

Dao-jun Guo · Hu-lin Li

Well-dispersed multi-walled carbon nanotube/polyaniline composite films

Received: 21 June 2004 / Accepted: 7 September 2004 / Published online: 15 February 2005
© Springer-Verlag 2005

Abstract Multi-walled carbon nanotube (MWNT)/ polyaniline (PANI) composite films with good uniformity and dispersion were prepared by electrochemical polymerization of aniline containing well-dispersed MWNTs. The results of transmission electron microscopy (TEM) show that aniline can be used to solve MWNTs via formation of donor–acceptor complexes. Scanning electron microscopy (SEM), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) revealed that the well arrangement of PANI-coated MWNTs in these films facilitated improved electron and ion transfer relative to pure PANI films and this may be due to the strong interaction between MWNTs and PANI.

Keywords Carbon nanotubes · Polyaniline · Electropolymerization

Introduction

Carbon nanotubes (CNTs) have demonstrated a wealth of exceptional structural, mechanical and electronic properties [1] that have made them show a lot of potential for a vast range of applications, including quantum wire [2], tips for scanning probe microscopy [3] and molecular octylthiophene [4]. Recent experimental studies have shown that, much attention has been paid to the use of CNTs in composite materials, e.g. the formation of nanotube/polymer composites is considered a promising approach to synergetic effects [5, 6]. Many polymers have

been used as matrix materials in CNT/polymer composites for various target applications. For example, CNTs can be used as a conductive filler for CNT/poly(3-octylthiophene) composites [7], and CNT/poly(phenylenevinylene) (PPV) [8], CNT/polypyrrole [9], CNT/PMMA [10] composites have also been reported. Moreover, conjugated polymers with the incorporation of CNTs show potential for electronic device applications [11], microelectromechanical systems (MEMS) to supercapacitors and sensors to solar cells and displays [12–14].

Among various conducting polymers, polyaniline (PANI) is a unique and promising candidate for practical applications due to its good processability, environmental stability, and reversible control of electrical properties by both charge-transfer doping and protonation [15, 16]. The dispersion of CNTs into PANI matrices for the fabrication of CNT/PANI composites has naturally stimulated significant interest among researchers. To date, several methods have been developed to prepare these polymer/nanotube composites efficiently including dissolving the polymer in an organic solvent containing the multi-walled carbon nanotube (MWNT) suspension [17], melt mixing [18], in situ polymerization [19], grafting macromolecules to the CNTs [20], and electrochemistry [9]. However, the development of such composites has been impeded by the inability to disperse CNTs in the polymer matrix due to the lack of chemical compatibility between the polymers and the CNTs [21–24]. This is, in part, because of the difficulties in material processing arising from insolubility of the pristine CNTs in most solvents. There is therefore interest in increasing the strength of the bonding between the nanotubes and the polymer matrix so that the interaction between the composite materials can be increased.

Recent studies have shown that the introduction of MWNTs to polyaniline composites enhances the electrical properties (the room temperature resistivity is decreased by one order of magnitude as compared to polyaniline) by facilitating charge-transfer processes between the two components [25]. Here, we report on the

D. Guo
College of Chemistry and Chemical Engineering,
Lanzhou University,
Lanzhou, 730000, People's Republic of China

H. Li (✉)
State Key Laboratory of Applied Organic Chemistry, Lanzhou,
730000, People's Republic of China
E-mail: lihl@lzu.edu.cn
Tel.: +86-931-8912517
Fax: +86-931-8912582

fabrication and characterization of MWNT/PANI composites by electrochemical polymerization of an aniline solution containing different MWNT contents. Electron microscopy showed that they have good uniform nanotube dispersion. The electrochemical impedance spectroscopy (EIS) analysis was used to investigate the doping effect of MWNTs on PANI film.

Experimental sections

Preparation of MWNT-aniline solutions

Multi-walled carbon nanotubes were produced via the chemical vapor deposition method. The samples—as produced—were purified by procedure already reported in the literature [26]. In a typical experiment, MWNTs were added to 5 ml of aniline with different contents of 0, 2, 4, and 8 wt% (weight percent with respect to aniline monomer). The mixture was heated at reflux for 5 h in the dark. After reflux for a short time, the original colorless aniline solution first became brownish and then turned dark red, indicating that MWNTs have been dissolved in the aniline. After being cooled to room temperature, MWNT/aniline solutions were obtained by filtration through 0.1 μm diameter Supor Membrane disc filters (Gelman).

