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Determination of Norepinephrine Tartrate at Oxidized Graphene Nanoribbon Modified Glassy Carbon Electrode

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In this paper the oxidized graphene nanoribbons for a sensor were prepared with glassy carbon electrode, and the electrochemical behavior of norepinephrine tartrate at the modified electrode was studied. It was found that the norepinephrine tartrate at the oxidized graphene nanoribbon modified glassy carbon electrode can be catalyzed significantly. The proposed method was used for determination of norepinephrine tartrate injection. The linear range and limit of detection were 6.0×10^{-6}- 7.6×10^{-5}-1.5×10^{-4} M and 2.1×10^{-8} M, respectively. The recoveries were in the range from 96.0 to 104.4% with RSD of 1.2～3.0% (n=6) in the range of 0.0～50.0 mg.L^{-1}. The recoveries were in the range from 96.0 to 104.4% with RSD of 1.2～3.0% (n=6) in the range of 0.0～50.0 mg.L^{-1}.

Keywords: oxidized graphene nanoribbons, norepinphrine tartrate, electrochemical sensor

1. INTRODUCTION

The sensor modified with graphene has been documented to result in high sensitivities, low detection limits, promotion electron-transfer, resistance to surface fouling and reduction of over potentials. It has been reported that many graphene modified electrodes were successfully applied to detect many organic molecules [1-5]. Thin and elongated strips of graphene represent a particularly versatile variety of graphene [6]. Several lithographic [7], chemical [6] and synthetic [8] procedures are known to produce microscopic samples of graphene nanoribbons (OGNs).

Norepinephrine is important catecholamine neurotransmitters in the central nervous system of mammals, and plays crucial physiological roles [9]. Norepinephrine tartrate is used for the treatment of various diseases, and the determination of norepinephrine in clinical medicine is of great significance

[10]. Various modified electrodes, such as ZrO_2 nanoparticles-modified carbon paste electrode [11], nanotubes modified edge plane pyrolytic graphite electrode [12], ionic liquid/multiwall carbon nanotubes paste electrode [13], carbon-coated nickel magnetic nanoparticles modified electrode [14], and ultrathin polymer film modified electrode [15], have been used for determination of norepinephrine. However, These preparation methods are tedious or time-consuming.

In present work, a simple method was proposed for the electrochemical sensor using glassy carbon electrode (GCE) modified by the OGNs, and the electrochemical behavior of norepinephrine tartrate at the modified electrode was studied.

2. EXPERIMENTAL

2.1. Chemicals

Norepinephrine tartrate was from Aldrich. Multiwalled carbon nanotube (MWCNTs) were obtained from Shenzhen Nano-Technologies Port Co.,Ltd. (China). Double-distilled water was used throughout. 0.1M phosphate buffer solution (PBS) was prepared by dissolving 0.1mol NaCl and 0.1mol Na_2HPO_4 in the double-distilled water of 1000mL and adjusted desired pH values with 6 mol.L^{-1}HCl or 1mol.L^{-1}NaOH. All other reagents were analytical grade.

