Int. J. Electrochem. Sci., 7 **(2012)** 3205 - 3214

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

The Composite Film of Polypyrrole and Functionalized Multi-Walled Carbon Nanotubes as an Electrode Material for Supercapacitors

Xiaofei Sun[1,2], *Youlong Xu*[1,2,*], *Jie Wang*[1,2], *Shengchun Mao*[1,2]

[1] Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, P. R. China
[2] International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, P. R. China
[*] E-mail: ylxuxjtu@mail.xjtu.edu.cn

Received: 2 February 2012 / *Accepted:* 5 March 2012 / *Published:* 1 April 2012

The composite film of polypyrrole and functionalized multi-walled carbon nanotubes (PPy/F-MWNTs) was prepared by an optimized route according to our previous work. MWNTs were pretreated by sonicating with a concentrated H_2SO_4/HNO_3 (3/1 volume ratio) solution in a water bath for 24 h, and were then co-electropolymerized with pyrrole to synthesize the PPy/F-MWNTs composite. MWNTs were cut into smaller nanorods and a lot of functional groups such as –COOH and –OH were produced during the pretreatment. After electropolymerization, MWNTs were coated by PPy via these functional groups resulting in a homogeneous, stable and porous composite film. When used as an electrode material for supercapacitors, PPy/F-MWNTs composite shows a specific capacitance of 243 F g^{-1} at the scanning rate of 10 mV s^{-1}, and over 220 F g^{-1} at 200 mV s^{-1}. It retains 94% of its initial capacitance after 1000 cycles of galvanostatic charge/discharge and the columbic efficiency is higher than 98.7% during cycling.

Keywords: Polypyrrole; Carbon nanotubes; Supercapacitors; Capacitance; Functionalization

1. INTRODUCTION

As the fossil resource is being exhausted gradually and has made severe pollution to global environment, it is crucial to use energy more economically and more efficiently. Supercapacitor (Electrochemical capacitor) is a promising energy storage device for efficient energy usage [1]. It has higher energy density than convential capacitors and higher power density than batteries, thus could be widely applied in a variety of fields such as portable electronics, hybrid vehicles, and stationary energy storage to build a low carbon society [2-3].

Carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) are being widely studied as supercapacitor electrodes due to their unique properties such as high surface area, high conductivity, and chemical stability that suitable for double layer capacitance [4-6]. However, the general specific capacitance of raw CNTs is usually less than 100 F g^{-1}. On the other hand, electrically conducting polymers (ECPs) such as polyaniline (PANi), polypyrrole (PPy), polythiophene (PTh), and their derivatives, are also interested electrode materials for supercapacitors due to the higher capacity they can provide from pseudocapacitance [7-11], but the cyclability and rate performance still needs to be improved. Therefore, CNTs are reported to modify conducting polymers so as to get both higher capacitance and better cycling performance [12-14].

In our previous work [15, 16], a systematic investigation was carried out to study the influence of functionalization time of MWNTs on the electrochemical performance of PPy/F-MWNTs composite films. It is found that when MWNTs are functionalized for 24 h, the resulted PPy/F-MWNTs composite exibits higher specific capacitance as well as faster charge/discharge capability and longer cycling life. In the present paper, this specific composite film is closely investigated for their structure, morphology and electrochemical performance as an electrode material of supercapacitors.

2. EXPERIMENTAL

2.1. Materials

Py (Fluka, 99%) was distilled prior to use and was stored at - 10 ^{o}C under a nitrogen atmosphere. MWNTs (Purity > 95%) were purchased from Shenzhen Nanotech Port Co., Ltd. The as-received MWNTs were first refluxed in HNO_3 to remove the impurities such as residual catalysts and carbon ashes, and were then functionalized by sonicating with a concentrated H_2SO_4/HNO_3 solution (3/1 volume ratio) in a water bath for 24 h. Details of functionalization can be found in ref. 17. Other reagents were obtained from commercial sources and were used without further treatment.

Field Emission Scanning Electron Microscope (FESEM, JEOL, JSM-6700F) and High Resolution Transmission Electron Microscope (HRTEM, JEOL, JEM-3010) were used to compare the morphology of the as-received MWNTs and the functionalized ones.

