



Electrochemical sensing platform of natural estrogens based on the poly(L-proline)-ordered mesoporous carbon composite modified glassy carbon electrode

Liqliang Luo*, Fang Li, Limei Zhu, Yaping Ding*, Dongmei Deng

College of Sciences, Shanghai University, Shanghai 200444, PR China

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ABSTRACT

A novel poly(L-proline)-ordered mesoporous carbon film with controllable thickness on the glassy carbon electrode surface was fabricated by one-step electrochemical technique and further used for the construction of electrochemical sensing platform of natural estrogens. Scanning electron microscopy, Fourier transform infrared spectroscopy and electrochemical impedance spectroscopy were employed to characterize the surface morphology, structure and interface property of the polymer. The voltammetric behaviors of estrogens involving estradiol, estrone and estriol were investigated on the modified electrode, and the proposed electrode exhibited strong electrocatalytic activity toward the oxidation of three estrogens especially for estradiol, making it a promising electrochemical sensing platform for sensitive detection of estrogens. Under the optimum conditions, the linear range of estradiol obtained by square-wave voltammetric determination was 1.0×10^{-8} – 2.0×10^{-6} mol/L with a low detection limit of 5.0×10^{-9} mol/L. The developed modified electrode was also applied to the determination of estradiol in female blood serums with satisfactory results.

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1. Introduction

Natural estrogens, also called endogenous estrogens, mainly involving estrone (3-hydroxy-1,3,5-(10)-oestratrien-17-one; E1), estradiol (estra-1,3,5-(10)-triene-3 β ,17 β -diol; E2) and estriol ((16 α , 17 β)-estra-1,3,5(10)-triene-3,16,17-triol; E3), are essential bioactive substance of 18-carbon steroid hormones. Among them, E2 is the most potent and active estrogen primarily generated by the ovary, and E1 and E3 are the metabolites of E2 with limited estrogenic activity [1,2]. Three estrogens take part in intracellular communication, affecting the development and maintenance of sex characteristics, and their concentrations and changes are closely related to human's health status [3,4]. Thus, the determination of natural estrogens is of great importance.

Currently, several methods have been proposed for the detection of estrogens, such as chromatography [5,6], chromatography–mass spectrometry [7,8], immunoassay [9–11] suspension array technology [12] and electroanalytical method [13–18]. Owing to the operational simplicity, low expense, fast response and high sensitivity [3,19], electroanalytical method attracts great concern and a variety of modified electrodes have

been reported for estrogens determination. For example, a nano- Al_2O_3 film modified glassy carbon electrode (GCE) [13], a Congo red-functionalized multi-walled carbon nanotubes (MWNTs) modified GCE [14], a MWNTs-Nafion modified GCE [15], a poly(L-serine) film-modified GCE [16], a DNA aptamer immobilized gold electrode chip [17] and a boron doped diamond thin film electrode [18] have been put forward to detect E2.

Ordered mesoporous carbon (OMC), with well-ordered structures and unique properties, is an excellent electrode modified material, and has been widely used in electroanalysis [20–22]. To obtain OMC modified electrode, several methods have been developed [22–24], mainly by directly casting OMC dispersion onto the electrode surface [21,22]. However, in this way, the thickness of the resulting film is not easy to be controlled, and the poor surface coverage of OMC on the substrate electrode often leads to large interfacial capacitance [24,25].

Like other carbon nanomaterials, such as carbon nanotubes and graphene, OMC film can also be deposited on GCE surface by cyclic voltammetry, which can control the thickness of the film by adjusting the experimental parameters such as scan rate and sweep segments [25,26]. To the best of our knowledge, however, the fabrication of OMC film on the surface of electrode by direct electrodeposition technique has not ever been reported. In this work, we tried to prepare a novel nanohybrid film of poly(L-proline)-OMC (PPOMC) by one-step cyclic voltammetry technique

* Corresponding authors. Tel.: +86 21 66134734; fax: +86 21 66132797.

E-mail addresses: luoliqw@yahoo.com.cn (L. Luo), wdingyp@sina.com (Y. Ding).

directly in a mixed dispersion containing L-proline and OMC. The obtained PPOMC modified GCE exhibited strong electrocatalytic activity toward the oxidation of three natural estrogens, making it a promising electrochemical sensing platform for sensitive detection of estrogens.

2. Experimental

2.1. Reagents and apparatus

E1, E2 and E3 were purchased from Sigma. L-Proline was obtained from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Stock solutions of E1, E2 and E3 (1.0 mmol/L) were prepared in ethanol. HPLC grade of acetonitrile was purchased from Sigma–Aldrich. All other chemicals were of analytical grade and double distilled water was used throughout the experiment. 0.1 mol L^{-1} phosphate buffer solutions (PBS) with different pH values adjusted by K_2HPO_4 and KH_2PO_4 , were employed as a supporting electrolyte.

Electrochemical experiments were carried out on a CHI 842B electrochemical workstation (Shanghai Chenhua Co., Ltd., China) with a conventional three-electrode system consisting of a PPOMC/GCE working electrode, a saturated calomel reference electrode (SCE) and a platinum foil counter electrode. Scanning electron micrographs (SEM) measurements, Fourier transform infrared (FTIR) spectra and electrochemical impedance spectroscopy (EIS) were operated on scanning electron microscope (JSM – 6700F, 15.0 kV), AVATAR 370 Fourier transform infrared spectrometer (America) and Solartron 1255B Frequency Response analyzer/SI 1287 electrochemical interface (Scribner Associates, Inc.), respectively. High performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) was performed on a Qstar XL HPLC–MS/MS system (Applied Biosystems, USA) coupled with electrospray ionization (ESI) source. A C18 analytical column of $250 \text{ mm} \times 3.0 \text{ mm}$ I.D., $5 \mu\text{m}$ (Shimadzu, Kyoto, Japan) was employed. The mobile phase was a mixture of acetonitrile and water (40:60, v/v).

