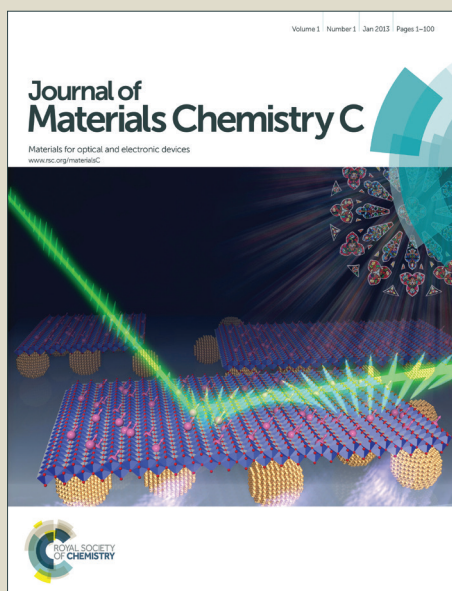


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Fabrication and evaluation of adhesion enhanced flexible carbon nanotube transparent conducting films

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Single-walled carbon nanotubes (SWCNTs) were dispersed in water with the help of a combination of surfactants to achieve high concentration SWCNT ink. Transparent conducting films (TCFs) were fabricated through rod-coating method using the SWCNT ink. The addition of binders (polyacrylic acid or carboxymethyl cellulose) greatly enhanced the adhesion of SWCNT films to substrate and the cohesion between CNTs, which produced a uniform film of SWCNTs by preventing damage during the post-treatment process. The thickness of SWCNT films is controlled by the amount of SWCNTs in the solution and the diameter of the wire used. To test the film adhesion, Scotch™ tape was then used to detach some loosely bound SWCNTs. Then the SWCNT films were further post-treated with nitric acid to improve the conductivity. The additive of polyacrylic acid to the SWCNT dispersion improved the film adhesion obviously without decrease its electrical conductivity. This rod-coating method demonstrates great potential for the scalable fabrication of flexible SWCNT-TCFs.

Introduction

Transparent conducting films (TCFs) are widely used for electrodes in electro-optic devices. Indium tin oxide (ITO), the representative transparent and conductive substrate in current use, has limitations when applied to next-generation devices owing to insufficient flexibility, the scarcity and rising prices of the raw materials and the poor adhesion to flexible substrates¹. Hence, there has been an active demand to develop TCFs for flexible electrodes that employ cost-effective materials and processes. As known to all, carbon nanotubes (CNTs) have high conductivity and high optical transparency making the CNT films with relatively low sheet resistance an ideal candidate to replace the relatively expensive and brittle ITO film^{2,3}, and recently CNT films were used as transparent electrodes in OLEDs⁴, solar cells⁵ and touch-screen devices⁶ to replace existing metal oxide-based materials.

Many kinds of methods have been used for the fabrication of CNT TCFs, including vacuum filtering^{7,8}, spin coating^{9,10}, dip coating^{11,12}, gel coating¹³, spray coating^{14,15}, and rod coating¹⁶ etc. The majority of existing coating methods can only be used for a small area of substrate on the laboratory scale. Among these methods, wire-wound rod-coating has been used to fabricate CNT TCFs¹⁷, because it offers several advantages such as low cost, simplicity, large scale and easy film-thickness control. Previous reports have suggested methods for preparing CNT-TCFs with a desirable adhesion to the substrates. Especially for scalable

fabrication of CNT films, excellent adhesion could guarantee the film undamaged during the post-treatment process. Some agents, such as N-methyl-2-pyrrolidone (NMP), were used to improve the adhesion of SWCNTs to the substrate¹⁸. A common method for achieving good adhesion of CNTs to polymeric films is by using binders, such as polymethyl methacrylate (PMMA)¹⁹, conductive polymers^{20,21} and depolymerized chitosam were used to enhance the interfacial adhesion between CNTs²². Since they can not be easily removed by water washing or acid-treatment, due to the nature of electrically insulating materials, they will remarkably increase the sheet resistance and may also decrease film transparency.

