

Short Communication

Polyaniline Nanofiber Modified Platinum Electrode Used to Determination of Dopamine by Square Wave Voltammetry Technique

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A polyaniline nanofibers modified platinum electrode (PANI-NF/Pt) is fabricated for detection of Dopamine (DA) by square wave voltammetry technique. The performance of the prepared PANI-NF/Pt electrode toward to DA was investigated by square wave voltammetry (SWV) and cyclic voltammetry (CV) techniques. Experimental results demonstrate that the oxidation of DA at PANI-NF/Pt electrode requires lower potential with higher current response than that at bare Pt electrode. Under optimal experimental conditions, PANI-NF/Pt electrode exhibits a low detection limit of 33.3 μM DA (signal-to-noise ratio, S/N=3) and a linear range from 62.5 μM to 603.0 μM . DA can be determined with high selectivity and sensitivity at the PANI-NF/Pt electrode. This PANI-NF/Pt electrode shows great promise in the detection of DA.

Keywords: Polyaniline, Dopamine, Square wave voltammetry

1. INTRODUCTION

Intrinsically conducting polymer (ICP) has a great promising application in modify electrode surface due to their electrochemical activity, mechanical flexibility, tunable conductivity and easy preparation. Among ICPs, polyaniline (PANI) has received particular attention because of its unique protonic acid doping/dedoping process, reversible redox reactions, electrocatalytic activity and environmental stability [1]. It has been reported that PANI can be used in many fields, including sensors [2], gas-separation membranes [3], supercapacitors [4, 5] and anticorrosion coatings [6]. In particular, PANI nanomaterials usually exhibit unique electronic and chemical properties from their

bulk counterparts. The corresponding current of an electrochemical sensor towards electroactive substance is usually proportional to the surface area of electrode, the concentration of electroactive substance, amount of active sites and the concentration effect of the electrode. PANI nanofibers usually have high surface area and active sites. The amine and imine groups along the molecular chains can form hydrogen bond with dopamine which can concentrate dopamine at the electrode surface. So, modify electrode with PANI nanofibers can improve the current response of the sensors. [7-9].

The square wave voltammetry (SWV), a technique applied a square wave with a certain frequency and amplitude on the cyclic voltametric curves, has the advantage over the ordinary scanning voltammetric technique (like CV) in higher signal/noise ratio and more significant discrimination of signals come from the different electroactive substances. The SWV, a peak shaped response to electroactive materials and obvious peak separation, makes it suitable to determine electroactive substances under the condition of interference materials co-exist. [10].

Dopamine (DA), an important neurotransmitter, has an important role in regulation human and/or animal behaviors. Its levels in brain, blood and cells have close relationship with many kinds of diseases, such as Parkinson's disease, Schizophrenia[11]. Therefore, the accurate determination of DA is important in clinical. Until now, techniques such as spectroscopic, mass spectroscopic, and electrochemical methods have been used to determine DA, [12-15]. Because of its relatively sensitive, accurate, quick response, cost-effective and convenience, electrochemical methods have been extensively investigated in recent years. But, when DA is oxidized at electrodes, the high oxidation potential and the adsorption of the oxidized products will contaminate and inactivate the bare electrode surface, which will make the analytical method with poor sensitivity and selectivity. In order to improve the determination sensitivity and selectivity, materials such as carbon nanomaterials, metallic oxides, metallic nano-particles, ionic liquids, conductive polymers and their composites have been used to modify the bare electrodes.[16-24] Nevertheless, these approaches still suffer one or more disadvantages, for instance, complex electrode fabrication process, poor stability, and bad adhesion of modifier substances to the basic electrode. So, assemble high sensitivity, good selectivity and high stability electrochemical sensor used to determine DA is a still a challenge task.

In this work, a PANI nanofibers modified platinum plate electrode (PANI-NF/Pt) was prepared for the determination of Dopamine (DA). Square wave voltammetry (SWV) and cyclic voltammetry (CV) techniques were used to character the performance of the PANI-NF/Pt electrode. The experimental results showed that the potential required for oxidizing DA at PANI-NF/Pt electrode was lower than that at bare Pt electrode, and the oxidation peak current of DA at PANI-NF/Pt electrode was larger than at bare Pt electrode. Under the optimized experimental conditions, DA was determined at PANI-NF/Pt electrode, and the results show that the method has low detection limit, fast response, cost effective. A linear dynamic range is from 62.5 μM to 603.0 μM for DA and the detection limit was 33.3 μM .

