Zn/Al complex-SWCNT ink for transparent and conducting homogeneous films by scalable bar coating method

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Abstract

It is shown that the viscosity of SWCNT inks is essential to produce highly homogeneous SWCNT films on the PET substrate with bar coating method. The Zn/Al complex-aided SWCNT ink has a viscosity threshold of 1.30 mPa·s for the preparation of homogeneous films. The local flows of the film are suppressed above this viscosity, allowing homogeneous film formation. The Zn/Al complex dispersant can be easily removed from SWCNTs coated on PET by 1M HNO₃, giving a pure SWCNT film with the sheet resistance of 150 ohm/sq and transmittance of 90 % at 550 nm immediately after HNO₃ treatment.

1. Introduction

Rapid development of the transparent electronics, including touch panel displays and transparent electrodes requires new materials for the transparent and conducting film (TCF) fabrication. So far, Indium Tin Oxide (ITO) film has been widely used as an electrode for the fabrication of transparent conductors.^{1,2} However, ITO has several obstacles for this application: Limited resources, high cost and non-flexibility.^{3,4} Thus, Single Wall Carbon Nanotube (SWCNT), having excellent opto-electrical and mechanical properties,^{5,6} which is superior to ITO, have attracted attention of scientists and engineers to make use of this unique material in the TCF fabrication.⁷⁻¹¹

Despite many attempts for the application of SWCNT in the transparent electronics, preparation of high quality TCF is still challenging. Thus, Y. Zhou et al. reported the stable doping of SWCNT film by CuI with the sheet resistance of 55-65 ohm/sq at the transmittance of 80%.¹² Also the films prepared by dry printing of SWCNTs on the substrate with the sheet resistance of 86 ohm/sq at 90%¹³ and 53 ohm/sq at 80%¹⁴ have been reported. The free self-standing films of SWCNT with the sheet resistance of 84 ohm/sq and transmittance 90 % have been developed as well.¹⁵ Although these techniques give highly transparent and conductive films, easy and scalable methods for the TCF fabrication are still required.

The film fabrication with the SWCNT inks is a promising route for the SWCNT films on a large scale, if we have an excellent dispersant for SWCNTs. The efficient debundling of the SWCNTs is requested for the TCF fabrication technology.¹⁶ Organic dispersants such as surfactants have been widely used to disperse SWCNTs in aqueous media; Sodium Dodecylbenzene Sulfonate (SDBS) and Sodium Dodecyl Sulfate (SDS) have been used for the film fabrication up to date.^{7,17-19} However, the application of surfactants is not suitable for the TCF fabrication because of its non-transparency and non-conductivity in a dry state. This implicates that the surfactants need to be removed from the SWCNT film in order to maintain the high electrical conductivity and optical transparency of the SWCNT film. Several studies have shown that the surfactants are removable with concentrated HNO₃ treatment for 30 or 60 min.^{7,17-19} Indeed, the film with sheet resistance of 70 ohm/sq at the transmittance of 80% has been obtained after

removal of SDS.¹⁷ Reducing of the removal time as well as concentration of HNO₃ for the film treatment should improve efficiency in the scalable TCF fabrication technology. Thus we have an intensive demand for the new type of SWCNT dispersant which can overcome these drawbacks of the surfactants.

Variety of techniques have been employed for the fabrication of homogeneous TCF such as spray coating,²¹ spin coating,²¹ vacuum filtration,²² Langmuir-Blodgett²³ and bar coating^{24,25} methods. Bar coating method can be applied to the scalable film fabrication, because it is easy and practical to be used for this purpose. Thus, we have chosen bar coating technique as the most efficient technique for the preparation of the uniform TCF.²⁵ The films prepared using SWCNT ink stabilized with surfactants such as SDS and SDBS have poor homogeneity due to the low viscosity, which is not fit for the production of homogeneous film.^{25,26} The additive such as nonionic surfactant, TX-100, needs to be added to increase viscosity of the surfactant-based SWCNT inks for better homogeneity of the TCF.^{25,26} However, the additives suppress electrical conductivity of the film, which is an obstacle toward efficient TCF fabrication.

