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Electrochemical oxidation and detection of paeonol on modified electrode with acetylene black nanoparticles

Huajie Zhang, Miaomiao Gao, Xiaofeng Yang*

School of Pharmacy, Wenzhou Medical College, Wenzhou 325000, China

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ABSTRACT

With an aim to construct a sensing platform for the electrochemical detection of paeonol, we modified the glassy carbon electrode with acetylene black nanoparticle (AB). A sensitive oxidation peak of paeonol was observed with remarkably increased peak current on the modified electrode because the electrode has a big surface area due to three dimensional structure of AB nanoparticles. The optimization of detection conditions was performed, including pH value of the buffer, the amount of AB nanoparticles on the electrode surface, the accumulation potential and time of paeonol. Under the optimized conditions, the oxidation peak current of paeonol increased linearly with its concentration over the range from 5×10^{-7} to 1×10^{-4} M. The detection limit was calculated to be 1×10^{-7} M. The modified electrode was successfully applied to detect the content of paeonol in cortex moutan, a common traditional Chinese medicine. The method is new, sensitive, rapid and convenient for the detection of paeonol.

1. Introduction

Paeonol, the main active ingredient of cortex moutan, is a common traditional Chinese medicine. Its chemical structure is shown in Fig. 1. It has been used to treat many diseases for a thousand years since paeonol possesses extensive pharmacological activities, such as anti-atherosclerosis, antioxidant, anti-tumor, promoting blood circulation, strengthening the immune system and anti-inflammatory activity [1]. Therefore, it is quite important to identify and quantify paeonol in traditional Chinese medicines.

Several methods have been developed to identify and quantify paeonol, such as fluorescence [2], liquid chromatographic–mass spectrometric (LC–MS) [3], gas chromatography–mass spectrometry (GC–MS) [4], micellar electrokinetic capillary chromatography [5], high-performance liquid chromatography [6] and micellar capillary electrophoresis [7]. Electrochemical detection is another way to identify and quantify paeonol due to its electrochemically active phenolic hydroxyl group. The irreversible oxidation process was observed at different solid electrodes [8,9]. For example, a Nafion/multi-wall carbon nanotubes composite film-modified electrode has been used to identify and quantify paeonol [9]. The linear range was 6×10^{-7} to 6×10^{-5} M and the detection limit of was 4×10^{-7} M.

We are interesting in utilizing acetylene black nanoparticle-modified electrode to identify and quantify paeonol, which still missing in literature. Acetylene black nanoparticle (AB), a special type of carbon black with porous structure, exhibits many fascinating properties such as excellent electric conductivity, large surface area due to three-dimensional structure, and strong adsorptive ability towards analytes. Therefore, the electrode modified with AB nanoparticles is promising to improve the sensitivity and detection limits of the detections. For instance, a sensitive and rapid electroanalytical method was developed for the detection of erythromycin, resulting from the remarkably enhanced oxidation process on the AB nanoparticles modified electrode [10]. Similarly, sensitive detections of other targets on the AB nanoparticles modified electrode have been reported, e.g. the detection of the 1-naphthylacetic acid [11], 6-benzylaminopurine [12], kojic acid [13], 2-chlorophenol [14] and Pb^{2+} ions [15].

In order to fabricate the modified electrode, we dispersed AB nanoparticles into water in the presence of dihexadecyl hydrogen phosphate (DHP). A homogeneous and stable AB suspension was obtained. We then dropped the suspension on the electrode. After evaporation of water, an AB film-modified electrode was formed. The electrochemical behavior of paeonol was examined on the AB film-modified electrode. The optimization of experimental conditions for the detection of paeonol was performed. Based on the electrochemical response of paeonol on the modified electrode, a novel electrochemical method to detect paeonol was proposed. This method was tested for the detection of paeonol in Chinese medicine in the last section of the paper.

* Corresponding author.
E-mail address: yang_xiaofeng@163.com (X. Yang).

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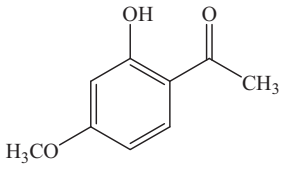

Fig. 1. Chemical structure of paeonol.

2. Experimental

2.1. Reagents

All the reagents were of analytical grade and used as received. Acetylene black (purity > 99.99%) was purchased from STREM Chemicals (Massachusetts, USA) and dihexadecyl hydrogen phosphate (DHP) from Sigma (Steinheim, Germany). Paeonol was obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Stock solution of paeonol (0.01 M) was prepared with ethanol and stored at 4 °C in a fridge.

2.2. Instruments

Electrochemical measurements were performed on a CHI 650B electrochemical workstation (Chenhua Instrument Co. Ltd., Shanghai, China) with a conventional three-electrode system. Either an AB film-modified glassy carbon electrode (GCE) or a bare glassy carbon electrode was used as the working electrode. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum wire.

