



Letter

Highly conductive and transparent carbon nanotube composite thin films deposited on polyethylene terephthalate solution dipping

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ABSTRACT

In this letter we present highly conductive and transparent thin films of single-walled carbon nanotubes (SWCNT) and conductive polymer composite deposited on polyethylene terephthalate film substrates by solution dipping. The initial results show that $66 \Omega/\square$ sheet resistance can be achieved with 80% transmission at the wavelength of 550 nm. This result is much superior to the performances of the pure SWCNT thin films deposited using the same technique. The improvement is attributed to the increase of effective electric conductive tube–tube junctions in the CNT network.

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As an integral part of the flexible displays and solar cells, the flexibility of the transparent electrodes is essential. The conventional transparent and conductive thin films, such as indium tin oxide (ITO), are brittle. When deposited on flexible substrates, the conductivity of those thin film electrodes tends to deteriorate significantly after subjecting to thermal and/or mechanical strain [1–3]. For instance, Na et al. [1] found that the resistance of ITO on Polyethylene Terephthalate (PET), increased by ~40 times after ~2500 bending cycles at a radius of ~8 mm. On the other hand, transparent carbon nanotube (CNT) conductive thin films have shown great potential in addressing this issue [4,5]. Ng et al. [4] tested the changes of the sheet resistance of a single-walled CNT (SWCNT) thin film dip-coated on PET surface and found that the resistance of the sample remains almost unchanged during a 10,000 two-point bending test cycle (with the bending radius of curvature of 12.5 mm), and only showing a 10% increase at the end of the test. In addition to its flexibility, CNT films also show high transparency in a large range of solar spectrum as compared to ITO which has excellent transparency in the visible range. In recent years, transparent CNT thin films have been studied and tested in a variety of optoelectronic devices [6–10].

Though great progresses have been made in the development of transparent conductive CNT thin films, the performances of the carbon nanotube films are lagging behind those of the ITO thin films. The main challenge here is to address the trade-off between transparency and conductivity. Many factors have been studied in

order to improve the conductivity of the CNT thin films without sacrificing their transparency [4,11–15]. For example: processing techniques and parameters [4,11]; length of the CNT [12]; doping [13,14]; and metallic amount of the CNT in the mixture [14]. In this letter, we report an alternative approach to improve both transparency and conductivity of the CNT thin films. Specifically, we introduce conductive polymers into the CNT network to reduce the resistance between tubes and lower the percolation threshold.

Commercially available SWCNTs (outer diameter: 1–2 nm; length: 5–30 μm) from the Chinese Academy of Science were used in this work. The conducting polymer used was poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT) purchased from H.C.Starck. The preparation of the SWCNT/PEDOT solution included three steps. Firstly, the as-received SWCNT was dispersed in distilled water by magnetic stir and sonication with the help of surfactant X-100 (from Sigma-Aldrich). Secondly, the CNT mixture was centrifuged to remove the particles and large bundles in the mixture. Thirdly, the above prepared SWCNT solution was mixed with the PEDOT. The flexible substrate employed in this work is PET films from Dupont. It is first cleaned by ethanol, then treated by air plasma for 10 min and then coated with amino propyl trimethoxy silane (APTMS). The SWCNT/conducting polymer composite thin film was formed by dip coating the above prepared solution on the PET surface and dried at 110 °C for 5 min. The final films were rinsed in nitric acid (HNO_3) and water in order to remove the surfactants in the thin films.

Fig. 1 shows the transmission spectra of two SWCNT composite thin films with different sheet resistances. For comparison reason, we also show the spectrum of a pure SWCNT thin film prepared with the same

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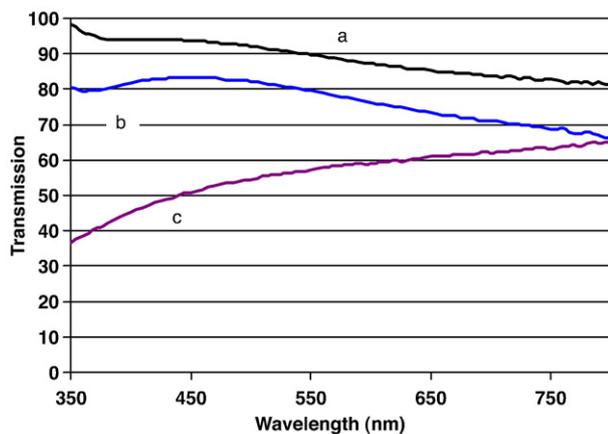


Fig. 1. Transmission spectra of SWCNT/PEDOT composite films and SWCNT thin film, (a), SWCNT/PEDOT composite thin film, sheet resistance: $94 \Omega/\square$, (b), SWCNT/PEDOT composite thin film, sheet resistance: $66 \Omega/\square$, (c) SWCNT thin film, sheet resistance: $67 \Omega/\square$.

