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Epinephrine electrochemical sensor based on a carbon paste electrode modified with hydroquinone derivative and graphene oxide nanosheets: Simultaneous determination of epinephrine, acetaminophen and dopamine

Marzieh Dehghan Tezerjani, Ali Benvidi *, Afsaneh Dehghani Firouzabadi, Mohammad Mazloum-Ardakani, Ali Akbari

Department of Chemistry, Faculty of Science, Yazd University, Yazd 89195-741, Iran
Department of Chemistry, Faculty of Science, University of Jiroft, Kerman 89195-741, Iran

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ABSTRACT

In this paper, an electrochemical sensor was constructed for determination of epinephrine based on carbon paste electrode (CPE) modified with graphene oxide (GO) and 2-(5-Ethyl-2,4-dihydroxyphenyl)-5,7-dimethyl-4H-pyrido[2,3-d][1,3]thiazine-4-one (EDDPT) as modifiers. The modified electrode was applied as an electrochemical sensor for oxidation of epinephrine (EP). Under the optimum conditions, the over potential of EP oxidation decreased about 279 mV at the modified CPE more than a non-modified CPE. Electrochemical behavior of EP was investigated on the fabricated electrode by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods, and some kinetic parameters of EP were obtained, too. The linear range and the detection limit for EP were found to be 1.5–600.0 μM and 0.65 μM (based on 3 s/m), respectively using the EDDPT/GO/CPE sensor and the differential pulse voltammetry (DPV) method. Also, the designed electrochemical sensor was applied to determine EP in the drug sample and simultaneous determination of epinephrine (EP), acetaminophen (AC) and dopamine (DA) in human serum solutions.

1. Introduction

Recently, new methods for measuring the various drugs have been introduced such as spectroscopic and electrochemical methods [1]. Characteristics such as higher selectivity, better sensitivity, higher speed, repeatability, cost and time made electrochemical methods more suitable for measurement of some drugs [2]. The electrochemical sensors based on modified electrodes have been improved due to some advantages such as being inexpensive, reproducible, simple analytical method with high detection sensitivity, and ease of miniaturization [3,4]. Carbon paste electrode (CPE) is widely used in electrochemical analysis due to some advantages such as possessing low cost, easy manufacturing, ease of use, low back ground current, wide potential window, high sensitivity and easy modification [5–7]. Epinephrine (EP) and dopamine (DA) are the best known catechol amines, which constitute a group of compounds with an alkyl amine chain attached to a benzene ring with two hydroxyl groups [8]. Epinephrine (EP) as a neurotransmitter is synthesized biologically in the adrenal medulla and sympathetic nerve terminals. It has a key role in the functioning of central nervous system (CNS), renal, hormonal, and cardiovascular system [9]. The existence of abnormal levels of EP causes several diseases such as phaeochromocytoma, hypoglycaemia and myocardial infarction [10]. Several methods have been reported for EP analysis [11–13] and due to electro active nature of EP, it can also be determined electrochemically [14–16].

Also, dopamine (DA) as a catecholamine neurotransmitter plays a key role in the central nervous and hormones in the mammalian system [17]. If the value of DA is lower than normal it may cause some neurological disorders such as Schizophrenia, Huntington's disease, and Parkinson's diseases [18]. Other investigated material in this research was acetaminophen (N-acetyl-p-aminophenol (AC)). It has been used comprehensively as a pharmaceutical pain reliever for patients who are susceptible to aspirin [19]. Therefore a suitable selective, simple, inexpensive, fast, sensitive and accurate detection method is required for determining EP, especially in the presence of DA and AC.

* Corresponding author.
E-mail addresses: abenvidi@yazd.ac.ir, benvidi89@gmail.com (A. Benvidi).

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Recently, various techniques have been developed for biocomponents determination such as enzyme based biosensors [20]. According to the existence of some bio components and drug in the human bodies, some methods have been reported for determination of EP, DA and AC based on the chemical modification of traditional electrode materials [21,22].

Recently, carbon-based nanostructures such as carbon nanofibers, carbon nanotubes (CNTs), and mesoporous carbons have been noticeably used in the construction of modified electrodes. These modified electrodes can be applied in both analytical and industrial electrochemistry, due to their low price, suitable electrocatalytic activity for different redox reactions, possessing a broad potential window, and relatively inert electrochemistry [23–27].

As known, graphene nano sheets, has a single layer of carbon atoms in a honeycomb two-dimensional lattice [28]. The structure of graphene can lead to specific properties such as suitable mechanical strength, large surface area, high conductivity and electron mobility at room temperature. The modified electrodes with graphene have paid more attention due to high electron conductivity and good biocompatibility [29]. Graphene oxide (GO) holds favorable features of electronics and π-π stacking interaction [30]. Other properties of GO are facile synthesis, high water dispensability, tunable surface functionalization, and good biocompatibility [31]. It has various applications such as transparent conductors [32], sensors [33], super capacitors [34], batteries, hydrogen storage [35] and nanocomposite materials [36]. In addition, the electrochemical sensors based on modified electrodes with nanomaterials are applied for the detection and determination of bio components such as EP and DA [37]. So, in the preset research GO nano sheets were used due to the mentioned benefits for electrode modification together with 2-(5-Ethyl-2,4-dihydroxy phenyl)-5,7-dimethyl-4H-pyrido[2,3-d] [1,3] thiazine-4-one (EDDPT).

