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Electrochemical properties of the poly(3,4-ethylenedioxythiophene)/single-walled carbon nanotubes composite synthesized by solid-state heating method

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ABSTRACT

The poly(3,4-ethylenedioxythiophene)/single-walled carbon nanotubes (PEDOT/SWNTs) composites with content of SWNTs varying from 4 wt% to 12 wt% were prepared by a simple solid-state heating method. The results from FTIR and UV–vis spectra showed that the composites were successfully performed by this method, and the strong interactions between the PEDOT and SWNTs occurred in the composite with 8 wt% SWNTs as compared to other composites. The galvanostatic charge–discharge measurements indicated that the PEDOT/SWNTs composite had higher specific capacitances than PEDOT, and the composite with 8 wt% SWNTs had the highest specific capacitance among the composites. The morphological studies showed that the composite with 8 wt% SWNTs exhibited a mixture of the plate-like PEDOT and nonuniformly distributed SWNTs. The further electrochemical tests on the composite with 8 wt% SWNTs showed that the composite had a high specific capacitance of 188 F g^{-1} at 0.5 mA cm^{-2} and a capacity retention of 66% over 1300 cycles.

1. Introduction

Electrochemical capacitors (ECs), known as supercapacitors, have attracted great interest as promising energy storage devices for many applications [1,2]. Supercapacitors are classified into two types based on their charge storage mechanism: electrical double layer capacitors and pseudo-capacitors. A conducting electro-active electrode with large surface area holds the key to high performance supercapacitors [1,2]. To fabricate such electrode, various materials including different types of carbon (active carbon, carbon fiber, graphene and carbon nanotubes), conducting polymers (PANI, PPy, PEDOT) and transition metal oxides (RuO_2, IrO_2) have been extensively investigated [3–7].

The conducting polymers, such as polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethenedioxythiophene) (PEDOT) are regarded as promising pseudo capacitor materials due to their good environmental stability, high electrical conductivity, low cost and high reversible performance [8–10]. However, the poor cycling stability and relatively low discharge capacitance caused by repeated influx and outflow of counter ions during charging–discharging are the limiting elements for practical applications in supercapacitors [11]. Therefore, the composites containing conducting polymers (PANI, PPy, PEDOT) and nanomaterials (carbon nanotube, graphene, metal oxides) have been widely studied to overcome the challenge of the conducting polymer electrode materials [12–15].

Among various conducting polymers, PEDOT, a derivative of polythiophene, has been exploited as a charge–storage material due to its large electroactive potential window and high cycling stability than PANI and PPy, although, the mass-specific capacitance of PEDOT is lower than PANI and PPy [16–19]. Therefore, the extensive efforts have been devoted to synthesize of PEDOT to increase its specific capacitance or energy density. The results from recent studies show that the combination of PEDOT and carbon nanotube (CNTs) is an effective way to increase the mass-specific capacitance of PEDOT because of the interconnected high surface area network of carbon nanotubes [20,21], and the PEDOT/CNTs composite can be prepared via chemical synthesis, electrochemical deposition on pre-formed carbon nanotube electrodes, or by electrochemical co-deposition [21–23].

In this paper, we developed a novel simple solid-state heating method for preparation of poly(3,4-ethylenedioxythiophene) /single-walled carbon nanotubes (PEDOT/SWNTs) composites, and the content of SWNTs in the composites was varied from 4 wt% to 12 wt%. The correlation between the structures and properties of the PEDOT/SWNTs composites were discussed based on the results from FTIR and UV–vis. Moreover, the morphological studies, galvanostatic charge–discharge measurement, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and cycle life

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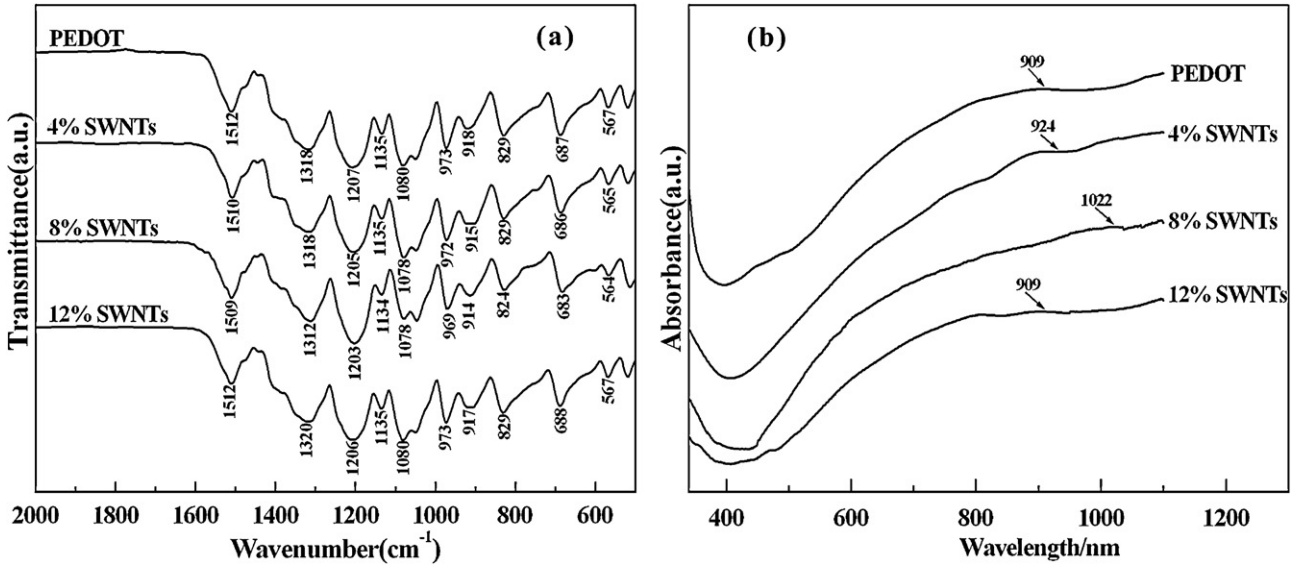

