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Electropolymerized composite film of polypyrrole and functionalized multi-walled carbon nanotubes: effect of functionalization time on capacitive performance

Xiaofei Sun · Youlong Xu · Jie Wang

Abstract The composite film of polypyrrole and functionalized multi-walled carbon nanotubes (PPy/F-MWNTs) was prepared by electropolymerization. MWNTs were functionalized by sonicating with a concentrated solution of H_2SO_4/HNO_3 (3/1, volume ratio) in a water bath for different times. The carbon nanotubes (CNTs) are cut into smaller portions with more functional groups introduced on their surface when the sonicating time (nominated as functionalization time hereafter) is increased. However, the specific capacitance of the composite film reaches a maximum of 240 Fg^{-1} at the scanning rate of 10 $mV\ s^{-1}$ when MWNTs are functionalized for 24 h, which is about 205 Fg^{-1}, 225 Fg^{-1} and 232 Fg^{-1}, respectively, when MWNTs are functionalized for 6 h, 12 h and 48 h. At a current load of 1.0 A g^{-1}, PPy/F-MWNT composite film functionalized for 24 h (PPy/F-MWNTs (24 h)) retains 93.49% of its initial capacitance after 1,000 cycles of galvanostatic charge/discharge, and the discharge efficiency is higher than 98.15% during cycling. High specific capacitance, good rate performance, fast charge/discharge ability and long cycling life are ascribed to the synergistic effect of the two components to form a porous composite film as well as the easy accessibility of counter ions into the film. Therefore, PPy/F-MWNT (24 h) composite film is a kind of promising electrode material for supercapacitors. The mechanism of underfunctionalization and overfunctionalization of carbon nanotubes is also discussed.

X. Sun · Y. Xu (✉) · J. Wang
Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University,
Xi'an 710049, People's Republic of China
e-mail: ylxuxjtu@mail.xjtu.edu.cn

X. Sun · Y. Xu · J. Wang
International Center for Dielectric Research,
Xi'an Jiaotong University,
Xi'an 710049, People's Republic of China

Introduction

Supercapacitor (Electrochemical Capacitor) [1] is an attractive energy storage device for high efficiency energy utilization under the low carbon economy. It lies between conventional capacitors and lithium ion batteries in Ragone plot [2] and has more energy density than the former while more power density than the latter. Thus, it can be wildely used in portable electronics, railways, power stations, aeronaustics and astronaustics, etc. [2, 3]. Considering the limitation of fossil resources and their severe pollution to the global environment, supercapacitor has also been found a variaty of applications in electric vehicles (EVs) due to its fast charge/discharge ability and long lifetime merits [4–7].

Electrode material [2, 8] is one of the key issues restricting the commercialization of supercapacitors. Worldwide reseach has been devoted to develop high performance electrode materials. Among them, carbon nanotubes [9–12] (CNTs) including single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) are paid special attention due to their benificial properties for electronic double layer capacitance (EDLC) [13] such as high surface area, high conductivity and chemical stability. On the other hand, electrically conducting polymers [14–16] (ECPs) such as polyaniline (PANi), polypyrrole (PPy) and polythiophene (PTh) are also prospective electrode materials for supercapacitors because of the high fradaic pseudocapacitance they can provide from redox reactions [17] during charge/discharge. For example, polypyrrole [18] (PPy) and its derevatives are broadly investigated as high capacitance, low cost and environmentally friendly

electrode materials for supercapacitors. However, raw CNTs can only generate limited specific capacitance (typically lower than 100 F g^{-1}), while ECPs can't endure the volume change [19] during long life charge/discharge. Therefore, the concept of composite material emerges with an aim of combining the advantages of each component [20–24].

In this work, the composite film of polyppyrole and functionalized multi-walled carbon nanotubes (F-MWNTs) was systematically studied as an electrode material for supercapacitors. With an objective of scaling up the practical application of carbon nanotubes, MWNTs were first functionalized with different times to modify their physical and chemical properties and were then electropolymerized with PPy to prepare the PPy/F-MWNTs composite film. The electrochemical performance of the composite film as an electrode material for supercapacitors was investigated with special attention to the effect of functionalization time of MWNTs on the performance of the composite film.

Experimental

Materials

MWNTs (purity of CNTs >95%) were purchased from Shenzhen Nanotech Port Co., Ltd. The as-received MWNTs were purified in refluxing HNO$_3$ for 12 h to remove the impurities such as ash carbon and catalyst residues and were then functionalized as reported in Ref. [25]. The refluxed MWNTs were sonicated with a concentrated solution of H$_2$SO$_4$/HNO$_3$(3/1, volume ratio) in a water bath for 6 h, 12 h, 24 h and 48 h, respectively, to make the nanotubes smaller and to generate functional groups on their surface. Py (Fluka, 99%) was distilled prior to use and was stored at −10 °C. All other reagents were obtained from commercial sources and were used without further treatment.

