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Electrocatalytic and simultaneous determination of isoproterenol, uric acid and folic acid at molybdenum (VI) complex-carbon nanotube paste electrode

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ABSTRACT

This paper describes the development, electrochemical characterization and utilization of a novel modified molybdenum (VI) complex-carbon nanotube paste electrode for the electrocatalytic determination of isoproterenol (IP). The electrochemical profile of the proposed modified electrode was analyzed by cyclic voltammetry (CV) that showed a shift of the oxidation peak potential of IP at 175 mV to less positive value, compared with an unmodified carbon paste electrode. Differential pulse voltammetry (DPV) in 0.1 M phosphate buffer solution (PBS) at pH 7.0 was performed to determine IP in the range from 0.7 to 600.0 μM, with a detection limit of 35.0 nM. Then the modified electrode was used to determine IP in an excess of uric acid (UA) and folic acid (FA) by DPV. Finally, this method was used for the determination of IP in some real samples.

1. Introduction

Nanomaterials have received great attention in recent years in different fields due to their enormous potential. Among them, carbon nanotubes (CNTs) have become the subject of intense investigation since their discovery in 1991 by Iijima [1]. Such considerable interest reflects the unique behavior of CNTs, including their remarkable electrical, chemical, mechanical and structural properties that make them a very attractive material for a wide range of applications [2–4]. The advantages of both single-wall (SW) and multi-wall (MW) CNTs, such as high surface area, good conductance, favorable electronic properties and electrocatalytic effect make them adequate for the construction of electrochemical sensors and biosensors [5–10].

Isoproterenol (IP) is a sympathomimetic beta adrenergic agonist medication. It had been used for bradycardia or heart block. By activating β1-receptors on the heart, it induces positive chronotropic, dromotropic, and inotropic effects [11]. IP has positive inotropic and chronotropic effects on the heart. In skeletal muscle arterioles it produces vasodilatation. It's inotropic and chronotropic effects elevate systolic blood pressure, while its vasodilatory effects tend to lower diastolic blood pressure. This drug is used to bronchitis, cardiac chock and heart attack. Nevertheless, the excess of this substance can causes heart failure and arrhythmias [12]. Therefore, determination of this compound is very important. Various methods including chromatography [13], chemiluminescence [14], spectrophotometry [15], and electrochemical methods [16–20] have been used for the detection of IP.

Also, as one of the important biomolecules present in physiological fluids, uric acid (UA) is the ultimate product of catabolism of the purine nucleosides [21]. Abnormal UA level is symptoms of several clinical conditions such as kidney damage, gout, hyperuricaemia and Lesch–Nyan diseases [22]. Hence, explore a simple, accurate and reliable determination method for UA becomes urgent. Various methods have been attempted, such as chemiluminescence [23], chromatography [24], spectrofluorometry [25] and enzymatic methods [26]. While these methods are often time consuming, inherently expensive or complicate, electrochemical methods for determination of UA present advantages such as simple, rapid, inexpensive and easy to use [27–31].

Folic acid (FA) is a water-soluble vitamin and can act as coenzyme in the transfer and utilization of one-carbon groups and in the regeneration of methionine from homocysteine [32]. Deficiency of FA is a common cause of anaemia and it is thought to increase the likelihood of heart attack and stroke. Many studies suggest that diminished folate status is associated with enhanced carcinogenesis as FA with vitamin B_{12} participates in the nucleotide synthesis, cell division and gene expression [33]. Periconceptual supplementation of FA has been demonstrated to reduce significantly the incidence and reoccurrence of neural tube defects, such

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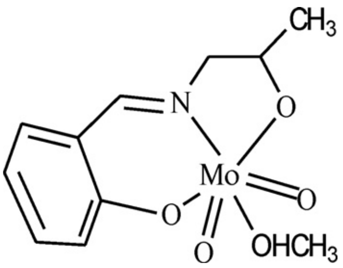

Scheme 1. Structure of dioxo-molybdenum (VI) complex [$MoO_2(L)(CH_3OH)$].

as spina bifida of women [34]. In January 1998, the US Food and Drug Administration introduced mandatory fortification of cereal grain products with FA at a concentration of 140 mg/100 g [35]. In the UK, the Department of Health proposed fortification of flour with FA at 240 mg/100 g [36].

