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A highly sensitive electrochemical sensor for simultaneous voltammetric determination of noradrenaline, acetaminophen, xanthine and caffeine based on a flavonoid nanostructured modified glassy carbon electrode

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ABSTRACT

For the first time, simultaneous voltammetric determination of Noradrenaline (NA), Acetaminophen (AC), Xanthine (XN) and Caffeine (CF) has been investigated at a flavonoid nanostructured sensor. The construction of modified electrode was performed through the electrodeposition of luteolin on a functionalized multi-wall carbon nanotube immobilized on the surface of a glassy carbon electrode (Lt/fMWCNT/MGCE). During modification process, luteolin is oxidized to the corresponding o-quinone derivative and attached to the surface of fMWCNT/GCE through Michael type addition reaction. Electrochemical properties of the modified electrode were investigated by electrochemical impedance spectroscopy (EIS). The Lt/fMWCNT/MGCE offered substantially lower overpotential for electro-oxidation of NA, AC, XN and CF in phosphate buffer solution (pH 7.0) compared with Lt/GCE, fMWCNT/GCE and bare GCE. Differential pulse voltammogram peak currents of NA, AC, XN and CF increased linearly with their concentration at the ranges of 0.7–100.0 μM, 0.9–80.0 μM, 1.0–70.0 μM and 10.0–110.0 μM, respectively, and the detection limits for NA, AC, XN and CF were sequentially 0.53 μM, 0.78 μM, 0.65 μM and 3.54 μM. Furthermore, this electrochemical sensor was successfully implemented for the determination of NA in pharmaceutical samples using standard addition method and the obtained results were found to be satisfactory.

1. Introduction

Noradrenaline (1-(3,4-Dihydroxyphenyl)-2-aminoethanol, Norepinephrine, NA), an endogenous adrenoceptor agonist, is present mainly in mammalian central nervous systems. It is released supra-spinally, spinally and peripherally at sites expressing adrenoceptor such as neurons in the spinal cord [1]. It is used for treating myocardial infarction hypertension, bronchial asthma and organic heart disease. Extreme abnormalities of NA concentration levels may lead to the occurrence of many diseases such as ganglia neuroblastoma, ganglion neuronal, paraganglioma and Parkinson' disease [2].

Acetaminophen, (N-acetyl-p-aminophenol, AC), is a widely used analgesic and antipyretic drug, which is considered safe at therapeutic levels for humans with normal drug use [3]. It is mainly used for the reduction of fever and as a pain killer for the relief of moderate pain associated with backache, headache, arthritis and postoperative pain. Overdoses of acetaminophen produce toxic metabolites accumulation in liver, which may cause severe and sometimes fatal hepatoxicity [4,5] and nephrotoxicity [6].

Xanthine (3,7-dihydro-purine-2,6-dione, XN) is an intermediate of the purine metabolism and is produced after adenosine triphosphate decomposition [7]. The concentration level of XN in biological fluids may provide sensitive indicators of certain pathologic states, especially for xanthinuria. It is a rare genetic disorder where the lack of xanthine oxidase leads to high concentration of XN in body fluids and can cause health problems such as renal failure.

Caffeine (1,3,7-trimethylxantine, CF) is a natural alkaloid belong to N-methyl derivatives of xanthine. It is found in various kinds of beverages such as coffee, Coca-Cola and tea. It has many physiological effects, such as gastric acid secretion, diuresis, and stimulation of the central nervous system [8]. Caffeine is used therapeutically in combination with nonsteroidal anti-inflammatory drugs in analgesic formulations. However, high amounts of caffeine can cause trembling, nausea, nervousness and seizures [9] and mutation effects such as inhibition of DNA [10]. Drugs consisting of CF (as a XN derivative) and AC combination are mostly used as pain relief, central nervous system stimulant and an analgesic agent [6,11,12]. This combination produces a significant reduction in dopamine release and a dramatic increase in NA release from striatal slices

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[13]. Extreme abnormalities of NA concentration levels may lead to the occurrence of many diseases [2]. Therefore, it is very important to develop a simple and rapid method for simultaneous determination of these biomolecules in routine analysis. Several methods for the determination of these biomolecules have been described in literature including liquid chromatography [14], spectrophotometry [15] and capillary electrophoresis [16,17]. However, most of these methods are complicated because they need derivatization or combination with various detection methods. Compared to these options, electrochemical methods have the advantages of high sensitivity, low cost and simple instrumentation [18].

Currently, much attention has been focused on developing nanomaterials, which are used for signal amplification in electrochemical sensors. Nanomaterials are usually used to take advantage of a larger surface area for biomolecules to be immobilized. This generally increases the number of binding sites available for the detection of a specific chemical analyte [19]. Various types of nanomaterials are used in electrochemical sensors. Carbon nanotubes (CNTs) [20] are one of the most exciting materials because of their unique electronic, chemical, and mechanical properties [21]. The subtle electronic properties suggest that CNTs, when used as an electrode material in electrochemical reactions, have the ability to promote electron-transfer reactions, which represents a new application of CNTs [22,23].

