

Fabrication of Highly Conductive and Transparent Thin Films from Single-Walled Carbon Nanotubes Using a New Non-ionic Surfactant *via* Spin Coating

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ABSTRACT Oligothiophene-terminated poly(ethylene glycol) was synthesized and used as a non-ionic and amphiphilic surfactant for fabricating high-quality single-walled carbon nanotube (SWCNT) films by a simple spin coating method. The absence of charge repulsion between SWCNT/surfactant complexes successfully leads to formation of a dense network of SWCNTs on the substrate through a single deposition of spin coating. When the SWCNT film was treated with nitric acid and thionyl chloride after washed with dichloromethane and water, a high-performance SWCNT film with the sheet resistance of 59 ohm/sq and the transparency of 71% at 550 nm was successfully obtained. Since the SWCNT film exhibits a high value of $\sigma_{\text{td}}/\sigma_{\text{ac}}$ (~ 17) and excellent dimensional stability after releasing from the substrate, the film can be used as a transparent electrode in flexible optoelectronic devices.

KEYWORDS: single-walled carbon nanotube · spin coating · transparent film · electrode · free-standing film

Transparent and electrically conductive films have been widely used as an electrode for organic electronics such as organic light-emitting diodes and organic photovoltaics. Recently, single-walled carbon nanotube (SWCNT) films attract much attention as an alternative to metal oxide electrodes due to their unique electrical conductivity, excellent mechanical properties, and feasibility of solution process, which satisfies the industrial demand for flexible and low-cost electrodes.¹

For fabricating SWCNT films, some approaches based on the direct growth of SWCNTs on the substrate have been reported.^{2–5} However, these methods are unsuitable for plastic substrates because of the high temperature required for the chemical vapor deposition process. Therefore, development of a solution-based SWCNT deposition process, which is simple and low-cost, is strongly demanded. Various methods of solution-based SWCNT deposition including vacuum filtration (VF),^{6–9} spraying,^{10,11} dip coating,¹² bar coating,^{13,14} and spin coating^{15,16} have

been reported. Among these methods, the spin coating has been recognized as the most promising process for mass production and industrialization of SWCNT thin films because of the uniformity of the film, ease of thickness control, short coating time, low-temperature fabrication, and high reproducibility.

Although the spin coating process is the most effective method for fabricating the SWCNT thin film, a few reports on the SWCNT films fabricated by the spin coating have been reported because of the lack of appropriate surfactant for dispersion of SWCNTs in solvent. The most conventional surfactants used for dispersion of SWCNTs are sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS).^{8,10,11,13,17–20} Although these surfactants have been well-known to disperse SWCNTs effectively in aqueous media for the spin coating process, the strong charge repulsion between complexes of SWCNT/surfactant due to ionic groups of surfactant prohibits deposition of SWCNTs on the substrate, and as a result, the thickness of the SWCNT film is limited. For this reason, the preparation of SWCNT thin film prepared by the spin coating has not been thoroughly studied. Particularly, a high-performance SWCNT film which fulfills the requirement for flat panel displays (transmittance >80% at 550 nm and sheet resistance <100 ohm/sq) has not been fabricated yet through a single deposition of spin coating.

To overcome the problem, two types of spin coating processes have been proposed, *viz.* repeated spin coating of SWCNT solution without surfactant¹⁶ and the dual spinning method,²¹ which exclude the repulsive effect of surfactant during the spin

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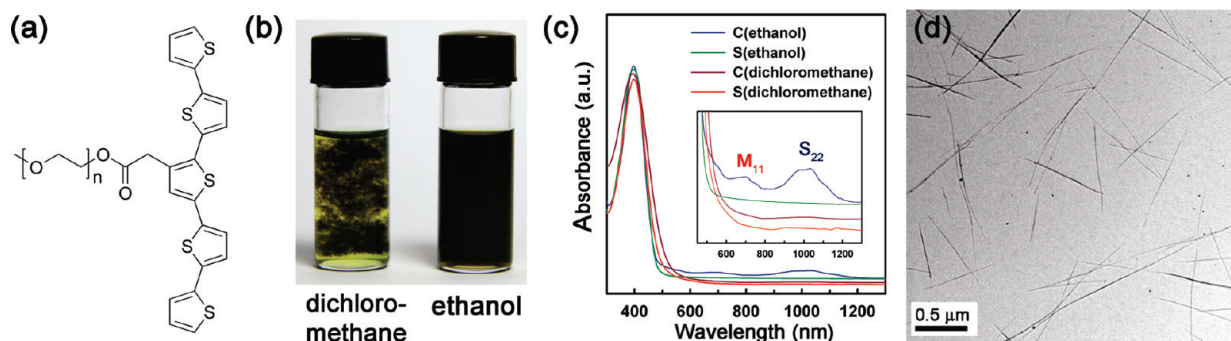


Figure 1. (a) Chemical structure of 5TN-PEG, (b) comparison of SWCNT dispersion in dichloromethane and ethanol, (c) UV–visible–NIR absorption spectra of 5TN-PEG (S) and SWCNT/5TN-PEG complex (C) in two different solvents, and (d) TEM image of exfoliated SWCNT/5TN-PEG complex in ethanol. Dispersions of SWCNT/5TN-PEG (SWCNT/5TN-PEG = 1/10 w/w) complexes are prepared by sonication and centrifugation.

coating process. However, these processes can not only solve the fundamental problem of spin coating process of SWCNTs but also are unpractical. Recently, Hellstrom *et al.*¹⁵ have reported that SWCNT thin films can be successfully fabricated by a single deposition of spin coating with a non-ionic surfactant (polythiophene) and exhibit high performance (80 ohm/sq at transmittance 72% at 550 nm).