We have found that nanosilica can be used as an efficient dispersant for carbon nanotubes.²⁷ However, its dispersibility changes with aging time, which is not desirable for the TCF fabrication. Then, we developed a quite stable Zn/Al complex dispersant for the fabrication of SWCNT based film.²⁸ The Zn/Al complex is amphiphilic, containing amorphous Al-acetate and Zn-nitrate. Here, the Al-acetate can be adsorbed on the hydrophobic surface of SWCNTs and Zn-nitrates have affinity to water phase.²⁸ Thus, the SWCNTs are stabilized in an aqueous media for at least one year. The Zn/Al complex dispersant has two merits of an easy removal of the dispersant from the film by simple washing treatment with 1M HNO₃ during 10 min and of an appropriate viscosity for the production of uniform SWCNT films with bar coating method.

As the homogeneity and opto-electrical properties of the SWCNT film depend on the viscosity of SWCNT ink and substrate for the film fabrication, we must examine the optimum conditions for the high

quality SWCNT films. This paper reports that Zn/Al complex aided SWCNT ink of an optimum viscosity is an excellent candidate for homogeneous TCF fabrication with bar coating method.

2. Experimental section

2.1. Materials and ink for TCF preparation

The SWCNT (eDIPS) for the ink preparation was synthesized by Chemical Vapor Deposition (CVD) method after the established procedures.²⁹ The Zn/Al complex dispersant was prepared by sol-gel technique. The salts $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Al}(\text{NO}_3)_3$ for the synthesis of Zn/Al complex dispersant were purchased from Sigma Aldrich. $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Al}(\text{NO}_3)_3$ of 1.00 g at the 1:1 weight ratio were dissolved in 40 g of ethanol and mixed for 2 h to produce the Zn/Al complex dispersant. The obtained Zn/Al complex was dried in vacuum at 303 K after evaporation of ethanol. We prepared Zn/Al complex-SWCNT inks with the concentration of SWCNT from 0.01 to 0.05 wt.%. to examine the concentration effect on the film homogeneity. The concentration of Zn/Al complex dispersant of 1.00 wt.% was used for the preparation of SWCNT ink. The inks were prepared by sonication for 20 min using the homogenizer tip (SONIC, VS 505) with power of 100 W at the frequency of 20 kHz. Commercial polyethylene terephthalate (PET) was used as a transparent substrate for the SWCNT film preparation (OHP, A450). The SWCNT dispersion was coated onto the PET substrate by use of a bar coater (Kobayashi Engineering Works).

2.2. Characterization of SWCNT ink and TCF

The wettability of the SWCNT ink was examined using a contact angle measuring instrument (DMC-MC3). The viscosity of the SWCNT inks was measured using an Ostwald viscometer at 298 K. The sheet resistance was measured using four point probe method (LORESTA-GP, MCP-T610). Optical absorption spectra and the transmittance at 550 nm were measured using a UV-vis spectrophotometer (JASCO, V-670). The SWCNT bundles before and after dispersion-treatment were observed using a High-Resolution Transmission Electron Microscope (HRTEM, JEOL JEM 2100). Atomic force microscope (AFM, Agilent Technologies) was used for the observation of the SWCNT films on the PET and WSxM

software³⁰ was used for the image processing. Effect of the removal of dispersants from the SWCNT film was examined by X-ray Photoelectron Spectroscopy (XPS; AXIS-ULTRA, DLD, Al K α). The Raman spectral change of SWCNT films on the PET with HNO₃-treatment was examined using a Raman microscope (Renishaw, inVia) with the excitation using lasers of 532 and 785 nm.

3. Results and discussion

3.1. Homogeneity of the SWCNT film

Homogeneity of the SWCNT film prepared using bar coating method is closely related with the concentration of SWCNT ink. Figure 1 shows the sheet resistance and optical transmittance versus the coordinates of the film (x, y), whose unit is cm; the film size is 23 cm x 17 cm. The variation of sheet resistance and transmittance at different coordinates is ascribed to the inhomogeneity of SWCNT film. The SWCNT ink of 0.005 wt.% gives the highly transparent film, whose transmittance is 99 %, as shown in Figure 1a and a₀. Extremely high transmittance suggests that the film is thin with randomly distributed SWCNT network. The sheet resistance of SWCNT film markedly varies from 10⁵ to 10⁷ ohm/sq, indicating that the SWCNT film is non-conductive and inhomogeneous. In case of 0.02 wt.% SWCNT transmittance of the film slightly decreases to 98 %, while the sheet resistance lies in the range from 10³ to 10⁵ ohm/sq, showing presence of inhomogeneously distributed SWCNTs on the PET substrate (Figure 1b and b₀). The ink of 0.05 wt.% SWCNTs provides quite homogeneous SWCNT film with the uniform transmittance of 90 % and the sheet resistance of 307 $\pm$ 35 ohm/sq, as shown in Figure 1c and c₀.