2.2. Electrode preparation

The PPy/F-MWNTs composite film was galvanostatically prepared at a current density of 1 mA cm^{-2} on a tantalum substrate (Ta) in an aqueous solution of 0.1 mol L^{-1} Py and 0.1 wt. % - 1 wt. % functionalized MWNTs. The supporting salt was 0.3 mol L^{-1} p-toluenesulfonate acid (TOS) and the polymerization charge was 3.6 coulumb.

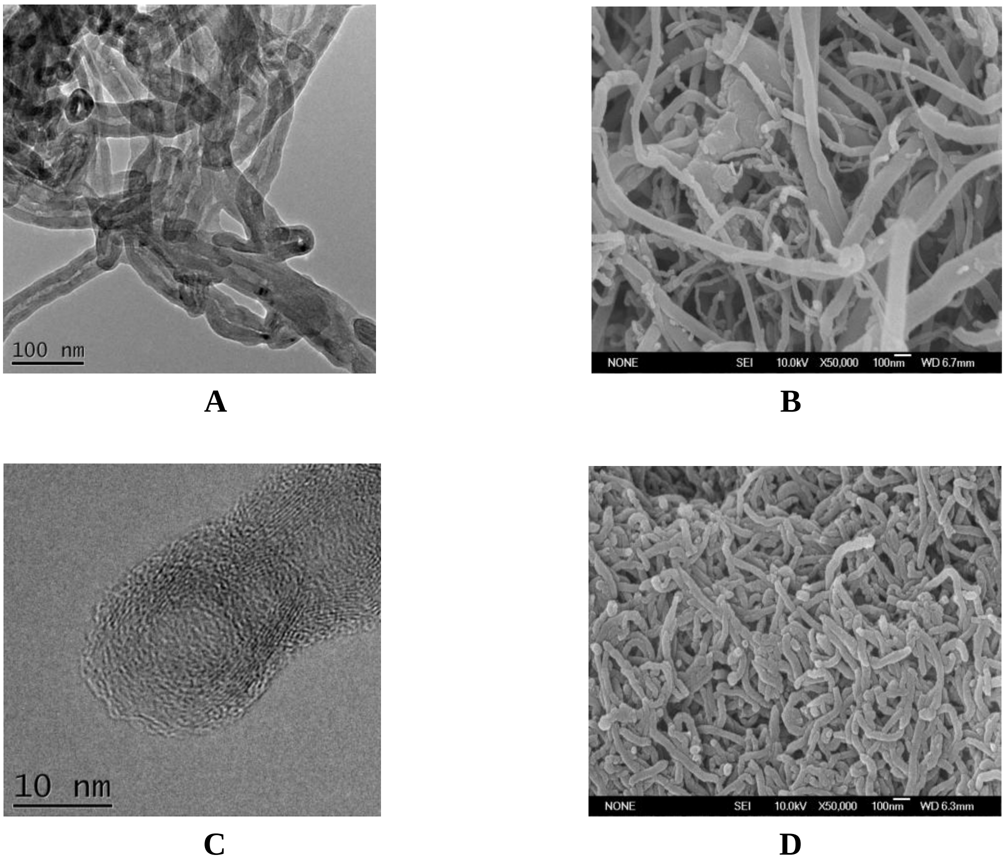
Fourier Transform Infrared Spectroscopy (FTIR, Bruker, VERTEX 70) and Thermogravametric Analysis (TGA, NETZSCH, STA 449C) were carried out to study the structure and the thermal behavior of PPy/F-MWNTs composite respectively. The morphology of the composite film was observed by the same FESEM in section 2.1.

2.3. Electrochemical performance

The electrochemical performance was tested on a Versatile Multichannel Potentiostat 2/Z (VMP 2, Princeton applied research). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GC) properties were investigated in a 2 mol L^{-1} KCl aqueous solution by a symmetric two-electrode testing system. The EIS was measured between 100 kHz – 10 mHz using an ac voltage of 10 mV at different dc potentials. The cycling performance was evaluated by GC approach with a current load of 1.0 A g^{-1} and a voltage window of 0-0.6 V.

