



ELSEVIER

Contents lists available at ScienceDirect

Talanta

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

Pristine multi-walled carbon nanotubes/SDS modified carbon paste electrode as an amperometric sensor for epinephrine



Tony Thomas^a, Ronald J. Mascarenhas^{a,*}, Ozma J. D' Souza^a, Simon Detriche^b, Zineb Mekhalif^b, Praveen Martis^a

^a Electrochemistry Research Group, Department of Chemistry, St. Joseph's College, Lalbagh Road, Bangalore 560027, Karnataka, India

^b Laboratoire de Chimie et d'Electrochimie des Surface, University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium

ARTICLE INFO

Article history:

Received 18 December 2013

Received in revised form

12 March 2014

Accepted 13 March 2014

Available online 20 March 2014

Keywords:

Multi-walled carbon nanotubes

Sodium dodecyl sulfate

Epinephrine

Modified carbon paste electrode

Diffusion coefficient

ABSTRACT

An amperometric sensor for the determination of epinephrine (EP) was fabricated by modifying the carbon paste electrode (CPE) with pristine multi-walled carbon nanotubes (pMWCNTs) using bulk modification followed by drop casting of sodium dodecyl sulfate (SDS) onto the surface for its optimal potential application. The modified electrode showed an excellent electrocatalytic activity towards EP by decreasing the overpotential and greatly enhancing the current sensitivity. FE-SEM images confirmed the dispersion of pMWCNTs in the CPE matrix. EDX analysis ensured the surface coverage of SDS. A comparative study of pMWCNTs with those of oxidized MWCNTs (MWCNTs_{OX}) modified electrodes reveals that the former is the best base material for the construction of the sensor with advantages of lower oxidation overpotential and the least background current. The performance of the modified electrode was impressive in terms of the least charge transfer resistance (R_{ct}), highest values for diffusion coefficient (D_{EP}) and standard heterogeneous electron transfer rate constant (k^0). Analytical characterization of the modified electrode exhibited two linear dynamic ranges from 1.0×10^{-7} to 1.0×10^{-6} M and 1.0×10^{-6} to 1.0×10^{-4} M with a detection limit of $(4.5 \pm 0.18) \times 10^{-8}$ M. A 100-fold excess of serotonin, acetaminophen, folic acid, uric acid, tryptophan, tyrosine and cysteine, 10-fold excess of ascorbic acid and twofold excess of dopamine do not interfere in the quantification of EP at this electrode. The analytical applications of the modified electrode were demonstrated by determining EP in spiked blood serum and adrenaline tartrate injection. The modified electrode involves a simple fabrication procedure, minimum usage of the modifier, quick response, excellent stability, reproducibility and anti-fouling effects.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Epinephrine (EP, adrenaline) is one of the largest catecholamine neurotransmitters in the mammalian central nervous system and a hormone possessing various physiological and pharmacological functions [1]. It serves as a chemical mediator for transmitting nerve impulses to efferent organs [2]. EP is secreted from the chromaffin cell of the suprarenal gland which exists as a large organic cation in nerve cells and body fluids [3,4]. It is synthesized naturally in human system from L-phenylalanine and L-tyrosine [5]. Clinically, EP is used as a common emergency health care medicine in the treatment of severe allergic reactions, anaphylaxis, sepsis, emphysema and myocardial infarction [6,7]. It is also used in the treatment of glaucoma [8]. Low levels of EP are found in patients of Parkinson's disease and orthostatic hypotension [9].

High levels of EP are associated with stress and thyroid hormone deficiency [10]. EP prepares the body for actions during perceived emergency situations by boosting the supply of oxygen and glucose to the brain and muscles [11]. It simultaneously elevates the blood sugar level by inducing the conversion of glycogen to glucose in liver and lipolysis in adipose tissue. Hence, it can be used as a potent doping agent and its use is banned by World Anti Doping Agency in competitive games [12]. Therefore, it is necessary to develop a simple, fast and accurate method for the determination of EP which would play an important role in neurophysiology, clinical diagnosis and quality control.

Many analytical methods have been developed for the determination of EP in various samples. These methods include spectrophotometry, fluorimetry, liquid chromatography, capillary electrophoresis, thermal lens microscopy (TLM), chemiluminescence, electrochemiluminescence and flow injection analysis [13,14]. However, these techniques involve cumbersome procedures, expensive instrumentation, lack of selectivity or specificity and prolonged analysis time. Therefore, these techniques are less

* Corresponding author. Tel.: +91 9448756584; fax: +91 8022245831.

E-mail address: ronaldmasc2311@yahoo.co.in (R.J. Mascarenhas).

desirable in the routine analysis of EP. Being an electroactive compound, electroanalytical techniques are commonly employed for the quantification of EP. These techniques make possible a simple, fast-and-inexpensive path to estimate EP with high sensitivity and selectivity [15]. Nevertheless, the electroanalysis of EP faces certain challenges. The redox process of EP occurs at high overpotential due to the sluggish electrode kinetics at traditional bare working electrodes like Au, Ag, Pt, glassy carbon (GC) and graphite. Voltammetric response of EP at these electrodes is very close to the other electroactive biomolecules such as ascorbic acid (AA), dopamine (DA) and uric acid (UA), and their signals usually overlap [16]. Adsorption of EP causes the passivation of the electrode [17]. These facts limit the accuracy and sensitivity of the determination of EP. Hence, it is necessary to resolve these problems by modifying the electrodes with suitable materials. CPE has been widely used in the development of electrochemical sensors for biomolecules because of its simple method of preparation, renewable surface, low background current, acquiescence with various types of modification procedures and above all, its biocompatibility [18].

