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Facile synthesis of polyaniline nanofibers/porous carbon microspheres composite for high performance supercapacitors

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ABSTRACT

Conductive polyaniline (PANI)/porous carbon microspheres (PCMs) composite (PANI/PCMs) was synthesized by simple solution polymerization method with PCMs as carbon support. The morphology and structure were analyzed by scanning electron microscope and X-ray diffraction. Electrochemical performances were analyzed by Cyclic Voltammetry and constant-current Charge and Discharge. The results show that the carbon support (PCMs) plays a vital role in regulating the morphology and structure of PANI. In PANI/PCMs composite, small and uniform PANI nanofibers were grown on the surface of PCMs, but only micronfibers were formed for the pristine PANI. The PANI/PCMs composite shows excellent capacitance performances in 1 M H_2SO_4 aqueous electrolyte. At a current density of 1 A/g, the PANI/PCMs composite represents a maximum specific capacitance of 242.5 F/g, which is much higher than those of pristine PANI (135.2 F/g) and PCMs (37.2 F/g).

1. Introduction

In view of the growing problems of fossil fuel energy shortage and environmental pollution, the development of sustainable energies as well as efficient energy storage systems becomes a very important and urgent task [1–3]. As a class of highly promising energy storage devices, supercapacitors have drawn great attention due to their outstanding advantages, *e.g.* the high power supply, high energy efficiency, long cycle life-time and low maintenance cost [4–6]. Porous carbon materials and conducting polymers are currently the two categories of promising electrode materials for the application of supercapacitors [7,8].

Among numerous capacitance materials, carbon materials is by far one of the most ideal materials, which can deliver desirable electric double layer capacitance (EDLC), owing to their a lot of nanopores, large specific surface area, high electrochemical stability, etc. [9–15]. Conducting polymers, such as polyaniline and polypyrrole, are considered to be one promising electrode materials for supercapacitors, which can exhibit extremely high pseudocapacitance (PC) relying on the quick redox reaction [16–18]. Particularly, integrating porous carbon materials and conducting polymers into composite materials is a highly efficient method for the designing of high-performance electrode for supercapacitors [19].

Compared with carbon-based electric double layer supercapacitor, the polymer-based pseudocapacitor usually has higher energy density, because the polymer can stores charge inside the entire material, and the carbon only stores charge on its surface [20]. However, the diffusion rate of electrolyte ions in the polymer is very low, so the discharge rate (or power density) of the pseudocapacitor is far lower than the electric double layer capacitor, which greatly limits its prospect in practical application [21]. The advantages of polymer/carbon composite material include two aspects [22–24]: (i) carbon is able to improve the charge transfer efficiency and mechanical strength of polymer; (ii) the high surface area and porous structure of carbon can improve the utilization ratio of polymer and increase the diffusion rate of electrolyte ions.

In this study, we report the synthesis of polyaniline (PANI)/porous carbon microspheres (PCMs) composite (PANI/PCMs) by a simple solution polymerization method with PCMs as carbon support. The PCMs are pre-synthesized by the efficient hydrothermal synthesis and heat treatment with glucose as raw material and lithium acetate as activating agent. Significantly, very small and uniform PANI nanofibers were successfully synthesized on the surface of PCMs, which can provide higher specific surface area and more abundant electrochemical active sites than the PANI micronfibers. With these merits, we investigated that the high performance electrode of supercapacitors could be designed with the PANI/PCMs composite material.

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2. Experimental

2.1. Sample preparation

2.1.1. The preparation of the PCMs support

Typically, 6 g of glucose and 35 ml of deionized water were added into a 50 ml Teflon reaction pot. The reaction pot was sealed with stainless steel shell and heated at a temperature of 180 °C for 8 h After the reaction, the sample was collected and washed with deionized water, and dried under vacuum. Afterwards, 0.5 g of as-prepared sample was mixed with 0.5 g of lithium acetate in 100 ml alcohol under ultrasonic treatment. Then the mixture was heated at a temperature of 850 °C for 1 h under oxygen-deprived environment. The product was washed with 1 mol/L HCl aqueous solution and deionized water, and dried under vacuum.

2.1.2. The preparation of PANI/PCMs composite

A certain amount of PCMs and monomer aniline were added into a round-bottomed flask, where 100 ml of 1 mol/L HCl aqueous solution was added in advance. Then some ammonium persulfate (APS) solution was slowly dripped into the flask under magnetic stirring and ice water bath condition (0 °C). After reaction of 12 h, the product was finally filtered, washed with alcohol and dried under vacuum. The PANI/PCMs composite samples with three carbon contents of 5%, 10% and 20%, namely PANI/PCMs (5%), PANI/PCMs (10%) and PANI/PCMs (20%) were synthesized according to the above steps.

2.2. Sample characterization

2.2.1. Characterization of materials

The crystal structures of the materials were analyzed by X-ray diffraction (XRD) recorded on a Diffractometer (D/max 2500 v/pc). The morphologies of the materials were investigated by a scanning electron microscope (SEM) (JSM-6510LV). The microstructures of the materials were investigated by a transmission electron microscope (TEM) (JEOL-2010). The thermal stability of polymer crystals was investigated by thermogravimetric-differential scanning calorimetry (TG-DSC) analysis.