In this paper, we report a large-scale coating of SWCNTs on polyethylene terephthalate (PET) substrates by wire-bar rod-coating. Comparison of the two additives, carboxymethyl cellulose (CMC) and polyacrylic acid (PAA), affect the properties of the film, including electrical conductivity and adhesion, and its possible causes were discussed. The addition of water-borne PAA to the CNT dispersion improved the CNT film adhesion obviously without decrease the electrical conductivity.

Experimental

High purity (95 wt%, diameter of 0.8-1.6 nm, length of 5-30 μm) SWCNTs grown by the chemical vapor deposition (CVD) were purchased from the Chengdu Organic Chemicals Co. Ltd, China. Other chemicals including TritonX-100 (TX100), CMC, and PAA were purchased from Aladdin and were used as received.

SWCNTs were dispersed in deionized water at a concentration of 1 mg/ml using sodium dodecyl benzene sulfonate (SDBS) (1wt%) as a dispersant. The solution was sonicated in a bath sonicator at 150 W for 10 h followed by centrifugation at 8000 rpm for 20 min. The 80% suspension was carefully decanted and fed into a beaker. TX100 (1wt %) was added into the above SWCNT/SDBS dispersion stirring at 60 °C in water bath for one min, then PAA (1wt%) or CMC (1wt%) was added into the SWCNT suspensions keeping on stirring for 10 min, respectively.

A typical coating procedure was as follows: 0.2 ml of SWCNT suspensions was coated onto PET substrates using the Mayer rod equipped with wire diameters of 0.27 mm and 0.4 mm (R. D. Specialties) wrapped on the wire-bar coating rods (correspond to wet film thicknesses are 30 μm and 45 μm, respectively). Then, the SWCNT-coated film was dried at 80 °C for 3 min. To test adhesion, the Scotch™ tape (3M Magic Tape) was adhered to the film by rubbing the entire surface area using constant pressure, and then the CNT films were peeled from the PET substrate. In order to explore the additives on the influence of the electrical properties of CNT-TCFs, post-treatment of CNT-TCFs is necessary. The TCFs were rinsed in deionized water for several times to remove the surfactants and additives and dried at 80 °C. Finally, TCFs were further immersed in 12 M nitric acid for 30 minutes followed by washing with deionized water and dried again.

Surface tension of SWCNT solution was characterized by automatic surface tensionmeter (BYZ-1) and shear viscosity was performed by rheometer (Ar1000) at room temperature. Transmittance of films was measured by UV-vis spectrophotometer at the wavelength of 400–600 nm. Solution-phase visible-near-infrared (vis-NIR) absorption was tested using a spectrophotometer (TU-1810, wavelength range 190-1100 nm). The sheet resistance of the film was measured by a four-point probe (Keithley 2400). The morphology of the films was observed using field emission scanning electron microscope (FE-SEM, HITACHI S-4800).

Results and discussion

The properties of different types of SWCNT solution are displayed in Fig.1. Fig.1a shows the surface tension and zero-shear viscosity of different types of solution. We know that surface tension of water is 71.9 mN/m. Water act as Newtonian fluid, its viscosity doesn't change over the rate of shearing, remaining 1.01×10^{-3} Pa.s. When the surfactants were added into water, the surface tension reduced to about 30 mN/m rapidly. This can attribute to one end of the surfactant molecules are soluble in water and the other end is insoluble in water. Result from this dual nature, surfactant molecules in aqueous solution gathering at the surface. The strong attractive forces among the water molecules in the solution were relaxed and led to a sharp reduction in the surface tension of the water from 71.9 to 30 mN/m, and in turn a reduction in the surface tension forces between the air-solution²³. After reaching the critical micelle concentration of surfactants, the surface tension will not reduce again. So when the organic additive such as PAA or CMC is added to the SWCNT/SDBS/TX100 dispersions, the surface tension of the system remains unchanged. It can be seen from the viscosity curve in the graph, after adding the same proportions of surfactant (SWCNT: SDBS = 1:10), SWCNT solution viscosity

