

Short Communication

Synthesis, Properties and Application of Polyaniline/Titanium Carbide Nanoparticles Modified Electrode

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A novel chemically modified electrode based on polyaniline/titanium carbide nanoparticles (PANI/nano-TiC) was developed by electrochemically co-polymerization of aniline and nano-TiC. The physical and chemical properties of PANI/nano-TiC modified electrode were investigated by cyclic voltammetry (CV), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Experimental results of them indicated that the existence of TiC can improve the conductivity, change the morphology of the modified electrode. PANI/nano-TiC modified electrode shows excellent electrocatalytic ability for the reduction of nitrite.

Keywords: Polyaniline; titanium carbide nanoparticles; electrocatalysis; nitrite; chemically modified electrode

1. INTRODUCTION

Titanium carbide nanoparticles (nano-TiC) is a typical transition metal carbide, which shows not only small size, distribution uniformity, specific surface area and high surface activity, but also high thermostability, antioxidation, strength and hardness, nice thermal conductivity, toughness, electrical conductivity, and so on[1]. Because of its advantages, TiC has been widely applied in biosensors[2], methanol electrooxidation[3], supercapacitor[4], direct fuel cells[5] and energy-related applications[6], also many other fields. However, its application in electrochemistry was seldom reported.

On the other hand, with the characteristics of high conductivity, homogeneity of film formation, ease of preparation, and good stability[7], polyaniline (PANI) has become the most attractive conducting polymers[8]. Therefore, the development of new electrochemical sensors for selected analytes could be expected based on the use of polyaniline and related conducting polymers as electrode modifiers. Polyaniline modified electrodes are known to catalyze electrochemical redox processes of selected inorganic and organic species.

Nitrite is commonly used as an additive in some foods[9], as a corrosion inhibitor[10] and is widely ubiquitous within environment, food and physiological systems. The nitrite ions can interact with amines to form carcinogenic nitrosamines[11]. As its potential toxicity, determination of nitrite is then important for environmental reason and public health.

In this work, a PANI/nano-TiC composite modified electrode has been fabricated by electropolymerization of aniline in solution which nano-TiC were dispersed in. The composite material of this work was prepared by coating the nano-TiC in the process of polymerizing the aniline without bonding or modifying layer-by-layer[12]. The existence of nano-TiC can improve the performance of the PANI and change the morphology of the PANI. Cyclic voltammetry was used to investigate the electrochemical behavior of target electrode, as well as its electrocatalytic property for the reduction of nitrite. Effects of scan rate and pH value have been investigated and discussed, the electrocatalytic ability for the reduction of nitrite of the target electrode is better compared with the other work[8].

2. EXPERIMENTAL

2.1. Materials and apparatus

H₂SO₄ was supplied by Sinopharm Chemical Reagent (Shanghai, China). Nano-TiC was purchased from Nanjing Emperor Nano Material Co., Ltd. (Nanjing, China). Aniline was supplied by Tianjin Kemiou Chemical Reagent Co., Ltd.(Tianjin, China). All other reagents were of analytical grade and were used without further purification. Double-distilled water was used throughout.

2.2. Fabrication of PANI/nano-TiC modified glassy carbon electrode

Putting 0.4 mg nano-TiC and 182 μ L into 20 ml 0.5M H₂SO₄, and then maintain ultrasonic agitation for 30 minutes. Before being modified, the GCE was polished with 0.3 and 0.05 μ m aluminum slurry, rinsed thoroughly with redistilled water, then ultrasonically rinsed with alcohol, redistilled water for 1 min each and dried by a hairdryer. After the GCE was cooled and then copolymerized by cycling between -0.2 - 1.0V for 24 segments, a dark green film can be observed at the electrode surface. After rinsing with double-distilled water, the target electrode can be obtained.

