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Electrochemical Determination of Diethylstilbestrol in Animal Food Using a Poly Polylysine/Graphene Modified Electrode

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A polylysine/graphene modified electrode was prepared. The electrochemical behaviour of diethylstilbestrol on the surface of this electrode was studied. A new method for the direct determination of diethylstilbestrol in food was developed. The experimental results showed that there was a pair of reversible redox peaks for diethylstilbestrol on this modified electrodes in 0.5~1.0 V range in a phosphate buffer solution (pH 3.0). Compared with the effects of a glassy carbon electrode and a polylysine modified electrode, it was concluded that the polylysine/graphene modified electrode has a higher electrocatalytic effect on the oxidation of diethylstilbestrol. In the range of 8.00×10^{-8} ~ 1.00×10^{-5} mol/L, the concentration of diethylstilbestrol was directly proportional to its oxidation peak current, and the detection limit is 1.20×10^{-9} mol/L. The relative standard deviation（RSD） was 1.7% over six parallel tests. The modified electrode had a high sensitivity and good selectivity and better stability than the control electrode and could be used to determine the concentration of diethylstilbestrol in beef, mutton and milk with recovery rates of 97.0% ~ 103.0%.

Keywords: polylysine; graphene; modified electrode;cyclic voltammetry;diethylstilbestrol

1. INTRODUCTION

Diethylstilbestrol (DES), a synthetic non-steroidal oestrogen, is mainly used to treat functional haemorrhage and amenorrhea oestrogen deficiency caused by hormone imbalance. Due to its low price and excellent curative effect, it was widely used in clinical medicine from the 1940s to 1960s. In addition, DES has the functions of reducing fat synthesis, accelerating the synthesis of metabolic proteins and increasing animal weight; as such, it has been widely used as a growth accelerator in the animal husbandry industry [1, 2]. However, DES is associated with high rates of side effects, including breast

and prostate cancers and clear-cell adenocarcinoma of the cervix [3-8]. DES is currently considered an endocrine disrupter reference compound by the USA Environmental Protection Agency [9]. However, the overuse of DES continues because it can economically benefits to the food and animal breeding industry. Thus, there is a worldwide concern regarding monitoring DES in food and the environment.

Various approaches have been developed for the determination of DES, such as high-performance liquid chromatography (HPLC) [10], gas chromatography-mass spectrometry (GC–MS) [11-14], liquid chromatographic tandem mass spectrometry (LC–MS/MS) [15], capillary electrophoresis [16] and fluorometry [17]. Although these methods can enable the detection of DES, they are relatively expensive and time consuming and their steps are tedious. Due to Due to having two hydroxyl groups in its chemical structure, DES can show a strong electrochemical response [18-23]. Traditional sample pretreatment technologies are cumbersome and time-consuming to operate, requiring a large number of organic solvents that aretoxic and harmful to the human body and environment. Therefore, it would be very significant to develop time-saving, efficient and green detection methods.

Electrochemical detection method have been studied and widely applied due to the advantages of their sensitivity, rapidity and low equipment costs. In recent years, chemically modified electrodes have been rapidly developed, and the modifying material determines the stability, selectivity and sensitivity of the modified electrode. Graphene has good conductivity and a large specific surface area, and can increase the electron transfer rate after modifying the surfaces of glassy carbon electrodes. In recent years, conductive polymer films, as a modified material, have attracted extensive attention because of their good porosity and solid structure, which can increase the specific surface area of the electrode and enable good electrocatalysis properties. In this experiment, a polylysine/graphene modified glassy carbon electrode (PLYS/GM/GCE) was prepared, and the electrochemical behaviour of DES was studied by using the synergistic electrocatalytic properties of graphene and polylysine. A new electrochemical method for the determination of DES was established. This modified electrode had the advantages of a simple preparation process, good selectivity, fast response and good stability. The determination of DES had a high sensitivity and wide linear range.

2. EXPERIMENTAL

2.1 Instruments and reagents

ACHI660E (Shanghai Chenhua Company) electrochemical analysis system with a three-electrode system (glassy carbon electrode, Ag/AgCl electrode and platinum wire electrode) was used for electrochemical experiments; a KQ-100 ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd.) was used in this experiment; the SEM was performed on a electron scanning microscope Sirion 200 (FEI, America); and doubly distilled high-purity water was prepared by using an SYZ-500 quartz azeotropic high-purity water distiller (Jiangsu Jintan Co., Ltd.). Graphene was prepared in the laboratory. Lysine was purchased from Sinopharm Chemical Reagent Co., Ltd., DES was obtained from Chengdu Aikeda Chemical Reagent Co., Ltd. A phosphate buffered saline solution (PBS) with a pH value of 2.2~8.0 was prepared in the laboratory. The reagents used were analytically pure, and the water was

doubly distilled.

