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Carboxyl Multiwalled Carbon Nanotubes through Ultrasonic Dispersing in Dimethylfomamide Modified Electrode as a Sensitive Amperometric Sensor for Detection of Sulfonamide

Baoshan He[*], *Wenbo Chen*

School of Food Science and Technology, Henan University of Technology, Zhengzhou 450001, People's Republic of China
[*]E-mail: hebaoshan@126.com

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A modified glassy carbon electrode (GCE) was fabricated by coated with a layer of carboxyl multiwalled carbon nanotubes (MWCNTs) treated with ultrasonic dispersing in dimethylfomamide (DMF) media. The modified electrode showed excellent electrochemical catalytic properties for the electrical oxidation polymerization of sulfonamide. In the BR buffer system, the oxidation peak current was proportional to the concentration of sulfanilamide. Based on this, a sensitive method for detection of sulfonamide was established. The linear range was 1.0×10^{-6}~1.0×10^{-4} mol/L of sulfonamide and the linear correlation coefficient was 0.999. The detection limit was 5.0×10^{-7} mol/L and the recovery was in the range of 95%~103%. Repeatability and stability of the modified electrode were also satisfied.

Keywords: Sulfonamide; Carboxyl multiwalled carbon nanotubes; Ultrasonic dispersing; Dimethylfomamide; Electrical oxidation polymerization

1. INTRODUCTION

Sulfonamides (SAs) are widely used in veterinary medicine clinic, aquaculture and other fields because of its function of antibacterialanti-inflammatory. But improper utilizations will cause the SAs residues in animal body and accumulation in the human body, which can lead to allergic reactions, making urinary system damaged, inhibiting leukocyte generation and even cause cancer. Therefore, many countries have developed several very strict standards about the content of SAs in food. The maximum residue of SAs is 0.1mg/kg. The current methods for the determination of SAs include liquid chromatography [1-4], high performance liquid chromatography (HPLC) [5-9], spectrophotometry [10-11], chemiluminescence [12-13], and capillary electrophoresis-mass

spectrometry [14]. Although these methods can determine SAs accurately, they need more rigorous conditions and are not suitable for on-site detection.

Electrochemical method can output electric signal directly as well as functions of fast response, simple to use, easy combination with other testing, provides a way to realize the field test. Right now, this sensor technology has been widely used in the field of food safety [15-18]. As the working electrode of electrochemical sensors, bare GCE has many problems, such as passivation, electric displacement, poor stability, weak repeatability and so on. As a result, the electrodes often need to be modified in the electrochemical measurements [19-21]. MWCNTs can promote the electron transfer between electroactive species and electrodes and have excellent electrocatalytic properties for various molecules and biomolecules. Therefore, they have been extensively used in many research regions since they were discovered [22-26]. However, the insolubility of MWCNTs is a major drawback limiting their use in electrochemical sensors and biosensors because they usually exist as parallel aggregated bundles in aqueous solution. Surfactants have been examined to be an effective approach for achieving the solubility without impairing their physical properties.

In this paper, sulfonamide was selectively determined based on the carboxyl MWCNTs treated with ultrasonic dispersing in DMF media. At this modified electrode, sulfonamide had sensitive electrical oxidation polymerization peaks and peak current was proportional to the concentration of sulfanilamide. The constructed method was convenient, high selectivity and sensitivity.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

Sulfonamide and DMF were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). MWCNTs were purchased from Beijing Gaoke Technological Material Co., Ltd. (Beijing, China). The BR buffer solution was prepared in our laboratory with 0.04 mol/L phosphate, 0.004 mol/L acetic acid, 0.04 mol/L boric acid, and 0.04 mol/L sodium hydroxide. All chemicals were analytical grade and all aqueous solutions were prepared by double distilled water.

The studies were performed with an electrochemical work station CHI660E (Shanghai Chen Hua Instrument Co., Ltd, China) and a conventional three-electrode system was used throughout. A bare or modified GCE was used as the working electrode, a platinum wire was the counter electrode and a saturated calomel electrode was the reference electrode. KQ-3200E ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd., China), UB-7 pH meter (Sartorius Scientific Instruments (Beijing) Co., Ltd., China).