In this paper, we report that a highly conductive and transparent SWCNT thin film has been successfully fabricated by a single deposition of spin coating using an amphiphilic surfactant, quinquethiophene-terminated poly(ethylene glycol) (5TN-PEG). Although 5TN-PEG does not have ionic groups in the molecule, it has been reported that 5TN-PEG can effectively stabilize nanotube dispersions.²² Moreover, since the molecular weight of 5TN-PEG (~2000 g/mol) used in this study is lower than other commercial non-ionic surfactants such as Pluronic or Triton-X,²³ it is expected that the surfactant can be easily washed out after deposition of SWCNTs. When the film was treated with nitric acid and thionyl chloride after the surfactant was washed with dichloromethane and water, highly conductive and transparent SWCNT films were obtained due to effective removal of surfactant and chemical doping. Furthermore, the film was easily separated from the substrate by floating the sample on water because the SWCNT thin film is dimensionally stable. Consequently, these high-performance and free-standing SWCNT films can be used for various optoelectronic devices.

RESULTS AND DISCUSSION

To disperse SWCNTs homogeneously in organic solvent, the non-ionic, amphiphilic surfactant (5TN-PEG), whose chemical structure is shown in Figure 1a, was used. It has been known that the oligothiophene part (5TN) in 5TN-PEG is strongly physisorbed onto the nanotube surface *via* strong $\pi-\pi$ interaction,^{24–27} while PEG is soluble in various organic solvents. Ethanol is chosen as a solvent to disperse SWCNTs in the presence of 5TN-PEG because ethanol has a low boiling point and low surface energy. The SWCNT solution was

prepared by mixing 1.7 mg/mL SWCNTs and 17 mg/mL 5TN-PEG in ethanol for 8 h using a bath-type ultrasonicator. After sonication, the solution was centrifuged at 5500 rpm for 90 min, and the upper 50% of solution was decanted. The dispersion of SWCNTs with 5TN-PEG in dichloromethane was also prepared by the same method. When the UV–vis–NIR absorption spectra of 5TN-PEG and SWCNT/5TN-PEG complex in ethanol are compared with those in dichloromethane, as shown in Figure 1c, it reveals that two additional absorption peaks are observed in the SWCNT/5TN-PEG in ethanol, while 5TN-PEG in ethanol shows one absorption peak (410 nm) corresponding to the absorption of oligothiophene. Observation of these two absorption peaks indicates the dispersion of nanotubes in solution because the peaks at 700 and 1000 nm are attributed to the first metallic ($M_{1,1}$) and the second semiconducting van Hove transition ($S_{2,2}$) of SWCNTs, respectively.²⁸ However, the solution in dichloromethane after centrifugation does not show a significant absorption in the regions corresponding to the absorption of nanotubes. This is because oligothiophene in 5TN-PEG, which can interact with CNTs by $\pi-\pi$ interaction, is dissolved in dichloromethane and thus loses the function to disperse SWCNTs.²⁹ Hence, dichloromethane should not be used for dispersion of SWCNTs, but can be used as an effective solvent to wash excess 5TN-PEG after formation of CNT films.

Figure 1d shows a transmission electron microscope (TEM) image of dispersed SWCNTs with 5TN-PEG, where the sample for the TEM image was prepared by depositing droplets of the dispersed solution onto the carbon-coated copper grid. TEM image indicates that 5TN-PEG can homogeneously disperse SWCNTs and effectively exfoliate SWCNT bundles in ethanol.

Films of SWCNTs on the substrate are fabricated from SWCNT/5TN-PEG (1/10 w/w) dispersion by a simple spin coating method. The thickness of the SWCNT film is controlled by changing the rpm of spin coating. After deposition, SWCNT films are washed with dichloromethane and water to remove the surfactant

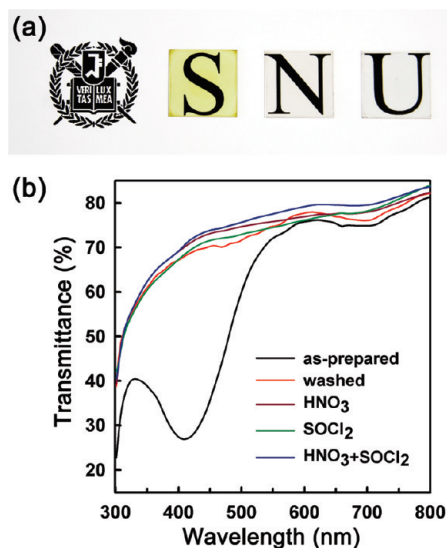


Figure 2. (a) Visual transparency of SWCNT films after depositing on the glass of 25 mm × 25 mm by spin coating (left), after washing with dichloromethane and water (middle), and after chemical treatment (right); (b) transmittance spectra of SWCNT films.

