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ORIGINAL PAPER

Mesoporous silica-based electrochemical sensor for simultaneous determination of honokiol and magnolol

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Abstract A kind of mesoporous SiO_2 was synthesized using cationic surfactant as the structure-directing template. After that, the resulting mesoporous SiO_2 was used to modify the carbon paste electrode (CPE). The electrochemical behaviors of honokiol and magnolol were examined. In pH 6.5 phosphate buffer, two well-shaped oxidation peaks at 0.31 and 0.44 V were observed at the mesoporous SiO_2-modified CPE. Compared with the unmodified CPE, the mesoporous SiO_2-modified CPE remarkably enhances the oxidation peak currents of honokiol and magnolol. This suggests that mesoporous SiO_2 exhibits considerable surface enhancement effects to honokiol and magnolol. After optimizing the parameters such as pH value, amount of mesoporous SiO_2, and accumulation time, a sensitive and simple electrochemical method was proposed for the simultaneous determination of honokiol and magnolol. As to honokiol, the calibration curve is from 2.0 to 100.0 μg L^{-1}, and the limit of detection is 0.5 μg L^{-1} (1.8×10^{-9} mol L^{-1}). For magnolol, the linear range is from 20.0 to 200.0 μg L^{-1}, and the limit of detection is 10.0 μg L^{-1} (3.8×10^{-8} mol L^{-1}). Finally, the newly proposed method was successfully employed to determine honokiol and magnolol in Chinese traditional medicines.

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1 Introduction

Honokiol and magnolol are the effective components of Magnoliae Cortex that is a useful drug prescribed in many Chinese traditional medicines as an anodyne, a sedative, a stomach medicine or a cough remedy. Until now, various methods, such as high-performance liquid chromatography (HPLC) [1, 2], capillary electrophoresis [3, 4], liquid chromatography with mass spectrometry [5], and synchronous fluorescence spectroscopy [6], were reported for the determination of honokiol and magnolol. From their molecular structures, it is very clear that honokiol and magnolol contain phenolic hydroxy group, which can be oxidized and exhibit electrochemical activity. Therefore, electrophoresis [7, 8] and HPLC [9] with electrochemical detector were also reported for the determination of honokiol and magnolol. However, to the best of our knowledge, electrochemical determination of honokiol and magnolol using mesoporous SiO_2-modified electrode has not been reported.

Since the ordered mesoporous silica was reported in 1992 [10], the interest in this field has expanded all over the world. With distinctive characteristics such as highly uniform channels, large surface area, narrow pore-size distribution, and tunable pore sizes over a wide range, mesoporous materials have obtained wide applications in catalysis as well as in other realms of chemistry [11–14]. In this work, we wish to develop a novel electrochemical method for sensitive determination of honokiol and magnolol utilizing the excellent properties of mesoporous SiO_2. Thus, a kind of mesoporous SiO_2 was synthesized

according to the published work [15], and then used to modify the carbon paste electrode (CPE). At the mesoporous SiO_2-modified CPE, two well-defined oxidation peaks are observed at 0.31 and 0.44 V for honokiol and magnolol. Moreover, the oxidation peak currents of honokiol and magnolol greatly increase at the mesoporous SiO_2-modified CPE in comparison with those at the unmodified CPE. The remarkable peak current enhancement reveals that mesoporous SiO_2 possesses considerable surface enhancement effects to honokiol and magnolol. Undoubtedly, the sensitivity of determination of honokiol and magnolol will be greatly improved when using mesoporous SiO_2. Compared with other reported methods, the mesoporous SiO_2-modified CPE possesses rapid response, excellent simplicity, low cost and high sensitivity.

2 Experimental

2.1 Reagents

All the chemicals were of analytical grade and used directly. Honokiol and magnolol were obtained from National Institute for the Control of Pharmaceutical Biological Products (Beijing, China). Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), graphite powder (spectral reagent), and paraffin oil were purchased from the Sinopharm Chemical Reagent Co. Ltd., China.

2.2 Instruments

All the electrochemical measurements were performed using 610B electrochemical analyzer (CH Instruments, USA). A conventional three-electrode system, consisting of a mesoporous SiO_2-modified carbon paste working electrode, a saturated calomel reference electrode (SCE), and a platinum wire auxiliary electrode, was employed.