Field Emission Scanning Electron Microscope (FESEM, JEOL, JSM-6700 F) and High Resolution Transmission Electron Microscope (HRTEM, JEOL, JEM-3010) were applied to compare the morphology of the as-received MWNTs and the functionalized ones. The carbon to oxygen ratio (C/O) in carbon nanotubes before and after functionalization was semiquantitatively anyalized by an Energy Dispersive X-ray spectrometer (EDX, Oxford INCA) affiliated to the FESEM. Confocal Laser Raman Spectroscopy (Jobin Yvon, LabRam HR 800) and Fourier Transform Infrared Spectroscopy (FTIR, Bruker, VERTEX 70) were also carried out to study the bonding structure in these CNTs.

Electrode preparation and characterization

The PPy/F-MWNTs composite film (1 cm×1 cm) was prepared on a tantalum (Ta) substrate in an aqueous solution of 0.1 mol l^{-1} Py and 0.1 wt.%–1 wt.%F-MWNTs. p-Toluenesulfonate acid (TOS) (0.3 mol l^{-1}) was added as a surfactant and supporting salt. The pH value was controlled less than 6 by TOS, too. A two-electrode synthesis system with Ta metal as both the counter electrode and the reference electrode was set up to galvanostatically electropolymerize the composite film. The current density was 1 mA cm^{-2} and the electropolymerization time was 1 h corresponding to an accumulated anodic charge of 3.6 C.

X-ray Diffraction (XRD, PANalytical, X'pert Pro) was applied to study the crystallinity of the PPy/F-MWNTs composite film. Its morphology was observed by the same FESEM in "Materials". An accurate electronic balance (AG 135, Mettler-Toledo) was used to determine the mass of the composite film.

Electrochemical tests

The electrochemical performance of the composite film as an electrode material of supercapacitors was investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GC) techniques in a symmetric two-electrode system where the counter electrode also acted as the reference electrode and was the same material as the working electrode. The electrolyte was 2 mol l^{-1} KCl aqueous solution. All the measurements were performed on the Versatile Multichannel Potentiostat 2/Z (VMP 2, Princeton Applied Research). The scanning rate of CV tests ranged from 10 mV s^{-1} to 200 mV s^{-1} between 0 and 0.6 V. The current load and voltage window of GC tests were 1.0 A g^{-1} and 0–0.6 V, respectively.

Results and discussion

The agglomeration of CNTs in aqueous solutions [26] prevents its practical application in synthesizing composite materials. In this work, the as-received MWNTs were first purified by refluxing in HNO$_3$ for 12 h to remove the residual catalyst and ash carbon and were then functionalized with a concentrated solution of H$_2$SO$_4$/HNO$_3$ for 6 h, 12 h, 24 h and 48 h, respectively, in a water bath. Figure 1 shows the morphology of the as-received MWNTs and that of the functionalized ones. The diameter and length of the as-received MWNTs are measured to be 40–60 nm and 5–15 μm, respectively, which are in good agreement with the nominal size the manufacturer provided. Both the diameter and length have significant wide distributions among bundles. Meanwhile, these bundles appear to be easily stacked together forming a rope network. By comparison, they are cut into smaller rods with shorter diameter and shorter length in F-MWNTs. More importantly, with the increase of functionalization time, the

Fig. 1 SEM images of the as-received MWNTs (**a**) and the MWNTs functionalized for 6 h (**b**), 12 h (**c**), 24 h (**d**) and 48 h (**e**), respectively
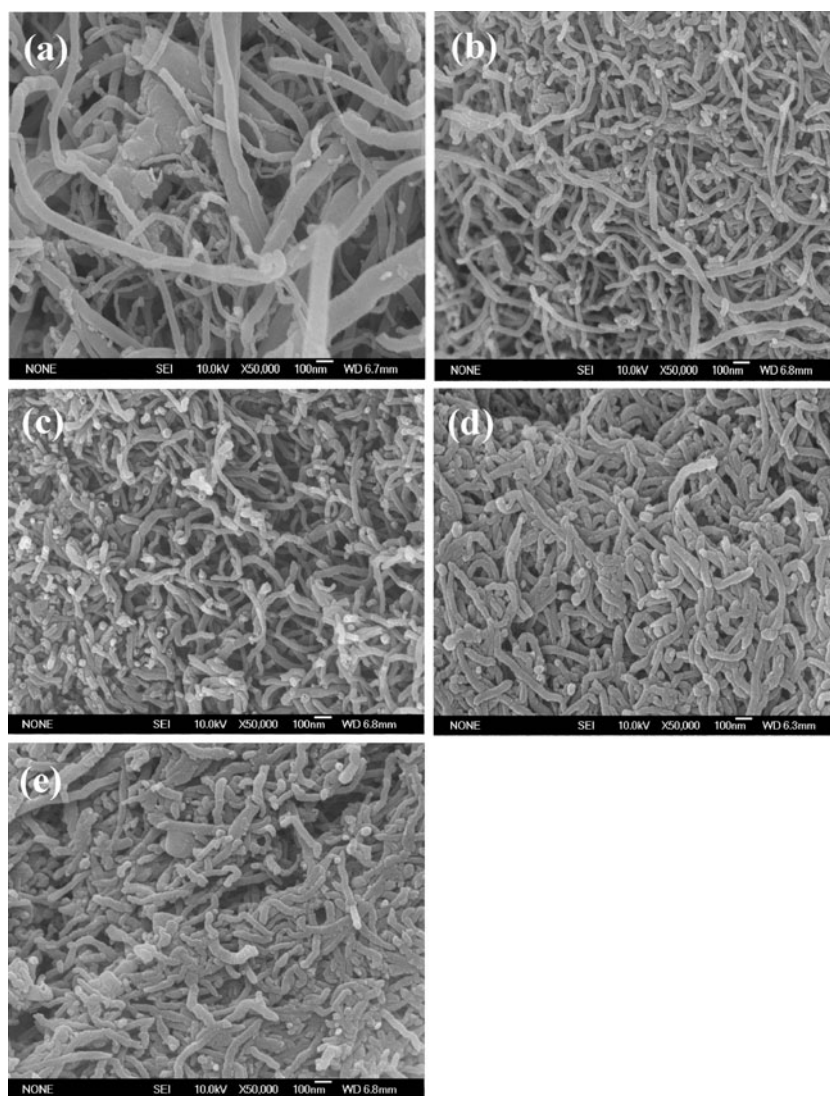
diameter becomes smaller and the length becomes shorter. When MWNTs are functionalized for 24 h (Fig. 1c), the diameter is about 25–35 nm and the length is about 300–400 nm, much less than the as-received ones. The multiple layers of the CNTs can be confirmed by HRTEM as shown in Fig. 2. It can be seen again that the as-received MWNTs are twisted together, while the F-MWNTs are less agglomerated, thus, clearly giving a layer number of more than 10. One may also note that the caps of the F-MWNTs are partially broken in Fig. 2b indicating the structure and morphology change accompanied with functionalization.