and baked at 120 °C to enhance adhesion between nanotubes and substrate. When the washed SWCNT films are treated with HNO₃ and SOCl₂ to improve electrical and optical properties of films,^{10,30–34} transparent and homogeneous films are obtained (Figure 2a). It should be noted that the color of films changes from yellowish (as-prepared) to gray (after washing and after treatment with both SOCl₂ and HNO₃) due to the removal of yellow-colored 5TN-PEG. To identify the removal of surfactant, UV–visible spectra of SWCNT/5TN-PEG films are measured. In Figure 2b, as-prepared film has a strong absorption in the range of 330–550 nm corresponding to the absorption of oligothiophene, whereas the absorption peak is drastically decreased after the film is washed with dichloromethane and water. Quantitatively, the transmittance at 408 nm is increased from 26.9 to 67.9%. The transmittance at 408 nm is further increased to 68.3, 70.0, and 70.4% when treated with SOCl₂, HNO₃, and both HNO₃ and SOCl₂, respectively, indicating that the chemical treatment with HNO₃ and/or SOCl₂ contributes to the removal of residual surfactant and that HNO₃ is more effective than SOCl₂ for removing the surfactant.

When the nanoscale morphology of SWCNT films is examined by scanning electron microscopy (SEM), as shown in Figure 3, the directional orientation of nanotubes is not observed in our films, unlike earlier reports.^{21,35,36} Individual SWCNTs are randomly distributed, forming a uniform network. The diameters of nanotube bundles are in the range of 5–20 nm. Recently, Lyons *et al.*³⁷ have demonstrated that the exfoliation of CNTs is required to obtain high electrical conductivity in the SWCNT network because nanotubes with smaller bundle size provide a larger number of pathways for charge transport. Nirmalraj *et al.*³⁸ have also shown that

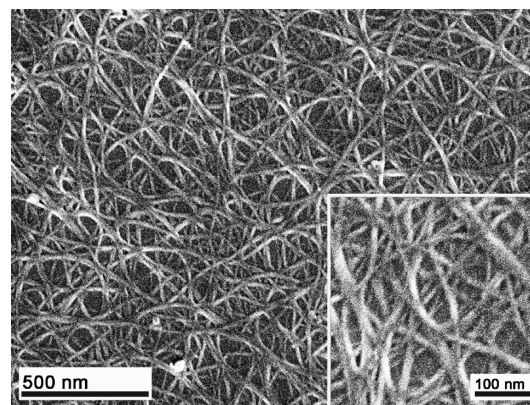


Figure 3. SEM images of SWCNT network film. The film was prepared by spin coating in the presence of 5TN-PEG, and then 5TN-PEG is removed by dipping in dichloromethane and water followed by chemical treatment with both HNO₃ and SOCl₂. Inset shows a highly magnified image of the network structure.

the resistance of electron transport at a junction is decreased as SWCNTs are debundled. Compared with the previous report on SWCNT film fabricated by the spin coating with polymeric surfactant,¹⁵ the size of SWCNT bundles in our system is much smaller, and therefore, our SWCNT films are expected to exhibit higher performance.

When the sheet resistance of SWCNT films is plotted against the transmittance, as shown in Figure 4a, SWCNT network films have very low sheet resistance of 59 ohm/sq with 71% transmittance at 550 nm after the films are treated with both HNO₃ and SOCl₂. Furthermore, the sheet resistance of the SWCNT films after chemical doping remained nearly constant within 10% deviation after exposure to ambient atmosphere for 4 days (see Figure S1 of Supporting Information). The effect of HNO₃ and SOCl₂ on the enhancement of electrical conductivity of SWCNTs has still been controversial: the electrical conductivity is enhanced by removal of surfactant by HNO₃ and/or SOCl₂, or the enhancement of electrical conductivity is due to p-doping of HNO₃ and/or SOCl₂ physisorbed on the CNT surface. Nevertheless, there is agreement that the treatment of HNO₃ and SOCl₂ would enhance the electrical conductivity of SWCNT network films.^{10,15,30,32–34,38} In our system, the sheet resistance of the SWCNT films was reduced by 90% when dipped in HNO₃ or SOCl₂, as compared with the washed sample, and further reduced up to 94–95% when the films are treated with both HNO₃ and SOCl₂. It is also noteworthy that SOCl₂ is slightly more effective than HNO₃ in our system at enhancing the performance of the SWCNT film, although the washing efficiency of HNO₃ is slightly better than SOCl₂ (Figure 2b).

The effect of SOCl₂ and HNO₃ on the SWCNT films fabricated using 5TN-PEG as a surfactant was examined by X-ray photoelectron spectroscopy (XPS) (Figure 4b) and TEM (Figure 4c–e). The C 1s peak of the car-