2.2. Instrumentation

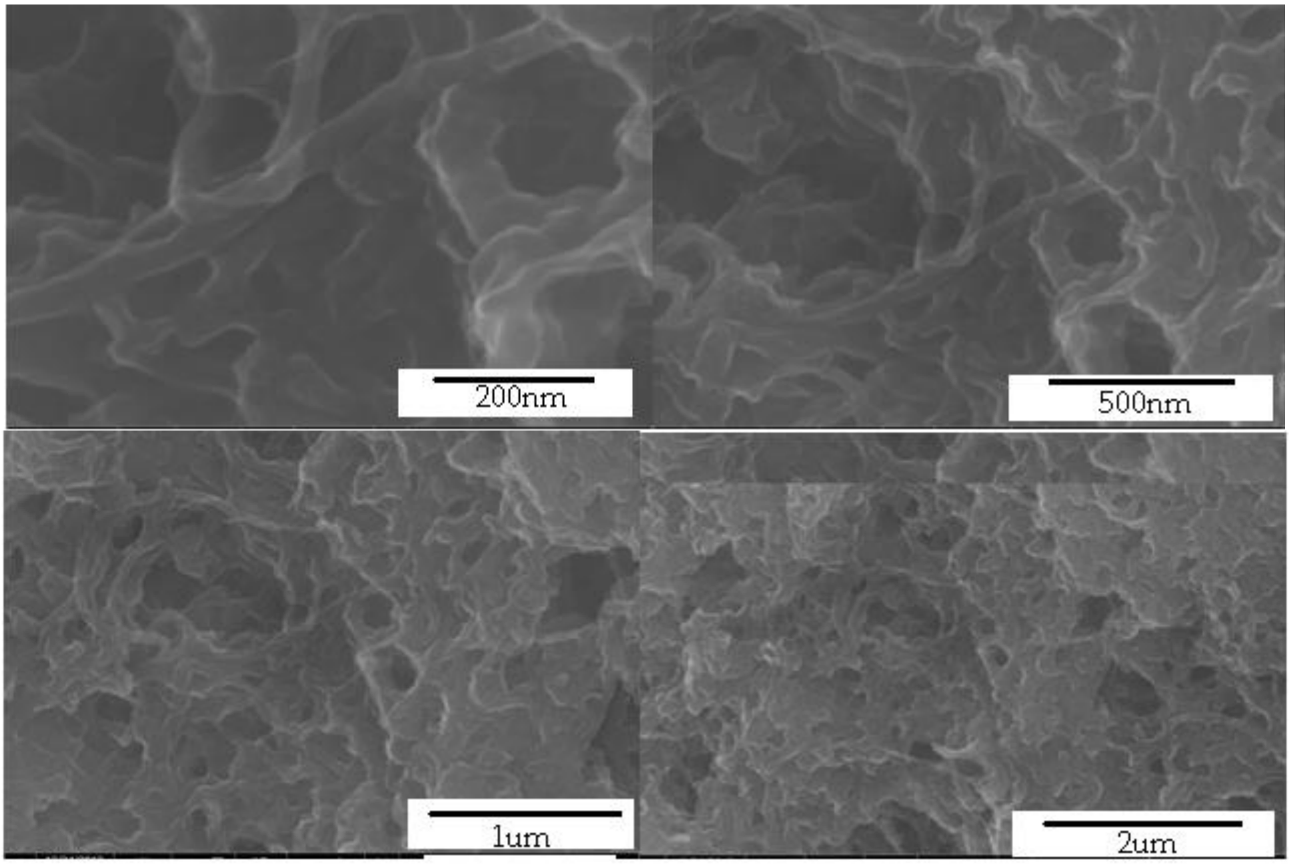
For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The electrochemical cells consisted of a three electrode, a 3 mm GCE modified by OGNs was used as working electrode. A platinum wire and a saturated calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively. The OGN material was characterized by scanning electron microscopy (SEM) (QUANTA FEG 450, USA.).

2.3. Preparation of oxidized MWCTs and Modified GCE

According to the previous work the OGNs were prepared as the literature [6]. One gram MWCNTs and 0.5 g sodium nitrate were poured into 70 mL concentrated H_2SO_4 (under ice bath), then 3 g $KMnO_4$ was gradually added. The mixture was stirred for 24 h and then diluted with double distilled water. After that, 6% H_2O_2 was added into the solution until the color of the mixture changed to brilliant yellow. The oxidized MWCTs were sonicated for 3 h. The mixture was washed with acidic water and ethanol, respectively, and tried in atmosphere at 60°C.Thus the OGNs were obtained. The modifier suspension was prepared by dispersing the OGNs in 5.0 ml of N, N-dimethylformamide under sonication for 30 min. The OGN modified GCE was prepared by casting 5μl of the mentioned above black suspension on the surface of GCE using a micropipette and left to dry at room temperature. Before the voltammetric measurements, the modified electrode was cycled between -1 and 1 V (scan rate 100 mV. s-1) in 0.1 M phosphate buffer solution (PBS) of pH 7.3 for several times until acquiring the reproducible responses. In order to compare with the behavior of norepinephrine tartrate at original MWCNTs, the MWCNT/GCE is also prepared with the MWCTs at same method.

