



Application of glassy carbon electrode modified with a carbon nanoparticle/melamine thin film for voltammetric determination of raloxifene



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ABSTRACT

As a selective estrogen receptor modulator, raloxifene (RXF) prevent of osteoporosis in postmenopausal women by estrogenic actions on bone and decreases the risk of invasive breast cancer by anti-estrogenic actions on the breast and uterus tissue. However, RXF may increase the risk of blood clots, including deep vein thrombosis and pulmonary embolism. For the first time glassy carbon electrode modified with a thin film of melamine/carbon nanoparticles (CNPs/Mela) was constructed and used for the sensitive voltammetric determination of RXF. In comparison with unmodified electrode, the presence of the CNPs/Mela film resulted in a remarkable increase in the peak currents and sharpness of the waves, so that sub-micromolar concentrations of RXF became detectable. The surface morphology of the modified electrode, prepared by drop-casting of the CNPs/Mela suspension on the GCE surface, was characterized by scanning electron microscopy. The electrochemical response characteristics of the modified electrode toward RXF were studied by means of cyclic and differential pulse voltammetry. Experimental variables, such as the deposited amount of the modifier suspension, pH of the supporting electrolyte, the accumulation time and the potential scan rate were optimized by monitoring the electrochemical responses of RXF. Under the optimum conditions, the modified electrode showed a wide linear dynamic range of 0.04–2.0 μM with a detection limit of 10.0 nM for the voltammetric determination of RXF. The prepared modified electrode showed high sensitivity, stability and good reproducibility in response to RXF, confirming its usability for the accurate determination of trace amounts of RXF in pharmaceutical and clinical preparations.

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1. Introduction

Raloxifene (RXF) is a polyhydroxylated non-steroidal compound with a benzothiophene core. It is a selective estrogen receptor modulator (SERM); which acts as an agonist for the estrogen receptor in some areas of the body and as an antagonist in the reproductive system [1–5]. At present, it is applied to the prevention of osteoporosis [6], breast cancer [7–9], the inhibition of the growth of uterine leiomyoma's [10] and the therapy of cardiovascular disease [8], etc. Furthermore, RXF has shown the ability to significantly lower the incidence of coronary events in postmenopausal women younger than 60 years [1]. Like tamoxifene, in men, RXF also significantly increases serum testosterone levels albeit to a lower extent [11]. Therefore, RXF is included in the list of drugs prohibited by the World Anti-Doping Agency (WADA) [12]. However,

the mechanism of RXF's action on various tissues is not completely understood yet. It is known that RXF is subjected to an extensive first pass metabolism: 60% of the per-oral dose is absorbed and only 2% reaches the systemic circulation [13].

Up to now, only few methods have been developed for the analysis of RXF such as spectrophotometric determination in pharmaceutical formulations [14–16], HPLC determination in tablets [17–19], HPLC determination in rat plasma [20], capillary electrophoresis [21], LC-MS-MS determination in human urine [22], and Rayleigh scattering [8]. Up to now, only few electrochemical methods have been developed for the analysis of RXF including bare glassy carbon electrode (GCE) [23] and multi-walled carbon nanotubes (MWCNT) modified GCE [24].

The preparation and application of various composites of carbon nanomaterials such as functionalized forms of reduced graphene oxides [25–27] and multi-walled carbon nanotubes [28–31] with metal nanoparticles as electrode modifiers caused to development sensitive electrochemical sensors for the determination of trace amounts of pharmaceutical and clinical preparations.

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Application of carbon nanoparticles (CNPs) in electroanalytical studies displays advantages over conventional electrodes including enhanced mass transport and catalysis, highly effective surface area, high porosity, more adsorption and reactive sites, and control over the electrode macro-environment [32–36].

Melamine (Mela) has the potential to improve the selectivity and sensitivity of electrochemical determinations at a relatively small cost. Notably, Mela has a large surface area for the surface modification of the electrodes [37,38].

In the present work, we synthesized a modifier made of CNPs/Mela immobilized on GCE by a simple method. The obtained results demonstrated that CNPs/Mela modified electrode could bring new capabilities for the electrochemical devices by combining the advantages of carbon nanoparticles and melamine, and can be readily used for determination of very low amount of RXF.

2. Experimental

2.1. Chemicals and reagents

Functionalized carbon nanoparticles (ca. 8 nm diameter, with phenyl sulfonate surface functional groups, Emperor 2000) were obtained from Cabot Corporation. Mela was purchased from Sigma-Aldrich. Pure sample of RXF is kindly provided by Iran Hormone Co. (Tehran, Iran). Stock solutions of RXF were freshly prepared as required in appropriate buffer solutions. The working solutions for all the electrochemical experiments were prepared by diluting with stock Britton–Robinson (BR) buffer solutions (containing 0.04 M acetic acid, orthophosphoric acid and boric acid) to obtain the desired pHs. Tablets of RXF were purchased from Loghman Pharmaceutical Co. (Tehran, Iran). All other chemicals were of analytical reagent grade from Merck. All aqueous solutions were prepared in doubly distilled, deionized water. High purity nitrogen (99.999%, Roham Gas Company, Iran) was used for deaeration of the solutions.

2.2. Real sample preparation

Fresh human blood serum samples were obtained from Razi Institute of Vaccine and Serum (Tehran, Iran). The serum samples were centrifuged, filtered and diluted with 0.1 M BR solution of pH 3 and applied for the recovery tests in spiked samples.

