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Improving the Electrical Conductivity of Multi-walled Carbon Nanotube Thin Films Using Ag-nanowires

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Abstract: ***Background*:** Transparent and conductive films (TCF) are the principal core for fabricating electronic devices. The traditional TCFs, indium tin oxide (ITO) thin films have been used for such devices which have their own drawbacks. In the present study, multi-walled carbon nanotubes (MWCNTs) thin films were fabricated and their electrical conductivity was improved by adding Ag nanowires to the CNTs for the first time in literature.

***Methods*:** The initial multi-walled carbon nanotubes with the diameters less than 10 nm and 5-15 µm length were oxidized in a mixture of sulfuric and nitric acids. Silver nanowires were synthesized by solvothermal method through reducing silver nitrate with ethylene glycol (EG) in the presence of polyvinylpyrrolidone (PVP). Different solutions including 1.8, 3.5, 5.1, and 10.5 wt.% of Ag/MWCNTs were prepared and coated on a cleaned and functionalized glass substrate by spin coating technique.

***Results*:** For low thicknesses, dc conductivity of the films was thickness-dependent but appeared to become bulk-like for film thicknesses of about 300 nm. A sheet resistance of 1006 ohm/sq with 82% transmittance at 550 nm in wavelength was attained for 5.1wt.% Ag nanowires in MWCNTs. Using the deduced data, the DC conductivity to optical conductivity ratio for a percolated network 92.4 was calculated for 5.1wt.% of Ag nanowires in MWCNTs which was much higher than 37 for the films without using Ag nanowires.

***Conclusions*:** It was observed that the conductivity and figure of merit of different films of MWCNTs-Ag nanowires composite were improved by increasing Ag nanowires concentration. The electrical conductivity and optical transmittance were affected by different Ag wt.% and different film thicknesses. The low sheet resistance of thin conductive films was due to the increased contact areas between MWNTs and Ag nanowires on the MWNTs surfaces.

Keywords: Ag nanowires, carbon nanotube, sheet resistance, transparent conductive film.

1. INTRODUCTION

Generally, transparent and conductive films (TCF) are the principal core for fabricating electronic devices such as flexible displays, digital papers, liquid crystal displays, solar cell and touch screen panels [1-4]. The traditional generations of TCFs were indium tin oxide (ITO) thin films. Because of their higher transparency and low sheet resistance, ITO thin films were used in the mentioned devices.

The increase in sheet resistance due to crack formation, the need to be produced at high temperatures in vacuum, its expensiveness due to high demands for fabricating thin films and also its brittleness under small strains, have all contributed to the replacement of ITO with materials that are cost-effective and do not have the drawbacks in ITO films [5-7]. To this aim, carbon nanotubes, graphene and silver nanowires can be used for fabrication of TCFs. These nanostructures can overcome many of restrictions of ITO films and can be highly conductive with a suitable transparency and thus applicable in flexible films [8-10]. Among these nanostructures, silver nanowires thin films have been prepared by different techniques and their ratio of bulk-DC conductivity to optical conductivity is more than 500 [8]. One of the major restrictions of this material as TCFs is the weak adhesion of silver nanowires to Poly Ethylene Tetra phetalat (PET) [8]. While graphene has a very good conductivity and good transparency for fabricating TCFs, there are some problems with its reproduction for commercial applications and also the methods for producing TCFs of this material are not as simple as those of CNTs [9]. However, because of the exclusive properties of CNTs including inherent mechanical and electrical properties, CNTs can be considered as a good candidates for fabricating TCFs and overcome many of the mentioned drawbacks. One of the advantages of using CNTs for fabricating TCFs on flexible substrates is the good adhesion of CNTs to the PET substrates [11-15]. Since large tube-tube contact resistance provides a high sheet resistance for CNTs networks, improving sheet resistance becomes a requirement. Metallic nanoparticles improve the electrical conductivity of CNTs films by providing the bridge between separated CNTs [9].