2.2. Preparation of carboxyl/DMF/MWCNTs/GCE

Prior to modification, the GCE end-face was successively polished to mirror-like with metallographic abrasive paper and different graininess (1.0, 0.3, 0.05 μm) Al_2O_3 emulsion. 60 mg MWCNTs were dispersed with 60 mL mixed acid solution (the concentrated H_2SO_4 and HNO_3 volume

ratio is 3: l) in ultrasonic bath for 100 min. Afterwards, MWCNTs was washed until the pH 7.0 of filtrate, and dried under 100 ^{o}C vacuum environment. The Carboxyl MWCNTs formed subsequently. Then 5 mg MWCNTs were dispersed with 10mL DMF solution of 0.25 mg/mL in ultrasonic bath for 100 min. 10 μL the dispersed Carboxyl MWCNTs was dropped on the surface of the pretreated GCE and dried under the infrared light. The modified electrode was named as carboxyl/DMF/MWCNTs/GCE.

2.3. Experimental procedures

In this way, the integrated three-electrode assembly composed of the carboxyl/DMF/MWCNTs/GCE working electrode, the platinum wire counter electrode and the saturated calomel reference electrode. The cyclic voltammograms were recorded in solution of sulfonamide in the potential range of 0.6~1.5 V with the scan rate of 100 mV/s.

Each time before the experiment, the working solution must be ventilated with high purity nitrogen for 10 minutes. All measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. SEM characterization of carboxyl MWCNTs

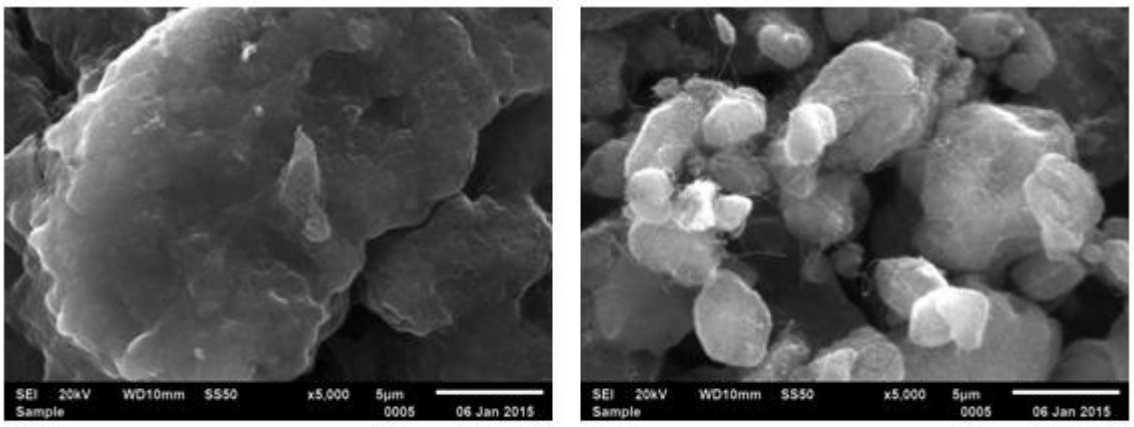


Figure 1. SEM images of MWCNTs (a) and carboxyl/DMF/MWCNTs (b).

Fig. 1 presents a set of the SEM micrographs of MWCNTs and carboxyl/DMF/MWCNTs powders. Compared with MWCNTs, It is easily found that the carboxyl/DMF/MWCNTs particle sizes become somewhat smaller and large particles are split into smaller particles, hinting that more homogenized particles can be obtained by the carboxyl method and ultrasonic dispersing in DMF media. This indicates that the carboxyl/DMF/MWCNTs powders have larger specific surface area and

higher catalytic activity. BET test results showed that higher sensitivity of carboxyl/DMF/MWCNTs/GCE as comparison with the MWCNTs/GCE, which is well agreeable to the SEM analysis.

