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ORIGINAL PAPER

Electrochemical capacitance of the composite of poly (3,4-ethylenedioxythiophene) and functionalized single-walled carbon nanotubes

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Abstract The homogenous coating of poly (3,4-ethylenedioxythiophene) (PEDOT) on carbon nanotubes was realized by using functionalization of single-walled carbon nanotubes (SWNTs) in this study. Consequently, the PEDOT/functionalized SWNTs (PEDOT/F-SWNTs) composites, with size of around 100nm, which is much smaller than that of PEDOT, were prepared by the electrochemical method. Its small granule increased the active/nonactive mass ratio and reduced the ions diffusion length. Therefore, its specific capacitance of the composite was up to 200F g^{-1}, which was remarkably greater than that of PEDOT. Furthermore, the PEDOT/F-SWNTs composites had very rapid charge/discharge ability with specific capacitance of 180F g^{-1} at scanning rate of 200mV s^{-1} and 170F g^{-1} at frequency of 1Hz, which is an important practical advantage. In addition, such composite had a good cycling performance and a wide potential window.

Keywords Supercapacitors · Poly (3, 4-ethylenedioxythiophene) · Carbon nanotubes · Composites · Functionalization

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Introduction

Owing to the unique characteristic of switching between their oxidized state (conductive state) and reduced state (nonconductive state), the electronically conducting polymers (ECPs) can be used as energy storage devices (electrochemical capacitors [1, 2] and secondary batteries [3]), sensors [4], and actuators [5, 6]. One of the most promising applications is the development of high-power-density electrochemical capacitors (supercapacitors), which have played an increasingly important role in applications such as electric vehicles and short-term power sources for mobile electronic devices [7–11].

Among ECPs, poly (3,4-ethylenedioxythiophene) (PEDOT), as a member of polythiophene family, has drawn a wide interest in supercapacitor application because of its fast charge/discharge ability [12], wide potential window [13], and environment-friendly feature [14] as well as high room temperature conductivity (easily up to 500S/cm), high thermal, and chemical stability. However, PEDOT also has inevitable shortcomings as all ECPs, that is, low conductivity and electrochemical activity in its reduced state and mechanical deterioration during long-term cycling.

To overcome these problems, ECPs/carbon nanotubes (CNTs) composites were prepared [13]. The mesoporous structure of CNTs was able to adapt to the mechanical stress during the cycling, and the high conductivity of CNTs can enhance that of the composite [13, 15–17]. However, compared with other ECPs, such as polyaniline, which can homogenously coat on CNTs, PEDOT has a strong tendency for polymerization on itself rather than CNTs [18].

In this study, the composite of PEDOT and functionalized single-walled CNTs (F-SWNTs) was investigated, with its morphology and electrochemical capacitance properties

carefully examined. In this study, the fast charge/discharge ability and cycling stability of the composite as the electrode of supercapacitor were emphasized.

Experimental

Materials 3,4-Ethylenedioxythiophene monomer (EDOT, Bayer) was distilled before use and stored at −10 °C in a nitrogen atmosphere. SWNTs (Purity of CNTs > 90wt%, Outer diameter < 8nm, Length 0.5–2μm, Ash < 1.5%) were purchased from Chengdu Organic Chemistry, Chinese Academy of Science. The SWNTs were functionalized by suspending in concentrated H_2SO_4/HNO_3 solution (3:1 volume ratio, 98 and 70% gravimetric concentrations, respectively) and sonicating in a water bath with the temperature of 60–70°C. All other reagents were obtained from commercial sources and were used as received.

Electrode preparation and characterization PEDOT/F-SWNTs electrodes (1 × 1cm) were galvanostatically prepared on tantalum electrodes (Ta) in aqueous mixture solution containing 0.05M EDOT, 0.01–0.1wt% F-SWNTs, and 0.1M *p*-toluenesulfonate sodium, which was used as a surfactant and supporting salt. PEDOT were prepared in the solution without F-SWNTs to investigate the role of F-SWNTs through comparison. In all the preparations, the current density was 2mA cm^{-2}, and the quantity of polymerization charge was 2mA h cm^{-2}. Owing to good dispersive capacity of F-SWNTs, ultrasound was not used in polymerization.