3. RESULTS AND DISCUSSION

The PPy/F-MWNTs composite film was synthesized by two steps.



A **B**

C **D**

Figure 1. Morphology of the as-received MWNTs and F-MWNTs. (a) and (b) are HRTEM and FESEM images of the as-received MWNTs, (c) and (d) are that of F-MWNTs respectively.

The as-received MWNTs were first purified by refluxing in HNO_3 and were functionalized by sonicating in mixed H_2SO_4/HNO_3 so as to remove the impurities such as residual catalysts and carbon ashes, and more importantly to cut the long tubes shorter and to introduce functional groups on the surface of MWNTs for better connecting organic molecules in the next step. The final composite film was then obtained by electrochemical polymerization in a mixed aqueous solution of F-MWNTs, Py and TOS. As can be confirmed in Fig.1 (a) by HRTEM, the as-received MWNTs contain several tens of layers. FESEM picture in Fig.1 (b) further describes the diameter is about 40 - 60 nm and the length ranges from 5 μm to 15 μm. One also needs to note that the size distribution of the as-received MWNTs is very large and a lot of bundles are densely packed because of the one dimensional nano effect. By comparison, they are cut into homogeneous small rods after functionalization, where the diameter is only 25-35 nm and the length is about 300 – 400 nm as can be seen in Fig.1(c) and (d). Our previous work [15, 16] indicates that a lot of functional groups such as -COOH and -OH are introduced by this pretreatment, hence, the solubility and wettability [18] of carbon nanotubes are noticeably improved.

After electrochemical polymerization, F-MWNTs are coated by PPy via these functional groups and PPy is doped [19] by F-MWNTs, thus forming a porous film that is ideal for electrodes of supercapacitors.

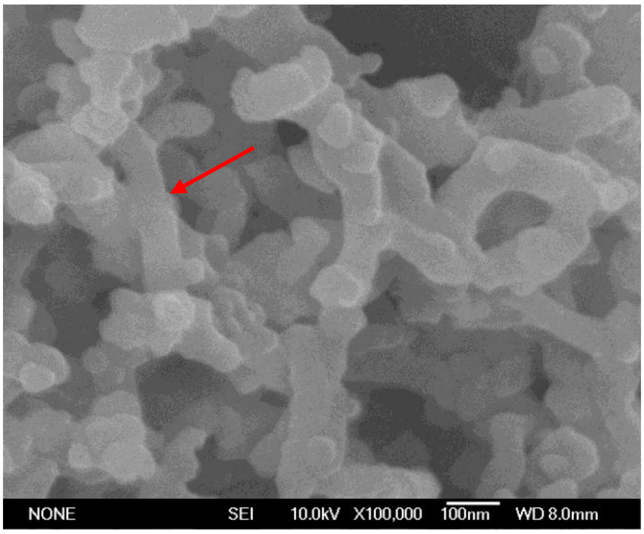


Figure 2. FESEM image of the PPy/F-MWNTs composite film.

As the FESEM image shown in Fig.2, the arrow indicates one of the carbon nanotubes, the outside of which is wrapped by PPy and a composite nano-rod is thus produced. A lot of these nano-rods stack together to form a porous film with the skeleton of carbon nanotubes. Fig.3 shows the FTIR patterns of the as-received MWNTs, pristine PPy film without CNTs and the PPy/F-MWNTs composite film. The PPy/F-MWNTs composite contains both the characteristic peaks of PPy and MWNTs which confirms their existence in the composite. In addition, those peaks of PPy/F-MWNTs locate in the middle of their counterparts of PPy and MWNTs, which suggests the interaction of the two components [20]. As a result, a stable porous composite film is formed.