3.2. Electrochemical impedance spectroscopy of the electrode

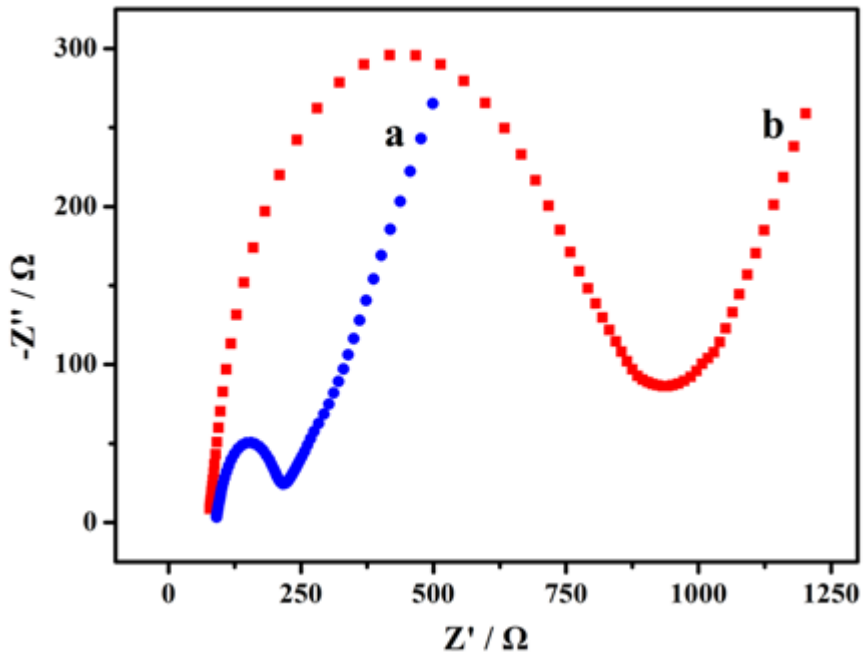


Figure 2. EIS plots for the carboxyl/DMF/MWCNTs/GCE (a), bare GCE (b) in a solution of 10 mM $[Fe(CN)_6]^{3-/4-}$ + 0.1 mol/L KCl as the supporting electrolyte. Frequency range: 0.19 Hz to 10 kHz.

Electrochemical impedance spectroscopy (EIS) was used to characterize the preparation process of carboxyl/DMF/MWCNTs/GCE. As shown in Fig. 2, the electron transfer resistance of the carboxyl/DMF/MWCNTs/GCE (~120 Ω, Fig. 2a) was smaller than that of the bare GCE (~810 Ω, Fig. 2b), which indicated that the presence of carboxyl/DMF/MWCNTs on the electrode surface improved the reactive site, reduced the interfacial resistance, and made the electron transfer easier, which can be ascribed to their great mesopore volume, high accessible surface, and excellent conductive property [27-28].

3.3. Electrochemical response of sulfonamide

The cyclic voltammograms of sulfonamide in pH 1.80 BR buffer solution were recorded on the bare GCE, carboxyl/DMF/MWCNTs/GCE in the potential range of 0.6~1.5 V with the scan rate of 100 mV/s. As shown in Fig. 3, no obvious redox peak appeared on the bare GCE in the whole electrochemical scanning range when the working solution had no sulfanilamide (curve a). When some sulfanilamide was added in, an oxidation peak current of sulfanilamide was found at about 1.085 V

and no reductive peak currents on the bare GCE (curve b). Owing to its electroactive properties, the anodic oxidation of sulfanilamide could occur at aromatic amino group (-NH_2) with the potential range of 0.6~1.5 V. However, the reduction of sulfonamide group (-SO_2-) could occur only at the higher negative potential value. Therefore, only anodic peak of sulfonamide group was investigated as shown in Fig. 3. The behavior of sulfonamide was in agreement with profiles reported for it in literatures [29-32]. On the carboxyl/DMF/MWCNTs/GCE (curve c, d), the oxidative peak currents of sulfanilamide increased significantly and the peak potential had somewhat negative shift to 1.082 V compared with that on the bare GCE, indicating that the carboxyl/DMF/MWCNTs had good catalytic properties for the electrical oxidation polymerization of sulfanilamide.