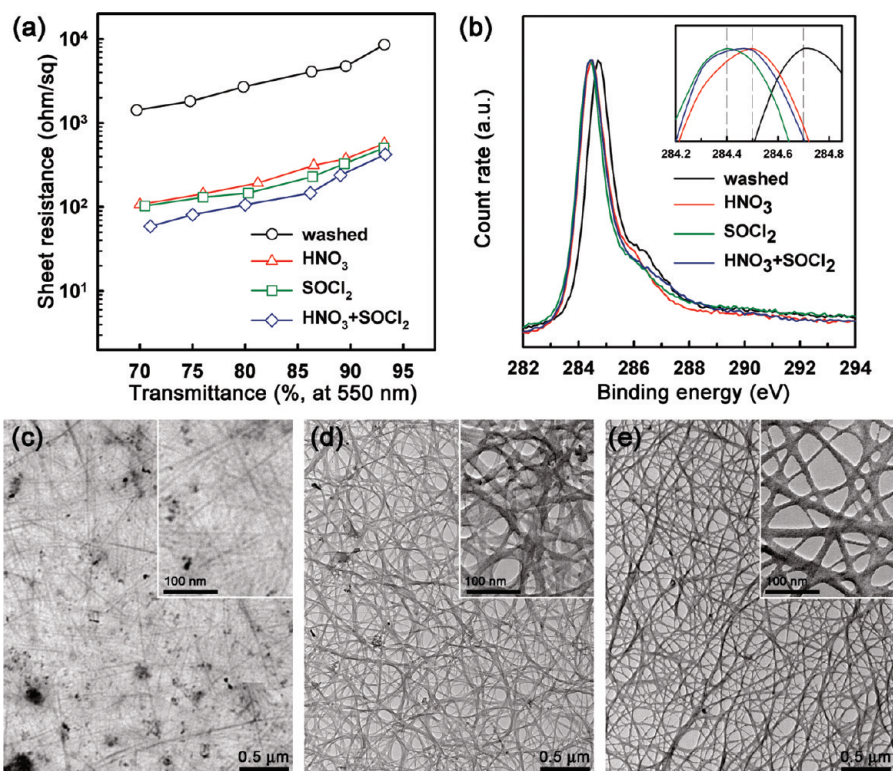


Figure 4. (a) Plot of sheet resistance as a function of transmittance at 550 nm for spin-coated SWCNT films, and (b) XPS spectra of C 1s core level of SWCNT. TEM images of the SWCNT network of (c) as-prepared, (d) washed, and (e) HNO₃- and SOCl₂-treated films. Insets show highly magnified images of SWCNT films.

bon sp² orbital, observed at 284.7 eV for washed film, was downshifted to 284.5 eV for HNO₃-treated film and to 284.4 eV for SOCl₂ or both treated film. This downshift associated with the charge transfer between CNTs and absorbates provides evidence of p-type doping.^{18,39,40} Additional evidence for doping is the observation of the change of the full width at half-maximum (fwhm) of the C 1s peak that is closely related to electron delocalization.⁴¹ As listed in Table 1, the fwhm values of the C 1s peak of SOCl₂ and both treated films are, respectively, 0.12 and 0.11 eV broader than the washed film, whereas the fwhm of HNO₃-treated film is not changed. Therefore, it is concluded that SOCl₂ has better ability to dope SWCNTs than HNO₃.

Comparison of TEM images of samples reveals that SWCNTs in the as-prepared film are buried in the 5TN-PEG matrix (Figure 4c), while SWCNT bundles with uniform network are clearly exposed after washing (Figure 4d). Although most of the 5TN-PEG is removed by wash-

ing, some surfactants still remain on the nanotube junctions and thus block the pathway of charge transport. When films are treated with HNO₃ and SOCl₂, these residual surfactants that are locally concentrated on junctions are completely removed, and consequently, individual nanotube bundles contact each other directly without an insulating barrier (Figure 4e). In short, the enhancement of electrical conductivity of SWCNT films arises from not only p-type doping but also removal of surfactant by HNO₃ and SOCl₂.

The most important parameters for evaluating the performance of transparent electrodes are generally the transparency and the sheet resistance. However, since the sheet resistance of the SWCNT film is strongly dependent upon the transparency, it is not informative to directly compare each property of SWCNT films. Recently, it has been proposed that the ratio of the direct current conductivity, σ_{dc} , to the optical conductivity, σ_{ac} (at typically 550 nm), is considered as a figure of merit (FOM)^{9,11,15,17,42} and that a higher value of σ_{dc}/σ_{ac} indicates better performance of the SWCNT network. This FOM comes from the relationship with transparency, T , and sheet resistance, R_s , as given by

$$T = \left(1 + \frac{188.5 \sigma_{ac}}{R_s \sigma_{dc}} \right)^{-2}$$

The average value of σ_{dc}/σ_{ac} for SWCNT films is increased from 0.64 (washing), 8.8 (HNO₃ treatment),

TABLE 1. Peak Positions and Full Width at Half-Maximum Values of C 1s Core Level in SWCNT Films before and after Chemical Treatments

treatment	binding energy (eV)	fwhm (eV)
washing	284.7	1.133
HNO ₃	284.5	1.132
SOCl ₂	284.4	1.254
HNO ₃ + SOCl ₂	284.4	1.232

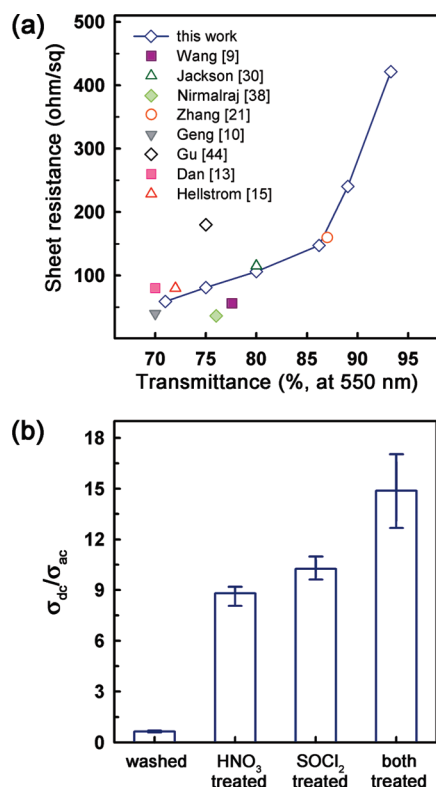


Figure 5. (a) Comparison of electro-optical performances of SWCNT films with those of other SWCNT films previously reported in the literatures (b) σ_{dc}/σ_{ac} values of our spin-coated films before and after chemical treatment.

