Journal of Molecular Liquids 252 (2018) 75–82

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Novel graphene modified carbon-paste electrode for promazine detection by square wave voltammetry

Khaled M. AlAqad [a], Rami Suleiman [b], Othman Charles S. Al Hamouz [a], Tawfik A. Saleh [a,*]

[a] Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[b] Center of Research Excellence in Corrosion, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:
Received 2 November 2017
Received in revised form 8 December 2017
Accepted 20 December 2017
Available online 24 December 2017

Keywords:
Graphene
Promazine
Electroanalysis
Determination
Electrode

ABSTRACT

Graphene nanosheet prepared from graphite via a modified Hummers method was used to design a graphene-modified carbon-paste electrode (GCPE). The electrochemical behavior was investigated by studying the electrocatalytic behavior of the ferrocyanide redox couple on its surface by using cyclic voltammetry. The GCPE showed voltammetric responses with a higher level of sensitivity and a lower background current compared to the carbon paste electrode. The analytical applicability of the newly prepared electrodes was demonstrated by the powerful quantitative determination of promazine (PZ). The electrochemical behavior of promazine at the surface of the fabricated electrode was evaluated using cyclic voltammetry and square wave voltammetry. The voltammogram of promazine showed two oxidation peaks at 0.6 V and 0.9 V and one signal of a reduction peak at 0.57 V. A mechanism was proposed to explain the oxidation-reduction process of PZ. Square wave voltammetry (SWV) technique has been successfully applied in this study for the determination of PZ using the prepared graphene-based electrode. A linear dynamic range of 0.1 μM to 8 μM, regression factor (R^2) of 0.9979, and a limit of detection (LOD) of 8 nM were obtained. The effective and straightforward method reported here to prepare the GCPE offers a high electrochemical activity and a relatively low background current. The GCPE has an excellent stability and can be recommended for promazine determination in various formulations.

1. Introduction

Graphene is an intrinsic two-dimensional sheet in a hexagonal configuration with carbon atoms bonded by sp2 carbon hybridization. Graphene has attracted extensive attention due to its unique electronic structure, two-dimensional nature, flexibility, and chemical stability. It is considered to be of good electronic conductivity and high surface area [1,2,3]. Graphene was used in various areas, such as corrosion, adsorption and electrochemical sensing using modified electrocatalytic nanoparticles, in addition to being used as the anode in lithium batteries [4–8]. Graphene is widely used in electrochemistry-related applications because of its high signal of electrical conductivity, high surface area, low cost of production and heterogeneous electron transfer rate [9–13]. Graphene can be used in the sensing of various targets, such as in the biosensing of glucose [14], assaying of hydrogen peroxide [15], and in the determination of bimolecular, organic molecules and pharmaceutical compounds. This is related to its individual properties, such as good conductivity and good carrier charge mobility [18]. Graphene plays a key role in electrochemistry-based applications as it characterized by having the properties of the individual planar structure [16,17].

Various classes of the carbon substrates such as graphite, carbon nanotube, and glassy carbon have been applied successfully in the fabrication of modified carbon paste electrodes via different methods [18–22]. Graphite is commonly used in electrochemistry because of its wide potential window and low background current [23]. A graphite paste electrode was used for the determination of a redox reaction by using the electrochemical technique, which has a high sensitivity and low cost [24]. Graphite is used as a carbon paste electrode because of its low current compared to solid graphite electrodes. A graphite paste electrode is used as a working electrode in electrochemical techniques, such as cyclic voltammetry measurements, as a characterization tool, and in the identification of pharmaceutical compounds. Examples for its use include the determination of phenolic compounds [25] and glutathione [26]. Graphite paste is now a very popular material due to its low background and the easiness in its modification and miniaturization.

Promazine hydrochloride (PMH), chemically known as 3-(10Hphenothiazin-10-yl)-*N*,*N*-dimethylpropan-1-amine hydrochloride, is a phenothiazine drug with an aliphatic side chain, used in the management of psychotic conditions [27]. The monitoring of promazine is significant for quality assurance in the pharmaceutical industry.

* Corresponding author.
E-mail address: tawfik@kfupm.edu.sa (T.A. Saleh).

https://doi.org/10.1016/j.molliq.2017.12.108
0167-7322/

Therefore, the detection of this drug is important in biological samples such as urine and drug tablets. Several analytical techniques have been reported for the determination of promazine including electrophoresis [28], spectrophotometry [29], and electrochemistry [30,31]. Most of these techniques suffered from serious limitations that include the usual need for time-consuming sample preparations and, in some cases, a derivatization as well.

Encouraged by the above, the present work reported on the successful use of a graphene prepared from graphite in the fabrication of an efficient graphene-modified carbon-paste electrode (GCPE). The electrochemical behavior of the fabricated electrode was evaluated using cyclic voltammetry and square wave voltammetry. The electrode was investigated for the quantitative determination of promazine powder.

2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were conducted using the CHI1140A electrochemical measuring station (CH instrument Inc., Austin, TX, US). The configuration of the electrochemical setup includes an electrochemical analyzer device, Ag/AgCl as a reference electrode (in 1 M potassium chloride (KCl) CHI11, CH Instruments INC), a platinum wire as an auxiliary electrode (CHI115, CH Instilments Inc.) and a paste composite electrode as a working electrode. The electrodes were inserted into a cell glass using a stand of Teflon cover. The CVs show two oxidation peaks of promazine. The first one is reversible while the second one is irreversible.

