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Selective voltammetric determination of norepinephrine in the presence of acetaminophen and tryptophan on the surface of a modified carbon nanotube paste electrode

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ABSTRACT

A new electrochemical sensor for the determination of norepinephrine (NE), acetaminophen (AC) and tryptophan (TRP) is described. The sensor is based on carbon paste electrode (CPE) modified with 5-mino-3′,4′-dimethyl-biphenyl-2-ol (5ADB) and takes the advantages of carbon nanotubes (CNTs), which makes the modified electrode highly sensitive for the electrochemical detection of these compounds. Under the optimum pH of 7.0, the oxidation of NE occurs at a potential about 170 mV less positive than that of the unmodified CPE. Also, square wave voltammetry (SWV) was used for the simultaneous determination of NE, AC and TRP at the modified electrode.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], they have received considerable attention in the fields of biotechnology and medicine due to their unique optical, magnetic, electronic and chemical properties, which differ greatly from those of the bulk material [2]. There are four main advantages to the use of a nanotube-modified electrode compared with a macroelectrode: high effective surface area, mass transfer, catalysis and control over local microenvironment [3,4]. The catalytic properties of some nanotubes can cause a decrease in the overpotential or producing a more reversible voltammetry than that displayed by the same material in a macroelectrode form. In addition, CNTs can effectively promote an electron-transfer reaction. The better performance of the CNT electrode compared to carbon electrode may be due to the carbon nanotube dimensions, the electronic structure, and the topologic defects present on the tube surface [5–9]. Several types of CNT electrodes have been reported, including CNT film coated electrode [10], CNT powder microelectrode [11], CNT paper electrode [12], and CNT paste electrode [13,14]. Carbon nanotube paste electrodes (CNPE) are prepared in an easy, fast and effective way using mineral oil as binder. The resulting CNPE not only retains the advantages of the classical carbon paste electrode (CPE) such as low background currents, the feasibility to incorporate different substances, easy renewal and composite nature, but also keeps the ability of the CNTs to promote electron-transfer reactions. CNPE shows considerable improvements in the electrochemical behavior of biologically important compounds [15–17].

The electrochemical determination of biomolecules has been intensively investigated over the past two decades. Among these biomolecules, norepinephrine (NE) is one of the most important catecholamine neurotransmitters in the central nervous system [18]. NE is one of the derivatives of cathecholamines secreted in the adrenal medulla and plays important physiological roles in the central nervous system. It affects muscle and tissue control, stimulates arteriole contraction, decreases peripheral circulation, and activates lipolysis in adipose tissue. It is also critical in mental disease, heart failure; DNA breaks in cardiac myoblast cells, and diabetes. Recent reports have indicated that NE enhances adhesion of human immunodeficiency virus-1 (HIV-1)-infected leukocytes to cardiac microvascular endothelial cells and also accelerates HIV replication via protein kinase [19].

NE determination is usually executed by high-performance liquid chromatography [20], gas chromatography [21], and spectrophotometry [22]. Meanwhile, NE is an electroactive species and can be detected with electrochemical oxidation at various modified electrodes [23–25].

Acetaminophen (AC) is a widely used analgesic antipyretic drug with actions similar to aspirin. It is a suitable alternative for the patients who are sensitive to aspirin and is safe up to therapeutic doses. Unfortunately, easy availability has resulted in its increased use in attempted suicides. Hence, the need has arisen for the development of rapid and reliable methods for the determination of AC

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concentration. Many methods have been used for the determination of AC in pharmaceutical formulations and biological fluids including titrimetry, UV–vis spectrophotometry, spectrofluorimetry, near infrared transmittance spectroscopy, and chromatography. Also, electrochemical methods have attracted much attention because of their quick response, high sensitivity, as well as ability to miniaturize [26–29].

Tryptophan (2-amino-3-(1H-indol-3-yl)-propionic acid, TRP), is an essential amino acid for humans and a precursor for serotonin (a neurotransmitter), melatonin (a neurohormone), and niacin [30]. It has been implicated as a possible cause of schizophrenia in people who cannot metabolize it properly. This compound is sometimes added to dietary, food products and pharmaceutical formulas due to the scarce presence in vegetables [31]. Therefore simple, sensitive and less expensive detection of TRP is of great interest. Therefore, various methods have been reported for the determination of TRP. Concentration of amino acids in biological samples is low; therefore it is necessary to use a highly sensitive method that provides determination of these analytes at subordinate concentrations. Electrochemical analytic technique is an attractive method due to simplicity, low expense, high sensitivity and possibility of miniaturization [32–35].