2.2 Preparation of modified electrode

The GCE was polished sequentially with metallographic sandpaper and alumina powder, rinsed with secondary distilled water after each polishing, ultrasonically cleaned in 50% nitric acid, anhydrous ethanol and distilled water, and then dried in air. Five microliters of a graphene suspension (0.7 mg/mL) was dropwise added onto the surface of the treated GCE and then dried under infrared light. Thus, the modified graphene electrode (GM/GCE) was prepared. The PLYS/GM/GCE was obtained by using a CHI660E electrochemical work station with a three-electrode system with GM/GCE as the working electrode, platinum wire as the counter electrode, and Ag/AgCl electrode as the reference electrode in PBS (pH 8.0) containing 1.0×10^{-4} mol/L lysine for circularly scanning 20 times over the potential range of -1.6-2.4 V. The scan rate was 60 mV/s.

2.3 Analytical procedure

Certain amount of DES and PBS were added to the electrolytic cell. With PLYS/GM/GCE as the working electrode, Ag/AgCl electric reference electrode and platinum electric opposite electrode and after stirring for 60 s, cyclic scanning was conducted over the potential range of -0.5 ~ 1.0 V with a 100 mV/s scanning rate, and the peak potential and peak current were recorded. After each scan, the electrode was placed in a pH 5.0 PBS solution for circular scanning until the potential peak disappeared. The electrode was rinsed with doubly distilled water prior to being used for the next measurement.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Optimization of *preparation conditions* of PLYS/GM/GCE

The experimental results (Figure 1) show that the amount of grapheme (Figure 1A), the pH of the polymer stock solution (Figure 1B), the scan rate (Figure 1C), the number of electropolymerizations canning cycles (Figure 1D), the low-potential electrochemical polymerizationpotential (Figure 1E) and the high-potential electrochemical polymerizationpotential (Figure 1F) influence the performance of the modified electrodes.

3.1.1 Effect of the amount of graphene

The experiment was carried out by changing the dropwise addition of graphene from 1 to 9 μL. The results showed that the peak current of DES on the modified electrode initially increased up to 5 μL and then decreased with the further increase of graphene (Figure 1A), which may be due to the fact that the catalytic site of graphene has not been fully utilized and electron transfer has been hindered.

3.1.2 The effect of the pH of the stock solution

The pH of the 1.0×10^{-4} mol/L lysine solution has a substantial influence on the catalytic performance of the modified electrode. The experiment was carried out by changing the pH of a buffer system consisting of citric acid and disodium hydrogen phosphate. The results showed that the current of DES on the modified electrode increased gradually with an increase in the pH of the polymer stock solution and reached a maximum value (Figure 1B) at pH 8.0; as such a pH of 8.0 was chosen for the polymer solution.

3.1.3 Effect of the scan rate during polymerization

For the preparation of PLYS/GM/GCE, the scan rate was varied from 20 to 100 mV/s. The peak current of DES on the modified electrode reached a maximum at 60 mV/s (Figure 1C). Therefore, a scan rate of polymerization of 60 mV/s was chosen.

3.1.4 Effect of scan cycles during polymerization

The number of scanning cycles affected the thickness of the PLYS/GM/GCE as well as the electrocatalytic effect towards DES. The peak current of DES on the modified electrode increased with increasing number of scanning cycles. When the number of scanning cycles reached 20, the peak current reached its maximum value and then decreased for subsequent cycles. Therefore, the optimal number of scanning cycles was 20 (Figure 1D).

3.1.5 Effect of the polymerization potential

The polymerization potential affected the thickness of the modified electrode film. The results showed that PLYS/GM/GCE had the best catalytic effect towards DES when the low-end of the potential range was -1.6 V (Figure 1E) and the high-end of the potential range was 2.4 V (Figure 1F); therefore the range of the polymerization potential was -1.6-2.4 V.

As discussed above, the electrocatalytic effect of the modified electrode towards DES and the response current of DES were optimized when the amount of the graphene solution was increased to 5 μL, and the PLYS/GM/GCE was prepared in a pH 8.0 PBS solution containing 1.0×10^{-4} mol/L lysine over the potential range of -1.6-2.4 V with a 60 mV/s scan rate for 20 scanning cycles.