2.3. Characterization of the modified electrode

All electrochemical experiments were carried out in a conventional three-electrode cell controlled by electrochemical work station (CHI 660D, Chenhua Instruments, Shanghai, China). With

a platinum flag as the counter-electrode and a Ag/AgCl electrode as the reference electrode, a PANI/nano-TiC modified electrode was used as the working electrode. Before being modified, the glassy carbon disk electrode substrate was polished with 0.3 and 0.05 μm aluminum slurry, rinsed thoroughly with redistilled water, then ultrasonically rinsed with alcohol and redistilled water for 1 min each, and dried. The micrographs of modified electrodes were obtained by scanning electron microscopy (SEM, Hitachi S-4800 microscope, Japan.). The element composition of modified electrodes was investigated by energy dispersive X-ray spectroscopy (EDS, Vantage 4105, NORAN). All measurements were carried out at room temperature.

2.4. Study of electrochemical properties of the modified electrode in H_2SO_4

Electrochemical characterization of the PANI/nano-TiC modified electrode was investigated by cyclic voltammetry. The PANI/nano-TiC modified glassy carbon electrode (PANI/nano-TiC/GC) was placed in voltammetric cell with 10 ml 0.5 M H_2SO_4 solution. The voltammetric experiments were carried out in the potential range from -0.2 to 1.0 V at a scan rate of 100 mVs^{-1} . As compared, the bare GC and polyaniline modified glassy carbon electrode (PANI/GC) electrode were performed under the same conditions. CV detections of nitrite at PANI/nano-TiC/GC electrode were carried in 0.1 M H_2SO_4 solution (pH = 1) in the potential range from -0.2 to 0.6 V.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammograms of the GC, PANI/GC, and PANI/nanoTiC/GC electrodes in 0.5 M H_2SO_4 solution

Various composite materials by combining PANI and other materials including carbon nanotubes[8] and titanium dioxide[13] can improve the physical properties of PANI but not affect the electrochemical properties of PANI. Cyclic voltammograms of the GC, PANI/GC, and PANI/nano-TiC/GC electrodes in 0.5 M H_2SO_4 solution from -0.2 to 1.0 V with the scan rate of 100 mV s^{-1} are presented in Fig. 1. Obviously, there was no redox peak that can be observed at the bare GC electrode in the scan ranges. There appears three pairs of redox peaks at about +0.23, +0.45, +0.78 V which were caused by the PANI at the GC electrode. However, at the PANI/nano-TiC /GC electrode, it can be seen that there are three pairs of redox peaks the same as PANI/GC, and there is no peak of nano-TiC. Voltammetric behavior of the PANI/nano-TiC/GC electrode is in accordance with that of the glassy carbon electrode adsorbed with PANI. Moreover, if the PANI/nano-TiC is polymerized on the surface of electrode, only the redox peaks of PANI appear while the TiC peaks are disappeared, but the existence of nano-TiC can improve the conductivity of the modified electrode compared with the electrode only modified with PANI.