2. EXPERIMENTAL

2.1. Materials

Aniline (Tianjin Guangfu Chemical Reagent Co.) was distilled and stored at 5°C prior to use. Dopamine (DA, 99.7%, Aladdin), Ascorbic acid (AA, 99.7%, Aladdin), Potassium iodate (KIO₃, Tianjin Jiangtian Chemical Reagent Co.) and hydrochloride (HCl, 37 wt %, Tianjin Jiangtian Chemical Reagent Co.) were all analytical grade and used without further purification.

2.2. Synthesis of Polyaniline Nanofibers (PANI-NF)

PANI-NF was synthesized by chemical oxidative polymerization. Typically, solution A was prepared by dissolving 0.10 M aniline in 1.00 M HCl, and solution B was prepared by dissolving 0.50M KIO₃ in 1.00 M HCl. Then these two solutions were mixed with a 3:2 volume ratio and shaken to ensure sufficient mixing before polymerization begins, and the mixture was allowed to stand still at room temperature for 5 hours. The product was filtered with membrane (pore diameter 0.22µm) and washed with double distilled water until the filtrate became filter liquor was colorless to collect PANI-NF product.

2.3. Preparation of the PANI-NF/Pt Electrode

Before used, the platinum plate electrode was cleaned under ultrasonic condition for 10 min and then washed with ethanol and double distilled water successively. The prepared PANI-NF was dispersed in distilled water ultrasonically for 20 min with PANI-NF content being 1.00 wt %. Then a certain amount of PANI-NF solution was spread on the pretreated Pt electrode surface and dried in vacuum at 40°C for 24h. The weight of the PANI-NF on the Pt electrode was controlled by adjusting the amount casted solution.

2.4. Characterization of the PANI-NF

The morphology of the prepared PANI-NF was characterized Scanning Electron Microscope (SEM) by Nanosem 430. Square wave voltammetry (SWV) techniques were used to characterize the performance of the PANI-NF/Pt electrode for DA. All of the measurements were carried out on an electrochemical station (VersaSTAT, USA) controlled by a computer. The SWV tests were carried out using a conventional three-electrode system using the PANI-NF/Pt electrode as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode.

3. RESULTS AND DISCUSSION

3.1. Characterizations of PANI-NF

Fig. 1 shows the SEM image of the prepared PANI, in which the PANI exhibits uniform nanofiber morphology with the diameter similar to 100nm. The morphology of PANI should be beneficial to improve the specific surface area of electrodes. The high specific surface area of electrodes will have more available active sites for DA. Therefore, the prepared PANI-NF should be an effective sensing material with high current response and analytical sensitivity.

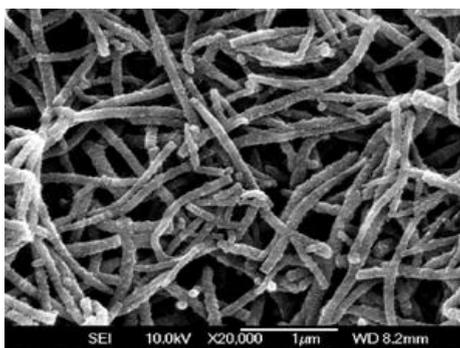


Figure 1. The SEM image of the prepared PANI-NF

3.2. Effect of PANI-NF Film on oxidation DA

Fig. 2 presents the square wave voltammetry (SWV) curves of DA at bare Pt and PANI-NF/Pt electrodes in 1.00 M HCl with the concentration of 0.20 mM. As shown in Fig. 2A and 2B the DA oxidation peak has distinct negative shift and the oxidation current increase. The oxidation peak potential of DA moved from 698 mV *vs* SCE at the bare Pt electrode to 566 mV *vs* SCE at the PANI nanofiber modified electrode. The corresponding current was increased about 6.7 times and from 1.22 μ A at the bare Pt electrode to 8.2 μ A at the PANI nanofiber modified electrode. This phenomenon is attributed to the electrocatalytic effect of PANI-NF[25]. The electrocatalytic effect is come from the strong interaction between dopamine and PANI through hydrogen bond and the facilitate transportation of electrons between dopamine and PANI. The high specific surface area of PANI-NF/Pt electrode is also helpful to increase the oxidation current of DA. The experimental results suggest that the PANI-NF/Pt electrode can be used to detect DA with a low potential and a high response current.