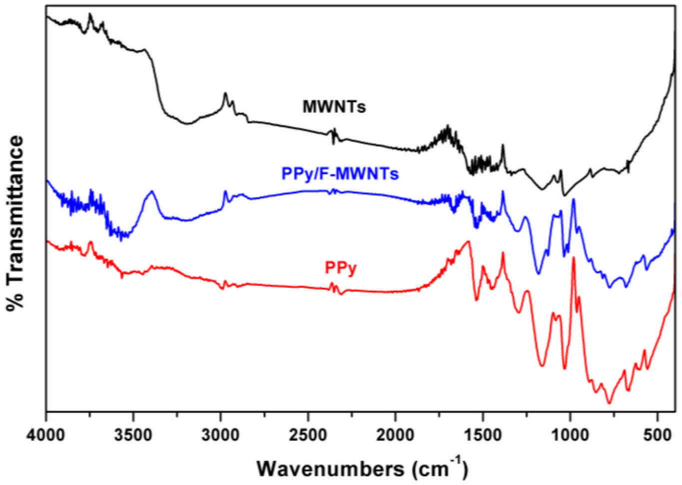


Figure 3. FTIR spectra of the as-received MWNTs, pristine PPy film and the PPy/F-MWNTs composite film.

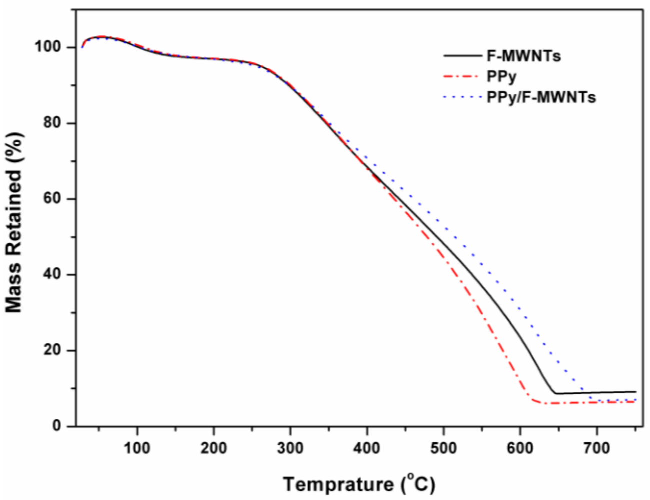
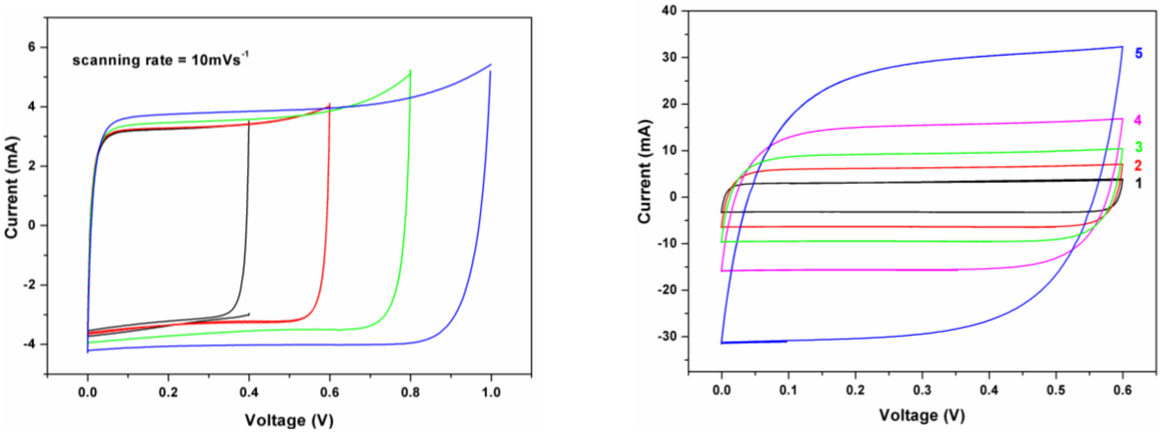


Figure 4. TGA curves of F-MWNTs (line), pristine PPy film (dash-dot) and the PPy/F-MWNTs composite film (dot).