Preparation of MWNT/PANI composite films

Multi-walled carbon nanotube/polyaniline composite films were formed on the platinum disk working electrode with an area of 1 cm^2 by the cyclic voltammetry (CV) technique at 100 mV s^{-1} between -0.2 and 1.2 V for 50 cycles in a solution of 0.5 M H_2SO_4 containing 0.325 M aniline dissolved MWNTs in various mixture ratios.

Measurements

All electrochemical experiments were performed with a CHI660A potentiostat/galvanostat using a glass cell with

a three-electrode configuration. The working electrode was a platinum disk encapsulated in epoxy resin and the working surface was the round face of the disk. A platinum sheet was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials in this paper are presented on the SCE scale. The working electrode was polished mechanically using emery paper (grade 1,200–1,500) to a mirror surface and then cleaned by potential cycling between -1.0 and 1.2 V at 50 mV s^{-1} in 0.5 M H_2SO_4 until a stable voltammogram was obtained.

Electrochemical impedance spectroscopy measurements for the MWNT/PANI composite films electrode were performed in 0.5 M H_2SO_4 solution under open circuit potential in an a.c. frequency range 10 kHz–10 MHz with an excitation signal of 5 mV.

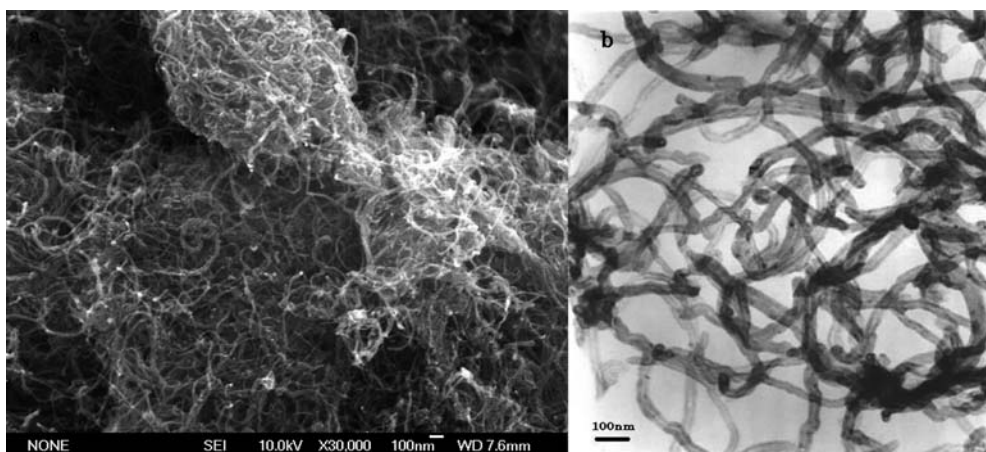
The morphology and microstructure of the MWNT/PANI composite films were characterized using transmission electron microscopy (TEM) (Hitachi600, Japan) and scanning electron microscopy (SEM) (Model JSM-6700F, Japan). All the electrochemical experiments were carried out at 20 ± 1 $^\circ\text{C}$.

Results and discussion

MWNT-aniline solutions

Figure 1a shows the typical SEM image of the purified MWNTs. It can be seen that the MWNTs are very long and highly entangled in the solid state to form a dense, robust, network structure. It is very difficult for the MWNTs to be well dispersed in the polymer matrix. However, after refluxing in aniline, the experiment indicates that the MWNTs exhibit high dissolution in most solvents such as acetone, THF, DMF and other common organic solvents that are compatible with aniline [27, 28]. Figure 1b shows the typical TEM image of a MWNT-aniline solution diluted with acetone after evaporation. It was obvious that the MWNTs have been completely peeled off and present as individual tubes and showed similar structural features to that before

Fig. 1 Typical SEM image of purified MWNTs (a) and TEM image of dissolved MWNTs (b) after evaporation of the solvent



dissolution, suggesting no damage had occurred to the MWNTs (of course, TEM would not reveal evidence of a chemical reaction of the MWNTs).