2.3. Preparation of AB film-modified GCE

We dispersed 5 mg AB nanoparticles and 5 mg DHP in 5 mL water with an aid of ultrasonication, giving a stable and homogeneous suspension. One hour needed to achieve this suspension. Prior to surface modification of the electrode with AB nanoparticles, the GCE was polished carefully with 0.05 μm alumina slurry and then sonicated in water for 2 min. After that, the GCE was coated with 8 μL AB suspension, and the water was evaporated from the surface under an infrared lamp in air. For the formation of the DHP film-modified GCE, the DHP solution without AB nanoparticles was used.

2.4. Sample preparation

The cortex moutan used in this work was purchased from a local Pharmacy. The samples were pulverized and then treated in the following way. The powder (about 4 g) was weighed, and then ultrasonicated in 20 mL ethanol at 40 °C for 2 h. The extraction was repeated three times. The extract was collected in a 100-mL volumetric flask and then diluted to 100 mL with ethanol. Spiked samples were prepared by adding a known amount of paeonol to a dry powder sample before extraction.

2.5. Analytical procedure

The supporting electrolyte used for the detection of paeonol was 0.1 M pH 7 phosphate buffer solution. The accumulation of paeonal on the modified electrode was conducted at open-circuit potential for 90 s. Differential pulse voltammograms of accumulated paeonal on the modified electrode were then recorded. The peak current at 0.78 V was plotted as a function of the concentration of paeonal. The pulse amplitude was 50 mV, the pulse width was 40 ms and the scan rate was 40 mV s^{-1}.

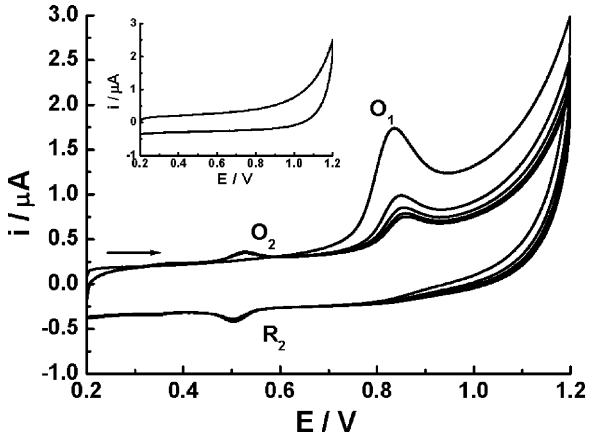

Fig. 2. CVs of 5×10^{-5} M paeonol in pH 7 phosphate buffer on the AB film-modified GCE. The insert is CV response on the AB film-modified electrode without paeonol. Scan rate = 100 mV s^{-1}.

3. Results and discussion

3.1. Electrochemical behavior of paeonol

The electrochemical response of paeonol on the AB film-modified GCE was studied using cyclic voltammetry (CV). Fig. 2 shows the successive CV curves of 5×10^{-5} M paeonol in pH 7 phosphate buffer. During the anodic sweep from 0.2 to 1.2 V, an oxidation peak (O_1) was observed at 0.84 V. In the reverse scan from 1.2 to 0.2 V, a reduction peak (R_2) appeared at 0.5 V. Another oxidation peak (O_2) was observed at 0.53 V on the second anodic sweep. Moreover, the peak current of O_1 decreased while the peak current of R_2/O_2 increased. When the positive potential was below 0.84 V, the peaks of R_2/O_2 vanished. The insert in Fig. 2 shows the CV response of AB film-modified GCE in pH 7 phosphate buffer without paeonol. The curve was featureless. These phenomena suggest that the peak O_1 is due to the direct oxidation of paeonol and the R_2/O_2 peaks are attributed to the oxidative reaction product.

In order to examine the oxidation mechanism of paeonol, the oxidation currents and potentials of peak O_1 were investigated at different scan rates using linear sweep voltammetry (LSV). The oxidation peak current of peak O_1 increased linearly with the square root of scan rate (ν) over the range from 0.05 to 0.2 V s^{-1}, revealing a diffusion-controlled oxidation process. Additionally, we found that the oxidation peak potential of peak O_1 (E_{pa}) shifted positively as an increase in the scan rate. These suggest that the oxidation of paeonol on the modified electrode is an irreversible process. For an irreversible and diffusion-controlled oxidation process, the E_{pa} is proportional to $\ln(\nu)$, and the slope is equal to $RT/2\alpha nF$. For paeonol, the E_{pa} of peak O_1 increased linearly with $\ln(\nu)$ in the form of

$$E_{pa} = 0.891 + 0.0232 \ln(\nu)$$

The slope was 0.0232, giving a value of 0.55 for αn. Since the value of α is generally considered as 0.5, only one electron is then transferred for the oxidation of paeonol. Additionally, the oxidation peak currents of peak O_1 in 0.1 M phosphate buffer solutions were studied as a function of pH value. With increasing the pH value, the oxidation peak potentials of O_1 shifted linearly to more negative potentials with a slope of −53.4 mV/pH, suggesting that the number of proton transferred is equal with that of electron. Therefore, the oxidation of paeonol involves one proton and one electron, which is consistent with the reported results [8,9]. From the molecular structure in Fig. 1, we speculate that the oxidation of paeonol occurs at the hydroxyl group together with the radicals' formation.