The mass of composite films was determined by the electronic balance (AG 135, Mettler-Toledo, precision = 0.01mg). Scanning electron microscopy (SEM) observations of the samples were carried out on field emission scanning electron microscope (JEOL, JSM-6700F).

Electrochemical tests All electrochemical tests were performed on the Versatile Multichannel Potentiostat 2/Z with the ability for impedance measurements (VMP2, Biologic). In three-electrode system, a platinum sheet was used as counter-electrode and saturated calomel electrode (SCE) as the reference electrode. Two-electrode system consisted of two almost identical PEDOT/F-SWNTs composite electrodes. The electrolyte was 1M KCl aqueous solution. The electrochemical performance was investigated by using cyclic voltammetry (CV), galvanostatical charge/discharge, and electrochemical impedance spectroscopy (EIS) techniques. The scanning rates of CV tests ranged from 10 to 200mV s^{-1}. The current load of galvanostatical charge/discharge was 0.5A g^{-1}. EIS tests were made in the frequency range from 100kHz down to 10mHz, using an alternating current (ac) signal amplitude of 10mV at various direct current (dc) bias. The data were recorded after the dc potential being applied for 10min because the composite on the electrodes need a period to reach an electrochemical steady state. The specific capacitance (C_{spec}) of the composite was calculated by,

$$C_{spec} = C/m \quad (1)$$

$$C_{spec} = 2C/m \quad (2)$$

in the three- and two-electrode systems, respectively. In these equations, the C is the measured value of capacitance and m presents the mass of the composite on one electrode.

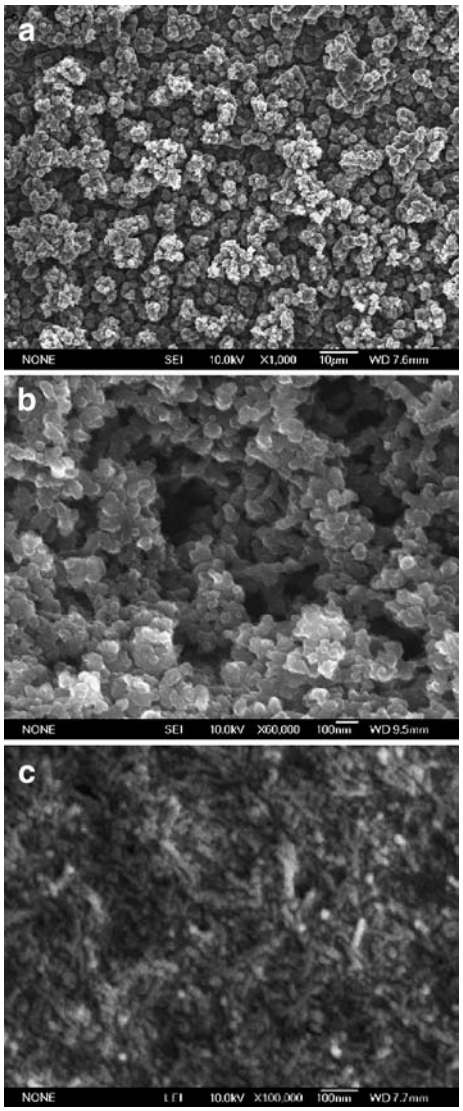

Fig. 1 SEM images of PEDOT (**a**), PEDOT/F-SWNTs (**b**), and F-SWNTs (**c**)

Results and discussion

Figure 1a shows the SEM image of PEDOT. PEDOT has a granular morphology with size of 1–2μm. The morphology of PEDOT/F-SWNTs, as presented by Fig. 1b, was also granular, but its size was only about 100nm, which is smaller than that of PEDOT by one order of magnitude. Moreover, it can also be seen that PEDOT coats on F-SWNTs homogenously, although it is well known that PEDOT is very difficult to coat on CNTs [18]. This progress can make the performance of PEDOT greatly improved by the high conductivity and mesoporous structure of CNTs. The small size of PEDOT/F-SWNTs comes from a great quantity of F-SWNTs existing in solution with the size less than 100nm, as shown by Fig. 1c. These F-SWNTs play a role of nucleus of polymerization. The even coating may result from the decrease in Fermi level of SWNTs by functionalization [19].