In the present study, we used silver nanowires as a nanostructure that improves the electrical conductivity of CNTs films. For this purpose, we used different silver nanowires

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percentages. Using silver nanowires expands the contact area between MWCNTs films and decreases the sheet resistance of thin films. Briefly, the steps for using Ag-nanowires and fabricating Ag-MWCNTs films are as follows: oxidation of MWCNTs under sulfuric and nitric acids with a ratio of 3:1, attaching Ag-nanowires to functionalized MWCNTs, spin coating on glass as substrate and finally post-heat treatment at 285 °C for 30 minutes, at ambient pressure. The annealing step causes the Ag-nanowires to melt between MWCNTs and enhances the electrical conductivity.

2. EXPERIMENTAL METHOD

2.1. Preparation of Functionalized MWCNTs Suspensions

The initial multi-walled carbon nanotubes with the diameters less than 10 nm and 5-15 µm length were purchased (Shenzhen Co., China). MWCNTs were oxidized in a mixture of sulfuric and nitric acids, which is a well-known chemical treatment for carbon nanotubes functionalization. Oxidizing carbon atoms at the caps generates defects in the sidewalls of the CNTs. Researchers -have used this oxidation method to functionalize the MWCNTs and produce short CNTs [16-19]. The functionalized MWCNTs were dispersed in ethanol and then sonicated for 30 minutes without any surfactants.

2.2. Silver Nanowires Synthesis

For synthesis of silver nanowires by solvothermal method, 11.1 ml EG solution of 0.15 M PVP/0.1 mM NaCl was injected drop by drop into 11.1 mL of a magnetically stirred EG solution of 0.1 M $AgNO_3$ using a syringe pump at a rate of 45 mL/h. The resulting solution was homogeneously mixed by stirring for 5 minutes and then put into a 50 ml Teflon-lined autoclave. The autoclave was sealed and heated at 160 ºC for 2.5 hours and afterward cooled to room temperature. The synthesized nanowires were separated from EG solution by centrifugation (3500 rpm, 15 min) and washed with acetone once. Finally, the silver nanowires were dispersed in ethanol for further characterization and use.

The XRD pattern of synthesized Ag nanowires exhibited five diffraction peaks that corresponded to pure silver metal with fcc crystal structure (JCPDS 04 -0783). The mean Ag nanowires diameter was 155 nm and the lengths of Ag nanowires were ranged from 3 to 40 µm with average size of 10 µm.

2.3. Preparation of MWCNTs-Ag Solutions

Different solutions including 1.8, 3.5, 5.1, and 10.5 wt.% of Ag/MWCNTs were prepared. The prepared solutions were ultra-sonicated for 30 minutes in an ultrasonic bath (42 KHz, 100 W), and after that the suspension was centrifuged to remove the possible particles and large bundles in the suspension. The suspension was coated on a cleaned and functionalized glass substrate with 3-aminopropyltriethoxysilane (APTES) binder by spin coating technique. The films were annealed at 285 ºC for 30 minutes and the sheet resistance and optical transmittance (at 550 nm) of the films were measured before and after the annealing process. It was observed that by annealing, the Ag nanowires partially melted on the MWCNTs surfaces caused an increase in the contact area between MWCNTs. It is noteworthy that at such a temperature, the CNTs maintain their structure and will not burn [20].

2.4. Characterizations

A scanning electron microscope (SEM: MIRA, TESCAN- Czech Republic) was used to observe the surface morphology of MWCNTs films and to measure the films' thickness. To this aim, the glass substrates were tilted in order to have a better view for imaging. Sheet resistance of the films was measured by a 4-point probe standard technique at room temperature and their optical transmittance was measured by means of a UV-Vis spectrophotometer (Cintra 101, GBC - Australia).

3. RESULTS AND DISCUSSION

There are two approaches for the establishment of sheet resistance in CNTs films, namely creating large sheet resistance between tube-tube MWCNTs and reducing the resistivity of MWCNTs networks [21]. The resistivity of CNTs networks was reduced by using metallic nanoparticles [22]. Decorating CNTs by metallic nanoparticles and nanowires is considered a good method for enhancing the electrical conductivity of CNTs films. Ag nanoparticles and Ag nanowires act like a nano-bridge between CNTs increasing the contact area between individual CNTs. Therefore, by using these metallic nanostructures, the conductive path between CNTs is enhanced and electrical conductivity is improved.

Fig. (**1**) shows a typical SEM images of Ag nanowires which are embedded in CNTs.