2.3. Apparatus

All electrochemical measurements were performed using a Metrohm potentiostat/galvanostat model 797VA. A three-electrode system was used, including a glassy carbon working electrode ($d = 2.0$ mm, purchased from Azar Electrode Co., Urmia, I.R. Iran), an Ag/AgCl (saturated KCl) reference electrode and a Pt wire auxiliary electrode. All the potentials are quoted vs. the Ag/AgCl reference electrode. A digital pH/mV/Ion meter (Metrohm, pH Lab 827) was used for pH measurements and preparation of the buffer solutions.

An ultrasonic bath (KODO Model JAC 1002) was used for cleaning the electrode surface and preparing modifier suspensions. The scanning electron microscopy (SEM) experiments were performed on a HITACHI S4160 (Japan) scanning electron microscope. All experiments were done at room temperature (25 ± 1 °C).

2.4. Preparation of CNPs/Mela/GCE

Before the modification process, the GCE was polished with 0.1 μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water and sonicated for 5 min. A homogenous suspension of CNPs/Mela was prepared by dispersing 1 mg CNP powder and 1 mg Mela powder in 1 mL of a mixture solvent of DMF and deionized water (50% V/V) under sonication for 15 min. The CNPs/Mela/GCE electrode

was prepared by casting appropriate volumes of the prepared modifier suspension on the GCE surface and drying in an oven at 55 °C for 5 min.

Prior to voltammetric measurements, the modified electrode was cycled 5 times between 0.2 and 1.3 V (a scan rate of 100 mV s^{-1}) in BR buffer solution of pH 3.0, to obtain a reproducible voltammetric response. The modified electrode was also cycled 3 times in the same buffer solution between the measurements to remove any adsorbed RXF as well as renewing the electrode surface.

3. Results and discussion

3.1. Characterization of CNPs/Mela/GCE

The surface morphology of the bare and CNPs/Mela modified electrodes were characterized by SEM. Fig. 1A displays typical image of CNPs/Mela film with $100 \text{ k}\times$ magnification. These images demonstrate that, in comparison to bare GCE, the surface morphology is considerably changed in the presence of the modifier on the electrode surface. From the SEM images, the size of carbon nanoparticles immobilized on the GCE was estimated to be 10–20 nm. The nano-clogs structure of CNPs provided a large active surface area, which is advantageous to the electron transfer and electrochemical sensing.

The FTIR spectra of Mela (Green line, curve a), CNPs (blue line, curve b) and CNPs/Mela (Red line, curve c) in the range of $400\text{--}4000 \text{ cm}^{-1}$ were exhibited in Fig. 1B. Obviously, similarity of obtained curves of Mela and CNPs/Mela samples revealing the presence of Mela at modifier composite. Notably, the FTIR result of Mela obtained in present work was similar to the previously reported by Liu et al. [39].

Electrochemical impedance spectroscopy (EIS) was used to study the impedance changes and also the interfacial characterization of the electrode surface during the modification processes. Fig. 1C shows the Nyquist plots of $\text{Fe}(\text{CN})_6^{3-/4-}$ as redox probe at the bare GC, CNPs/GC and CNPs/Mela/GC electrodes. Obtained results showed that the semicircle section of impedance spectrum almost vanished at the CNPs/GCE (Table 1). It can be mainly ascribed to the improved electrical conductivity of GCE modified by CNPs thin films compared to bare GCE. However, although, the diameter of the semicircle of CNPs/Mela/GCE is smaller than the bare GCE, it is larger than the CNPs/GCE. Notably, Mela is not as conductive as carbon nanoparticles alone, but its positive property such as adsorption capability and increasing the effective surface area make it a suitable choice in drug investigations using corresponding modified electrodes. The improved signal of CNPs/Mela/GCE than CNPs/GCE is an evidence on this issue.

The effective surface areas of used electrodes were evaluated by cyclic voltammetry in 1.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution containing 0.1 M KCl at different scan rates. For a reversible process, the effective surface area can be estimated based on the Randles-Sevcik equation. The effective surface area of the CNPs/Mela/GCE, CNPs/GCE and bare GCE were obtained 0.127, 0.096 and 0.035 cm^2 , respectively. These results indicate that the microscopic surface area of the GCE increased significantly after modification.

3.2. Electrochemical behavior of RXF on the surface of various electrodes

The electrochemical behavior of RXF was investigated by means of DPV and CV on the surface of bare GCE and CNPs/Mela/GCE. Fig. 2A depicts CVs for the electrochemical oxidation of $10.0 \mu\text{M}$ RXF at the modified GCE in a BR buffer solution of pH 3.0, recorded at a scan rate of 100 mV s^{-1} . The first scan presents an anodic peak ($I_{p1,a}$), at $E_{p,a} = +0.690 \text{ V}$, and on the reverse scan, two cathodic peaks, $I_{p1,c}$ at $E_{p,c} = +0.607 \text{ V}$ and $I_{p2,c}$ at 0.256 V . In the successive scans a new anodic peak ($I_{p2,a}$) at 0.298 V is observed, while peaks currents of $P_{1,a}$ and $P_{1,c}$ gradually decreased. The redox peak pair (2) is related to the redox activity of the product of RXF oxidation, which adsorbed on the electrode surface. As regards to $E_{p1,a} - E_{p1,c} = 87 \text{ mV}$ and ratio less than 1.0 for $I_{p1,c}/I_{p1,a}$, it seem that RXF has a quasi-reversible redox in this area. As

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