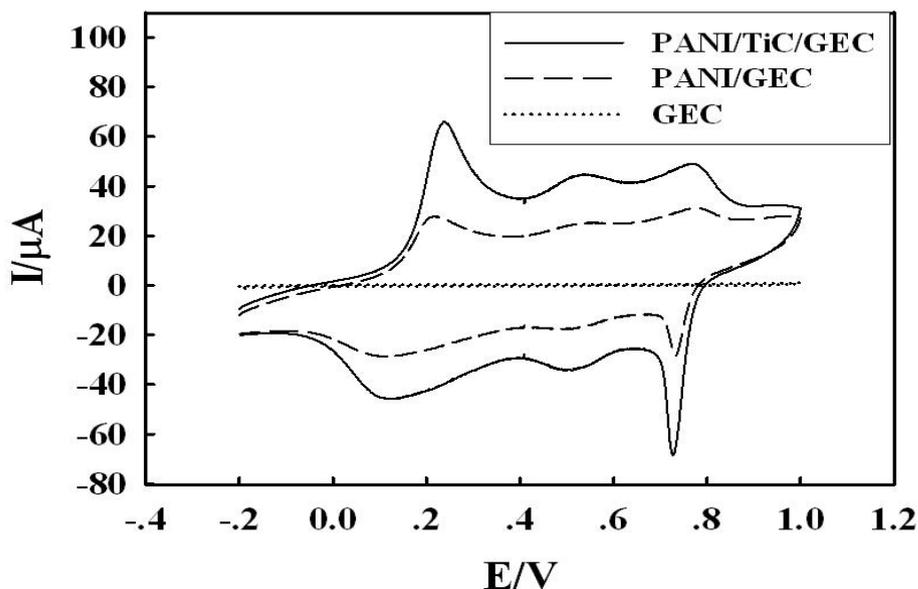


Figure 1. Cyclic voltammograms of the bare GC, PANI/GC and PANI/nano-TiC/GC in 0.5 M H₂SO₄ solutions. Scan rate: 100 mV s⁻¹.

3.2. Morphology of PANI/nano-TiC electrode

In present work, in order to describe the morphology of PANI/nano-TiC nanocomposites, SEM was employed. Figure 2 illustrates the typical SEM photographs of PANI (Fig. 2a) and PANI/nano-TiC (Fig. 2b). It can be observed from Fig. 2a that PANI exhibits at the surface of the electrode. The diameter of PANI is almost 80-100 nm. However, the SEM picture of PANI/nano-TiC shows significant differences. PANI performs multiform morphology, such as schistose[14], porous[15], owing to the difference of preparation method. The material of PANI fabricated in the present paper is porous. SEM picture shows the morphology of the composited material is starchy after the addition of TiC. The reason maybe is that the presence of TiC affects the process of the polymerizing of aniline and moreover lead to the change of morphology. Furthermore, from the EDS result (Fig. 3a), C, O, S and N are the major elements of PANI modified electrode while C, O, S, N and Ti are the major elements of PANI/nano-TiC (Fig.3b) modified electrode. And that C and N come from PANI, S comes from H₂SO₄. Nano-TiC, which is diluted in the solution of sulfuric acid with aniline, moves towards electrode through free diffusion and then is fixed on the surface of glassy carbon electrode during the polymerization process. The existence of Ti element indicates that nano-TiC has been modified on the electrode together with the PANI.

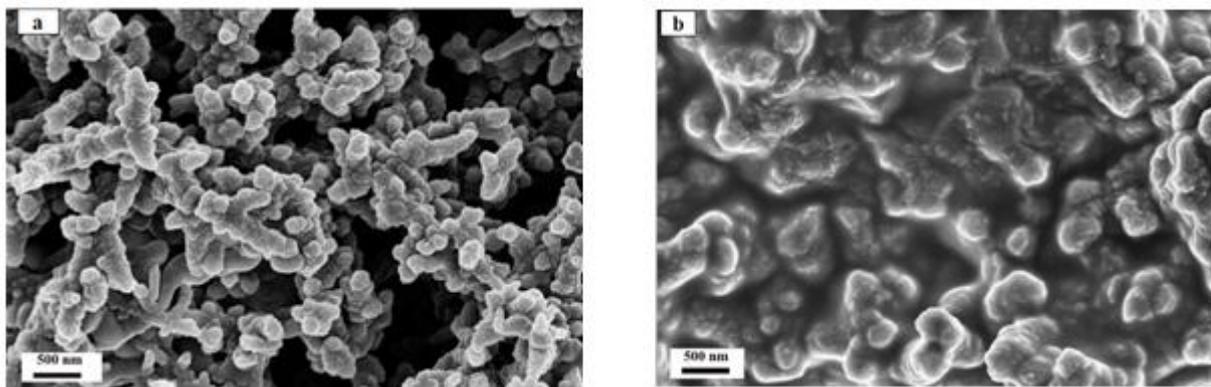


Figure 2. SEM images of PANI (a) and PANI/nano-TiC (b) modified glassy carbon electrode.