Electropolymerization of MWNT/PANI composite films

The MWNT/PANI composite films were formed by electropolymerization of aniline dissolved MWNTs with different concentrations. Figure 2 shows the typical CV growth of MWNT/PANI film in aqueous 0.5 M H_2SO_4 + 0.325 M aniline dissolved with MWNTs of 8 wt%. Continuous potential scanning at 100 mV s^{-1} in the potential range between -0.2 and 1.2 V gives a thin, uniform green coating on the platinum electrode. The CV exhibited three pairs of redox current peaks centered roughly at 0.2 , 0.5 and 0.8 V , respectively, and their peak heights increased with the increase of number of potential cycles, suggested that the films were conductive and also electroactive. According to the literature [29], the oxidation peaks A and C can be assigned to the oxidation of PANI in the leucoemeraldine oxidation state to the emeraldine oxidation state, and the further oxidation of the emeraldine oxidation state, respectively. The interpretation of the middle peaks B/B' corresponding to the benzo/hydroquinone (BQ/HQ) couple [30].

Electrochemical response of the MWNT/PANI composite films

To elucidate the effect of MWNTs on the property of PANI films, electrochemical performance of composite films was evaluated by carrying out CV measurements in $0.5 \text{ M H}_2\text{SO}_4$, as shown in Fig. 3. The cyclic voltammograms of the MWNT/PANI films (Fig. 3a) showed a

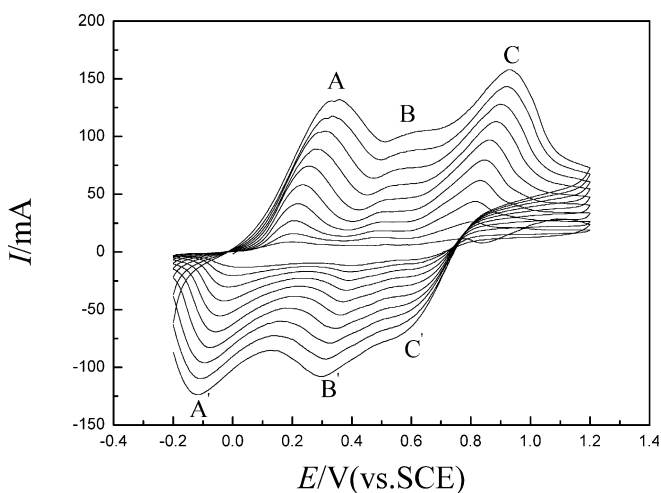


Fig. 2 Cyclic voltammograms of the first ten potential cycles on Pt electrode in aqueous $0.5 \text{ M H}_2\text{SO}_4$ + 0.325 M aniline dissolved with MWNTs of 8 wt%, scan rate, 100 mV s^{-1}

couple of strong and broad oxidation and reduction waves. Their wave currents were much stronger than that of pure PANI films electrode s(Fig. 3b). The voltammograms reveal the electrodes are stable in sulfuric acid solution within the sweeping potential range. Close comparisons of CV curves between MWNT/PANI electrode and pure PANI electrode show that a MWNT/PANI electrode not only displays a higher background current in the potential sweep but also there exist faradaic currents, which is believed to arise from the contribution of the loaded MWNT. It has been reported that PANI was considered as a promising material for electrochemical capacitors due to the existence of different oxidation states. Owing to the higher current in the voltammograms of the MWNT/PANI electrode than a pure PANI electrode, a larger capacitance for capacitors equipped with MWNT/PANI electrode can be anticipated.

To illustrate the performance of the resulting electrodes in supercapacitors, constant current charge–discharge cycling was performed to measure the capacitance in a $0.5 \text{ M H}_2\text{SO}_4$ solution. Typical galvanostatic charge–discharge curves at a current of 0.5 mA between 0 and 0.8 V are shown in Fig. 4. It can be clearly seen that the MWNT/PANI electrode cell presents higher capacitance than the pure PANI and this has been considered as the contribution of faradaic pseudocapacitance of MWNT/PANI.