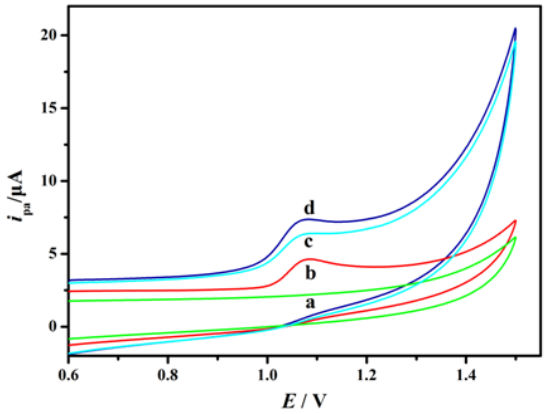
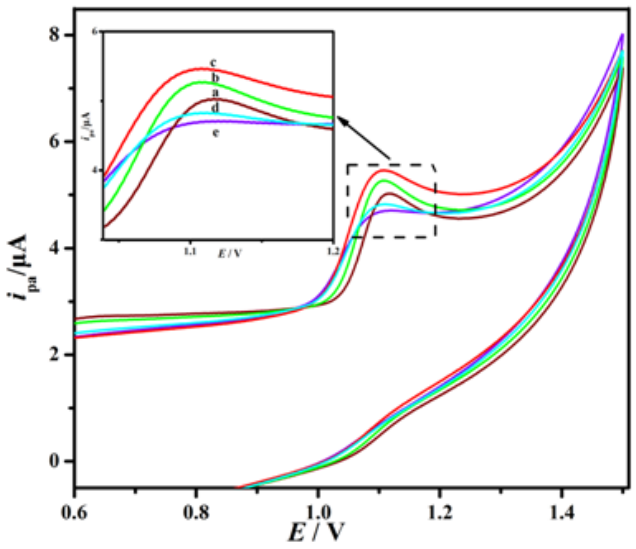


Figure 3. Cyclic voltammograms of BR buffer solution at bare GCE (curve a), 7.0×10^{-5} mol/L sulfonamide at bare GCE (curve b), 7.0×10^{-5} mol/L sulfonamide at carboxyl/DMF/MWCNTs/GCE (curve c), 1.0×10^{-4} mol/L sulfonamide at carboxyl/DMF/MWCNTs/GCE (curve d) in pH 1.80 BR buffer solution with the scan rate of 100 mV/s.

3.4. Effect of pH on the response



(a)

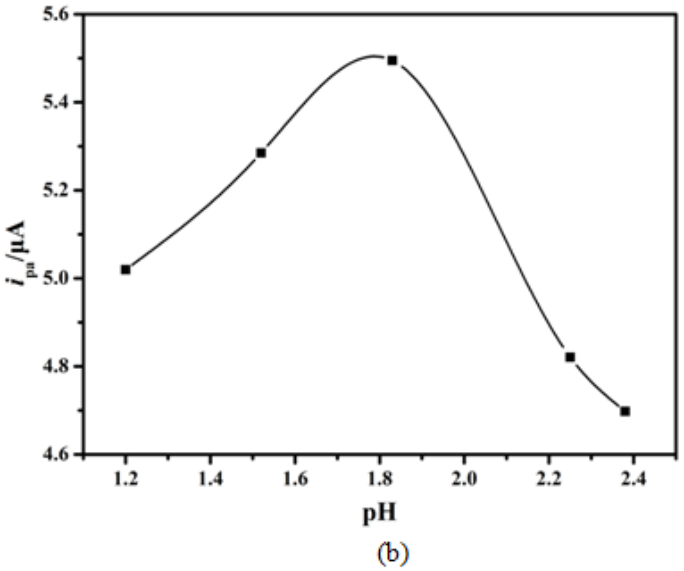


Figure 4. (a) Cyclic voltammograms of 1.0×10^{-4} mol/L sulfonamide in different pH of BR buffer solution with the scan rate of 100 mV/s. The curves of a~e correspond to the pH values of 1.20, 1.52, 1.83, 2.25, 2.38. (b) Effects of the solution pH on the oxidation peak current of 1.0×10^{-4} mol/L sulfonamide.