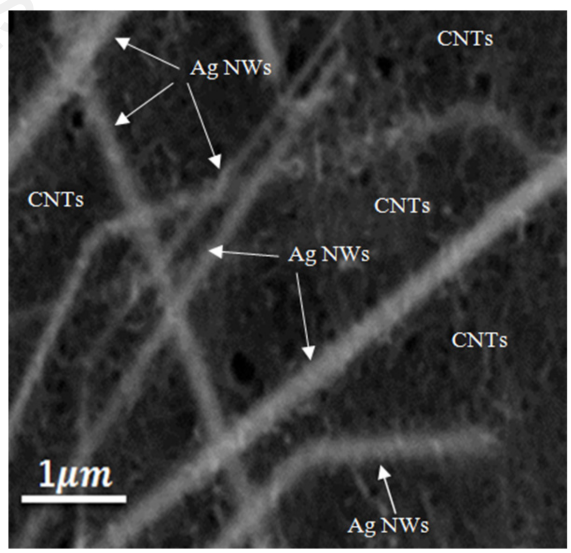

Fig. (1). SEM image of Ag nanowires-MWCNTs films. The Ag nanowires are embedded in CNTs.

Fig. (**2**) shows the transmittance (λ=550 nm) of the films with various thicknesses as a function of Ag nanowires wt.%. It is clear from Fig. (**2**), that not only by increasing the thickness the transmittance is reduced but also for all thicknesses by increasing the Ag nanowires wt.%, the transmittance of the films is reduced almost with the same slope.

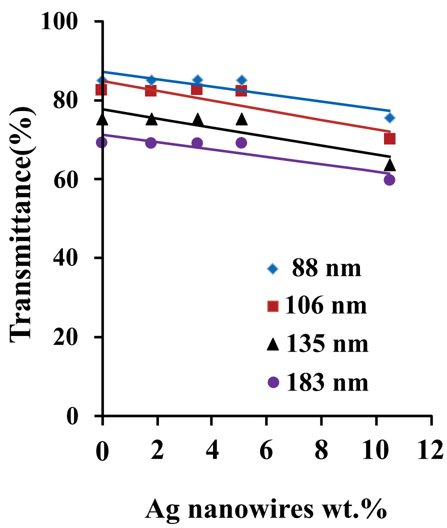

Fig. (2). Transmittance at 550 nm of various film thicknesses versus Ag nanowires wt.(%).

Also, it can be observed that for films prepared using low wt.% of Ag nanowires, the transmittance was nearly the same but reduced by increasing the wt.% of Ag nanowires. By increasing the Ag nanowires wt.% to higher than 10.5%, the transmittance was remarkably reduced, possibly due to the filling of the empty spaces between the nanotubes by Ag nanowires. Indeed, by increasing the Ag nanowires' percentage, their concentration increases in the empty spaces between the CNTs resulting in the reduction of the films' transmittance. However, if so many Ag nanowires are attached to the MWCNTs' surfaces, they will fill the empty spaces between MWCNTs and act like an obstacle for light passing through, hence reducing the films' transmittance.

Fig. (**3**) shows the optical transmittance of the films with different Ag wt.% as a function of sheet resistance. The Ag nanowires react with carboxyl-terminated MWCNTs and are attached physically to the surface of MWCNTs. The sheet resistance and the optical transmittance can be controlled by Ag wt.%. By increasing the number of the attached nanowires on the MWCNTs surfaces and increasing the contact area between MWCNTs, the conductivity of the films improves. On the other hand, by adding more Ag nanowires, the films' transmittance reduces. The lowest value for the sheet resistance was 1006 ohm/sq for 5.1% wt.% of Ag nanowires. Such a film showed 85% transparency and its conductivity was enhanced compared to that of the films without Ag nanowires. It is clear from Fig. (**3**) that by adding Ag nanowires up to 10.5%, the films' transmittance as well as sheet resistance is reduced. In fact, adding Ag nanowires provides some good links between the nanotubes thereby their electrical conductivity is enhanced, but by adding Ag nanowires above a certain value, the films' transmittance reduces because of the increase in the light scattering centers. The conductivity and transmittance of the films depends on the films' thickness. By increasing the films' thickness, the conductivity enhances but their transmittance is reduced. However, the increasing and decreasing rates were different for various wt.% of Ag nanowires. In general, transmittance and sheet resistance for thin metallic films are related by [23]:

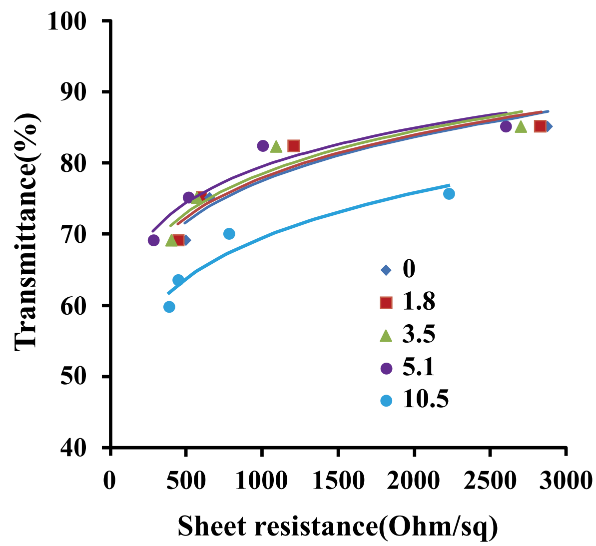

Fig. (3). Films' transmittance versus their sheet resistance for different percentages of Ag nanowires. The solid lines are power fitting and drawn as guide for eyes.

$$T=\left(1+\frac{Z_0}{2R_s}\frac{\sigma_{op}}{\sigma_{DC.B}}\right)^{-2} \qquad (1)$$

where Z_0 is the free space impedance (377Ω), σ_{op} is the optical conductivity and $\sigma_{DC,B}$ is the bulk DC conductivity. For a thin film, DC conductivity is thickness-dependent and is proportional to t^n, where t is the film's thickness and n is the percolation exponent. De *et al*. [24, 25] using a simple model have shown that there is another relation between T and R_s of transparent conductors in percolative regime at which the conductivity is thickness-dependent as [25]:

$$T=\left(1+\frac{1}{\Pi}\left(\frac{Z_0}{R_s}\right)^{\frac{1}{1+n}}\right)^{-2} \qquad (2)$$

Π is a dimensionless parameter called percolative figure of merit and its higher values mean higher T and lower R_s. In order to investigate the effect of different Ag nanowires concentration, these equations were applied to the films prepared with different Ag wt.%. In a recent study we have found DC conductivity to optical conductivity ratio 37 for CNTs without using Ag nanowires [26]. It is evident that with increasing the Ag nanowires concentration, the figure of merit increases. The maximum of the DC conductivity to optical conductivity ratio was 92.4 for 5.1 wt.% of Ag nanowires. Such an increase was due to the increase in transmittance and a decrease in sheet resistance at 5.1 wt.% of Ag nanowires. Also, it was found that the percolative figure of merit increased from 5, to 5.8 when Ag wt.% was increased from 1.8 to 5.1 wt.%. For 10.5 wt.% Ag nanowires percolative figure of merit was 3.6. At higher Ag nanowires concentrations, despite the enhancement of electrical conductivity, the optical transmittance of the films was reduced. The component n for 1.8, 3.5 and 5.1 wt% Ag nanowires had values from 1.3, 1.2 to 1.1 respectively while it increased to 1.7 for

10.5 wt% Ag nanowires. The parameters Π and n were calculated through a power fitting of log-log plot of $T^{-0.5}$ -1 versus R_s on equation 2, while the $\frac{\sigma_{DC,B}}{\sigma_{op}}$ ratio was found by fitting on equation 1.

Fig. (**4**) shows the sheet resistance versus Ag nanowires wt.% for different film thicknesses. For thinner films, the reduction in sheet resistance by increasing Ag wt.% is clear, but for thicker films the slope of sheet resistance vs Ag nanowires concentration is smaller. Nanowires, due to having a very high surface-area-to-volume ratio, provide a large driving force for diffusion, especially at higher temperatures. Annealing can increase the conductivity of the MWCNT-Ag films. It was found that by increasing the annealing temperature from 200 to 285 ºC for 30 minutes, the sheet resistance was reduced significantly.

