

Microwave-assisted synthesis and electrochemical capacitance of polyaniline/multi-wall carbon nanotubes composite

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Received 1 October 2007; received in revised form 11 October 2007; accepted 19 October 2007

Available online 26 October 2007

Abstract

Polyaniline/multi-wall carbon nanotubes composite (PANI/MWNTs) was rapidly synthesized by microwave-assisted polymerization. Transmission electron microscope (TEM) image revealed that this composite was a core-shell structure with PANI layers (50–70 nm). Electrochemical behavior of the composite was evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge tests with a two-electrode system. An enhanced specific capacitance of 322 F/g with a specific energy density of 22 W h/kg was about 12 times that of MWNTs. This composite also exhibited a good rate capability, retaining up to 87% of initial capacity at a current density of 5 mA/cm². © 2007 Elsevier B.V. All rights reserved.

Keywords: Polyaniline; Multi-wall carbon nanotubes; Microwave-assisted; Supercapacitor

1. Introduction

Supercapacitors, known as important charge storage devices, are attracting great interest owing to their application in electrical vehicles, portable computers and cellular devices [1–4]. Among various materials, carbon nanotubes (CNTs) are frequently studied for supercapacitor applications because of their unique electric properties and nano-scale size [5–7]. However, CNTs possess lower capacitance than many electronically conducting polymers (ECPs) [8,9]. On the other hand, many studies have proved that ECPs represent promising pseudo-capacitive materials due to versatility of structure, low cost and high specific capacitance [10–13]. Thus, the combination of ECPs with CNTs offers an attractive way to improve the capacitance of materials resulting from the large specific surface of CNTs and redox contribution of the ECPs [14–17].

Generally, the chemical or electrochemical polymerization is considered efficient in preparing the ECPs/CNTs composite. Recently, Milena et al. [18] provided a new polyaniline/nanotube composite obtained by ultrasonically initiated emulsion polymerization. To our knowledge, no reports are published on the microwave-assisted synthesis of the ECPs/CNTs composite and its capacitance. However, the advantages of this method are evident such as quick thermal reactions, low energy consumption and the controllable thickness of polymer layers [19–21]. Herein, a novel microwave-assisted strategy, for the first time, is developed to synthesize PANI/MWNTs composites as electrode materials for supercapacitors. And all the electrochemical tests demonstrate that the prepared composite possesses better electrochemical performance.

2. Experimental

MWNTs (Shenzhen Nanoport Corporation of China) were purified by refluxing in 6 M HNO₃ for 24 h, and then thoroughly washed with deionized water and ethanol before to be dried at 120 °C during 24 h. Aniline was

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distilled under reduced pressure before use. Ammonium persulfate (APS) was used as received. Purified MWNTs (0.08 g) and aniline (5 mmol) were dispersed in 0.2 M H_2SO_4 (20 mL) solution and sonicated for 30 min to facilitate aniline to adsorb on the wall of MWNTs. Upon stirring, 0.2 M H_2SO_4 solution (5 mL) containing APS (5 mmol) was slowly added to the above mixture. Then the mixture was heated using a commercial microwave oven equipped with a reflux condenser through the microwave irradiation (XH-100B, 100–850 W, Beijing Xianghu Science and Technology Development Co. Ltd, Beijing, PR China). The reaction was carried out for 3 min, and then cooled to room temperature naturally. The resulting powders were filtered and rinsed with deionized water and ethanol several times, and then dried at 50 °C overnight under vacuum.

Fourier transformation infrared spectrum was recorded using BRUKER-EQUINOX-55 FT-IR spectrometer (KBr pelleting). The morphology of the composite was conducted on a Hitachi 600 transmission electron microscope.

Electrodes for supercapacitors were prepared by mixing active materials (3 mg) with 15 wt.% carbon black and 5 wt.% polytetrafluoroethylene to form slurry. The slurry was pressed on a graphite current collector (area: 1 cm²). The prepared electrode was dried at 40 °C for 24 h and pressed again. The active material mass on an electrode was 3 mg. Electrochemical studies were carried out in a two-electrode system consisted of two identical electrodes, using a CHI660A electrochemical working station. The electrolyte was 1 M H_2SO_4 solution. Cyclic voltammograms were recorded from –0.2 to 0.8 V at scan rates of 10, 20 and 30 mV/s. Charge–discharge tests were conducted at different current densities, with cutoff voltage of –0.2–0.8 V.

