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Electrochemical Determination of Sudan I at a Silver Nanoparticles/Poly(Aminosulfonic Acid) Modified Glassy Carbon Electrode

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In this paper, a novel silver nanoparticles/poly(aminosulfonic acid) modified glassy carbon electrode (Ag-PASA/GCE) for the determination of Sudan I was fabricated through electrochemical immobilization. Electrochemical behavior of Sudan I at the Ag-PASA/GCE was studied by cyclic voltammetry. The polymer-modified electrode showed excellent electrocatalytic activity for the redoxidation of Sudan I. Under optimal experimental conditions, the oxidation peak current of Sudan I was linearly proportional to its concentration in a range from 4.0×10^{-8} to 4.0×10^{-6} mol/L with a correlation coefficient of 0.9986 and a detection limit of 8.0×10^{-9} mol/L. The application of the modified GCE for the determination of Sudan I in food samples showed good recovery, reproducibility and high sensitivity.

Keywords: Modified electrode, Cyclic voltammetry, Linear sweep voltammetry, Sudan I, Silver nanoparticle, Aminosulfonic acid

1. INTRODUCTION

Sudan I is a synthetic lipophilic azo dye extensively used in many industrial fields such as oils, plastics, waxes, petrol, shoes, printing inks and floor polishing [1]. Its carcinogenicity was discovered in 1970s, and confirmed in recent studies. The International Agency for Research on Cancer, a part of the World Health Organization, has assessed Sudan I as a group 3 carcinogen [2]. Due to the carcinogenicity, use of Sudan I as coloring agent in food products is forbidden in most countries. However, some food manufacturers still purposefully add it into foodstuffs such as ketchup, chili powder to increase luster because of its low cost. Therefore, development of specific and convenient analytical methods for Sudan I is very necessary. There are a number of reported methods for Sudan I determination, including HPLC with detection by UV-visible spectroscopy [3], mass spectrometry [4, 5], chemiluminescence [4] and photodiode array [6], GC with detection by mass spectrometry [7], capillary electrophoresis [8], and electrochemical methods using modified electrodes with various modifiers [9-14]. Among these reported methods, chromatography methods require expensive equipments, large amount of organic solvents and are time-consuming, capillary electrophoresis method is not very sensitive. Electrochemical methods are obviously better due to its convenience, fastness, higher sensitivity and reproducibility. For electrochemical determination of Sudan I using modified electrode, the modifier is a key factor that can heavily influence the determination sensitivity and selectivity. Various modifiers such as montmorillonite calcium [9], gemini surfactantionic liquid-multiwalled carbon nanotube composite film [10], Fe_3O_4 nanoparticles [13], mesoporous carbon [12], single-walled carbon nanotubes and iron(III)-porphyrin [14], and multiwall carbon nanotubes [11] have been reported.

Electrically conductive polymer films have received extensive interest and have been used as modifiers in preparing modified electrode in recent years due to their good chemical stability, reproducibility, more active sites, homogeneity, and strong adherence to electrode surface [15, 16]. In the preparation of polymer film modified electrodes, electropolymerization is an effective technique for immobilizing polymer films onto electrodes with different thickness and has been used in preparing various modified electrode [15, 17]. Furthermore, polymers films have been proven to be suitable matrices for dispersing metallic nanoparticles. Silver nanoparticle, one of these typical metallic nanoparticles, has attracted growing interest in constructing electrochemical sensors due to its conductivity and excellent catalytic activity [18-21]. Owing to the synergistic effect of metal ion and electric polymer, performance of the modified electrode such as the sensitivity and catalytic capability can be greatly improved [22-24].

