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ORIGINAL PAPER

Electrochemical determination diethylstilbestrol by a single-walled carbon nanotube/platinum nanoparticle composite film electrode

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Abstract Platinum nanoparticles (Pt_{nano}) were prepared and used in combination with single-wall carbon nanotube (SWNT) for fabricating electrochemical sensors with remarkably improved sensitivity toward diethylstilbestrol (DES). The glassy carbon (GC) electrode modified with SWNT/Pt_{nano} composite film exhibited excellent electrochemical behaviors toward the redox of DES. Compared with the bare GC electrode and SWNTs film modified GC electrode, the redox peak currents at the SWNTs/Pt_{nano} composite film modified GC electrode was enhanced greatly. The experimental parameters, which influence the peak current of DES, were optimized. Under optimal conditions, a linear response of DES was obtained in the range from 1.0×10^{-7} to 2.0×10^{-5} mol L^{-1} (R = 0.997) and with a limit of detect (LOD) of 1.5×10^{-8} mol L^{-1}. The proposed procedure was successfully applied to determine the active ingredient in the DES tablet with satisfactory results.

Keywords Diethylstilbestrol · Platinum nanoparticles · Single-walled carbon nanotube · Voltammetry

1 Introduction

There is an increasing interest in that the normal operation of the endocrine (hormonal) system can be disrupted by a number of anthropogenic and naturally occurring chemicals, thereby affecting those physiological processes which are under hormonal control [1]. These compounds, the so-called endocrine-disrupting chemicals (EDCs) or endocrine disruptors, which defined by the European Commission as "an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function" [2]. This term describes both the synthetic chemicals and natural compounds that may affect the endocrine system. EDCs may potentially cause adverse effects on human health and wildlife not only at the level of the individual, but also at that of the population and the community, by interfering with endogenous hormones in the body [3].

Diethylstilbestrol (DES) is a synthetic estrogen that was widely used in livestock production to promote growth rate and is used as a treatment for estrogen-deficiency disorders in veterinary medicine, and it is included in the US Protection Agency list of endocrine disrupter reference compounds [4]. Today, the unfortunate effects of such treatment are well known; children exposed in utero to DES exhibit numerous abnormalities in reproductive tract development and function, and females experience a low but significant increase in vaginal and breast cancer [5, 6]. Moreover, transgenerational neoplastic effects of DES have been recently reported [7]. Therefore efforts to develop new degradation [8] and detection methods are very important.

The current methods for the analysis of DES are gas chromatography (GC) [9, 10], liquid chromatography (LC) with mass spectrometry (MS) [11, 12], enzyme-linked immunosorbent assay (icELISA) [13], electrochemiluminescence

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[14], time-resolved fluoroimmunoassay [15]. However, seldom have electrochemical techniques, which are often simple and less expensive, been used to determine DES [16, 17]. Here, a direct electrochemical method based on single-walled carbon nanotube/platinum nanoparticle (SWNT/Pt_{nano}) composite film modified glassy carbon (GC) electrode was developed for the determination of DES.

Recently, multifarious nano-materials have been applied in electroanalytical chemistry. Metallic and metal-oxide nanoparticles are capable of increasing the activities for many chemical reactions due to the high ratio of surface atoms with free valences to the cluster of total atoms. In addition to a high surface area-to-volume ratio for nanoparticle derivatized materials, the size controllability, chemical stability, and surface tenability provide an ideal platform for exploiting such nanostructures in sensing/biosensing and catalytic applications [18]. In particular, platinum nanoparticles (Pt_{nano}) have been an intensive research subject for the design of electrodes because of their easy preparation and stabilization [19].

