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Article

New modified multiwalled carbon nanotubes paste electrode for electrocatalytic oxidation and determination of warfarin in biological and pharmaceutical samples

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ABSTRACT

A novel sensor for the determination of warfarin based on a simple and sensitive method was developed on multiwalled-carbon-nanotube modified $ZnCrFeO_4$ carbon paste electrodes (MWCNT/$ZnCrFeO_4$/CPEs). Cyclic voltammetry, differential pulse voltammetry, chronoamperometry, and electrochemical impedance spectroscopy were used to investigate the electrochemical behavior of warfarin at the chemically modified electrode. According to the results, MWCNT/$ZnCrFeO_4$/CPEs showed high electrocatalytic activity for warfarin oxidation, producing a sharp oxidation peak current at about +0.97 *vs* Ag/AgCl reference electrode at pH = 4.0. The peak current was linearly dependent on warfarin concentration over the range of 0.02–920.0 μmol/L with a detection limit of 0.003 μmol/L. In addition, chronoamperometry was also used to determine warfarin's catalytic rate constant and diffusion coefficient at MWCNT/$ZnCrFeO_4$/CPEs.

1. Introduction

Warfarin is a blood anticoagulant that inhibits the function of vitamin K dependent coagulation. Warfarin is used to inhibit the coagulation of blood to reduce or prevent the chance of developing heart attacks, strokes, and venous and other blood clots. The common side effects of warfarin are easy bruising and bleeding, nausea, vomiting, stomach pain, bloating, gas, or altered sense of taste. The most serious drawback of using warfarin is hemorrhage, which can be life-threatening and even cause death. Therefore, detection of warfarin in biological and clinical samples is very important [1–3]. Several analytical techniques have been developed for determination of warfarin in biological fluid including micellar electrokinetic chromatography electrospray ionization mass spectrometry (MEKC-ESI-MS) [4], supercritical fluid chromatography-tandem mass spectrometry (SFCMS/MS) [5], high performance liquid chromatography (HPLC) using ultraviolet or fluorescence detection [6–12], capillary zone electrophoresis (CZE) [13–15] and square-wave adsorptive cathodic stripping voltammetry with hanging mecury electrode [16]. However, these methods suffer from serious problems such as expensive chemical materials for electrode modification, low stability, and high toxicity, and they are time consuming. Recently, several papers have introduced new modified electrodes for the determination of warfarin in pharmaceuticals and biological fluids like urine and plasma [17–19].

Chemically modified carbon paste electrodes (CPEs) are endowed with many good qualities, such as ease of handling and applicability to anodic oxidations. Different modifiers for carbon paste have been reported in the last years for the electrochemical analysis of drugs. In recent years, magnetic nanoparticles (MNPs) have attracted a growing interest in the development and fabrication of sensors and biosensors. MNPs

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exhibit the best performance at sizes of 10–20 nm owing to supermagnetism, which makes them especially suitable when looking for a fast response, large surface area, and high mass transfer [20,21]. In 2015, Gholivand et al. [17] reported an electrochemical sensor based on Fe_3O_4 MNPs modified CPE for the determination of warfarin. Although this method is sensitive, its application is difficult because of stability limitations. Therefore, a modified material is needed to make them more stable and to prevent their aggregation.

In this work, we describe a novel strategy for the determination of warfarin using a paste electrode containing multiwalled carbon nanotubes (MWCNTs) plus a new magnetic nanoparticles ($ZnCrFeO_4$). The modified electrode has a catalytic effect on the oxidation current of warfarin and it shows advantages in terms of high sensitivity, reproducibility, and selectivity. Moreover, the stability is enhanced greatly compared with previously modified electrodes owing to the introduction of spinel-structured $ZnCrFeO_4$ nanoparticles. The analytical feasibility of the approach is examined by measuring warfarin content in different real samples with satisfactory results.

