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NiO nanoparticle decorated on single-wall carbon nanotubes and 1-butyl-4-methylpyridinium tetrafluoroborate for sensitive raloxifene sensor

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ABSTRACT

In this study, carbon paste electrode (CPE) modified with NiO/SWCNTs and 1-butyl-4-methylpyridinium tetrafluoroborate (1B4MPTFB) was used for the effective determination of raloxifene as a sensor. The use of NiO/SWCNTs and 1B4MPTFB in the electrode matrix showed great conductivity for electro-oxidation of raloxifene and nanomolar determination of raloxifene in buffering the solution. The CPE/NiO/SWCNTs/1B4MPTFB improved the oxidation current of raloxifene and reduced the oxidation overvoltage compared to an unmodified sensor. The CPE/NiO/SWCNTs/1B4MPTFB showed a linear dynamic range of 0.03–520 μM with a detection limit of 7.0 nM using the square-wave voltammetric method. The CPE/NiO/SWCNTs/1B4MPTFB showed good sensitivity for the analysis of raloxifene in table and pharmaceutical serum samples. The obtained data for real samples analysis were checked with other analytical method and statistical tests such as F-test and *t*-test were used for study the accuracy of data.

1. Introduction

Estrogen receptor drugs are the main category of drugs used in the treatment of cancer, especially breast cancer [1]. Raloxifene is one of the most important among selective estrogen receptor modulators. The side effects of raloxifene are minimal compared to tamoxifen in the treatment of breast cancer [2]. In addition, raloxifene was suggested for the deterrence and treatment of postmenopausal osteoporosis. Although consuming raloxifene can be useful for treating some diseases, overdosing on it can be harmful to human health [3]. Its side effects include breathing trouble, birth defects, lung, and chest pain. Due to the high consumption and adverse effects of raloxifene, many analytical methods were used to determine raloxifene in biological and blood serum [4–9]. Analytical methods for the analysis of raloxifene were punctuated with electrochemical methods based on voltammetric analysis because of easy operation, fast response, and high selectivity [10–17]. In addition, voltammetric sensor sensitivity was improved by the modification of the working electrodes with nanomaterials, ionic liquids, organic ligands, and other electroactive mediators [18–30]. Only four electrochemical modified sensors were suggested for the analysis of raloxifene in real samples. Bagheri and Hosseini reported a glassy carbon electrode as a working electrode for the analysis of raloxifene in pharmaceutical formulations with dynamic range 0.2–50.0 μM and detection limit of 0.075 μM [7]. Shahrokhian et al. modified glassy carbon electrode with melamine/carbon nanoparticles and used this modified sensor for the analysis of raloxifene in the concentration range of 0.04–2.0 μM with limit of detection 0.01 μM [9]. Ghoneim et al. used a mercury electrode as a sensor for the determination of raloxifene in the concentration range of 0.005–0.01 μM with limit of detection 2.0 nM [8]. In the final report, Cheraghi et al. suggested carbon paste electrode (CPE) modified with ZnO/CNTs nanocomposite and 1-methyl-3-octylimidazolium tetrafluoroborate as a highly sensitive sensor for the determination of raloxifene in the concentration range of 0.08–400.0 μM with limit of detection 0.04 μM [3]. In comparison to the previously suggested electrochemical sensor for the analysis raloxifene, the CPE/NiO/SWCNTs/1B4MPTFB showed better limit of detection or linear dynamic range due to the application of a highly conductive mediator (NiO/SWCNTs and 1B4MPTFB) (see Table 1).

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Table 1
The analytical data reported by the presence sensor and some different electrochemical sensors for raloxifene analysis.

Electrode	pH	LDR (μM)	LOD (μM)	Sensitivity (μA/μM)	Ref.
Carbon paste	7.0	0.08–400.0	0.04	0.0987	[3]
Glassy carbon	3.0	0.2–50.0	0.07	0.198	[7]
Mercury electrode	5.0	0.002–0.1	0.0006	0.00074	[8]
Glassy carbon	3.0	0.04–2.0	0.01	7.3	[9]
Carbon paste	7.0	0.03–520	0.007	0.1584	This work

2. Experiment

2.1. Apparatus and chemicals

Single-wall carbon nanotubes (D ~25 nm) were purchased from Neutrino Company, Iran. Raloxifene, sodium hydroxide, 1-butyl-4-methylpyridinium tetrafluoroborate, and nickel (II) nitrate hexahydrate were purchased from Sigma-Aldrich. Graphite powder and nujol oil were purchased from Merck and used for the fabrication of a working electrode. The morphological structures of the NiO/SWCNTs were investigated by a Philips CM30, 300-kV scanning transmission electron microscope. The potentiostatic investigation was performed with a μ-Autolab type III coupled with an electrochemical cell in the presence of Ag/AgCl/KCl_{sat}, CPE/NiO/SWCNTs/1B4MPTFB, and platinum. NiO/SWCNTs nanocomposite was synthesized according to a reported procedure by Sanati et al. [31].

2.2. Preparation of CPE/NiO/SWCNTs/1B4MPTFB

CPE/NiO/SWCNTs/1B4MPTFB was created by mixing 0.05 g of NiO/SWCNTs and 0.95 g of graphite powder in a mortar and pestle. This was then mixed by hand for 45 min along with liquid nujol oil and a suitable amount of 1B4MPTFB as a conductive binder. The CPE/NiO/SWCNTs/1B4MPTFB was added to the end of a glass tube (A = 0.284 cm^2) and a copper wire was inserted into the paste for connecting electrical devices.