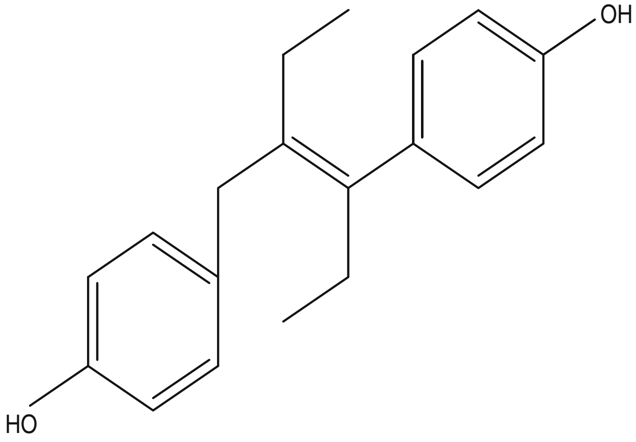
Carbon nanotubes (CNTs), a unique class of one-dimensional functional structures, are a promising building block for nanoscience and nanotechnology because of their high-surface-area, good mechanical strength and rich electronic properties [20, 21]. The subtle electronic behavior of carbon nanotubes reveal that they have the ability to promote electron-transfer reactions when used as an electrode material in electrochemical reactions [22, 23]. To exploit the potential applications in future nano-devices, it is necessary to develop versatile approaches to assemble or integrate CNTs onto solid surfaces. In recent years, considerable efforts have been made to fabricate different CNTs morphologies and explore their application in various fields including composites, electrochemical devices and sensors, among others [24–26].

In this article, Pt_{nano} and SWNT were combined to modify GC electrodes to improve their electroactivity and selectivity for DES. Pt_{nano} were in electrical contact, through the SWNT, with the GC backing, enabling the composite structure to be used as an electrode [19]. Consequently, a voltammetric method based on the SWNT/Pt_{nano} composite film modified electrode was developed for the determination of DES. This newly proposed method possesses advantages such as high sensitivity, rapid response, low cost and simplicity.

2 Experimental

2.1 Reagents and apparatus

Diethylstilbestrol (DES, Scheme 1), purchased from Chinese National Institute for the Control of Pharmaceutical and Biological Products, was used without further purification. A stock solution of DES (1.0×10^{-3} mol L^{-1}) was prepared with ethanol and stored in a refrigerator at 4 °C. Dihexadecyl hydrogen phosphate (DHP) was purchased from Fluka. All other chemicals were of analytical grade. Double-distilled water was used throughout. The commercially available drug tablets were purchased from the market.



Scheme 1 The structure of DES

Single-wall carbon nanotube (SWNT, obtained from the Chengdu Organic Chemicals Co., Ltd., CAS, China) were synthesized by a catalytic pyrolysis method and purified with oxidative acid treatment. All electrochemical measurements were performed with a computer controlled Model CHI 830B electrochemical analyzer (Chenghua Instrument Co., Shanghai, China). A three-electrode cell was employed with a platinum wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode and a SWNT/Pt_{nano} composite film modified GC electrode as working electrode. All potentials were quoted with respect to SCE.

2.2 Preparation of platinum nanoparticles (Pt_{nano})

Platinum nanoparticles (diameter 2–3 nm) were prepared as described [18]. A solution consisting of 1 mL of K_2PtCl_6 (4.7% aqueous solution) and 85 mL of distilled water was heated to 80 °C with stirring in a 100-mL round-bottom flask. After the addition of freshly prepared 15 mL of sodium citrate (1% aqueous solution), the resulting solution was maintained at 80 ± 0.5 °C for about 3 h. The wavelength was scanned in the range 200–500 nm using a UV spectrophotometer. As can be seen from Fig. 1, the disappearance of absorption bands of $PtCl_6^{2-}$ at 262 nm was observed at the end of the reaction (3 h), indicating the formation of platinum nanoparticles. This procedure consistently provided stable Pt nanoparticles 2–3 nm in diameter [19]. No obvious changes in the particle size were noticed after 6 months when the Pt colloid was stored in the dark at 4 °C.

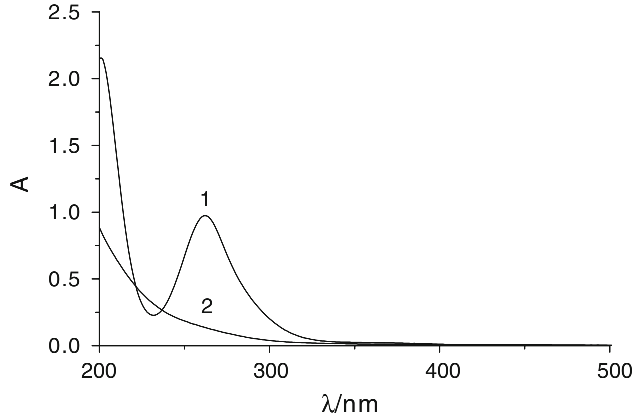


Fig. 1 Absorption spectroscopy: (1) 4.05 × 10^{-5} mol L^{-1} K_2PtCl_6 solution; (2) 4.05 × 10^{-5} mol L^{-1} Pt_{nano} solution

2.3 Preparation of the SWNT/Pt_{nano} composite film modified GC electrode

A GC electrode of 3-mm diameter was used. It was polished with 0.3 and 0.05 μm alumina slurry (CH instrument, Inc.) in sequence, and then sonicated in ethanol and doubly distilled water, respectively.