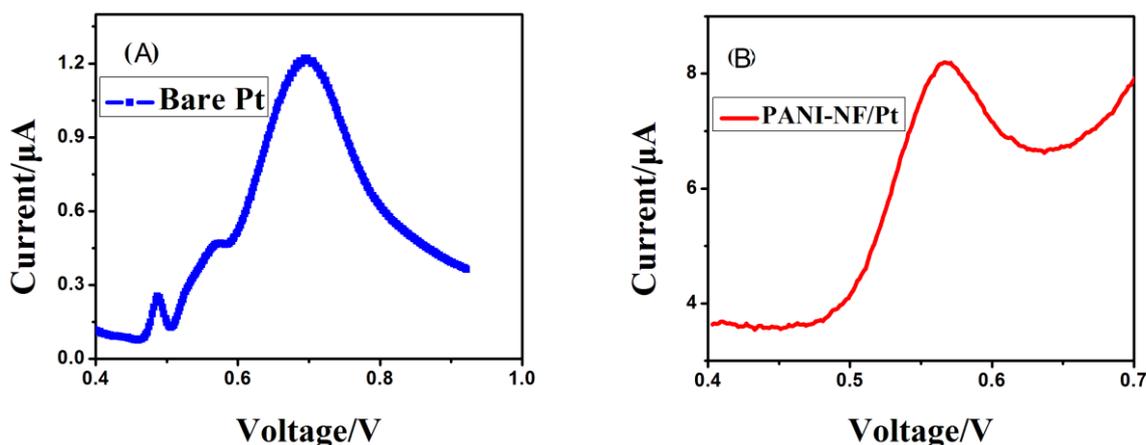


Figure 2. SWV curves of DA at bare Pt electrode (A) and at PANI-NF/Pt electrode.

3.3. Determination of DA under the condition of AA co-exist.

Fig. 3 presents the square wave voltammetry (SWV) curves of DA and ascorbic acid (AA) at bare Pt (Fig. 3 A) and at PANI-NF/Pt (Fig. 3 B) electrodes in 1.00 M HCl solution with the concentration of DA and AA being 0.20 mM, respectively. At the bare Pt electrode (Fig. 4 A), DA demonstrates an oxidation peak at 632 mV while AA at 792 mV. Compare with the electro-oxidation curve appeared in figure 2A, the oxidation potential of dopamine was negative shift from 698 mV to 632 mV at the bare Pt electrode, and the oxidation current increase from 1.22 μA to 6.44 μA . This phenomenon is attributed adsorption of one component (a base or acid) will facilitate the adsorption of the other through acid-base reaction (here, DA is a base and AA is an acid). The curve appeared in figure 3A also demonstrate that the oxidation current of DA is much higher than that of AA at Pt bare electrode. This might attribute to the priority adsorption of DA at the Pt electrode. The figure 3A clearly shows that the oxidation peak potential separation between DA and AA is not big enough to measure DA without interference from AA at the bare Pt electrode. While the oxidation peaks of DA and AA at PANI-NF/Pt electrode (shown in Fig. 3 B) were at about 311 mV and 568 mV, respectively, which have obvious negative shift compare with that at bare Pt electrode. The figure 3B also clearly indicates that the oxidation current of DA is much lower than that of AA, which is against the results appeared in figure 3A. This phenomenon is ascribed to the doping effect of AA to PANI. Under this condition, AA competition with DA for active site at PANI molecular chains, and obviously the interaction between dopant (AA) and PANI is much higher than that of hydrogen bond (DA). The difference between DA and AA oxidation peak potentials is above 250 mV, which is big enough to distinguishing DA from AA. The currents observed at the PANI-NF/Pt electrode (shown in Fig. 3B) are much enhanced compare with that at the bare Pt electrode. This is attributed to the catalytic activity of the PANI-NF/Pt electrode toward different electroactive substances.[25] Above experimental results demonstrate that the PANI-NF/Pt electrode can not only catalyze the oxidation process of DA and AA, but also can make peak separation more obviously. The obvious peak potential's separation, coupled with the increased sensitivity, is helpful to determination of DA under the condition of AA co-exist.