has been improved from 1.01×10^{-3} Pa.s to 0.01 Pa.s. Especially, after joined the non-ionic surfactant TX100, SWCNT solution viscosity has improved to 0.25 Pa.s, more than a dozen times. According to the previous literature research, the best solution viscosity range between 0.02-1 Pa.s for rod coating method²⁴. The additive PAA or CMC has less influence on the viscosity of SWCNT dispersions. The dispersions of SWCNT:SDBS:TX100:PAA=1:10:20:20 and SWCNT:SDBS:TX100:CMC=1:10:20:20 both can be used by rod-coating method to fabricate large area of SWCNT film with high performance. Fig. 1(b) shows the rheological behaviour of SWCNT suspensions prepared with SDBS and TX100 as adding binder PAA or CMC. Comparing with SWCNT/SDBS/TX100 suspensions, the addition of PAA or CMC has only a minimal impact on the high-shear behavior. And all the suspensions exhibit shear-thinning behavior in different shear rate. In the process of coating, solution viscosity is also declining, conducive to the solution to flow level in a short period. So we choose these three types of solution to prepare SWCNT films for comparison. These solutions can fabricate scalable CNT TCFs by rod-coating. A large area uniform TCF sample, like A3 paper size, with excellent transmittance fabricated using PAA solution is shown in Fig. S1.

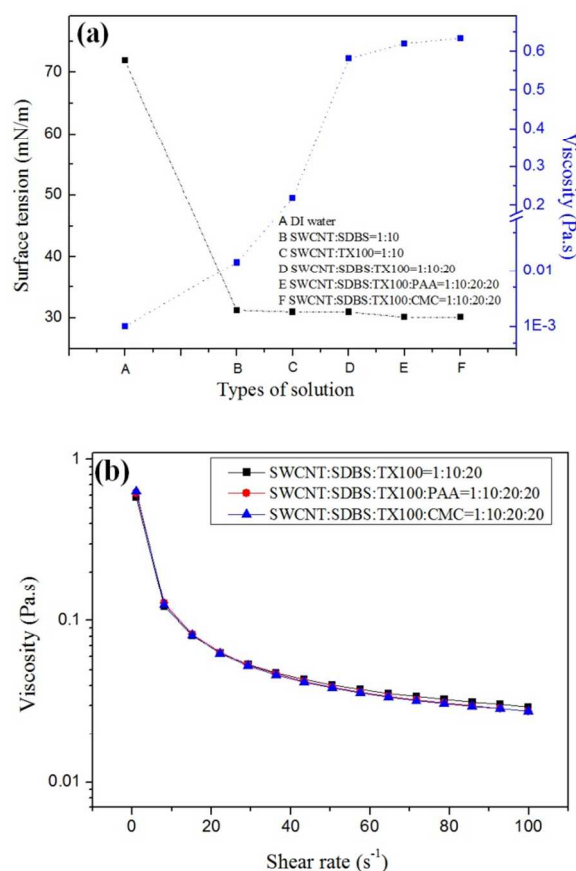


Fig.1 (a) The surface tension and zero-shear viscosity and (b) apparent viscosity vs. an ascending shear rate for different types of SWCNT suspensions.

Fig. 2 shows the optical images of the film before and after (dashed rectangle) taping trials and corresponding SEM images. After taping trials, the comparison of SWCNT/TX100 film

(TX100 film) is the most obvious as shown in Fig. 2a, and SWCNT/TX100/CMC film (CMC film) changed a little (Fig. 2b). On contrast, the SWCNT/TX100/PAA film (PAA film) is almost unchanged (Fig. 2c). From the SEM images, the PAA film also has the maximum residual SWCNTs (Fig. 2f). Compared with

PAA film, only less SWCNTs left on TX100 film (Fig. 2d). The CMC film always show the moderate performance (Fig. 2e). This phenomenon is due to that, after trials, some weakly bound individual or small-size bundled SWCNTs were removed.

