

Gold nanoparticles modified carbon paste electrode for differential pulse voltammetric determination of eugenol



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ABSTRACT

In the present study, a carbon paste electrode chemically modified with gold nanoparticles was used as a sensitive electrochemical sensor for determination of eugenol. The differential pulse voltammetric method was employed to study the behavior of eugenol on this modified electrode. The effect of variables such as percent of gold nanoparticles, pH of solution, accumulation potential and time on voltammogram peak current were optimized. The proposed electrode showed good oxidation response for eugenol in 0.1 mol L⁻¹ phosphate buffer solution (pH 8) and the peak potential was about +285 mV (vs. Ag/AgCl). The peak current increased linearly with the eugenol concentration in the range of 5–250 μmol L⁻¹. The detection limit was found to be 2.0 μmol L⁻¹ and the relative standard deviation was 1.2% (n = 7). The effect of interferences on the eugenol peak current was studied. The method has been applied to the determination of eugenol in different real samples, spiked recoveries were in the range of 96%–99%.

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1. Introduction

Eugenol [1-hydroxy-2-methoxy-4-allylbenzene] (Fig. 1) is a major component of clove essential oil, which has been widely used as a herbal drug [1]. It has demonstrated several biological activities such as an anti-inflammatory [2], anti-oxidation [3] and anti-bacterial activity against both gram positive and gram negative microorganisms [4]. This compound is also widely used in dentistry as a cement material with zinc oxide or as a sedative agent [5]. Determination of eugenol and related components is significant in neurochemistry and brain science studies. Many studies report that natural aromatic essential oils contain eugenol [6–9]. Several techniques such as Headspace solid-phase microextraction–gas chromatography–mass spectrometry (HS-SPME/GC/MS) [10], high performance liquid chromatography (HPLC) [11], dropping mercury electrode (DME), direct current polarographic (DCP) and differential pulse polarographic (DPP) [12] have been proposed for its determination. There are few electrochemical theories reported in eugenol determination [12–14]. In comparison with various analytical techniques, using the modified electrode is significantly better at detection and determination of important chemical compounds due to its easy preparation method, compatibility,

reliability and wide electro analytical applications [15–18]. The chemical modifications of bare electrodes offer significant advantages in the design and development of electrochemical sensors [19,20]. In operation, electrode surface modification has been tried as a means to reduce overvoltage and to overcome the slow kinetics of many electrode processes [21]. A further advantage of the chemically modified electrodes is that they are less prone to surface fouling compared to bare electrodes [22]. The ease and speed of preparation and obtaining a new reproducible surface, low residual current, porous surface and low cost are advantages of modified carbon paste electrodes (MCPEs) over all other solid electrodes [23]. In recent years nanomaterials modified electrode has been used in the electrochemical sensor. Gold nanoparticle (GN) is a commonly used metal nanomaterial with the characteristics such as high metal conductivity and good biocompatibility, which has been widely used in the field of chemically modified electrodes [24–27]. Moreover, gold nanoparticle has a catalytic effect on peak current and potential in modified electrodes [28,29]. The voltammetric sensor based on gold nanoparticles for determination of biological molecules such as cysteine [30], carcinoembryonic antigen [31], norepinephrine [32] and protein [33] has received much attention due to its good stability and biocompatibility.

In this study we introduce a carbon paste electrode chemically modified with gold nanoparticles used as a sensitive electrochemical sensor for determination of eugenol. This modified electrode showed significant response for the detection of eugenol in lab and real samples using differential pulse voltammetric method.

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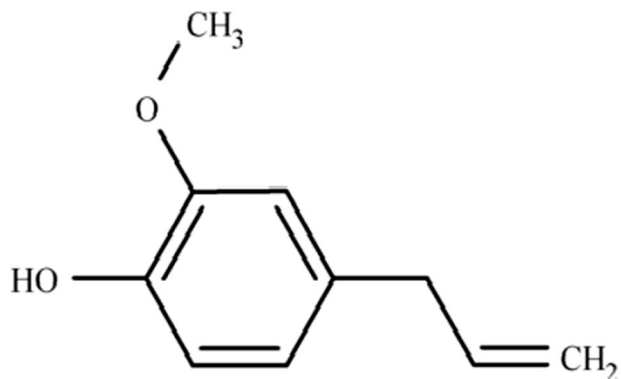


Fig. 1. Structure of [1-hydroxy-2-methoxy-4-allylbenzene] (Eugenol).