and 10 (SOCl₂ treatment) to 15 (both HNO₃ and SOCl₂ treatment). The highest record of FOM is about 17 after both HNO₃ and SOCl₂ are treated (Figure 5b), which satisfies the minimum requirement for flat panel display (80% transparency at 550 nm, sheet resistance 100 ohm/sq, FOM ~ 16).¹⁰ Figure 5a and Table 2 compare our result with other reported data for SWCNT films. Our film prepared by the simple spin coating ex-

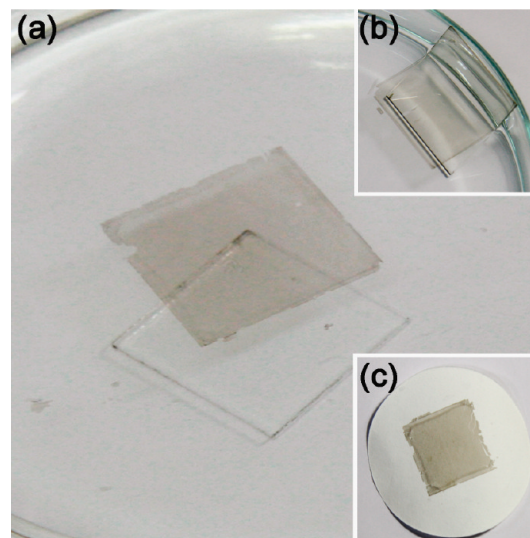


Figure 6. Photographs of free-standing films: (a) floating on the water surface, (b) releasing from the glass substrate, and (c) transferred to filter paper.

hibits better optical and electrical performance as compared with other transparent and conductive SWCNT films.

Another advantage of our films is dimensional stability. When the SWCNT film is floated on water, it is easily separated from its substrate and can be transferred to other substrate. This “free-standing” SWCNT film has an important advantage for microelectronic applications.⁴³ Especially, the transfer of the SWCNT film on a flexible substrate such as polyethylene terephthalate (PET) and polydimethylsiloxane is essential for fabrication of flexible electronics. Figure 6 shows the photographs of the preparation of free-standing film. When the film is immersed into deionized water, the film is floated on the water surface and then released from the glass (Figure 6a,b). Transference of this free-standing

TABLE 2. Comparison of Electro-optical Performance of Our SWCNT Network Films with Other SWCNT Films Reported in the Literature

type of SWCNT	surfactant	method	treatment	σ_{dc}/σ_{ac}	ref
laser ablation	Triton X-100	VF	SOBr ₂	25	9
arc-discharge	SDS	VF	HNO ₃ + SOCl ₂	14	30
arc-discharge	SDBS	VF	HNO ₃	35	38
arc-discharge	PEDOT:PSS ^b	VF		15	8
HiPco	SDS	VF	HNO ₃ + SOCl ₂	~4.6	33
arc-discharge	SDS	VF + stamp	SOCl ₂	16	21
arc-discharge	Nafion	spray coating	HNO ₃	16	18
arc-discharge	SDS	spray coating	HNO ₃	24	10
arc-discharge ^d	no surfactant	dip coating		~3.3	12
HiPco	P3HT ^c	drop casting	I ₂	6.8	43
HiPco	SDBS + Triton X-100	bar coating	oleum	12	13
arc-discharge	no surfactant	spin coating ^e	HNO ₃	19	16
arc-discharge	P3DT ^d	spin coating ^f	SOCl ₂	13	15
arc-discharge	5TN-PEG	spin coating ^f	HNO ₃	8.8	this work
			SOCl ₂	10	
			HNO ₃ + SOCl ₂	17	

^aPretreatment with HNO₃ before film fabrication. ^bPoly(3,4-ethylenedioxythiophene):poly(styrene sulfonate). ^cPoly(3-hexylthiophene). ^dPoly(3-dodecylthiophene). ^eSpin coating repeated 100 times. ^fSingle deposition.

film onto another substrate can be easily achieved by scooping up the floating one. We successfully transferred the films on filter paper (Figure 6c). The free-standing film exhibited high bending stability (see Figure S2 of Supporting Information).

CONCLUSIONS

We have successfully fabricated high-performance SWCNT films by a single deposition of spin coating. For successful spin coating, a non-ionic and amphiphilic surfactant, 5TN-PEG, was used to avoid charge repul-

sion between complexes of SWCNT/surfactant. After washing the surfactant with solvent followed by chemical treatment with HNO_3 and SOCl_2 , the SWCNT films exhibited high performance (71% transmittance at 550 nm, 59 ohm/sq of sheet resistance, and $\sigma_{dc}/\sigma_{ac} = 17$). Furthermore, free-standing SWCNT films can be prepared and easily transferred to another substrate. These results lead us to conclude that the chemical structure and property of the surfactant should be taken into account for fabrication of high-performance SWCNTs via the spin coating process.