The CV curves of PEDOT and the PEDOT/F-SWNTs composite at a scanning rate of 10mV s^{-1} were presented in Fig. 2. Both of the curves are close to a rectangle, which indicates a fast charge/discharge process [20]. The specific capacitance of PEDOT from Fig. 2 is 120F g^{-1}. Compared with PEDOT, the composite exhibits a much greater capacitance, 210F g^{-1}. This value is also greater than the best specific capacitance of functionalized CNTs, which has been reported as 130F g^{-1} so far [21], according to the literature available. The large specific capacitance of PEDOT/F-SWNTs comes from the synergy effect of PEDOT and F-SWNTs. That is, F-SWNTs play a role of the nucleus of polymerization reaction so that composite granule with size of around 100nm was obtained. The small granule can increase the active/nonactive mass ratio so as to fully extract energy of PEDOT. Their normalized capacitance values are displayed in Fig. 2b. The capacitance of PEDOT at a scanning rate of 200mV s^{-1} remains 66% of the value at a scanning rate of 10mV s^{-1}, which indicates comparatively fast charge/discharge ability with respect to other ECPs. Better than PEDOT, the capacitance of PEDOT/F-SWNTs remained 86% when the scanning rate ranged from 10 to 200mV s^{-1}; that is, specific capacitance was still up to 180F g^{-1} at a scanning rate of 200mV s^{-1}. The reason of its novel fast charge/discharge ability is that its small granules and large amount of meso-tunnel in the composite, as shown in Fig. 1b, can effectively reduce the diffusion length of ions (L) so as to reduce the diffusion time (t), which can be estimated as (L^2/D) where D is diffusion coefficient. It should be noted that the area-specific capacitance of PEDOT/F-SWNTs in Fig. 2 was 0.8F cm^{-2}, and that of PEDOT was 0.46F cm^{-2}. A thinner PEDOT film will have a faster charge/discharge ability, but