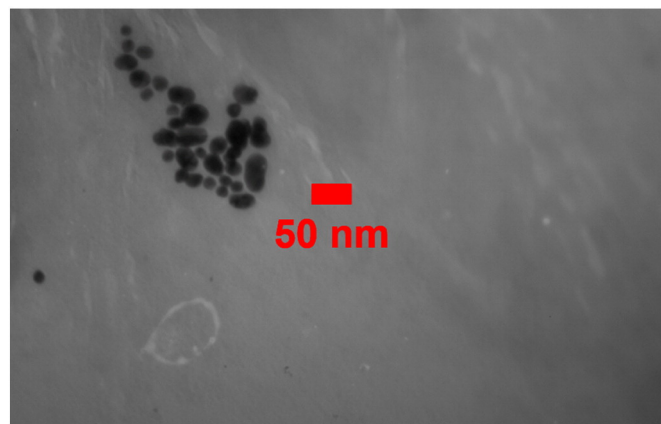


Fig. 2. TEM image of gold nano particles.

2. Experimental

2.1. Reagents and solutions

The standard solution of eugenol, tetrachloroauric acid (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and sodium citrate were purchased from Merck (Darmstadt, Germany). Working solutions were prepared daily by appropriate dilution. All solutions were prepared using double distilled water. Clove essential oils and pharmaceutical products were purchased from Merck. Phosphate buffer (0.1 mol L^{-1}) was prepared by dissolving appropriate amount of phosphoric acid in water and $\text{pH} = 8$ was adjusted by adding 1.0 mol L^{-1} NaOH to this solution. Highly pure graphite powder, sulfuric acid, acetic acid and boric acid were purchased from Merck.

2.2. Apparatus

All voltammetric experiments were performed using Autolab electro analyzer, Model PG-STAT-101 from Metrohm (Switzerland). A conventional three-electrode cell was used at room temperature with a carbon paste modified electrode as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode and a platinum wire as the auxiliary electrode. A RH B-KT/C magnetic stirrer was employed for deposition step (Germany).

2.3. Synthesis and functionalization of gold nanoparticles

Gold nanoparticles were prepared following the method of Gopu et al. [8]. Briefly, 95 mL of an aqueous chloroauric acid solution containing 5 mg of Au was brought to boil and then 5 mL of 1% sodium citrate solution was added to the boiling solution. The color of the solution first changed to bluish, then to purplish and eventually to ruby red. The solution was further boiled for 30 min and left to cool to ambient temperature [8]. TEM image shows that spherical particles with a diameter of $9 \pm 2 \text{ nm}$ Fig. 2. The particle size distribution curve for synthesized GNs. is given in Fig. 3.

2.4. Preparation of the modified carbon paste electrode

The carbon paste electrode was prepared by mixing fine graphite powder with paraffin (70:30, w/w) in a mortar and pestle. A portion of the composite mixture was packed into the end of a glass tube (3.4 mm inner diameter). Electrical contact was made by forcing a copper wire down into the tube and into the back of the composite. A small amount of carbon paste was forced out from the tube and cut off with a scalpel. The electrode surface was smoothed by polishing on a piece of graph paper while a slight manual pressure was applied to the piston. To prepare the modified composite electrode, 500 mg of the graphite

powder was mixed with 3 mL of GN solution. This modified composite was air dried for 24 h and then used in the same way as the unmodified composite. TEM image is shown in Fig. 4.

2.5. General procedure

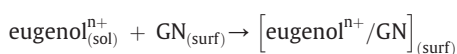
The analytical procedure consisted of a closed-circuit accumulation of eugenol onto the modified carbon paste electrode surface. The preconcentration/voltammetric determination was used in all differential pulse adsorptive anodic stripping voltammetric experiments. In the first step the MCPE was immersed in 10 mL of phosphate buffer which worked as an electrolyte containing a known amount of eugenol. The deposition potential of +0.1 V was applied for 100 s while the solution was stirring. The stirring was then stopped for a period of 10 s and the potential was scanned in differential pulse mode (with 15 mV s^{-1} scan rate, 100 mV pulse amplitude and 40 ms pulse period) from 150 to 500 mV. The resulted oxidation peak registered at about +285 mV and its currents were used as a measure of eugenol concentration. Each scan was repeated three times with a new surface of electrode for each analyzed solution and the mean of these voltammograms was obtained. All experiments were carried out at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

3. Results and discussion

3.1. Electrochemical behavior of eugenol at the carbon paste electrode modified with gold nanoparticles

The studies of the voltammetric behavior of the eugenol were performed using differential pulse voltammetry. DPV was used in the voltammetric measurement owing to its good sensitivity. Fig. 5 compares typical differential pulse voltammograms of $100 \mu\text{M}$ eugenol recorded at two different working electrodes (i.e. bare CPE (curve b) and GN-CPE (curve a)) after 100 s accumulation under close circuit condition in a phosphate buffer ($\text{pH} = 8.0$) solution. As seen in Fig. 5a, at the GN-CPE, compared to the bare CPE, the oxidation peak of eugenol shifted to more negative values direction and also the peak current increased. The enhanced peak current response and shift in the oxidation potential are clear evidences of the catalytic effect of the GN-CPE toward oxidation eugenol.

Based on the results and under the conditions of the experiment, the possible pathways for the analysis cycle are postulated below ("sol", and "surf" subscripts mean that compound is in solution or surface):



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