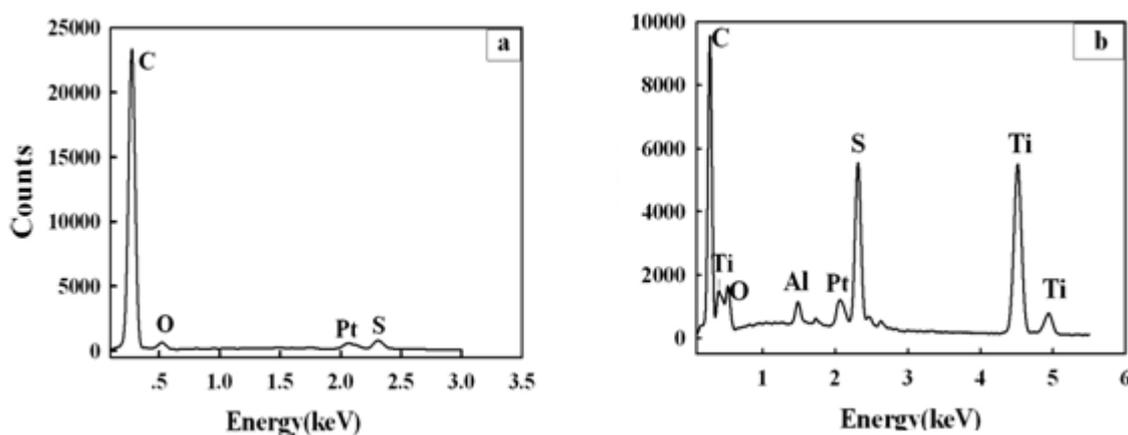


Figure 3. EDS pattern of PANI (a) and PANI/nano-TiC (b) modified electrode.

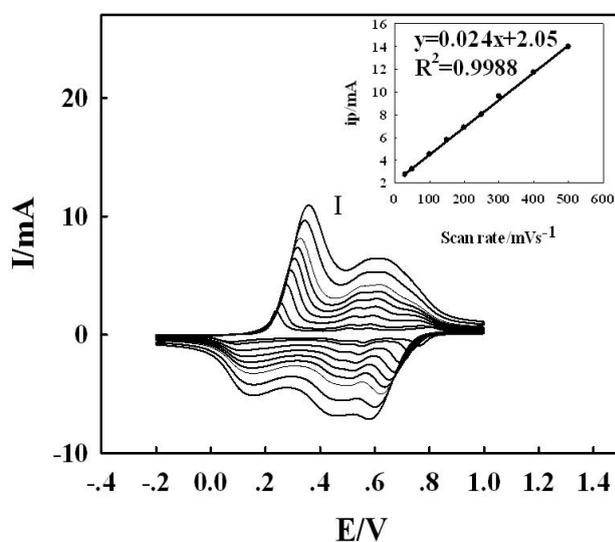


Figure 4. Cyclic voltammetric behavior of the PANI/nano-TiC electrode in 0.5 M H₂SO₄ solution at different scan rates: 50, 100, 150, 200, 250, 300, 400, and 500 mV s⁻¹ (from inside to outside).

3.3. Cyclic voltammetric behavior of the PANI/nano-TiC modified electrode at different scan rates

Fig. 4 shows the voltammetric behavior of the PANI/nano-TiC electrode at different scan rates in 0.5 M H₂SO₄ solution. As can be observed, all the peak potentials do not change with increasing scan rate, and the cathodic peak current is almost as same as the corresponding anodic peak current. The good linearity (up to 500 mV s⁻¹) between peak current and scan rate (the inset plot in Fig. 4) reveals that the electrochemical behavior of PANI/nano-TiC shows a surface confined redox process.