Fig. 2 TEM images of the as-received MWNTs (**a**) and the MWNTs functionalized for 48 h (**b**)
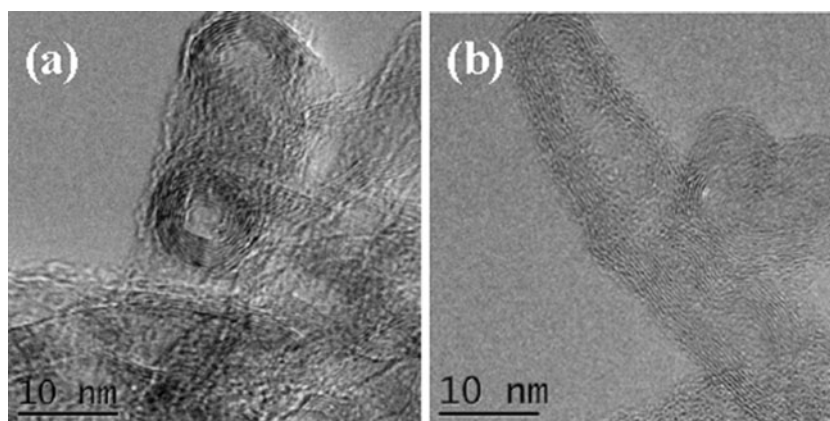
Although EDX is not an accurate quantitative technique, it can be used here under the same condition to compare the carbon to oxygen ratio (C/O) in MWNTs before and after functionalization. The results are shown in Table 1. The oxygen content increases with the increase of functionalization time but not very dramatically after 24 h. For one thing, it implies that some functional groups containing oxygen is introduced to the MWNTs after functionalization, and for another, it reveals that neither all surface nor all MWNTs can be functionalized. It seems 24 h is a good choice of cost-effective time for functionalizing MWNTs at first glance, which needs to be confirmed later by the electrochemical performance of the composite film. To determine what the functional groups are, FTIR spectra [27] of MWNTs functionalized for 48 h is shown Fig. 3. The IR peak at 1,510 cm^{-1} is assigned to the C=C streching mode from MWNTs. The peaks observed at 3,400 cm^{-1} and 1,650 cm^{-1} are –OH streching and C=O streching of the –COOH groups, respectively. The peaks at 1,200 cm^{-1} and 1,040 cm^{-1} corresponds to C–O streching. The peaks at 2,960 cm^{-1} and 2,870 cm^{-1} are due to –CH$_3$ streching. Comparing with the mere carbon groups in CNTs, functional groups such as –COOH, –C–O and –CH$_3$ are produced on MWNTs after functionalization. In Fig. 4, Raman spectroscopy [28] is further taken to clarify the influence of functionalization time on the structure of MWNTs. The peak at 1,600 cm^{-1} is called the tangential mode (G band) and the one at 1,350 cm^{-1} is the disorder mode (D band). The intensity ratio of D band to G band (D/G) nearly reaches one after refluxing in HNO$_3$ indicating that not only are the impurities removed but also that the initial functionalization has started in this step [24]. When the functionalization time is extended, the increasing D/G ratio demonstrates a higher level of functionalization that is in good agreement with the EDX data in Table 1. Another small characteristic peak in Raman spectra at 1,610 cm^{-1} shows the –COOH groups on the sidewalls of F-MWNTs [29], which is consistent with FTIR in Fig. 3.