The thermal stability of the composite was investigated by TGA technique. The ramp rate was 10 ^{o}C min^{-1} from room temperature to 750 ^{o}C under an air flow of 30 mL min^{-1}. The thermogram is shown in Fig.4 together with that of F-MWNTs powders and pure PPy film without CNTs doping. Although the three materials present similar thermal trend in air, carbon nanotubes have better stability than PPy as have been known. It is of great interest that F-MWNTs/PPy composite exhibits the best thermal stability. We think the functional groups play a great role here as the two components (F-MWNTs and PPy) are strongly bonded by these groups, and the synergistic effect [15] creates a 1+1>2 result. The good thermal stability is no doubt helpful to the cycling performance of the composite film as a supercapacitor electrode, which will be validated by the electrochemical properties in the rest of this paper.



A **B**

Figure 5. CV curves of the PPy/F-MWNTs composite film: (a). under different voltages of 0.4 V, 0.6 V, 0.8 V and 1.0 V at the scanning rate of 10 mV s^{-1}; (b). at different 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) between 0-0.6 V. Data are collected by a symmetric two-electrode system.

Fig.5 depicts the cyclic voltammetry property of PPy/F-MWNTs film in a 2 mol L^{-1} KCl solution. It would be found in Fig.5(a) that at higher voltages of 0.8 V and 1.0 V, there is a sharp tale at the end of charging, which might comes from hysterisis of Fradic reaction during voltammetric sweeping. Therefore, the voltage window was set between 0-0.6 V in Fig.5(b) to study the electric response at different scanning rates. The CV curves are rectangle-like indicating an ideal capacitance behavior when the scanning rates are 100 mV s^{-1} and lower. Although the CV curve changs a little bit to parallelogram shape at 200 mV s^{-1}, it is still much better than PPy without CNTs which shows a resistance-like electrochemical behavior [21] in Fig. 8 (a) . The specific capacitance (C_m, F g^{-1}) at different scanning rates in Fig. 5 can be calculated by the following equation:

$$C_m = \frac{4\times\int i\frac{dt}{dv}}{m} \qquad (1)$$

where i is the current (A), v is the voltage (V), t is the time (s), and m is the total mass of active materials in both positive and negative electrodes, respectively. A caculation factor 4 is applied here in the equation because the materials are being tested in symmetric two electrode systems. The results are shown in Fig.6. PPy/F-MWNTs composite holds a specific capacitance of 243 F g^{-1}, 237 F g^{-1}, 235 F g^{-1}, 228 F g^{-1} and 220 F g^{-1} respectively at the scanning rates of 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1} and 100 mV s^{-1}, and 200 mV s^{-1}. On the other hand, the specific capacitance of pristine PPy film is only 185 F g^{-1} at 10 mV s^{-1} which decreased quickly to 25.44 F g^{-1} at 200 mV s^{-1} [22]. This demonstrates the fast charge/discharge capablility and the good rate performance of the composite film as a supercapacitor electrode. In Fig.2, MWNTs are coated by PPy and act as the skeleton of the film network. Since cabon nanotubes are good electron conductors, they can provide electron transfer path in the composite and contribute to the fast charge/discharge trait of the composite film.

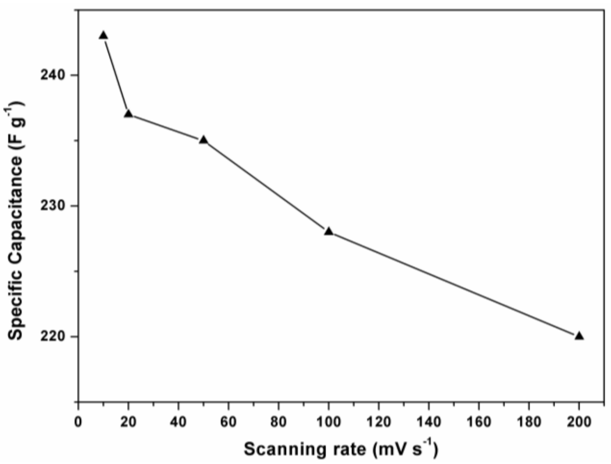


Figure 6. Specific capacitance of the PPy/F-MWNTs composite film at different scanning rates on the symmetric two-electrode testing system.