METHODS

Arc-discharge SWCNTs were purchased from Hanwha Nanotech Co., Ltd. (South Korea) and used without further purification. Quinquethiophene-terminated poly(ethylene glycol) (5TN-PEG) was synthesized according to our previous report.²² To disperse SWCNTs in organic solvent, SWCNTs (5.1 mg) and 5TN-PEG (51 mg) were added in 3 mL of ethanol and stirred for 5 min to dissolve 5TN-PEG. The SWCNT solution was then sonicated in a bath-type sonicator (Hwashin Instrument, Power Sonic 410) for 8 h and centrifuged at 5500 rpm for 90 min (Hettich, DE/EBA 20). The supernatant was carefully decanted and saved.

Bare glasses of 25 mm × 25 mm were cleaned with acetone and isopropyl alcohol and then dried at 200 °C for 30 min. After complete drying, the glass was treated with a UV–ozone cleaner for 15 min. SWCNT films on glass were prepared from the above decanted solution by spin coating (Laurell, WS-400A-6TFM-LITE). The thickness of the SWCNT film was controlled by adjusting the rpm of spin coating. After spin coating, the samples were soaked in dichloromethane for 30 min to remove surfactant and annealed at 120 °C for 30 min. For further removal of surfactant, films were rinsed with deionized water for 30 min and baked at 120 °C for 30 min. Finally, washed films were chemically treated for hole doping and/or further removal of surfactant with three different methods: (1) dipping in SOCl_2 (Fluka, ≥99%) for 30 min and drying in air, (2) dipping in HNO_3 (60%) for 1 h and drying in air followed by soaking in deionized water for 30 min and then drying in air, and (3) HNO_3 treatment followed by dipping in SOCl_2 .

For preparation of free-standing films, SWCNT films spin-coated on glass were annealed for a short period of time (<1 min) at 120 °C. When the films were dipped in deionized water, films were immediately released from the glass and floated on the water surface.

The absorption spectra of the SWCNT dispersion were obtained from a UV–visible–NIR spectrophotometer (Varian, Cary 5000), and the transmittance of SWCNT films was measured by a UV–visible spectrophotometer (HP 8452A). The morphologies of SWCNT films were observed by a transmission electron microscope (JEOL, JEM-1010) and field emission scanning electron microscope (JEOL, JSM-6700F). Electrical properties of SWCNT films were characterized by a four-point probe measurement system (Napson, CRESBOX). X-ray photoelectron spectra were obtained on AXIS-His (Kratos).

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Supporting Information Available: Stability of SWCNT films after HNO_3 and SOCl_2 treatments, and bending stability of free-standing film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Cao, Q.; Rogers, J. A. Ultrathin Films of Single-Walled Carbon Nanotubes for Electronics and Sensors: A Review of Fundamental and Applied Aspects. *Adv. Mater.* **2009**, *21*, 29–53.
- Peng, H. S. Aligned Carbon Nanotube/Polymer Composite Films with Robust Flexibility, High Transparency, and Excellent Conductivity. *J. Am. Chem. Soc.* **2008**, *130*, 42–43.
- Pint, C. L.; Xu, Y. Q.; Pasquali, M.; Hauge, R. H. Formation of Highly Dense Aligned Ribbons and Transparent Films of Single-Walled Carbon Nanotubes Directly from Carpets. *ACS Nano* **2008**, *2*, 1871–1878.
- Tawfik, S.; O'Brien, K.; Hart, A. J. Flexible High-Conductivity Carbon-Nanotube Interconnects Made by Rolling and Printing. *Small* **2009**, *5*, 2467–2473.
- Zhang, H. L.; Wei, D. C.; Liu, Y. Q.; Wu, B.; Huang, L. P.; Xi, H. X.; Chen, J. Y.; Yu, G.; Kajjura, H.; Li, Y. M. A New “Bones/Muscles” Strategy for Preparing Highly Conducting Single-Walled Carbon-Nanotube Films with Ultrahigh Transparency. *Small* **2009**, *5*, 2392–2396.
- Hu, L.; Hecht, D. S.; Gruner, G. Percolation in Transparent and Conducting Carbon Nanotube Networks. *Nano Lett.* **2004**, *4*, 2513–2517.
- Wu, Z. C.; Chen, Z. H.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. Transparent, Conductive Carbon Nanotube Films. *Science* **2004**, *305*, 1273–1276.
- De, S.; Lyons, P. E.; Sorel, S.; Doherty, E. M.; King, P. J.; Blau, W. J.; Nirmalraj, P. N.; Boland, J. J.; Scardaci, V.; Joimel, J.; Coleman, J. N. Transparent, Flexible, and Highly Conductive Thin Films Based on Polymer–Nanotube Composites. *ACS Nano* **2009**, *3*, 714–720.
- Wang, Y.; Di, C. A.; Liu, Y. Q.; Kajjura, H.; Ye, S. H.; Cao, L. C.; Wei, D. C.; Zhang, H. L.; Li, Y. M.; Noda, K. Optimizing Single-Walled Carbon Nanotube Films for Applications in Electroluminescent Devices. *Adv. Mater.* **2008**, *20*, 4442–4449.
- Geng, H. Z.; Kim, K. K.; So, K. P.; Lee, Y. S.; Chang, Y.; Lee, Y. H. Effect of Acid Treatment on Carbon Nanotube-Based Flexible Transparent Conducting Films. *J. Am. Chem. Soc.* **2007**, *129*, 7758–7759.
- Tenent, R. C.; Barnes, T. M.; Bergeson, J. D.; Ferguson, A. J.; To, B.; Gedvilas, L. M.; Heben, M. J.; Blackburn, J. L. Ultrasoft, Large-Area, High-Uniformity, Conductive Transparent Single-Walled-Carbon-Nanotube Films for Photovoltaics Produced by Ultrasonic Spraying. *Adv. Mater.* **2009**, *21*, 3210–3216.
- Jang, E. Y.; Kang, T. J.; Im, H. W.; Kim, D. W.; Kim, Y. H. Single-Walled Carbon-Nanotube Networks on Large-Area Glass Substrate by the Dip-Coating Method. *Small* **2008**, *4*, 2255–2261.
- Dan, B.; Irvin, G. C.; Pasquali, M. Continuous and Scalable Fabrication of Transparent Conducting Carbon Nanotube Films. *ACS Nano* **2009**, *3*, 835–843.
- Kitano, T.; Maeda, Y.; Akasaka, T. Preparation of Transparent and Conductive Thin Films of Carbon Nanotubes Using a Spreading/Coating Technique. *Carbon* **2009**, *47*, 3559–3565.
- Hellstrom, S. L.; Lee, H. W.; Bao, Z. N. Polymer-Assisted Direct Deposition of Uniform Carbon Nanotube Bundle

