Current Applied Physics 10 (2010) e101–e104

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Effect of surfactant and coating method on the electrical and optical properties of thin conductive films prepared with single-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 29 December 2009
Received in revised form
12 May 2010
Accepted 10 June 2010
Available online 18 June 2010

Keywords:
Single-walled carbon nanotubes
Surfactant
Coating method
Thin conductive film

ABSTRACT

Single-walled carbon nanotubes were purified by conventional method of thermal oxidation followed by acid treatment and coated as a thin conductive film on flexible poly(ethylene terephthalate) substrate. The morphology and sheet resistance of the conductive films were largely dependent on the surfactant used for dispersing the nanotubes and the coating method. We achieved a sheet resistance of 332 Ω sq^{-1} with 80% optical transmittance at a wavelength of 550 nm for an optimized thin film. The highly conductive, transparent and flexible thin film prepared by our method is expected to be competent for the flexible electronic applications.

1. Introduction

There have been a lot of studies on carbon nanotubes since their discovery by Lijima [1]. The superlative electronic, optical and mechanical properties of single-walled carbon nanotubes (SWCNTs) make them one of the promising candidates for applications in transparent coatings [2–5], transistors [6], sensors [7], solar cells [8], actuators [9], light emitting diodes (LEDs) [10] and so on. Optically transparent and highly conductive indium tin oxide (ITO) has been widely used in a variety of optoelectronic applications. However, there are some major limitations for using ITO films in such applications: i) requirement of high deposition temperature, ii) high cost due to the accelerated depletion of indium sources, iii) lack of mechanical flexibility, and iv) higher sheet resistance on plastic substrates compared to SWCNT thin films [11]. These limitations can be overcome to a great extend by using SWCNTs. SWCNTs are essentially insoluble in aqueous medium owing to their non-polar nature. Covalent [12,13] and ionic [14,15] functionalizations were used to get stable suspensions of nanotubes. Air brushing, dip coating, bar coating and spin coating [3,16,17] are some of the methods for fabricating a thin conductive film (TCF) with SWCNTs. The electrical properties of nanotubes as a TCF depend on the method of SWCNT synthesis, purity of the material, nature of nanotubes, type of surfactants for dispersion, coating method and so forth. Our interest is to optimize the type of surfactant and coating method in order to obtain highly transparent and conductive thin film from the well-purified SWCNTs. In this study, we prepared aqueous dispersions of SWCNTs with various surfactants, and evaluated the electrical and optical properties of TCFs formed on poly(ethylene terephthalate) (PET) by different coating method.

2. Experimental

2.1. Purification of SWCNTs

The raw arc-discharge SWCNTs were purchased from Hanhwa Nanotech (product number: ASA–100F, diameter: 1.0–1.2 nm, length: 5–20 μm). These nanotubes were purified by thermal oxidation followed by acid treatment. We used HCl (henceforth SWCNT-H) and nitric acid (henceforth SWCNT-N) separately for the purification process. The typical procedure is as follows: raw SWCNTs were thermally oxidized at 425 °C for 2 h in air atmosphere. They were then bath sonicated with concentrated HCl for 4 min. The nanotubes were washed several times with Millipore water (resistivity greater than 18 MΩ cm) until the solution showed a pH of 7, and dried at 80 °C in a vacuum oven for 5 h. In the case of

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doi:10.1016/j.cap.2010.06.008