The surface tension and viscosity of SWCNT inks play a key role in the production of homogenous films.^{25,26} The surface tension of SWCNT inks of 70.50 mN/m does not change with the concentration of SWCNTs, allowing uniform spreading of the ink onto the PET substrate. Figure 2a shows a briefly proportional increase of viscosity with the concentration of SWCNTs which can be explained by more entangled network formation at the higher concentration of SWCNTs.²⁶ This viscosity change directly governs the film homogeneity with the relevance to local flow of the SWCNT ink on the PET substrate. An evident irregularity in the thickness of the coated SWCNT film is formed immediately after coating,

which depends on the diameter of the bar wound wire (Figure S1 in Supplementary Data Section). Flattening of the SWCNT film occurs spontaneously in a wet state by the local flow of the SWCNT ink. Thus, the local flow is controlled by the viscosity of SWCNT ink. The local flow is significant at viscosity below 1.30 mPa·s, leading to local thinning and inhomogeneous film formation. However, the rapid and local flow is suppressed at viscosity above 1.30 mPa·s, allowing a uniform SWCNT film formation.

The surface coating quality is also strongly influenced by the affinity of the substrate against the SWCNT ink. Figure 2b shows hydrophilicity/hydrophobicity of the PET substrate determined by contact angle measurements. The contact angle of SWCNT ink against PET substrate is 77.5° , indicating a sufficient wettability. The wettability of PET substrate is associated with the hydrophilicity and surface roughness as well. The hydrophilicity can be attributed to the presence of hydrophilic functionalities such as C-O, O=C-O and C=O, inducing negative charges to the surface.³¹ The zeta potential measurement in the preceding study²⁸ showed that SWCNTs coated with Zn/Al complex were positively charged. Thus, the stable SWCNT deposition should be guaranteed by the electrostatic attractive interactions between SWCNTs and PET substrate in the presence of Zn/Al complex. The surface roughness of the PET substrate additionally supports the deposition of the SWCNTs onto the substrate (Figure S2 in Supplementary Data Section).

3.2. Change in opto-electrical properties of the film with acid treatment

Removal of the Zn/Al complex from the SWCNT surface with the HNO₃ solution lowers the sheet resistance; the HNO₃ concentration affects intensively the removal of the Zn/Al complex from SWCNTs, as shown in Figure 3a. The minimum sheet resistance of 150 ohm/sq at 1M HNO₃ indicates that even diluted acid can remove the Zn/Al complex efficiently without deterioration of the SWCNT film. The sheet resistance against the treatment time shows the minimum, as shown in Figure 3b. The minimum sheet resistance comes from two contrary effects: 1.) dissolution of the Zn/Al complex from the film surface, decreasing the sheet resistance and 2.) detachment of SWCNT from the film surface, increasing

the sheet resistance. The most conducting film is obtained by the washing treatment with 1M HNO₃ for 10 min, being derived from the compromising condition of the opposite effects. Then, we adopted this washing condition as a standard procedure for the removal of Zn/Al complex dispersant.

We need to understand the arrangement of SWCNTs coated on the PET substrate. The HR-TEM observation of SWCNTs shows that SWCNTs form an ordered bundle structure which is partially debundled by dispersion treatment with Zn/Al complex (Figure S3 in Supplementary Data Section). Here, these HR-TEM images on the Cu grid are shown, because we cannot observe directly SWCNT on the PET substrate. The Zn/Al complex dispersants are adhered on the fine SWCNT bundles to separate the bold bundles. The SWCNT bundles on the PET substrate after the dispersion treatment are assumed to be finer than those on the Cu grid, because SWCNT interacts more strongly with the PET than with the Cu grid. The HR-TEM observation of the SWCNT with Zn/Al complex dispersant on the Cu grid with the acid treatment should be challenged in the future. Instead of HR-TEM observation, AFM gives important information on the SWCNT structure coated on the PET substrate before and after HNO₃ treatment. Figure 4a and b shows the AFM micrographs and the size distribution histograms of the SWCNT on PET before and after HNO₃ treatment. The average size of SWCNT bundles with Zn/Al complex is evaluated to be 310 nm, whereas the acid treatment decreases this value to 48 nm in size. The AFM studies clearly show the effectiveness of the removal treatment of Zn/Al complex with diluted HNO₃. The efficient removal of Zn/Al complex improves the electrical contact between fine SWCNT bundles, lowering the electrical resistivity as observed.