Since the addition of the above functional groups, the solubility and wettability [28, 30] of MWNTs are expected to be improved. Figure 5 presents the photo of dispersed MWNTs in deionized water. The well-dispersed F-MWNTs are maintained for more than 1 month without any obvious change, whereas the as-received MWNTs always float on the upper surface of water even under stirring. It is known that the functional groups such as –COOH could result in partial ionic bonds and transform the nonpolar MWNTs to
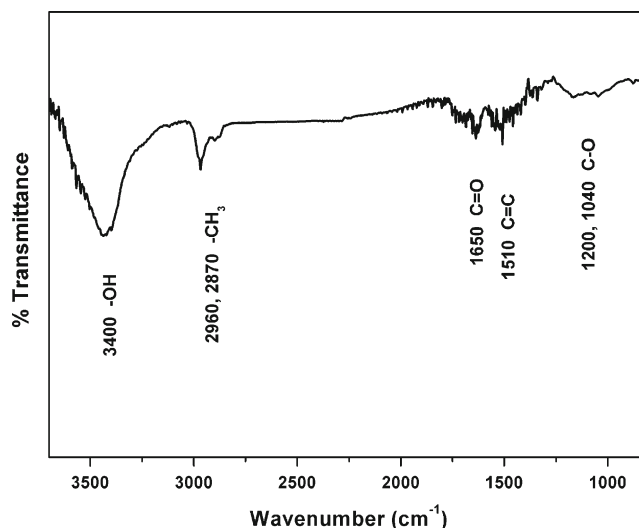

Fig. 3 FTIR spectra of the MWNTs functionalized for 48 h

polar ones. Therefore, the functionalized carbon nanotubes have better solubility and wettability in aqueous solutions than their as-received counterparts. This, no doubt, is beneficial for fabricating composite electrodes based on CNTs and is favorable in promoting the electrochemical performance of supercapacitors.

The F-MWNTs are then dissolved in deionized water to synthesize the PPy/F-MWNTs composite film. The X-ray diffraction patterns of pristine PPy film without CNTs and PPy/F-MWNTs composite film functionalized for 24 h are shown in Fig. 6. The composite holds the amorphous pattern of PPy except that the main broad peak at 25.4° in PPy shifts a little to a higher angle of 26.1° due to the addition of F-MWNTs which have two peaks at 26.5° and 43.8° [29]. The low magnification SEM image in Fig. 7a displays the porous structure of the composite film. With higher amplification in Fig. 7b, a special nanotube is observed to be partially coated by PPy while the other part is almost bare MWNT. Perhaps, the uncoated segment is not functionalized since functionalization is inhomogeneous as pointed out earlier by EDX. The unfunctionalized MWNT has a very weak bonding with PPy, so there is not much PPy coated on its surface. This nanotube happens to give a direct picture of the morphology of the composite film: PPy is coated on the surface of MWNTs and the two constituents (PPy and MWNTs) are interacted closely [31] resulting in a porous composite film that is beneficial to its supercapacitor performance. In summary, the synthesis mechanism [32] of the PPy/F-MWNTs composite film could be illustrated in Fig. 8. The as-

Table 1 C/O (carbon/oxygen) ratio characterized by EDX in MWNTs before and after functionalization

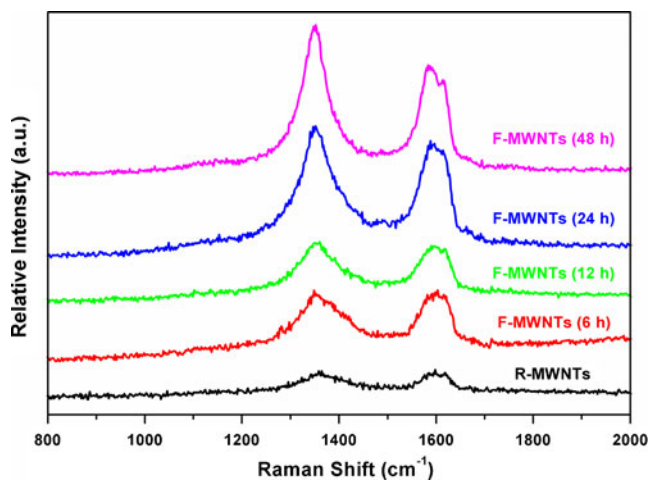| Functionalization time	As-received	6 h	12 h	24 h	48 h
C/O ratio (%)	99.38/0.62	88.50/11.50	82.56/17.44	76.67/23.33	75.94/24.06

Fig. 4 Raman spectroscopy of the refulxed MWNTs (R-MWNTs) and the subsequent functionalized ones for 6 h, 12 h, 24 h and 48 h, respectively

Fig. 6 XRD patterns of F-MWNTs powders, pristine PPy film and PPy/F-MWNTs (24 h) composite film. The F-MWNTs are functionalized for 48 h. The *inset zooms* in the peak region of 18°–34° (2θ)

received MWNTs are pretreated by purification and functionalization in mixed acid to remove the impurities and to introduce functional groups on the surface of MWNTs. Meanwhile, the MWNTs are cut into smaller rods with better solubility and wettability. At the beginning of electropolymerization, Py is polymerized on the surface of MWNTs with TOS^- doping and is connected to the substrate by electrostatic adsorption [33]. With continuous electropolymerization, the composite nanorods are covered by more PPy and grow larger in three dimensions [34]. As a result, a porous composite film with the skeleton of MWNTs is fabricated.