High performance liquid chromatographic determination was carried out with an Agilent 1100, coupled with a UV–VIS detector. The mobile phase was methanol–dichloromethane–water–phosphoric acid (81:3:16:0.12, v/v/v/v), filtered through a 0.45-μm Millipore filter and degassed prior to use. The flow rate was 0.5 mL min^{-1}. Detection was performed at a wavelength of 290 nm at room temperature. The sample injection volume was 20 μL.

2.3 Synthesis of mesoporous SiO_2

Mesoporous SiO_2 was synthesized according to the published work using CTAB as the template [15]. A solution of CTAB in NaOH solution was prepared and stirred at 298 K. After that, the silica source (TEOS) was added to this solution under stirring to give gel mixtures with the molar compositions: 1 SiO_2/0.25 NaOH/0.1 CTAB/100 H_2O. After 30 min of stirring at 298 K, the mixture was sealed and heated at 343 K for 24 h under static conditions. The resulting solid precipitate was recovered by filtration, washed with deionized water and then dried at 80 °C overnight. Finally, the dried solid precipitate was calcined at 823 K for 6 h to remove CTAB.

2.4 Preparation of mesoporous SiO_2-modified CPE

The synthesized mesoporous SiO_2 (0.2 g) was mechanically mixed with graphite powder (0.8 g) and paraffin oil (0.3 mL) in a carnelian mortar to give a homogenous modified carbon paste. After that, the resulting carbon paste was tightly pressed into the end cavity (3 mm in diameter) of working electrode, and the surface was polished on a smooth paper.

2.5 Sample preparation

The Cortex Magnoliae Officinalis (i.e. Magnolia Bark) used in this study was purchased from a local Pharmacy. The samples were dried at 60 °C for 2 h and then pulverized. The extraction of honokiol and magnolol was performed as follows [8]. One gram of the powder was accurately weighed and dispersed in 100.0 mL of methanol. The mixture was kept in a 60 °C water bath for 3 h. After cooling, it was sonicated for 30 min, then filtered and the volume made up to 100.0 mL for measurement.

2.6 Analytical procedure

Unless otherwise stated, pH 6.5 phosphate buffer (0.1 mol L^{-1}) was used as the supporting electrolyte for honokiol and magnolol. After 3-min accumulation, the differential pulse voltammograms were recorded from 0.10 to 0.70 V with following parameters: pulse amplitude = 40 mV, pulse width = 20 ms, and scan rate = 40 mV s^{-1}.

3 Results and discussion

3.1 Electrochemical behaviors of honokiol and magnolol

Figure 1 shows the cyclic voltammograms of honokiol in pH 6.5 phosphate buffer. During the cyclic potential sweep from 0.00 to 0.80 V, a pair of reversible redox peak is observed at the mesoporous SiO_2-modified CPE (curve a) and the unmodified CPE (curve b). The oxidation peak

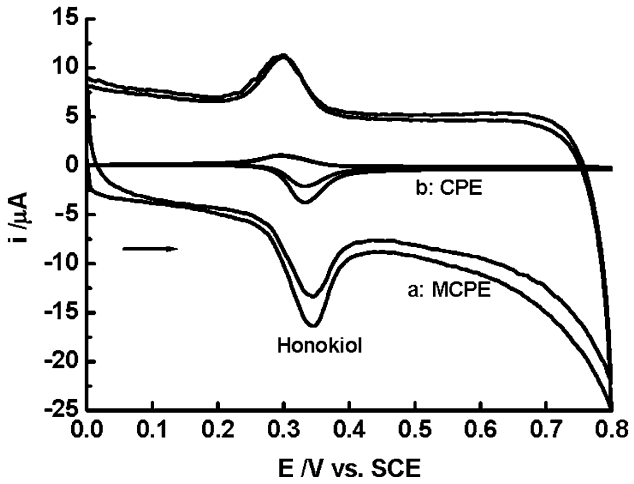

Fig. 1 Cyclic voltammograms of 5.0 mg L^{-1} honokiol in pH 6.5 phosphate buffer at mesoporous SiO_2-modified CPE (*curve a*) and CPE (*curve b*). Scan rate = 100 mV s^{-1}

potential (E_{pa}) is 0.34 V, and the reduction peak potential (E_{pc}) is 0.30 V. So the peak potential separation ($\Delta E_p = E_{pa} - E_{pc}$) is 40 mV. From the comparison, it is apparent that the peak currents of honokiol remarkably increase at the mesoporous SiO_2-modified CPE. The peak current enhancement suggests that the mesoporous SiO_2-modified CPE is more active to the oxidation of honokiol.

