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Voltammetric behavior of tiopronin on carbon paste electrode modified with nanocrystalline $Fe_{50}Ni_{50}$ alloys

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ABSTRACT

A simple and sensitive sensor was proposed for the rapid determination of tiopronin (TP) using a carbon paste electrode (CPE) modified with synthesized nanocrystalline Ni_{50}–Fe_{50} alloys (nano-Ni_{50}–Fe_{50}) and ferrocene carboxylic acid (FcCa). The synthesized nano-Ni_{50}–Fe_{50} was characterized by different methods such as TEM, SEM and XRD. The electrochemical oxidation of TP on the nano-Ni_{50}–Fe_{50}/FcCa carbon paste electrode (nano-Ni_{50}–Fe_{50}/FcCa/CPE) was studied. The nano-Ni_{50}–Fe_{50}/FcCa/CPE exhibited good electrocatalytic properties towards oxidation of TP in phosphate buffer solution (pH 7.0) with an overpotential of about 500 mV lower than that of the bare electrode. The rate constant for the catalytic oxidation of TP was evaluated by rotating disk voltammetry and the value of k_c was found to be 3.2×10^7 $cm^3 mol^{-1}$ s^{-1}. Using differential pulse voltammetry (DPV), the determination of TP was explored at the modified electrode. The results indicated that the differential pulse response of TP was linear with its concentration in the range of 0.01–50.0 μM. The detection limit was 7.46 nM (S/N = 3). The proposed sensor was successfully applied for the determination of TP in tablet and urine samples.

1. Introduction

Tiopronin (2-mercaptopropionylglycine; TP) is a pharmaceutically important thiol drug used for the treatment of cystinuria, rheumatoid arthritis and heavy metal poisoning, even at low doses [1,2]. TP is also used in the treatment of hepatic diseases and as a mucolytic in respiratory disorders [3]. TP reduces cystine excretion and stone recurrences in up to 70% of patients [4]. Urinary excretion of TP after single oral dose (500 mg) was mainly confined to the first 6 h (74%) and was almost complete (98%) within 12 h [5]. It was similar in efficacy to penicillamine (PA) as a sulfhydryl compound. However, TP is preferred because the incidence of its side effects is lower than PA [6,7]. Numerous side effects including ageusia or dysgeusia rash, pemphigus, thrombocytopenia, myasthenia gravis, agranulocytosis, polymyositis, proteinuria, or hypersensitivity nephritic syndrome have been reported for TP in subjects who had started abrupt incremental dosing of the drug [8]. Therefore, determination of TP is an important aspect of quality control in pharmaceutical formulations and its determination in biological fluids is also important for medical field. Hence, it is very important to develop a simple, fast, economically advantageous, sensitive and accurate detection method for TP.

A range of methods including spectrometric [9], chromatographic [10–14], and chemiluminescence [15,16] have been proposed for TP determination. In most cases, several drawbacks, such as being time-consuming and low sensitivity, limit their practical applications [17,18]. To date, electrochemical techniques have been narrowly explored for TP detection. Compared with the other analytical techniques, electroanalytical methods have the advantages of simplicity, low expense, and high sensitivity [19–24]. However, at traditional electrode surfaces, TP only exhibits sluggish voltammetric response. Thus, considerable efforts are necessary to develop modified electrodes to enhance the voltammetric response and analytical performance for TP detection. Many different strategies have been employed for the electrode modifications [25–31]. Among them, preparing bulk-modified electrode materials has been of particular interest [32–34]. It has been shown that bulk modification is flexible and easy to perform. When the electrode surface has become inactive by, for instance, poisoning of the catalyst by impurities, a fresh surface layer containing the catalyst is easily obtained by polishing.