procedure. The results clearly demonstrate that the composite films are much more transparent than the pure SWCNT thin film is in the wavelength range from 350 nm to 800 nm, suggesting a thinner and more transparent SWCNT composite film can offer the same conductivity as a thicker pure SWCNT film. Specifically, composite thin films with the sheet resistances of $66 \Omega/\square$ and $94 \Omega/\square$ show 80% and 90% transmission at the wavelength of 550 nm respectively, while the pure SWCNT thin film with the sheet resistance of $67 \Omega/\square$ can only transmit $\sim 58\%$ of the light at the wavelength of 550 nm. This result is surprising as single SWCNTs have significantly better conductivity than most conducting polymers do.

When CNTs are deposited on a substrate by solution methods, they are randomly tangled together on the surface and normally form an isotropic network. Due to the large aspect ratios of the CNTs, the solution deposition methods tend to form a large amount of voids in the film, as revealed by a Hitachi S-4700 field emission scanning electron microscope (FE-SEM) with a 3 kV acceleration voltage. A typical example of those SEM analyses was presented in Fig. 2. The electric conductivity of the SWCNT thin films is attributed to the formation of a percolating network of CNTs. The charge carriers move between neighboring CNTs via quantum-mechanical tunneling process. The conductivity of the thin film σ , according to the statistical percolation theory, can be expressed by [16]:

$$\sigma = \sigma_0(p - p_c)^t, p > p_c$$

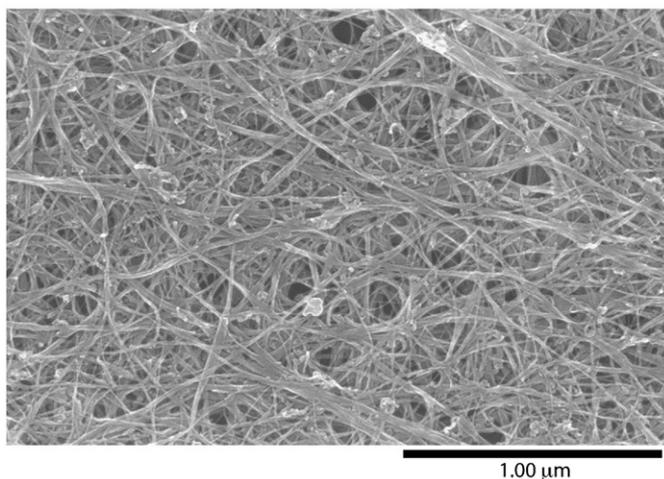


Fig. 2. A typical SEM picture of pure SWCNT thin film deposited on PET surface by dip coating (sheet resistance: $136 \Omega/\square$).

where σ_0 is the conductivity of an element of the percolating network, p is the concentration of the nanotubes (for the thin film illustrated in Fig. 2, air can be treated as the matrix); p_c is the percolation threshold, t is related to sample dimensionality, i.e. $t \approx 1, 1.33$ or 2 for one, two, or three dimensions, respectively [17].

From this equation, it is obvious that the conductivity of the CNT thin films depends on three factors: the first one is the conductivity of SWCNT itself, which is excellent [18]. The second one is the concentration of the SWCNTs, i.e. the amount of free carriers per unit area in the film. The third one is the percolation threshold, in other words, the capability of free carriers moving between the tubes in the film. As shown in Fig. 2, the CNTs are loosely and randomly entangled. When two hard tubular objects meet each other, as the case of CNT tube to CNT tube, it is very difficult to achieve intimate contact between these two objects due to physical shape restriction and the stiffness of the material. Therefore, tunnel barriers to different extent are formed in the tube-tube junctions. Some of those junctions are electrically conductive, where free carriers can tunnel from one SWCNT into an adjacent SWCNT; some other junctions are less electrically conductive, where free carriers have difficulty to cross over; the remaining junctions are not conductive, where free carriers remain localized upon the SWCNT. Obviously, those carriers crossing the tube-tube junctions and moving between tubes contribute to the conductivity of the network while the carriers remaining localized do not. Hence, if we are able to increase the number of the effective electrically conductive tube-tube junctions per unit area without increasing the number of the SWCNTs, we will improve the transport of free carriers between the tubes and lower the percolation threshold, thus improving the conductivity of the CNT networks. Recent work by Blackburn et al. [14] supports this analysis. Those workers found that the DC conductivity of the SWCNT film is several orders of magnitude lower than expected by considering the total carrier density within the conduction band of individual SWCNTs (approximately 1 electron per carbon atom). They suggested that the tube-tube junctions primarily control the resistivity in the SWCNT films.