One milligram of SWNT was added into 2 mL plastic centrifuge tube, then 1 mL DHP (1 mg mL^{-1}) and 1 mL Pt_{nano} was also added. A well-dispersed suspension of SWNT/Pt_{nano} was obtained by ultrasonication for about 10 min. The GC electrode was coated by a drop of 6 μL SWNT/Pt_{nano} suspension and dried under an infrared lamp in air. A uniform composite film containing a network of SWNT and Pt nanoparticles was formed. The SWNT film coated GC electrode was prepared by the same procedure as explained above. The freshly prepared SWNT/Pt_{nano} modified electrodes were activated in 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} phosphate buffer (pH 7.0) using successive cyclic scans from 0.6 to −0.2 V in sequence until stable voltammograms were obtained. After each measurement the electrode surface was refreshed by the same methods as above.

2.4 Procedure

The supporting electrolyte for electrochemical measurements was 0.1 mol L^{-1} phosphate buffer (pH 7.0). A certain volume of standard solution of DES was added to the 10 mL cell containing phosphate buffer. Then the accumulation step was performed at open circuit for 120 s in a stirred solution, and linear sweep voltammograms were recorded from 0.6 to −0.20 V after 2 s quiescence. The reduction peak currents were measured at 0.140 V for the quantification of DES.

3 Results and discussion

3.1 SEM characterization

The morphology of platinum nanoparticles and the SWNT/Pt_{nano} composite film were characterized by SEM. A high and homogeneous dispersion of spherical Pt_{nano} is shown in Fig. 2a and the Pt_{nano} and SWNT are dispersed well on the substrate as shown in Fig. 2b.

3.2 Electrochemical behavior of DES at different electrodes

To investigate the electrochemical behavior of DES at the SWNT/Pt_{nano} composite film modified GC electrode, the cyclic voltammetry was performed at three different electrodes (Fig. 3). As can be seen from Fig. 3a almost no obvious redox peak is obtained at the bare GC electrode but at the SWNT film modified GC electrode, (Fig. 3b), a well-defined reduction peak at 0.140 V (R_1) and two oxidation peaks at 0.218 V (O_1) and 0.572 V (O_2) are observed. The highest currents of all three peaks occur at the SWNT/Pt_{nano} composite film modified GC electrode (Fig. 3c), and this can be attributed to the combination of strong interfacial accumulation abilities of SWNT toward DES, together with enhanced electroactive surface area and electron transfer due to the presence of Pt nanoparticles.