Metal nanoparticles possess an extreme small size, a high specific surface area, a high surface-to-volume ratio and unique physicochemical characteristics [35]. The use of nanoparticle superstructures for the creation of electrochemical devices is an extremely promising prospect. These superstructures hold important applications as catalysts. Several advantages of nanomaterial as electrode materials have been attested for the analysis of diversified chemicals of cancer investigation, food quality, clinical, pharmaceutical and environmental interest [36–42]. Recently several types of nanoparticles have been successfully introduced such as Au [43], Cu [44], Ag [45] and $Ni(OH)_2$ [46] for fabrication of sensors. Also, over the past decades, Fe–Ni and other bimetallic nanoparticles have been widely investigated for applications in magnetic

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devices, such as sensors, transformers, inductive devices and electric motors [47]. The bimetallic nanoparticles are promising materials that exhibit high permeability [48]. High surface-to-volume ratio for nanomaterial is also a definite asset towards the development of electrochemical sensing platforms for single-molecule detection [49–51].

Due to their catalytic activity for a wide range of redox processes, organometallics are a possible choice for preparing voltammetric modified (bio)sensors [52–54]. The sensitivity and selectivity of the sensors can be greatly improved as a result of the electrocatalysis by organometallics [55–57]. Ferrocene and its derivatives as organometallic compounds have attracted much attention in recent years due to their electrochemically reversible behavior, pH-independence of the redox potential and good stability [52]. Since they can be poorly adsorbed onto the electrode surfaces, many methods have been used to improve their attachment to the electrode surfaces such as incorporation into carbon paste electrodes. The modified electrodes based on the incorporation of catalysts within carbon paste are gaining considerable attention. Short response times accrue from the absence of supporting membranes and the close proximity of the catalytic and graphite site. For example, Gholivand and Khodadadian [58] studied the electrocatalytic activity of a graphene/ferrocene composite to simultaneous determination of captopril and hydrochlorothiazide at its modified carbon paste electrode. Murr et al. reported an amperometric biosensor using diaphorase/ferrocene modified carbon paste electrodes for electrocatalytic oxidation of NADH [59]. The electrocatalytic behavior of these sensors towards oxidation of species is believed to be mediated by the Fe^{III}/Fe^{II} couple [52].

In this paper, we described the electrocatalytic oxidation and differential pulse voltammetry detection of TP by using an electrochemical sensor which was prepared by co-incorporation ferrocene carboxylic acid and nanocrystalline Ni_{50}–Fe_{50} alloys in a carbon paste electrode. To the best of our knowledge, there is no report on the application of nanocrystalline Ni_{50}–Fe_{50} alloys/FcCa modified carbon paste electrode (nano-Ni_{50}–Fe_{50}/FcCa/CPE) or other modified electrode for the determination of TP. The electrochemical behavior of TP at nano-Ni_{50}–Fe_{50}/FcCa/CPE, at carbon paste electrode modified with ferrocene carboxylic acid (FcCa/CPE), at nano-Ni_{50}–Fe_{50}/CPE, and at carbon paste electrode (CPE) was investigated. The results showed the superiority of nano-Ni_{50}–Fe_{50}/FcCa/CPE to the other electrodes in terms of both provision of better reversibility and higher sensitivity.

2. Experimental

2.1. Materials

Ferrocene carboxylic acid and TP were obtained from Fluka. Solutions of TP were prepared in twice distilled water prior to use. Phosphate buffer solutions (PBS) were prepared from orthophosphoric acid and its salts in the pH range of 5.0–9.0. Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode substrate. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. The biological samples used in this work were obtained from Medical Diagnostic Laboratory, Sabzevar, Iran. The solvent used for the electrochemical studies was twice distilled water. All other regents used were of analytical grade.