Morphology of the MWNT/PANI composite films

Figure 5a, b shows SEM micrographs of the surface of the pure polyaniline and the MWNT/PANI composite films on the Pt electrode, respectively. As can be seen, the pure polyaniline films are a loose and fibrillar. For the MWNT/PANI composite films, SEM images re-

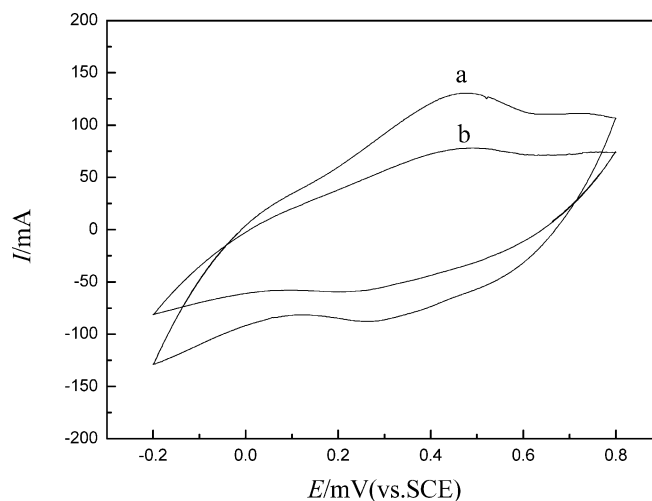


Fig. 3 Cyclic voltammograms of the MWNT/PANI films dissolved with MWNTs of 8 wt% (a) and pure PANI films (b) coated Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$, scan rate, 100 mV s^{-1}

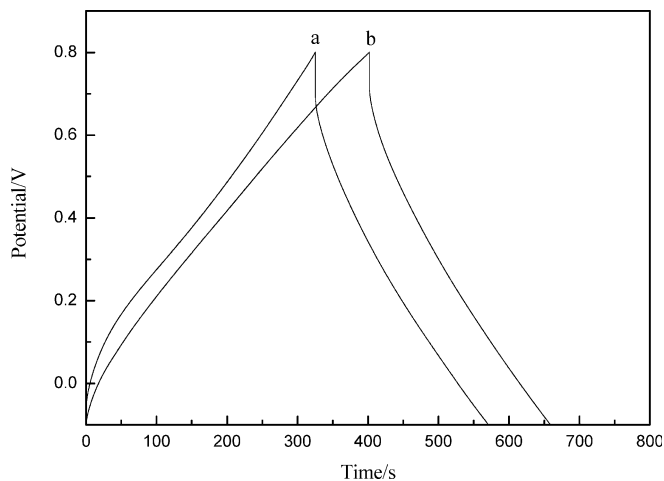


Fig. 4 Charge–discharge curves with a 0.5 mA current of capacitors equipped with **a** PANI and **b** MWNT/PANI films dissolved with MWNTs of 8 wt%

vealed the uniform and cable-like morphology of the nanostructures in which the outer layers were polyaniline and the inner layer were comprised of MWNTs [31]. The rough outer amorphous polyaniline layer had an average thickness of about several tens of nanometers. It is to be expected that this difference in surface morphology will play an important role in subsequent processes, e.g., impedance spectra.

Impedance spectra of the MWNT/PANI composite films

It is well known that CNTs can be dissolved in aniline via the formation of a donor–acceptor complex [32]. The solubility of single-walled carbon nanotubes (SWNTs) in aniline is up to 8 mg ml^{-1} . Therefore, the dependence of impedance spectra of the conducting polymer composite may be considered for studying the characteristics of film structures and the kinetics and mechanisms of charge transfer and ion transport in the MWNT/polymer film interface and polymer film/electrolyte interface. Figure 6 shows the impedance spectra of the MWNT/