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [19], these materials have turned out to hold great promise in various fields in science and technology. In the 21st century, the applications of CNTs include lab-on-chip sensors, drug delivery vehicles, conducting nanowires, energy storage devices and electrochemical sensors [20,21]. Electrochemical sensors based on CNTs are reported to have certain advantages such as increased heterogeneous electron transfer rates, prevention of surface fouling, high sensitivity, quick response time and electrocatalytic activity towards wide varieties of compounds [22,23]. Various types of CNT modified electrodes such as CNT-polymer nanocomposite electrodes, CNT-paste electrodes, CNT/sol-gel nanocomposite electrodes and layer-by-layer assembly of CNT film electrodes, have been used as electrochemical sensors for catecholamines [24].

Surfactants have been widely used in electroanalysis because of their ability to improve the properties of the electrode/solution interface [25]. Surfactant modified electrodes have been used as an electrochemical sensor for catecholamines [26–28]. The drop-cast method of modification is endowed with a dual advantage: entire coverage of the electrode surface with the modifier and minimum utilization of the modifier [29]. Hence, it is but natural that this method gets a preference over other methods of modification. There is no report of sodium dodecyl sulfate (SDS) being used in combination with pMWCNTs as an amperometric sensor for the quantification of EP.

In keeping with our endeavor to modify CPE using different materials and also to use them as sensor for different applications [30–36], our objective in the present work was to develop a simple amperometric sensor for the determination of EP by combining properties of pMWCNTs as well as that of SDS. Here, in order to optimize the potential application of the sensor, we have exploited the advantages of MWCNTs such as electrocatalytic activity, favorable charge transfer, good conductivity, good adsorptive properties in combination with the properties of SDS such as increased surface area, high columbic forces and amenability to adsorption on the electrode surface through the hydrophobic end of the chain. The modified electrode was intended to be free from the interference of other molecules so that it would provide a better detection limit and linear dynamic range. To minimize the usage of MWCNTs, we bulk modified the CPE with MWCNTs. In order to investigate a better support to drop cast SDS onto the electrode surface, a parallel study was carried out using CPE bulk modified with oxidized MWCNTs (MWCNTs_{ox}). Our study demonstrates that the CPE bulk modified with pMWCNTs is a better supporting material for this purpose. This inspired us to bulk modify the CPE

with pMWCNTs and use this surface for further modification with SDS by the drop cast method. Electrochemical behavior of EP was thoroughly investigated at the modified electrode. The interference studies were carried out in the presence of other biomolecules. Analytical performance of the modified electrode was examined by estimating the EP in pharmaceuticals and the blood serum. The modification of the electrode in the present study results in a reduction in oxidation overpotential and a better linear dynamic range for EP as compared to our previous report [37].

2. Experimental

2.1. Chemicals and reagents

Epinephrine hydrochloride, dopamine hydrochloride, serotonin hydrochloride (Sigma-Aldrich), L-tryptophan (Trp), L-tyrosine (Tyr), L-cysteine (Cys), UA, and folic acid (FA) were obtained from SRL, acetaminophen (AAP) was procured from Micro Labs Ltd., and AA, KH₂PO₄, H₃PO₄, NaOH pellets, HClO₄, silicone oil, and SDS were from Merck; all the chemicals were of analytical grade and were used as received. All aqueous solutions were prepared with ultra pure water (> 18.2 MΩ cm) from Milli-Q Plus system (Millipore). The stock solutions of 25.0 × 10⁻³ M EP, DA and serotonin (5-HT) were prepared in 0.1 M HClO₄, UA, Cys, FA and Tyr in 0.1 M NaOH and Trp, AAP and AA were prepared in water. Phosphate buffer solutions were prepared from KH₂PO₄ and NaOH and pH was adjusted using H₃PO₄ or NaOH. The graphite powder was obtained from Graphite India Ltd. The thin pristine MWCNTs (NC7000 series), obtained from Nanocyl S.A. (Belgium), are produced via the catalytic carbon vapor deposition (CCVD) process. The MWCNTs were used as received. The MWCNTs have an average diameter of 9.5 nm and length of 1.5 μm.

2.2. Apparatus

All electrochemical experiments were performed using a ChemiLink model EA-201 Electro Analyzer. A conventional three electrode system was used for all electrochemical experiments, which comprises of a bare or modified CPE as working electrode, a platinum wire as auxiliary electrode and all potentials were measured and applied using saturated calomel electrode (SCE) as a reference electrode. The tip of the Lugin capillary was set at a fixed distance from the working electrode surface throughout the experimental studies. The cyclic voltammetric (CV) studies were performed in quiescent solution and the amperometric experiments were carried out under hydrodynamic conditions. The electrochemical experiments and voltammetric curves were recorded at room temperature (~300.0 K). The surface morphology of the electrodes was studied using field-emission scanning electron microscopy (FE-SEM) and the energy dispersive X-ray analysis (EDX) using Quanta 200, FEI, Germany; SUPRA 40 VP, Gemini, Zeiss, Germany. A Philips Tecnai 100 transmission electron microscope (TEM) was used to observe the morphology of MWCNTs. Electrochemical impedance spectroscopy (EIS) was performed using VersaSTAT 3. A digital pH/mV meter (ELICO LI 614) was employed to measure the pH of the prepared buffer solutions.

2.3. Generation of oxygen functionalities on pMWCNTs

Since the oxygen functionalities on the surface of the MWCNTs improve their electrochemical properties, the same were generated by treating 2.2 g of NC7000 with 170.0 mL of a mixture of nitric acid (38.0 mL at 70 wt%) and sulfuric acid (132.0 mL at 98 wt%). This mixture was then heated at 50 °C for 4 h under

Download English Version:

<https://daneshyari.com/en/article/7680850>

Download Persian Version:

<https://daneshyari.com/article/7680850>

[Daneshyari.com](https://daneshyari.com)