A recent publication [19] reports that aligning the CNTs can improve the electric conductivity of CNT/polymer composite. This can be attributed to the increase of both free carrier concentration and the effective electrically conductive tube-tube junctions per unit area. Adding conductive polymer to the SWCNT network plays the similar roles. Fig. 3 presents a typical example of the surface morphology of SWCNT/conducting polymer composite thin films characterized by the same SEM technique mentioned above. As it can be seen, the polymer has filled most voids existed in the CNT network. There are only few large CNT bundles existing on the film surface, which can be removed by proper solution purification procedures. In addition, the

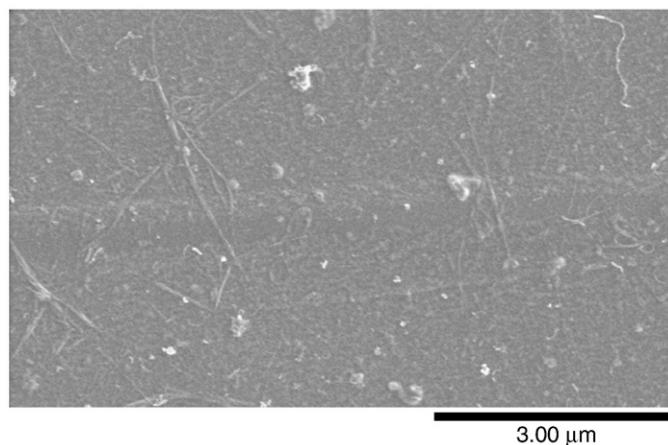


Fig. 3. A typical SEM picture of SWCNT/PEDOT composite thin film deposited on PET surface by dip coating (sheet resistance: $116 \Omega/\square$).

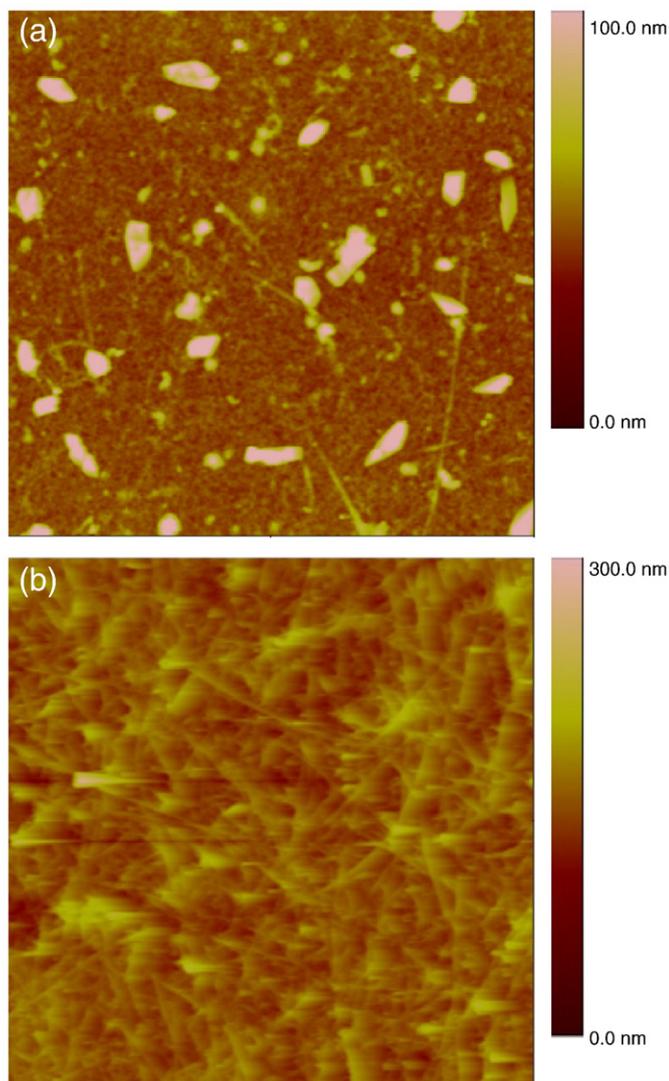


Fig. 4. Examples of AFM pictures for CNT thin films. (a) Single-walled CNT/PEDOT composite thin film deposited on glass slide by dip coating. (b) Pure single-walled CNT thin film deposited on glass slide by dip coating.

surface of the composite film is much smoother than that of the pure CNT films, as determined by the morphology analyses using an atomic force microscope (AFM) in tapping mode (typical examples are shown in Fig. 4). This is very important for organic solar cell applications as rough CNT network might short the circuit. Since the charge carrier mobility of the SWCNT is ~ 4 orders higher than that of conductive polymers [20], and most conductive polymers have low

free charge carrier density at room temperature, the contributions from the free carriers in the polymer probably can be neglected when the CNT percolation network is formed. On the other hand, conductive polymer helps forming electric contacts between CNT tubes and increasing the effective electric conductive tube-tube junctions in the CNT network. This facilitates the transport of free carriers between adjacent CNTs and decreases the percolation threshold, hence reducing the sheet resistance of the CNT networks.