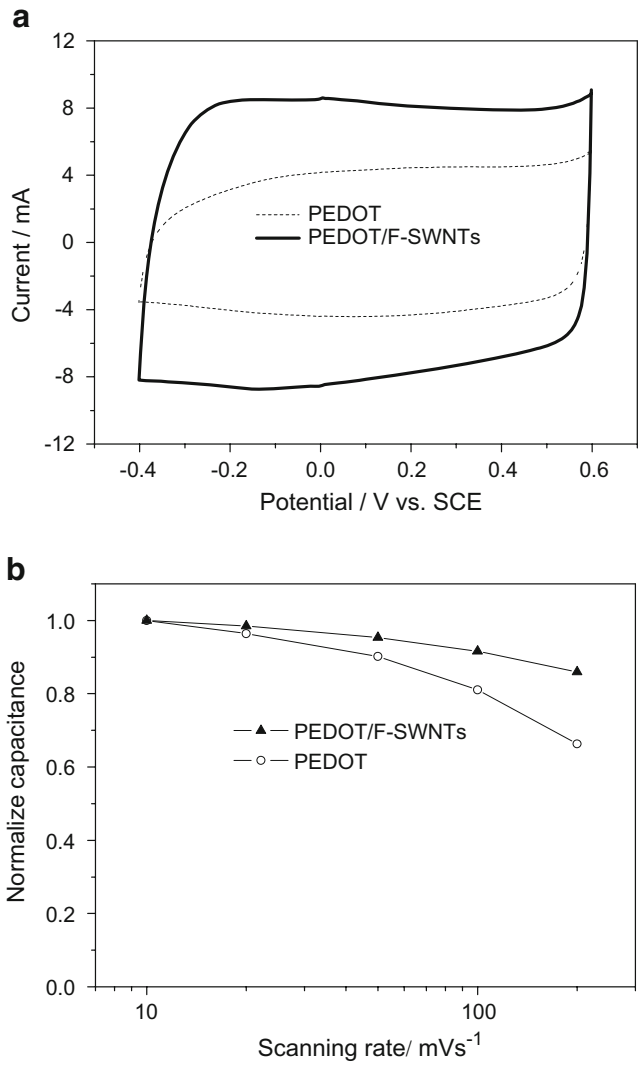

Fig. 2 CV curves of PEDOT and PEDOT/F-SWNTs at scanning rate of 10 mVs^{-1} (**a**) and their normalized capacitance as function of scanning rate (**b**) in 1 M KCl solution, three-electrode system

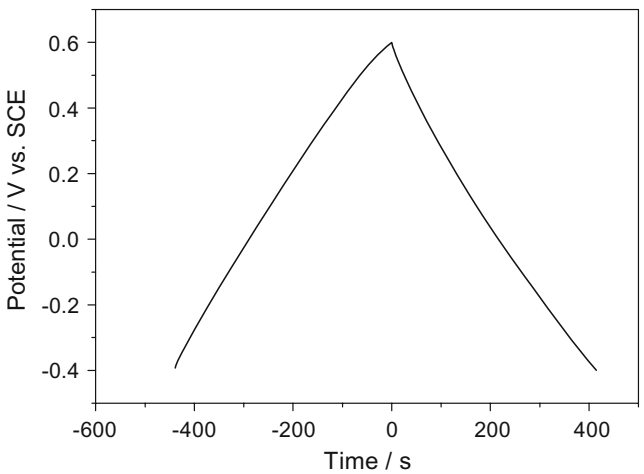

Fig. 3 Charging/discharging curve of PEDOT/F-SWNTs composite at current load of 0.5 Ag^{-1} in 1 M KCl solution, three-electrode system

such a thin film with its area-specific capacitance going even lower hardly has any impractical value.

Figure 3 displays the galvanostatical charge/discharge curve of PEDOT/F-SWNTs at a current load of 0.5A g^{-1}. The curve is linear in the whole range of potential without any obvious ohmic polarization (IR drop), which confirms an ideal capacitance behavior. The discharge-specific capacitance of the composite from Fig. 3 is 207F g^{-1}, which agrees with the values from the CV test at a scanning rate of 10mV s^{-1}.

The electrochemical behavior of the novel composite was also examined by the EIS method. Nyquist plots of the composite from 100kHz down to 10mHz at different potentials are presented in Fig. 4a. The arc in high frequency, as shown in the down-right corner of Fig. 4a, is related to the interfacial process. The imaginary part in the low frequency is almost vertical with the real part of the impedance in the plots, which suggests an ideal capacitive behavior again. The difference in the real part between low and high frequency can be used to evaluate the charge transfer resistance (R_{ct}). The values of R_{ct} of the composite at an open circuit potential (OCP) and 0.5V (vs SCE) were all smaller than 0.5Ω (electrode surface area 1cm^2). The