In this paper, a novel silver doped poly(aminosulfonic acid) modified glassy carbon electrode (Ag-PASA/GCE) was fabricated by electropolymerization, the electrochemical behavior of Sudan I at the Ag-PASA/GCE was investigated by cyclic voltammetry, and a new method for determination of Sudan I in foodstuffs was established. It was found that the poly(aminosulfonic acid) film exhibited obvious catalytic activity toward the oxidation of Sudan I due to the hydrogen bonding interaction between the poly(aminosulfonic acid) and Sudan I, and the electron transfer rate and sensitivity of the modified electrode were further enhanced by the silver nanoparticles, resulting a clear increase of redox peak currents of Sudan I. The oxidation peak current showed a linear relationship with the concentrations of Sudan I in the range of 4.0×10^{-8} to 4.0×10^{-6} mol/L, with the detection limit of 8.0×10^{-9} mol/L. This new method for the determination of Sudan I is of great simplicity, high sensitivity, good accuracy and low cost. The practical application of the system has been demonstrated by determining Sudan I in foodstuffs such as ketchup and chili powder.

2. EXPERIMENTAL

2.1 Reagents and solutions

Sudan I was purchased from Acros (Germany) and 8.0×10^{-4} mol/L Sudan I stock solution was prepared by dissolving it in absolute ethanol. Aminosulfonic acid，$AgNO_3$ and all other chemical reagents (analytical-reagent grade) were obtained from Beijing Chemical Reagent Company (Beijing, China). Phosphate buffer solutions (PBS) were prepared by mixing the stock solutions of 0.2 mol/L Na_2HPO_4 and 0.1 mol/L citric acid. All aqueous solutions were prepared in double distilled water.

2.2 Apparatus

Electrochemical measurements were conducted on a CHI 660C Electrochemical Workstation (Chen-hua, Shanghai, China). Scanning electron microscope (SEM) image was obtained using a field emission SEM Sirion 200 (FEI, America). All electro-chemical experiments were carried out using a three-electrode system consisted of a working electrode (a bare GCE or Ag-PASA/GCE, 3 mm in diameter) a counter electrode (a platinum wire electrode), and a reference electrode (a Ag/AgCl electrode). Acidity was measured by a PHS-3B Precision pH Meter (Shanghai, China), and all sonication was done using a KQ-100 Ultrasonic Cleaner (Kunshan, China).

2.3 Preparation of Ag-PASA/GCE

Prior to modification, the bare glassy carbon electrode (GCE, ∅ = 3 mm) was polished successively with grit 2000 gold sand paper and 0.05 μm alumina powder slurry to mirror-like smoothness, the bare GCE was rinsed thoroughly with doubly distilled water after each polishing step. Then, the electrode was subjected successively to 1:1 nitric acid, absolute ethanol and doubly distilled water in ultrasonic bath for 2 min, respectively. After being cleaned again with distilled water, using the GCE as working electrode, a Ag/AgCl electrode as reference electrode and a platinum as counter electrode, the GCE was modified by cyclic scanning from – 0.7 to 1.9 V at 80 mV/s for 11 cycles in a solution containing 100 mmol/L nitric acid, 1 mmol/L $AgNO_3$, 1 mmol/L aminosulfonic acid and 150 mmol/L KNO_3. Finally, the modified electrode was rinsed with doubly distilled water and dried in air to give a silver nanoparticles/poly(aminosulfonic acid) modified GCE (Ag-PASA/GCE).

2.4 Electrochemical measurement

All electrochemical measurements were performed with a CHI 660C Electrochemical Workstation. The electrochemical system consisted of a Ag-PASA/GCE as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as reference electrode. Unless otherwise stated, a mixture of PBS (pH 4.0), ethanol and water with a ratio of 10:4:6 was chosen as the supporting electrolyte. During measurement, preconcentration was firstly performed at the surface under open-circuit for 120 s with stirring. Then, cyclic voaltammograms (CVs) or linear sweep voltammograms (LSVs) were obtained by scanning in the potential range from – 0.6 to 0.8 V and – 0.2 to 0.4 V, respectively, at a scan rate of 100 mV/s. Upon completion of each scan, the modified electrode was placed in a mixed solution of ethanol and pH 4.0 PBS (ethanol:PBS = 1:1) and cyclic scan was continued until no redox peaks came out, then the electrode was washed with doubly distilled water and dried in air for reuse.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Modification of Silver and poly(aminosulfonic acid) on GCE