3. RESULTS AND DISCUSSION

3.1. SEM imagine of oxidized OGN/GCE



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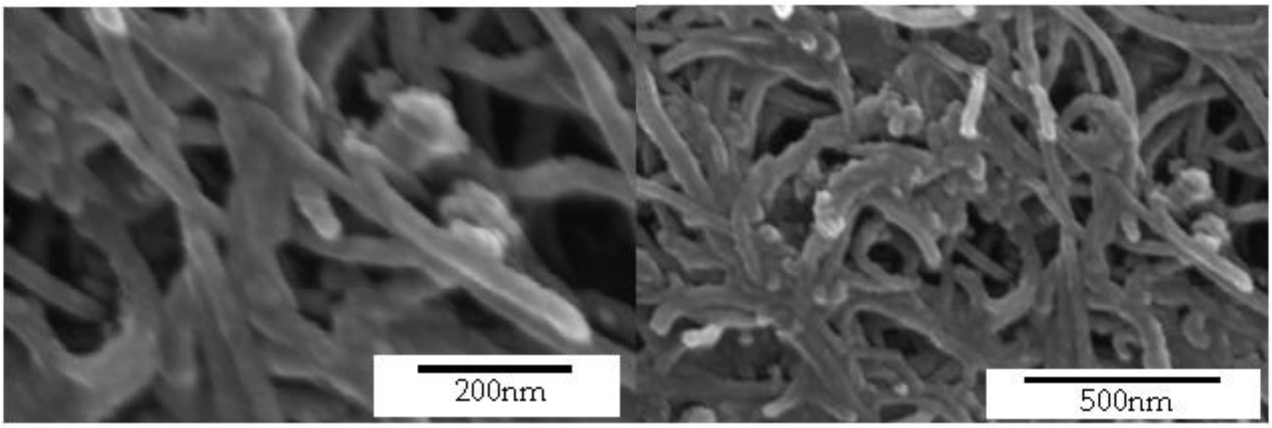

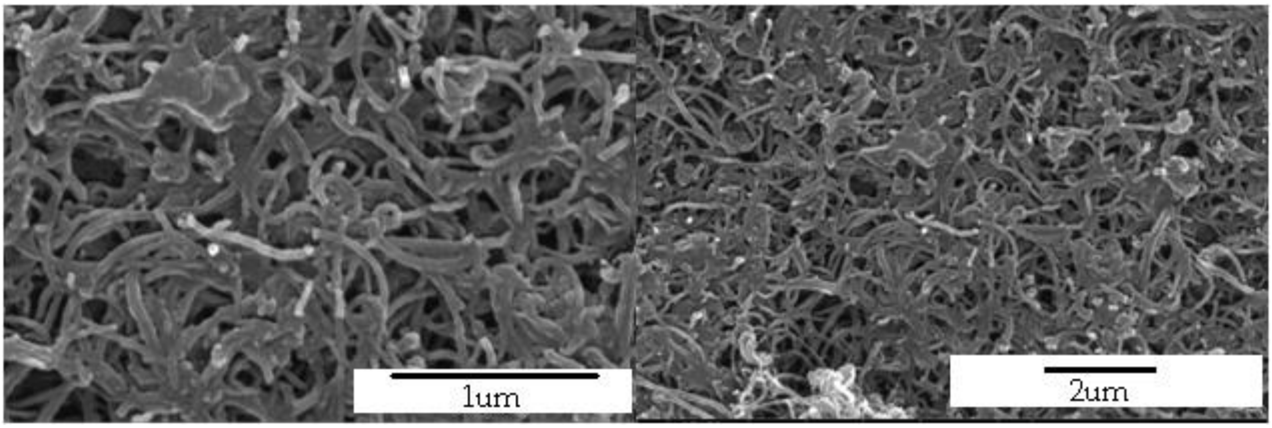

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Figure 1. SEM imagine of OGNs on the surface of GCE (a) and original MWCNTs (b)

SEM is applied to confirm the formation of a layer of the film on the surface of bare GCE. The SEM imagines of OGNs (a) on the surface of GCE and original MWCNTs (b) are shown in Fig.1, compared with MWCNTs, the sheet and elongated OGNs were observed.

3.2. CVs of the modified GCE in the $K_3Fe(CN)_6$–$K_4Fe(CN)_6$

An electrochemical method was used to characterize the modified electrode. The cyclic voltammograms (CVs) of the modified electrode in the $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ system are shown in Fig.2. The peak currents of $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ at the OGN/GCE were less than that of MWCNT/GCE, and the reduction peak of $K_3Fe(CN)_6$ shifted to positive direction. The anodic-cathodic peak separations were approximately 220 and 108 mV for the OGN/GCE and MWCNT/GCE, respectively, indicating that the groups on the surface of OGNs are different from those of MWCNTs. The peak and peak currents were influenced by the functional groups of OGNs such as –COOH and –OH [6], which could absorb the $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$.

