Macromolecular Research, Vol. 16, No. 1, pp 76-80 (2008)

Electrical Properties of Composite Films Using Carbon Nanotube/Polyelectrolyte Self-Assembled Particles

Byung-Soo Kim† and Kyung-Do Suh*

Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

Bumsu Kim†

Division of Inorganic Chemistry Exam, Bureau of Chemistry & Biotechnology Exam, Korean Intellectual Property Office (KIPO), Daejeon 302-701, Korea

Received September 3, 2007; Revised October 17, 2007

Introduction

Carbon nanotubes (CNTs)/polymer composites have been widely investigated to use the excellent properties of CNTs, such as electrical, thermal, and mechanical properties.[1-3] Recently, electrical properties of CNT/polymer composites have been studied for potential applications, such as fuel cell, sensor, transparent electrode for electric devices, and so on.[4-9] Especially, the CNT/polymer composite film with excellent electric conductivity is a promising candidate for industrial applications, such as electromagnetic interference (EMI) shielding material.[10] EMI shielding materials have been paid an attention to develop the long lifetime and the high efficiency of equipment in various fields, such as telecommunication, computer, military and aerospace, etc. Although metals have conventionally been used for EMI shielding, they have many defects such as corrosion, heavy weight and high hardness. To overcome these problems, the CNT/polymer composite was considered as promising EMI shielding material because of light weight, easy process and flexibility.[11]

However, the uniform dispersity of CNTs in polymer matrix is a challenge for applications because of aggregation by strong van der waals forces among CNTs. To improve the dispersity of CNTs in polymer matrix, some approaches have already been suggested, such as, using efficient mixing apparatus, functionalizing CNTs, and mixing surfactants (dispersants), and so on.[12-16]

In this study, to enhance the dispersity of CNTs in polymer matrix, CNTs coated polymer particles were used as building block for CNT/polymer composite films. The Layer-by-Layer (LbL) self-assembly was used to fabricate CNTs coated polymer particles because LbL self-assembly readily controlled the amount of CNTs on polymer particles by changing the number of adsorption cycles.

The CNTs coated polystyrene (PS) particles were synthesized by LbL self-assembly method with functionalized multiwall CNTs (fMCNTs) and polyelectrolytes (poly(diallyldimethylammonium chloride) (PDDA), poly(sodium 4-styrenesulfonate) (PSS)). To prepare negatively charged PS particle as core particle for LbL self-assembly, PS particles were chemically reacted with sulfonic acid. The amount of CNTs on the surface of PS particles was precisely controlled by the stepwise growth of fMCNT/polyelectrolyte multilayers on polymer particles. Composite particles with different quantity of fMCNTs were changed to fMCNT/PS composite films by hot press. The morphologies of fMCNT/polyelectrolyte self-assembled particles and fMCNT/PS composite films were observed by SEM. And fMCNT/polyelectrolyte multilayer on PS particles was confirmed by zeta potential analysis. In addition, the electrical conductivity and EMI shielding effectiveness of fMCNT/PS composite films were measured. It was suggested that electrical properties of fMCNT/PS composite films were efficiently adjusted by controlling the number of self-assembled multilayers on the surface of particles.

Experimental

Materials. Purified multiwall carbon nanotubes (MCNTs, CVD, 95%) were obtained from Iljin Nanotech Inc. Sulfuric acid (95%) and nitric acid (60-62%) were obtained from Junsei Chemical. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in water, M_w = 100,000 - 200,000), poly(sodium 4-styrenesulfonate) (PSS, M_w = 70,000) and poly(methyl methacrylate) (PMMA, M_w = 120,000) were purchased from Aldrich. Styrene monomer (Junsei) was purified through a removing column before use and ethanol (EtOH, 99.9%, J. T. Baker) and methylene chloride (99.9%, J. T. Baker) was regent grade. Poly(vinyl pyrrolidone) (PVP-40T, weight average molecular weight (M_w) = 4.0×10^4 g·mol^{-1}, Sigma) and di-2-ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, Wako) were purchased. 2,2-azobis(isobutyronitrile) (AIBN, Junsei) was recrystallized from methanol.