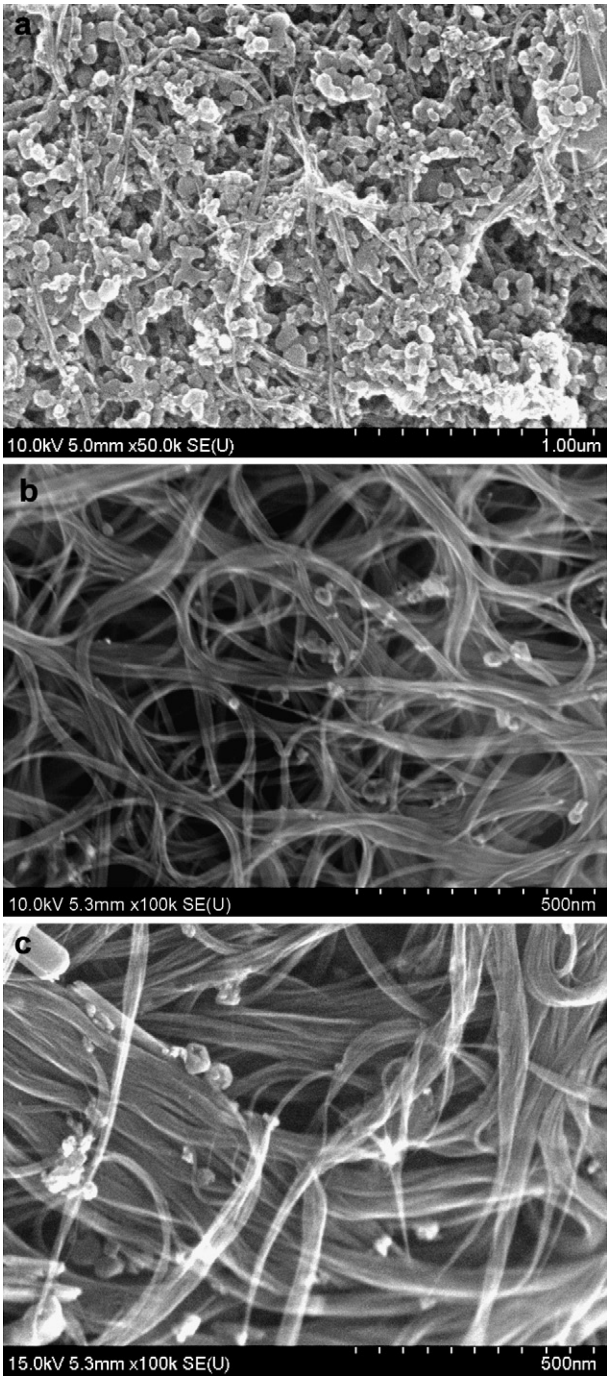

Fig. 1. FESEM images of (a) raw SWCNTs, (b) SWCNT-H and (c) SWCNT-N.

nitric acid process, the SWCNTs were treated with 60% HNO_3 prior to the HCl process.

2.2. Preparation of TCF on PET substrate

Aqueous dispersions of the purified SWCNTs were achieved by using different surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and triton X-100. All the chemicals were purchased from Sigma–Aldrich and used as received. In a typical procedure, a mixture of 0.3 mg SWCNT and 3 mg mL^{-1} surfactant in water was first bath sonicated for 30 min and subsequently tip-sonicated (Sonic Vibra-cell, 750 W) for 5 min.

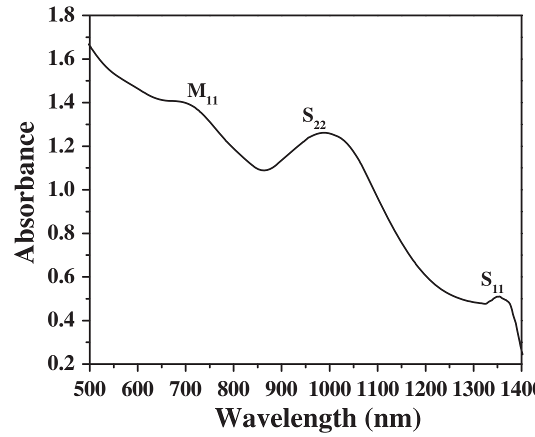

Fig. 2. VIS–NIR spectrum of the purified SWCNT-N/SDS dispersion in water.

After sonication, the solution was centrifuged at 8000 rpm for 30 min. The well-dispersed supernatant was carefully decanted and was used for dip and spray coating onto a PET substrate. The obtained film was then treated with 60% HNO_3, rinsed with water and dried in a vacuum oven. The scotch tape test was conducted over the thin films formed on PET. It was found that the adhesion between the nanotube TCFs and PET substrate is strong, irrespective of type of surfactant and coating method.

2.3. Characterization

The morphological features of SWCNTs and TCFs were analyzed by FESEM (Hitachi S-4800) images. The optical properties of the film were measured using a UV–VIS–NIR spectrophotometer (JASCO V 570) and the transmittance (400–800 nm) values were recorded at a wavelength of 550 nm. Sheet resistances of TCFs were measured by a four point probe method with a surface resistance measurement system (CMT-SR1000 N, Changmin Tech.).