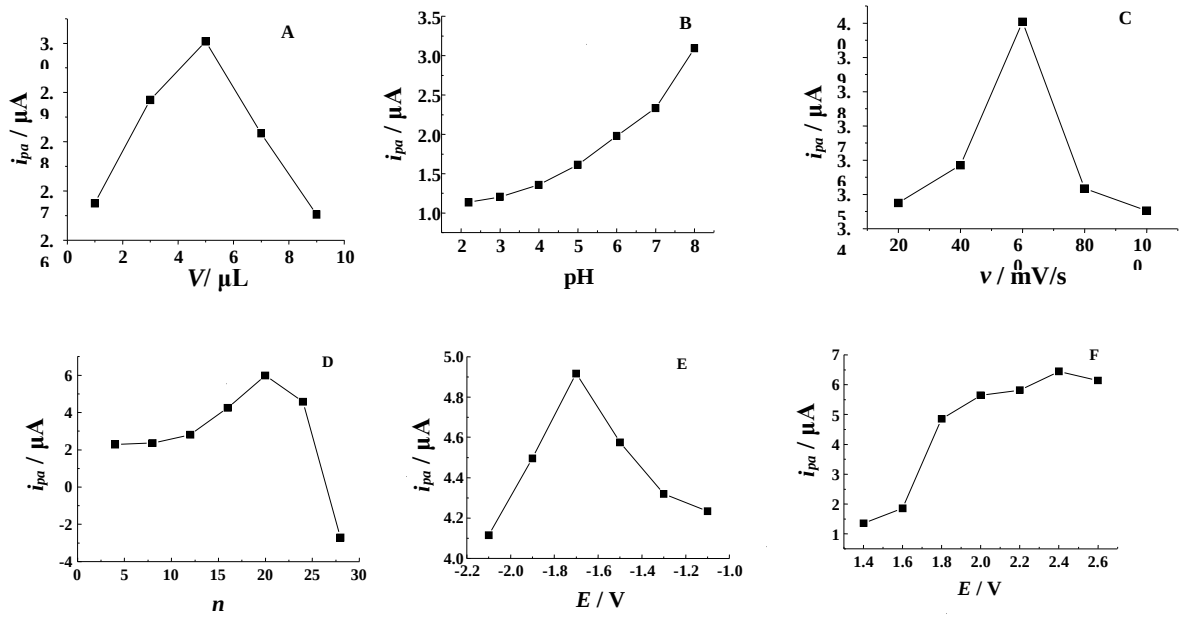


Figure 1. Optimization of preparation conditions of PLYS/GM/GCE (A) Amount of graphene; (B) pH of the polymer stock solution; (C) scan rate; (D) number of electropolymerization cycles; (E) low potential for electrochemical polymerizationand; (F) high potential for electrochemical polymerization.

3.2 The polymerization cycle voltammetry curve of lysine on GM/GCE

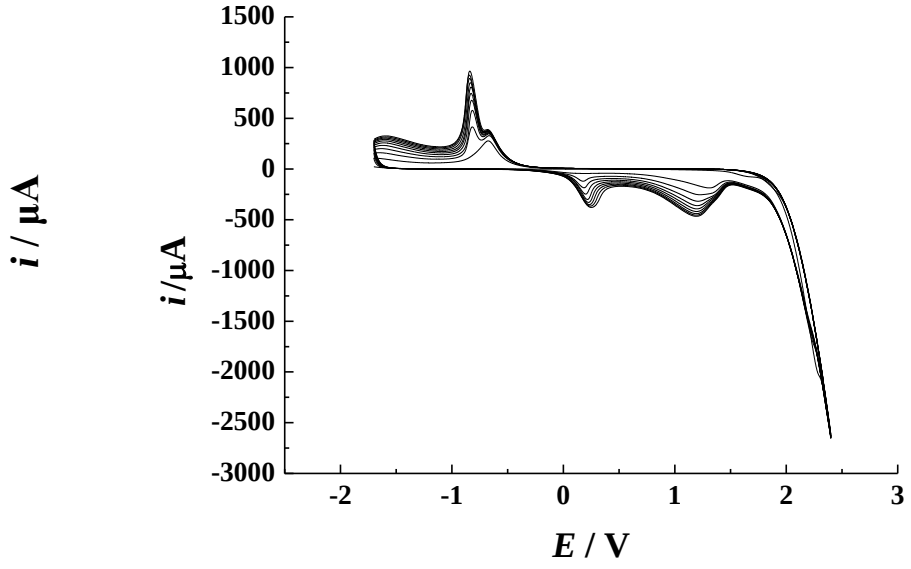
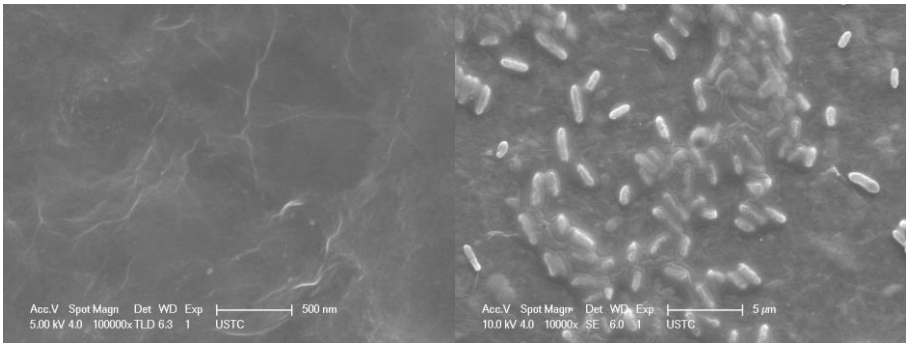