The cyclic voltammetric responses of magnolol in pH 6.5 phosphate buffer were examined, and the results are shown in Fig. 2. During the anodic sweep from 0.00 to 0.80 V, an oxidation peak at 0.46 V is observed at the unmodified CPE (curve a) as well as at the mesoporous SiO_2-modified CPE (curve c). On the reverse scan, no reduction peak appears, indicating that the oxidation of magnolol is totally irreversible. During the second anodic sweep, the oxidation peak currents of magnolol remarkably decrease, may be attributed to the fact that the oxidative product of magnolol adsorbs at electrode surface. In addition, it was found that the oxidation peak currents of magnolol obviously increase after 1-min accumulation at the unmodified CPE (curve b) and the mesoporous SiO_2-modified CPE (curve d). Accumulation improves the surface concentration of magnolol, so the oxidation peak currents correspondingly increase. From Fig. 2, it is also found that the mesoporous SiO_2-modified CPE remarkably improves the oxidation signals of magnolol, which attributed to the excellent properties of mesoporous SiO_2.

The electrochemical behaviors of coexistence of honokiol and magnolol were investigated since they usually co-exist. Figure 3 depicts the differential pulse voltammograms of honokiol and magnolol in pH 6.5 phosphate buffer. After 3-min accumulation, two separate oxidation peaks are observed at the unmodified CPE (curve a) and the mesoporous SiO_2-modified CPE (curve c). The peak potentials are 0.31 and 0.44 V for honokiol and magnolol, and the oxidation peak potential difference is as large as 130 mV. From the comparison of curves (a) and (c), it was found that the oxidation peak currents of honokiol and magnolol significantly increase at the mesoporous SiO_2-modified CPE. Mesoporous SiO_2 with regular and specific mesoporous channels offers huge surface area and numerous active sites, therefore, the mesoporous SiO_2-modified CPE exhibits highly efficient accumulation efficiency to honokiol and magnolol. As a result, the oxidation peak currents of honokiol and magnolol remarkably

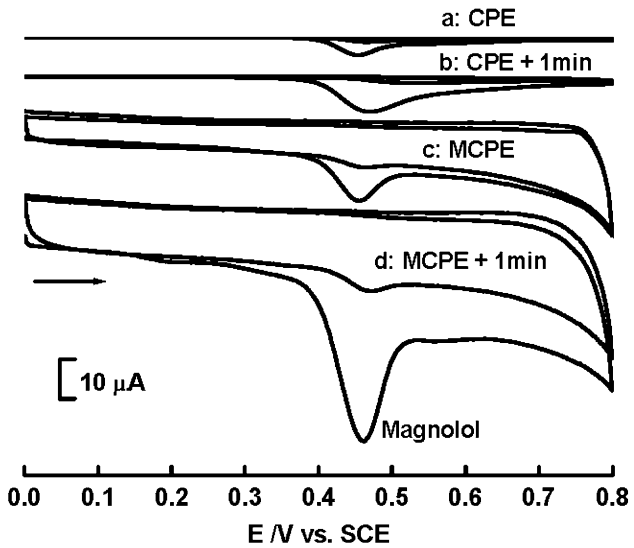

Fig. 2 Cyclic voltammograms of 5.0 mg L^{-1} magnolol at CPE (*a*, *b*) and mesoporous SiO_2-modified CPE (*c*, *d*). (*b*, *d*) after 1-min accumulation. Scan rate = 100 mV s^{-1}

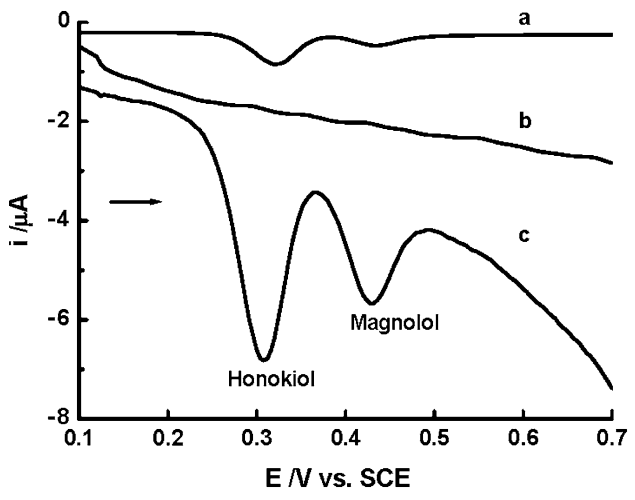

Fig. 3 DP voltammograms of 0.1 mg L^{-1} honokiol and magnolol at CPE (*a*) and mesoporous SiO_2-modified CPE (*c*). (*b*) blank voltammograms of mesoporous SiO_2-modified CPE. Accumulation time = 3 min, pulse amplitude = 40 mV, pulse width = 20 ms, scan rate = 40 mV s^{-1}

