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Electrochemical sensor based on graphene doped gold nanoparticles modified electrode for detection of diethylstilboestrol

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ABSTRACT

An electrochemical sensor for detection of diethylstilboestrol (DES) was successfully developed. At first, graphene-modified glassy carbon electrode (Gr/GCE) was fabricated by casting graphene (Gr) on the surface of the pretreated glassy carbon electrode (GCE). Then, gold nanoparticles (Nano-Au) were produced by reducing gold chloride tetrahydrate ($HAuCl_4$) employing cyclic voltammetry (CV). Electrochemical behavior of DES at the graphene doped gold nanoparticle modified glassy electrodes (Gr/Nano-Au/GCE) was studied and a new method was developed for the electrochemical analysis of DES. Gr/Nano-Au/GCE showed a good catalytic performance for the electrochemical oxidation of DES in pH = 6.0 phosphate buffer solution (PBS). The oxidation peak currents of DES showed a linear relationship with their concentrations in the ranges of 1.20×10^{-8}–1.20×10^{-5} mol L^{-1}. The estimated detection limit is 9.80×10^{-9} mol L^{-1}. When the relative error is less than ±5%, no interference was found when detection was performed in the presence of some common ions, estradiol, estriol, estrone and folic acid. The modified electrode has good selectivity and stability and has been successfully applied to the detection of DES in food samples.

1. Introduction

Diethylstilbestrol (DES) is a kind of synthetic estrogens. It is used widely as a growth stimulant in animals for food and as a treatment for estrogen-deficiency disorders in veterinary medicine [1,2]. It was also prescribed to pregnant women to prevent miscarriage, premature labor, and related complications of pregnancy. But the unfortunate side-effects of such treatment are well known [3]. Its presence as a residue in meat and its proven carcinogenic nature for human beings and laboratory animals has led to the regulation of its use. Therefore, it is of great importance to develop a fast and efficient method for its detection to prevent illegal usage.

Various methods such as gas chromatography–mass spectrometry [4–6], liquid chromatography–mass spectrometry [7–10], electrochemical immunoassay [11] or chemiluminescence [12] have been reported for the detection of DES. However, the above noted techniques usually require expensive instruments and/or materials, large amount of highly purified solvents, and are time-consuming.

Recently, chemically modified electrodes have been used widely in analytical chemistry. Electrochemical methods provide a simple, convenient, and fast means for detecting biological and environmental molecules. DES has the property of electrochemical activity because of hydroxyl groups in its molecule. In the past few years, electrochemical detection of DES has been reported [13–15]. However, there is no report on detection of DES using Gr/Nano-Au/GCE by electrochemical method, to our best knowledge.

Due to its extraordinary structure and properties, graphene exhibits excellent electronic, optical, mechanical and thermal properties [16–18]. It has been used to modify electrodes for electrochemical studies [19–26]. Metal nanoparticles also have been used widely as sensing material to modified electrode because of its excellent conductivity, good electrocatalytic activity and chemical stability [27–31]. Among various metal nanoparticles, gold nanoparticles have been extensively studied in electroanalytical chemistry because of their unique properties [32–34], such as good biological compatibility and conductivity. They have synergistic effects on the chemical and physical properties, which can enhance the sensitivity and the stability of the graphene modified electrode.

In this work, a Gr/Nano-Au/GCE was prepared. The electrochemical behavior of DES was studied and a new method for the detection of DES was developed. The results showed that the oxidative peaks increased linearly with DES concentration in the range

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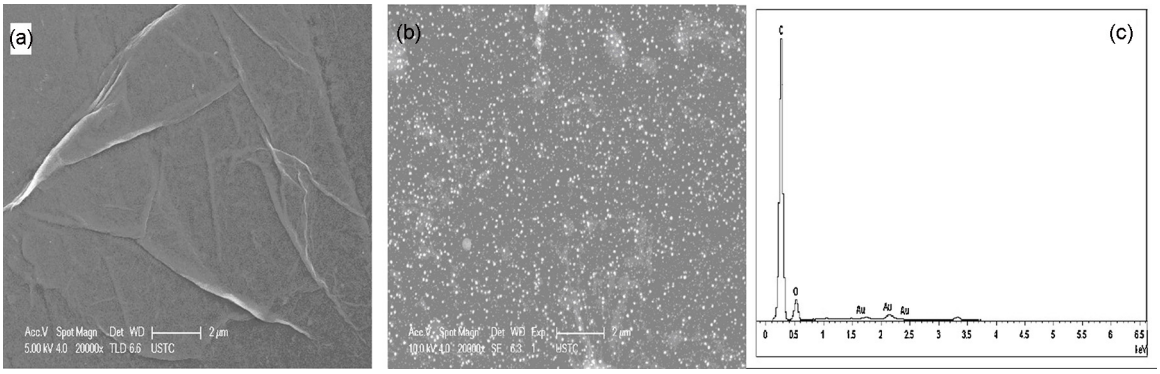

Fig. 1. (a) SEM image of Gr/GCE. (b) SEM image of Gr/Nano-Au/GCE. (c) EDS spectrum of Gr/Nano-Au/GCE film.

of $1.20 \times 10^{-8}$and 1.20×10^{-5}mol L^{-1}, with a detection limit of 9.80×10^{-9} mol L^{-1}. The method was successfully applied to the quick detection of DES in food samples with good results.