3. Results and discussion

Typical TEM images of purified MWNTs and PANI/MWNTs composite are shown in Fig. 1. MWNTs display a hollow structure with an outer diameter between 20

and 40 nm, and exhibit regular morphology. In Fig. 1b, the core-shell composite with 150–180 nm in diameter can be clearly observed, in which PANI acts as a shell and MWNTs as a core. The growth of thick PANI layers (50–70 nm) within short reaction time may be importantly dependent on special microwave heating. This kind of special nanostructure enlarges the liquid–solid interfacial area and gives more opportunity for ions insertion-extraction, ensuring a high reaction rate.

Fig. 2 shows FTIR spectra of PANI and PANI/MWNTs composite. The spectrum of the composite exhibits the main IR bands similar to that of PANI. For example, the C=C stretching deformation of quinoid (1577 cm⁻¹) and benzenoid ring (1488 cm⁻¹), the C–N stretching vibration (1297 cm⁻¹), the C–H in plane bending vibration (1137 cm⁻¹), and the C–H out of plane bending vibration (809 cm⁻¹) can be observed in spectrum of the composite, endorsing the presence of doped PANI on MWNTs. Meanwhile, this composite shows a higher intensity ratio of ~1580 and ~1490 cm⁻¹ than PANI, indicating the pres-

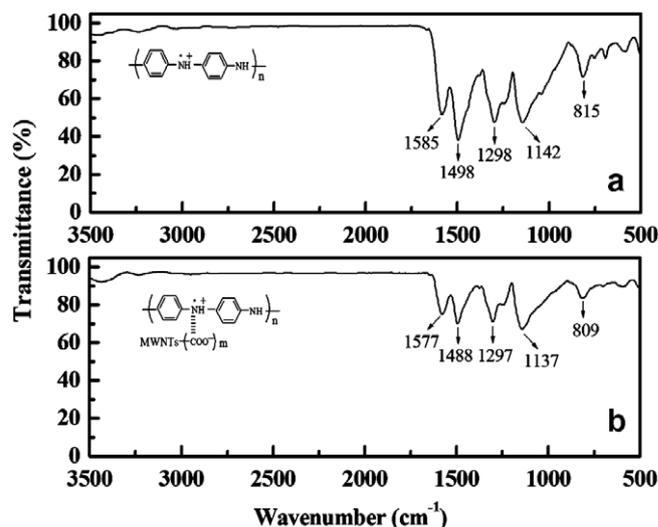


Fig. 2. FTIR spectra of (a) PANI and (b) PANI/MWNTs composite.

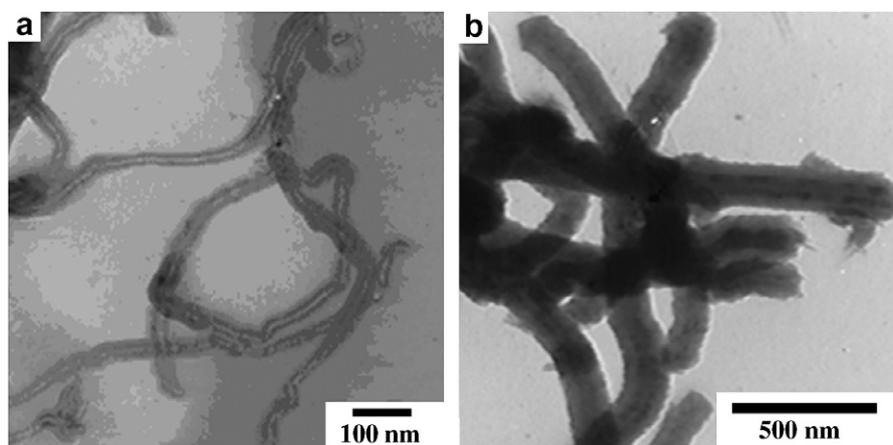


Fig. 1. TEM images of (a) MWNTs and (b) PANI/MWNTs composite.

ence of strong interaction between MWNTs and the quinoid ring of PANI [18].