Figure 2. Cyclic voltammetry curves of the lysine polymerization process

Figure 2 shows the cycle voltammetry curve for the polymerization of lysine obtained on the GM/GCE under the optimum polymerization conditions. It can be seen that there is a reduction peak at - 0.70 V and two oxidation peaks at 0.20 V and 1.35 V during at the first cycle. In subsequent scanning

cycle, the oxidation peak at 1.35 V, and the reduction peak were negatively shifted, while the oxidation peak at 0.20 V was positively shifted. The peak current gradually increased, but the amplitude gradually decreased until the values were stable, indicating that lysine had been polymerized on the electrode surface. A dark blue film was observed on the electrode surface after polymerization. From scanning electron microscopy images, it could be observed that a graphene-modified electrode was formed on the surface of the GCE with a three-dimensional spatial structure (see Figure 3). It can be deduced that lysine monomers oxidize to form amino radicals at higher positive potential and then bond to the surface of glassy carbon electrodes [24].



(a) (b)

Figure 3. SEM image of the GM/GCE (**a**) and the poly lysine film on the GM/GCE (**b**)

3.3 The electrochemical behaviour of DES on a PLYS/GM/GCE

The electrochemical behaviour of DES on a GCE, a PLYS/GCE, and a PLYS/GM/GCE, as well as that of a PLYS/GM/GCE in the absence of DES, were investigated by CV as shown in Figure 4. The value of the oxidation peak current (i_{pa}) of DES on the PLYS/GM/GCE (i_{pa} = -12.27 μA and E_{pa} = 0.54 V) was significantly increased in contrast to the poor response at the GCE (i_{pa} = -0.70 μA and E_{pa} = 0.59 V); additionally, the PLY/GCE had values of i_{pa} = -3.46 μA and E_{pa} = 0.51 V in the presence of DES, and no response was seen for the PLYS/GM/GCE in the absence of DES, which suggested that the PLYS/GM/GCE film on the electrode had good electrocatalytic activity towards the electrochemical oxidation of DES. Because the anodic values were i_{pa} = -12.27 μA and E_{pa} = 0.54 V and the cathodic values were i_{pc}= 3.9 μA and E_{pc} = 0.31 V， the ratio of i_{pa} / i_{pc} > 1 and ΔE = 0.23 V; therefore, the reaction is a quasi-reversible reaction. The electrocatalytic activity might be attributed to the formation of hydrogen bonds between hydroxyl groups in DES and nitrogen atoms in polylysine. The hydrogen bonds weaken the bond energy between hydrogen and oxygen, and electron transfer occurs easily between N-H-O bonds [24].

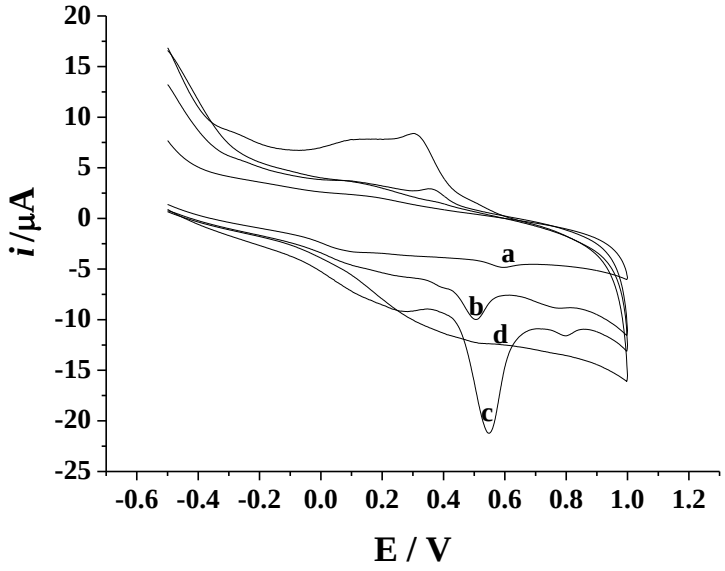


Figure 4. CV curves of DES on a GCE (**a**), a PLYS/GCE (**b**), and on a PLYS/GM/GCE (**c**) as well as that of PLYS/GM/GCE in the absence of DES (**d**)