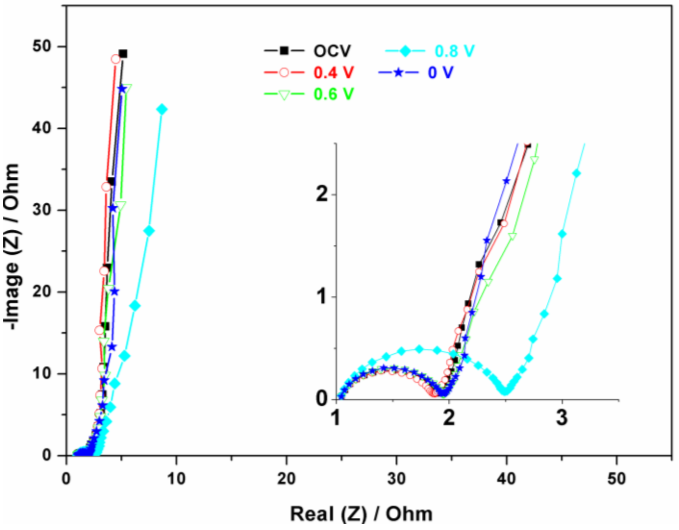
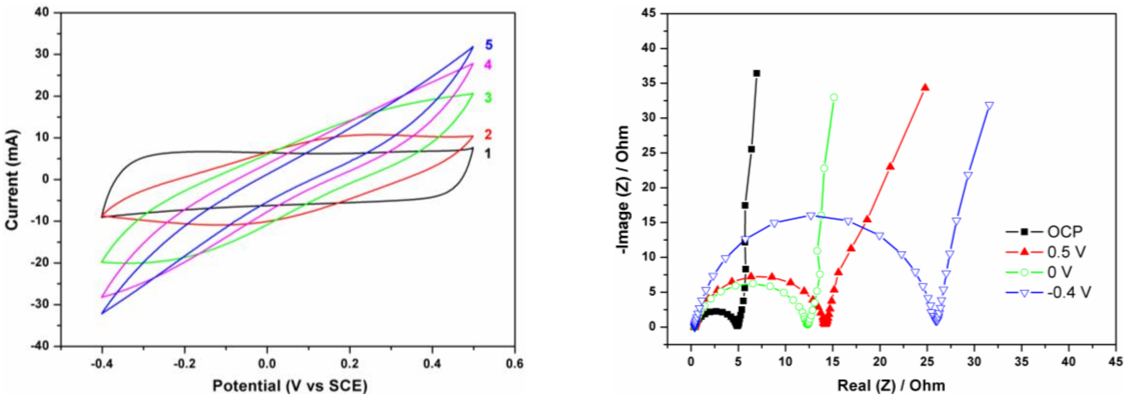


Figure 7. EIS of the PPy/F-MWNTs composite film under different voltages. Tested on a symmetric two-electrode system.

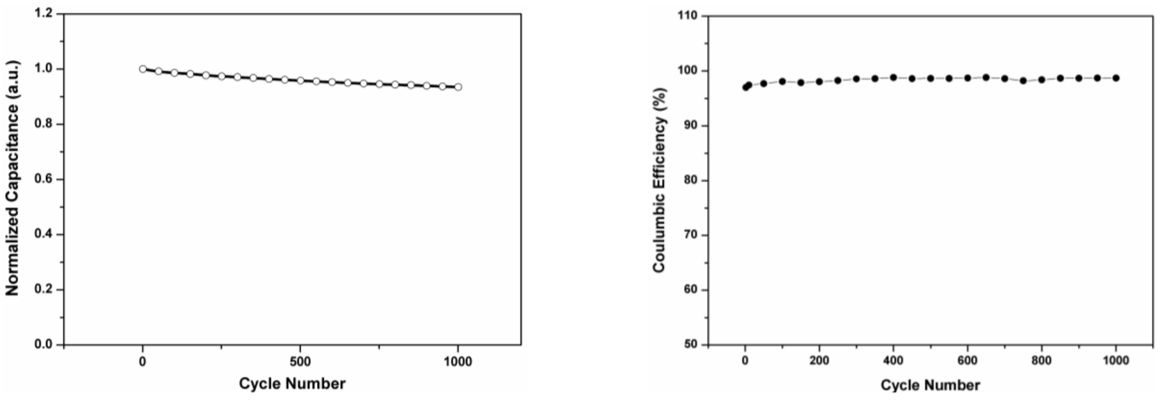
Electrochemical impedance spectroscopy was then used to measure the impedance of the composite film at different voltages in Fig.7. The Nyquist plot consists of two parts: the charge transfer resistance (Rct) at high frequencies and the warburg diffussion resistance (Rw) at low frequencies. At open circuit voltage (OCV), the charge transfer resistance (semi-circle) is 1 Ω, which increases to 1.5

