Preparation and Characterization of PSS/Pt/GR/GCE Graphene Composite Modified Electrode

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Abstract

The Poly (Sodium Styrene sulfonate) / nano Pt / graphene (PSS/Pt/GR) composite modified electrode material was prepared and characterized by transmission electron microscopy (TEM), infrared spectroscopy and alternating current impedance. The electrochemical behavior of tyrosine was determined on PSS/Pt/GR/GCE composite modified electrode. The results show that the PSS/Pt/GR composite modified electrode material is synthesized well. This electrode can be used to determine tyrosine with high sensitivity and accuracy, which could have promising applicability for the determination of other substances.

Keywords: Graphene composite modified electrode, Characterization, Tyrosine.

1. Introduction

Two-dimensional graphene nanomaterials are widely used in industry since Andre Geim and Konstantin Novoselov of the University of Manchester in the United Kingdom obtained monolayer graphene from graphite by mechanical stripping in 2004 [1], which opened the prelude to two-dimensional nanomaterials. As a new carbon material[2], grapheme is an ideal electrode modifier[3, 4]. The excellent mechanical properties, thermodynamic stability, high conductivity and large specific surface area[5] of graphene have inspired researchers to study new graphene-like materials. There are abundant surface active sites on the surface of two-dimensional graphene nanomaterials [6], which is beneficial to the increase of electrochemical signals. Tyrosine is one of the essential amino acids in the human body. It is a key precursor for the synthesis of melanin and neurotransmitters in human body. It is an important indicator for the diagnosis of melanoma [7], neurological diseases [8] and early cancer [9].Currently, a variety of methods have been reported for the determination of tyrosine, such as colorimetry[10], the Acc Q-Tag method [11], fluorescence spectroscopy[12], capillary electrophoresis[13], high performance liquid chromatography-tandem mass spectrometry[14, 15], etc. These methods have the disadvantages of expensive instruments, complicated operation and low sensitivity. The subject adopts an electrochemical method, which has the advantages of low cost, simple operation, good selectivity and high sensitivity[16, 17]. In this paper, the preparation and characterization of PSS/Pt/GR composite modified electrode materials were studied. The electrochemical behavior of tyrosine on the surface of PSS/Pt/GR/GCE composite modified electrode was determined.

2. Materials and Methods

2.1 Instruments and reagents

CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd.); Three-electrode system: the

working electrode was PSS/Pt/GR/GCE composite modified electrode, the reference electrode was saturated calomel electrode, the auxiliary electrode was platinum electrode.

The graphene oxide (GO) and composite modifier PSS/Pt/GR used in this paper were self-made suspension dispersions of 1 mg/mL, tyrosine (Shanghai Yuanye Biotechnology Co., Ltd.), sodium polystyrene sulfonate (PSS), other reagents were analytical pure reagents, and distilled water was secondary deionized water.

2.2 Preparation of PSS/Pt/GR electrode materials

The GO dispersant of 1 mg/mL was poured into a three-necked flask, and the PSS of 200 mg was added to dissolve ultrasonically for 1 h. Then 0.8 mL K_2PtCl_4 solution (1%) was added to stir continuously for 0.5 h. The 20 mg $NaBH_4$ solid was dissolved in 10 mL distilled water and added with disposable straw. Heat up to 50 ℃, continued stirring reaction 24 h. The product was centrifuged three times at 12000 r/min for 20 min each time. The black precipitate was rinsed into a weighing bottle with distilled water and dried in an oven at 60 ℃ for 12 h. The resulting solid was a PSS/Pt/GR nanocomposite. Using the above method, the other conditions were not changed, and the K_2PtCl_4 solution was not added as a control, and the obtained composite was PSS/GR.