Figure 9 shows the cyclic voltammetry property of the PPy/F-MWNTs composite film in 2 mol l^{-1} KCl solution. It could be found that the CV curves of the PPy/F-MWNTs (6 h) composite film are rectanglelike when the scanning rates are 100 mV s^{-1} and lower, which indicate an ideal capacitance behavior. However, when the scanning rate is increased to 200 mV s^{-1}, the CV curve changes to a
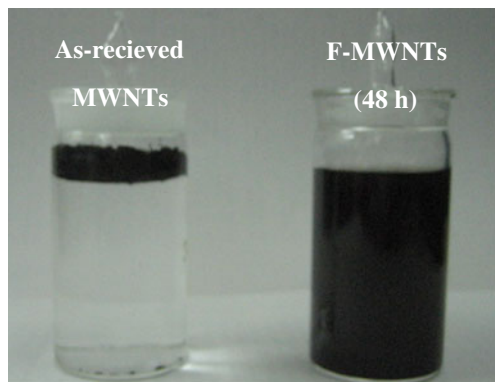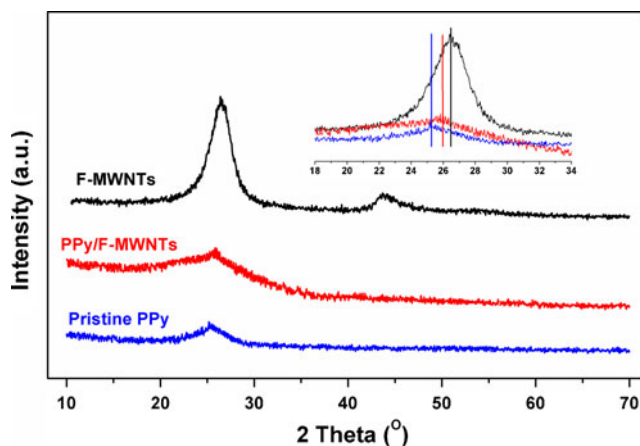

Fig. 5 Photograph of dispersed MWNTs in deionized water after 30 days (*left*: the as-received MWNTs, *right*: MWNTs functionalized for 48 h)

parallelogram shape indicating a resistancelike electrochemical behavior. Similarly, this shape transformation of CV curves starts at a scanning rate of 100 mV s^{-1}, 100 mV s^{-1} and 50 mV s^{-1}, respectively, when MWNTs are functionalized for 12 h, 24 h and 48 h. Hence, the composite film functionalized with less time exhibits faster charge/discharge ability. With increasing functionalization time, the MWNTs are cut into smaller size and are coated compactly by more PPy in the composite film. Consequently, the mesopores that counterions intercalate during charge/discharge are less accessible in the composite film, and the fast charge/discharge ability is deteriorated. Interestingly, the CV curves of PPy/F-MWNTs composite films functionalized for 12 h and 24 h are much alike, and the fast charge/discharge ability of the latter is even better at the scanning rate of 200 mV s^{-1}. All of the above suggests that the electrochemical performance of the composite film is not always better with the extension of the functionalization time and that there must be an apt time that the composite film exhibits excellent integrated perfomance.

The specific capacitances caculated from Fig. 9 are presented in Fig. 10. At the scanning rate of 10 mV s^{-1}, the specific capacitances of the four composites are 205 F g^{-1}, 225 F g^{-1}, 240 F g^{-1} and 232 F g^{-1}, respectively. When MWNTs are functionalized for less time, e.g. 6 h, carbon nanotubes take up a large fraction in the composite as long tubes and big rods, the composite thus shows rapid charge/discharge process and low capacitance like a double-layer capacitor. When the functionalization time is increased, MWNTs are cut into shorter and smaller rods which are wrapped densely by PPy in the composite film thus the PPy content is largely increased. As a result, the specific capacitance of the composite film is promoted by the pseudocapacitance from the conducting polymer. Here again, the PPy/F-MWNTs composite film functionalized for 24 h is found to have the highest specific capacitance at each scanning rate and the variation of capacitance among different

Fig. 7 SEM images of the PPy/F-MWNTs composite film where MWNTs are functionalized for 24 h. **b** is a higher magnification picture of **a**
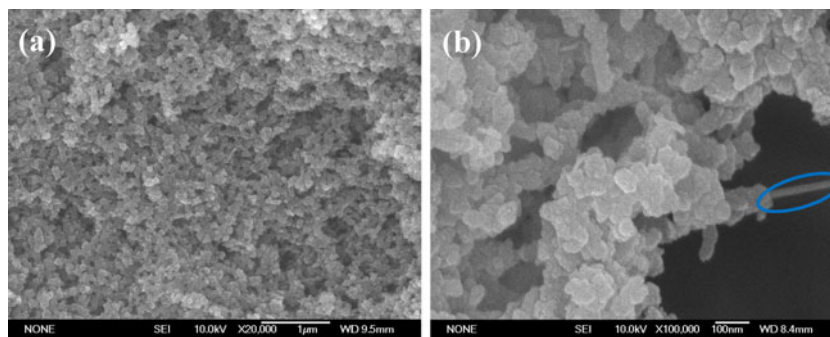
scanning rates is also smaller. At the scanning rate of 200 mV s^{-1}, this composite film still holds a specific capacitance of 220 F g^{-1} demonstrating its fast charge/discharge trait and excellent rate performance.