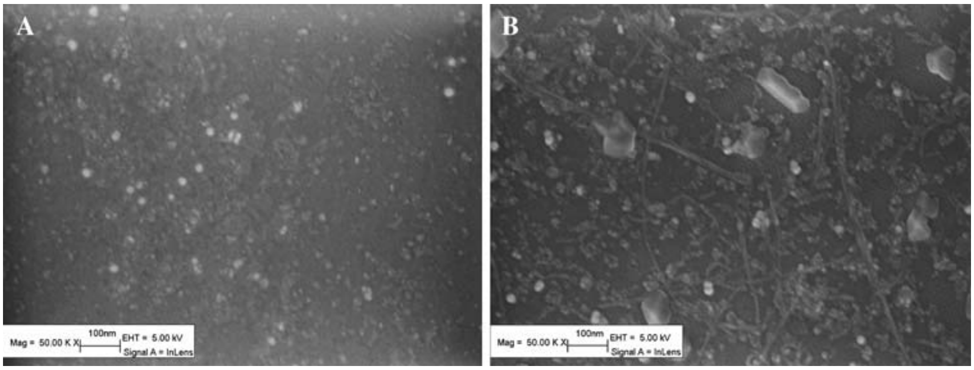


Fig. 2 SEM of Pt_{nano} and SWNT/Pt_{nano} composite film

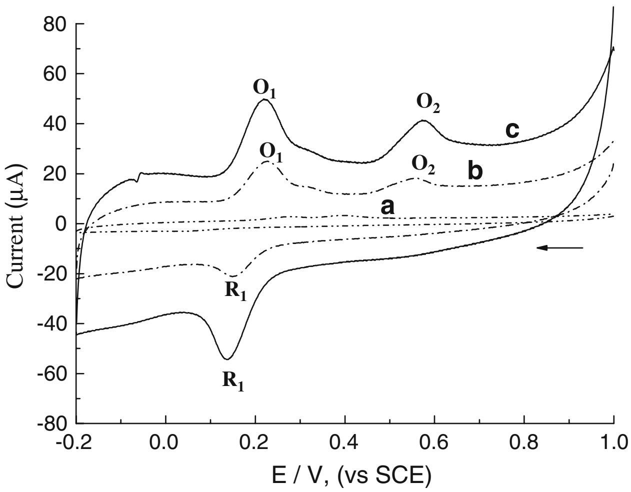


Fig. 3 Cyclic voltammograms of 3.75×10^{-5} mol L^{-1} DES at (a) SWNTs/Pt_{nano} composite film coated GCE; (b) SWNTs film coated GCE; (c) bare GCE in 0.1 M phosphate buffer (pH 7.0) from 1.0 to −0.2 V. Scan rate is 100 mV s^{-1}

The role of DHP was to allow the SWNT/Pt_{nano} suspension formation and to stabilize and protect the Pt_{nano}, resulting in both stability and longevity of nanocomposite films on the GC surface. The bare Pt electrode under the same conditions gave no response with DES (figure not shown).

In order to better understand the electrochemical properties of SWNT/Pt_{nano} composite film modified GC electrode, the electrochemical active surface areas of bare and modified electrodes were measured by cyclic voltammetry using 20 mmol L^{-1} potassium ferrocyanide as the redox probe. Steady-state CVs (second cycle recorded) for the bare and the two modified GC electrodes in 20 mmol L^{-1} $Fe(CN)_6^{4-}$ and 0.2 mol L^{-1} KCl at 20 mV s^{-1} versus Ag/AgCl (3 mol L^{-1} KCl) reference electrode show well-defined oxidation and reduction peaks due to the Fe^{3+}/Fe^{2+} redox couple at about +0.30 and +0.17 V versus Ag/AgCl in the forward and reverse scans, respectively. The peak currents of $K_4[Fe(CN)_6]$ are proportional to the square root of the scan rate, indicating a diffusion-controlled process. Hence the electrochemical active surface areas of electrodes was calculated according to the Randles–Sevcik equation [27] and the SWNT/Pt_{nano} composite film modified electrode exhibited the highest electrochemical active surface area.

$$i_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} \upsilon^{1/2} C \qquad (1)$$

where n is the number of electrons participating in the redox reaction, A is the area of the electrode (cm^2), D is the diffusion coefficient of the molecule in solution (cm^2 s^{-1}), C is the concentration of the probe molecule in the bulk solution (mol cm^{-3}), and υ is the scan rate of the potential perturbation (V s^{-1}). The $Fe(CN)_6^{4-/3-}$ redox system used in this study is one of the most extensively studied redox couples in electrochemistry and exhibits a heterogeneous one-electron transfer ($n = 1$). C is equal to 20 mM, and the diffusion coefficient (D) is $(6.70 \pm 0.02) \times 10^{-6}$ cm^2 s^{-1}. The experiment results showed that the electrochemical active area of a bare GC electrode, 0.5 mg mL^{-1} SWNT-DHP modified GC electrode and 0.5 mg mL^{-1} SWNT/Pt_{nano} composited film modified GC electrode were 3.7×10^{-2}, 5.4×10^{-2}, and 6.8×10^{-2} cm^2, respectively. Hence the enhanced responses of DES at SWNT/Pt_{nano} composite film modified GC electrode may arise from the large active area of the SWNT/Pt_{nano} composite film for the adsorption of DES.