Polymerization conditions exhibit great influence on the performance of the modified electrode. To obtain the optimum polymerization conditions, we examined the influence of polymerization potential, scan rate, number of cycles and concentration of silver ions on the oxidation response of Sudan I at the Ag-PASA/GCE (Figure 1). Varying the terminal potential from 1.1 to 2.5 V with a gradual increase of 0.2 V each time while keeping the initial potential fixed at – 0.7 V, oxidation peak response of Sudan I at the Ag-PASA/GCE first increase with increasing terminal potentials and reach maximum at 1.9 V, then decrease with the continuing increase of terminal potentials (Figure1 A). Therefore, 1.9 V was chosen as the optimum terminal potential. Similarly, – 0.7 V was obtained as the optimum initial potential (Figure1 B). As a result, a potential range of – 0.7 to 1.9 V was chosen for the polymerization. Ag-PASA/GCE prepared at a scan rate of 80 mV/s gives the largest peak current of Sudan I (Figure1 C). Experiments show that thicker film was obtained at a lower scan rate because of longer polymerization time, which hinders electron transport; While higher scan rate gave thinner film, which has weaker catalytic activities. The thickness of the polymer film grows with increasing number of scan when the concentration of aminosulfonic acid is fixed. Ag-PASA/GCE prepared with 11 cycles gives maximum oxidation peak response of Sudan I (Figure1 D). The concentration of silver ion during polymerization also exhibits great influence on the oxidation peak responses of Sudan I at the Ag-PASA/GCE. Silver ion concentration of 1.0 mmol/L gives the highest response (Figure1E).

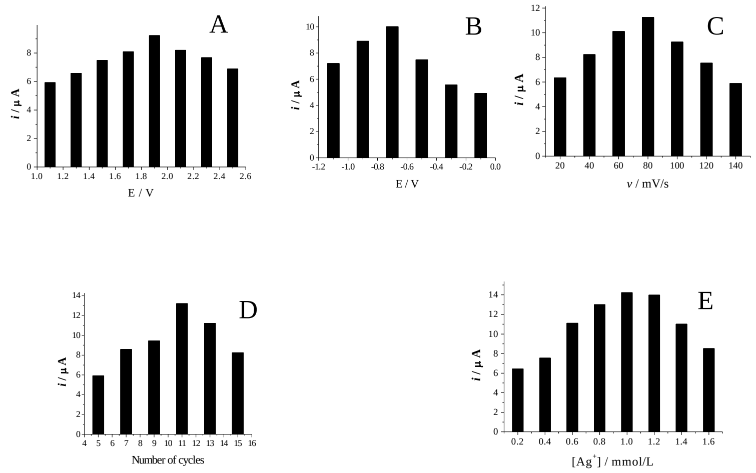

Figure 1. Variations in oxidation peak response of Sudan I as a function of (A) the terminal potential, (B) the initial potential, (C) scan rate, (D) number of scan cycles, and (E) concentration of silver ions in the electrode modification.

Figure 2 shows the continuous cyclic voltammograms of polymerization under the above optimized conditions. As can be seen, in the potential range of – 0.7 to 1.9 V, only a reduction peak was observed with peak potential at – 0.21 V when the solution was in the absence of silver ion (Figure 2, inset); When silver ion and aminosulfonic acid coexisted in the solution, In addition to a reduction peak observed at – 0.25 V, a pair of redox peaks of silver at 0.50 V and 1.51 V were also observed, which may be resulted from the deposition of silver on the GCE. Furthermore, the peak current increased with the increase of scan cycles, but the current increase became smaller, indicating that the mass deposition of poly(aminosulfonic acid) and silver on the GCE became slower. When the polymerization was finished, a blue film was observed at the electrode surface.