Chemical Oxidation of MCNTs. MCNTs were functionalized by a sonification treatment in a mixture of sulfuric acid and nitric acid (3:1) for 6 h at room temperature.[17] Functionalized MCNTs (fMCNTs) were diluted with deionized water and separated by centrifugation. They were continuously subjected to repeated redispersion/centrifugation in deionized water. Finally, fMCNTs obtained through these procedures were diluted to 0.0005 g fMCNTs/1 g deionized water.

*Corresponding Author. E-mail: kdsuh@hanyang.ac.kr
†These authors contributed equally to this work.

Preparation of Sulfonated PS Microspheres. Monodisperse polystyrene (PS) particles were synthesized by dispersion polymerization.[18] AIBN, PVP, Aerosol-OT, styrene and ethanol were weighted into 250 mL 4-necked glass reactor equipped with a mechanical stirrer, a refluxing condenser and a nitrogen inlet system. After mixing, the reactor with homogeneous solution was dipped into oil bath. Homogenous solution was polymerized at 70 °C for 24 h and stirring speed 40 rpm. The produced particles are repeatedly centrifuged and dried in vacuum at ambient temperature. The PS particles (0.5 g) were modified by mechanical stirrer with H_2SO_4 (50 g) at 18 h under room temperature.[19] The sulfonated PS particles were finally obtained by four centrifugations with ethanol and deionized water, and dried in vacuum at ambient temperature.

fMCNTs/Polyelectrolyte Multilayers on PS Particles by LbL Self-assembly. Polyelectrolyte (PDDA/PSS/PDDA) self-assembled PS particles were fabricated by LbL assembly method. The sulfonated PS particles (0.5 g) were mixed through mechanical stirrer in polyelectrolyte (PDDA and PSS) solutions consecutively. Modified PS particles were washed by centrifugation with deionized water. Polyelectrolytes (PDDA and PSS) were dissolved in deionized water at a concentration of 10 mg/mL. Prepared PS particles with PDDA/PSS/PDDA multilayer were poured and mixed in the amount of 6 wt% fMCNTs solution. After the exceeded fMCNTs were removed by three centrifugations, the polyelectrolyte/fMCNTs coated PS particles were obtained. Desirable $(PDDA/fMCNTs)_n$ multilayers coated PS particles were fabricated by alternating adsorptions of PDDA and fMCNTs on PS particles.

Preparation of fMCNT/PS Composite Layer on PMMA. fMCNT/PS composite films were fabricated to measure electrical properties. First, a PMMA substrate was prepared by the solvent removal from the PMMA dissolved in methylene chloride. Then, fMCNT/polyelectrolyte self-assembled particles were dropped on the PMMA film. Finally, bilayer films comprising of a PMMA layer and a fMCNT/polymer (PS) composite layer were obtained by hot press method for 2 h at 120 °C.[20] The procedure was shown in Figure 1.

Characterizations. The sulfonic groups on the surface of PS particles were confirmed by FT-IR (Nicolet, Mahgna IR-550). The zeta-potential of fMCNTs/polyelectolyte self-assembled particles was measured by zeta-potential analyzer (Otsukael, ELS-8000). The morphology of fMCNTs composite particles was observed with scanning electron microscope (SEM, JSM-6300, JEOL). A thermogravimetric analysis (TGA) was carried out in the temperature range of 25-800 °C at a heating rate of 10 K/min under a nitrogen atmosphere using a SDT2960 (TA instrument, Inc.) To confirm electric conductivity of fMCNTs composite films, the four-probe method was used at room temperature in the range of 0.1 Hz-10 MHz. In addition, electromagnetic interference (EMI) shielding effect was examined in the frequency range of 50 MHz-1.5 GHz by ASTM D4935-99 method (HP 8719ES).

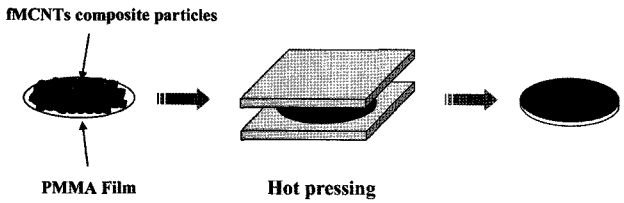

Figure 1. Schematic illustration for preparing fMCNT/PS composite layer on PMMA.