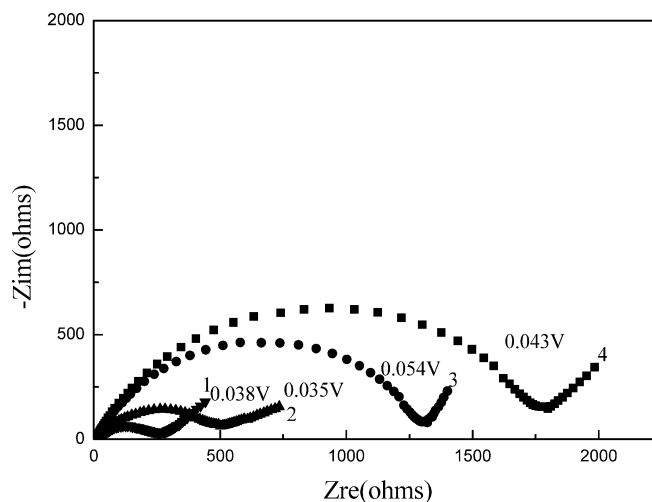
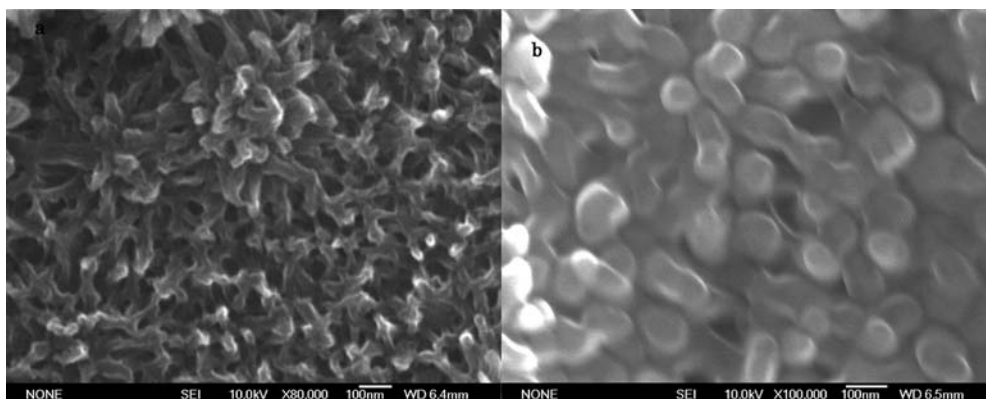


Fig. 6 The impedance spectra of MWNT/PANI composite films with content of 8 wt% 1, 4 wt% 2, 2 wt% 3, 0 wt% 4 prepared using similar conditions in 0.5 M H_2SO_4 solution at open circuit potential

PANI composite films containing different amounts of MWNTs in 0.5 M H_2SO_4 solution. It can be seen that the plot in Fig. 6 shows a single semi-circle in the high-frequency region and a straight line in the low-frequency region for all spectra can be observed. The high-frequency arc is the overall contact impedance generated from the electrical connection between MWNT/PANI composites and the backing plate as well as the charge transfer at the contact interface between the electrode and the electrolyte solution.

In spite of the similar shape of the impedance spectra, there is an obvious difference between the diameters of the four semi-circles. That is, the diameters of the semi-circles declines greatly with the increasing doping content of MWNTs in aniline. In other words, the bulk-film transport of electrons and the charge transfer resistance (R_{ct}) of MWNT/PANI composite films are much lower than that of the pure polyaniline films. This means that the MWNTs inside the polyaniline matrix may lead to a faster electron transport in the bulk-film and charge transfer in the parallel polyaniline film/solution interface

Fig. 5 Typical SEM images of the pure polyaniline (**a**) and MWNT/PANI composite films (**b**) with a content of MWNTs 8 wt%



and MWNTs/solution interface, compared to that in the originally single polyaniline film/solution interface. In conducting polymer/carbon nanotubes (CP/CNs) composites, it has been suggested that either the polymer functionalizes the CNs [33, 34], or the CPs are doped with CNs, i.e., a charge transfer occurs between the two constituents. This fact may suggest that the MWNT has an obvious improvement effect, which makes the composites have more active sites for faradaic reactions and a larger specific capacitance than pure PANI. Also, this results in enhanced electric conductivity, lowers the resistance, and facilitates the charge-transfer of the composites.

Conclusions

The MWNT/PANI composite films were synthesized successfully by electropolymerization of aniline containing well-dissolved MWNTs. Aligned MWNT films were encapsulated in the cores of the growing polymer chains, resulting in the formation of a PANI-MWNT hybrid material. Owing to the specific and complex nature of MWNTs, the results revealed an improvement in various physical and chemical properties of PANI, such as thermal stability, conductivity and charge carrier mobility. The improvements made in the various properties of the present MWNTs are expected to enhance the application potential of the conducting polymer without hampering its chemical properties. The method described here may be useful for developing new applications of these nanocomposite films in molecular electronics and other fields.