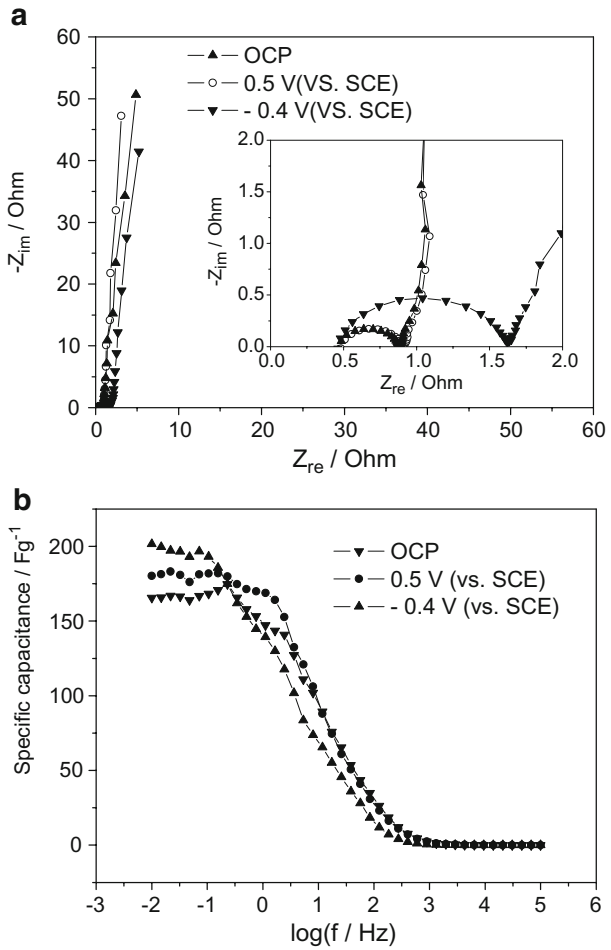

Fig. 4 Nyquist plots (**a**) and capacitance as function with frequency (**b**) of PEDOT/F-SWNTs at various potential in 1 M KCl solution, three-electrode system

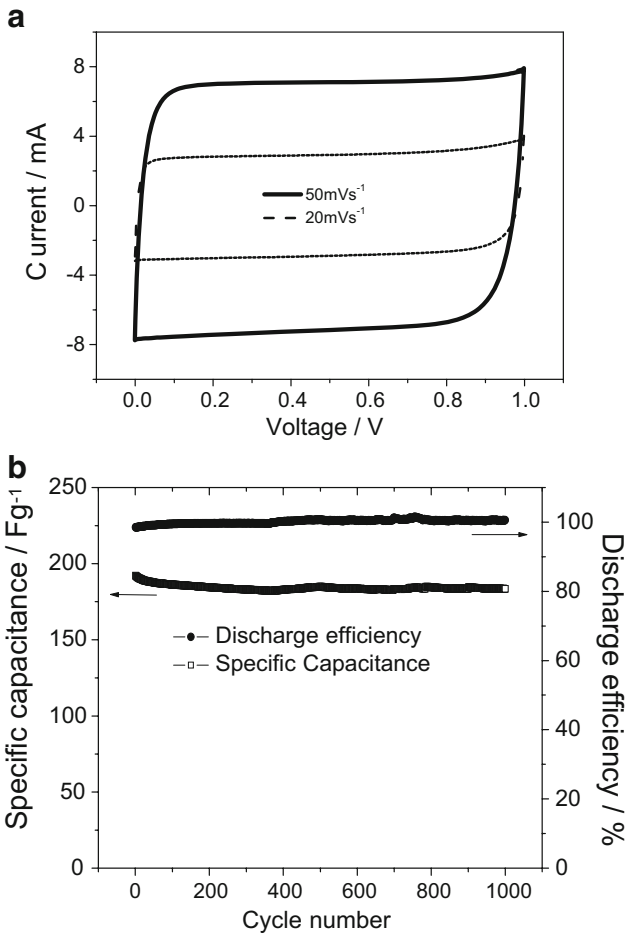

Fig. 5 CV curves of PEDOT-Functional SWNT at 20 and 50 mV s^{-1} (**a**) and discharge-specific capacitance and discharge efficiency (**b**), in two-electrode system

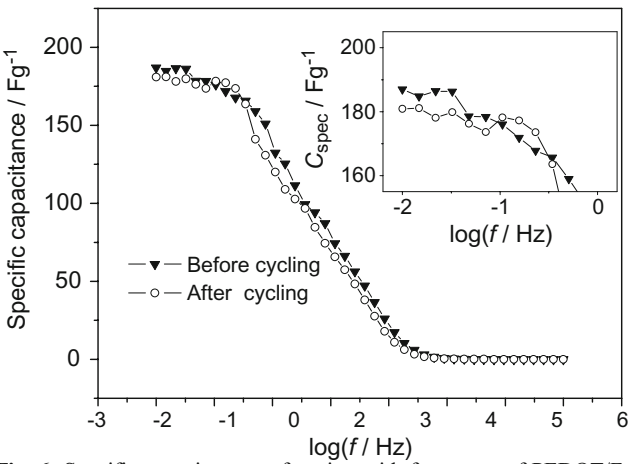

Fig. 6 Specific capacitance as function with frequency of PEDOT/F-SWNTs before and after 1000 cycles in 1 M KCl solution, two-electrode system