2.2.2. Electrochemical measurements

The electrochemical properties of the samples in 1 mol/L H_2SO_4 aqueous solution were tested by Cyclic Voltammetry (CV) and constant-current Charge and Discharge (CDC) on an electrochemical work station (CHI 660E). The test system was a typical three-electrode system, with platinum sheet as auxiliary electrode, reversible hydrogen electrode as reference electrode. The working electrode was prepared as follows: 10 mg of sample was dispersed in 0.9 ml alcohol and 0.1 ml binder (0.05% Nafion, Dupont) under ultrasound, then 5 μL of mixed slurry was coated on the glassy carbon electrode ($\Phi = 5.0$ mm), and dried under infrared lamp.

3. Results and discussion

3.1. Morphologies and structures

The crystalline structures of the as-prepared samples are first investigated by means of the XRD technique. Fig. 1 shows the XRD patterns of PCMs, PANI/PCMs (5%), PANI/PCMs (10%) and PANI/PCMs (20%). From Fig. 1(A), it can be seen that the PCMs sample has two broad diffraction peaks at about 23 and 43° of 2-Theta, which indicates a typical amorphous structure of carbon materials [25]. From Fig. 1 (B–D), it is obvious that the PANI/PCMs samples possess three additional characteristic diffraction peaks at about 14.5, 20.4 and 25.3° of 2-Theta, which demonstrates the

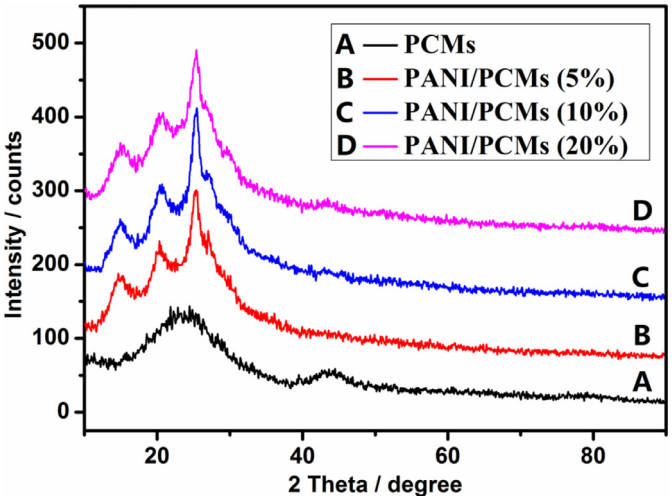

Fig. 1. XRD patterns of (A) PCMs, (B) PANI/PCMs (5%), (C) PANI/PCMs (10%) and (D) PANI/PCMs (20%).

PANI component has been integrated with the PCMs and composite structrue is formed [26].

The morphologies of the as-prepared samples are further investigated by means of the SEM technique, with the results shown in Fig. 2. Fig. 2(A) and (B) display the typical SEM images of the PCMs in different magnification, indicating that the sample has a well-shaped spherical morphology with the diameter from 300 to 500 nm. For the PANI/PCMs (20%) composite (Fig. 2(C)), a great amount of microspheres with a larger diameter from 500 to 800 nm can be observed. Remarkably, from the high magnification image (Fig. 2(D)), it can be seen that numerous well-dispersed PANI nanofibers (about 20 nm in diameter) have been successfully grown on the surface of PCMs. However, only micronfibers structures (more than 200 nm in diameter) were formed for the pristine PANI sample (Fig. 2(E) and (F)). The results show that the PCMs play an important role in regulating the morphology and structure of PANI. It is deduced that the spherical carbon support would be beneficial to the uniform deposition and controlled growth for the polymer nanostructures.

The microstructures of the as-prepared samples are also investigated by means of the TEM technique, with the results shown in Fig. 3. From the result of TEM, it is obvious that the surface roughness and dimension of pristine PANI and PANI in composites are quite different. Fig. 3 (A, B) shows that the PANI nanofiber in PANI/PCMs (20%) is very slender and has a higher roughness. Fig. 3 (C, D) shows that the micronfibers of pristine PANI is more bulky and display a lower roughness. The increased surface roughness of the electrode materials means higher electrochemical activity area and better performances for supercapacitor applications.

In order to analyze the relationship between polymer crystallinity and corresponding supercapacitor performances, the thermal stability of polymer crystals was investigated by the TG-DSC technique (see Fig. 4). Form the TG-DSC curves in Fig. 4, it can be seen that the pristine PANI and PANI/PCMs (20%) completed decomposition between 300 °C and 700 °C. In the TG curves, the PANI/PCMs (20%) shows a little early initiate temperature at 335 °C (350 °C for pristine PANI), and a later end temperature at 676 °C (640 °C for pristine PANI). In the DSC curves, the PANI/PCMs (20%) shows a lower maximum heat-release temperature of 384 °C, compared with the 435 °C of pristine PANI. The early initiate temperature for decomposition of PANI/PCMs (20%) is due to the smaller nanostructures and lower crystallinity of PANI, and later end temperature is mainly attributed to the better heat-resisting property of PCMs. The decrease in nanoscale and

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