, the glassy carbon electrode was polished with 1.0 μm, 0.3 μm and 0.05 μm α-alumina powders in sequence and rinsed thoroughly with pure water after each polishing step. The polished glassy carbon electrode was sonicated in HNO_3 (1:1), ethanol, and ultra-pure water for 5 min, respectively, and dried in nitrogen atmosphere. 12 μL of the graphene oxide suspension was dropped onto the glassy carbon electrode surface and dried in an infrared lamp to get graphene oxide modified glassy carbon electrode (GO/GCE). The GO/GCE was then transferred to 0.1 M PBS (pH 5.0). The graphene oxide sheets coated on the surface of the glassy carbon electrode were electrochemically reduced by applying a constant potential of −1.3 V for 400 s to form the electrochemically reduced graphene oxide modified glassy carbon electrode (ERGO/GCE). After washing repeatedly with ultrapure water, the ERGO/GCE was treated in 0.1 M PBS (pH 7.0) containing 1 mM of 4-ABA by carrying out voltammetric cycling between −1.5 and 2.5 V at 100 mV s^{-1} for 5 circles, and poly(4-aminobenzoic acid)/electrochemically reduced graphene oxide composite film modified glassy carbon electrode (4-ABA/ERGO/GCE) was obtained. Finally the 4-ABA/ERGO/GCE was thoroughly washed with ultrapure water to remove physically adsorbed substances and stored in 0.1 M PBS (pH 7.0) for use.

2.4. Preparation of real samples

The acetaminophen tablet was purchased from a local pharmacy. Four tablets (equivalent to 250 mg of acetaminophen in each tablet) of acetaminophen pharmaceutical formulation were accurately weighed and finely powdered in an agate mortar. An adequate amount of the powders was weighed and dispersed in 50 mL of ultrapure water with ultrasonic agitation for 30 min. Then the mixture was filtrated. After filtration, the filter cake was washed five times with 8 mL of ultrapure water, and all filtrates were collected in a 100 mL volumetric flask and diluted to the designated volume with ultrapure water for further analysis.

3. Results and discussion

3.1. Cyclic voltammograms of electropolymerization of 4-ABA

The cyclic voltammograms (CVs) describing the formation of 4-ABA film on the surface of ERGO/GCE are given in Fig. 1. It can be seen that with the increase of the number of voltammetric cycles, two anodic peaks gradually appeared at about 0.18 V and 1.55 V, and two reduction peaks appeared at 0.30 V and −0.75 V, respectively. The result is consistent with previously published studies [27]. Moreover, the peak current increased with the number of voltammetric cycles. This indicates the polymeric film continued to grow on the surface of ERGO/GCE. After drying in air, a blue film could be seen at the electrode surface, which shows a fact that 4-ABA film was successfully introduced onto the surface of ERGO/GCE.

3.2. Characterization of the modified electrodes

The surface morphologies of the modified electrodes were characterized by TEM and SEM. The TEM image of GO (Fig. 2A) shows that the as-prepared graphene oxide sheets are corrugated and scrolled,

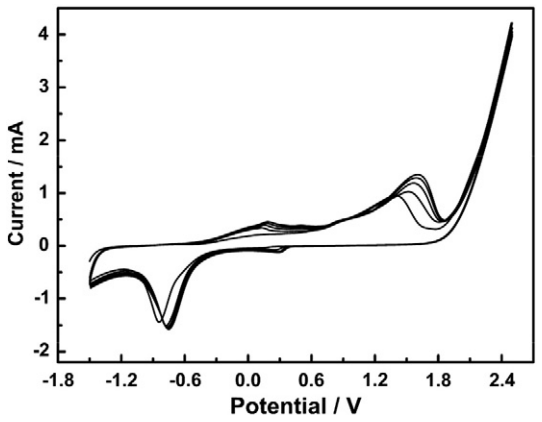

Fig. 1. The CVs describing the formation of 4-ABA film on the surface of ERGO/GCE. Scan rate: 100 mV s^{-1}.