2.3 Preparation of PSS/Pt/GR/GCE composite modified electrode

The bare electrode was rotated and polished with 80 nm and 50 nm alumina polishing powder on the wet deer skin in turn. After each polishing of the glassy carbon bare electrode, the surface of the electrode was washed with distilled water, and then ultrasonically washed with 1：1 nitric acid solution（HNO_3：H_2O=1：1）, absolute ethanol and double distilled water for 2 min, and dried under natural conditions. The 6 μL PSS/Pt/GR dispersions were removed by a pipette gun and dripped evenly onto the surface of the treated glassy carbon electrode. The surface of the electrode was dried under an infrared lamp. The composite modified electrode with a strong, uniform and stable PSS/Pt/GR dispersions was obtained. The PSS/Pt/GR/GCE composite modified electrode can be used again in citric acid-sodium citrate buffer solution with pH=3.60.

3. Results and discussion

3.1 Transmission electron microscopy characterization

The morphology of synthesized graphene composite modified electrode materials was characterized by TEM. The TEM images of samples are shown in Fig.1. It can be seen from Fig. 1(a) that there are a large number of wrinkles on the surface of GO. It is because of the existence of wrinkles that GO has a relatively large specific surface area and special electrical and chemical properties; as shown in Fig. 1(b), there are a large number of nanometers. The platinum metal particles are distributed on the surface of the graphene layer. The results show that the PSS/Pt/GR composite modified electrode material has been successfully synthesized.

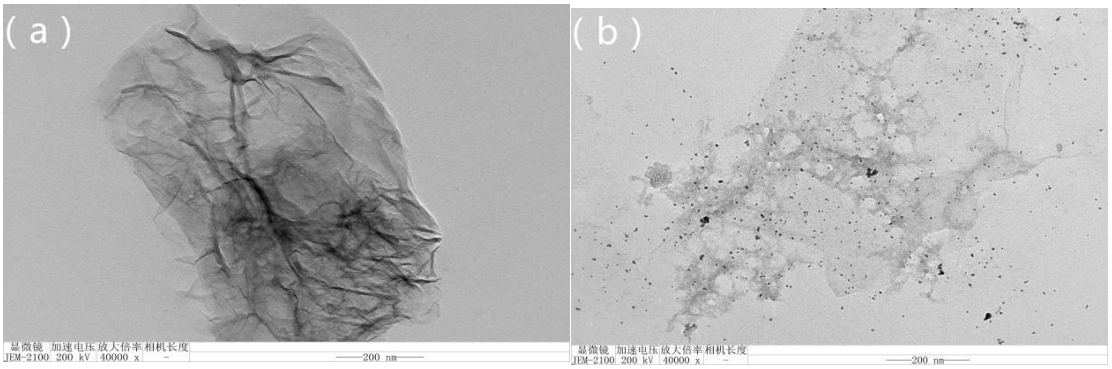

Fig.1.TEM images of GO (a) and PSS/Pt/GR (b).

3.2 Infrared spectroscopy characterization

It can be seen from the infrared spectrum Fig.2 that the curve a GO has an obvious absorption peak at 1720 cm^{-1}, which belongs to C=O stretching vibration, indicating that there are a large number of oxygen-containing functional groups on the surface of GO. The other three characteristic absorption peaks (1365 cm^{-1}, 1250 cm^{-1}, 1060 cm^{-1}) correspond to the stretching vibration peaks of C-OH, C-O-C and C-O respectively. The 1007 cm^{-1} and 830 cm^{-1} of the curve c are the stretching vibration peaks of the phenyl group and it can be seen that almost all of the oxygen-containing functional groups disappear, indicating that the PSS/GR composite modification material was synthesized.

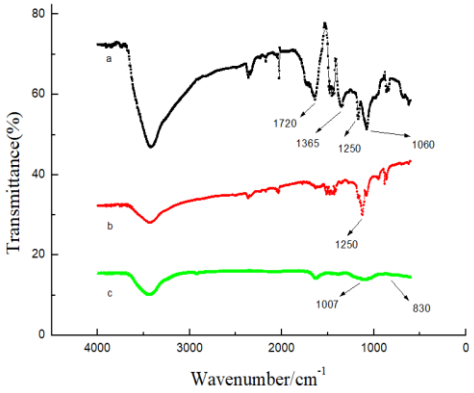

Fig.2. Infrared Spectra of GO, GR, PSS-GR

a: GO; b: GR; c: PSS-GR.