Fig. (**5**) shows the DC-conductivity to optical conductivity versus annealing temperature for different Ag nanowires

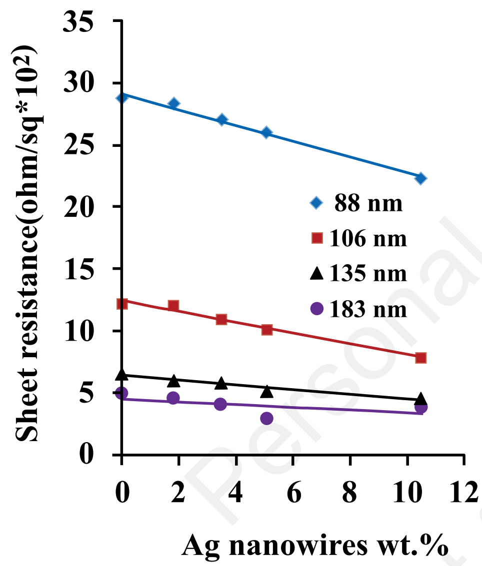

Fig. (4). Sheet resistance versus Ag-nanowires wt.% for different film thicknesses.

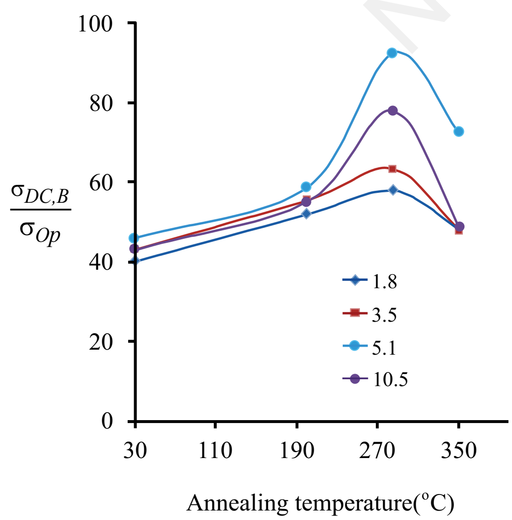

Fig. (5). DC-conductivity to optical conductivity ratio versus annealing temperature.

percentages. It is clear from Fig. (**5**) that figure of merit for all different Ag nanowires percentage is increased. The maximum figure of merit found 92.4 for 5.1wt.% of Ag nanowires.

CONCLUSION

In this study, thin films of MWCNTs-Ag nanowires composite were fabricated for the first time. It was shown that the conductivity and figure of merit of different films were improved by increasing Ag nanowires concentration. The maximum conductivity was observed for the films containing 5.1wt.% of Ag nanowires. The DC conductivity to optical conductivity ratio for 5.1wt.% Ag nanowires was 92.4. The electrical conductivity and optical transmittance were affected by different Ag wt.% and different film thicknesses.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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REFERENCES

[1] Ratcliff, E.L.; Lee, P.A.; Armstrong, N.R. Work function control of hole-selective polymer/ITO anode contacts: an electrochemical doping study. *J. Mater. Chem.*, **2010**, *20*, 2672-2679.

[2] Sun, Q.; Kim, J.H.; Park, J.H.; Seo, S. Characteristics of a pentane thin film transistor with periodic groove patterned poly (methyl methacrylate) dielectrics. *Appl. Phys. Lett.*, **2010**, *96*, 103301.

[3] Wang, S.J.; Geng, Y.; Zheng, Q.B.; Kim, J.K. Fabrication of highly conducting and transparent graphene films. *Carbon*, **2010**, *48*, 1815-1823.

[4] 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.

[5] Hu, Y.; Diao, X.; Wang, C.; Hao, W., Wang, T. Effect of heat treatment on properties of ITO films prepared with rf magnetron sputtering. *Vacuum*, **2004**, *75*, 183-188.

[6] Blandenet, G.; Court, M.; Lagarde, Y. Thin layers deposited by the pyro sol process". *Thin Solid Films*, **1981**, *77*, 81-90.

[7] Gruner, G. Carbon nanotube films for transparent and plastic electronics. *J. Mater. Chem.*, **2006**, *16*, 3533-3539.

[8] Sukanta, D.; Higgins, T.M.; Lyon, P.E.; Doherty, E.M.; Nirmalraj, P.N.; Blau, W.J.; Boland, J.J.; Coleman, J.N. Silver nanowire networks as flexible, transparent, conducting films: extremely high DC to optical conductivity ratios. *ACS Nano*, **2009**, *3*, 1767-1774.