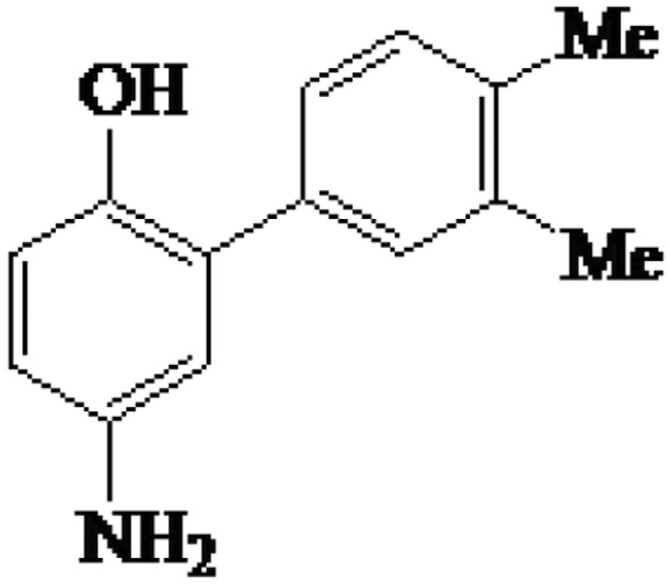
TRP is the essential amino acid that plays an integral role in the synthesis of the neurotransmitter serotonin (5-HT) [36]. AC administration is known to increase brain 5-HT levels because AC alters TRP metabolism by inhibiting tryptophan 2, 3-dioxygenase (TDO) thus increasing the availability of TRP for the production of 5-HT [37] and 5-HT is known to play a role in NE release in the brain [38,39]. Therefore the simultaneous determination of NE, AC and TRP is important.

Therefore, in the continuation of our recent studies concerning the preparation of modified electrodes [6,17,19,24,26,32,33,40–42], in the present work, we describe the preparation of a new electrode composed of CNPE modified with 5-amino-3′,4′-dimethyl-biphenyl-2-ol (Scheme 1) (5ADBCNPE) and investigate its performance for the electrocatalytic determination of NE in aqueous solutions. We also evaluate the analytical performance of the modified electrode for quantification of NE in the presence of AC and TRP.

2. Experimental

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 12, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the (5ADBCNPE) were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 827 pH/Ion Meter was used for pH measurements.



Scheme 1. Structure of 5-mino-3′,4′-dimethyl-biphenyl-2-ol (5ADB).

All solutions were freshly prepared with double distilled water. NE, AC, TRP and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Graphite powder and paraffin oil (DC 350, density = 0.88 g cm^{-3}) as the binding agents (both from Merck) were used for preparing the pastes. Multiwalled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, i.d. between 5 and 10 nm, and tube length from 0.5 to 200 μm were prepared from Nanostructured & Amorphous Materials, Inc. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–9.0. 5-amino-3′,4′-dimethyl-biphenyl-2-ol was synthesized in our laboratory as reported previously [6].

2.2. Preparation of the electrode

The 5ADBCNPEs were prepared by hand mixing 0.01 g of 5ADB with 0.89 g graphite powder and 0.1 g CNTs with a mortar and pestle. Then, ~0.7 mL of paraffin oil was added to the above mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, 5ADB modified CPE electrode (5ADB-CPE) without CNTs, CNT paste electrode (CNPE) without 5ADB, and unmodified CPE in the absence of both 5ADB and CNTs were also prepared in the same way.

3. Results and discussion

3.1. Electrochemical properties of 5ADBCNPE

To the best of our knowledge there is no prior report on the electrochemical properties and, in particular, the electrocatalytic activity of 5ADB in aqueous media. Therefore, we prepared 5ADBCNPE and studied its electrochemical properties in a buffered aqueous solution (pH 7.0) using CV (Fig. 1). It should be noted that one of the advantages of 5ADB as an electrode modifier is its insolubility in aqueous media. Experimental results showed reproducible, well-defined, anodic and cathodic peaks with E_{pa} = 0.28 V and E_{pc} = 0.18 V. The observed peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 100 mV, was greater than the value of 59/n mV expected for a reversible system [43], suggesting that the redox couple of 5ADB in 5ADBCNPE has a quasi-reversible behavior in aqueous medium. The effect of the potential scan rate (ν) on electrochemical properties of the 5ADBCNPE was also studied by CV. Plots of the both anodic and cathodic peak currents (I_p) were linearly dependent on ν in the range of 10 to 800 mV s^{-1} (Fig. 1A), indicating that the redox process of 5ADB at the modified electrode is diffusionless in nature.

The apparent charge transfer rate constant, k_s, and the charge transfer coefficient, α, of a surface-confined redox couple can be evaluated from CV experiments by using the variation of anodic and cathodic peak potentials with logarithm of scan rate, according to the procedure of Laviron [44]. Fig. 1B shows such plots, indicating that the E_p values are proportional to the logarithm of scan rate for ν values higher than 3 V s^{-1} (Fig. 1B). The slopes of the plots in Fig. 1B can be used to extract the kinetic parameters α_c and α_a (cathodic and anodic transfer coefficients, respectively). The slope of the linear segments is equal to $-2.303\ RT/\alpha nF$ and $2.303\ RT/(1-\alpha)nF$ for the