value increased obviously at −0.4V (vs SCE) because the PEDOT had been reduced (dedoped). However, the value was still about 1Ω, which is much smaller than that of PEDOT [11]. This confirms that the F-SWNTs enhanced the conductivity and electrochemical activity of PEDOT effectively.

The capacitance could be evaluated from the low-frequency data of the EIS spectra by the equation:

$$C = -1/(2\pi f Z_{\text{im}}) \quad (3)$$

In this equation, f represents frequency, and Z_{im} the is image (Z). The results from Eqs. 3 and 1 are shown in Fig. 4b. In the case of OCP, a capacitance plateau was achieved with frequency range from 230 to 10mHz. This means that the electric signal can reach the active position of the composite even at 230mHz. The capacitance plateau was wider and the specific capacitance is up to 170F g^{-1} at a frequency of 1Hz in the case of 0.5V (vs SCE) because of the open structure of PEDOT in an oxidized state. As for −0.4V (vs SCE), the plateau was narrow, which results from the compact structure of PEDOT in a reduced state. However, the specific capacitance was greatest in this case, which may be caused by the entrance of cations into PEDOT films to neutralize the negative charge of the F-SWNTs, as the F-SWNTs are immobile [22].

The electrochemical capacitance performance of the composite was also tested in a two-electrode system, which is more similar to the impractical operation than the three-electrode one does. Figure 5a presents the CV curves of the cell at 20 and 50mV s^{-1}. Although the pseudocapacitance behavior based on the faradaic charge transfer occurs at the three-electrode system, as shown by the wide peak around −0.1V in Fig. 2a, an ideal capacitive behavior is demonstrated from the voltammogram in the two-electrode system and even the scanning rate up to 50mV s^{-1}. Cycleability experiments with an operating voltage of 1V were performed at scanning rate of 50mV s^{-1} in the cell. The values of 192F g^{-1} at the beginning of cycling maintain stable over 1,000 cycles at such a high charge/discharge rate. A drop of only 8F g^{-1} is observed. More importantly, the discharge efficiency (discharging capacitance divided by charging capacitance) is almost 100% during the 1,000 cycles. In a word, the composite performed well in such a wide potential window [23]. Because the electrical energy storage (W) is proportional to capacitance (C) and voltage (U) according to

$$W = 1/2CU^2 \quad (4)$$

comparatively large W can be stored in this composite, despite C is not its advantage.

The relation of specific capacitance (calculated from Eqs. 2 and 3) and frequency of the two-electrode cell is shown in Fig. 6. The value of specific capacitance is 187F g^{-1} before cycling and still remains 180F g^{-1} at 10mHz and 170F g^{-1} at 230mHz after 1,000 cycles. Although there is a drop of 7F g^{-1}, the capacitance plateau is wider after 1,000 cycles, which indicates an even faster charge/discharge ability.

Conclusions

The homogenous coating of PEDOT on CNTs was successfully realized by functionalization of SWNTs. The short F-SWNTs allow the PEDOT/F-SWNTs composite prepared with a size of 100nm. The unique micro/nanotextural effectively increases the active/nonactive mass ratio and significantly reduces the ions diffusion length. Therefore, the energy can be fully extracted from PEDOT, so that the specific capacitance of the composite reached 210F g^{-1}, which is much higher than that of PEDOT (120F g^{-1}). Furthermore, the composite has a very fast charge/discharge ability (specific capacitance up to 170F g^{-1} at frequency of 1Hz) and stable cycleability with a discharge efficiency of almost 100%. All of above suggest that the PEDOT/F-SWNTs composite is among the excellent electrode materials for supercapacitors.

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