Results and Discussion

The surfaces of PS particles prepared by dispersion polymerization were sulfonated by a reaction with sulfuric acid. The sulfonated PS particles were confirmed by FT-IR spectroscopy as shown in Figure 2. The characteristic peak of

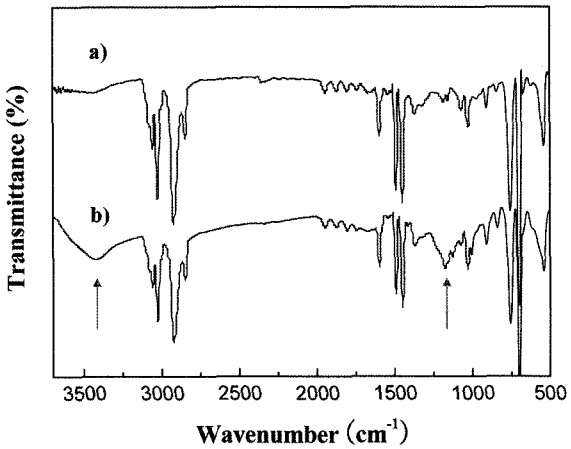

Figure 2. FT-IR spectra of the pure PS particles (a) and sulfonated PS particles (b).

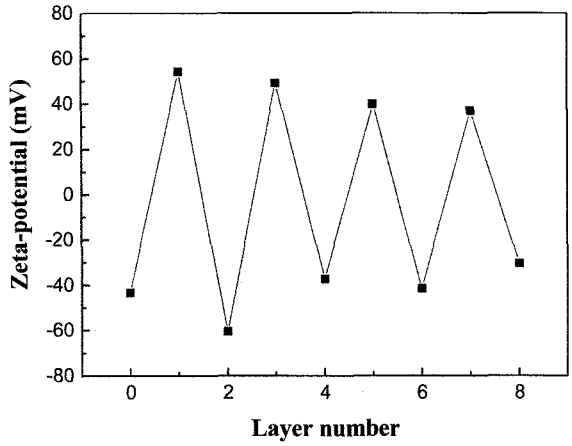

Figure 3. The zeta-potential of fMCNT/polyelectrolyte self-assembled PS particles (0: sulfonated PS particles; 1,3,5,7: PDDA; 2: PSS; 4,6,8: fMCNTs).

sulfonic group appeared at 1250 cm^{-1} (S = O bond) and 3400 cm^{-1} peaks (O-H bond).

Figure 3 shows the zeta-potential of each layer of fMCNTs and polyelectrolytes on sulfonated PS particles. Sulfonated PS particles had negative surface charges because of sulfonic groups on particle surfaces. Oppositely charged polyelectrolytes (PDDA and PSS) were adsorbed on sulfonated PS particles. PDDA/PSS/PDDA multilayers on sulfonated PS particles were fabricated by the subsequent adsorptions of polyelectrolytes and confirmed by zeta-potential analysis.

fMCNTs were adsorbed on positively charged PDDA layer which was the utmost layer of PDDA/PSS/PDDA self-assembled PS particles. fMCNT layers were charged negatively because fMCNTs had carboxyl functional groups by chemical oxidation of CNTs in acid solutions. When fMCNTs and PDDA were alternately coated on particles by LbL self-assembly, the repeating changes of negative and positive surface charges were observed as shown in Figure 3 (from the 4th layer to the 8th layer). These variations of zeta potential indicated that surfaces of PS particles were successfully coated by PDDA and fMCNTs subsequently.