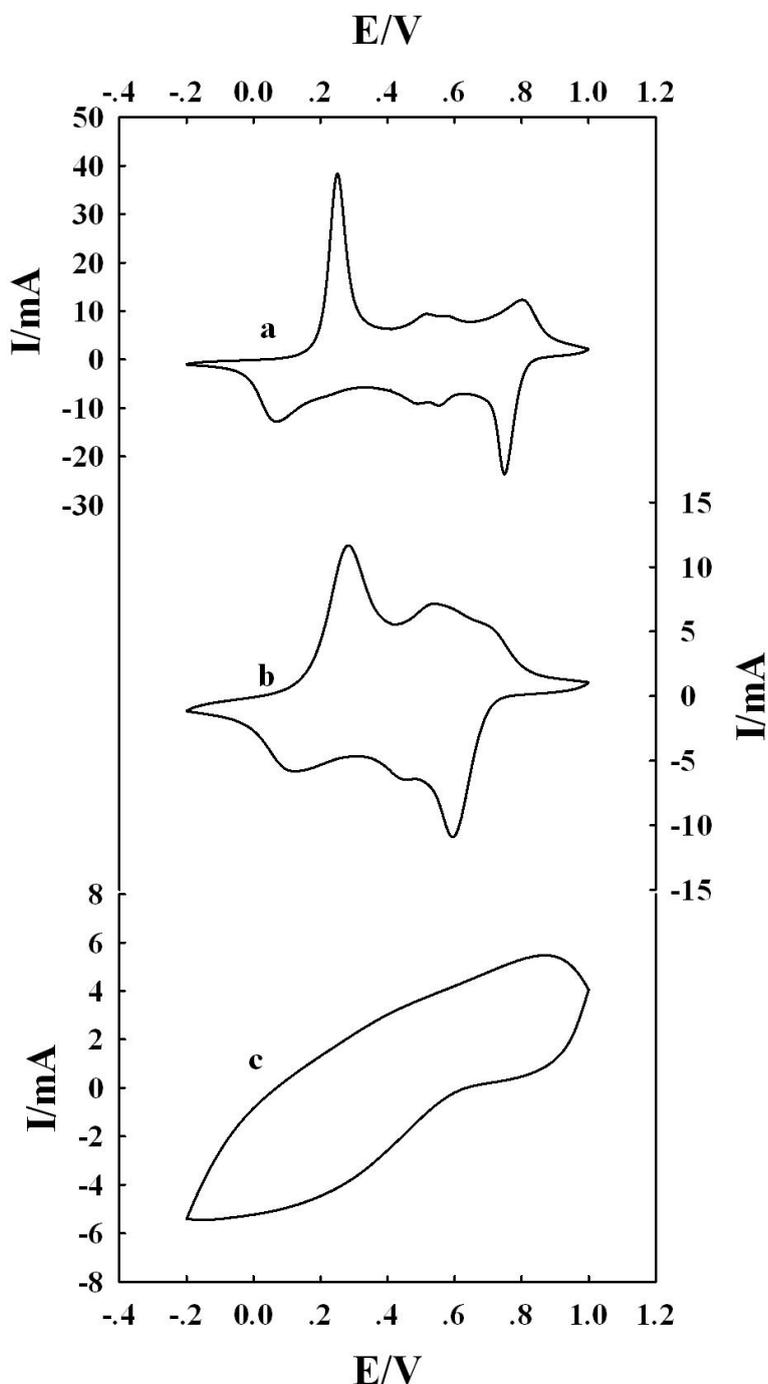


Figure 5. Cyclic voltammograms of PANI/nano-TiC electrode in H₂SO₄ solution with different pH values: (a) 0, (b) 1, and (c) 2. Scan rate: 100 mV s⁻¹.

3.4. Effect of pH value on the electrochemical behavior of PANI/nano-TiC electrode

pH value has a profound influence on the electrochemical behavior of PANI/nano-TiC. Fig.5 presents the cyclic voltammograms of PANI/nano-TiC electrode in H_2SO_4 solution with different pH values. Three pairs of redox peaks (I, II and III) can be observed obviously in the solution with pH 0, 1. With the increase of pH, the redox peaks of PANI come to disappear. The peaks of PANI/nano-TiC are obvious in pH 0 solution, then the peak current begins to decrease in pH 1 solution. However, there is a curve without any peaks in pH 2 solution. This implies that the electrochemical properties of PANI/nano-TiC depend strongly on the pH value of the solution.