increase. Otherwise, the differential pulse voltammograms of mesoporous SiO_2-modified CPE in pH 6.5 phosphate buffer were given in curve (b) for a better understanding. The curve is smooth and no oxidation peak is observed, revealing that the oxidation peaks at 0.31 and 0.44 V are assigned to honokiol and magnolol.

3.2 Optimization of detection

The electrochemical responses of honokiol and magnolol at the unmodified CPE and mesoporous SiO_2-modified CPE were examined in pH 5.5, 6.0, 6.5, 7.0, 7.5, 8.0 phosphate buffer (0.1 mol L^{-1}). When increasing pH value from 5.5 to 6.5, the oxidation peak currents of honokiol and magnolol gradually increase. As further improving pH value from 6.5 to 8.0, the oxidation peak currents gradually decrease. Therefore, pH 6.5 phosphate buffer was employed to achieve high sensitivity. In addition, the oxidation peak potentials of honokiol and magnolol shift negatively with increasing pH value, indicating that proton is involved in their oxidation.

The effects of amount of mesoporous SiO_2 on the electrochemical responses of honokiol and magnolol were evaluated. When gradually improving the amount of mesoporous SiO_2 from 0 to 10%, the oxidation peak currents of honokiol and magnolol increase dramatically. As further increasing the amount to 20%, the oxidation peak currents increase slightly. When improving the amount of mesoporous SiO_2, the active sites for honokiol and magnolol also increase. So, their oxidation peak currents correspondingly increase. However, the oxidation peak currents begin to decrease when the amount of mesoporous SiO_2 is higher than 20%, maybe due to poor electric conductivity of mesoporous SiO_2. Therefore, the amount of mesoporous SiO_2 is selected as 20%.

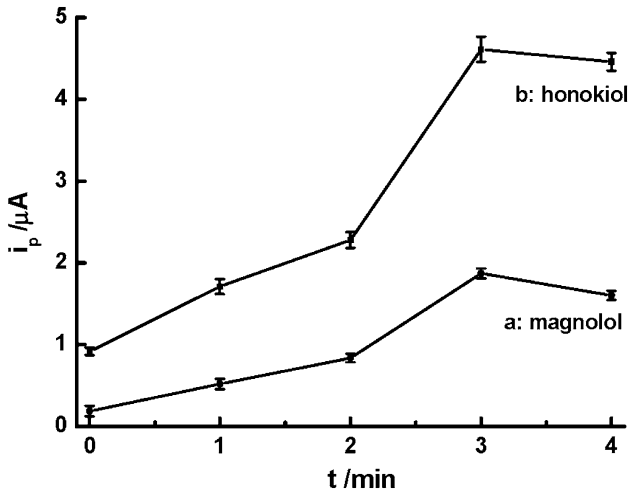

Fig. 4 Effects of accumulation time on the oxidation peak currents of 0.1 mg L^{-1} magnolol (*a*) and honokiol (*b*)

Figure 4 shows the influence of accumulation time on the oxidation peak currents of honokiol and magnolol. As gradually improving the accumulation time from 0 to 3 min, the oxidation peak currents of honokiol and magnolol significantly increase. When further increasing the accumulation time, the oxidation peak currents change very slightly, suggesting that the amount of honokiol and magnolol tends to a limiting value. Considering sensitivity and working efficiency, 3-min accumulation is employed.

3.3 Reproducibility, linear range, and limit of detection

The mesoporous SiO_2-modified CPE was used for single measurement in this work. The reproducibility between multiple modified electrodes was estimated by measuring the oxidation peak currents of honokiol and magnolol. The RSD of 10 mesoporous SiO_2-modified CPEs is 5.8 and 5.3% for 0.1 mg L^{-1} honokiol and magnolol, indicative of excellent reproducibility.