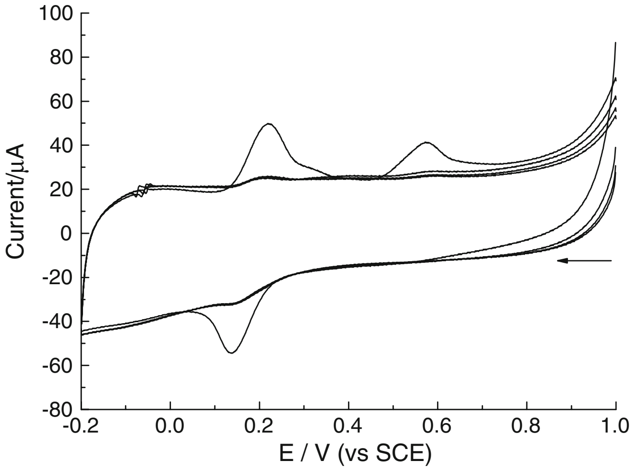


Fig. 4 Multi-cyclic voltammograms of 3.75×10^{-5} mol L^{-1} DES at SWNTs/Pt_{nano} composite film modified GC electrode in phosphate buffer (pH 7.0) from 1.0 to −0.2 V. Scan rate: 100 mV s^{-1}

The multi-cyclic voltammograms of a SWNT/Pt_{nano} composite film modified GC electrode in phosphate buffer at pH 7.0 with 3.75×10^{-5} mol L^{-1} DES are illustrated in Fig. 4. In the potential range 1.0 to −0.2 V, there are three obvious redox peaks in the first sweep. However, the redox peaks currents of DES decrease remarkably from the second sweep and the redox peak current stays constant during the successive cyclic potential sweeps, indicating that the redox products of DES have absorption properties. In contrast to two oxidation peaks of DES, the reduction peak of DES has higher sensitivity. So we chose the reduction peak to analyze and detect DES.

The effect of potential scan rate, υ, on the electrochemical behavior of DES was evaluated by cyclic voltammetry in the scan rate range 50–250 mV s^{-1}. All the peak currents of R_1, O_1, and O_2 were proportional to scan rate, suggesting that an adsorption-controlled process was involved in the redox reaction of DES at the SWNT/Pt_{nano} composite film modified electrode. The peak potentials (E_p) of R_1, O_1, and O_2 were also investigated and the results showed that the E_p of R_1 shifted negatively and peak potentials of O_1, and O_2 shifted positively with increase in pH from 4.4 to 8.6. The slopes of E_p versus pH of O_1, O_2,

R_1 were 0.052, 0.049, 0.053 mV/pH, respectively, which shows that the number of protons transferred in the redox of DES equals that of the electrons. The complication of the redox process exhibited by DES and the lack of electrochemical constants, limits the application of Nernstian derived equations for the calculation of the number of electrons (*n*) of each redox process transferred. However, using Faraday's equation and the charged resulting from the complete electrolysis of the electroactive species provides a way of determining the total value of *n*. The controlled potential coulometry of DES at 0.7 V showed that the complete reaction mechanism involves two electrons.

3.3 Effect of the amount of SWNT/Pt_{nano} suspension

Since DHP film can prohibit the electron exchange between DES and the electrode and block the adsorption of DES, the concentration of DHP in the SWNT/Pt_{nano} suspension solution should be kept as low as possible. However, the lower concentration of DHP leads to a poor dispersion characterization and hence affects the casting of SWNT/Pt_{nano} composite film. In the present case the DHP concentration of 0.5 mg mL^{-1} is suitable. The relationship between the amount of SWNT/Pt_{nano} suspension on the GC electrode surface and the reduction peak current of DES were tested and the results are shown in Fig. 5. The peak currents initially increase gradually with increasing amount of SWNT/Pt_{nano} suspension over the electrode surface. When the amount of SWNT/Pt_{nano} suspension solution exceeds 6.0 μL, no obvious change in the peak current is observed, which suggests that the composite film has genuine catalytic function towards the electrochemical behavior of DES and that the electron transfer processes within the film and at the film-solution interface are sufficiently fast and not the rate-controlling steps. But with further increase of the amounts of SWNT/Pt_{nano} suspension (higher than 14 μL) the peak currents begin to decrease gradually. This is mainly due to the blocking behavior of DHP. Thus the amount of SWNT/Pt_{nano} suspension on the GC electrode surface was chosen as 6.0 μL.

3.4 Choice of supporting electrolyte

For optimization of the DES determination, the effects of pH and buffer systems, such as phosphate buffer, B-R buffer, acetate buffer, Macllvaine buffer, were examined. The highest reduction peak current of DES was obtained in phosphate buffer.