2.2. Materials

Sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$,), potassium ferrocyanide with CAS Number: 14459-95-1 and purity of 99%, and promazine powder (purity 99%) with the CAS number 53-60-1 were purchased from Sigma–Aldrich Company, US.

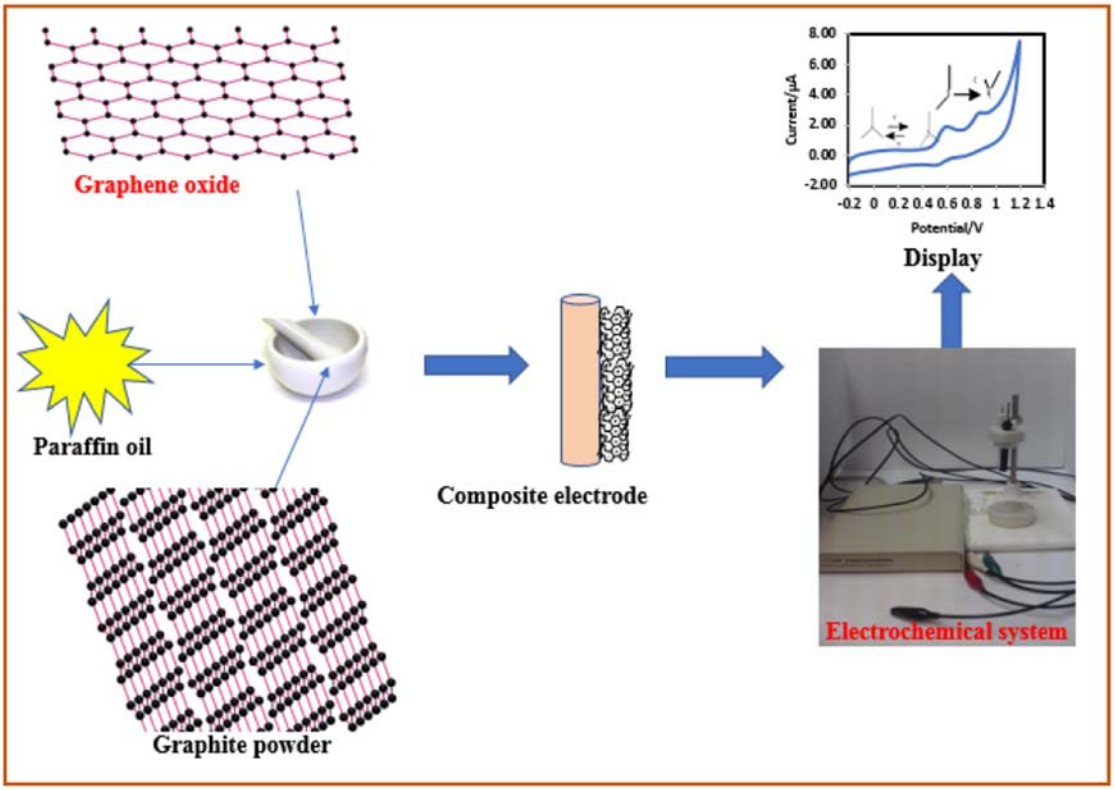
A solution of 10^{-4} M of PZ was prepared by dissolving a certain amount of PZ in a phosphate buffer (pH = 4.0) solution to make an analyte; the solution was placed under sonication for 10 min to allow complete desolvation. The buffer solution was prepared using phosphate powder buffer in a 100 mL volumetric flask and distilled water as a solvent. Other diluted solutions of PZ were prepared by diluting certain volumes of the standard solution with distilled water. Low-density Paraffin oil and carbon powder were obtained from Sigma–Aldrich Company. Phosphate buffer (0.5 M, pH = 4.0) was used as a supporting electrolyte and a solution of 0.02 M potassium ferrocyanide mixed with 0.2 M of KCl was used as a supporting electrolyte. All standard solutions were prepared using distilled water.

2.3. Synthesis of graphene oxide and electrode design

Graphene oxide (GO) was prepared using a modified Hummers method [32–33], and by using the graphite powder as a base material. The procedure for the synthesis of GO is as follows:

In 250 mL volumetric flask, graphite powder (1 g) was added to a 23 mL of concentrated sulfuric acid (H_2SO_4) and 100 g of sodium nitrate ($NaNO_3$). The resulting solution was stirred then for 30 min at 5 °C in an ice-bath. After that, potassium permanganate ($KMnO_4$,) powder (3 g) was slowly added to the flask, and the mixture was heated to 35–40 °C and stirred for another 30 min. Distilled water (46 mL) was added then to the above mixture over a period of 25 min. Finally, 140 mL of water and 10 mL of 30% H_2O_2 were added to the mixture. The unexfoliated graphite in this mixture was removed by repeated centrifugation and filtration (first by 5% HCl and then with water) and the final product was washed thoroughly with water and dried under vacuum at 65 °C for overnight [34].

The carbon paste electrode was prepared by a hand mixing of 70% graphite and 30% paraffin oil. The resulting paste was packed into the electrode cavity (0.1 mm diameter) of the PTFE sleeve. Electrical contact



Scheme 1. Illustration of the preparation of the composite GCPE used in the determination of the promazine drug.