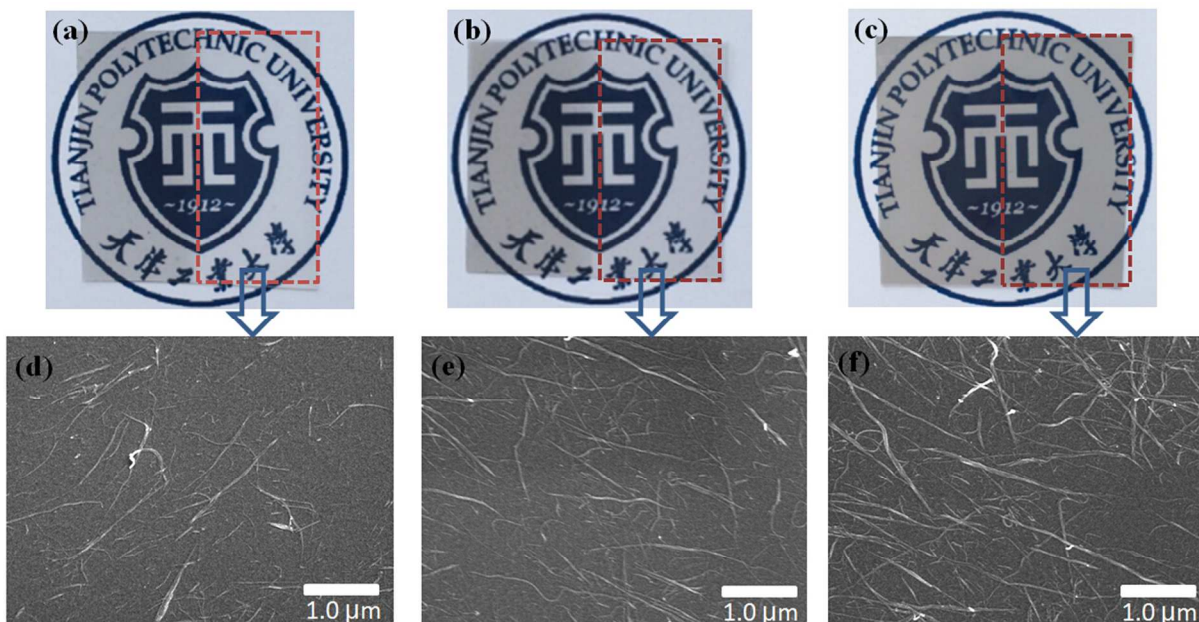


Fig.2 Optical images of the films before and after (dashed rectangle) taping trials (a-c) and corresponding SEM images after taping trials (d-f): (a,d) SWCNT/TX100 film, (b,e) SWCNT/TX100/CMC film, (c,f) SWCNT/TX100/PAA film.

In order to quantitative characterization of adhesion, we can use an adhesion factor incorporating transmittance which can be easily measured from absorption spectroscopy²⁵:

$$f = 1 - \frac{T_n - T_0}{100 - T_0} = 1 - \frac{\Delta T}{100 - T_0} \quad (1)$$

where f is the adhesion factor, T_n and T_0 are transmittance of the detached film after trial and pristine samples, respectively. When $T_n = T_0$, $f = 1$, and no CNTs are detached, demonstrating perfect adhesion and cohesion. When $T_n = 100\%$ (base substrate without CNTs), $f = 0$, and no CNTs are left on the film, demonstrating no adhesion.

The transmittance before and after detaching the tape of three types SWCNT films was shown in Fig. 3. Transmittance of three pristine samples is about 78.5 % at 550 nm. After trial, the transmittance of TX100 films increase to 90.4 % at 550 nm. However, the transmittance of CMC films and PAA films only increase to 84.8 % and 80 % at 550 nm, respectively. According to Eq. (1), the adhesion factor of three types SWCNT films is 0.45, 0.71, and 0.93, respectively. The addition of PAA and CMC both could enhance the adhesion of SWCNT films obviously.