2. Experimental

2.1. Apparatus and chemicals

Electrochemical measurements were performed on a CHI 660C Workstation (CH Instruments, Shanghai, China) with a conventional three-electrode system, which composed of a bare or modified GCE as the working electrode, and a saturated calomel electrode and a platinum wire electrode as the reference and counter electrodes, respectively. Ultrasonic cleaning was performed using a KQ-100 ultrasonic cleaner (Kunshan, China) and solution pH was measured using a pHS-3B pH meter (Shanghai, China). SYZ-550 Quartz Sub-Boiling High-purified Water Distiller (Jiangsu, China) and MT Infrared lamp (Guangzhou, China) were used.

DES was purchased from Chengdu Aikeda Chemical Reagent Co., Ltd (Chengdu, China). Food samples (beef, fish, and milk powder) were obtained from the local markets (Heze, China). The concentration of 1.00×10^{-3} mol L^{-1} standard solution of DES was prepared in alcohol. Graphene was synthesized from graphite powder according to our previously reported method [35]; 0.3 mg suspension graphene was dispersed in 10 mL water after sonication to prepare a suspension solution of 0.3 mg mL^{-1}. Buffer solution was obtained by mixing the stock solutions of 0.20 mol L^{-1} sodium phosphate dibasic (Na_2HPO_4) and 0.10 mol L^{-1} citric acid. All reagents were obtained as analytical grade and used without further purification. Double distilled water was used throughout the experiments. All experiments were performed at room temperature.

2.2. Preparation of Gr/Nano-Au/GCE

A glassy carbon electrode (Φ = 3.8 mm) was polished before each experiment with gold sand paper (2000-Grit) and Al_2O_3 slurry, respectively, and was then rinsed with distilled water between each polishing step. Next, it was sonicated successively with 50% nitric acid, absolute alcohol and doubly distilled water, and dried in air. The Gr/GCE was prepared by casting 5 μL of graphene suspension (0.3 mg ml^{-1}) on the electrode surface and dried under an infrared lamp. A Gr/Nano-Au/GCE was prepared by immersing the Gr/GCE into an aqueous solution containing 0.1 mol L^{-1} KNO_3 and 5 mmol L^{-1} $HAuCl_4$ with a scan rate of 50 mV s^{-1} in the potential range of −0.2 V to 1.0 V for two cycles. A Nano-Au/GCE was prepared for comparison studies by immersing the pre-treated GCE into an aqueous solution containing 0.1 mol L^{-1} KNO_3 and 5 mmol L^{-1} $HAuCl_4$ under the same conditions.

Table 1
Content of C, O and Au elements.

Element	Weight/5	Atom/%
C	42.42	54.65
O	45.95	44.44
Au	11.63	0.91
Total	100.00	100.00

The morphology and chemical composition of the Gr/GCE and Gr/Nano-Au/GCE surface were investigated and verified by SEM and EDS, as shown in Fig. 1. From the Fig. 1b, it can be observed that large amounts of gold nanoparticles were well-dispersed on the surface of the Gr/GCE. At the same time, EDS spectrum of Gr/Nano-Au/GCE film was carried out, as shown in Fig. 1c. The content of C, O and Au are lasted in the Table 1. The EDS image confirmed the presence of Au elements on the surface of Gr/GCE.

2.3. Analytical procedure

Certain amounts of pH 6.0 PBS and DES standard solutions were pipetted into a 50 mL electrolytic cell. Electrochemical measurements were performed with a CHI 660 C Workstation having a three-electrode cell configuration comprising a bare GCE, a Gr/GCE, a Nano-Au/GCE or a Gr/Nano-Au/GCE as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum as the counter electrode. After stirring for 90 s, cyclic voltammograms (CVs) were obtained by scanning in the potential range from −0.2 V to 0.8 V. Scan rate was 100 mV s^{-1}. The modified electrode was placed in pH = 6.0 PBS and scanned until no peak for reuse.

3. Results and discussion

3.1. The choice of graphene volume

The redox peak current of DES was affected by the volume of graphene. Therefore, we investigated the effect of the volume of graphene casted on GCE. At the graphene concentration of 0.3 mg mL^{-1}, the current peak of DES increased as the volume of graphene increased from 1 to 5 μL, and then decreased while the amount of graphene suspension exceeded 5 μL. This may be due to high loading of graphene increased the thickness of the modified layer on GCE, then the catalyst on the surface cannot be utilized effectively and catalytic substrates have been hampered to spread to the electrode surface. Thus, we used 5 μL of a 0.3 mg mL^{-1} graphene suspension to prepare the modified electrodes in our experiments .