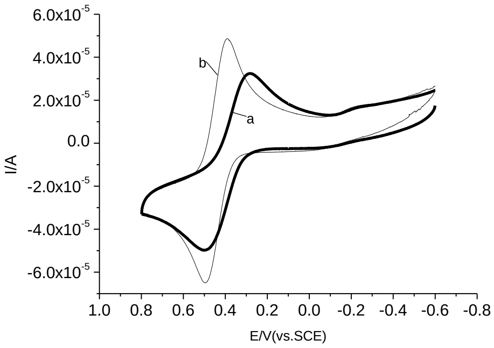


Figure 2. CVs of $K_4[Fe(CN)_6]$ (5 mM) at OGN/GCE (a) and MWCNT/GCE (b); Scan rate: 100.0 mV. s^{-1}. Supporting electrolyte: 5 mMK $_4[Fe(CN)_6]$ +0.1MKCl.

3.3. Electrochemical behavior of norepinephrine tartrate at modified electrode

The electrochemical response of norepinephrine tartrate at the modified electrode in 0.1 M PBS of pH 7.3 is shown in Fig.3. An oxidation peak for norepinephrine tartrate at MWCNT/GCE was observed at 0.398V, and a weak reduction peak appeared at 0.376V, which are in agreement with the results [16]. However, two oxidation peaks of 0.295 and 0.353V and three weak reduction peaks of 0.328, 0.049 and -0.030 V for norepinephrine tartrate at OGN/GCE were observed, and the peak currents at 0.328V are more than that of norepinephrine tartrate at MWCNT/GCE. These results indicated that the OGN modified electrode markedly promoted the electrochemical redox of norepinephrine tartrate by considerably accelerating the rate of electron transfer due to the functional groups of –COOH and –OH, and the electrochemical intermediates on the OGN could be found.

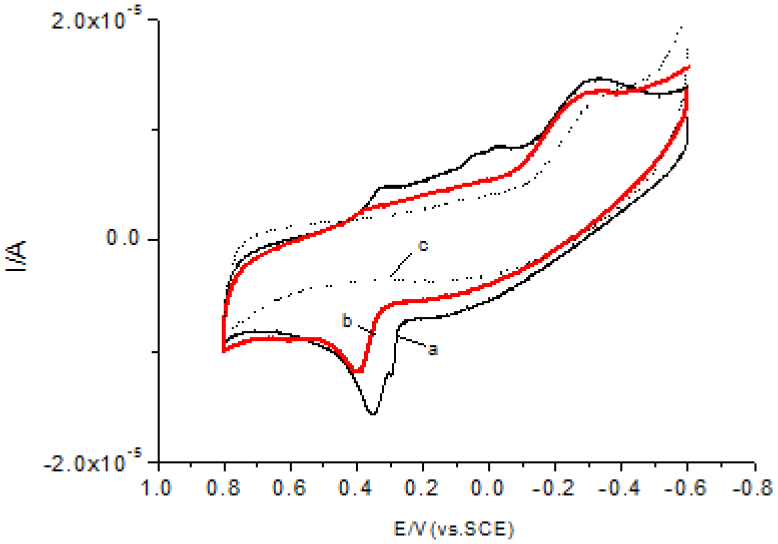
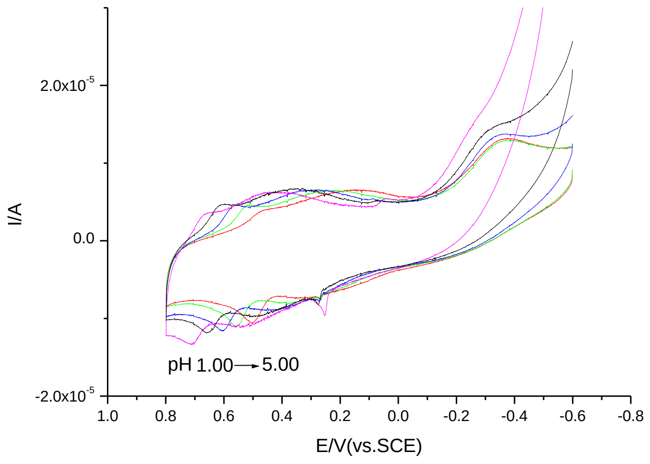


Figure 3. CVs of 6.0×10^{-5} M norepinephrine tartrate at OGN/GCE (a) and MWCNT/GCE (b) and CVs of the OGN/GCE (c); Scan rate: 100.0 mV. s^{-1}. Supporting electrolyte: 0.1 M PBS of pH 7.3.

