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Electrochemical mechanism of eugenol at a Cu doped gold nanoparticles modified glassy carbon electrode and its analytical application in food samples

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ABSTRACT

A simple one-step electrodeposition method was used to construct a glassy carbon electrode (GCE), which has been modified with Cu doped gold nanoparticles (GNPs), i.e. a Cu@AuNPs/GCE. This electrode was characterized with the use of scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The eugenol was electrocatalytically oxidized at the Cu@AuNPs/GCE. At this electrode, in comparison with the behavior at the GCE alone, the corresponding oxidation peak current was enhanced and the shift of the oxidation potentials to lower values was observed. Electrochemical behavior of eugenol at the Cu@AuNPs/GCE was investigated with the use of the cyclic voltammetry (CV) technique, and additionally, in order to confirm the electrochemical reaction mechanism for o-methoxy phenols, CVs for catechol, guaiacol and vanillin were investigated consecutively. Based on this work, an electrochemical reaction mechanism for o-methoxy phenols was suggested, and in addition, the above Cu@AuNPs/GCE was successfully employed for the analysis of eugenol in food samples.

1. Introduction

The electro-oxidation of phenol compounds on the electrode surface is important for many reasons, which include the treatment of phenolic wastewater [1] and the synthesis of quinines; also, the passivating layer made from phenols can act as a protective coating for metals or protect an electrode's surface from corrosion [2]. However, the electro- chemical oxidation of phenol is quite a complex process [3] and the distribution of the reaction products as well as the reaction pathway involved, may be affected by: the concentration of phenolic compounds, electrode material involved, pH of the reaction medium, current density, potential as well as other related properties [1]. Consequently, the knowledge of the electrochemical mechanism of phenol compounds is of considerable interest and usefulness in this field.

Phenolic phytochemicals are one broad class of nutraceuticals found in plants, which have been extensively researched in relation to their health-promoting potential [4]. Eugenol (4-allyl-2-methoxyphenol), an aromatic molecule, is found in plant products such as cloves, bay leaves and allspice, and it has been used for general pain relief [5–7].

In the central nervous system, eugenol is neuroprotective against excitotoxicity, cerebral ischemia, and the toxic effects of amyloid-β peptides [8]. It has been effective in animals against generalized seizures [9]. Also, eugenol has anti-viral, -oxidant, and–inflammatory properties [10,11]. On the other hand, it can be used in cosmetics and as a flavoring agent in food products. At low concentrations, it commonly acts as an anti-oxidant and an anti-inflammatory agent, whereas at higher concentrations, it acts as a strong oxidant causing increased generation of tissue-damaging free radicals [12]. Additionally, it has been reported to have anti-genotoxic activity [13].

Both the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) have recommended for humans, an acceptable daily intake of eugenol of 2.5 mg kg^{-1} body weight [14]. Also, the U.S. Food and Drug Administration (FDA) considered eugenol to be safe, and the compound is regarded to be non-carcinogenic and non-mutagenic. Various analytical methods for the determination of eugenol in real samples have been reported, and they included high-performance liquid chromatography (HPLC) [15,16], gas chromatography-mass spectrometry

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(GC-MS) [17], liquid chromatography-mass spectrometry (LC-MS) [18], and electrochemical methods [19,20]. Although these mentioned methods are relatively satisfactory, the instruments involved are often expensive and costly to run and maintain, and the pretreatment process for samples is generally complicated and time-consuming. Thus, some alternative relatively inexpensive and less complex analytical methods would be quite useful. Electrochemical techniques have certain advantages, such as low cost, fast analysis, miniaturization and high sensitivity. Often, these methods are not considered as an alternative and effective method for practical application.

Recent studies have suggested that eugenol may have anti-cancer properties [21,22], and additionally, the molecular mechanism of eugenol-induced apoptosis in melanoma, skin tumors, osteosarcoma, leukemia, gastric and mast cells has been well documented. However, the electrochemical mechanism of eugenol has not been reported so far in the literature.

In general, alloys usually have better properties than their individual metals. In addition, by incorporating common metals into noble metals, the consumption of noble metals can be reduced and more functions may be achieved. Consequently, they have been used in the fabrication of fuel cells and sensors [23–28], e.g. AuCu alloy [29,30]. Such information formed the basis of this investigation, the aims of which were: 1. to investigate the electrochemical mechanism of eugenol and other o-methoxyphenol compounds at the Cu@AuNPs/GCE; 2. to research and develop a quantitative electroanalytical method for eugenol at the Cu@AuNPs/GCE with the use of cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

2. Experimental

2.1. Instrumentation

Electrochemical measurements were carried out on a CHI-660A electrochemical workstation (Shanghai Chenhua Instruments, China). A conventional three-electrode system was used throughout the experiments.