In conclusion, SWCNT/conducting polymer composite thin films offer excellent conductivity and transparency in the visible light region. The preliminary results are close to those of the commercial available ITO thin films deposited on PET, such as the ones from Sigma-Aldrich ($35 \Omega/\square$, $>86\%$ transmission at 550 nm). With the optimization of the composition of the SWCNT composite, plus other techniques reported in the literature [11–15], SWCNT/conducting polymer composite thin films might potentially offer better or comparable performances as the conductive oxides.

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References

- [1] S. Na, S. Kim, J. Jo, D. Kim, *Adv. Mater.* 20 (2008) 4061.
- [2] J. Lewis, S. Grego, B. Chalamala, E. Vick, D. Temple, *Appl. Phys. Lett.* 85 (2004) 3450.
- [3] D.R. Cairns, R.P.W. II, D.K. Sparacin, S.M. Sachsman, D.C. Paine, G.P. Crawford, *Appl. Phys. Lett.* 76 (2000) 1425.
- [4] M.H.A. Ng, L.T. Hartadi, H. Tan, C.H.P. Poa, *Nanotechnology* 19 (2008) 205703.
- [5] M. Zhang, S. Fang, A.A. Zakhidov, S.B. Lee, A.E. Aliev, C.D. Williams, K.R. Atkinson, R.H. Baughman, *Science* 309 (2005) 1215.
- [6] J. van de Lagemaat, T.M. Barnes, G. Rumbles, S.E. Shaheen, T.J. Coutts, C. Weeks, I. Levitsky, J. Peltola, P. Glatkowski, *Appl. Phys. Lett.* 88 (2006) 233503.
- [7] M.W. Rowell, M.A. Topinka, M.D. McGehee, H.-J. Prall, G. Dennler, N.S. Sariciftci, L. Hu, G. Gruner, *Appl. Phys. Lett.* 88 (2006) 233506.
- [8] K. Lee, Z. Wu, Z. Chen, F. Ren, S.J. Pearton, A.G. Rinzler, *Nano. Lett.* 4 (2004) 911.
- [9] Y. Wang, C.-a. Di, Y. Liu, H. Kajiura, S. Ye, L. Cao, D. Wei, H. Zhang, Y. Li, K. Noda, *Adv. Mater.* 20 (2008) 4442.
- [10] Q. Cao, S.-H. Hur, Z.-T. Zhu, Y.G. Sun, C.-J. Wang, M.A. Meitl, M. Shim, J.A. Rogers, *Adv. Mater.* 18 (2006) 304.
- [11] R.C. Tenent, T.M. Barnes, J.D. Bergeson, A.J. Ferguson, B. To, L.M. Gedvilas, M.J. Heben, J.L. Blackburn, *Adv. Mater.* 21 (2009) 3210.
- [12] D. Simien, J.A. Fagan, W. Luo, J.F. Douglas, K. Miger, J. Obrzut, *ACS Nano* 2 (2008) 1879.
- [13] T.M. Barnes, J.L. Blackburn, J.V.D. Lagemaat, T.J. Coutts, M.J. Heben, *ACS Nano* 2 (2008) 1968.
- [14] J.L. Blackburn, T.M. Barnes, M.C. Beard, Y.-H. Kim, R.C. Tenent, T.J. McDonald, B. To, T.J. Coutts, M.J. Heben, *ACS Nano* 2 (2008) 1266.
- [15] Z. Li, H.R. Kandel, E. Dervishi, V. Saini, Y. Xu, A.R. Biris, D. Lupu, G.J. Salamo, A.S. Biris, *Langmuir* 24 (2008) 2655.
- [16] G. Stauffer, *Introduction to Percolation Theory*, Taylor & Francis, London, 1985.
- [17] S.A. Curran, J. Talla, S. Dias, D. Zhang, D. Carroll, D. Bix, *J. Appl. Phys.* 105 (2009) 073711.
- [18] K. Bradley, J.-C.P. Gabriel, G. Gruner, *Nano Lett.* 3 (2003) 1353.
- [19] H. Peng, X. Sun, *Chem. Phys. Lett.* 471 (2009) 103.
- [20] S. Hong, S. Myung, *Nat. Nanotechnol.* 2 (2007) 207.