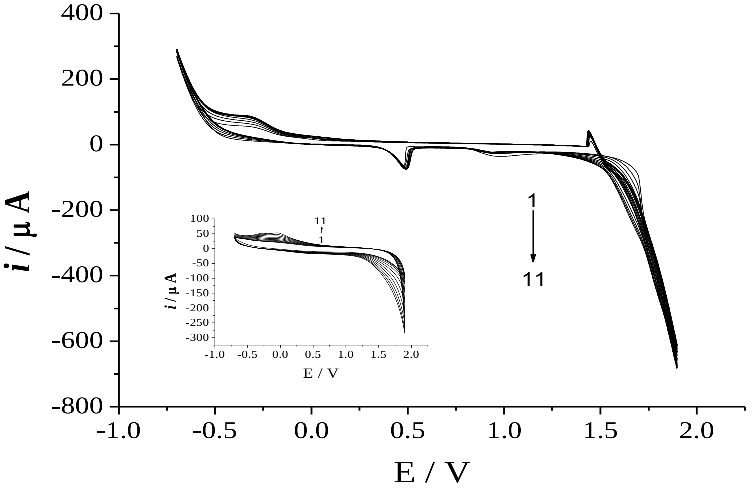

Figure 2. Cyclic voltammetric curves of silver ion and aminosulfonic acid in polymerization process. Inset is the cyclic voltammetric curves of aminosulfonic acid in polymerization process.

3.2 Characterization of the Ag-PASA/GCE

Figure 3 showed the SEM image of the Ag-PASA/GCE. From which we can see that silver nanoparticles were well dispersed on the surface of electrode with uniform size and good shape, and poly(aminosulfonic acid) also had been successfully polymerized onto the surface.

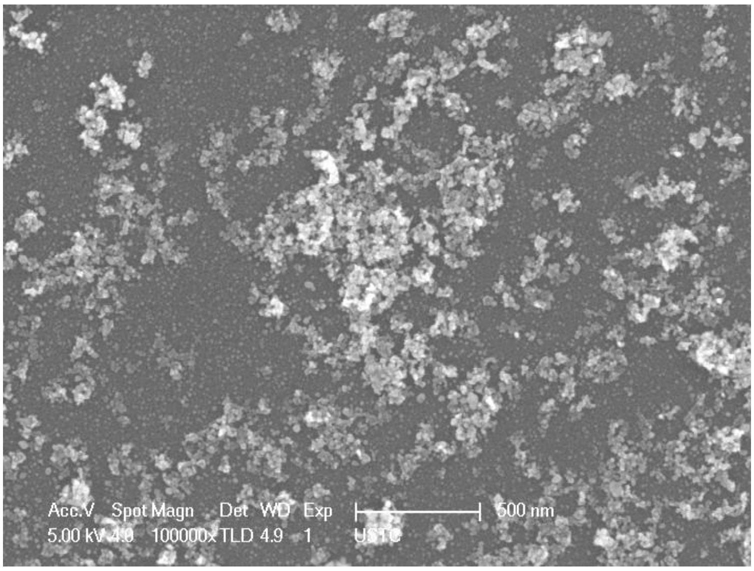

Figure 3. The SEM image of the Ag-PASA/GCE.

3.3 Electrochemical behavior of Sudan I at the Ag-PASA/GCE

Figure 4 shows the cyclic voltammograms of Sudan I at the bare GCE, the PASA/GCE and the Ag-PASA/GCE. From which we can see that very weak current response of 2.0 × 10^{-6} mol/L Sudan I was observed at the bare electrode (a), a pair of redox peaks with oxidation and reduction currents of i_{pa} = – 9.31 μA and i_{pc} = 6.90 μA, respectively, were observed at the PASA/GCE (b), while at the Ag-PASA/GCE, oxidation and reduction currents of 2.0 × 10^{-6} mol/L M Sudan I increased to i_{pa} = –18.12 μA and i_{pc} = 13.48 μA, respectively (c), both oxidation and reduction peak currents were almost doubled, indicating that the Ag-PASA film can significantly catalyze the oxidation process of Sudan I and the electron transfer rate of Sudan I in the film is much faster. From the cyclic voltammograms of Sudan I at the Ag-PASA/GCE, we can know that E_{pa} = 0.227 V, E_{pc} = 0.088 V, the potential difference is 139mV, i_{pa}/i_{pc} > 1, which indicates that the reaction process of Sudan I at the modified electrode is a quasi-reversible process.