Ω when the voltage is increased to 0.8 V. However, pristine PPy film [22] without carbon nanotubes has a Rct value as high as 5 Ω at open circuit potenial (OCP) which increases to 26 Ω when the potential is changed to -0.4 V (v.s SCE in three-electrode testing system) as shown in Fig. 8 (b). As stated above, the addition of carbon nanotubes increases the specific surface area of the composite and forms a porous film, which inturn improves the counterion diffusion from the elctrolyte into the film (vice versa). Therefore, the impedance angle at low frequency region is nearly -90^{o} and shows an ideal capacitance behavior. Besides the improvement of electron transfer by CNTs, the EIS explains that the fast charge/discharge capability is also a result of the reduction of ionic impedance in the composite film.



A B

Figure 8. CV curves at different scanning rates (a) and EIS under different potentials (b) of pristine PPy film. Data are collected by a three-electrode testing system where the counter electrode is Pt and the reference electrode is saturation mercury electrode (SCE). The scanning rate is 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) respectively in (a).



A B

Figure 9. Normalized capacitance (a) and discharge efficiency (b) of the PPy/F-MWNTs composite film during cycling in a 2 mol L^{-1} KCl aqueous solution. Tested on a symmetric two-electrode system.

Furthermore, the cycling performance of the PPy/F-MWNTs composite film is investigated by galvanostatic charge/discharge technic in Fig.9. It retains 94% of the initial capacitance after 1000 cycles (Fig.9 (a)) and the discharge efficiency (discharge capacitance divided by charge capacitance, Fig.9 (b)) is higher than 98.7% during cycling. Hence, PPy/F-MWNTs composite film can be used as a high efficiency supercapacitor electrode with excellent cyclability and fast charge/discharge ability. One needs to note that 0.6 V is a higher stable voltage than 0.4 V [23] that pristine PPy film can provide in KCl electrolyte on a two-electrode system. The elevated voltage is thought comes from the incorporation of volume change during cycling by CNTs and the more stable thermal behavior accompanied (see Fig.4). Thereby, the energy density and power density are enchanced.

In summary, the mechanism of the improved electrochemical performance of PPy/F-MWNTs composite film is considered to be the synergism [15,16] between PPy and F-MWNTs. After functionalization, MWNTs are cut into an appropriate size that could have a good connection with PPy via functional groups such as –COOH and –OH. During electropolymerization, F-MWNTs are coated by PPy and PPy is doped by F-MWNTs. With continous polymerization, a porous and loose [24] composite film is fabricated, which is very helpful for counterion diffusion in the electrolyte, thus promotes the rate performance of the composite film. On the other hand, carbon nanotubes can endure the volume change of PPy during cycling with good thermal behavior, thus prolongs the cycling life of supercapacitors. In addition, the specific capacitance is increased by the double layer capacitance from MWNTs and the pseudocapacitance from PPy [25]. Therefore, PPy/F-MWNTs composite film integrates both the merits of carbon nanotubes and polypyrrole. Carbon nanotubes have good conductivity, high surface area and excellent mechanical property, while PPy is high-capacity, low-cost and enviromental friendly. Consequently, the PPy/F-MWNTs composite film shows good electrochemical performance such as high capacity, fast charge/discharge ability, long cycling life, large energy and power density, therefore is a promising electrode material for high efficiency supercapacitors.