- Networks for High Performance Transparent Electrodes. *ACS Nano* **2009**, *3*, 1423–1430.
16. Yim, J. H.; Kim, Y. S.; Koh, K. H.; Lee, S. Fabrication of Transparent Single Wall Carbon Nanotube Films with Low Sheet Resistance. *J. Vac. Sci. Technol., B* **2008**, *26*, 851–855.
 17. Doherty, E. M.; De, S.; Lyons, P. E.; Shmeliov, A.; Nirmalraj, P. N.; Scardaci, V.; Joimel, J.; Blau, W. J.; Boland, J. J.; Coleman, J. N. The Spatial Uniformity and Electromechanical Stability of Transparent, Conductive Films of Single Walled Nanotubes. *Carbon* **2009**, *47*, 2466–2473.
 18. Geng, H. Z.; Kim, K. K.; Song, C.; Xuyen, N. T.; Kim, S. M.; Park, K. A.; Lee, D. S.; An, K. H.; Lee, Y. S.; Chang, Y.; Lee, Y. J.; Choi, J. Y.; Benayad, A.; Lee, Y. H. Doping and De-doping of Carbon Nanotube Transparent Conducting Films by Dispersant and Chemical Treatment. *J. Mater. Chem.* **2008**, *18*, 1261–1266.
 19. Zhang, D. H.; Ryu, K.; Liu, X. L.; Polikarpov, E.; Ly, J.; Tompson, M. E.; Zhou, C. W. Transparent, Conductive, and Flexible Carbon Nanotube Films and Their Application in Organic Light-Emitting Diodes. *Nano Lett.* **2006**, *6*, 1880–1886.
 20. Pei, S. F.; Du, J. H.; Zeng, Y.; Liu, C.; Cheng, H. M. The Fabrication of a Carbon Nanotube Transparent Conductive Film by Electrophoretic Deposition and Hot-Pressing Transfer. *Nanotechnology* **2009**, *20*, 235707.
 21. Meitl, M. A.; Zhou, Y. X.; Gaur, A.; Jeon, S.; Usrey, M. L.; Strano, M. S.; Rogers, J. A. Solution Casting and Transfer Printing Single-Walled Carbon Nanotube Films. *Nano Lett.* **2004**, *4*, 1643–1647.
 22. Lee, J. U.; Huh, J.; Kim, K. H.; Park, C.; Jo, W. H. Aqueous Suspension of Carbon Nanotubes via Non-covalent Functionalization with Oligothiophene-Terminated Poly(ethylene glycol). *Carbon* **2007**, *45*, 1051–1057.
 23. Shvartzman-Cohen, R.; Levi-Kalishman, Y.; Nativ-Roth, E.; Yerushalmi-Rozen, R. Generic Approach for Dispersing Single-Walled Carbon Nanotubes: The Strength of a Weak Interaction. *Langmuir* **2004**, *20*, 6085–6088.
 24. Kim, K. H.; Jo, W. H. Synthesis of Polythiophene-Graft-PMMA and Its Role as Compatibilizer for Poly(styrene-co-acrylonitrile)/MWCNT Nanocomposites. *Macromolecules* **2007**, *40*, 3708–3713.
 25. Kim, K. K.; Yoon, S. M.; Choi, J. Y.; Lee, J.; Kim, B. K.; Kim, J. M.; Lee, J. H.; Paik, U.; Park, M. H.; Yang, C. W.; An, K. H.; Chung, Y. S.; Lee, Y. H. Design of Dispersants for the Dispersion of Carbon Nanotubes in an Organic Solvent. *Adv. Funct. Mater.* **2007**, *17*, 1775–1783.
 26. Zou, J. H.; Liu, L. W.; Chen, H.; Khondaker, S. I.; McCullough, R. D.; Huo, Q.; Zhai, L. Dispersion of Pristine Carbon Nanotubes Using Conjugated Block Copolymers. *Adv. Mater.* **2008**, *20*, 2055–2060.
 27. Kim, K. T.; Jo, W. H. Synthesis of Poly(3-hexylthiophene)-Graft-Poly(*t*-butyl acrylate-co-acrylic acid) and Its Role of Compatibilizer for Enhancement of Mechanical and Electrical Properties of Nylon 66/Multi-walled Carbon Nanotube Composites. *Compos. Sci. Technol.* **2009**, *69*, 2205–2211.
 28. Hirano, A.; Maeda, Y.; Akasaka, T.; Shiraki, K. Synergistically Enhanced Dispersion of Native Protein–Carbon Nanotube Conjugates by Fluoroalcohols in Aqueous Solution. *Chem.—Eur. J.* **2009**, *15*, 9905–9910.