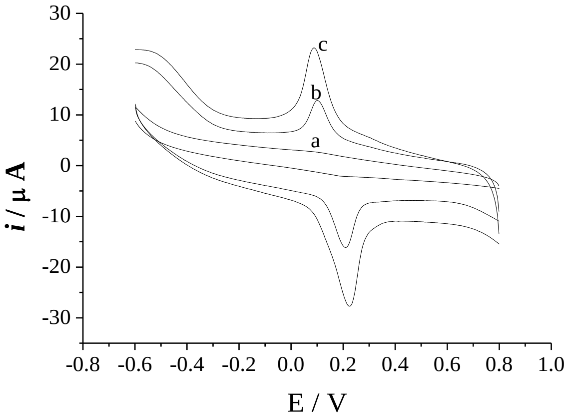

Figure 4 Cyclic voltammograms of 2.0 × 10^{-6} mol/L Sudan I at bare GCE (a), PASA/GCE (b), Ag-PASA/GCE (c) in PBS (pH = 4.0). Scan rate: 100 mV/s.

3.4 Optimization of conditions for the determination of Sudan I

3.4.1 Effect of pH

The effect of pH on the electrochemical signal was analyzed in phosphate buffer solution. Figure 5 shows the influence of pH on Sudan I redox peak potential and peak current. From which we can see that, in a range of pH 3.0 to 8.0, the oxidation peak of Sudan I shifts negatively with increasing pH, which indicates that the oxidation of Sudan I is a proton leaving process. E_{pa} and solution pH are linearly proportional in the pH range of 3.0 to 8.0 with the linear equation as E = 0.048 – 0.066pH, r = – 0.9967, the slope of the equation 66 mV/pH is close to 60 mV/pH, indicating that electron transfer number equals proton transfer number [11]. In a pH from 3.0 to 8.0, both oxidation peak current and reduction peak current firstly increase with increasing pH and reach maximum at pH 4.0, then decrease as pH continues to increase, thereby, a pH 4.0 PBS was chosen as the supporting electrolyte in this study.

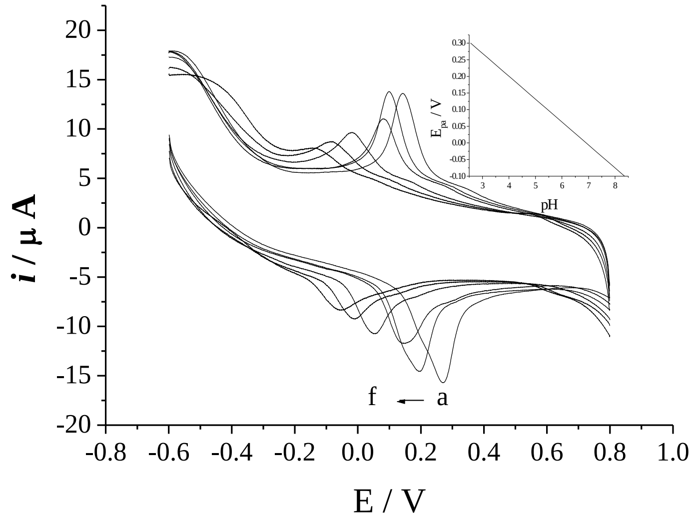

Figure 5. Cyclic voltammograms of 2.0 × 10^{-6} mol/L Sudan I at different pH values. Each of the letters from a to f corresponds to a pH of 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0, respectively. Inset is the plot of the peak potential of Sudan I versus pH value of buffer solutions. Scan rate: 100 mV/s.