3.4. Influence of pH



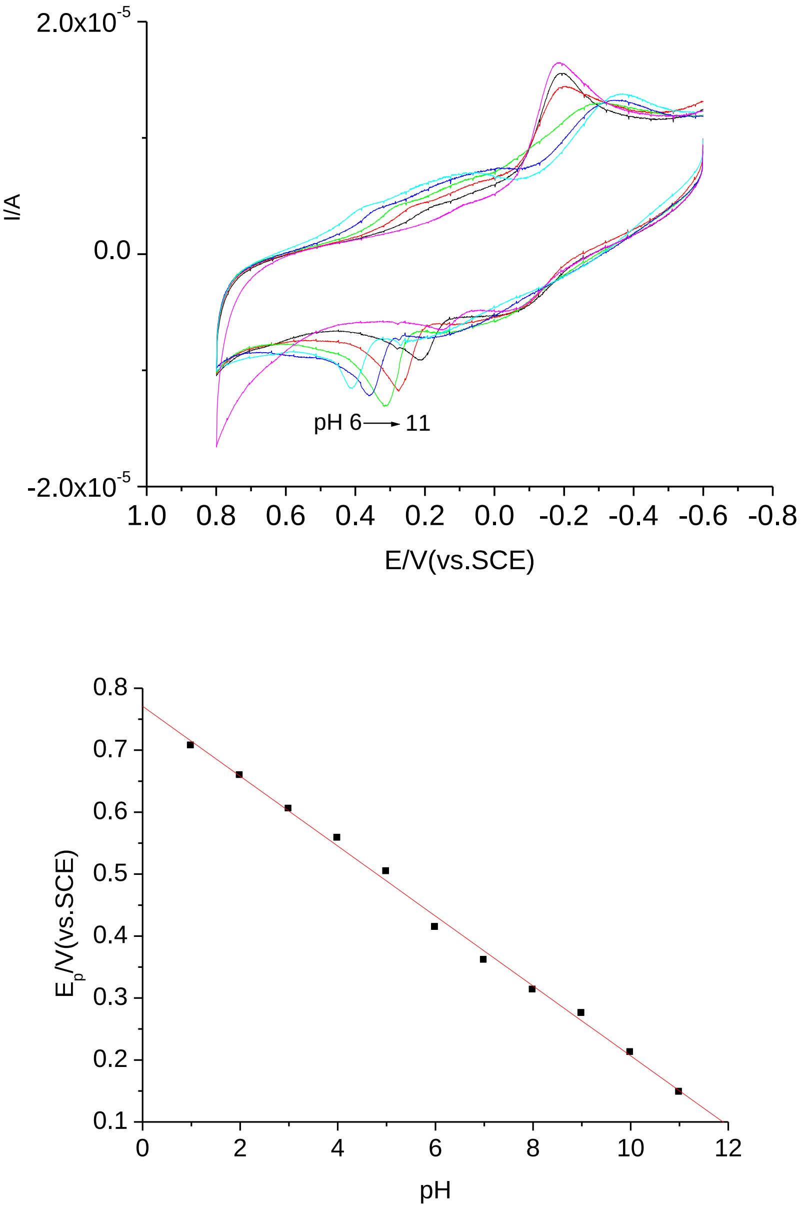


Figure 4. Influence of pH on the electrochemical behavior of norepinephrine tartrate at OGN/GCE; Scan rate: 100.0 mV. s^{-1}. Supporting electrolyte: 0.1 M PBS.

The influence of pH on the electrochemical behavior of norepinephrine tartrate at OGN/GCE in PBS was investigated at different pH values in the range of 1.0 to 11.0. Fig. 4 shows the CVs of 6.0×10^{-5} M norepinephrine tartrate on the surface of the modified electrode over the discussed pH range at scan rate of 100 mV.s^{-1}. It was found that the oxidation peak potential shifted negatively with pH increasing and a good linear relationship was observed between the Ep and pH values in the range of 1.0 to 11.0, a equation is obtained as $E_p(V)=-0.05641$ pH+0.77085 with the correlation coefficients (R) of 0.9982.

