STUDY ON CHARACTERIZATION OF THE PANi-SnO_2 COMPOSITE SYNTHESIZED BY ELECTROCHEMICAL METHOD

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Abstract: *PANi-SnO_2 composites were prepared successfully by electrochemical method. The morphology and crystal structure of samples were determined by scanning electron microscope (SEM) measurement and X-ray diffraction (XRD). The electrochemical characterization of material was determined by cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS). The investigated results indicated that PANi-SnO_2 composite has outstanding electrochemical properties in comparison with SnO_2.*

Keywords: PANi -SnO_2 composites; SnO_2 nanoparticles; Electrochemical properties.

1. INTRODUCTION

To meet the increasing energy demand, supercapacitors in energy storage devices are researched very necessarily. The new generation of energy storage devices requires high energy density, fast charging rates, and long service life. In research on supercapacitors, combining electrochemical active materials is essential, including the bonding between metal oxides and conductive polymers [1-3]. The properties of composite materials are completely different from those of the component materials due to interfacial interactions between semiconductors and polymers. The properties of these materials can be easily adjusted for the desired application through the variation of the particle size, shape, and distribution of the particles.

Metal oxides have a wide range of charge potentials, however, they have a small surface area and poor electrical conductivity. Among metal oxides, SnO_2 has a large specific capacitance (782 mAh/g), cheap and environmentally friendly [4, 5]. However, SnO_2 is a semiconductor (band gap is 3.6 eV), low conductivity, easy to clump, reduces the working surface area, which limits the application of SnO_2 for supercapacitors [6, 7]. To overcome this limitation, conductive polymers such as polyaniline (PANi) are used in combination with SnO_2 to form composite materials. PANi is a conductive polymer with high capacitance, good conductivity, low cost, easy to synthesize, friendly with the environment but less mechanical [8]. When PANi combines with SnO_2 to form SnO_2-PANi composite, it promises to have good properties for use in supercapacitors [9-11]. There are many methods to synthesize PANi-SnO_2 composite. Zhenyu Luo and et al. synthesized this composite by hydrothermal route using ammonium persulfate oxidant. The results show that the integrated composite is made up of PANi nanoparticles and SnO_2 particles [10]. Venkata S. Reddy Channu and et al., have been synthesized PANi - SnO_2 composite through a simple solution-technique method with chelating agent. The obtained results show that SnO_2-PANi are highly promising anode material for electrochemical applications [9].

In this study, we will focus on the synthesis of PANi-SnO_2 composite material by electrochemical method and study the morphology, crystal structure and the electrochemical properties of this composite material.

2. EXPERIMENTAL

2.1. Synthesis of SnO_2 nanoparticles

SnO_2 nanoparticles were prepared by the chemical method following the steps. The first, 12 g tin dichloride ($SnCl_2$) and 24 g sodium chloride (NaCl) were dissolved in deionized water. Then, the mixed solution was heated at 90 ^oC for 1 hour under continuous stirring. The resulting suspension was filtered and washed with distilled water and ethanol. After that, the resulting solids were calcined at 600 ^oC and kept for 24 hours. The obtained white powder (SnO_2) is to be used to synthesis composite PANi- SnO_2 in the next steps.

2.2. Synthesis of PANi – SnO_2 composite

The PANi – SnO_2 composites were prepared on the stainless steel electrode by the cyclic voltammetry (CV) method in the solution of 0.5 M H_2SO_4, 0.2 M aniline (Ani), and 6 g/ L SnO_2. Electrochemical parameters were set as follows: The potential window from -0.2 V to 1.4 V; The scanning rate of 20 mV/s for 10 cycles. The prepared electrode after the electropolymerization was washed gently with alcohol and acetone to remove the monomers.

2.3. The characterization of materials

The morphology of samples was determined by SEM images carried out on the equipment FE-SEM Hitachi S-4800 (Japan). XRD diffraction pattern used to recognize the crystal structure was measured by D8 ADVANCE of Bruker (Germany) with the 2θ range from 10^o to 70^o.

The electrochemical tests including cyclic voltammetry (CV) and EIS measurement were carried out on the electrochemical system IM6 (Zahner- Electric, Germany). All the experiments used a three-electrode cell including the reference electrode (calomel), working electrode (SnO_2/stainless steel, PANi-SnO_2/stainless steel), and counter electrode (Pt).