The influence of pH on the reduction of DES was studied in the pH range 4.4–8.6. The effect of pH on the reduction peak current is shown (Fig. 6). When the pH is lower than 6.0, the peak current increases with pH increase and little change in the peak current is observed over the pH range 6.0–7.5. At pH higher than 7.5 peak current decreases with pH increase.

3.5 Accumulation conditions

Accumulation, either open-circuit or close-circuit accumulation, is a common and effective tool to improve determining sensitivity. The influence of accumulation potential on the peak current of DES was investigated at different potentials and at open-circuit. The accumulation of DES at open-circuit was more efficient than that at other potentials. Hence accumulation was carried out at open-circuit.

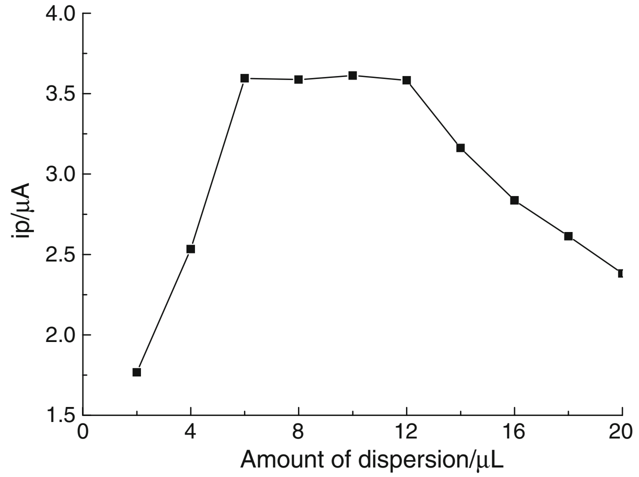


Fig. 5 Influence of amount of SWNTs/Pt_{nano} suspension on the reduction peak current of 6.25×10^{-7} mol L^{-1} diethylstilbestrol

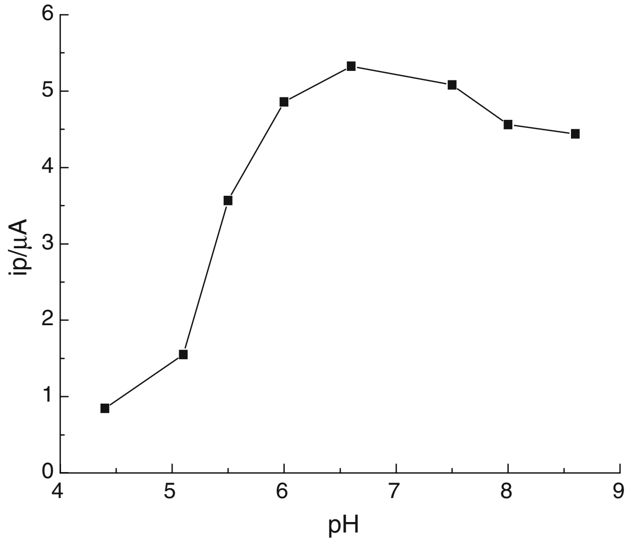


Fig. 6 Variation of peak current of 1.25×10^{-6} mol L^{-1} DES with different pH

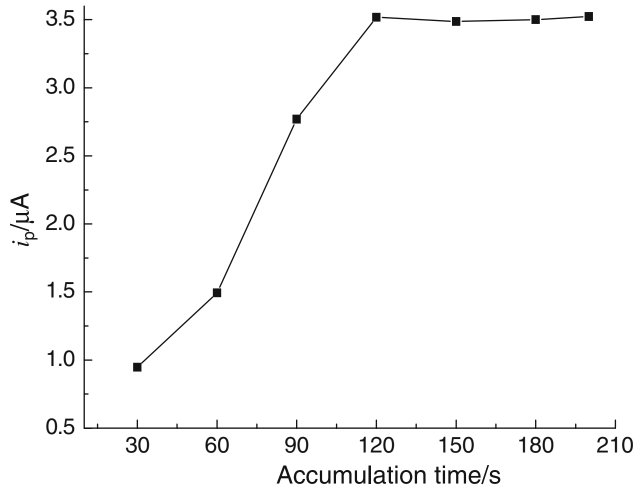


Fig. 7 Effect of accumulation time on the peak current of 6.25×10^{-7} mol L^{-1} diethylstilbestrol

The effect of accumulation time on the peak current of DES is also shown in Fig. 7. The peak current increases linearly with increase in accumulation time from 15 to 120 s. Rapid adsorption of DES on the surface of the SWNT/Pt_{nano} composite film modified GC electrode is responsible for this phenomenon. However, for a longer accumulation time the plot levels off indicating, presumably, that a limiting amount of DES on the electrode surface has been adsorbed. Further increase in accumulation time leads to only a slight increase in the amount of DES adsorbed on the electrode owing to surface saturation. The sensitivity for lower DES concentrations could be increased by increasing the accumulation time, but the linear concentration range was diminished.