The influence of pH of the assay solution on the amperometric response to sulfanilamide was investigated in the range from 1.20 to 2.38 at a fixed concentration of 1.0×10^{-4} mol/L (Fig. 4 (a)). The results showed that on the carboxyl/DMF/MWCNTs/GCE, sulfanilamide had an oxidation peak at the pH 1.20. With the increase of the pH values, the oxidation peak current increased and the biggest oxidation peak current was obtained at pH 1.80, and then declined when the pH value exceeded 1.80 (Fig. 4 (b)). This phenomenon indicates that the electrochemical oxidation of sulfanilamide involves the gain and loss of H^+. In strong acidic condition, the solution of the H^+ and sulfanilamide could combine and produce ammonium salt, reduce the electrochemical activity of sulfanilamide. Under the condition of appropriate acidity, sulfanilamide had good oxidation ability and the oxidation peak current reached the maximum at pH 1.80. Then the oxidation polymerization reaction of sulfanilamide on the electrode surface progressed smoothly. When the pH value exceeded 1.80, sulfanilamide oxidation current declined, and further illustrated H^+ was involved in the electrochemical reaction process and validated the electrochemical response of sulfonamide. So the pH 1.80 buffer solution was used in the subsequent experiments.

3.5. Effect of scan rates

The effect of scan rates on the oxidation peak current of 1.0×10^{-4} mol/L sulfanilamide was investigated, as shown in Fig. 5 (a). It was found that the oxidation peak current of sulfanilamide was linearly increase with the scan rates in the range of 10~500 mV/s, and the regressive equation was i_{pa} (μA) = 18.85 v (mV/s) + 3.00 with r = 0.988 (Fig. 5 (b)). The peak current was directly proportional with the first power of scan rate indicating that the electrochemical reaction of sulfanilamide was controlled by surface adsorption.