References

- Iijima S (1991) *Nature* 56:354
- Tans SJ, Devoret MH, Dai HJ et al (1997) *Nature* 386:474
- Dai HJ, Hafner JH, Rinzler AG, Colbert DT, Smalley RE (1996) *Nature* 384:147
- Tans SJ, Verschueren ARM, Dekker C (1998) *Nature* 393:49
- Hamon MA, Chen J, Hu H, Chen YS, Itkis ME, Rao AM et al (1999) *Adv Mater* 11:834
- Riggs JE, Guo ZX, Carroll DL, Sun YP (2000) *J Am Chem Soc* 122:5879
- Musa I, Baxendale M, Amaratunga GAJ, Eccleston W (1999) *Synth Met* 102:1250
- Coleman JN, Curran S, Dalton AB, Davey AP, Carthy MB, Blau W et al (1999) *Synth Met* 102:1174
- Chen GZ, Shaffer MSP, Coleby D, Dixon G, Zhou WZ, Fray DJ, Windle AH (2000) *Adv Mater* 12:522
- Pang SJ, Wu QD, Gao HJ, Xue ZQ (1996) *Solid State Commun* 97:579
- Friend RH, Gymer RW, Holmes AB et al (1999) *Nature* 397:121
- Williams OA, Whitfield MD, Jackman RB, Foord JS, Butler JE, Nebel CE (2001) *Appl Phys Lett* 78:3460
- Kleinsorge B, Ferrari AC, Robertson J, Milne WIJ (2000) *Appl Phys* 88:1149
- Drury CJ, Mutsaers CMJ, Hart CM, Matters M, deLeeuw DM (1998) *Appl Phys Lett* 73:108
- Skotheim TA, Elsenbaumer RL, Reynolds JR (1997) *Handbook of conducting polymers*. New York
- Premamoy G, Samir KS, Amit C (1999) *Eur Polym J* 35:699
- Jin L, Bower C, Zhou O (1998) *Appl Phys Lett* 73:1197
- Jin Z, Pramoda KP, Xu G, Goh SH (2001) *Chem Phys Lett* 337:43
- Jia ZJ, Wang ZY, Xu CL, Liang J, Wei BQ, Wu DH et al (1999) *Mater Sci Eng A* 271:395
- Zengin H, Zhou W, Jin J, Czerw R, Smith DW, Echehoyen L et al (2002) *Adv Mater* 14:1480
- Hadjiev VG, Iliev MN, Arepalli S, Nikolaev P, Files BS (2001) *Appl Phys Lett* 78:3193
- Peigney A, Flahaut E, Laurent C, Chastel F, Rousset A (2002) *Chem Phys Lett* 352:20
- Bower C, Rosen R, Zhou O (1999) *Appl Phys Lett* 74:3317
- Haggenmueller R, Gommans HH, Rinzler AG, Fischer JE, Winey KI (2000) *Chem Phys Lett* 30:219
- Cochet M, Maser WK, Benito AM, Callejas MA, Martinez MT, Benoit JM et al (2001) *Chem Commun* 1450
- Li QW, Yan H, Cheng Y, Zhang J, Liu ZFJ (2002) *Mater Chem* 12:179
- Sun Y, Wilson SR, Schuster DI (2001) *J Am Chem Soc* 123:5348
- Li XH, Wu B, Huang JE et al (2003) *Carbon* 41:1670
- Genies EM, Boyle A, Lapkowski M, Tsintavis C (1990) *Synth Met* 36:139
- Genies EM, Lapkowski M, Penneau JFJ (1988) *Electroanal Chem* 249:97
- Terrones M, Hsu WK, Kroto HW, Walton DRM (1999) *Top Curr Chem* 199:189
- Ajayan PM, Schadler LS, Giannaris C, Rubio A (2000) *Adv Mater* 12:750
- Baibarac M, Baltog I, Lefrant S, Mevellec JY, Chauvet O (2003) *Chem Mater* 15:4149
- Sun YP, Fu K, Li Y, Huang W (2002) *Acc Chem Res* 35:1096