The working electrode was a Cu@AuNPs/GCE (3 mm in diameter), the counter electrode was a platinum wire and a saturated calomel electrode (SCE) was the reference sensor. All potentials were reported with respect to the SCE. A cell stand (Model BAS-C1A, BAS Co., USA) was used to stir the testing solution during the pre-concentration step.

The samples were also measured by a well established HPLC method with the use of an Agilent 1100 series HPLC-DAD system equipped with a G1379A vacuum degasser, a G1311A quaternary pump, a G1313A autosampler, an injector with a 100 μL loop, and a G1315B diode array detector. For chromatographic measurements, an Agilent ZORBAX Eclipse XDB-C18 column (250 mm × 4.6 mm, 5 μm) was used together with an Agilent Zorbax high pressure reliance cartridge guard-column (C18, 12.5 mm×4.6 mm, 5 μm).

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) were obtained using a field emission scanning electron microscope (FESEM; JSM-6701F JEOL, Japan). The samples for SEM and EDS imaging were electro-deposited onto the detachable GCE. The magnification for all samples was 30,000x and the power level was 10.0 kV.

X-ray diffraction data were recorded with a Bede D1 System (Bede Scientific Instruments, Durham, UK) using Cu K_α radiation (λ=1.5406) and Bragg angle range ($10^\circ \sim 70^\circ$).

2.2. Reagents

Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$), eugenol and vanillin were purchased from Aladdin Reagent Database Co. (Shanghai, China). All other chemicals (analytical grade) were obtained from Beijing Chemical Reagent Co. (Beijing, China) without further purification. A Britton-Robinson (B-R) buffer was prepared by mixing sodium hydroxide (0.2 mol L^{-1}) with mixed acids containing 0.034 mol L^{-1} ortho-phosphoric, 0.040 mol L^{-1} acetic acid and 0.040 mol L^{-1} boric acid; the buffer (pH 2.00) was monitored with an Orion SA720 meter (Boston, MA, USA). Doubly-distilled water was used throughout the experiments.

2.3. Experimental procedure and voltammetic parameters

Eugenol, vanillin, guaiacol and catechol were investigated, and a suitable amount of each 100 μg mL^{-1} solution, together with 2.0 mL B-R buffer (pH 2.00), were transferred to the electrochemical cell and diluted to 10.0 mL with distilled water. The CV and LSV measurements were carried out with the use of the three electrode set-up, and the respective profiles were recorded at potentials between +0.2 - +1.0 V at a scan rate of 100 mV s^{-1}. The first anodic peak for eugenol was used for quantitative analysis of the substance. All experiments were carried out at room temperature ($25 \pm 0.5\,^\circ C$).

2.4. Preparation of Cu@AuNPs/GCE

Prior to its modification, the bare GCE (3 mm diameter) was polished, in order, with 1.0, 0.3 and 0.05 μm alumina slurries, and sonicated sequentially in dilute nitric acid, ethanol and distilled water. Then, the GCE was successively scanned in 0.25 mol L^{-1} H_2SO_4 over the potential range of -1.0 - 1.0 V at a scan rate of 100 mV s^{-1} until a steady state was reached. Finally, the clean GCE was immersed into 10.0 mL of 5.0×10^{-4} mol L^{-1} $HAuCl_4$ solution containing 2.0×10^{-4} mol L^{-1} $CuSO_4$, 0.01 mol L^{-1} Na_2SO_4 and 0.01 mol L^{-1} H_2SO_4, and the GCE was submitted to 10 successive potential sweeps from -0.50 V to 1.50 V with a scan rate of 0.1 V s^{-1}; thus, a Cu@AuNPs nano-particles were electrodeposited, and when the eugenol analyte was introduced under these conditions a maximum peak current was obtained. Finally, at the end of this electroanalytical process the Cu@AuNP/GCE was removed and rinsed with doubly distilled water.

2.5. Treatment of real samples

A spice or curry powder samples (5.0 g) was placed into a 100 mL Erlenmeyer flask (with a screw cap) and pure ethanol (5.0 mL) was added. The mixture was shaken vigorously for 30 min and transferred to a 10 mL centrifuge tube, and centrifuged at 3000 rpm for 10 min. After a settling time of 2 min, the supernatant was transferred quantitatively into a 50 mL volumetric flask. The above extraction procedure was repeated twice. All extracts were collected, and transferred into a 50 mL volumetric flask; then, the solution was diluted to the mark with ethanol. A 1.0 mL aliquot of this sample solution was analysed by the voltammetric procedure.

2.6. HPLC procedure

The analyses of eugenol in spice and curry powders samples were carried out with the use of an HPLC instrument equipped with UV-vis detection at 280 nm as mentioned in section 2.1. Two solutions were used for the mobile phase: (A) methanol and (B) 0.01 mol L^{-1} NaH_2PO_4. A gradient was developed as follows: the solution A (v/v) ratio was 65% within 0-10 min. The flow rate was kept at 1.0 mL min^{-1} and under this condition, the retention time for eugenol was 5.82 min. Each sample solution (10 μL) was