Sheet resistance of as-prepared SWCNT films on substrates was measured with 4-point probe multimeter at room temperature. Sheet resistance and calculated adhesion factor of coating films are shown in Table 1. This result suggests that SWCNT ink with PAA can not only strengthen the adhesion of CNT films stronger than CMC but also give low film sheet

resistance when used the same diameter wire-bar coating. This indicated that CMC was easier peeled off than PAA by Scotch™ tape before post-treatment.

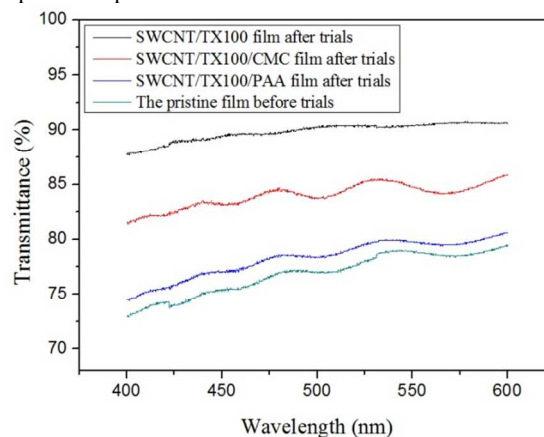


Fig.3 Transmittance spectra of the CNT films in the visible range before and after taping trials.

Table 1 Adhesion factor (f) and sheet resistance (R_s) of as-prepared coating films.

Diameter of wires (μm)	SWCNT with PAA		SWCNT with CMC	
	f	R_s (ohm/sq)	f	R_s (ohm/sq)
0.27	0.930	37000	0.710	52000
0.40	0.925	25650	0.704	39600

The strength of film adhesion is due to the additive of binders, PAA or CMC. The binders act as a bridge between CNT film and the PET substrates, which stick the CNT film to the substrates. For the two kinds of additives PAA and CMC, the different functional groups in the molecule is largely affected adhesive bonding capacity, as shown in Fig.4. For PAA binder, the interaction between the individual long-chain carboxyl group which forms a hydrogen bond. This allows PAA itself between cross-linked with a long-chain, result in a stronger adhesion²⁷. And also $-\text{COOH}$ in PAA is more hydrophilic than the $-\text{OH}$ in CMC, so SWCNTs with PAA solution performs good dispersion properties.

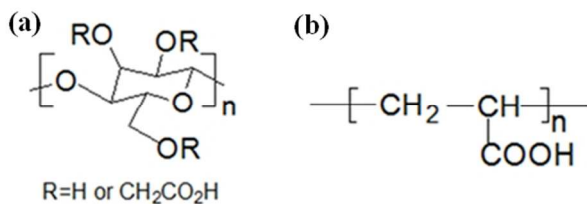


Fig.4 Structure diagram of (a) CMC and (b) PAA.

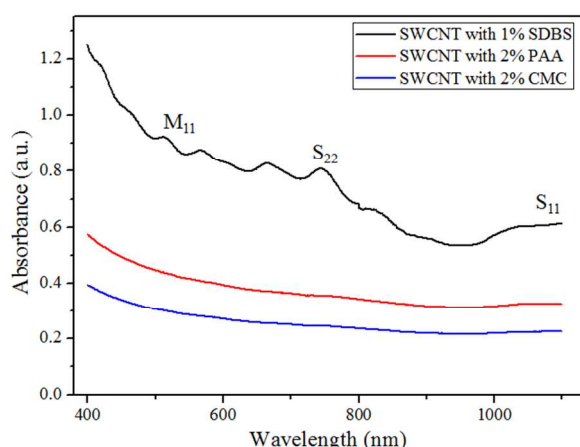


Fig.5 Absorption spectra of SWCNTs dispersed with (a) 1 wt.% SDBS (b) 2 wt.% PAA, and (c) 2 wt.% CMC.