Generally, when MWNTs are functionalized for 6 h, 12 h and 24 h, the composite film exhibits higher specific capacitance in order; however, the one functionalized for 48 h doesn't follow this trend and shows lower capacitance than that functionalized for 24 h. Combined with the CV curves in Fig. 9, the composite film functionalized for 24 h shows the best electrochemical performance. The mechanism is considered to be the synergistic effect between F-MWNTs and PPy. In addition to enhancing the specific capacitance by combining the double layer capacitance from CNTs and the pseudocapacitance from PPy, when MWNTs are functionalized for 24 h, the nanotubes are cut into an appropriate size that has good connection with PPy while keeping the porous [35] and loose [36] structure of the composite film, which are beneficial to the intercalation/deintercalation of counterions into/out of the film, thus improving the charge/
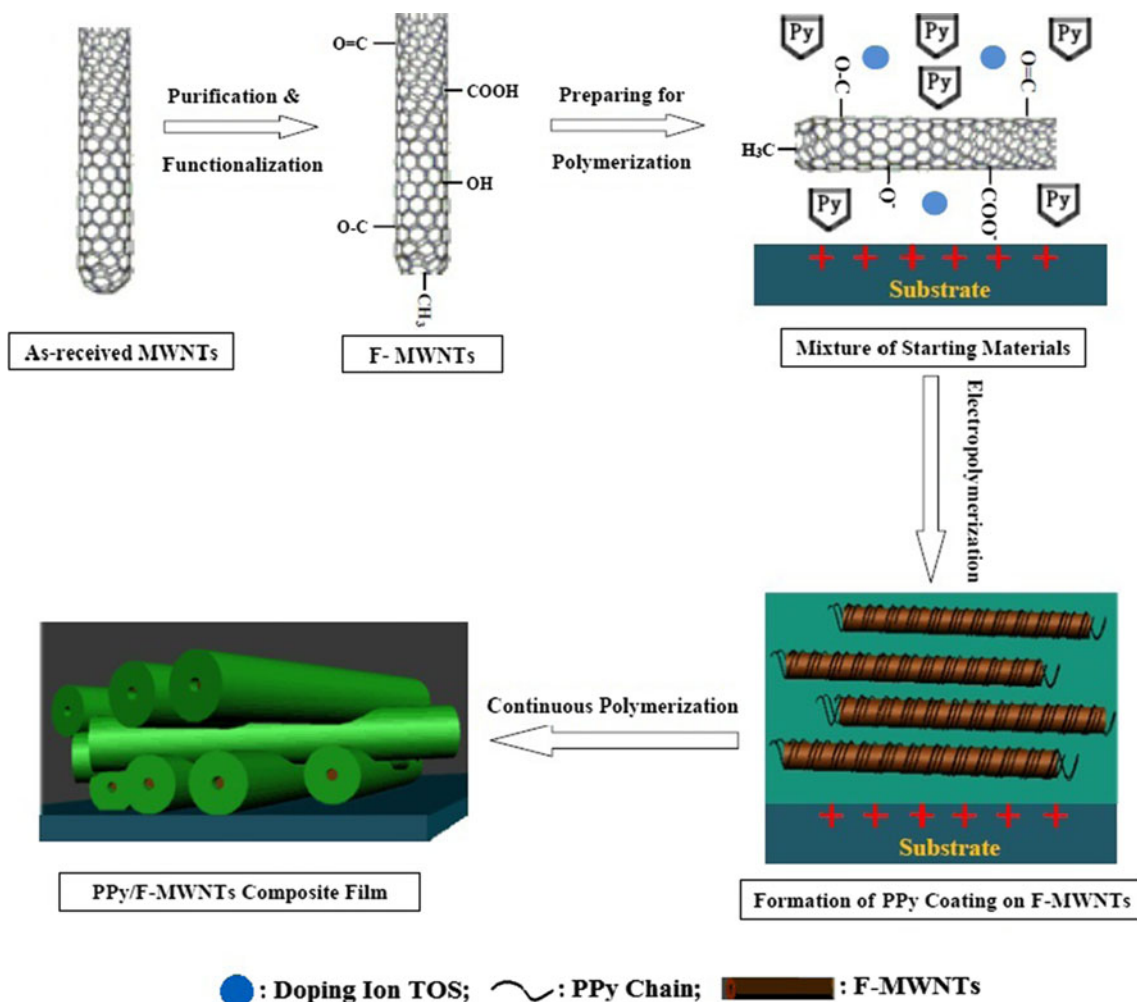