Fig. 1. FTIR spectra (a) and UV–vis spectra (b) of PEDOT/SWNTs composites and PEDOT.

measurement were done to evaluate the potential application of solid-state synthesized PEDOT/SWNTs as a supercapacitor material.

2. Experimental

2.1. Materials

SWNTs (diameter of <2 nm, length 5–15 μm, Shenzhen Nanoport Corporation of China) were purified by refluxing in 6 M HNO_3 for 5 h, and then thoroughly washed with deionized water and ethanol before to be dried at 60 °C during 24 h. 3,4-Ethylenedioxythiophene (EDOT) was obtained from Aladdin Reagent Company (China). The 2,5-dibromo-3,4-ethylenedioxythiophene was synthesized according to the previous report [24]. All other chemicals and solvents were used as received without further purification.

2.2. Preparation of PANI/MWNTs composites

A typical solid-state heating synthesis procedure was as followed: a mixture of 0.56 g (2 mmol) 2,5-dibromo-3,4-ethylenedioxythiophene and 20 mg purified SWNTs in 30 mL chloroform was ultrasonicated for 30 min to facilitate monomer to adsorb on the wall of SWNTs. After ultrasonication, the mixture was placed in an vacuum oven at 60 °C to evaporate the chloroform, then the residue kept in an vacuum oven under same conditions for 24 h at 60 °C to prepare PEDOT/SWNTs composite. The different wt% (4 wt%, 8 wt%, 12 wt%) of SWNTs with respect to the EDOT was applied for preparation of PANI/MWNTs composites. For comparison, the pure PEDOT was also synthesized in the similar manner without SWNTs.

2.3. Structure characterization

The Fourier transform infrared (FTIR) spectra of the composites were obtained by using a BRUKERQEUINOX-55 Fourier transform infrared spectrometer (Billerica, MA) (frequency range 4000–500 cm^{-1}). UV–vis spectra of the samples were recorded on a Shimadzu UV-2450 spectrophotometer. Scanning electron microscopy (SEM) measurements were observed on a Leo1430VP microscope. Transmission electron microscopy (TEM) experiments were carried out in a Hitachi 2600 electron microscope. The samples for TEM measurements were prepared by placing a few drops of PEDOT/SWNTs ethanol suspension on copper supports.

2.4. Electrochemical tests

The electrodes were prepared by mixing 85 wt% active materials (3 mg), 10 wt% carbon black and 5 wt% polytetrafluoroethylene (PTFE) to form slurry. The slurry was pressed on a graphite current collector (area: 1 cm^2), then dried at 60 °C for 24 h. Half-cell electrode tests were performed with the three-electrode cells using standard calomel reference electrode (SCE) and Pt foil of counter electrode in the electrolytes of 1 M H_2SO_4. The galvanostatic charge–discharge and CV tests were performed in the potential window ranged from −0.2 to 0.8 V and conducted at different scan rates and current densities using CHI660C electrochemical working station. Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential, 0.5 V and 1 V by using Zennium40084, and the data were collected in the frequency range of 0.1 Hz to100 kHz. The cycle life measurement of composite electrode was recorded by sequential CV cycling (over 1300 cycles) at a scan rate of 10 mV s^{-1}.

3. Results and discussion

Fig. 1(a) represents the FTIR spectra of PEDOT/SWNTs composites and PEDOT prepared by solid-state heating method. As can be seen in Fig. 1, the FTIR spectra of composites are identical to that of PEDOT. The main characteristic bands of PEDOT appear in the spectra of composites as follows: the two bands appearing at ∼1509–1512 and ∼1312–1320 cm^{-1} can be assigned to the asymmetric stretching mode of C=C and inter-ring stretching mode of C—C, respectively. The bands appearing at ∼1203–1207, ∼1134–1135 and ∼1078–1180 cm^{-1} are attributed to the C—O—C bending vibration in ethylenedioxy, while the bands at ∼969–973, ∼914–918, ∼824–829 and ∼683–688 cm^{-1} are the characteristic bands of stretching vibrations of the C-S-C bond in thiophene ring [25–27]. Furthermore, the comparison of the FTIR spectra of PEDOT/SWNTs composites and PEDOT reveals that the bands of composites with 4 wt% and 12 wt% SWNTs are similar to those of PEDOT, while the bands of composite with 8 wt% SWNTs shifts slightly from their corresponding positions to the lower