Materials Science and Engineering C 69 (2016) 1–11

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Simultaneous determination of ascorbic acid, acetaminophen and codeine based on multi-walled carbon nanotubes modified with magnetic nanoparticles paste electrode

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ARTICLE INFO

Article history:
Received 13 March 2016
Received in revised form 30 May 2016
Accepted 5 June 2016
Available online 7 June 2016

Keywords:
$ZnCrFeO_4$
Multi-walled carbon nanotubes
Ascorbic acid
Acetaminophen
Codeine

ABSTRACT

Based on incorporating $ZnCrFeO_4$ into multi-walled carbon nanotubes paste matrix (MWCNTs/$ZnCrFeO_4$/CPE), a chemically modified electrode was prepared for the simultaneous determination of ascorbic acid (AA), acetaminophen (AC) and codeine (CO). The prepared electrode, MWCNTs/$ZnCrFeO_4$/CPE, was characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The MWCNTs/$ZnCrFeO_4$/CPE showed an efficient electrocatalytic activity for the oxidation of AA, AC, and CO. The separations of the oxidation peak potentials for AA–AC and AC–CO were about 250 mV and 630 mV, respectively. The calibration curves obtained for AA, AC, and CO were in the ranges of 0.4–730.0 μmol L^{-1}, 0.1–368.0 μmol L^{-1}, and 0.3–250.0 μmol L^{-1}, respectively. The detection limits ($S/N = 3$) were 0.03 μmol L^{-1}, 0.009 μmol L^{-1}, and 0.01 μmol L^{-1} for AA, AC, and CO, respectively. The method was also successfully employed as a selective, simple, and precise method to determinate AA, AC, and CO in pharmaceutical and biological samples.

1. Introduction

Electroanalytical methods comprise a class of techniques in analytical chemistry studying chemical reactions which take place at the interface of an electrode, usually a solid metal or a semiconductor, and an ionic conductor, the electrolyte. These reactions involve electric charges moving between the electrodes and the electrolyte. Electrochemical detection was widely used to detect a large number of interesting and important compounds. Electrochemical methods are fast, simple, selective and sensitive for the determination of inorganic and organic compounds [1–3]. Due to their significant mechanical strength, high electrical conductivity, high surface area, good chemical stability, as well as relative chemical inertness in most electrolyte solutions and a wide operation potential window [4–11], multiwall carbon nanotubes (MWCNTs) can be used to promote electron transfer reactions when used as electrode materials in electrochemical devices, electrocatalysis and electroanalysis processes. The electronic properties of these nanomaterials depend on size (diameter and length), purity, topological defects (edge plane-like sites/defects) present on the MWCNTs surfaces, chemical functionalization, number of concentric tubes, and their orientation [12,13]. The modification of electrode substrates with MWCNTs for use in analytical sensing has been documented to result in low detection limits, high sensitivities, reduction of over-potentials, and resistance to surface fouling [4–11].

Carbon-pastes, prepared from graphite and a suitable water-immiscible binder, provide an appropriate medium for incorporating modifiers into electrodes. These electrodes offer advantages such as low background current, easy preparation and use, low cost, large potential window and simple surface renewal. Moreover, the feasibility of incorporating different substances such as MWCNTs during the paste preparation permits the fabrication of electrodes with desired composition and predetermined properties [2–8].

Spinel ferrites are represented by the formula unit $A^{2+}B_2^{3+}O_4$ where the oxide anions are arranged in a cubic close-packed lattice and the cations A and B occupy some or all of the octahedral and tetrahedral sites [14,15]. A and B can be divalent, trivalent, or quadrivalent cations including magnesium, zinc, iron, manganese, aluminum, chromium, cobalt, titanium, and silicon. Spinel ferrites are commercially essential materials because of their excellent structural, magnetic and electrical properties [16,17]. $ZnFe_2O_4$ is one of the most important ferrite binary oxides with ferromagnetic property. The substitution of Ti^{3+}, Cr^{3+} and Mn^{3+} in zinc ferrite enhances magnetization because of the substitution effect of the metal ions [18].