2.3. Preparation of raloxifene real samples

The raloxifene hydrochloride tablet and pharmaceutical serum were used for checking the performance ability of CPE/NiO/SWCNTs/1B4MPTFB in raloxifene determination in real samples. Ten raloxifene hydrochloride tablets (60 mg; Aurobindo Pharma USA) were purchased from the local pharmacy. They were then powdered in a mortar and continuously dissolved in 10 mL (1:1 (v/v)) ethanol/water solution for a real sample analysis. Also, the pharmaceutical serum sample was used directly for the analysis of raloxifene in the real sample by the standard addition method.

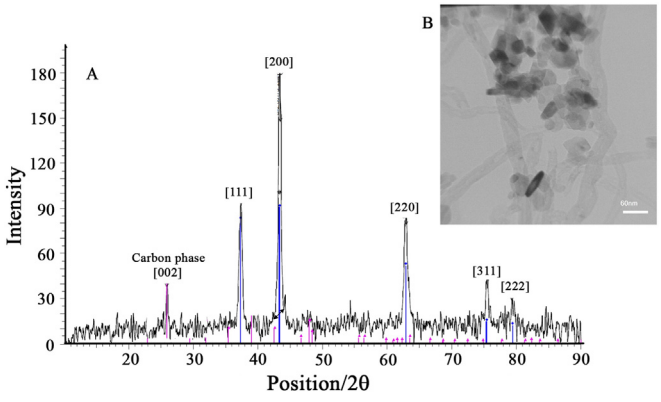

Fig. 1. A) XRD pattern of NiO/SWCNTs nanocomposite. B) TEM image of NiO/SWCNTs nanocomposite.

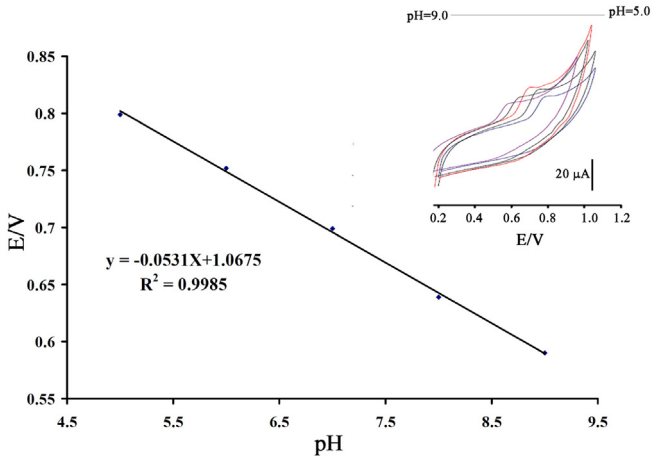

Fig. 2. Potential-pH curve for electro-oxidation of 300.0 μM raloxifene at a surface of CPE/NiO/SWCNTs/1B4MPTFB in the pH range 5.0–9.0. Insert) relative cyclic voltammograms of 300 μM raloxifene at a surface of CPE/NiO/SWCNTs/1B4MPTFB in the pH range 5.0–9.0.

3. Results and discussion

3.1. NiO/SWCNTs characterization

The XRD pattern of NiO/SWCNTs was recorded in Fig. 1A. The presence of [002] plane at 2θ~26° is relative to SWCNTs in NiO/SWCNTs nanocomposite structure. In addition, the presence of [111], [200], [220], [311] and [222] planes are relative to NiO nanoparticle. According to the XRD pattern data, we can suggest synthesis of NiO/SWCNTs nanocomposite structure. The TEM image of NiO/SWCNTs was recorded and the obtained figure can be seen in Fig. 1B. Fig. 1 shows the NiO nanoparticles with diameter ~20 nm decorated at a surface of single wall carbon nanotubes.

3.2. Electro-oxidation of raloxifene on a surface of CPE/NiO/SWCNTs/1B4MPTFB

Due to the phenolic structure of raloxifene, we assume that the electro-oxidation mechanism of this estrogen receptor drug is relative

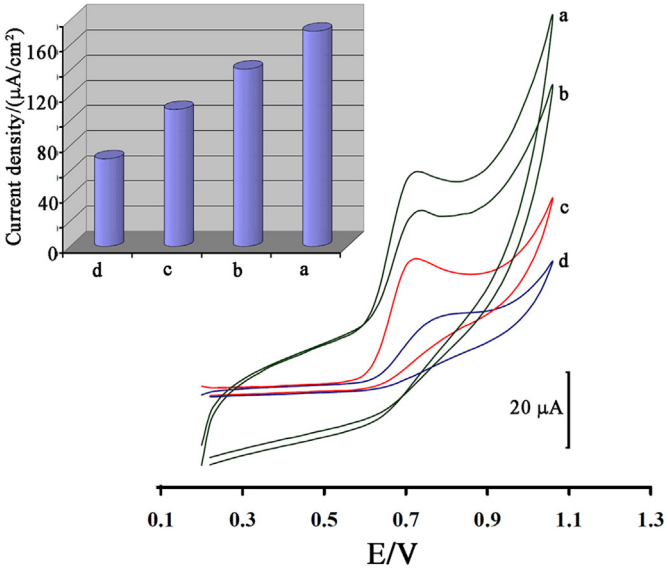

Fig. 3. Cyclic voltammograms of 500.0 μM raloxifene at a surface of a) CPE/NiO/SWCNTs/1B4MPTFB; b) CPE/1B4MPTFB; c) CPE/NiO/SWCNTs and d) CPE at pH = 7.0. Insert) current density obtained from this figure's data. Condition; Scan rate 100 mV/s and pH = 7.0.