The FE-SEM images of sulfonated PS particles and fMCNT/polyelectrolyte self-assembled PS particles having different number of PDDA/fMCNT multilayers are shown in Figure 4. The Figure 4(a) shows that the surfaces of sulfonated PS particles are clean. The size distribution of particle was very narrow (average diameter: 2 μm). However, fMCNT bundles were observed on particles after coating PDDA and fMCNT

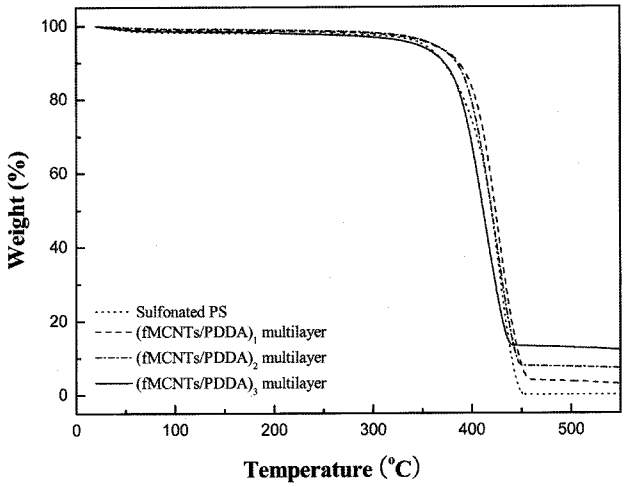

Figure 5. TGA thermograms of the sulfonated PS particles and $(PDDA/fMCNTs)_n$ multilayer particles.

as shown in Figures 4(b)-(d). As the number of fMCNT/PDDA multilayers increased, the amount of fMCNTs on particles gradually increased. Furthermore, the expansion of fMCNT coverages on surfaces was observed with increasing the number of fMCNT/PDDA multilayers. The interconnected networks formed by fMCNTs among particles were observed, also.

Thermal properties of sulfonated PS and fMCNT/polyelectrolyte coated PS particles were studied by TGA ther-

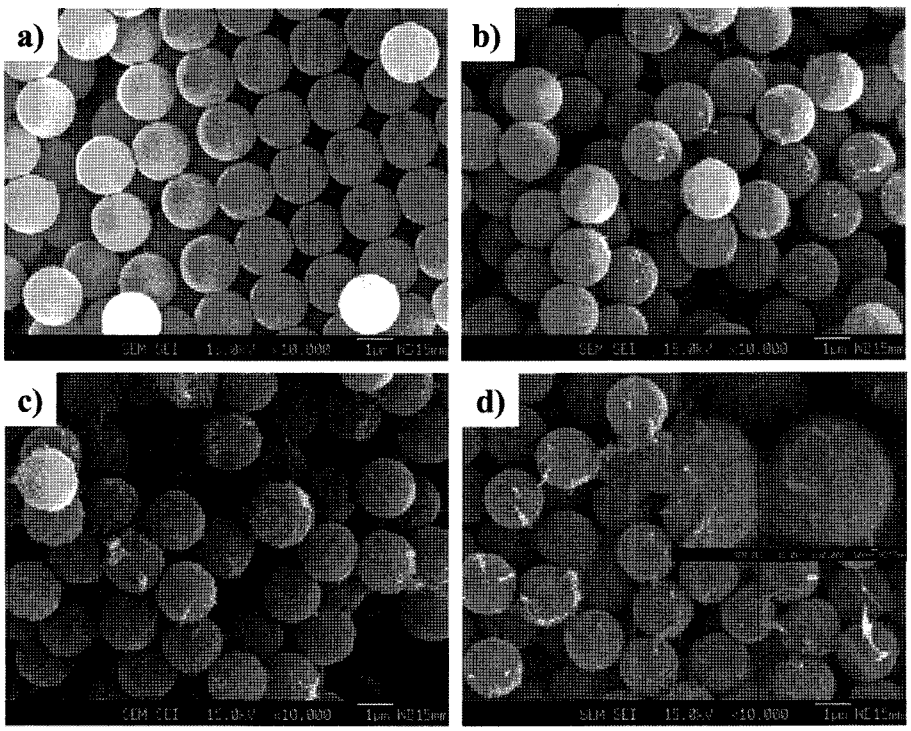

Figure 4. FE-SEM images of sulfonated PS particles (a), $(PDDA/fMCNTs)_1$ self-assembled particles (b), $(PDDA/fMCNTs)_2$ self-assembled particles (c), and $(PDDA/fMCNTs)_3$ self-assembled particles (d).