3. RESULTS AND DISCUSSION

3.1. The morphologies and structure

The crystal structure

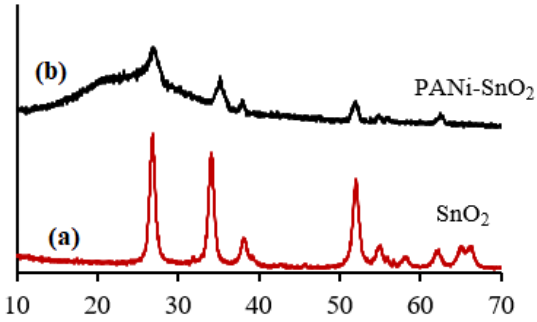


Figure 1. *XRD patterns of the PANi-SnO_2 and SnO_2.*

Figure 1 shows the X-ray spectra of SnO_2 nanoparticles and PANi-SnO_2 composite. The obtained diffraction peaks of SnO_2 powder (line a) are suitable with the standard data JCPDS (No. 41-1445), which evidence the tetragonal structure of SnO_2 [12]. The peaks located at 2 theta values (26 ^{o}, 34 ^{o}, 38 ^{o} and 52 ^{o}) observed on the XRD patterns of PANi- SnO_2 composite (line b) are major peaks of the tetragonal crystallization structure. However, the intensity of the peaks at line b is weaker than those of SnO_2 probably because of the link between PANi and SnO_2 in the sample [13, 14]. Those demonstrated that SnO_2 was successfully prepared by chemical method and SnO_2 existed into the matrix of composite material.

The morphological structure

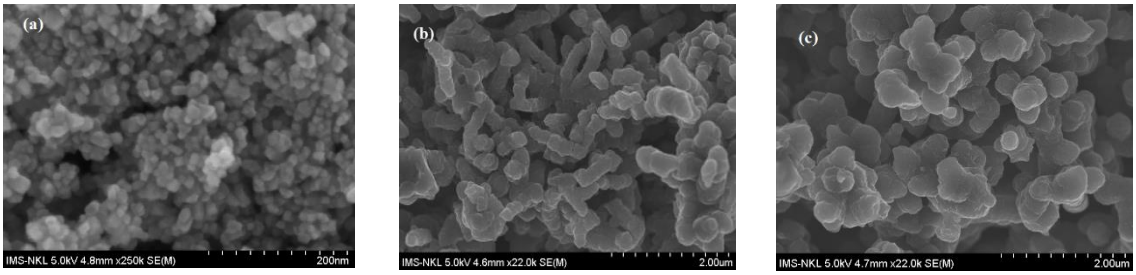


Figure 2. *SEM images of the SnO_2 (a), PANi (b), PANi-SnO_2 composite (c).*

The morphology of prepared SnO_2 powder seen clearly in figure 2a shows the shape of SnO_2 crystals is spherical with a diameter around from 15 to 20 nm. The SEM image shown in fig 2b indicates that the synthesized PANi polymers have the fibrous structure with the width of about 0.25 µm. That fibrous structure is also observed in PANi-SnO_2 composite but with a larger diameter of 0.4 µm and those fibers gather in tufts.

3.2. The electrochemical properties

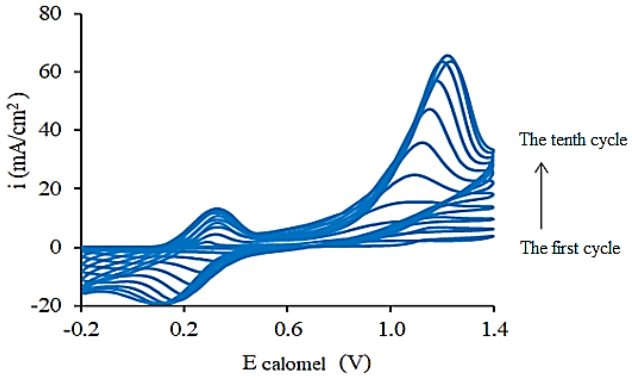


Figure 3. *The CV diagram of the synthesis process PANi-SnO_2 composites in solution of 0.5 M H_2SO_4, 0.2 M Ani, and 6 g/l SnO_2, , scanning rate of 20 mV/s for 10 cycles.*

Figure 3 gives the CV curves during the synthesis process of PANi-SnO_2 composite on the stainless steel electrode as substrate with the scanning rate of 20 mV/s for 10 cycles in the electrolyte solution. It's obvious that there are two oxidation peaks at 0.3 and 1.25 V during the anodic sweep and one peak approximately at 0.2 V during the cathode sweep. The oxidation peaks at 0.3 and 1.2 V are transferences of PANi structures from leucoemeraldine to emeraldine and from emeraldine to pernigraniline, respectively. The reduction peak at 0.1 V is to change PANi form from pernigraniline to emeraldine. The height of peak increasing during electrolysis time demonstrates that the PANi film develops on the working electrode surface [15, 16].