Fig. 3 gives CV curves of MWNTs and PANI/MWNTs composite electrodes with scanning rates 10, 20 and 30 mV/s in two-electrode system. Apparently, the MWNTs electrode reflects an ideal double-layer behavior except two weak redox peaks (P₁/P₂, P₃/P₄), which is likely ascribed to the redox processes of electroactive surface species such as quinone groups [22]. However, CV curves of the composite (Fig. 3b) not only present a large background current, but also appear obvious peak currents (P₅/P₆). It implies that the capacitance of the composite is much higher than that of MWNTs. This improvement should contribute to fast faradaic process of PANI. With increasing scan rate from 10 to 30 mV/s, the peak current at P₅ increases from 11 to 29 mA, showing good rate ability.

Fig. 4 shows galvanostatic charge–discharge curves of (a) MWNTs and (b) PANI/MWNTs composite electrodes between –0.2 and 0.8 V at a current density of 1 mA/cm² in two-electrode system. All the curves exhibit mirror-like images, indicating a reversible oxidation process among the electrode materials. The specific capacitance (C_m) of the electrode material is calculated by means of

$C_m = (I \times t) / (V \times m)$ [23], with I being charge–discharge current, t the discharge time, $V = 1$ V, and m the mass of active materials in an electrode. The rates are listed in Table 1. The highest specific capacitance for the composite (322 F/g) is almost 12 times that of MWNTs (25.4 F/g) at 1 mA/cm². Compared with the specific capacitance (360 F/g) of the composite obtained by the oxidative polymerization method [24], the result in our experiment is little lower. However, the microwave-assisted method is simpler and more efficient, and the two values are still comparable. When the current density increases to 5 mA/cm², the composite still shows a high value of 280 F/g. The capacitance retention is 87%, indicative of a good rate capability [25]. The reason may be that the core-shell structure of the electrode provides a relatively easy path for fluid/solid reactions and thus makes more redox faradic reactions to occur at higher scan rate.

Fig. 5 compared the specific energy density (E) and power density of MWNTs and PANI/MWNTs composite. The specific energy density (E) and power density (P) are evaluated according to Equations $E = (C_m V^2) / 4$ and $P = E / t$ [26], with C_m being the specific capacitance of the composite electrode, t the discharge time and

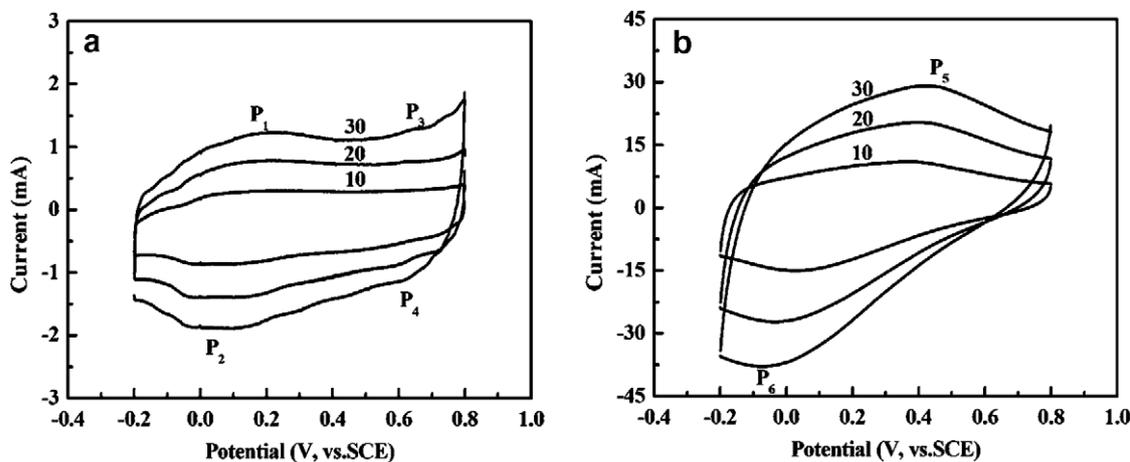


Fig. 3. CV curves of (a) MWNTs electrode and (b) PANI/MWNTs composite electrode at different scan rates in two-electrode system.