3.4.2 Effect of ethanol amount

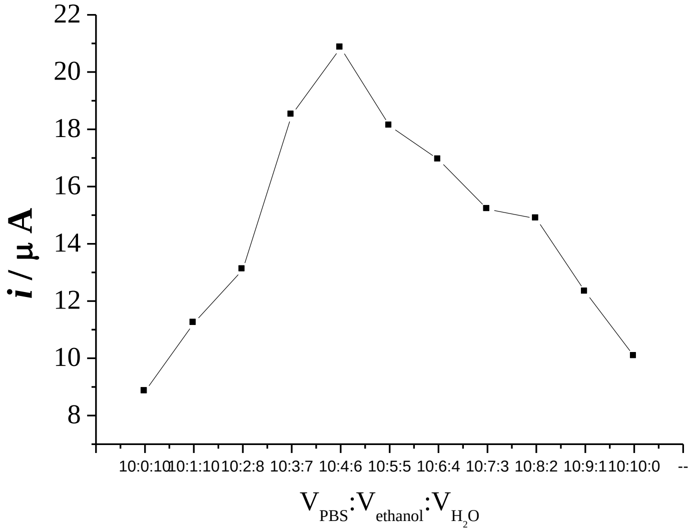

Figure 6. Plot of the oxidation peak current of 2.0 × 10^{-6} mol/L Sudan I versus the ratio of PBS (pH 4.0), ethanol and water.

Sudan I is insoluble in water whereas soluble in ethanol. In this study, a certain amount of ethanol was added into the solution to increase the solubility of Sudan I. The amount of ethanol exerts great influence on electrochemical response of Sudan I at the Ag-PASA/GCE. Measurements were made with different amounts of ethanol added into the solution and results are shown in Figure 6. It was found that the maximum redox peak current was obtained when PBS (pH 4.0), ethanol and water were in the ratio of 10:4:6. Thereby, a supporting electrolyte with a ratio of 10:4:6 among PBS (pH 4.0), ethanol and water was chosen in this study.

3.4.3 Effect of accumulation time

Accumulation is a simple and effective way to enhance the determining sensitivity. In this work, open-circuit accumulation was employed to further improve the redox peak current of Sudan I. Peak currents of 2.0×10^{-6} mol/L Sudan I were measured with various stirring time. When the accumulation time increased from 0 to 120 sec, the oxidation peak current increased with increasing accumulation time. However, the oxidation peak current did not increase as further increasing the accumulation time. Considering both sensitivity and working efficiency, an accumulation time of 120 sec was employed.

3.4.4 Effect of scan rate

The effect of scan rate on the redoxidation of Sudan I was investigated at a concentration of 2.0×10^{-6} mol/L in pH 4.0 PBS in a range of from 40 to 600 mV/s (Figure 7). It was found that both the oxidation current and the reduction current increased with increasing scan rates. The oxidation peak currents linearly increased with the scan rates. The linear regression equation are expressed as $i_{\mathrm{pa}}(\mathrm{A}) = 3.94 \times 10^{-7} + 2.59 \times 10^{-8}\, v$ (mV/s), r = 0.9967, indicating that the process of Sudan I on the electrode is an adsorption process. The electrode process is similar to the process of Sudan I at a Fe_3O_4 nanoparticles modified glassy carbon electrode [13].

Figure 8 shows the correlation between the oxidation and reduction peak potentials and the logarithms of scan rates, log (ν/mV/s). According to Laviron's theory of quasi-reversible voltammetry of adsorbed species [25], variations in the peak potential values are a function of logarithms of scan rates and the following equations can be used to determine the electron transfer number and coefficient:

$$E_{pa} = a + (2.303RT/(1-\alpha)n_{\alpha}F)\lg v \quad (1)$$

$$E_{pc} = b - (2.303RT/\alpha n_{\alpha}F)\lg v \quad (2)$$

where a and b are constants.

From Figure 7 we can see that, In a pH 4.0 PBS and a scan rate range of 160 to 600 mV/s, $E_{pa} = -0.077 + 0.099\lg v$, R=0.9993; $E_{pc} = 0.38 - 0.12\lg v$, R = 0.9984. Based upon equations (1) and (2), the calculated electron transfer number (n_{α}) and the electron transfer coefficient (α) are 1.06 and 0.45, respectively. The electron transfer coefficient is close to theoretical value 0.5, proving that the electrode process is quasi-reversible.