3.3 Changes in surface chemistry and electrical properties of SWCNT on HNO₃ treatment

XPS examination clearly evidences the effectiveness of removal of the Zn/Al complex from SWCNT film, as shown in Figure 5a. The Zn 2p peaks in the range from 1050 to 1020 eV and peaks of Al 2s, 2p, Zn 3p, 3s in the range from 140 to 70 eV disappear after acid treatment, indicating SWCNT film free of Zn/Al complex. The atomic percentages of the elements before and after acid treatment are shown in Table 1.

The C content becomes almost twice, while the O content almost triples after acid treatment. The resultant XPS data clearly indicate an effective removal of Zn/Al complex from the SWCNT film. Figure 5 b, c and d shows the C1s XPS spectra of the bare PET, SWCNT film before and after acid treatment with their deconvoluted spectra, respectively. The bare PET has C1s peaks coming from the surface oxygen groups (C-O at 286.19 eV and O=C-O at 288.77 eV) in addition to the C1s peak from the C-C bonding at 284.36 eV.³¹ The C1s XPS spectrum of the SWCNT film before acid treatment has a weak peak coming from sp² SWCNTs at 284.94 eV in addition to the C1s peak from the C-C bonding.³² The C1s peaks of the surface oxygen groups are relatively weak in comparison with those of the bare PET. The Zn/Al complex dispersant should partially cover the PET surface. The acid treatment gives a distinct C1s peak having a strong sp² carbon peak at 285.02 eV and evident surface oxygen peaks due to removal of the Zn/Al complex. A slightly higher energy shift of the sp² carbon peak from 284.94 eV to 285.02 eV after HNO₃ treatment³³ must be noted. The literature³³ reported that the sp² carbon peak of SWCNTs gave the higher energy shift after doping with HNO₃. Also it is well known that simple treatment with HNO₃ decreases the electrical resistivity of SWCNTs due to creation of holes by doping effect.³⁴ Consequently the treatment of SWCNT-Zn/Al complex with the diluted HNO₃ for 10 min should induce the doping effect.

Doping effect is also evidenced by the optical absorption spectra, as shown in Figure 6a. We clearly observe the S11 and S22 transitions of the semiconducting SWCNT and a weak M11 transition of metallic SWCNT. The dispersion treatment of SWCNT with Zn/Al complex decreases slightly the absorbance of these transitions. This can be explained by the charge transfer between SWCNT and Zn/Al complexes according to our preceding study.²⁸ We observe the pronounced depression of these transitions after the acid treatment even for only 10 min with diluted HNO₃, which evidences the doping of SWCNT with HNO₃ according to the literature.^{34,35} Nevertheless, this doping effect is not stable under an ambient condition. The sheet resistance of the film increases with the exposure time to air, as shown in Figure 6b. This indicates evolution of doped nitrogen species, losing doping effect; the sheet resistance becomes almost constant of 320 ohm/sq after 30 days.

The Raman spectroscopy using the excitation wavelengths of 532 nm and 785 nm gives the information inherent to semiconducting and metallic SWCNTs, respectively. Figure 6c and d shows Raman spectra of SWCNT film on the PET substrate before and after the acid treatment with excitation using 532 and 785 nm. The RBM peaks of semiconducting and metallic SWCNTs almost disappear after coating on the PET with Zn/Al complex dispersant. The acid treatment does not recover the RBM peak due to loss of the resonance enhancement induced by doping with NO_3^- ions.³⁴ The intensity ratio of the disordered peak (I_D) to graphite like band (I_G) is 0.1, indicating quite high crystallinity of this SWCNT. The preceding study²⁸ showed the blue-shift of both of G and G'-bands of SWCNT with Zn/Al complex due to the charge transfer interaction. The acid treatment also induces similar blue shift of G and G'-bands of SWCNT. This also indicates p-type doping of SWCNT on the HNO_3 treatment.