The linear range and limit of detection for honokiol and magnolol were individually examined using differential pulse voltammetry (DPV) under the optimized conditions. For honokiol, the linear range is over the range from 2.0 to 100.0 μg L^{-1} with correlation coefficient of 0.997. After 3-min accumulation, the limit of detection is as low as 0.5 μg L^{-1} (1.8×10^{-9} mol L^{-1}). As to magnolol, the calibration curve is from 20.0 to 200.0 μg L^{-1} with correlation coefficient of 0.996, and the limit of detection is 10.0 μg L^{-1} (3.8×10^{-8} mol L^{-1}) after 3-min accumulation.

3.4 Interference

The possible interferences of other species on the determination of honokiol and magnolol were examined. It was found that 1000-fold concentrations of Cd^{2+}, Pb^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, 4-nitrophenol, 2-chlorophenol; 500-fold concentrations of xanthine, uric acid, hypoxanthine, phenol, resorcinol, lysine, cysteine; 100-fold concentrations of dopamine, ascorbic acid, and catechol, almost do not interfere with the oxidation signals of honokiol and magnolol since the peak current change is below 5%.

3.5 Analytical application

Under the optimized conditions, the mesoporous SiO_2-modified CPE was used to determine honokiol and magnolol in several Cortex Magnoliae Officinalis. Figure 5a depicts the DP voltammograms of sample solution in pH 6.5 phosphate buffer after 3-min accumulation. During the potential sweep from 0.10 to 0.70 V, two oxidation peaks

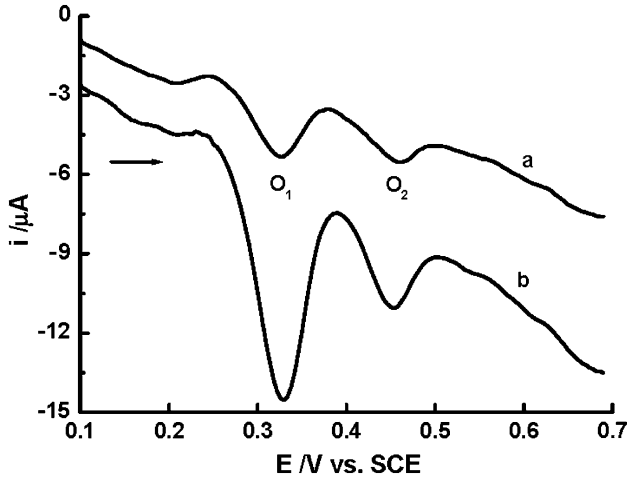

Fig. 5 DP voltammograms of honokiol and magnolol at mesoporous SiO_2-modified CPE in sample solution (*a*) and after addition of standard solutions (*b*)

Table 1 Determination of honokiol and magnolol in Cortex Magnoliae Officinalis

Sample		By HPLC/ mg g^{-1}	By this method/ mg g^{-1}	RSD (%)	Recovery (%)
A	Honokiol	14.8	15.2	4.2	101.3
	Magnolol	30.4	29.3	4.0	96.5
B	Honokiol	41.9	41.3	3.2	97.7
	Magnolol	35.2	36.6	3.1	96.8
C	Honokiol	9.5	10.2	4.3	96.7
	Magnolol	9.6	10.8	4.7	98.2

(O_1 and O_2) appear. After addition of honokiol and magnolol standard solution, the peak currents of O_1 and O_2 increase (Fig. 5b). So, the content of honokiol and magnolol can be easily achieved from the peak current ratio. Each sample was determined in triplication with RSD below 5%. The results are summarized in Table 1. In order to testify the accuracy of this method, the content of honokiol and magnolol was also detected by HPLC [1]. The results obtained by two methods are in good agreement, indicating that the newly developed method is reliable and accurate. In addition, the recovery for honokiol and magnolol was also tested, and the value is in the range from 96.5 to 101.3%, also revealing that the mesoporous SiO_2-modified CPE is effective and reliable for the determination of honokiol and magnolol.

4 Conclusion

A kind of mesoporous SiO_2 was synthesized using CTAB as the template, and then used to modify the CPE. Owing to specific and uniform mesoporous networks, large surface area and high sorption capacity, the mesoporous SiO_2-modified electrode significantly improves the response signals of honokiol and magnolol. Based on this, a sensitive and simple method was proposed, which successfully employed to determine honokiol and magnolol in Chinese traditional medicines.

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