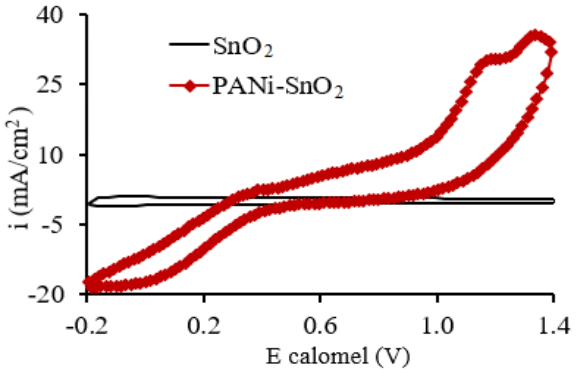


Figure 4. *The CV diagrams of SnO_2 and PANi-SnO_2 in 0.5 M H_2SO_4 with scanning rate of 20 mV/s.*

Figure 4 illustrates the CV diagrams of pure SnO_2 and PANi-SnO_2 composite with scanning rate of 20 mV/s in 0.5 M H_2SO_4. The obtained results show that the response current density of SnO_2 is lower significantly than that of PANi-SnO_2 composite because SnO_2 is a semiconductor having poor conductivity. The CV diagram of PANi-SnO_2 has two peaks in the potential area from 1.0 to 1.4 V which corresponds to the process of changing PANi structure between emeraldine and pernigraniline forms. The above results demonstrated the electrochemical activity of composite was much higher than SnO_2.

EIS measurement was carried out with the frequency range from 100 kHz to 10 mHz and the amplitude of 5 mV. Nyquist plots of PANi-SnO_2 composite and SnO_2 in 0.5 M H_2SO_4 given in figure 5 presents a semicircle in the high frequency region. It is ascribed the charge-transfer resistance (R_{ct}) between the electrolyte and the surface of the composite electrode. According to theory, the smaller the semicircle is, the higher the electrochemical property is. The results in figure 5 show that the charge-transfer resistance of composite (R_{ct} = 4.5 kΩ) is smaller than that of SnO_2 (R_{ct} = 6.0 kΩ). It can be explained that PANi is a good conductive polymer so it improves the conductivity of composite, while SnO_2 is poorly conductive so the resistance will be large. These results are suitable with the above CV investigation.

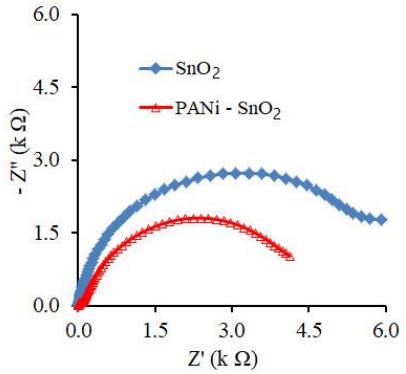


Figure 5. *Nyquist plots of PANi-SnO_2 composite and SnO_2 in 0.5 M H_2SO_4 (Frequency range: 100 kHz to 10 mHz; amplitude: 5 mV).*

5. CONCLUSIONS

SnO_2 nanoparticles and PANi-SnO_2 composites were synthesized successfully by the chemical and electrochemical methods, respectively. SnO_2 had the uniform particles size of roughly 15-20 nm and the composite had a fibrous structure with the fibrous diameter of 0.4 µm. The response current density of SnO_2 is lower significantly than that of PANi-SnO_2 composite at the same potential. Besides, the charge-transfer resistance of composite (R_{ct}) is 4.5 kΩ, which is 1.5 kΩ less than that of SnO_2. The results showed that the presence of PANi in the composites greatly improved the electrochemical properties of the material which will be used for further studying in the future.

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TÓM TẮT

NGHIÊN CỨU ĐẶC TRƯNG TÍNH CHẤT CỦA VẬT LIỆU COMPOZIT PANi-SnO_2 ĐƯỢC TỔNG HỢP BẰNG PHƯƠNG PHÁP ĐIỆN HOÁ

Compozit PANi-SnO_2 được tổng hợp thành công bằng phương pháp điện hóa. Hình thái và cấu trúc tinh thể của các vật liệu đã được xác định bằng phương pháp chụp kính hiển vi điện tử quét (SEM) và giản đồ nhiễu xạ tia X (XRD). Đặc trưng điện hóa của vật liệu được xác định bằng phương pháp quét thế tuần hoàn (CV) và đo phổ tổng trở điện hóa (EIS). Kết quả nghiên cứu cho thấy compozit PANi-SnO_2 có tính chất điện hóa vượt trội so với SnO_2.

Từ khóa: Compozit PANi-SnO_2; Nano SnO_2; Tính chất điện hoá.

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