The suspension stability was estimated by measuring the optical absorption intensity of the characteristic bands of SWCNTs as shown in Fig. 5. The dispersion was diluted 10 times with mixed solvent because of the high dispersibility of SWCNTs. Usually, there are three characteristic absorption peaks for SWCNTs are observed in the absorbance spectra^{28, 29}. The first two bands are attributed to electronic transitions between the first (S_{11}) and second (S_{22}) pairs of van Hove singularities in semiconducting SWCNTs. The other is attributed to the first pair (M_{11}) of singularities in metallic SWCNTs. The vis-NIR spectrum of SWCNT/SDBS solution shows fine S_{11} , S_{22} and M_{11} peaks as shown in Fig. 5, similar peak position of similar diameter of SWCNTs with our previous report³⁰. The S_{11} , S_{22} and M_{11} peaks in SWCNT solution with PAA and CMC are seriously depressed due to the absorption of PAA and CMC molecules to the CNT walls. This also indicates that the strong interaction between PAA and CMC with CNTs, giving strong adhesion. The higher absorbance of SWCNT/PAA suspension than

SWCNT/CMC suspension, showing a higher concentration of SWCNT/PAA solution than that with CMC.

The SWCNT dispersions adding 2% PAA and 2% CMC were used as dispersions for the film coating, respectively. After coating, the SWCNT films on the PET substrates were washed with water and post-treated with nitric acid to remove residual dispersants¹⁴. Surface morphology was examined using SEM (Fig. 6). From the images, it can be clearly seen there are a few surfactant and binder residues on the film surface before acid treatment. The remainders of surfactant and binder increase the contact resistance between SWCNTs, resulting high sheet resistance, as shown in Table 1. After acid treatment, the majority of surfactants and binders contained in the SWCNT films were successfully removed by the strong acid on the film surface and obtained a dense and homogeneous network of SWCNTs.

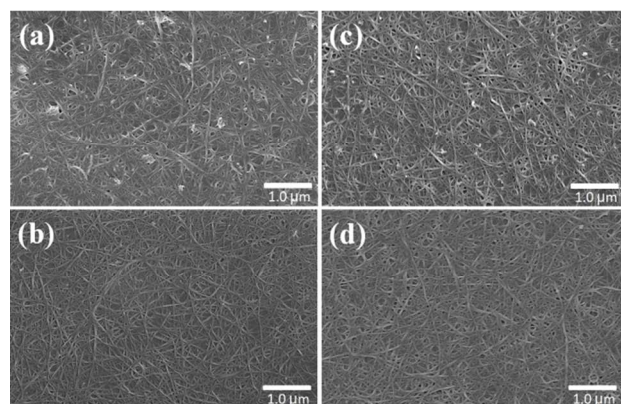


Fig.6 SEM image of SWCNTs coated onto PET films. SWCNTs dispersed with CMC (a,b) and PAA (c,d), before (a,c) and after (b,d) acid treatment.

Table 2 shows the calculated adhesion factor and sheet resistance of coating films after acid treatment. After post-treated, the adhesion factors of CMC film and TX100 film were both improved. However, the adhesion factor of PAA film was decreased after post-treatment compared with Table 1. At post-treatment process, the removed binders contained in the SWCNT films decreased the adhesion factor. On the contrary, the process of SWCNT film dried at 80°C could enhance the film adhesion. For binders PAA and CMC, from Table 1, CMC was easier peeled off than PAA by ScotchTM tape before post-treatment. So there were more SWCNTs peeled off in CMC films. After post-treatment, most of binders PAA or CMC contained in the SWCNT films were removed by the strong acid from the film surface. The amount of SWCNTs and CMC peeled off from CMC films was relatively reduced and the adhesion factor was relatively increased comparing with the pristine films. CMC film and PAA film still show higher adhesion factor compared with that of TX100 film. We evaluate that there are residual binders exist in the inside of CNT films and also exist between CNT network and PET substrate. After acid treated, chemical functionalities have been directly attached to SWCNT sidewalls incorporation of active functional groups of carboxylic acids and hydroxyl groups, oxidized with HNO_3 which were illustrated in our previous work³¹. Since the molecular structure of a carboxyl

functional group are presented in both PAA and CMC binders, the long-chain carboxyl group and the active material particles may form an ester linkage structure with CNT walls, hence increase adhesion between CNTs and substrate.