A value of about -56.41 mV per pH unit indicates that equal numbers of electrons and protons are involved in the electro-reduction of norepinephrine tartrate on the surface of the modified electrode [12].

3.5. Effect of potential scan rate on peak current

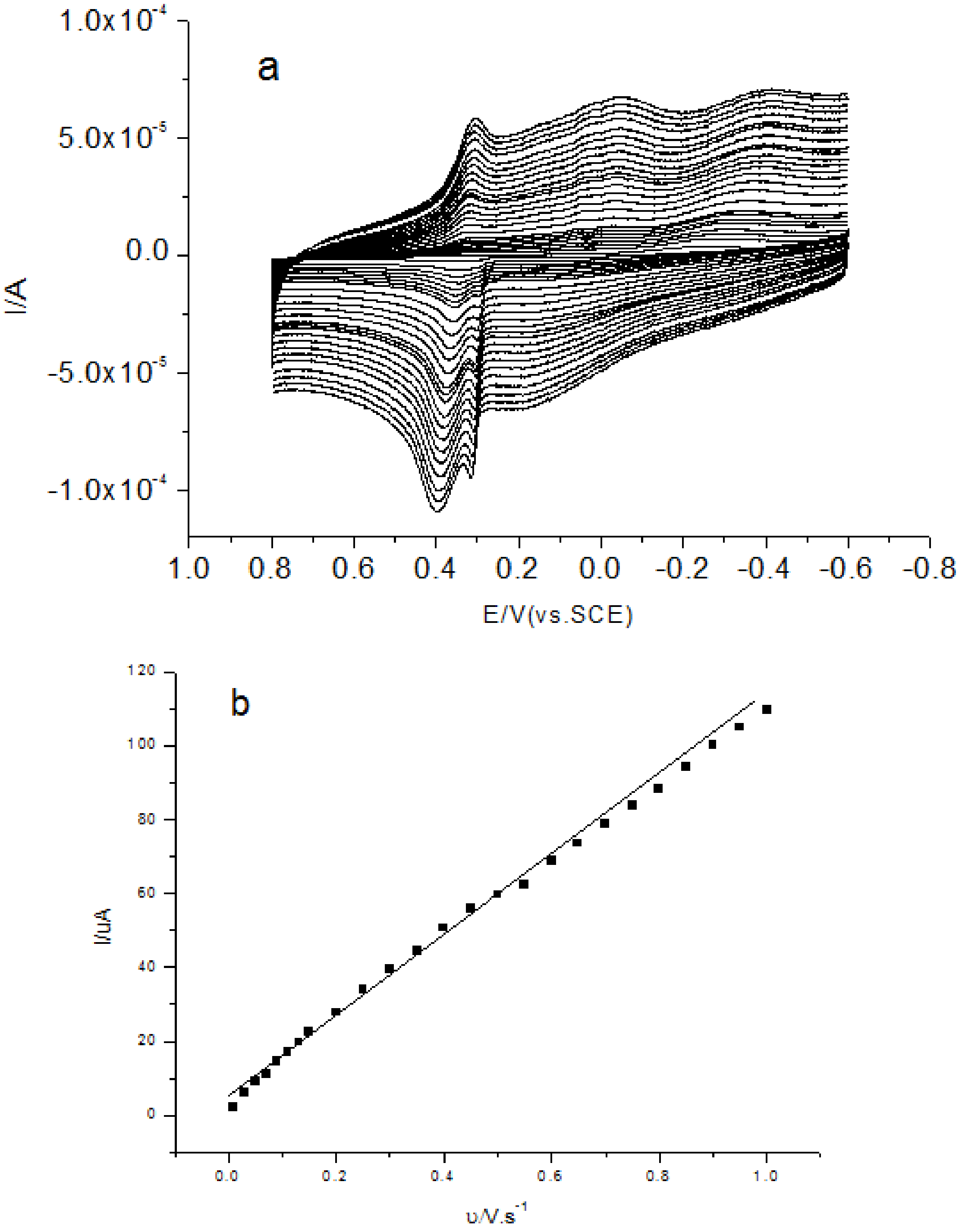
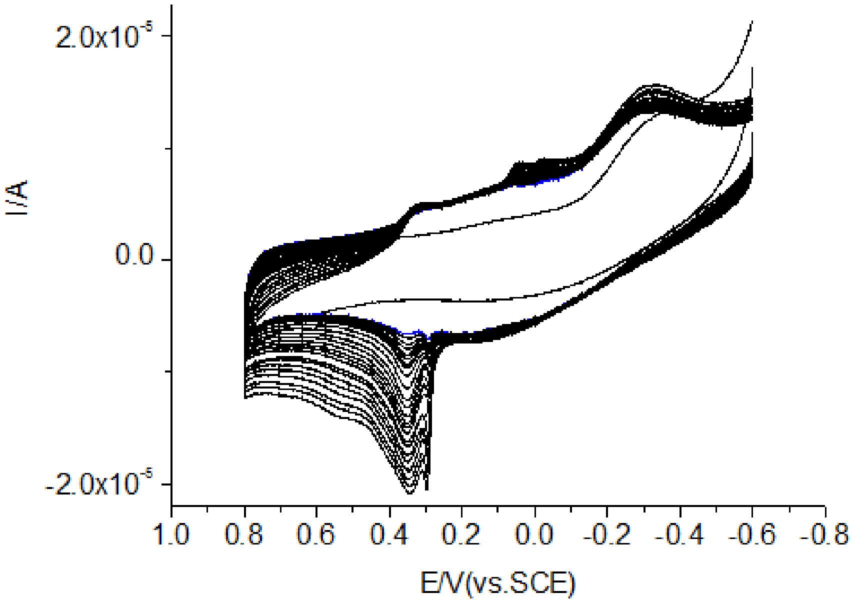