mograms as shown in Figure 5. The main degradation of all samples appeared between 350 and 470 °C under nitrogen atmosphere. The sulfonated PS particles were entirely burned out over 450 °C. However, the residues of fMCNT/polyelectrolyte coated PS remained at 500 °C because of fMCNTs attached on particles. Therefore, the amount of fMCNTs coated on particles was checked by removing core polymer particles during heating at 500 °C. With increasing the number of PDDA/fMCNT multilayers (from the 1st layer of fMCNTs to the 3rd layer of fMCNTs), the amount of fMCNTs on particles increased (3.6%, 7.5%, and 12.7%, respectively). The increasing amount of fMCNTs on particles with increasing the number of PDDA/fMCNT multilayer was well consistent with the observation of FE-SEM as shown in Figure 4. These results showed that the amount of fMCNTs on the particles was successfully controlled by LbL self-assembly.

fMCNT/PS composite films were fabricated on PMMA substrates by using fMCNT/polyelectrolyte self-assemble particles. When fMCNT/PS composite films were prepared without PMMA substrates by hot press technique, produced composite films were very brittle. Therefore, the PMMA

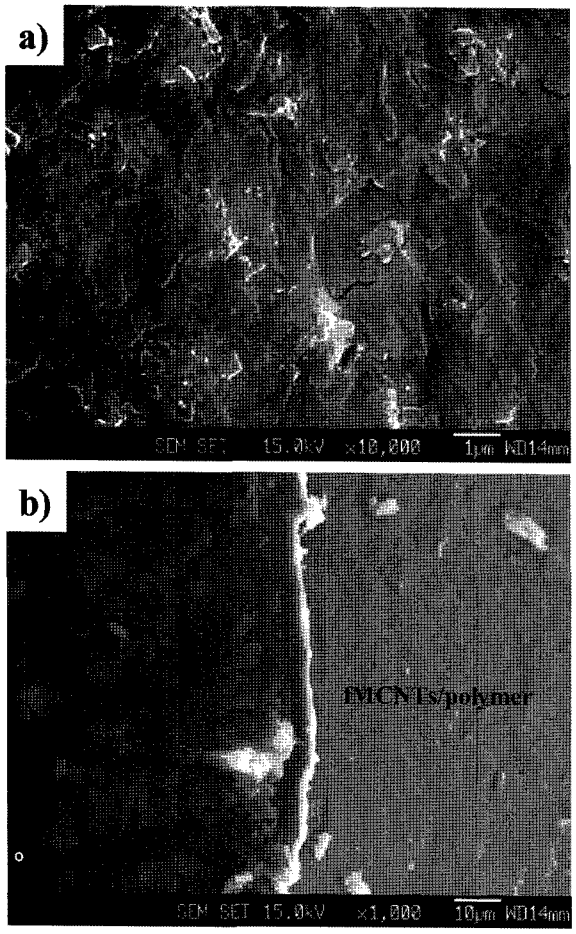

Figure 6. FE-SEM images of fMCNT/fMCNT/PS composite layer on PMMA (a: top view, b: side view).

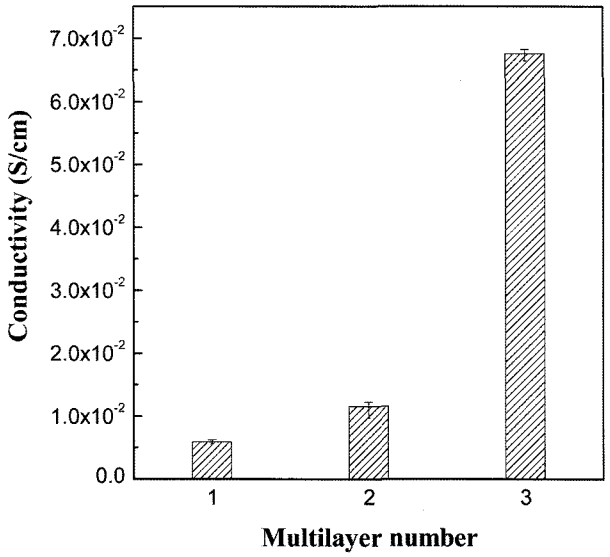

Figure 7. Electrical conductivity of fMCNT/PS composite layer on PMMA using the different number of PDDA/fMCNT multilayers self-assembled particles at room temperature.

with superior flexibility was used as substrate for fMCNT/PS composite films. fMCNT/polyelectrolyte self-assembled particles were hot pressed on the PMMA substrate at 120 °C. The average thickness of fMCNT/PS composite layer on PMMA was 525 μm. Figure 6(a) shows the surface of fMCNT/PS composite layer on PMMA. The barrier between the PMMA substrate and fMCNT/PS composite layer is shown in Figure 6(b). It was observed that the PMMA layer and the fMCNT/PS composite layer were not mixed each other during hot pressing at 120 °C.

