Sensors and Actuators B 213 (2015) 285–294

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Simultaneous voltammetric determination of paracetamol and domperidone based on a graphene/platinum nanoparticles/nafion composite modified glassy carbon electrode

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ARTICLE INFO

Article history:
Received 12 September 2014
Received in revised form 22 January 2015
Accepted 16 February 2015
Available online 26 February 2015

Keywords:
Paracetamol
Domperidone
Graphene
Platinum nanoparticles
Electrodeposition
Nafion

ABSTRACT

Graphene oxide and hexachloroplatinic acid were electrochemically reduced on a glassy carbon electrode (GCE) surface so as to form a graphene (Gr)–platinum nanoparticles (PtNP) composite. This nano composite was then coated with nafion (NAF) film so as to form NAF/PtNP/Gr/GCE. In this work, an electrochemical method based on adsorptive stripping square wave voltammetry (AdSSWV) employing NAF/PtNP/Gr/GCE has been proposed for the subnanomolar determination of paracetamol (PCT) and domperidone (DOM) simultaneously. The electrode material was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction. The electrochemical performance of PCT and DOM on modified electrode was investigated by cyclic voltammetry, electrochemical impedance spectroscopy, and chronocoulometry. A sixteen fold enhancement in the AdSSWV signal was observed at NAF/PtNP/Gr/GCE in pH 6.0, phosphate buffer, as compared to GCE. Under the optimized conditions, the method allowed simultaneous determination of PCT and DOM in the linear working range of 8.2×10^{-6}–1.6×10^{-9} M with detection limits ($3 \times SD/s$) of 1.06×10^{-10} and 4.37×10^{-10} M for PCT and DOM respectively. The practical analytical utilities of the modified electrode were demonstrated by the determination of PCT and DOM in pharmaceutical formulations, human urine, and blood serum samples. This proposed method was validated by HPLC and the results are in agreement at the 95% confidence level. Simultaneous voltammetric determination of PCT and DOM has been reported for the first time.

1. Introduction

Paracetamol (PCT) is widely used all over the world as a pharmaceutical analgesic and antipyretic agent [1]. Domperidone (DOM), chemically, known as 5-chloro-1-[1-[3-(2,3-dihydro-2-oxo-1H-benzimidazol-1-yl) propyl]-4-piperidinyl]-1,3-dihydro-2H-benzimidazol-2-one. DOM is a dopamine antagonist used as an antiemetic for the short term treatment of nausea and vomiting of various etiologies [2]. A combination of PCT and DOM works in a synergistic manner. PCT relieves symptoms of migraine and DOM increases the contractions of the stomach and intestines, which aids in a quick absorption of PCT. However, an overdose of DOM may results in high accumulation of PCT. Symptoms of DOM overdose also include drowsiness, dizziness, confusion, twitching, and irregular heartbeats. Therefore, the development of a sensitive and selective method for their simultaneous determination is highly desirable for analytical applications and diagnostic research.

Literature survey reveals several analytical methods for simultaneous determination of PCT and DOM including capillary electrophoresis [3], chromatography [4], and spectroscopy [5]. However these methods are lengthy, overpriced, complicated, require expert knowledge, and often need the pretreatment step that makes them unsuitable for routine analysis. On the other hand, electrochemical methods are used extensively over other methods due to simplicity, low cost, and relatively short analysis time. There are several voltammetric methods reported for individual determination of PCT [6–11] but only two voltammetric methods are available for DOM determination [12,13]. There is no official electrochemical method reported for simultaneous determination of PCT and DOM. Hence, it is essential to develop simple yet sensitive method for simultaneous determination of PCT and DOM.

Over the past two decades, chemically modified electrodes (CMEs) have attracted broad interest in sensor development due

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http://dx.doi.org/10.1016/j.snb.2015.02.090
0925-4005/

to low background current, wide range of potential window, easy surface renewal, lower detection limit, and low sensitivity to dissolved oxygen. Because of these advantages CMEs have been used in various analyses [14–17]. In Recent years, our group has reported chemically modified electrodes for determination of various organic [18–24] as well as inorganic species [25,26].

Graphene (Gr) is a two dimensional (2D) one atom thick nanomaterial consisting of sp^2 hybridize carbon, has attracted tremendous attention due to its unique properties, such as high surface area, excellent electrical conductivity, and well electrocatalytic activity [27,28]. Because of these properties graphene has been used as an ideal electrode material in supercapacitors [29], field effect transistors [30], and chem/bio sensors [31]. Graphene has been used for the sensitive determination of various drugs molecules, due to their excellent conductivity because of π–π stacking and synergetic effects with other materials [32–34]. Platinum nanoparticles (PtNPs), on the other hand, due to their large aspect ratio (surface area to volume), biocompatibility, and high electrical conductivity have also been widely employed as a modifier in voltammetry for analysis of organic molecules [35,36]. The introduction of metal nanoparticles into the dispersion of graphene sheets could inhibit the aggregation of graphene sheets, and result in mechanically jammed, exfoliated graphene agglomerate with very high surface area [37]. Nafion, a perfluorinated sulphonated cation exchanger with properties of excellent antifouling capacity, chemical inertness, and high permeability to cations, has been extensively employed as an electrode modifier for organic molecules [38–40]. Thus, a synergistic effect of Gr, PtNP, and NAF composite film modified GCE can enable a sensitive determination of PCT and DOM.