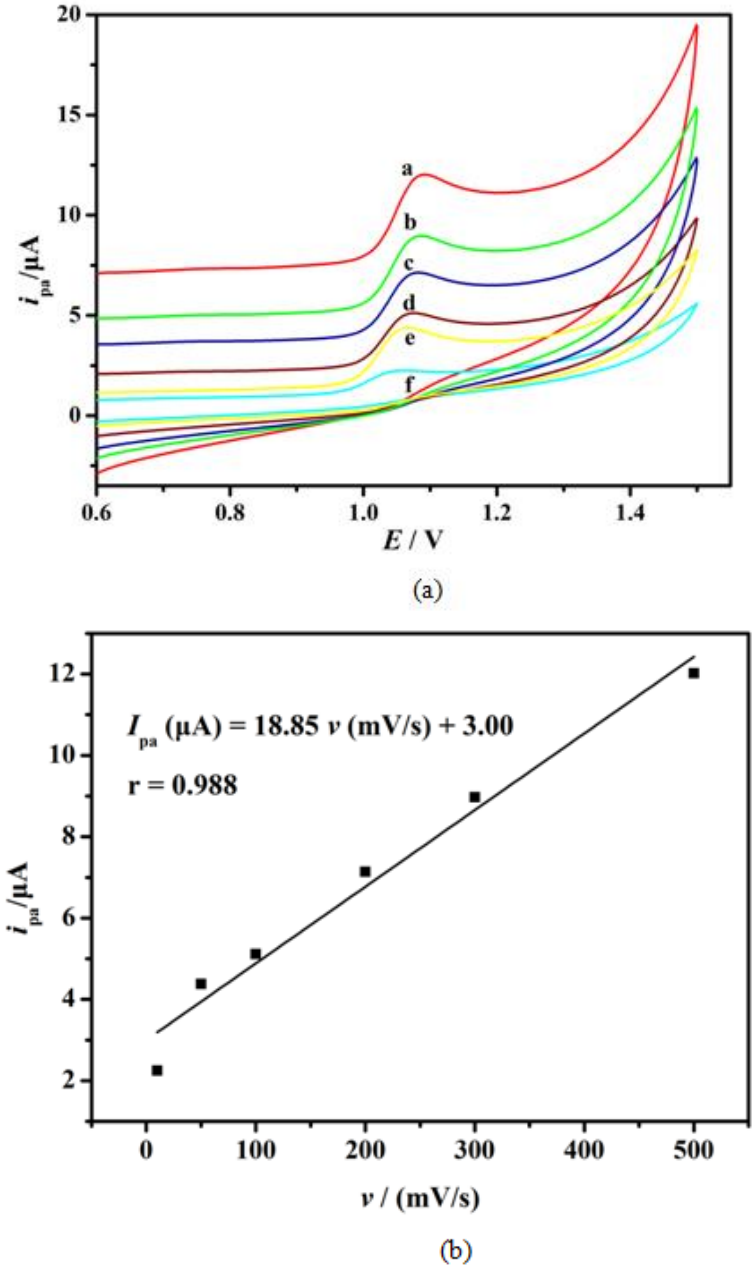


Figure 5. (a) Cyclic voltammograms of 1.0×10^{-4} mol/L sulfonamide on the carboxyl/DMF/MWCNTs/GCE in pH 1.80 of BR buffer solution at different scan rates. Curve a to f corresponds to the scan rates: 10 mV/s; 50 mV/s; 100 mV/s; 200 mV/s; 300 mV/s; 500 mV/s, respectively. (b) Relationship between oxidation peak currents and the scan rates.

3.6. Determination of sulfanilamide concentration

The cyclic voltammograms of different concentrations of sulfanilamide on the carboxyl/DMF/MWCNTs/GCE were examined under the optimized experimental conditions. Fig. 6 (a) shows the oxidation peak current increased with the successive addition of sulfanilamide. The modified electrode exhibited a linear calibration in the concentration range of sulfanilamide from

1.0×10^{-6} to 1.0×10^{-4} mol/L, and the regressive equation was i_{pa} (μA) = 0.350 c (10^{-5} mol/L) + 3.76 with a correlation coefficient of 0.999 (Fig. 6 (b)).