Figure 7 shows the electrical conductivity of fMCNT/PS composite layer on PMMA having different number of PDDA/fMCNT multilayers. The conductivity of composite films increased dramatically with increasing the number of PDDA/fMCNTs multilayers (5.929×10^{-3} S/cm (the 1st PDDA/fMCNT layer), 1.153×10^{-2} S/cm (the 2nd PDDA/fMCNT layer), and 6.756×10^{-2} S/cm (the 3rd PDDA/fMCNT layer). Because the amount of fMCNTs on the multilayers increased with increasing the number of fMCNT/polyelectrolyte multilayers, conductive pathways contributing to the conductivity of composite layer were extended, also. It was suggested that the enhanced conductivity of composite films were caused by the extended fMCNT network in polymer matrix. In addition, it was suggested that the fMCNTs may be well dispersed in fMCNT/PS composite films films by using fMCNT/polyelectrolyte self-assembled particles

The EMI shielding efficiency (SE) represents relation between a transmitted power and an incident power. The EMI SE is defined as $SE(dB) = 10 \log P_i/P_t = 20 \log E_i/E_t$, where P_i is the incident electromagnetic power, P_t is the transmitted electromagnetic power, E_i is the incident electric field, and E_t is the transmitted electric field.[21,22]

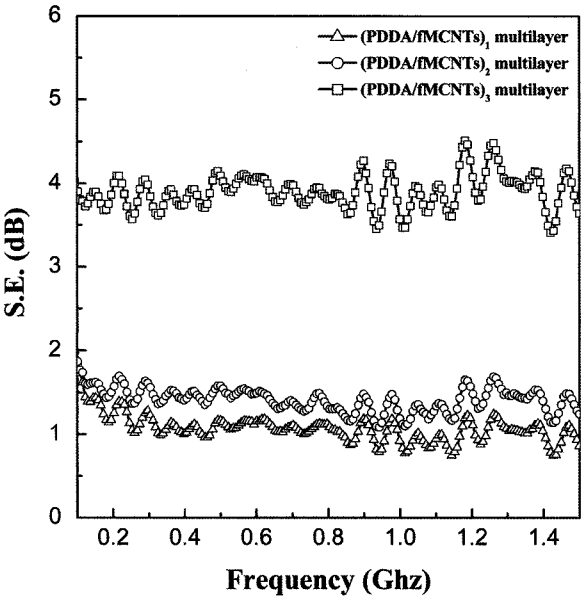

Figure 8. EMI shielding efficiency of fMCNT/PS composite layer on PMMA using the different number of PDDA/fMCNT multilayers self-assembled particles over frequency rage of 50 MHz - 1.5 GHz.

Figure 8 shows the EMI SE over the frequency range (50 MHz -1.5 GHz) of fMCNT/PS composite layer on PMMA with the different number of PDDA/fMCNT multilayers. The EMI SE over frequency rage of 50 MHz - 1.5 GHz was measured to be 1-5 dB. Though the EMI SE of films was observed as shown in Figure 8, the EMI SE was too low to be applied for practical applications. This result may be caused by the low aspect ratio and the surface damages of functionalized fMCNTs. In addition, the reduced number of metal catalysts in fMCNTs during functionalization may be another factor to lower the EMI SE.[23]

Conclusions

fMCNT/polyelectrolyte coated PS particles were synthesized by LbL self-assembly to enhance dispersity of CNTs in CNT/PS composite films. The amount of fMCNTs on particles was efficiently controlled by adjusting the number of PDDA/fMCNT multilayers. The electrical properties of fMCNT/PS composite layer on the PMMA using fMCNT/polyelectrolyte self-assembled particles were investigated. The fMCNT/PS composite layer on the PMMA showed the high electric conductivity because fMCNTs were well dispersed in composite films. Also, EMI SE over frequency rage of 50 MHz - 1.5 GHz was weakly measured around 1-5 dB depending on the different number of PDDA/fMCNT multilayers. Though the EMI SE of composite films was observed, the EMI SE was too low to be applied for practical applications. The electrical conductivity of fMCNT/PS composite layer on PMMA continuously increased with the stepwise growth of PDDA/fMCNT multilayers. It was suggested that electrical properties of composite films were efficiently controlled by using fMCNT/polyelectrolyte self-assembled particles.