2.2. Synthesis of OMC

OMC was synthesized using template method in which SBA–15 acted as the template and sucrose acted as the carbon source [27,28].

2.3. Electrode preparation and modification

Before experiments, GCE was polished on a chamois leather with $0.05 \mu\text{m}$ α -alumina powder. Then, the electrode was rinsed successively with 1:1 nitric acid, absolute alcohol and double distilled water in ultrasonic bath, and allowed to dry at room temperature. With the aid of ultrasonication, 1 mg OMC and 10 mmol L-proline were dispersed in 10 mL 0.1 mol L^{-1} PBS (pH 9.0) to yield a homogeneous dark black suspension.

Afterwards, the prepared GCE was put into the above black suspension containing 0.1 mg mL^{-1} OMC and 1.0 mmol L^{-1} L-proline, and swept for 10 segments at the scan rate of 100 mV s^{-1} in the potential range from -0.8 to 2.4 V (Fig. 1). Finally, the PPOMC/GCE was carefully washed with double distilled water for use. For comparison, similar procedure was performed to get PP/GCE and OMC/GCE.

2.4. Electrochemical measurement

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were used for electrochemical measurements. For SWV, the pulse amplitude was set at 25 mV , frequency 40 Hz and potential step

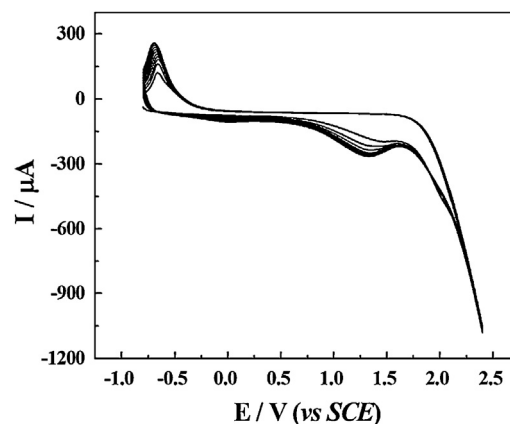


Fig. 1. The electropolymerization of PPOMC on GCE surface was carried out using cyclic sweeps between -0.8 V and 2.4 V for 10 cycles in 0.1 mol L^{-1} PBS (pH 9.0) containing 1 mmol L^{-1} L-proline and 0.1 mg mL^{-1} OMC.

10 mV . Prior to measurements, the prepared PPOMC/GCE was placed in 0.1 mol L^{-1} PBS (pH 7.4) and swept in the potential range of 0.2 – 0.9 V until stable voltammograms were obtained. Then, E2 solution was added. After accumulation for 5 min under open-circuit potential and then keeping quiet for 30 s, the voltammetric responses were recorded in 0.2 – 0.9 V , and the peak current was measured at about 0.60 V . After each measurement, the PPOMC/GCE was activated by five cyclic sweeps in 0.2 – 0.9 V in the blank PBS (pH 7.4) to remove any adsorbates and give a reproducible electrode surface.

2.5. Pre-treatment of real samples

Several female blood serums were obtained from Shanghai University Hospital. The samples were deproteinized by adding $150 \mu\text{L}$ perchloric acid to 0.5 mL serum, vortex-mixing for 30 s and centrifuging at $1795 \times g$ for 5 min. The supernatant was spiked with certain amount of E2 stock solution for real sample determination.

3. Results and discussion

3.1. Characterization by SEM and FTIR spectra

The typical morphologies of PPOMC film and OMC film obtained by deposition were observed by SEM, as shown in Fig. 2. The inset of Fig. 2 shows that OMC film is made up of linked ordered finger-like carbon flakes, which indicates that the structure of OMC film could significantly increase the effective electrode surface. Compared with OMC film, the PPOMC film is characterized by light dots, which suggests that L-proline has been incorporated into or modified on the OMC film.

In order to further demonstrate that OMC and L-proline have been co-modified on the surface of GCE, FTIR spectra of OMC (a), L-proline (b) and PPOMC film (c) were analyzed in the range of 400 – 4000 cm^{-1} , as seen in Fig. 3. In curve a, the band around 1650 cm^{-1} is attributed to C=O stretch vibration, and the band around 1150 cm^{-1} is assignable to C–O stretch vibration, while the band around 3450 cm^{-1} is due to the carboxylic acid O–H stretch vibration. These indicate that oxygen-containing functional groups exist on the surface of OMC [22]. In curve b, L-proline is constituted of the peaks of C=O stretching vibration at 1623 cm^{-1} , and C–H, N–H, O–H stretching vibration in the range of 2500 – 3500 cm^{-1} . While in the copolymer of PPOMC film (c), the peaks of C=O stretching vibration shifts to 1639 cm^{-1} , and the peaks at 3447 cm^{-1} , corresponding to C–H, N–H, O–H stretching vibration, become broad obviously. This can be explained by poly-reaction of L-proline

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