3.4 Optimum measurement conditions

3.4.1 Effect of solution pH

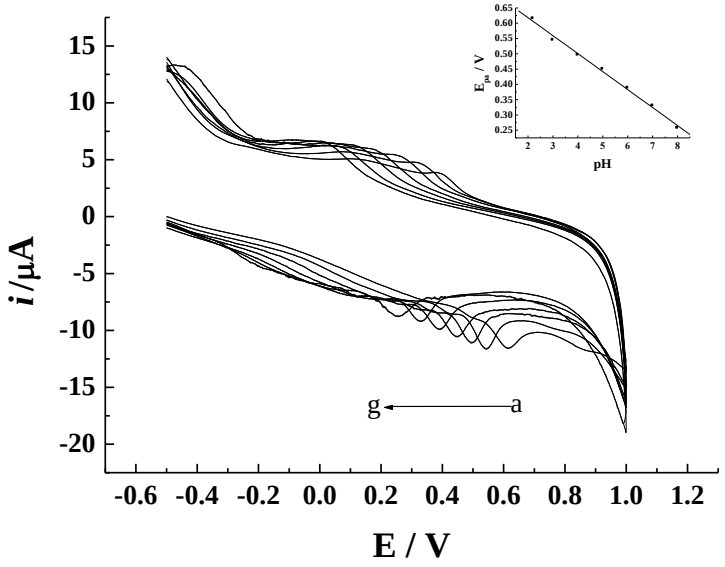


Figure 5. CVs of a 1.00×10^{-6} mol/L solution of DES at different pH values on the PLYS/GM/GCE. Letters a-g correspond to pH values of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0, respectively. The inset shows a plot of the peak potential of DES versus the pH value of the buffer solutions. The can rate was 100 mV/s.

The experimental results showed that the redox peak currents changed with changes in the pH of the solution. When the other conditions remained constant, the redox peak currents reached their maximum when the pH of the solution was 3.0. Therefore, the optimal pH for testing of the substrate was 3.0. In addition, the oxidation peak negatively shifted (Figure 5) with increasing pH. The linear regression equation for the oxidation peak potential vs. pH was E_{pa} = 0.72-0.060 pH, and its slope was close to 0.059, indicating that the redox process of DES involved protons and that the proton transfer number was equal to the electron transfer number. These results are consistent with those of other study in the literature [25, 26].

3.4.2 Effect of the potential

The oxidation peak current of DES on PLYS/GM/GCE was related to the high and low scanning potential. If the low potential was fixed to -0.4 V and the high potential was changed, it was found that the response current of DES on the modified electrode was the largest when the high potential was 1.0 V; thus, the optimum high potential was 1.0 V. When the high potential was fixed at 1.0 V, the response current of DES on the modified electrode was the largest when the low potential was -0.5 V. The optimal potential range was in this experiment -0.5 ~ 1.0 V.

3.4.3 Effect of the scan rate

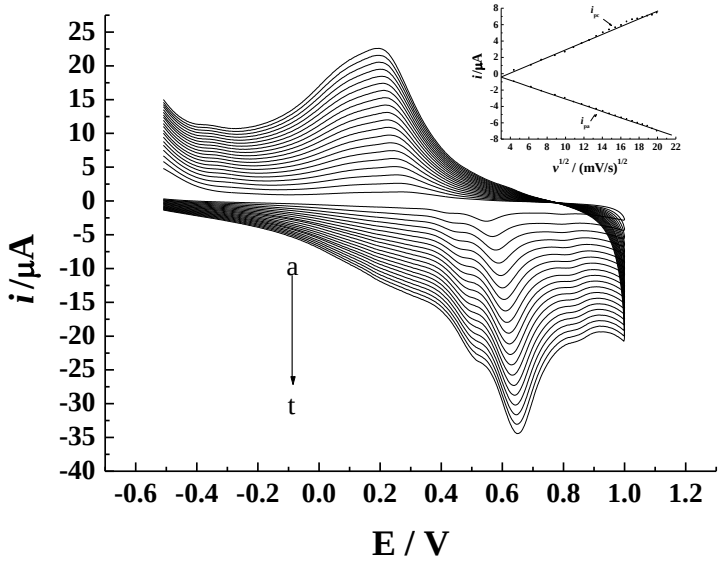


Figure 6. CVs of a 1.0 ×10^{-6} mol/L DES solution on the PLYS/GM/GCE. The inset shows a plot of oxidation peak currents of DES versus the scan rates. The letters from a-t correspond to scan rates of 20, 40, 60,80, 100, 120, 140, 160, 180, 200, 220, 240,260, 280, 300, 320, 340, 360, 380 and 400 mV/s.