3.6 Influence of surfactants

The influence of surfactants, such as cationic surfactants (Cetyl trimethyl ammonium Bromide, CTAB), anionic surfactant (sodium dodecyl sulfonate, SDS) and non-ionic surfactants (β-cyclodextrin) on the reduction peak current of DES were examined. All these surfactants reduced the reduction peak current of DES, especially the β-cyclodextrin. These phenomenon also demonstrate that the reduction of DES is controlled by absorption.

3.7 Interferences

Under this system, the interferences of some inorganic ions and organic compounds were examined and the results are as follows: 1,000-fold concentration of Cl^-, 600-fold concentration of NO^{3-}; 500-fold concentration of K^+, Mg^{2+}; 400-fold concentration of Zn^{2+}; 300-fold concentration of Pb^{2+}; 200-fold concentration of Cu^{2+} and 100-fold concentration of dopamine, ascorbic acid; 300-fold concentration of alanine; 20-fold concentration of L-histidine hardly influence the current response of 6.25×10^{-7} mol L^{-1} DES (signal change below 5%).

3.8 Calibration plot

Under optimized experimental parameters the calibration curve was obtained in pH 7.0 phosphate buffer by linear sweep voltammetry. The linear segment increases from 1.0×10^{-7} to 2.0×10^{-5} mol L^{-1}, with a regression equation of $i_p = 2.37 + 10.03 \times 10^6\ C$ ($r = 0.997$, C in mol L^{-1}, i_p in μA). For concentrations of DES higher than 2.0×10^{-5} mol L^{-1}, the peak current increased only slightly and approached a constant value due to saturation of the SWNT/Pt_{nano} composite film modified electrode surface. The detection limit was 1.5×10^{-8} mol L^{-1} at a 3:1 signal-to-noise ratio for an accumulation time of 120 s. The relative standard deviation (RSD) of 3.56% for 1.25×10^{-6} mol L^{-1} DES ($n = 7$) showed good reproducibility. In order to investigate the stability of the SWNT/Pt_{nano} composite film modified GC electrode, the modified electrode was stored at room temperature. The experimental results showed that the current response of DES suffered a 2.2% decrease during the first 2 days, 4.1% for 5 days and 6.3% for the following 15 days, showing that the SWNT/Pt_{nano} composite film modified GC electrode possesses good long-term stability.

3.9 DES assay in pharmaceutical formulations

Thirty tablets were weighted accurately and crushed to a fine powder. Some of this powder was weighed accurately, transferred to a 50 mL flask and dissolved in 50 mL ethanol. After sonication it was filtered. The prepared solution from drug tablets was detected on SWNT/Pt_{nano} composite film modified GC electrode by linear sweep voltammetry. The amount of DES present in a tablet was calculated by the standard additional curve method and the average result was 0.48 mg for each tablet, which is similar to the label claim (0.5 mg). The recoveries of DES were tested and the results listed in Table 1 were in the range 94.1–101.7%, which indicates that this method is accurate enough for practical application.

4 Conclusions

An easily prepared SWNT/Pt_{nano} composite film modified GC electrode was prepared to investigate the electrochemical behavior of DES. The modified electrode increased the electrochemical response of DES significantly, which clearly demonstrates the excellent electrocatalytic activity of the SWNT/Pt_{nano} composite film

Table 1 The analytical results of the DES tablet sample

Determined content (mg)	Average content (mg)	Relative deviation (%)	Added amount (mg mL^{-1})	Found amount (mg mL^{-1})	Recovery (%)
0.51	0.48	2.52	0.056	0.053	94.6
0.45			0.058	0.059	101.7
0.49			0.085	0.081	95.3
0.48			0.102	0.096	94.1

toward the electrochemical behavior of DES. Based on this a sensitive voltammetric method was proposed for the determination of DES in real samples. The results show promise for further sensor development.

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