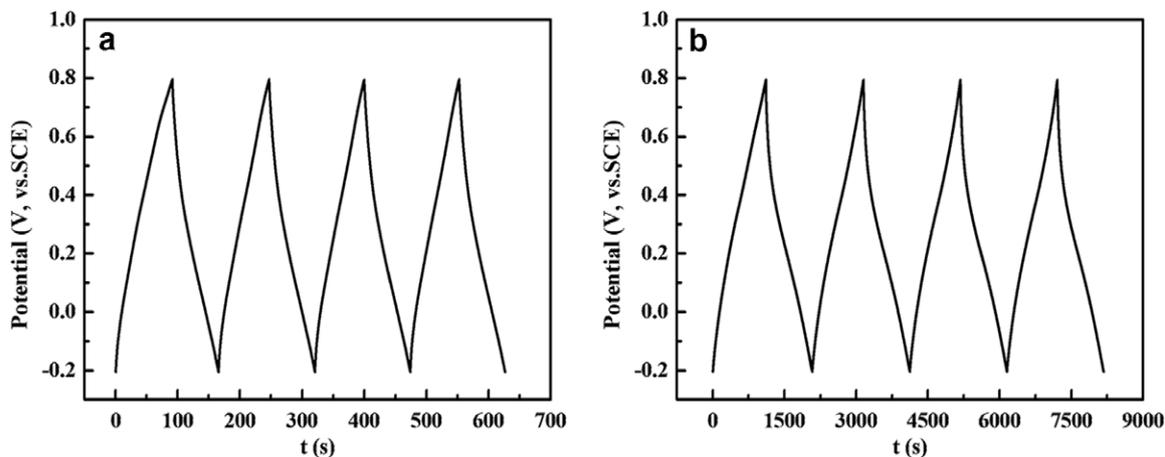


Fig. 4. Charge–discharge curves of (a) MWNTs electrode and (b) PANI/MWNTs composite electrode at 1 mA/cm² in two-electrode system.

Table 1
The specific capacitances of MWNTs and PANI/MWNTs composite electrodes at different currents evaluated from charge–discharge tests

Current density (mA/cm ²)		1	2	3	4	5
Specific capacitance (F/g)	MWNTs	25.4	24.2	23.6	22.8	22.2
	PANI/MWNTs	322	310	300	292	280

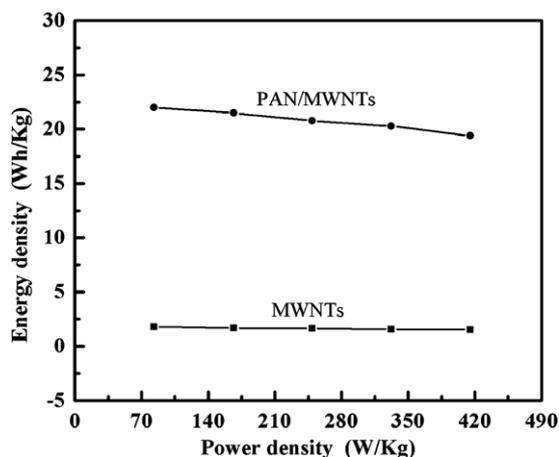


Fig. 5. Regone plot of specific power vs. specific energy for MWNTs electrode and PANI/MWNTs composite electrode.

$V = 1$ V. As shown in Fig. 5, the specific energy densities of two kinds of electrodes reduce slowly with increasing power densities. The energy density of the composite can reach 22 W h/kg at a power density of 83 W/kg, and still remains 19.4 W h/kg at a power density of 415 W/kg. Its energy density is also 12 times that of MWNTs. Thus, the microwave-assisted process is proved to be an effective strategy in preparing the PANI/MWNTs composite with good electrochemical performance. About the study on the energy density, Hashmi [27] reported polypyrrole prepared by electrochemical polymerization. The electrochemical results show that the energy density of polypyrrole is 16.7–24.7 W h/kg, which is very similar to that of PANI/MWNTs prepared by the microwave-assisted method. Certainly, the future work will further improve the specific capacitance and energy density of electrode materials by this efficient method.

4. Conclusions

A microwave-assisted method was developed for the rapid fabrication of PANI/MWNTs composites. Electrochemical tests indicated that this composite had a high specific capacitance (322 F/g) and good rate capability. More importantly, the microwave-assisted technique might be applied in modifying CNTs with others materials including

organic and inorganic materials to obtain various electrode materials with better electrochemical properties.

Acknowledgments

This work was supported by National Basic Research Program of China (973 Program) (No. 2007CB209703), Natural Science Foundation of China (No. 20403014, No. 206330400) and Natural Science Foundation of Jiangsu Province (BK2006196).

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