Conclusion

The Zn/Al complex dispersant can offer for promising SWCNT inks producing uniform SWCNT films on PET substrate with bar coating method, whereas the surfactants cannot give the uniform films. This is because the Zn/Al complex-aided SWCNT ink for bar coating has enough viscosity ($> 1.30 \text{ mPa}\cdot\text{s}$) to avoid local flows inducing distinct heterogeneity. Also simple washing of SWCNT-Zn/Al complex with 1M HNO_3 for 10 min can remove completely the Zn/Al complex, leading to a marked decrease of the film resistance; the best film resistivity and optical transmittance at 550 nm are 150 ohm/sq and 90 %, respectively. However, SWCNT unraveled with Zn/Al complex dispersant in aqueous solution should form the re-bundled structure of SWCNT on drying process with the bar coating method. An intensive suppression of re-bundling of SWCNTs on drying must be challenged to obtain SWCNT-TCF better than ITO.

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Reference

- (1) Chopra, K. L.; Major, S.; Pandya, D. K. *Thin Solid Films* **1983**, *102*, 1.
- (2) Hösel, M.; Angmo, D.; Søndergaard, R. R.; dos Reis Benatto, G. a.; Carlé, J. E.; Jørgensen, M.; Krebs, F. C. *Adv. Sci.* **2014**, *1*.
- (3) Hecht, D. S.; Hu, L.; Irvin, G. *Adv. Mater.* **2011**, *23*, 1482.
- (4) Geng, H.Z.; Lee, Y. H. *Nanoscale phenomena: basic science to device applications*; Springer, 2008; pp. 15–28.
- (5) Bandaru, P. R. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1239.
- (6) Salvétat, J.-P. et al. *Appl. Phys. A Mater. Sci. Process.* **1999**, *69*, 255.
- (7) Y. Wang, H.J. Yang, H.Z. Geng, Z.C. Zhang, E.X. Ding, Y. Meng, Z.J. Luo, J. Wang, X. M. S. and S. X. D. *J. Mater. Chem. C* **2015**, *3*, 3796.
- (8) 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. *ACS Nano* **2009**, *3*, 714.
- (9) Rowell, M. W.; Topinka, M. a.; McGehee, M. D.; Prall, H.-J.; Dennler, G.; Sariciftci, N. S.; Hu, L.; Gruner, G. *Appl. Phys. Lett.* **2006**, *88*, 233506.
- (10) Zhang, D.; Ryu, K.; Liu, X.; Polikarpov, E.; Ly, J.; Tompson, M. E.; Zhou, C. *Nano Lett.* **2006**, *6*, 1880.
- (11) Hecht, D. S.; Heintz, A. M.; Lee, R.; Hu, L.; Moore, B.; Cucksey, C.; Risser, S. *Nanotechnology* **2011**, *22*, 075201.
- (12) Zhou, Y.; Shimada, S.; Saito, T.; Azumi, R. *Carbon N. Y.* **2015**, *87*, 61.
- (13) Reynaud, O.; Nasibulin, A. G.; Anisimov, A. S.; Anoshkin, I. V.; Jiang, H.; Kauppinen, E. I. *Chem. Eng. J.* **2014**, *255*, 134.