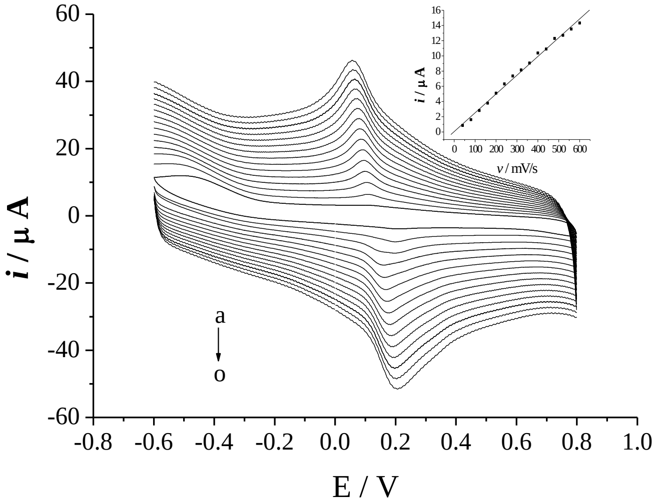

Figure 7. Cyclic voltammograms of 2.0 × 10^{-6} mol/L Sudan I at the Ag-PASA/GCE. Inset is the plot of oxidation peak currents of Sudan I versus scan rates. Each of the letters from a to o corresponds to scan a rate of 40, 80, 120, 160, 200, 240, 280, 320, 360, 400, 440, 480, 520, 560, 600 mV/s.

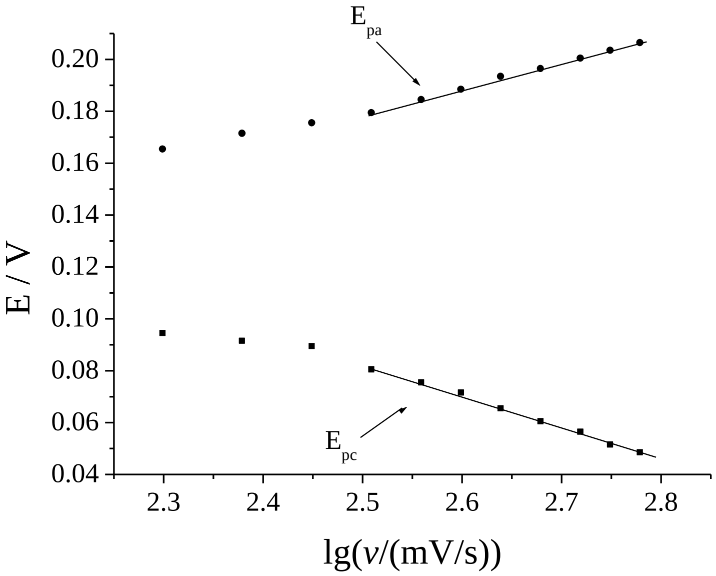

Figure 8. Plots of the peak potentials versus the logarithms of the scan rates.

3.5 Linearity range, detection limit and reproducibility

The variation of oxidation peak current with concentration was studied at the Ag-PASA/GCE in pH 4.0 PBS using linear sweep voltammetry (LSV). Figure 9 showed the oxidation peak current response of Sudan I at the GME with different concentrations. From which we can see that the oxidation peak current of Sudan I was linearly proportional to its concentration in a concentration range from 4.0 × 10^{-8} to 4.0 × 10^{-6} mol L^{-1}, with a linear regression equation of i_{pa}(A) = 3.36c + 1.74 × 10^{-6}, r = 0.9986 and a detection limit of 8.0 × 10^{-9} mol/L. The relative standard deviation (RSD) for six replicate determinations of 2.0 × 10^{-6} mol/L Sudan I at the Ag-PASA/GCE was 2.1%, suggesting that this method possesses excellent reproducibility. After each measurement, the Ag-PASA/GCE was regenerated by 10 cyclic sweeps in ethanol/pH 4.0 PBS (1:1).