2.2. Instruments

Voltammetric measurements (such as cyclic voltammetry, differential pulse voltammetry and rotating disk electrode) were carried out using a computerized Metrohm (797 VA Computrace, Switzerland). Chronoamperometry and electrochemical impedance spectroscopy were performed using IVIUM compact stat (the Netherlands) that was connected to a Pentium IV personal computer. All electrochemical studies were performed at 25 ± 2 °C with a three-electrode assembly including a carbon paste (unmodified or modified) as a working electrode, an Ag/AgCl/KCl (3 M) electrode as the reference electrode, and a platinum wire as a counter electrode. A digital pH-meter (780 pH meter, Metrohm) with precision of ±0.001 was used to read the pH value of the buffer solutions. X-ray diffraction patterns were recorded using D8 advanced model, product of 2002 in Bruker company (with CuKα radiation; λα = 1.54 Å). Transmission electron microscope (TEM) observations were carried out using a LEO 912AB transmission electron microscope operated at 120 kV. The scanning electron microscopy (SEM) was performed on a VEGA-Tescan scanning electron microscope.

2.3. Preparation of nanocrystalline Ni_{50}–Fe_{50} alloys

The nanocrystalline Ni_{50}–Fe_{50} alloy was synthesized by a published procedure by ball milling of elemental powders [60]. Briefly, mechanical alloying as mixture of pure Fe (99.9%) powder and Ni (99.8%) powder was carried out in a commercial Fritsch Pulverisette 7 planetary ball mill. To prevent oxidation phenomena, the mixed powder was sealed in a cylindrical vial under an argon atmosphere with stainless steel balls. The weight ratio of balls to powder was 30:1. To avoid excessive heating during milling, each 30 min of milling was followed by a stay during 10 min under the argon atmosphere at room temperature. The milling periods of 70 h at 300 rpm was used as optimum time for synthesis of nanocrystalline alloy. XRD measurement patterns reveal the phase and purity of as-obtained products. Fig. 1A shows typical XRD pattern of the pure Fe, pure Ni and nanocrystalline Fe_{50}–Ni_{50} alloy. The peaks at 2θ (45° and 51.8°) resulted from the nanocrystalline Fe_{50}–Ni_{50} alloy (curve c), indicating that the synthesized nanocrystallines are not the mixtures of individual pure Fe (curve a) and pure Ni (curve b) but rather alloy nanostructures [60–62]. According to Scherrer formula [49], the average size of the crystalline structure of the Fe_{50}–Ni_{50} alloys is about 13 nm. The morphology of the nanocrystalline Fe_{50}–Ni_{50} alloys was characterized by SEM and TEM techniques. Fig. 1B shows the SEM images of the synthesized product. Fig. 1C presents a typical TEM image of nanocrystalline Fe_{50}–Ni_{50} alloys. It is clear that in this case, a nanocrystalline Fe_{50}–Ni_{50} was successfully prepared.

2.4. Preparation of working electrode

The nano-Ni_{50}–Fe_{50}/FcCa/CPE was prepared by dissolving the 0.002 g of FcCa with 0.096 g graphite powder and 0.002 g nanocrystalline Fe_{50}–Ni_{50} in diethyl ether and hand mixing with a mortar and pestle. The solvent was evaporated by stirring. A 1:1 (w/w) resulting mixture and paraffin was blended by hand-mixing 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. For comparison, FcCa modified CPE without nano-Ni_{50}–Fe_{50} (FcCa-CPE), nano-Ni_{50}–Fe_{50} paste electrode without FcCa (nano-Ni_{50}–Fe_{50}/CPE), and unmodified CPE in the absence of both FcCa and nano-Ni_{50}–Fe_{50} were also prepared in the same way.

3. Results and discussion

3.1. Direct electrochemical reaction of sensor

Fig. 2A shows the cyclic voltammograms of the different electrodes in 0.1 M PBS (pH 7.0) at scan rate of 50 mV s^{-1}. As shown in Fig. 2A, a pair of redox peaks with separation of peak potential ΔE_p of about 100 mV, appears at the FcCa-CPE (curve b) that can be attributed to the oxidation of the ferrocenecarboxylic acid ($FcCa_{red}$) to ferroceniumcarboxylic acid ($FcCa_{ox}$) at the forward scan and reduction of ferrocenum ions to