- (14) Fukaya, N.; Kim, D. Y.; Kishimoto, S.; Noda, S.; Ohno, Y. *ACS Nano* **2014**, *8*, 3285.
- (15) Nasibulin, A. G.; Kaskela, A. et al. *ACS Nano* **2011**, *5*, 3214.
- (16) Biswas, C.; Lee, Y. H. *Adv. Funct. Mater.* **2011**, *21*, 3806.
- (17) Geng, H.-Z.; Kim, K. K.; So, K. P.; Lee, Y. S.; Chang, Y.; Lee, Y. H. *J. Am. Chem. Soc.* **2007**, *129*, 7758.
- (18) Rösner, B.; Guldi, D. M.; Chen, J.; Minett, a I.; Fink, R. H. *Nanoscale* **2014**, *6*, 3695.
- (19) Gao, J.; Wang, W. Y.; Cui, L. J.; Chen, L. T.; Hu, X. Y.; Li, H.; Geng, H. Z. *Adv. Mater. Res.* **2013**, *658*, 3.
- (20) Mirri, F.; Ma, A. W. K.; Hsu, T. T.; Behabtu, N.; Eichmann, S. L.; Young, C. C.; Tsentalovich, D. E.; Pasquali, M. *ACS Nano* **2012**, *6*, 9737.
- (21) Kim, S.; Yim, J.; Wang, X.; Bradley, D. D. C.; Lee, S.; DeMello, J. C. *Adv. Funct. Mater.* **2010**, *20*, 2310.
- (22) Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. *Science* **2004**, *305*, 1273.
- (23) Kim, Y.; Minami, N.; Zhu, W.; Kazaoui, S.; Azumi, R.; Matsumoto, M. *Japanese J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap.* **2003**, *42*, 7629.
- (24) Khim, D.; Han, H.; Baeg, K.-J.; Kim, J.; Kwak, S.-W.; Kim, D.-Y.; Noh, Y.-Y. *Adv. Mater.* **2013**, *25*, 4302.
- (25) Dan, B.; Irvin, G. C.; Pasquali, M. *ACS Nano* **2009**, *4*, 835.
- (26) Maillaud, L.; Poulin, P.; Pasquali, M.; Zakri, C. *Langmuir* **2015**, *31*, 5928.
- (27) Matsuda, T.; Minami, D.; Khoerunnisa, F.; Sunaga, M.; Nakamura, M.; Utsumi, S.; Itoh, T.; Fujimori, T.; Hayashi, T.; Hattori, Y.; Endo, M.; Isobe, H.; Onodera, H.; Kaneko, K. *Langmuir* **2015**, *31*, 3194.
- (28) Kukobat, R.; Minami, D.; Hayashi, T.; Hattori, Y.; Matsuda, T.; Sunaga, M.; Bharti, B.; Asakura, K.; Kaneko, K. *Carbon N. Y.* **2015**, *94*, 518.
- (29) Saito, T.; Ohshima, S.; Okazaki, T.; Ohmori, S.; Yumura, M.; Ijima, S. *J. Nanosci. Nanotechnol.* **2008**, *8*, 6153.
- (30) Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, a. M. *Rev. Sci. Instrum.* **2007**, *78*.
- (31) Setsuhara, Y.; Cho, K.; Shiratani, M.; Sekine, M.; Hori, M. *Thin Solid Films* **2010**, *518*, 6492.
- (32) Wang, J.; Sun, J.; Gao, L.; Wang, Y.; Zhang, J.; Kajiuira, H.; Li, Y.; Noda, K. *J. Phys. Chem. C* **2009**, *113*, 17685.

- (33) Morant, C.; Torres, R.; Jimenez, I.; Sanz, J. M.; Elizalde, E. *J. Nanosci. Nanotechnol.* **2008**, *8*, 1.
- (34) Kaskela, A.; Nasibulin, A. G.; Timmermans, M. Y.; Aitchison, B.; Papadimitratos, A.; Tian, Y.; Zhu, Z.; Jiang, H.; Brown, D. P.; Zakhidov, A.; Kauppinen, E. I. *Nano Lett.* **2010**, *10*, 4349.
- (35) Itkis, M. E.; Niyogi, S.; Meng, M. E.; Hamon, M. a.; Hu, H.; Haddon, R. C. *Nano Lett.* **2002**, *2*, 155.

Figure 1. Variations of the sheet resistance and transmittance with the coordinates (x, y) in cm of SWCNT film, at the constant concentration of the Zn/Al complex of 1.00 wt.%. The SWCNT concentration of ink: 0.005 wt. % (a) and (a₀), 0.02 wt.% (b) and (b₀), 0.05 wt.% (c) and (c₀).

Figure 2. Viscosity of Zn/Al complex-SWCNT ink against the concentration of SWCNT (a) and contact angle of SWCNT ink on the PET substrate (b). Here the concentration of Zn/Al complex dispersant is kept at 1.00 wt.% for all dispersion systems.

Figure 3. Sheet resistance against the concentration of HNO₃ used for the washing treatment (a) and sheet resistance versus the treatment time by 1M HNO₃ (b).

Figure 4. The AFM micrographs of SWCNT film on PET substrate (a) before and (b) after acid treatment and their size-distribution histograms of bundles corresponding to the above micrographs.

Figure 5. (a) XPS spectra of the film before and after acid treatment on the PET substrate. (b) Spectra of C 1s of PET substrate: Spectra of C 1s (c) before and (d) after the treatment with the deconvoluted spectra.

Figure 6. (a) Optical absorption spectra and (b) exposure time dependence of sheet resistance of SWCNT film after acid treatment. Raman spectra recorded at the laser wavelengths of (c) 785 and (d) 532 nm.

Table 1. Chemical composition change of the SWCNT film before and after acid treatment.

Table 1. Chemical composition change of the SWCNT film before and after acid treatment.

Element	Before treatment	After treatment
	at. %	at. %
Zn	5.9	0.0
Al	5.5	0.0
C	43.8	83.4
O	43.3	15.9

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6