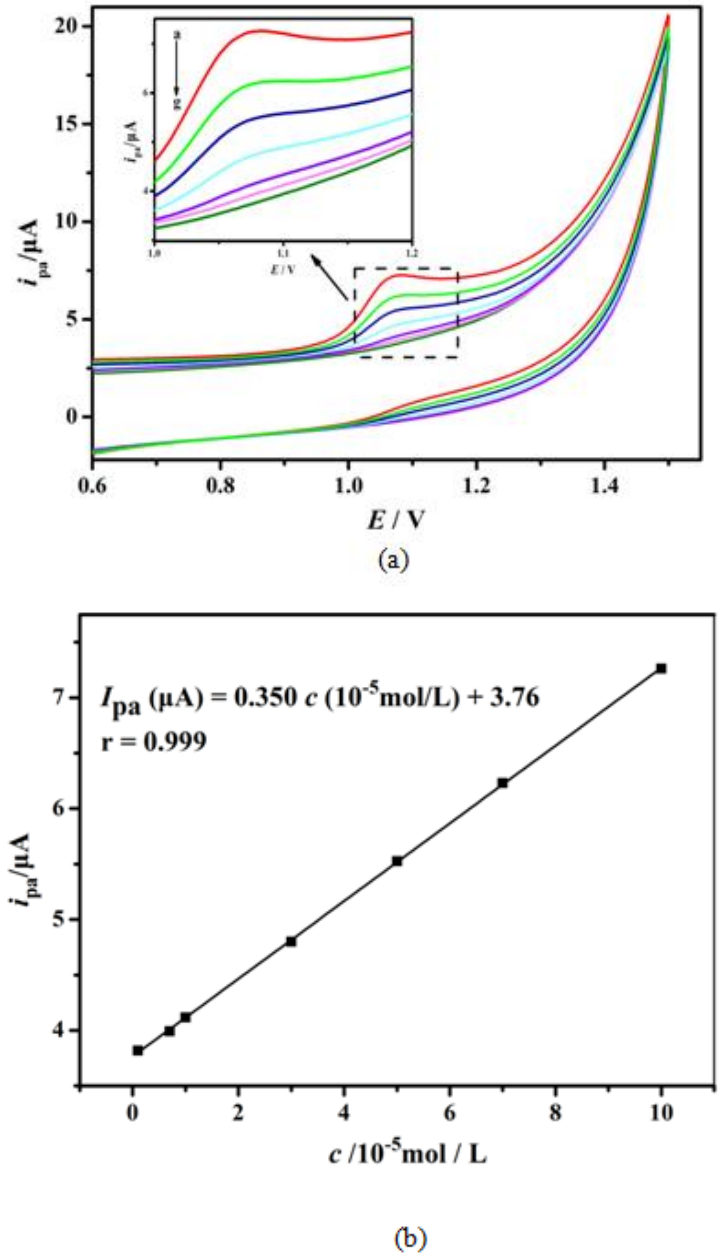


Figure 6. (a) Cyclic voltammograms for different concentrations of sulfonamide on the carboxyl/DMF/MWCNTs/GCE in pH 1.80 of BR buffer solution with the scan rate of 100 mV/s. Curve a to g corresponds to the concentrations of sulfonamide：1.0×10^{-4}mol/L; 7.0×10^{-5} mol/L; 5.0×10^{-5} mol/L; 3.0×10^{-5} mol/L; 1.0×10^{-5} mol/L; 7.0×10^{-6} mol/L; 1.0×10^{-6} mol/L, respectively. (b) Calibration curve between oxidation peak currents and the concentrations of sulfonamide.

The detection limit was 5.0×10^{-7} mol/L (signal-to-noise ratio = 3). These results show that the carboxyl/DMF/MWCNTs/GCE is useful for the simple and rapid determination of sulfanilamide samples.

3.7. Analysis of sulfanilamide in pork samples

The real sample analyses were performed using pork samples purchased from local market. The samples were pretreated by mixing 0.5 g mashed meat with 1 mL ethyl acetate into a 1.5 mL centrifuge tube. Then, meat samples were sonicated for 10 min. Next, this micro-centrifuge tube was centrifuged at 5000 rpm for 10 min. A 0.5 mL portion of supernatant liquid was ten times diluted in the BR buffer solution. Thereafter, the extracted pork samples were spiked with varying concentration of sulfanilamide, and were measured to evaluate the reliability of the proposed carboxyl/DMF/MWCNTs/GCE. As shown in Table 1, the recoveries were found to be between 95% and 103%. The better reproducibility showed less than 5% variation compared with the method (RSD less than 10%) described in the literature [33].

The results indicated that the proposed electrode is acceptably accurate and precise, and can be used for the analysis of samples from a real environment.

Table 1. Recovery studies for sulfonamide in pork (n=3)

sulfonamide	Addition (10^{-5} mol/L)	Found (10^{-5} mol/L)	Recovery(%)	RSD (%)
	0.94	0.97	103.2	4.1
	1.86	1.90	102.2	3.3
	2.78	2.66	95.7	4.7
	3.50	3.46	98.9	4.4
	4.64	4.52	97.4	3.8

4. CONCLUSIONS

The carboxyl/DMF/MWCNTs composite was successfully prepared and used to develop a novel modified electrode for the detection of sulfanilamide. Owing to the excellent property of carboxyl/DMF/MWCNTs composite such as high electrical conductivity and high accessible surface area, the application of the proposed method was verified by determination of sulfanilamide in real samples with higher sensitivity, lower detection limit, acceptable stability.

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