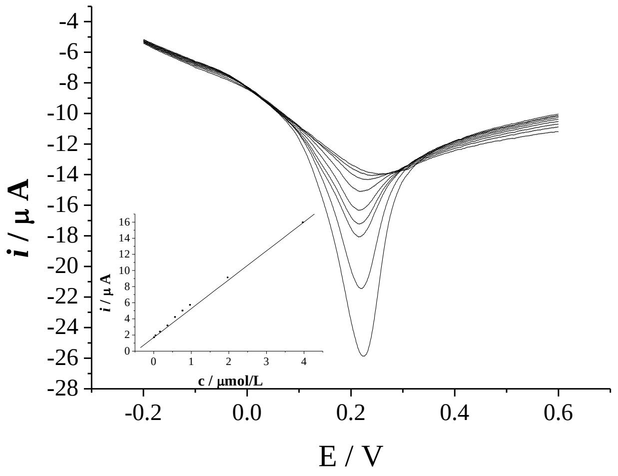

Figure 9. Linear sweep voltammograms of Sudan I at the Ag-PASA/GCE at different concentrations. Each of the letters from a to i corresponds to a concentration of 4.0×10^{-8}, 8.0×10^{-8}, 2.0×10^{-7}, 4.0×10^{-7}, 6.0×10^{-7}, 8.0×10^{-7}, 1.0×10^{-6}, 2.0×10^{-6}, 4.0×10^{-6}, respectively (in mol/L). Inset is the plot of the oxidation peak current versus concentration of Sudan I. Scan rate: 100 mV/s.

3.6 Interference Studies

Potential interference to the oxidation current of Sudan I from some interferents was investigated by cyclic voltammetry. Experiments show that, when the relative deviation is less than ±5%, no change in the current response was observed for 1.0 μM Sudan I in the presence of Na^+ (1000), Zn^{2+} (1000), Fe^{3+} (1000), Ca^{2+} (1000), K^+ (1000), Mg^{2+} (1000), glucose (100), ascorbic acid (100), caffeine (100), 4-nitrophenol (50), 4-chlorophenol (50), and phenol (50), indicating that the Ag-PASA/GCE is highly selective toward the determination of Sudan I, where the data in the parenthesis are the concentration ratios of those interferents to Sudan I. These results indicated good selectivity of the method for the determination of Sudan I.

4. ANALYTICAL APPLICATION

Measurements of Sudan I in chili powder and ketchup samples were performed by linear sweep voltammetry. 2.020 g of accurately weighed chili powder was extracted three times with ultrasound assistance, each time with 20 mL of absolute ethanol for 20 min. Extracts were combined, filtered and diluted to 100 mL. The determination conditions were set as discussed above and determinations were conducted in accordance with the analytical procedure in section 2.4. No peak current of Sudan I was observed, which indicates that the chili powder contained no Sudan I or the content is lower than the detection limit, and the determination was not interfered by other substances contained in the chili powder. Then certain amount of Sudan I standard solution was added into the chili powder. Extraction and determination were performed as above. The recoveries were calculated and the results are listed in Table 1. 2.052 g of Ketchup was similarly tested and the results are listed in Table 1 too.

Table 1. Determination results of Sudan I in chili powder and ketchup samples (n=6)

Sample	Added (μmol/L)	Found (μmol/L)	Recovery (%)	R.S.D. (%)
chili powder	0	0	-	-
	0.40	0.39	97.5	3.2
	0.80	0.77	96.2	3.6
	1.20	1.15	95.8	3.5
ketchup	0	0	-	-
	1.00	0.95	95.0	2.9
	1.50	1.45	96.7	3.4
	2.00	1.88	94.0	3.9

5. CONCLUSION

An electrochemical method for the determination Sudan I based on a novel silver nanoparticles/poly(aminosulfonic acid) modified glassy carbon electrode has been developed. The modified electrode showed excellent electrocatalytic activity toward the redoxidation of Sudan I. The oxidation peak current was linearly proportional to the concentration in the range 4.0×10^{-8} to 4.0×10^{-6} mol/L, with a correlation coefficient, and a detection limit of 0.9986 and 8.0×10^{-9} mol/L, respectively. The method is of good recovery, reproducibility and high sensitivity, and provides a practicable solution for determining Sudan I in food products.

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