CV curves with various scan rates were recorded for a 1.00×10^{-6} mol/L DES solution. As shown

in Figure 6, the oxidation peaks and the reduction peak of DES increased with an increase in the scan rate over the range from 20 to 400 mV/s, and a good linear relationship between the redox peak current of DES on the PLYS/GM/GCE and the square root of the scan rate was obtained. The linear regression equations were as follows： i_{pa} (μA) = -0.72 - 0.38 $v^{1/2}$ (mV/s) $^{1/2}$， R = -0.9995； i_{pc} (μA) = -1.95 + 0.47 $v^{1/2}$ (mV/s) $^{1/2}$， R = 0.9973, indicating that the electrochemical reaction of DES on the PLYS/GM/GCE was a diffusion control process. This is different from the electrode reaction of DES at conductive carbon black paste electrode in 0.2 M B-R buffer solution of pH 4.0 [26]. The oxidation peak was not obvious when the scan rate was too low. In addition, the detection sensitivity decreased when the scan rate was too high. Therefore, the optimal scan rate in this experiment was 100 mV/s.

Figure 7 shows the plots of the peak potentials versus the logarithms of the scan rates. The linear regression equations for E_{pa} and E_{pc} versus the scan rates are expressed as:

E_{pa} = 0.40 + 0.095 log ν (mV/s), R = 0.9980, E_{pc} = 0.41 - 0.083 log ν (mV/s), R = -0.9909.

According to Laviron theory, $E_{pa} = a + (2.303RT/(1-\alpha)n_a F)\log v$ (1)

$E_{pc} = b - (2.303RT/\alpha n_a F)\log v$ (2)

Where a and b are constants, F is the Faraday constant (96, 487 C), R is the universal gas constant (8.314 J·K $^{-1}$·mol $^{-1}$), T is the temperature in Kelvin (K), n is the number of electrons transferred and α is the electron transfer coefficient. By combining Eqs. (1) and (2), we obtained n = 1.34, and α = 0.53. Here, α is quite close to its theoretical value of 0.5.

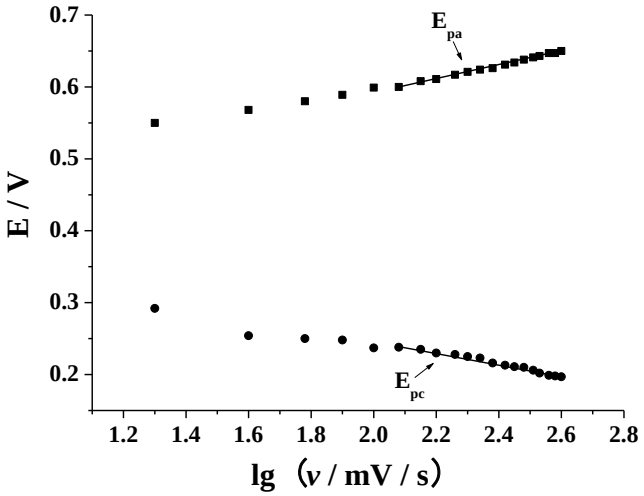


Figure 7. Plots of the peak potentials versus the logarithms of the scan rates

3.4.4 Effect of the amount of ethanol

The amount of ethanol also related to the peak current of DES in the experiment. To demonstrate the effect of the amount of ethanol, we varied the volume ratio of ethanol to water. When the total volume ratio of ethanol to water was 10%, the maximum oxidation peak current of DES was measured.

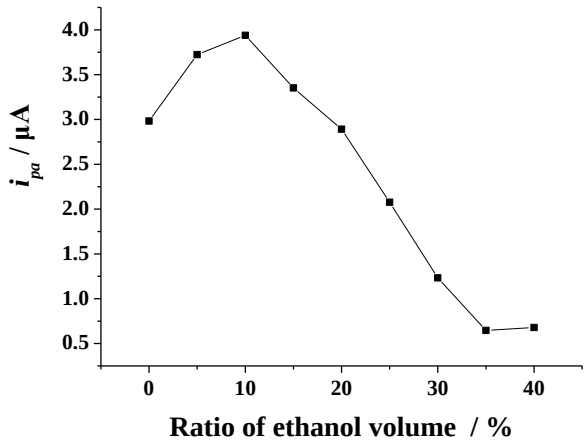


Figure 8. The plot of the volume ratio of ethanol to water

3.4.5 The optimal stirring time

The peak current of DES also related to the stirring time in the experimental process. The results showed that the peak current reached its maximum when the stirring time was 50 s. Therefore, in the experiment the optimal stirring time of the liquid prior to testing was 50 s.