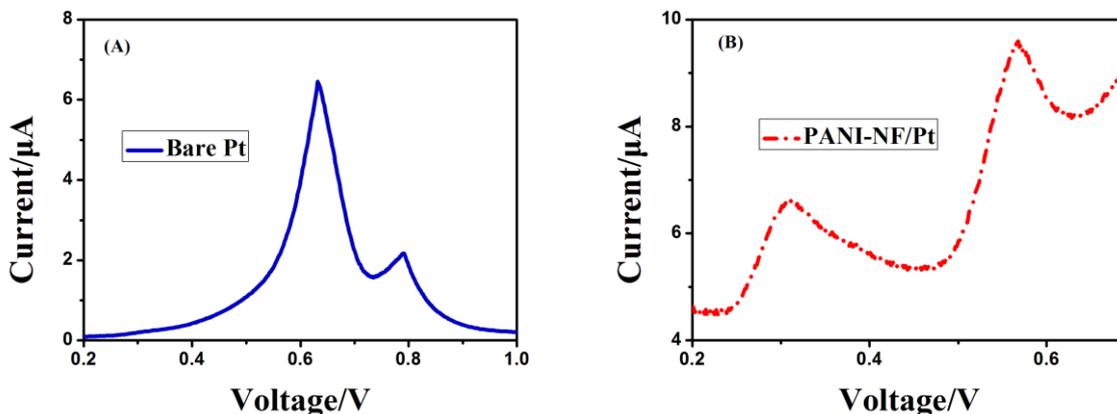


Figure 3. (A) SWV of 0.20 mM AA and 0.20 mM DA at the bare Pt electrode in 1.00 M HCl solution and (B) SWV of 0.20 mM AA and 0.20 mM DA at the PANI-NF/Pt electrode in 1.00 M HCl solution

3.4. Linearity and Detection Limit

Fig. 4A presents the SWV curves of different concentrations of DA oxidized at PANI-NF/Pt electrode in 1.00 M HCl solution, and Fig. 4B presents the peak currents of these SWV curves vs. the concentrations of DA. With the DA concentration ranging from 62.5 μM to 603.0 μM , the oxidizing peak current is linear related to the concentration of DA and the linear regression equation is $I_p (\mu\text{A}) = 0.002 C (\mu\text{M}) + 3.662$ ($R = 0.992$). The detection limit of this PANI-NF/Pt electrode for DA was $33.3 \times 10^{-6} \text{ M}$ ($S/N = 3$).

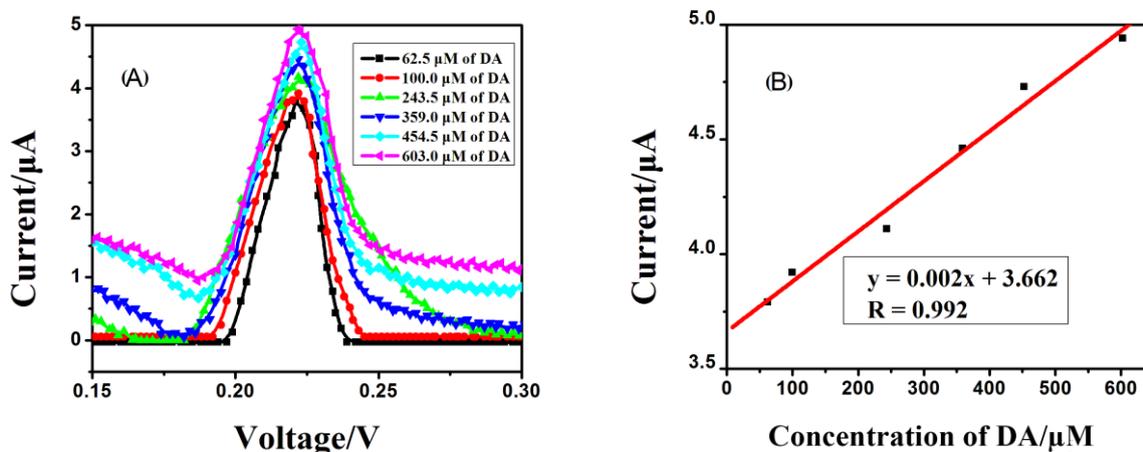


Figure 4. (A) SWV curves of different concentration DA at PANI-NF/Pt electrode in 1.00 M HCl solution; (B) The relationship between oxidizing peak currents and the concentration of DA.

These results suggest that the prepared PANI-NF/Pt electrode has great promising for the detection of DA, which has a relatively wider linear range and lower limit of detection. The

electrochemical behavior of dopamine at modified electrodes may be varied according to electrode materials, electrode modification substances, potential apply techniques and co-exist substances in the electrolyte, just as shown in above part of this paper. This research has the similar dynamic linear range to that reported by Feng who modified electrode with PANI nanotubes [8], but has obvious difference with that reported by Jin who modified electrode with PANI tetragonal starlike polyaniline microstructure [9].

4. CONCLUSIONS

PANI-NF was synthesized by chemical oxidative polymerization method and the PANI-NF/Pt electrode was assembled. The obtained PANI-NF/Pt electrode exhibits good analytical performance for the electrochemical determination of DA. The modified electrode has the detection limit of 33.3 μM , a linear range from 62.5 μM to 603 μM . This PANI-NF/Pt electrode detects quickly and accurately determinations of DA under the condition of AA coexist in a mixture.

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