Among the electrode modifiers reported in literature, flavonoids (especially contain o-dihydroxy catechol) are emerging as potent electron transfer mediator for the electrochemical determinations of biologically important compounds [24,25]. Luteolin (3′,4′,5,7-tetrahydroxyflavone, Lt) is an important member of the flavonoid family, which demonstrates a wide range of biochemical and pharmacological effects, including anti-oxidation, anti-bacteria, anti-inflammatory, anti-carcinogenic and other beneficial properties [26–28]. There have been some reports on the electrochemical behavior of Lt [29,30].

In the present work, as a continuation of our previous studies concerning the development of electrochemical sensors through electrocatalysis for the detection of some important biological compounds [25,31–36], we described the preparation of a modified electrode by electrochemical deposition of luteolin on a functionalized multi-walled carbon nanotube coated glassy carbon electrode (Lt/fMWCNT/MGCE) for selective and sensitive determination of noradrenaline, acetaminophen, xanthine and caffeine, simultaneously. To our best knowledge, no voltammetric procedure exists for simultaneous determination of noradrenaline, acetaminophen, xanthine and caffeine.

2. Experimental

2.1. Chemicals and reagents

Lt, NA, AC, XN and CF were purchased from Sigma–Aldrich and used as received. Stock solutions of Lt, NA, AC, XN and CF were freshly prepared as required. The MWCNT with 99% purity was obtained from Sigma–Aldrich. MWCNTs were chemically functionalized by ultra-sonication in a mixture of sulfuric acid and nitric acid (3:1, v/v) for 8 h (named fMWCNTs). fMWCNTs were washed with deionized water and separated by centrifuging three times. The fMWCNTs were immobilized onto the glassy carbon electrode, using ethanol as dispersing agent. All other reagents were analytical grade.

2.2. Apparatus

Electrochemical experiment including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy techniques (EIS) were recorded with an Autolab potentiostat/galvanostat (PGSTAT30, ECOCHEMIE, Netherlands) controlled by personal computer. The experimental conditions for voltammetric measurements and EIS were controlled with general purpose electrochemical system (GPES) and frequency response analyzer (FRA) software, respectively. The measurements were carried out using a conventional three-electrode cell using an Ag|AgCl|KCl (3 M) electrode as the reference and a Pt wire as the counter (auxiliary) electrode. The morphological characterizations of all electrodes have been examined by means of scanning electrochemical microscopy, SEM (TESCAN, VEGA II). A digital pH-meter (Ion Analyzer 250, Corning) with precision of ±0.001 was used to read the pH value of the buffered solutions. A glassy carbon disk electrode (Azar electrode Co., Iran) with a geometrical area of 0.0254 cm^2, bare or modified, was used as working electrode. The experiments were carried out at room temperature. All solutions were prepared in twice distilled water.

2.3. Electrode preparation

Prior to modification, the bare GCE was first polished with 0.05 μm alumina slurry using a polishing cloth to produce a mirror-like surface. Then it was rinsed thoroughly with distilled water, and sonicated in mixture of ethanol and water (1:1, v/v) for 5 min. The glassy carbon electrode was then pretreated in 0.1 M sodium bicarbonate solution with cyclic voltammetry in potential range from −0.5 V to 1.0 V at a scan rate of 50 mV s^{-1} by 20 cycles (named activated GCE). 1.0 mg fMWCNT was dispersed in 1.0 mL ethanol with the aid of ultrasonic agitation to give a 1.0 mg mL^{-1} black solution. The carboxylic groups of fMWCNTs were confirmed by FT-IR with stretching bands of carboxylic acid groups at 1710 cm^{-1} (not shown). 2.0 μL of the black solution was cast onto the activated GCE surface and then solvent was evaporated at room temperature for 5 min to prepare the fMWCNT/GCE. Finally to prepare Lt/fMWCNT/MGCE, the fMWCNT/GCE was rinsed with twice distilled water and was placed in a 0.1 mM solution of luteolin in 0.1 M PBS (pH 7.0), and it was modified by five cycles of potential sweep between −0.2 and 1.0 V at 50 mV s^{-1}. During this process, a deposited layer of luteolin is attached to the surface of fMWCNT/GCE. Subsequently, the modified electrode was rinsed with water to remove any physically adsorbed substances and placed in buffer solution (pH 7.0). To fabricate luteolin modified GCE (Lt/GCE), the activated GCE was placed in a 0.5 mM solution of luteolin in 0.1 M PBS (pH 7.0). It was modified with the same procedure that was described for Lt/fMWCNT/MGCE.

As well known, oxygen-containing groups are formed on the surface of carbon nanotubes by chemical treatment such as nitric acid [37]. The amount and type of oxygen-containing functional groups depends on the treatment methods. In the case of nitric acid, formation of acid groups like carboxyl and lactol is reported [38,39]. The carboxyl and/or other oxygen containing groups on the fMWCNT/MGCE surface can behave as nucleophiles against the o-quinone ring (as Michael acceptor) formed from luteolin oxidation, leading to bond formation between luteolin and surface active functional groups and hence to the deposition of luteolin on the fMWCNT/MGCE surface (Scheme 1).

3. Results and discussion

3.1. Characterization of Lt/fMWCNT/MGCE

Fig. 1 shows the cyclic voltammograms of Lt/fMWCNT/MGCE and Lt/GCE in a 0.1 M blank phosphate buffer solution (pH 7.0) as the supporting electrolyte (at potential scan rate 20 mV s^{-1}). It can be seen that the oxidation and reduction peak currents at the surface of Lt/fMWCNT/MGCE were larger than those obtained