3.3 Electrochemical impedance analysis

It can be seen from Fig. 3 that the impedance of the PSS/Pt/GR/GCE composite modified electrode is 57.11 Ω, which is about 1/4.5 of the impedance of the bare electrode; the impedance of the modified PSS/GR/GCE electrode is 146 Ω, which is about bare. The electrode impedance value is 1/1.7. It can be seen that the PSS/Pt/GR/GCE composite modified electrode has a large degree of impedance reduction and good electrical conductivity.

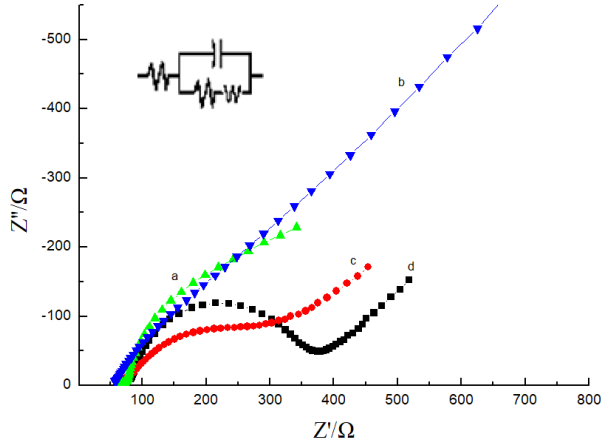

Fig.3. AC impedance curves of several electrodes

a: PSS/GR/GCE R=146 Ω; b: PSS/GR/Pt/GCE R=57.11 Ω; c: PSS/Pt/GCE R=140.7 Ω; d: GCE R=254.2 Ω.

3.4 Electrode potential measurement

The PSS/Pt/GR/GCE composite modified electrode is the working electrode, the saturated calomel electrode is the reference electrode, the platinum wire electrode is the auxiliary electrode, and the electrolytic cell is 10 mL. The three electrodes were placed in a 10 mL electrolytic cell for experiments, and all experiments were carried out at 25 ℃. The potential-current curves were recorded by cyclic voltammetry and linear sweep voltammetry to determine the tyrosine oxidation peak potential and peak current.

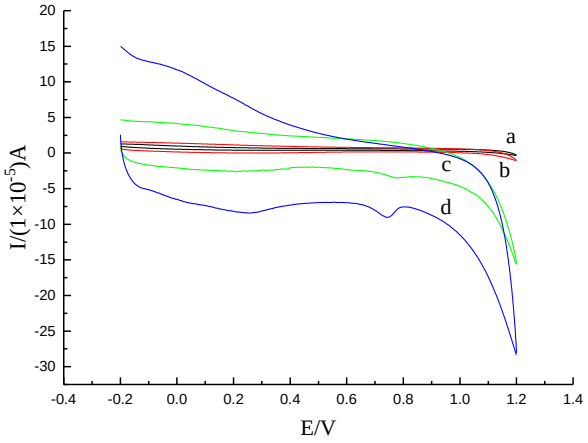

Fig.4. Cyclic voltammograms of tyrosine measured by several electrodes

a: GCE + blank solution; b: GCE + tyrosine; c: GR/GCE + tyrosine; d: PSS/Pt/GR/GCE+ tyrosine.

It can be seen from Fig. 4 that the peak current of tyrosine measured by PSS/Pt/GR/GCE composite modified electrode is the largest, and the peak shape is better, indicating that the composite modified electrode is closely related to the electron transfer rate of tyrosine on the electrode surface, and is more conducive to the electron

transfer.

4. Conclusions

PSS/Pt/GR composite modified electrode material was prepared on the basis of graphene oxide and characterized. PSS/PT/GR/GCE composite modified electrode was prepared and tyrosine was determined, showing better accuracy and selectivity. The satisfactory results indicated that the PSS/Pt/GR/GCE electrode would have promising application in determinating other substances.

Conflicts of Interest

The author declares no conflict of interests regarding the publication of this paper.

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