Ascorbic acid (vitamin C) is a vital component in human diet with the highest concentrations in such animal organs as liver, leukocytes, and anterior pituitary. Commonly known as vitamin C and used for its antioxidant effect, AA forms part of human diet in foods and drinks [19,20].

Acetaminophen (*N*-acetyl-*p*-aminophenol) with codeine (a naturally occurring methylated morphine) is a combination medicine used to relieve moderate to severe pain. It contains a narcotic pain reliever

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http://dx.doi.org/10.1016/j.msec.2016.06.014
0928-4931/

(codeine) and a non-narcotic pain reliever (acetaminophen). Codeine works in the brain to change how your body feels and responds to pain. Acetaminophen can also reduce a fever [21]. Recently, several papers have introduced new modified electrodes for the determination of CO and/or CO plus AC [22–33]. Zen et al. [22] used glassy carbon electrode (GCE) modified with Nafion/ruthenium oxide pyrochlore to determine codeine in human plasma and drug formulation. A nontronite clay modified screen-printed electrode (NC/SPE) has also been proposed to determine CO content in both urine and commercially available drugs [23]. Pournaghi-Azar et al. investigated the use of Prussian blue film modified-palladized aluminum electrode (PB/Pd-Al) prepared by a simple and rapid electroless method for the determination of codeine [24]. Carbon Paste electrode modified with TiO_2 Nanoparticles [25] and graphene–$CoFe_2O_4$ [26] were used for Simultaneous Determination of CO and AC in biological compounds. However, simultaneous determination of AA, AC, and CO has rarely been reported [27,28] in the literature. Table 1 shows comparisons of the proposed method and other electrochemical methods reported for the determination of AA, AC, and CO.

Magnetic nanoparticles (MNPs) have also attracted a growing interest in the development and fabrication of sensors and biosensors. They exhibit the best performance at sizes of 10–20 nm due to supermagnetism, which makes them especially suitable when looking for a fast response, large surface area and high mass transference [16,17]. Preparation of modified electrode with MWCNTs and nanoparticles may be in one stage [16,17] or in two stages [34]. For instance, Lee et al. reported one-pot synthesis of MWCNTs decorated with magnetic iron-oxide nanoparticles [17]. In fact, the synthesis of spinel was conducted in the MWCNTs suspension solution. In the present study, a two-stage preparation of modified electrode was applied. Actually, we described initially the preparation of spinel-type $ZnCrFeO_4$ magnetic nanoparticles from salts of zinc, chromium and iron. Then, these particles were mixed with MWCNTs for the electrode modification. We have used voltammetric and electrochemical impedance spectroscopic techniques at pH 4.0 to demonstrate the electrochemical behavior of AA, AC, and CO on MWCNTs/$ZnCrFeO_4$/CPE. The results showed that the detection limit, linear dynamic range, and sensitivity to AA, AC, and CO with MWCNTs/$ZnCrFeO_4$/CPE are comparable to, and even better than, those recently developed using voltammetric methods [22–33].

2. Experimental

2.1. Apparatus

All Voltammetric measurements were carried out using an electrochemical system comprising the Metrohm instrument (Herisau, Switzerland), Model 797 VA and a conventional three electrode cell assembly containing an Ag/AgCl electrode as reference electrode, a platinum wire as counter electrode and the MWCNTs/$ZnCrFeO_4$/CPE as 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, Sigma-Aldrich). The structure and morphology of the product were characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-K_α radiation), FE-SEM (Hitachi S-4160, Japan) with gold coating and Tunneling electron microscopy (Zeiss-EM10C-100 KV, Germany). FT-IR was recorded using a JASCO FT-IR (680 plus, Japan). The spectra of solids were obtained using KBr pellet. The analysis of chemical composition of the modified electrode was performed using an energy dispersive spectrometer (EDX).

2.2. Chemicals

All chemicals were of analytical reagent grade purchased from Merck (Darmstadt, Germany) except otherwise stated.