3. Results and discussion

The FESEM images of the raw SWCNTs and purified SWCNTs are shown in Fig. 1. Fig. 1(b) and (c) suggest that the carbonaceous and metallic impurities were removed by purification. SWCNT-H exhibits a spaghetti-like morphology whereas SWCNT-N has more dense and aligned morphology. The yields of nanotubes after purification by HCl and HNO_3 treatments were 8.0 and 4.0%, respectively, but in both the cases, the purity of the material was very high. So, we concentrated our studies on cost-effective SWCNT-H for the optimization of surfactant and coating method, and then finally applied the same to SWCNT-N.

The formation of dense nanotubes after acid treatment was verified by VIS–NIR spectroscopy (JASCO V 570), as shown in Fig. 2. The average nanotube diameter could be calculated from the spectrum using the following equations: $S_{11}(\mathrm{eV}) = 2\alpha\beta/d$, $S_{22}(\mathrm{eV}) =$

Table 1
Sheet resistance and optical transmittance of TCFs fabricated with different coating method from surfactant dispersions of SWCNT-H sample.

Surfactant	Sheet resistance (kΩ sq^{-1})		Transmittance (%)
	Spray coating	Dip coating	
SDS	2.1	35.2	85
Triton X-100	6.3	96.7	85
SDBS	15.9	400 000	85

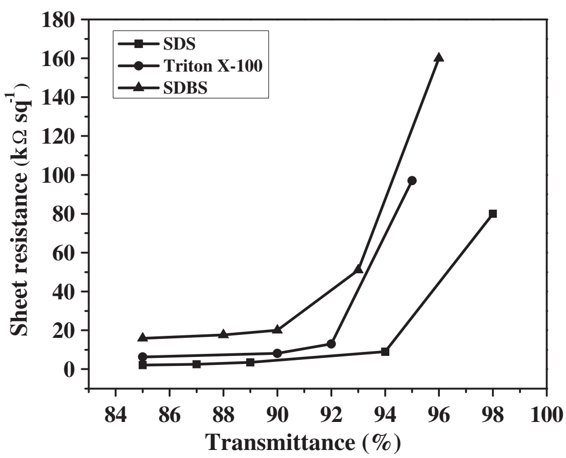

Fig. 3. Sheet resistance as a function of optical transmittance for the TCFs (SWCNT-H) prepared with different surfactants and spray coating method.

$4\alpha\beta/d$ and $M_{11}(eV) = 6\alpha\beta/d$; where α is the C–C bond distance (0.141 nm), β is the transfer or resonance integral between the pπ-orbitals (2.9 eV) and d is the diameter of the nanotubes [18]. Based on the above equations, the calculated diameter of the purified nanotubes lies between 1.3 and 1.4 nm. This indicates a slight densification of the nanotubes occurred after the acid purification process.

Highly purified SWCNTs (SWCNT-H) were dispersed using different surfactant (SDS, SDBS, triton X-100) and these dispersions were used to make TCFs by spray and dip coating methods. Sheet resistances of TCFs fabricated by different coating method are summarized in Table 1. It is clear that the sheet resistances of TCFs prepared by spray coating are lower than those of the dip coated films. It is believed that the air force during spray coating helps close packing of nanotubes in order to preserve better electrical continuity on the PET surface. Moreover, the spray coating method is simple, fast and needs only a very small volume of SWCNT dispersion. Thus, we applied the spray coating method to investigate the effect of surfactant on electrical properties of TCFs. The sheet resistance versus transmittance of the TCFs fabricated from dispersions of SWCNTs with different surfactant is shown in Fig. 3. It is found that the film of SWCNT/SDS system shows the lowest sheet resistance at all ranges of the transmittance. Sun et al. also reported that SDS could achieve better dispersion than any other surfactants because of the strong electrostatic attraction of SDS molecules with the carbon nanotubes [19]. The good dispersion of SWCNTs in the SWCNT/SDS aqueous solution resulted in low sheet resistance of the TCFs.