2. Experimental

2.1. Apparatus

All voltammetric measurements were carried out using an electrochemical system comprising a Metrohm instrument (Herisau, Switzerland), Model 797 VA and a conventional three-electrode cell assembly containing an Ag/AgCl electrode as the reference electrode, a platinum wire as the counter electrode and the MWCNT/$ZnCrFeO_4$/CPEs as the working electrode. All of the potentials were measured and reported *vs* Ag/AgCl reference electrode. The pH of the solutions was controlled with a Corning pH meter (model 146). The structure and morphology of the product were characterized by using X-ray diffraction (XRD) (Holland Philips Xpert, X-ray diffractometer with Cu-K_α radiation) and field emission scanning electron microscope (FE-SEM) (Hitachi S-4160) with gold coating. Fourier-transform infrared spectroscopy (FT-IR) was recorded using a JASCO FT-IR (680 plus). The spectra of solids were obtained using a KBr pellet. The analysis of the chemical composition of the modified electrode was performed using an energy dispersive spectrometer (EDX).

2.2. Chemicals

All chemicals were of analytical reagent grade and purchased from Merck (Darmstadt, Germany) except where otherwise stated. A stock solution of 0.01 mol/L warfarin was prepared by dissolving a suitable amount of sodium warfarin (Sigma-Aldrich) in water and the solution was diluted to 25-mL with water in a 25 mL volumetric flask. Working solutions were prepared by diluting the stock solution with deionized water.

Phosphate buffer solutions (0.10 mol/L) with different pH values were used. Pure graphite powder (particle size <50 μm) and MWCNT (>90% MWCNT basis, with a diameter of 20–30 nm and a length of 5–15 μm) were prepared from Iran's Research Institute of Petroleum Industry. High-viscosity paraffin (d = 0.88 kg/L) was used for the preparation of paste electrodes.

2.3. Preparation of $ZnCrFeO_4$ magnetic nanoparticles

The synthesis of $ZnCrFeO_4$ nanoparticles used for this study followed a method reported by Hamed et al. [21,22]. $Fe(NO_3)_3{\cdot}9H_2O$ (8.07 g), $Zn(NO_3)_2{\cdot}6H_2O$ (5.94 g), and $Cr(NO_3)_3{\cdot}9H_2O$ (8.00 g) were mixed with 100 mL methanol to form a sol and the mixed solution was adjusted to pH∼9 with ammonium hydroxide solution. After stirring the mixture for 20 min at 80 °C, stirring was continued for 24 h at room temperature. The product was washed with twice-distilled water several times and dried at 60 °C. After that, heat treatment of the product was carried out for 1 h at 700 °C, then for another 2 h at 900 °C.

2.4. Preparation of MWCNT/$ZnCrFeO_4$ modified electrode

To eliminate metal oxide catalysts within the nanotubes, MWCNTs were refluxed in 2.0 mol/L HNO_3 for 15 h, and then washed with twice-distilled water and dried at room temperature. HNO_3 usually causes a significant destruction of carbon nanotubes and introduces –COOH groups at the ends or at the sidewall defects in the nanotube structure.

The MWCNT/$ZnCrFeO_4$-modified electrode was prepared by mixing 30 mg of $ZnCrFeO_4$, 120 mg of MWCNT, and 850 mg of graphite powder. Diethyl ether was added and mixed to get a uniform mixture. After evaporation of the diethyl ether, 200 mg paraffin oil was added and the solid was mixed with mortar and pestle to obtain a uniformly wetted paste. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on weighing paper. The multiwalled carbon nanotubes/carbon-paste electrode (CNPE) was prepared in the same way, but without adding $ZnCrFeO_4$. The unmodified CPE was prepared by mixing fine graphite powder with the appropriate amount of paraffin and thorough hand mixing in a mortar and pestle.

2.5. Recommended procedure

MWCNT/$ZnCrFeO_4$/CPEs was polished with white and clean paper. To prepare a blank solution, 10.0 mL of buffer solution (PBS, pH 4.0) was transferred into an electrochemical cell. The initial and final potentials were adjusted to 0.70 and 1.15 V *vs* Ag/AgCl, respectively. The differential pulse voltammogram (DPV) was recorded with pulse amplitude of 100 mV, pulse time of 50 ms, and sweep rate of 50 mV/s to give the blank signal, and labeled as I_{pb}. Then, different amounts of warfarin solution were added to the cell using a micropipette, and the DPV was recorded again to get the analytical signal (I_{ps}). The difference in current ($I_{ps} - I_{pb}$) was considered as a net signal (ΔI) for each of the species. Calibration graphs were prepared by plotting the net peak currents versus warfarin concentra-