The present study deals with simultaneous determination of PCT and DOM using nafion/platinum nanoparticles/graphene modified glassy carbon electrode employing adsorptive stripping square wave voltammetry (AdSSWV). The morphological and electrochemical characterization of the electrode material has been carried out by using various techniques, such as scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronocoulometry (CC). The developed AdSSWV method based on nanocomposite shows good sensitivity and selectivity for determination of PCT and DOM in pharmaceutical formulations, urine, and blood serum samples. Moreover, the proposed voltammetric method has been validated by HPLC and the results obtained are in good accordance with those obtained by the proposed method.

2. Experimental

2.1. Chemicals and instrumentation

All chemicals were of A. R. grade and were used as received without any further purification. Paracetamol and domperidone (≥98%) have been procured from Sigma Aldrich. Graphite powder (99% trace metals basis) was purchased from S. D. Fine (India). Chloroplatinic acid hydrate ($H_2PtCl_6 \cdot \times H_2O$) was obtained from Sigma Aldrich. Nafion (NAF, 1100EW, 5 wt% aqueous alcoholic solution, Aldrich) was prepared as 0.1% solution by dilution with ethanol. All solutions were prepared using double distilled water of specific conductivity (0.3–0.8 μS). Phosphate buffer solution (PBS; 0.1 M, pH 6.0) was employed as a supporting electrolyte. The developed method was employed for analysis of the following pharmaceuticals: Crocin (500 mg), Tylenol (325 mg), Motilium (10 mg), Dom DT (5 mg), Acedome (PCT: DOM = 500 mg: 10 mg), Acemol-D (PCT: DOM = 500 mg: 10 mg), and Grenil (PCT: DOM = 500 mg: 20 mg).

The voltammetric measurement were performed using an Autolab PGSTAT 30 equipped with USB electrochemical interface using GPES software, version 4.9.005 and frequency response analyzer, software version 2.0 respectively. Conventional three-electrode system employing, a GCE (diameter = 3 mm) was used as working electrode, platinum wire, and Ag/AgCl (sat. KCl) were used as counter and reference electrodes, respectively. The pH measurements were performed using ELICO LI 120 pH meter. HPLC used for validating the method was an Agilent model 1100. XRD analysis was carried out on an X-ray diffractometer (Shimadzu 7000S, Shimadzu Analytical, Japan) equipped with CuK_α radiation (λ = 0.154 nm). Surface morphology of the materials was investigated by SEM.

2.2. Preparation of the nafion/platinum nanoparticles/graphene/GCE (NAF/PtNP/Gr/GCE)

The glassy carbon electrode was polished, at the start of the work, with aqueous slurries of alumina powders (1.0 μm and 0.3 μm α-Al_2O_3) on polishing cloth until mirror-like finish was obtained. After that, the electrode was ultrasonicated in distilled water for about 30 s, and finally allowed to dry under infrared lamp. Graphene oxide (GO) was synthesized directly from graphite by Hummers method [41]. The synthesized graphite oxide powder was exfoliated in doubly distilled water by ultrasonication for 120 min to form homogeneous GO dispersions with a concentration of 1.0 g L^{-1}. Graphene and PtNP were prepared according to literature procedure via electroreduction [42,43]. This procedure for fabrication of modified electrode is depicted pictorially in Scheme 1. Preparation of graphene–platinum nanocomposites is a two-step process. In the first step 10.0 mg L^{-1} GO solution was prepared. The GCE was placed into this solution, and five CV scans between +0.6 V and −1.5 V were carried out so as to convert GO to Gr. This modified GCE was then dipped into a solution of 10 mM H_2PtCl_6 (in 0.1 M NaCl). The electrochemical reduction to PtNP was performed under magnetic stirring by applying an electro-deposition potential of −0.7 V for 40 s. After electrochemical reduction, the working electrode was washed with doubly distilled water, and dried under I. R. lamp. Finally, NAF modification was carried out by drop casting (5.0 μL, 0.1%) on to the surface of the GCE, and the solvent was allowed to evaporate at room temperature. Thus, NAF/PtNP/Gr/GCE was fabricated. For comparison, GO/GCE, Gr/GCE and PtNP/Gr/GCE were prepared using same method.

2.3. Voltammetric procedures

Stock solutions of PCT and DOM were prepared in double distilled water. The required quantity of the stock solution was placed in to a 25.0 cm^3 standard volumetric flask, and the total volume was made to 25 cm^3 with PBS, pH 6.0 (0.1 M). An AdSSWV was used for determination of both the drugs, and optimized adsorptive stripping square wave voltammetric parameters were: accumulation potential: −0.3 V, accumulation time: 90 s, equilibrium time: 15 s, square wave frequency: 100 Hz, step potential: 5 mV, modulation amplitude: 50 mV. The voltammogram was then recorded by scanning the potential toward the positive direction from −0.2 to +1.1 V. Cyclic voltammetric experiments were carried by sweeping potential from −0.2 to +1.3 V. Double potential step chronocoulometry was carried out with a pulse period of 5 s vs. Ag/AgCl. EIS study has been done in the frequency range of 10^{-2}–10^6 Hz at open circuit potential with amplitude of 5 mV.

2.4. Treatment and determination of samples

Pharmaceutical formulations, urine, and blood serum samples were analyzed for determination of PCT and DOM. Twenty tablets were weighed, and then finely powdered using mortar and pestle