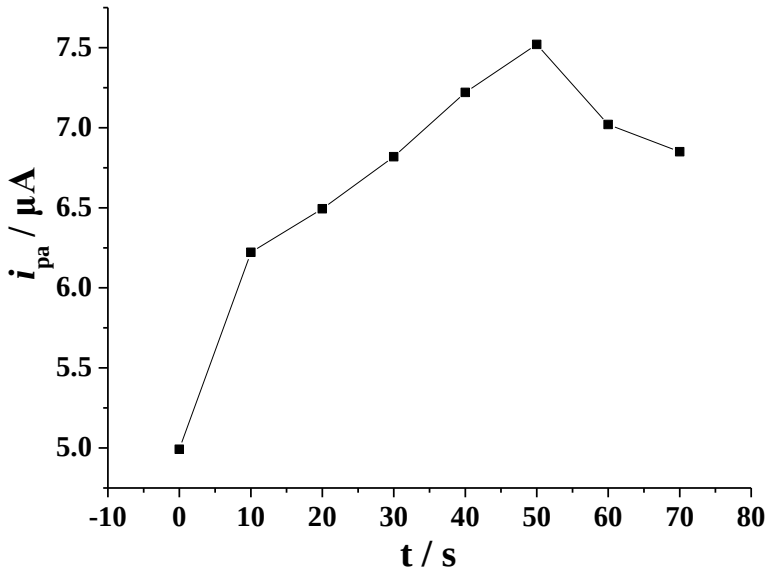


Figure 9. The plot of the oxidation peak current versus the stirring time

3.5 Linear range, detection limit and reproducibility

The concentration of a DES solution was determined by differential pulse voltammetry under the optimal experimental conditions. There was a good linear relationship between the oxidation peak current of DES and its concentration, ranging from 8.00×10^{-8} ~ 1.00×10^{-5} mol/L (Figure 8). The linear regression equations was i_{pa}(μA)=2.00×10^{-8}+0.12c (μmol/L), R=9978. The concentration of DES was

gradually decreased to obtain the detection limit. When the concentration was less than 1.20×10^{-9} mol/L, the oxidation peak disappeared. Therefore, the detection limit was 1.20×10^{-9} mol/L.

Under the optimal polymerization conditions, a 1.00×10^{-6} mol/L solution of DES was measured six times in parallel, and the relative standard deviation was 1.7%, indicating that the PLYS/GM/GCE has good reproducibility.

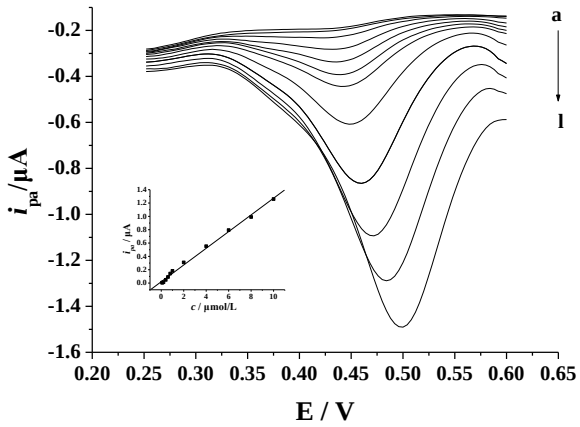


Figure 10. CV curves of different concentrations of DES on the PLYS/GM/GCE. The letters a to l correspond to concentrations of 8.00×10^{-8}, 1.00×10^{-7}, 2.00×10^{-7}, 4.00×10^{-7}, 6.00×10^{-7}, 8.00×10^{-7}, 1.00×10^{-6}, 2.00×10^{-6}, 4.00×10^{-6}, 6.00×10^{-6}, 8.00×10^{-6} and 1.00×10^{-5} mol/L respectively. The insert shows a plot of i_{pa} versus the concentration of DES. The scan rate was 100 mV/s.