Fig. 8 A schematic diagram of the preparation of the PPy/F-MWNTs composite film
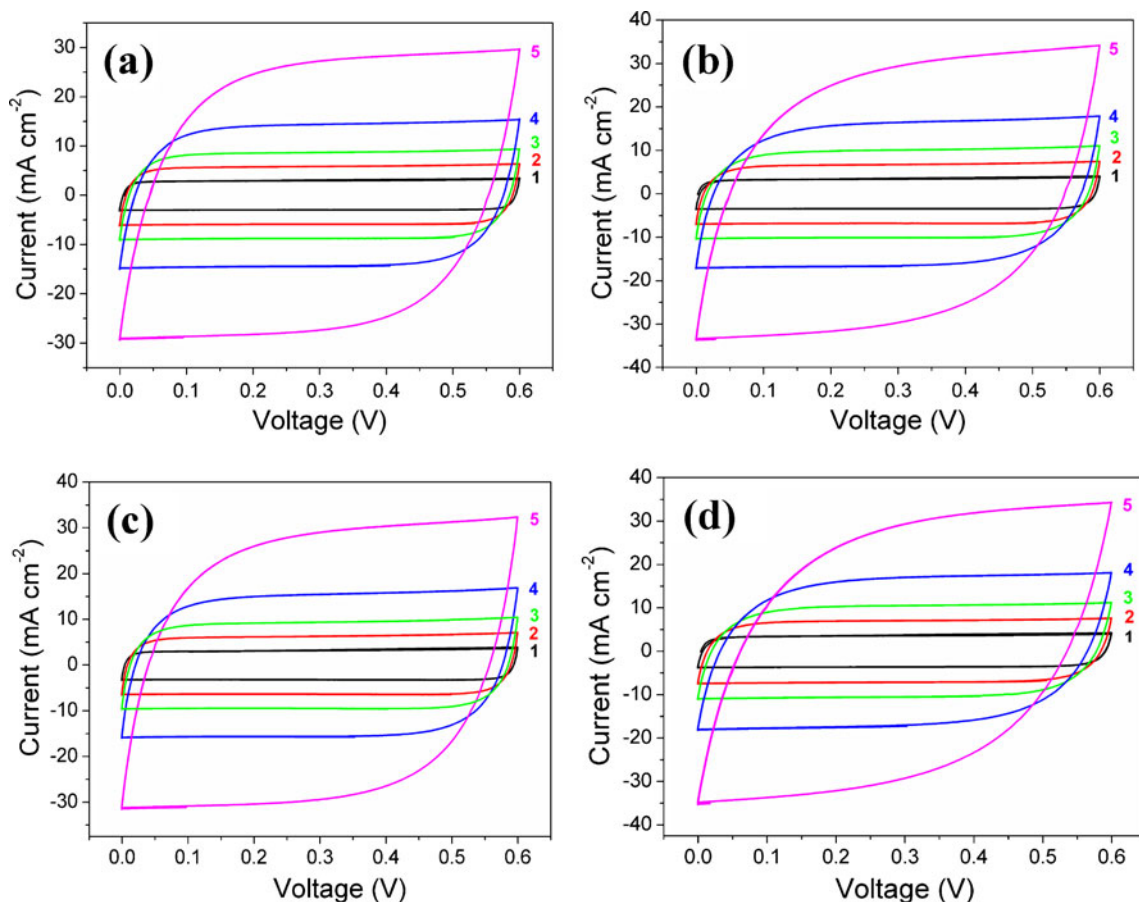
Fig. 9 CV curves of the PPy/F-MWNTs composite films at the scanning rates of 10 mV s^{-1} (*curve 1*), 20 mV s^{-1} (*curve 2*), 50 mV s^{-1} (*curve 3*), 100 mV s^{-1} (*curve 4*) and 200 mV s^{-1} (*curve 5*). MWNTs are functionalized for 6 h, 12 h, 24 h and 48 h, respectively in **a**, **b**, **c** and **d**.

The cyclic voltammetry is tested in a symmetric two-electrode system where the counter electrode also acts as the reference electrode and is the same material with the working electrode

discharge performance of the composite film. On the other hand, F-MWNTs could incorporate the volume change of PPy during cycling and prolong the cycle life of the
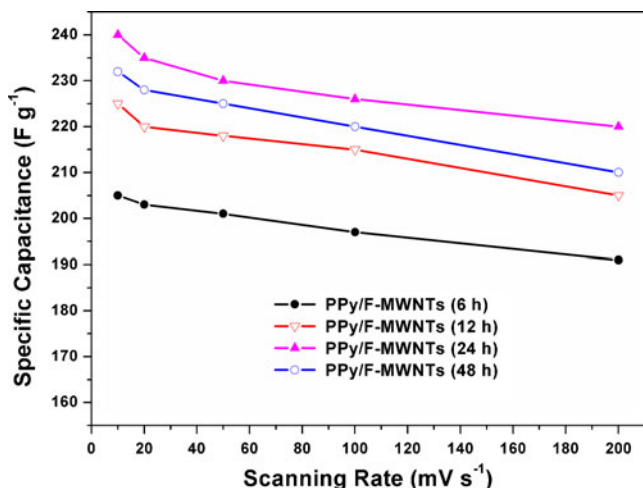