Fig.7 shows the relationship between the film sheet resistance and transmittance for the TCFs by three types of SWCNT solution after acid treated. We can see that the additive of PAA has almost no influence on the film sheet resistance after acid treatment compared with TX100 films in a wide range of transmittance, and the additive of CMC makes a little higher sheet resistance than TX100 films. From the adhesion property of the three types of SWCNT films, we demonstrate that there are residual binders exist in the inside of CNT films and also exist between CNT network and PET substrate. When more binders exist between the SWCNTs, it would increase the contract

resistance. However, if there fewer binders exist inside and between SWCNT networks, it will dense the CNT networks as shown in Fig. 6d and strengthen the contact of SWCNTs, hence increase the conductivity of SWCNT films. TCFs with relatively low sheet resistance of $124 \Omega \cdot \text{sq}^{-1}$ at 80 % transmittance were obtained. Additionally, TCFs of SWCNT/PET were significantly more flexible than the commercial TCFs of ITO/PET. We illustrated this issue on the basis of literature value^{3,32}. They can be bent all the way without a significant change in sheet resistance (Fig. S2). And after 3000 cycles test, the sheet resistance of CNT films has only a minor increase about 3% as shown in Fig. S3. Hence, TCFs of SWCNT/PET perform excellent flexibility.

Table 2 Adhesion factor (f) and sheet resistance (R_s) of coating films after acid treated.

T%	SWCNT with TX100		SWCNT with CMC		SWCNT with PAA	
	f	$R_s(\text{ohm/sq})$	f	$R_s(\text{ohm/sq})$	f	$R_s(\text{ohm/sq})$
76%	0.812	102	0.826	115	0.869	100
80%	0.814	120	0.827	148	0.872	124
84%	0.815	165	0.830	186	0.874	162

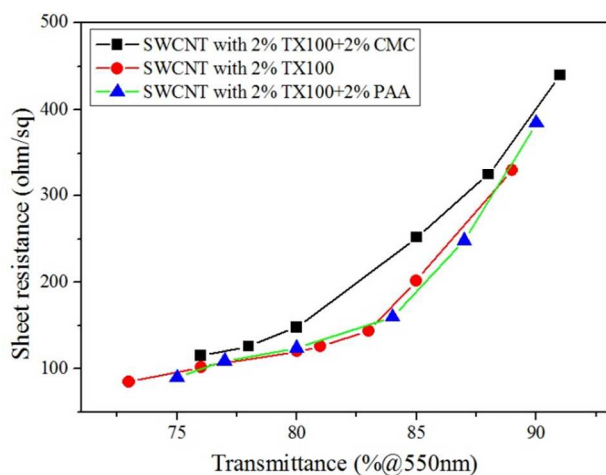


Fig.7 The relationship between transmittance and sheet resistance of SWCNT-TCFs after acid treated.

Conclusions

In this work, transparent and conductive SWCNT thin films were prepared using rod coating. Binders of PAA and CMC were added in SWCNT ink to improve the film adhesion. By comparing the suspension stability and the adhesion ability of the two binders, PAA act as the much better performance to improve the CNT adhesion on substrate. The surfactants on the surface of CNT films were mostly removed by nitric acid treatment. TCFs with relatively low sheet resistance of $124 \Omega \cdot \text{sq}^{-1}$ at 80 % transmittance and high adhesion factor of 0.87 were obtained. The additive PAA in SWCNT solution could improve the film adhesion obviously without decrease its electrical conductivity. This rod-coating method demonstrates great potential to fabricate large scale flexible CNT-TCFs. Specially, high adhesion could

protect the film undamaged during the post treatment processes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Fabrication and evaluation of adhesion enhanced flexible carbon nanotube transparent conducting films

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Graphical Abstract

The addition of polyacrylic acid to SWCNTs dispersion improved the film adhesion obviously without decrease its electrical conductivity.