[9] Lee, J.Y.; Connor, S.T.; Cui, Y.; Peumans, P. Solution-processed metal nanowires meshtransparent electrodes. *Nano Lett.*, **2008**, *8*, 689-692.

[10] Bae, S.; Kin, H.; lee, Y.; Xu, X.; Park, J.S.; Zheng, Y.; Balakrumar, J.; Lei, T.; Kim, H.R. Roll-to- roll production of 30- inch graphene films for transparent electrode. *Nat. Nanotechnol.*, **2010**, *5*, 574-578.

[11] Sreekumar, T.; Liu, K.; Ericson, L.; Hauge, R. Single-Wall Carbon Nanotube Films. *Chem. Mater.*, **2003**, *15*, 175-178.

[12] Meitl, M.; Zhou, Y.; Gaur, A.; Jeon, S.; Usrey, M.; Strano, M.; Rogers, J. Solution Casting and Transfer Printing Single-Walled Carbon Nanotube Films. *Nano Lett.*, **2004**, *4*, 1643-1647.

[13] 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. Transparent ,conductive carbon nanotube films. *Science*, **2004**, *305*, 1273-1276.

[14] Pasquier, A.D.; Unalan, H.E.; Kanwal, A.; Miller, S.; Chhowalla, M. Highly transparent and flexible field emission devices. *Appl. Phys. Lett*., **2005**, *87*, 203511-203513.

[15] Rowell, M.W.; Topinka, M.A.; Prall, H.J.; Dennler, G.; Sariciftci, N.S.; Hu, L.; Gruner, G.; McGehee, M.D. Organic solar cells with carbon nanotube network electrods. *Appl. Phys. Lett.*, **2006**, *88*, 233506-233509.

[16] Cao, Q.; Hur, S.H.; Zhu, Z.T.; Sun, Y.; Wang, C.; Meitl, M.A.; Shim, M.; Rogers, J.A. Highly bendable, transparentthin-film transistors that use carbon-nanotube-based conductors and semiconductorswith elastomeric dielectrics. *Adv. Mater*., **2006**, *18*, 304-309.

[17] Chen, J.; Hamon, M.A.; Hu, H.; Chen, Y.; Rao, A.U.; Eklund, P.C.; Haddon, R.C. Formation mechanism of properties of single-walled carbon nanotubes. *Science*, **1998**, 28295-28298.

[18] Chen, J.; Hamon, M.A.; Lynksyitove, S.; Itkis, M.E. Dissolution of full-length single-walled carbon nanotubes. *J. Phys. Chem. B*, **2001**, *105*, 2525-2528.

[19] Farbod, M.; Khajehpour -Tadavani, S.; Kiasat, A. Surface oxidation and effect of electric field on dispersion and colloids stability of multiwalled carbon nanotubes. *Colloids Surf. A: Physicochem. Eng. Aspects*, **2011**, *384*, 685-690.

[20] Faraji, S.; Stano, K.; Rost, C.; Maria, J.P.; Zhu, Y.; Bradford, P.D. Structural annealing of carbon coated aligned multi-walled carbon nanotube sheets. *Carbon*, **2014**, *79*, 113-122.

[21] Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y.H.; Kim, S.G.; Rinzler, A.G. Crystalline ropes of metallic carbon nanotubes. *Science*, **1996**, *273*, 483-487.

[22] Fischer, J.E.; Dai, H.; Thess, A.; Lee, R.; Hanjiani, N.M.; Dehaas, D.L.; Smally, R. Metallic resistivity in crystalline ropes of single-wall carbon nanotubes. *Phys. Rev. B*, **1997**, *55*, R4921.

[23] Dressel, M.; Gruner, G. *Electrodynamics of Solids: Optical Properties of Electrons in Matter*. Cambridge University Press: Cambridge, **2002**.

[24] Dan, B.; Irvin, G.C.; Pasquali, M. Continuous and scalable fabrication of transparent conducting carbon nanotube films. *ACS Nano*, **2009**, *3*, 835-843.

[25] De, S.; King, P.J.; Lyons, P.E.; Khan, U.; Coleman, J.N. Size effects and the problem with percolation in nanostructured transparent conductors. *ACS Nano*, **2010**, *4*, 7064-7072.

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