



Fabrication of a nanostructure-based electrochemical sensor for simultaneous determination of epinephrine and tryptophan



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ABSTRACT

A carbon-paste electrode modified with vinylferrocene and carbon nanotubes (CNTs) was used for the sensitive and selective voltammetric determination of epinephrine. The mediated oxidation of epinephrine at the modified electrode was investigated by cyclic voltammetry (CV). Square wave voltammetry (SWV) of epinephrine at the modified electrode exhibited two linear dynamic ranges with a detection limit of 3.0×10^{-8} M. SWV was used for simultaneous determination of epinephrine and tryptophan at the modified electrode, and quantitation of epinephrine and tryptophan in some real samples by the standard addition method.

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1. Introduction

Epinephrine (1-(3,4-dihydroxyphenyl)-2-methyloaminoethanol), a hormone secreted by the medulla of adrenal glands [1], is an important catecholamine neurotransmitter in the mammalian central nervous system [1]. Presence of epinephrine in the body affects the regulation of blood pressure and the heart rate, lipolysis, immune system, and glycogen metabolism. Low levels of epinephrine have been found in patients with Parkinson's disease [2]. From point of view of the medicine, it is a drug for emergencies treatment in severe allergic reaction, cardiac arrest and sepsis [3]. Therefore, the quantitative determination of epinephrine concentration in different human fluids, such as plasma and urine, is important for developing nerve physiology, pharmacological research and life science [4]. Compared to other choices, electrochemical methods provide useful alternatives since they allow faster, cheaper, safer analysis and high sensitivity [5–11].

L-tryptophan is one of the essential amino acids in protein biosynthesis of living organisms. Tryptophan concentration is a sensitive parameter to monitor the biochemical balance of the brain. It is very essential for people with sleep deprivation, anxiety and mood enhancement due to its ability to increase brain levels of serotonin and melatonin. Tryptophan functions as a biochemical precursor for serotonin (a neurotransmitter) and melatonin (a neurohormone) [12]. It is a routine constituent of most protein-based dietary foods. The common side effects in high dosage of tryptophan are drowsiness, nausea, dizziness, and loss of appetite. Therefore a rapid, simple, sensitive and low cost detection method for tryptophan is of great interest. To date, various methods have been reported on determination of tryptophan such as chemiluminescence [13], fluorometry [14], capillary electrophoresis [15], high-performance liquid chromatography [16] and spectrometry [17]. Electrochemical techniques have gained much attention for its high sensitivity, high accuracy and simple operation mode. The poor electron transfer behavior with high overpotential for tryptophan oxidation at the conventional electrodes has resulted in

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efforts to develop novel chemically modified electrodes (CMEs) to improve the sensitivity and reduce the overpotential for the electrochemical oxidation of tryptophan [18–22].

Electrochemical techniques in the field of pharmaceutical analysis have developed due to their simplicity, reasonable accuracy and precision, low cost, and rapidity. There is no need for derivatization or time-consuming extraction steps in comparison with other techniques because of less sensitivity of electroanalytical methods to the matrix effects [23–56]. Carbon-paste electrodes (CPEs) are widely utilized to perform the electrochemical determinations of a variety of biological and pharmaceutical species owing to their low residual current and noise, ease of fabrication, wide anodic and cathodic potential ranges, rapid surface renewal, and low cost. Moreover, chemically modified electrodes (CMEs) can be easily prepared by adding different substances to the bulk of CPEs in order to increase sensitivity, selectivity, and rapidity of determinations [57–59].

The integration of nanotechnology with electrochemistry is expected to produce major advances in the field of electrochemical sensors. There is growing interest in developing new enhanced materials and designing novel sensors with controlled features on a nanometric scale. The unique properties of metal nanoparticles (enhanced mass transport, high surface area and improved signal-to-noise ratio) can often be advantageous in electroanalytical techniques [60]. Carbon nanotubes (CNTs) are gaining popularity in the electrochemistry as a viable nanomaterial due to their extraordinary electronic, chemical and structural characteristics. CNTs display intrinsic properties that include high surface areas, high electrical conductivities, and their inherent size and hollow geometry, which make them extremely attractive as substrates for heterogeneous catalysis [61–63].

In the present work, we describe the preparation of a new electrode composed of CNPE modified with vinylferrocene (VFCNPE) and investigate its performance for the electrocatalytic determination of epinephrine in aqueous solutions. We also evaluate the analytical performance of the modified electrode for quantification of epinephrine in the presence of tryptophan.

2. Experimental

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302 N, 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 (Azar electrode, Urmia, Iran), a platinum wire (Azar electrode, Urmia, Iran), and the (VFCNPE) were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 827 pH/Ion meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. Epinephrine, tryptophan 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 agent (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. (USA). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0. Vinylferrocene was purchased from Sigma Aldrich (USA).

2.2. Preparation of the electrode

The VFNPEs were prepared by hand mixing 0.01 g of VF 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, VF modified CPE electrode (VF-CPE) without CNTs, CNTs paste electrode (CNPE) without VF, and unmodified CPE in the absence of both VF and CNTs were also prepared in the same way.

3. Results and discussion

3.1. Electrochemical properties of VFCNPE

VFCNPE was constructed and its electrochemical properties were studied in a 0.1 M PBS (pH 7.0) using CV. The experimental results show well-defined and reproducible anodic and cathodic peaks related to vinylferrocene/vinylferricenium ion redox system, with E_{pa} , E_{pc} and E° of 0.41, 0.3 and 0.355 V vs. Ag/AgCl/KCl (3.0 M) respectively. The observed peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 110 mV, was greater than the value of $59/n$ mV expected for a reversible system [41], suggesting that the redox couple of VF in VFCNPE has a quasi-reversible behavior in aqueous medium.

3.2. Influence of pH

The electrochemical behavior of epinephrine is dependent on the pH value of the aqueous solution, whereas the electrochemical properties of Fc/Fc⁺ redox couple are independent on pH. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of epinephrine. Thus the electrochemical behavior of epinephrine was studied in 0.1 M PBS in different pH values ($2.0 < \text{pH} < 11.0$) at the surface of VFCNPE by cyclic voltammetry. It was found that the electrocatalytic oxidation of epinephrine at the surface of VFCNPE was more favored under acidic conditions than in basic or neutral medium. This appears as a gradual growth in the anodic peak current and a simultaneous

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