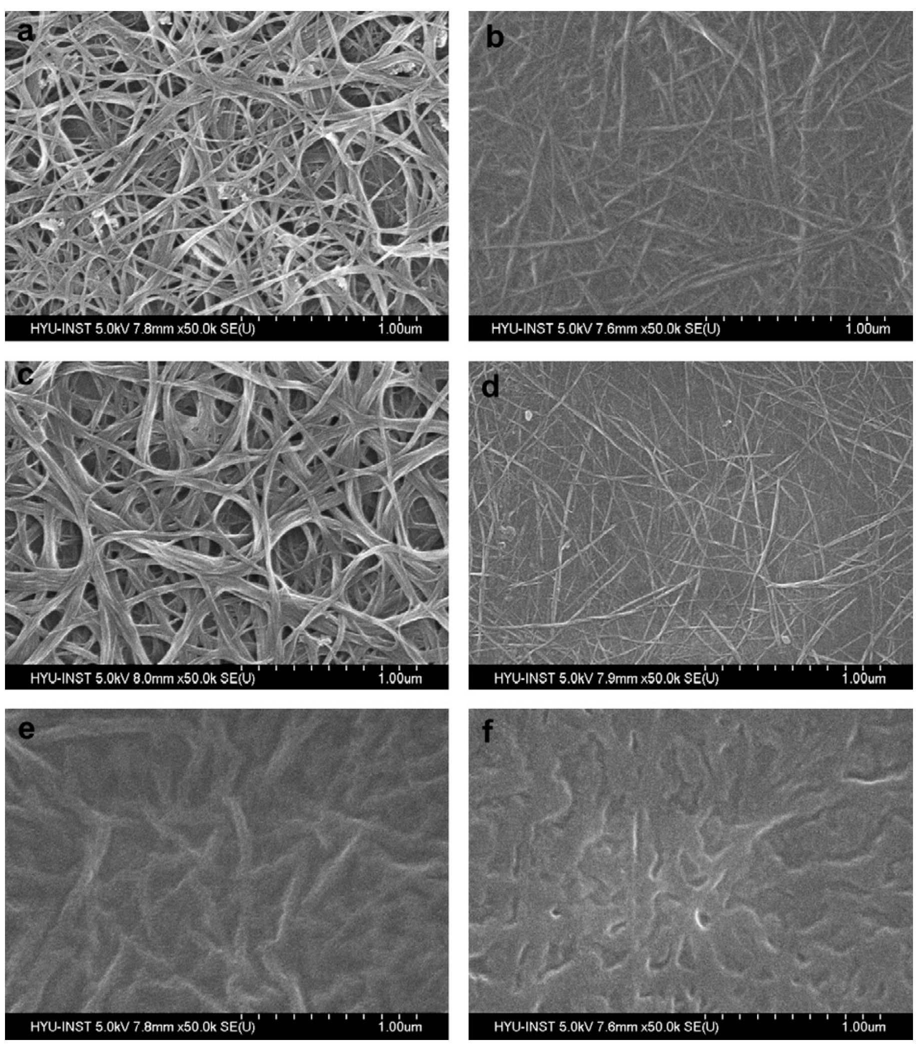

Fig. 4. FESEM images of the TCFs fabricated from dispersions of SWCNT-H material using different surfactant and coating method. (a) SWCNT/SDS(S), (b) SWCNT/SDS(D), (c) SWCNT/SDBS(S), (d) SWCNT/SDBS(D), (e) SWCNT/triton X-100(S), (f) SWCNT/triton X-100(D). S and D in parenthesis mean spray and dip coating, respectively.

The morphologies of TCFs fabricated by spray and dip coating method are compared in Fig. 4. A distinct morphology of thin film is observed with respect to type of surfactant and the coating method. Some sorts of morphological similarity are observed for the SWCNT films formed from the dispersions of SDS and SDBS, but SWCNT/triton X-100 film morphology is entirely different. For sprayed films shown in Fig. 4(a), (c), and (e), it is clear that more aggregation of tubes takes place when SDBS and triton X-100 are used. The less aggregated tubes with more entangled networks formed with SWCNT/SDS are assumed to be the least resistive pathways and hence exhibits the lowest sheet resistance. For the dipped films, most SWCNTs are separated rather than interconnected in case of sprayed films. As a result, a TCF with more interconnected networks shows lower sheet resistance as compared to that of a film with more independent tubes. As described previously, the TCF prepared from sprayed SWCNT/SDS dispersion showed the lowest sheet resistance and so we extended this system and same coating method to study the SWCNT-N material. The TCF prepared with SWCNT-N/SDS dispersion exhibited a sheet resistance of 956 Ω sq^{-1} with 85% optical transmittance, which is a much lower resistance compared to that of TCF made with SWCNT-H material. The sheet resistance was further decreased to 472 Ω sq^{-1} when the TCF was treated with 60% nitric acid, which did not affect the transmittance of the film. Finally, we achieved a low sheet resistance of 332 Ω sq^{-1} with an optical transmittance of 80% by spraying more quantity of SWCNT dispersion onto the PET substrate. The TCF with low sheet resistance and high optical transmittance may be considered as a potential candidate for flexible electronic applications.