Stock solutions of AA and AC (0.010 mol L^{-1}) were prepared daily by dissolving suitable amounts of them in water in a 10-mL volumetric flask. CO stock solution (0.010 mol L^{-1}) was prepared daily by dissolving Codeine phosphate 99% (provided from Temad Company, Tehran, Iran) in 10-mL water. Working solutions of the substances were prepared daily by appropriate dilution of the stock solutions with water.

Phosphate buffer solutions (0.10 mol L^{-1}) with different pH values were used. Pure graphite powder (particle size <50 μm) and MWCNTs (>90% MWCNTs basis, with a diameter of 20–30 nm and a length of 5–15 μm) were prepared from Aldrich (USA). High-viscosity paraffin (d = 0.88 kg L^{-1}) was used for the preparation of the paste electrodes.

2.3. Preparation of $ZnCrFeO_4$ magnetic nanoparticles

The $ZnCrFeO_4$ nanoparticles were prepared *via* sol–gel method [35,36]. 8.07 g $Fe(NO_3)_3 \cdot 9H_2O$, 5.94 g $Zn(NO_3)_2 \cdot 6H_2O$ and 8.00 g $Cr(NO_3)_3 \cdot 9H_2O$ were mixed with 100 mL methanol to form a sol, the mixed solution was adjusted to pH ~ 9 by the ammonium hydroxide solution. After stirring the mixture for 20 min at 80 °C, it was continued for 24 h at room temperature. The product was washed with double 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 it was continued for another 2 h at 900 °C.

2.4. Preparation of MWCNTs/$ZnCrFeO_4$/CPE

$ZnCrFeO_4$ (0.05 g) was dissolved in diethyl ether and hand mixed with 9.0-times its weight of graphite powder and 2.0-times its weight of carbon nanotubes in a mortar and pestle. The solvent was evaporated by stirring. Using a syringe, paraffin was added to the mixture and mixed well for 20 min until a uniformly wetted paste was obtained.

Table 1
Comparison of some characteristics of the different modified electrodes for the determination of AA, AC and CO.

Electrode	Limit of detection (μmol L^{-1})			Linear dynamic range (μmol L^{-1})			Interferences	Ref.
	AA	AC	CO	AA	AC	CO		
Nafion/ruthenium oxide pyrochlore modified GCE	–	–	0.01	–	–	0–32.0	Not reported	[22]
Clay-modified screen-printed carbon electrode	–	–	0.02	–	–	2.5–45	Not reported	[23]
Palladium-plated aluminum electrode	–	–	0.8	–	–	2.0–30.0	Not reported	[24]
CPE modified with TiO_2 nanoparticles	–	0.05	0.018	–	30.0–90.0	0.7–100	Cysteine and AA	[25]
Graphene/$CoFe_2O_4$ nanocomposite modified CPE	–	0.025	0.011	–	0.03–12	0.03–12	–	[26]
Palladium-plated aluminum electrode	–	–	–	1×10^3–1×10^5	290–3300	3×10^3–4×10^4	Not reported	[27]
Aluminum electrode modified by thin layer of palladium	–	5.0	5.0	1×10^2–3×10^3	1×10^2–3×10^3	1×10^2–3×10^3	Caffeine and Aspirin	[28]
Graphene-based modified Electrode	–	–	0.015	–	–	0.05–30	Ascorbic acid	[29]
Porous silicon/palladium nanostructure modified CPE	–	0.4	0.30	–	1–700	1–700	Ascorbic acid	[30]
Gold nanoparticles/MWCNTs modified GCE	0.76	0.03	–	1.0–150.0	0.09–35.0	–	Dopamine and uric acid	[31]
Flavonoid nanostructured modified GCE	–	0.78	–	–	0.9–80.0	–	Not found	[32]
Boron-doped diamond film electrode	–	–	0.08	–	–	0.1–60.0	Ascorbic acid	[33]
MWCNTs/ZnCrFeO4 modified CPE	0.03	0.009	0.01	0.4–730	0.1–368.0	0.3–250.0	–	This work