Figure 5. Effect of potential scan rate on peak current; Supporting electrolyte: 0.1 M PBS of pH 7.3.

The information involving electrochemical mechanism usually can be obtained from the investigation of CVs in the different potential sweep rates. Therefore, the CV investigations for 6.0×10^{-5} M norepinephrine tartrate were performed on the surface of the OGN/GCE in PBS of pH 7.3 at different potential sweep rates. Fig. 5a illustrates the influence of scan rate on the CVs of 6.0×10^{-5} M norepinephrine tartrate in the range of 10 to 1000 mV.s^{-1}. A slope of 105.35852 was revealed for the linear relation between the currents of the oxidation peak (I) at 0.352V and the ν (Fig.5b) indicating a mixed adsorption-diffusion controlled process on the surface of the modified electrode [17]. The regression equation for this relationship is obtained as I(uA)= 105.35852 ν（V.s^{-1}） +5.42575 with the R values of 0.9990.

3.6. Linearity range

The relationship between the oxidation current and the concentration was examined by CVs of norepinephrine tartrate at OGN/GCE in 0.1M PBS, and the results were shown in Fig.6. Under the previous conditions, the oxidation peak currents were proportional to norepinephrine tartrate concentrations over three intervals in the range of 6.0×10^{-6} to 1.5×10^{-4} M, 2.0×10^{-4} to 6.5×10^{-4} M and 7.6×10^{-4} to 1.5×10^{-3} M in 0.1 M PBS of pH 7.3. Three linear regression equations were obtained as I(μA)= 24.751 c（mM） +6.843 (R=0.9915), I(μA)= 10607c（mM） + 9.576(R= 0.9920), and I(μA)= 5.561 c（mM） + 12.03161(R= 0.9990), respectively. The detection limit at the sensor was evaluated by using the relation 3s/b, where s is the standard deviation of blank solution (PBS of pH 7.3) and b is the slope of the calibration curve and was found to be 2.1×10^{-8} M. The sensitivity of norepinephrine tartrate determination was calculated as 24.751 μA mM^{-1}. A comparison of electrochemical response of the sensor with previously reported electrochemical sensors for the determination of norepinephrine tartrate is shown in Table 1.