4. CONCLUSIONS

Composite film of PPy and F-MWNTs functionalized for 24 h is a good candidate electrode material for supercapacitors. The specific capacitance could reach 243 F g^{-1} at the scanning rate of 10 mV s^{-1}, and 220 F g^{-1} at 200 mV s^{-1}. Moreover, it shows very rapid charge/discharge ability and long cycling life due to the easy accessibility of counterions into the film and the synergistic effect of the two components. Further work is underway to study the detailed interaction between carbon nanotubes and PPy in the composite during charge/discharge by Electrochemical Quartz Crystal Microblance (EQCM).

ACKNOWLEDGEMENTS
Financial supports from the National Natural Science Foundation of China (Grant No. 20804030) and the Natural Science Foundation of Shaanxi Province (Grant No. 2009JQ6004) are gratefully acknowledged.

References

1. B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamental and Technological Applications*, Kluwer Academic/Plenum Publisher, New York (1999)
2. G. Lota, K. Fic and E. Frackowiak, *Energy Environ. Sci.*, 4 (2011) 1592
3. P. Simon and Y. Gogotri, *Nat. Mater.*, 7 (2008) 845
4. K. H. An, W. S. Kim, Y. S. Park, Y. C. Choi, S. M. Lee, D. C. Chung, D. J. Bae, S. C. Lim, and Y. H. Lee, *Adv. Mater.*, 13 (2001) 497
5. R. H. Baughman, A. A. Zakhidov and W. A. deHeer, *Science*, 297 (2002) 787
6. J. H. Kim, K. W. Nam, S. B. Ma, and K. B. Kim, *Carbon*, 44 (2006) 1963
7. H. Y. Mi, X. G. Zhang, X. G. Ye, and S. D. Yang, *J. Power Sources*, 176 (2008) 403
8. L. B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater.*, 12 (2000) 481
9. Y. Xu, J. Wang, W. Sun, and S. Wang, *J. Power Sources*, 159 (2006) 370
10. M. D. Ingram, H. Staesche, and K. S. Ryder, *Solid State Ionics*, 169 (2004) 51
11. J. H. Sung, S. J. Kim, and K. H. Lee, *J. Power Sources*, 124 (2003) 343
12. J. Xu. K, Wang, S. Z. Zu, B. H. Han, and Z. Wei, *ACS Nano*, 4 (2010) 5019
13. J. Wang, Y. Xu, F. Yan, J. Zhu, J. Wang, F. Xiao, *J. Solid State Electrochem.*, 14 (2010) 1565
14. C. Peng, J. Jin, and G. Z. Chen, *Electrochim. Acta*, 53 (2007) 525
15. X. Sun, Y. Xu, and J. Wang, *J. Solid State Electrochem.*, Published online, DOI: 10.1007/s10008-011-1619-x
16. X. Sun, Y. Xu, and J. Wang, presented at ICMAT 2011, Singapore
17. J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science*, 280 (1998) 1253
18. Z. Chen, K. Kobashi, U. Rauwald, R. Booker, H. Fan, W. F. Hwang, and J. M. Tour, *J Am. Chem. Soc.*, 128 (2006) 10568
19. G. Z. Chen, M. S. P. Shaffer, D. Coleby, G. Dixon, W. Z. Zhou, D. J. Fray, and A. H. Windle, *Adv. Mater.*, 12 (2000) 522
20. S. Lefrant, M. Baibarac and I. Baltog, *J. Mater. Chem.*, 19 (2009) 5690
21. J. Wang, Y. Xu, X. Sun, F. Xiao and S. Mao, *Acta Physio-Chimica Sinica*, 23 (2007) 877
22. X. Sun, Master Thesis, Graduate School of Xi’an Jiaotong University, Xi’an (2008)
23. J. Wang, Y. Xu, X. Chen, and X. Sun, *Compos. Sci. and Technol.*, 67 (2007) 2981
24. J. Wang, Y. Xu, X. Chen, X. Du, and X. Li, *Acta Physica Sinica*, 56 (2007) 4256
25. B. E. Conway and W. G. Pell, *J Solid State Electrochem.*, 7 (2003) 637