Fig. 10 Specific capacitances of the PPy/F-MWNTs composite films at different scanning rates
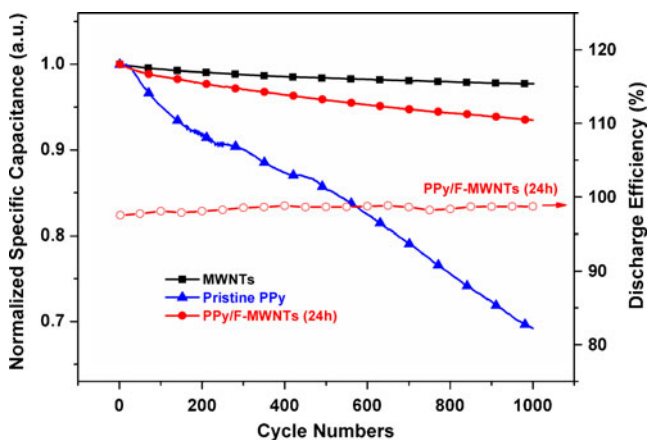

Fig. 11 Normalized specific capacitances of MWNTs, pristine PPy film and the PPy/F-MWNTs (24 h) composite film. The discharge efficiency of the composite during cycling is also plotted to the *right*. All data is collected by a symmetric two-electrode testing system between 0 and 0.6 V in 2 mol l^{-1} KCl aqueous solutions. The current load is 1.0 A g^{-1}. The preparation of MWNTs electrode could be found in Ref. [40]

composite film as will be discussed later. While for 48 h, the functionalization time might be too long and the nanotube structure might be destroyed to a certain degree. At the same time, MWNTs are cut so small that they are entirely coated with a thick PPy layer; hence, the skeleton network of MWNTs has less contribution and the composite forms a densely packed film that can't provide good diffusion path for counterions during charge/discharge especially at high rates. As a result, the composite film shows lower capacitance and poorer rate performance. In this case, the carbon nanotubes could be overfunctionalized. On the contrary, they are underfunctionalized when the functionalization time is 12 h or less.

Furthermore, the cycling performance of the PPy/F-MWNTs composite film functionalized for 24 h is investigated in Fig. 11 by the galvanostatic charge/discharge technique. The current load is 1.0 A g^{-1} and the voltage window is 0–0.6 V. MWNTs showing a capacitance retention as high as 97.75% after 1,000 cycles are also plotted for comparison. Pristine PPy film without MWNTs decays 30.8% of its initial capacitance under the same testing condition, which means the capacitance retention is only 69.2%. However, the capacitance retention of the PPy/F-MWNTs (24 h) composite film increases dramatically to 93.49%. Moreover, its discharge efficiency (discharge capacitance divided by charge capacitance) is higher than 98.15% during cycling. Therefore, the addition of MWNTs siganificantly improves the cyclability of PPy film. It is also noteworthy that the voltage window of symmetrical supercapacitors built by PPy electrodes with good cycling stability is only 0–0.4 V because of the shrinkages and cracks of electrodes during long life cycling [19]. However, the voltage window of PPy/F-MWNTs composite here is improved to 0.6 V thanks to the adaption of volume change by F-MWNTs and the smoother charge transfter [37] between PPy and F-MWNTs in the porous composite film. As a result, the energy density and power density of supercapacitors are improved. Besides CNTs, some other carbon materials such as carbon aerogel [38] and mesoporous carbon [39] have also been used to improve the electrochemical performance of polypyrrole in the literatures. Although the initial capacitance of PPy/F-MWNTs composite is lower than that of carbon aerogel modified PPy [38] which is 318 F g^{-1} at the scanning rate of 10 mV s^{-1}, the cycling performance of the former is much better, i.e., capacity retention of 93.49% after 1,000 cycles at 1 A g^{-1} comparing to that of 50% for the latter. Zou [39] et al. studied the supercapacitor performance of mesoporous carbon/polypyrrole composite which gives a specific capacitance of 261 F g^{-1}, 238 F g^{-1} and 203 F g^{-1}, respectively, at the scanning rate of 10 mV s^{-1}, 20 mV s^{-1} and 50 mV s^{-1}. However, PPy/F-MWNTs (24 h) composite in our work still holds a specific capacitance of 220 F g^{-1} even at the scanning rate of 200 mV s^{-1} demonstrating its better rate performance and faster charge/discharge trait. At the same time, the cycling performance of our material is also superior. Therefore, the composite film of PPy and functionalized cabon nanotubes shows outstanding rate performance and distincitve cycleability with high specific capacitance and will be a promising electrode mateiral for supercapacitors as high efficiency energy storage devices in a variety of applications such as hybrid electric vehicles.

Conclusions

Compared with underfunctionalization of 6 h or 12 h and overfunctionalization of 48 h, multi-walled carbon nanotubes functionalized for 24 h are cut into an appropriate size to form a porous film with PPy under electropolymerization. Synergistic effect of F-MWNTs and PPy in this condition makes the composite film integrate both the advantages of carbon nanotubes and polypyrrole, thus, having good electrochemical performance as an electrode material for supercapacitors. The specific capacitance could reach 240 F g^{-1} at the scanning rate of 10 mV s^{-1} and 220 F g^{-1} at the scanning rate of 200 mV s^{-1}. The capacitance retains 93.49% of its initial value after 1,000 cycles of galvanostatic charge/discharge and the discharge efficiency is higher than 98.15% during cycling. Further work is underway to closely study the interaction between CNTs and PPy in the PPy/F-MWNTs (24 h) composite film to optimize this kind of promising electrode material for supercapacitors.

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