As mentioned in the present study a novel electrode was fabricated using a modified carbon paste electrode (CPE) with graphene oxide (GO) and EDDPT. The combination of graphene oxide (GO) and EDDPT in the fabrication of EDDPT/GO/CPE for detection of EP was used. Due to the unique properties of GO [38] and using EDDPT, an increase in the peak current and a decrease in the overpotential of EP were observed at the designed electrode compared to the bare CPE. Under optimum conditions, some parameters of epinephrine such as the electron transfer coefficient (α), the electron transfer rate constant (k_s), the diffusion coefficient of species in a 0.1 M alkaline solution (pH = 7) were obtained. The obtained results revealed that the proposed sensor offers several advantages such as high sensitivity, repeatability and good stability. The applicability of the modified electrode was successfully tested by voltammetric determination of EP individually and simultaneous determination of EP, AC and DA.

2. Experimental method and materials

2.1. Instruments and chemicals

The electrochemical experiments were carried out using a potentiostat/galvanostat Autolab model PGSTAT 30 (Eco Chemic, Utrecht, Netherlands) and a NOVA 1.7 software at laboratory temperature (25 ± 1 °C). The working, counter and reference electrodes were, an EDDPT/GO/CPE, a platinum electrode and an Ag/AgCl (sat.), KCl (3 M) electrode, respectively. Graphite powder (particle diameter: 0.10 mm) from Merck was used as the working electrode (WE) substrate. For pH measuring a Metrohm model 691 pH/mV meter was used. Epinephrine, dopamine, acetaminophen and another applied reagents were used with analytical grade (Merck, Darmstadt, Germany). Phosphate buffer solutions (0.1 M) were prepared from 0.1 M H_3PO_4-NaH_2PO_4, and for pH regulating 0.1 M H_3PO_4 or NaOH was used.

2.2. The synthesis procedure of 2-(5-Ethyl-2,4-dihydroxyphenyl)-5,7-dimethyl-4H-pyrido[2,3-d] [1,3] thiazine-4-one (EDDPT) modifier

(2-(5-Ethyl-2,4-dihydroxyphenyl)-5,7-dimethyl-4H-pyrido[2,3-d] [1,3] thiazine-4-one (EDDPT)) as a modifier (Fig. 1) was synthesized by authors using the reported procedure [39]. Briefly, the synthesis of EDDPT is explained as follows: a mixture of 0.248 g 2-amino-4, 6-dimethylnicotinamide (Sigma-Aldrich, 1.5 mmol) and 0.616 g sulfonylbis [(5-ethyl-2,4-dihydroxyphenyl) methanethione] (1.5 mmol) in 10 cm^3 MeOH was heated to reflux for 3 h. The hot mixture was filtered. The filtrate was concentrated and the formed solid was crystallized from 4 cm^3 MeOH to give 0.34 g (68%) orange crystals of product. The obtained results for characterization of modifier by ^{1}H NMR, 13C NMR and IR are listed as follow:

^{1}H NMR (500 MHz, DMSO-d_6): δ = 14.27 (s, 1H), 10.29 (s, 1H), 8.06 (s, 1H), 7.89 (s, 1H), 6.45 (s, 1H), 2.53 (q, J = 7.48 Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H), 1.13 (t, J = 7.48 Hz, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.8, 153.3, 152.2, 147.8, 136.2, 136.0, 128.1, 128.7, 123.1, 123.2, 119.7, 111.2, 102.2, 22.0, 21.0, 19.0, 14.1 ppm; IR (ATR): 3299, 3131, 2967, 1650, 1600, 1556, 1491, 1430, 1390, 1349, 1278, 1249, 1217, 1140, 1032, 900, 874, 732, 680 cm^{-1}.

2.3. The synthesis process of graphene oxide

The graphene nano sheets were synthesized according to the procedure offered in the literature [40]. Briefly, a mixture of graphite/$KMnO_4$ (3:18 g) and a mixture of H_2SO_4/H_3PO_4 (360:40 mL) were prepared at 50 °C. These two mixtures were added by shaking and then stirring for 12 h. Then, the reaction product cooled down to 25 °C and was transferred into ice bath containing 6 mL 30% H_2O_2. The obtained solution was centrifuged and then filtered, and the obtained precipitate was washed with water, 30% HCl, and finally washed twice with 200 mL of ethanol. After sonication for 3 h, a colloidal suspension of graphene oxide nano sheets were obtained in purified water (150 mg/50 mL). Also, the prepared GO was characterized with FT-IR and UV/Vis spectroscopy methods.

2.4. Preparation of EDDPT/GO/CPE sensor

To prepare this electrochemical sensor, at first the ratios of EDDPT, GO and CPE were optimized. Carbon paste was prepared by hand mixing of graphite powder (0.48 g), EDDPT (0.005 g), GO (0.015 g) and Paraffin (Dc 350, Merck) using a mortar and pestle, and then was inserted in the bottom of a glass tube (internal radius: 2 mm and 10 cm long). Electrical contact was performed by pushing a piece of copper wire down the glass tube. When necessary, a fresh surface of electrode was obtained by pushing an excess of the paste out of the tube and polishing with a weighing

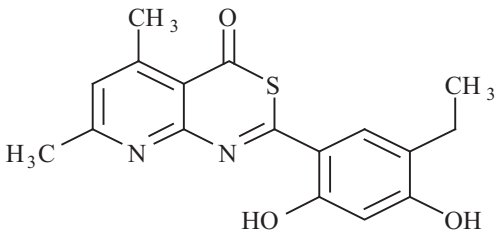

Fig. 1. The structure of 2-(5-Ethyl-2, 4-dihydroxyphenyl)-5,7-dimethyl-4H-pyrido [2,3-d] [1,3] thiazine-4-one (EDDPT) as a modifier.