References

(1) J. T. Wescotta, P. Kung, and A. Maitia, *Appl. Phys. Lett.*, **90**, 033116 (2007).
(2) J. Xiong, Z. Zheng, X. Qin, M. Li, H. Li, and X. Wang, *Carbon*, **44**, 2701 (2006).
(3) E. Kymakis and G. A. J. Amaratunga, *J. Appl. Phys.*, **99**, 084302 (2006).
(4) Y. Qiao, C. M. Li, S. J. Bao, and Q. L. Bao, *J. Power Sources*, **170**, 79 (2007).
(5) Y. H. Liu, B. Yi, Z. G. Shao, L. Wang, D. Xing, and H. Zhang, *J. Power Sources*, **163**, 807 (2007).
(6) B. Philip, J. K. Abraham, A. Chandrasekhar, and V. K. Varadan, *Smart Mater. Struct.*, **12**, 935 (2003).
(7) H. W. Chen, R. J. Wu, K. H. Chan, Y. L. Sun, and P. G. Su, *Sens. Actuator B-Chem.*, **104**, 80 (2005).
(8) U. Yogeswaran and S. M. Chen, *Electrochim. Acta*, **52**, 5985 (2007).
(9) A. D. Pasquier, H. E. Unalan, A. Kanwal, S. Miller, and M. Chhowalla, *Appl. Phys. Lett.*, **87**, 203511 (2005).
(10) N. Li, Y. Huang, F. Du, X. He, X. Lin, H. Gao, Y. Ma, F. Li, Y. Chen, and P. C. Eklund, *Nano Lett.*, **6**, 1141 (2006).
(11) Y. Yang, M. C. Gupta, K. L. Dudley, and R. W. Lawrence, *Nano Lett.*, **5**, 2131 (2005).
(12) X. Zhou, Y. Zhu, Q. Gong, and J. Liang, *Mater. Lett.*, **60**, 3769 (2006).
(13) Y. Wang, R. Cheng, L. Liang, and Y. Wang, *Compos. Sci. Technol.*, **65**, 793 (2005).
(14) X. Zhang, J. Zhang, and Z. Liu, *Carbon*, **43**, 2186 (2005).
(15) X. Gong, J. Liu, S. Baskaran, R. D. Voise, and J. S. Young, *Chem. Mater.*, **12**, 1049 (2000).
(16) B. Kim and W. M. Sigmund, *Langmuir*, **20**, 8239 (2004).
(17) Z. Shi, Y. Lian, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, Q. Gong, H. Li, and S. L. Zhang, *Chem. Commun.*, **6**, 461 (2000).
(18) J. W. Kim and K. D. Suh, *Colloid Polym. Sci.*, **276**, 870 (1998).
(19) Y. Yang, Y. Chu, F. Yang, and Y. Zhang, *Mater. Chem. Phys.*, **92**, 164 (2005).
(20) S. J. Han, B. Kim, and K. D. Suh, *Macromol. Chem. Phys.*, **208**, 377 (2007).
(21) Y. K. Hong, C. Y. Lee, C. K. Jeong, D. E. Lee, K. Kim, and J. Joo, *Rev. Sci. Instrum.*, **74**, 1098 (2003).
(22) N. F. Colaneri and L. W. Shacklette, *IEEE Trans. Instrum. Meas.*, **41**, 291 (1992).
(23) H. M. Kim, K. Kim, C. Y. Lee, J. Joo, H. S. Yoon, D. A. Pejakovic, J. W. Yoo, and A. J. Epstein, *Appl. Phys. Lett.*, **84**, 589 (2004).