4. Conclusions

The TCFs have been fabricated with well-purified SWCNTs by dip and spray coating method. The effect of surfactant and method of fabricating TCFs onto a flexible PET substrate was investigated to obtain a film with low sheet resistance and high optical transmittance. Spraying of SWCNT dispersion onto the PET substrate yielded consistently the TCFs with superior properties compared to dip coating process. The optimized SWCNT/SDS thin film on the PET exhibited lowest sheet resistance with high transmittance.

Acknowledgments

This work was supported by Basic Science Research Program through the National Research Foundation of Korea grant (No. 2010-0001842) and the Korea Center for Artificial Photosynthesis funded by the Ministry of Education, Science, and Technology (MEST) through the National Research Foundation of Korea (NRF-2009-C1AAA001-2009-0093879).

References

[1] S. Lijima, Nature 354 (1991) 56.
[2] J. Zhang, L. Gao, J. Sun, Y. Liu, Y. Wang, J. Wang, H. Kajiura, Y. Li, K. Noda, J. Phys. Chem. C. 112 (2008) 16370.
[3] N. Saran, K. Parikh, D.S. Suh, E. Munoz, H. Kolla, S.K. Manohar, J. Am. Chem. Soc. 126 (2004) 4462.
[4] Z. Li, H.R. Handel, E. Dervishi, V. Saini, Y. Xu, A.R. Biris, D. Lupu, G.J. Salamo, A.S. Biris, Langmuir 24 (2008) 2655.
[5] S. Paul, D.W. Kim, Carbon 47 (2009) 2436.
[6] S. Ju, A. Facchetti, Y. Xuan, J. Liu, F. Ishikawa, P. Ye, C. Zhou, T.J. Marks, D.B. Janes, Nat. Nanotechnol. 2 (2007) 378.
[7] P. Bondavalli, P. Legagneux, D. Pribat, Sens. Actuators B. 140 (2009) 304.
[8] J.E. Trancik, S.C. Barton, J. Hone, Nano Lett. 8 (2008) 982.
[9] J. Fraysse, A.I. Minett, G. Gu, S. Roth, A.G. Rinzler, R.H. Baughman, Curr. Appl. Phys. 1 (2001) 407.
[10] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M.E. Tompson, C. Zhou, Nano Lett. 6 (2006) 1980.
[11] Y. Song, C.M. Yang, D.Y. Kim, H. Kanoh, K. Kaneko, J. Colloid. Interface Sci. 318 (2008) 365.
[12] B. Vigolo, V. Mamane, F. Valsaque, T.N.H. Le, J. Thabit, J. Ghanbaja, L. Aranda, Y. Fort, E. McRae, Carbon 47 (2009) 411.
[13] E.T. Mickelson, I.W. Chiang, J.L. Zimmerman, P.J. Boul, J. Lozano, J. Liu, R.E. Smalley, R.H. Hauge, J.L. Margrave, J. Phys. Chem. B. 103 (1999) 4318.
[14] K.D. Ausman, R. Piner, O. Lourie, R.S. Ruoff, M. Korobov, J. Phys. Chem. B. 104 (2000) 8911.
[15] M.F. Islam, E. Rojas, D.M. Bergey, A.T. Johnson, A.G. Yodh, Nano Lett. 3 (2003) 269.
[16] M. Kaempgen, G.S. Duesberg, S. Roth, Appl. Surf. Sci. 252 (2005) 425.
[17] J.S. Moon, J.H. Park, T.Y. Lee, Y.W. Kim, J.B. Yoo, C.Y. Park, J.M. Kim, K.W. Jin, Diamond Relat. Mater. 14 (2005) 1882.
[18] M.A. Hamon, M.E. Itkis, S. Niyogi, T. Alvaraes, C. Kuper, M. Menon, R.C. Haddon, J. Am. Chem. Soc. 123 (2001) 11292.
[19] Z. Sun, V. Nicolosi, D. Rickard, S.D. Bergin, D. Aherne, J.N. Coleman, J. Phys. Chem. C. 112 (2008) 10692.