 29. Yang, A.; Kuroda, M.; Shiraiishi, Y.; Kobayashi, T. Chain-Length Dependent Stationary and Time-Resolved Spectra of α -Oligothiophenes. *J. Phys. Chem. B* **1998**, *102*, 3706–3711.
 30. Jackson, R.; Domercq, B.; Jain, R.; Kippelen, B.; Graham, S. Stability of Doped Transparent Carbon Nanotube Electrodes. *Adv. Funct. Mater.* **2008**, *18*, 2548–2554.
 31. Dettlaff-Weglikowska, U.; Skakalova, V.; Graupner, R.; Jhang, S. H.; Kim, B. H.; Lee, H. J.; Ley, L.; Park, Y. W.; Berber, S.; Tomanek, D.; Roth, S. Effect of SOCl_2 Treatment on Electrical and Mechanical Properties of Single-Wall Carbon Nanotube Networks. *J. Am. Chem. Soc.* **2005**, *127*, 5125–5131.
 32. Blackburn, J. L.; Barnes, T. M.; Beard, M. C.; Kim, Y. H.; Tenent, R. C.; McDonald, T. J.; To, B.; Coutts, T. J.; Heben, M. J. Transparent Conductive Single-Walled Carbon Nanotube Networks with Precisely Tunable Ratios of Semiconducting and Metallic Nanotubes. *ACS Nano* **2008**, *2*, 1266–1274.
 33. Parekh, B. B.; Fanchini, G.; Eda, G.; Chhowalla, M. Improved Conductivity of Transparent Single-Wall Carbon Nanotube Thin Films via Stable Postdeposition Functionalization. *Appl. Phys. Lett.* **2007**, *90*, 121913.
 34. Geng, H. Z.; Lee, D. S.; Kim, K. K.; Han, G. H.; Park, H. K.; Lee, Y. H. Absorption Spectroscopy of Surfactant-Dispersed Carbon Nanotube Film: Modulation of Electronic Structures. *Chem. Phys. Lett.* **2008**, *455*, 275–278.
 35. Schmidt, R. H.; Kinloch, I. A.; Burgess, A. N.; Windle, A. H. The Effect of Aggregation on the Electrical Conductivity of Spin-Coated Polymer/Carbon Nanotube Composite Films. *Langmuir* **2007**, *23*, 5707–5712.
 36. LeMieux, M. C.; Roberts, M.; Barman, S.; Jin, Y. W.; Kim, J. M.; Bao, Z. N. Self-Sorted, Aligned Nanotube Networks for Thin-Film Transistors. *Science* **2008**, *321*, 101–104.
 37. Lyons, P. E.; De, S.; Blighe, F.; Nicolosi, V.; Pereira, L. F. C.; Ferreira, M. S.; Coleman, J. N. The Relationship between Network Morphology and Conductivity in Nanotube Films. *J. Appl. Phys.* **2008**, *104*, 044302.
 38. Nirmalraj, P. N.; Lyons, P. E.; De, S.; Coleman, J. N.; Boland, J. J. Electrical Connectivity in Single-Walled Carbon Nanotube Networks. *Nano Lett.* **2009**, *9*, 3890–3895.
 39. Shin, D. W.; Lee, J. H.; Kim, Y. H.; Yu, S. M.; Park, S. Y.; Yoo, J. B. A Role of HNO_3 on Transparent Conducting Film with Single-Walled Carbon Nanotubes. *Nanotechnology* **2009**, *20*, 475703.
 40. Graupner, R.; Abraham, J.; Vencelova, A.; Seyller, T.; Hennrich, F.; Kappes, M. M.; Hirsch, A.; Ley, L. Doping of Single-Walled Carbon Nanotube Bundles by Bronsted Acids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5472–5476.
 41. Luong, J. H. T.; Hrapovic, S.; Liu, Y. L.; Yang, D. Q.; Sacher, E.; Wang, D. S.; Kingston, C. T.; Enright, G. D. Oxidation, Deformation, and Destruction of Carbon Nanotubes in Aqueous Ceric Sulfate. *J. Phys. Chem. B* **2005**, *109*, 1400–1407.
 42. Green, A. A.; Hersam, M. C. Colored Semitransparent Conductive Coatings Consisting of Monodisperse Metallic Single-Walled Carbon Nanotubes. *Nano Lett.* **2008**, *8*, 1417–1422.
 43. Gu, H.; Swager, T. M. Fabrication of Free-Standing, Conductive, and Transparent Carbon Nanotube Films. *Adv. Mater.* **2008**, *20*, 4433–4437.