3.5. Preliminary application of the PANI/nano-TiC electrode

Nitrite can induce methaemoglobinaemia and react with secondary and tertiary amines forming carcinogenic nitrosamines. The research on the determination of nitrite is still a trend. Here, the electrocatalytic reduction of nitrite in 0.1 M H_2SO_4 solution at PANI/nano-TiC electrode was investigated preliminarily and the corresponding results are shown in Fig.6. It can be observed obviously that the response currents decrease with the addition of the nitrite, which implies PANI/nano-TiC has electrocatalytic ability to the reduction of nitrite. This work studies the sensing function of PANI/nano-TiC against nitrite and compared with the other work[8], the sensitivity result of our work is better.

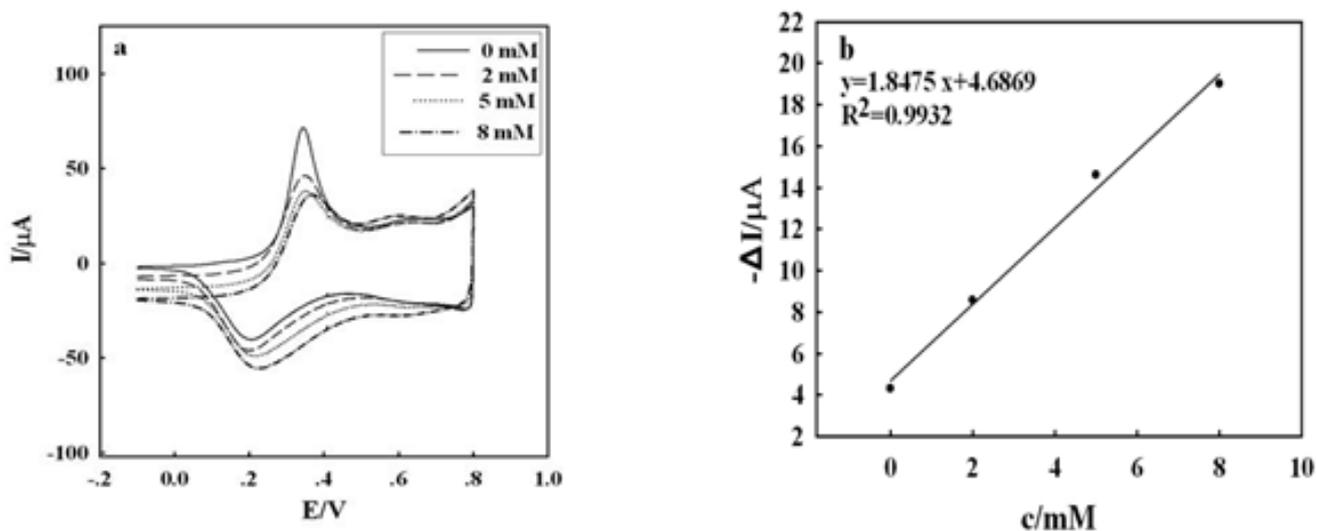


Figure 6. Electrocatalytic reduction of nitrite (a) on the PANI/nano-TiC modified electrode. The concentration of nitrite are 0, 2, 5 and 8 mM (from top to bottom). And Calibration curves for the determination of nitrite (b) by PANI/nano-TiC electrode. Supporting electrolyte: 0.1 M H_2SO_4 solution. Scan rate: 100 mV s^{-1} .

4. CONCLUSIONS

The immobilization of nano-TiC in PANI and the characteristics of the corresponding PANI/nano-TiC electrode have been investigated in this paper by SEM, EDS, electrochemical impedance analysis and cyclic voltammetry. In 0.5 M H₂SO₄, the PANI/nano-TiC electrode shows three reversible redox peaks with the formal potential of +0.23, +0.45, +0.78V respectively. The electrochemistry of the PANI/nano-TiC electrode depends strongly on the pH value of the solutions. With the increase of the pH value, the electrochemical property of PANI/nano-TiC electrode becomes weak. Furthermore, the PANI/nano-TiC electrode shows electrocatalytic ability for the reduction of nitrite.

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