A comparison of our sensor with other reported sensors based on the analytical performance of the proposed method and that of previous electrochemical methods for the determination of DES has been performed. The results are shown in Table 1. The proposed method was successfully applied to the determination of DES. Compared with several modified electrodes [21, 22, 26-33], the oxidation peak presents higher sensitivity for analyzing and detecting DES. It showed a wide linear range and a low LOD. The results indicate that PLYS/GM/GCE has a good catalytic effect on DES.

Table 1. Comparison of different electrodes for the determination of DES

Electrode	Method	Linear range (μmol•L^{-1})	LOD (μmol•L^{-1})	Reference
Pt/SWCNT/GCE	LSV	0.1-20	0.015	21
Pt/MWCNT/GCE	SWV	0.1-25	0.012	22
RGO-MWCNT /GCE	LSV	0.01-40	0.003	26
MWCNT/cobaltphtolocyanine/GCE	SWV	0.7-5.66	0.199	27
β-CD/RGO/GCE	DPV	0.01-13	0.004	29
PEDOT/GO-MWCNT/GCE	LSV	0.01-20	0.003	30
Graphene/GCE	DPV	0.025-3	0.011	31

Graphene/nano-Au/GCE	CV	0.012-12	0.0098	32
Mesoporous silica/CPE	DPV	0.0075-0.3	0.0025	33
PLYS/GM/GCE	DPV	0.08.00-10.0	0.0012	This work

3.6 Interference experiment

The interference effects of several common organics and ions on the determination of DES was studied. Under the optimal experimental conditions, the addition of 1.00×10^{-6} mol/L diestrol, and a 100-fold excess of glucose, sucrose, K^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cl^-, NO_3^-, SO_4^{2-}, dopamine, ascorbic acid, uric acid, vitamin E, estradiol, estradiol, estrone and folic acid did not interfere with the determination of a 1.0×10^{-6} mol/L solution of DES. The relative error was allowed to be within ±5%. It shows this sensor has excellent selectivity.

3.7 Determination of recovery

Pretreatment of meat (beef and mutton) sample.

A certain amount of meat was minced with a meat grinder, and then four portions of 5.000g each were weighed (labelled 1, 2, 3 and 4). A 3 mL acetonitrile-acetone (4: 1) mixed solution were added to each of four tubes. Different amounts of DES standard solutions were added to sample tubes 2, 3 and 4. Each sample tube was placed in an ultrasonic cleaner, left to dispersed for 30 minutes and then centrifuged for 10 minutes at 2000 r/min. The supernatant solution was transferred to four small beakers, A, B, C and D. Then, 3 mL acetonitrile-acetone (4 : 1) mixed solution was again added to the 4 small sample tubes. The samples were treated in the same way as before and the supernatants were combined with their respective supernatants from the previous treatment. The supernatants in the beakers were dried, and 4 mL of a pH=5.0 phosphate buffered solution and 1 mL of ethanol were added to dissolve the concentrate for use in the experimental determination.

A certain amount of milk sample was divided into four portions of each 5.000 g (labelled 1, 2, 3 and 4) and prepared with the same procedure as the meat samples.

Table 2. Recovery measurements of the DES in food samples (n = 6)

Sample	Addition standard ($\times10^{-6}$ mol/L)	Total ($\times10^{-6}$mol/L)	Recovery(%)	RSD(%)
Beef	-	1.52	-	2.6
	0.50	2.03	102.0	2.8
	1.00	2.49	97.0	3.1
	1.50	3.01	99.3	2.9
Mutton	-	1.02		
	0.50	1.51	98.0	3.3
	1.00	2.05	103.0	2.5
	1.50	2.54	101.3	2.3
Milk	-	-	-	

0.50	0.51	102.0	3.1
1.00	0.98	98.0	3.2
1.50	1.46	97.3	2.9

From Table 2, it can be seen that this system was successfully applied for the determination of DES in beef, mutton and milk samples with satisfactory recovery.

4. CONCLUSIONS

A polylysine/graphene modified electrode was prepared by optimizing the experimental conditions. The experimental results showed that the modified electrode had a good electrocatalytic effect towards DES and could be used for the electrochemical determination of DES in animal food. Over the range of 8.00×10^{-8} ~ 1.00×10^{-5} mol/L, the concentration of DES was directly proportional to its oxidation peak current, the detection limit is 1.20×10^{-9} mol/L, and the RSD was 1.7% over six parallel tests. The PLYS/GM/GCE can be used to detect diethylstilbestrol in beef, mutton and milk samples with recovery rate of 97.0% ~ 103.0%. The PLYS/GM/GCE could overcome the interference effects of dopamine, ascorbic acid, uric acid, vitamin E, oestradiol, folate, etc. Therefore, this method is sensitive, accurate, simple, rapid, highly selective and of practical value.

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