Numerous methods for the measurement of FA are available, including enzyme-linked immunosorbent assays (ELISAs) [37], liquid chromatography/tandem mass spectrometry (LC/MS/MS) [38], capillary electrophoresis (CE) [39], microemulsion electrokinetic chromatography (MEEKC) [40] and high-performance liquid chromatography (HPLC) [41]. As FA is an electroactive component, some electrochemical methods have been reported for its determination [42–48].

To our search, no study has reported the simultaneous electrocatalytic determination of IP, UA and FA by using modified carbon nanotube paste electrodes. Thus, in this paper, we described initially the preparation and suitability of a molybdenum (VI) complex-modified carbon nanotube paste electrode (MC-CNPE) as a new electrode in the electrocatalysis and determination of IP in an aqueous buffer solution, then we evaluated the analytical performance of the modified electrode in quantification of IP in the presence of UA and FA.

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 MC-CNPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 691 pH/Ion Meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. IP, UA, FA 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 10 to 30 μm were prepared from Nanostructured & Amorphous Materials, Inc. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0. Dioxo-molybdenum (VI) complex [$MoO_2(L)(CH_3OH)$] was synthesized in our laboratory as reported previously [49] (Scheme 1).

2.2. Preparation of the electrode

The MC-CNPEs were prepared by hand mixing 0.01 g of MC with 0.89 g graphite powder and 0.10 g CNTs with a mortar and pestle. Then, ~0.7 mL of paraffin 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 10 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.

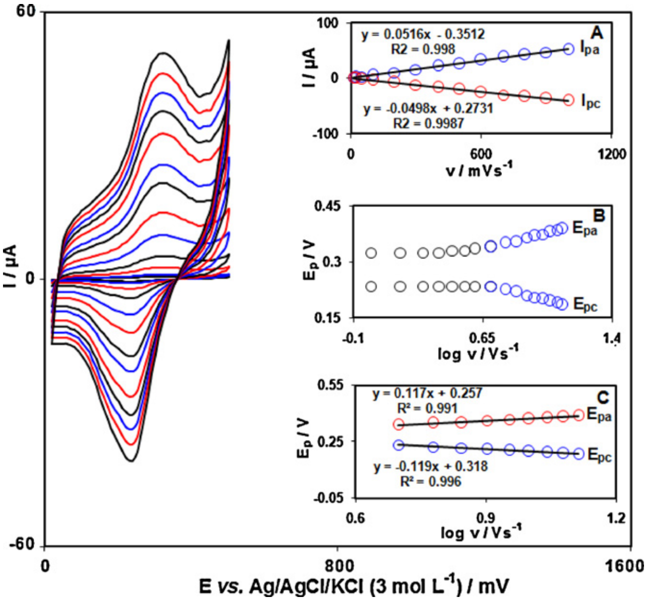

Fig. 1. CVs of MC-CNPE in 0.1 M PBS (pH 7.0), at various scan rates, from inner to outer, 10, 20, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mV s^{-1}. Insets: variation of (A) I_p *vs.* scan rate; (B) variation of E_p *vs.* the logarithm of scan rates and (C) variation of E_p *vs.* the logarithm of the high scan rates.

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

3. Results and discussion

3.1. Electrochemical properties of modified MC-CNPE

To the best of our knowledge there is no prior report on the electrochemical properties and, in particular, the electrocatalytic activity of MC in aqueous media. Therefore, we prepared MC-CNPE and studied its electrochemical properties in PBS (pH 7.0) using CV (Fig. 1). It should be noted that one of the advantages of MC as an electrode modifier is its insolubility in aqueous media. Experimental results showed reproducible, well-defined, anodic and cathodic peaks with E_{pa}, E_{pc} and $E^{\circ\prime}$ of 0.325, 0.235 and 0.28 V *vs.* Ag/AgCl/KCl (3.0 M), respectively. The observed peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 90 mV, was greater than the value of 59/*n* mV expected for a reversible system [50], suggesting that the redox couple of MC in MC-CNPE has a quasi-reversible behavior in aqueous medium. The effect of the potential scan rate (ν) on electrochemical properties of the MC-CNPE 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 10–1000 mV s^{-1} (Fig. 1A), indicating that the redox process of MC at the modified electrode is diffusionless in nature [50].

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 [51]. Fig. 1B shows such plots, indicating that the E_p values are proportional to the logarithm of scan rate for ν values higher than 5 V s^{-1} (Fig. 1C). The slopes of the plots in Fig. 1C