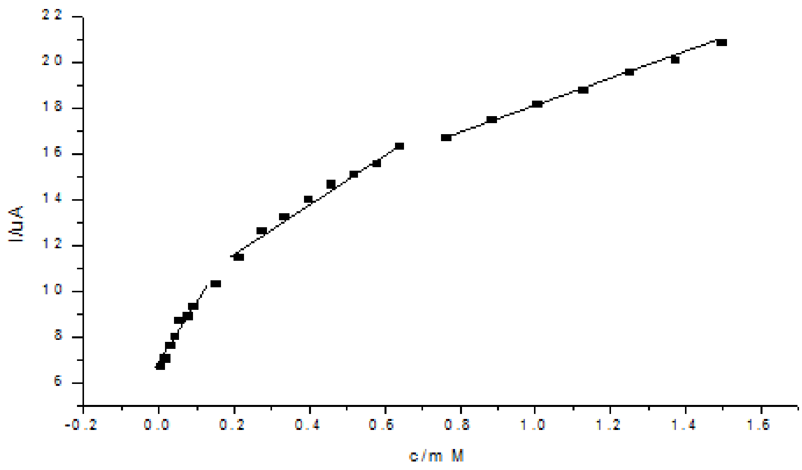


Figure 6. Linearity range of norepinephrine tartrate; Scan rate: 100mV.s^{-1}; Supporting electrolyte: 0.1 M PBS of pH 7.3.

Table 1. Comparison of electrochemical response of the sensor with previously reported electrochemical sensors for the determination of norepinephrine

No.	Electrochemical sensor	Linear range of concentration	Detection limit	Ref.
1	Imprinted sensor	5.0×10^{-8} to 10.0×10^{-6}M	4.9×10^{-10}M	[18]
2	MnO_2/CRGO/ GCE	2.0×10^{-7} to 8.0×10^{-4}M	2.0×10^{-9}M	[19]
3	TiO_2 / CPE	5.0×10^{-6} to 1.0×10^{-3} M	1.0×10^{-7} M	[20]
4	GR–DE–IL/CPE	0.015 to 1000 μM	5.0 ± 1 nM	[21]
5	OGN/GCE	6.0×10^{-6} to 1.5×10^{-4} M	2.1×10^{-8} M	This work

3.7. Selectivity

To examine the selectivity of the sensor towards norepinephrine tartrate, influence of some inorganic ions （K^+,Na^+,Na^+,Ca^{2+},Mg^{2+},Zn^{2+},Cl^-,SO_4^{2-},NO_3^-,Ac^-） and potential interfering substances such as uric acid, ascorbic acid and serotonin was evaluated. For this purpose CVs of a solution having a mixture of norepinephrine tartrate and10–100 folds amount of aforementioned interfering substances was recorded at pH 7.3. The experimental results show that no significant changes in peak current response of norepinephrine tartrate were observed for these interfering substances up to100 fold amounts. These results are consistent with the previous reports [22].

3.8. Repeatability of the modified electrode

The repeatability of the OGN/GCE was investigated by repetitive recording at a fixed norepinephrine tartrate concentration of 6.0×10^{-5} M. The relative standard deviation (RSD) for the peak currents in CVs based on 6 replicates was 2.5%, indicating excellent repeatability of the response of the modified electrode. Also, on using the OGN/GCE daily and storing under ambient conditions over a period of 2 weeks, the electrode retained 96.3% of its initial peak current response for a norepinephrine tartrate concentration of 6.0×10^{-5} M, which shows long-term stability of the film modifier on the surface of GCE. The results indicate that the modified electrode has an excellent repeatability and reproducibility.

3.9. Application

To assess the applicability of the proposed method, the OGN/GCE was used for determination of the content of norepinephrine tartrate injection by applying CV method in the linear range of 6.0×10^{-6} to 1.5×10^{-4} M. 2.00 ml of 2000.0 mg/L norepinephrine tartrate injection was diluted to 100.00 ml with 0.1M phosphate buffer solution of pH 7.3, the content of diluted norepinephrine tartrate using CV method were found to be 40.5mg/L (expected 40.0mg/L). The recoveries were in the range from 96.0 to 104.4% with RSD of 1.2～3.0% (n=6) in the range of 0.0～50.0 mg.L^{-1}.

4. CONCLUSIONS

In present work, the OGN materials were prepared. It was demonstrated that modification of GCE with the OGN is a simple and effective method for obtaining highly sensitive electrodes for determination of norepinephrine tartrate. The procedure enables preparation of highly stable and reproducible uniform modifier films, which leads to a considerable enhancement in repeatability and reproducibility in the voltammetric measurements. High sensitivity and improved detection limit of the OGN/GCE are promising for the determination of amounts of norepinephrine tartrate injection.

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