Carbon Nanotube Based Transparent Conductive Thin Films

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Carbon nanotube (CNT) based optically transparent and electrically conductive thin films are fabricated on plastic substrates in this study. Single-walled carbon nanotubes (SWNTs) are chemically treated with a mixture of concentrated sulfuric acid and nitric acid before being dispersed in aqueous surfactant-contained solutions. SWNT thin films are prepared from the stable SWNT solutions using wet coating techniques. The 100 nm thick SWNT thin film exhibits a surface resistivity of 6 kΩ/□ with an average transmittance of 88% on the visible light range, which is three times better than the films prepared from the high purity as-received SWNTs.

Keywords: Carbon Nanotube, Transparent, Conductive, Thin Film, Acid Treatment.

1. INTRODUCTION

Transparent conductive thin film electrodes are widely used for liquid crystal displays (LCDs), touch screens, solar cells, and flexible displays. Due to high electrical conductivity and high optical transparency, indium tin oxide (ITO) thin films are often used in these applications. Typically, ITO thin films needs to be deposited or post-annealed at high temperatures (>300 °C) to achieve an optimal combination of electrical and optical properties.[1, 2] However, high processing temperatures are not suitable for many plastic substrates, such as polyethylene terephthalate (PET) films, which are often used for touch panels and flexible electro-optical devices. Another shortcoming of ITO films prepared by conventional methods is their brittleness, a 2% strain will make the films crack and thus lose conductivity.[3] Recently investigated wet coating techniques can provide ATO/polymer films with flexibility[4] (ATO, antimony tin oxide, is a material similar to ITO), but the conductivity is greatly reduced to about 10^{-2} S/cm, which limits its applications.

An alternative material to ITO is poly(3,4-ethylenedioxythiophene)-poly(4-stryrenesulfonate) (PEDOT:PSS) which is a conductive polymer material. With PEDOT:PSS, flexible films can be made that can continue to conduct beyond 60% strain.[5] However, the low transparency and conductivity (∼1 S/cm) (Ref. [6]) of PEDOT:PSS restricts its suitability for many applications.

With high conductivity (in the order of $10^3 \sim 10^4$ S/cm (Ref. [7])) and high aspect ratio (>100), single-walled carbon nanotubes (SWNTs) have been investigated for fabricating transparent conductive thin films/coatings. One approach is to add carbon nanotubes into a polymer matrix, such as polyimide[8] or ASTAA (alkoxysilane terminated amide acid) polymer.[9] These polymeric composites have good mechanical properties but low conductivity. Therefore, they are just suitable for those applications that do not require high electrical conductivity such as electrostatic charge mitigation. To improve the conductivity, films fabricated directly from SWNT solutions have also been investigated. In previously published work, SWNTs were first dispersed in aqueous solutions, then thin films were made by wet coating techniques,[10] or filtering through membrane and transferring to substrates thereafter.[11] Thin films made by these methods show much better conductivity than the CNT-based composites. Since SWNTs are insoluble in most organic solvents and water, a surfactant (such as Triton X-100 or SDS) has to be used to make a stable SWNT solution. However, the surfactant adsorbed on the surface of SWNTs will greatly affect electrical properties. Therefore, removing surfactant in the coatings is one important issue for making transparent conductive SWNT thin films. The cited filtration method in Ref. [11] is effective for washing away the surfactant, but the fabrication process in Ref. [11] is not easy to be scaled up and the bonding between the SWNT film and the substrate is quite weak. This motivates the need to improve the fabrication processes so as to achieve CNT thin films with improved electrical and optical transmission properties.

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Oxidizing carbon nanotubes with a mixture of sulfuric acid and nitric acid is a well-know chemical treatment for nanotubes, which was first used to cut SWNTs into short tubes.[12] The introduced carboxylic acid groups (–COOH) from the acid treatment could also be utilized to dissolve SWNTs in organic solutions by amide or noncovalent functionalization of these carboxylic groups.[13, 14] It is to be noted that the carboxylic groups can also help SWNTs to be stably dispersed in water with less surfactant. Hence SWNTs were treated with the mixed acids in this work before being dispersed in aqueous surfactant solutions to prepare CNT thin films. The experimental results show that this chemical treatment can improve the conductivity of SWNT thin films by three times while retaining the same optical properties.

2. THIN FILM FABRICATION

The high purity SWNTs (>90%) for this study were synthesized using a chemical vapor deposition (CVD) method and were supplied by Timesnanoweb (Chengdu, China).

A schematic of the fabrication process is shown in Figure 1. In a typical acid treatment procedure, 100 mg nanotubes were added to 40 ml of acid mixture of sulfuric acid (98 wt%) and nitric acid (69 wt%) in a ratio of 3:1, and stirred for 15 min on a 110 °C hot plate. The suspension was then diluted to 200 ml. Finally, the SWNTs were collected by membrane filtration (0.45 μm pore size), and washed with enough deionized (DI) water to remove residual acids. The acid treated SWNTs (10 mg)

was added into 10 ml of a 0.5% Triton-X 100 aqueous solution. To reduce the aqueous surface tensions (thus contact angles), a small percentage (less than 0.05 wt%) of DuPont™ Zonyl® FSO was also added, which is a water-soluble nonionic fluorocarbon-based surfactant. The suspension was bath ultrasonicated for 1 hour and settled for a few hours at room temperature. The solutions was applied to a 50 mm × 100 mm poly(ethylene terephthalate) (PET) substrates by a manually controlled wire-wound rod, i.e., pushing the solution on top of the substrate with a wire-wound rod. After drying in an oven at the temperature of 50 °C, the films were shaken in water to remove residual surfactant on the surface of coatings, the shaking stopped when there is no change on the surface resistivity of the thin films. For comparison, thin films were also made with as-received SWNTs solutions with the same procedures as above except that the Triton-X 100 aqueous solution is 1%, because it was found that at least 1% of Triton-X 100 is needed to fully disperse 0.1% as-received SWNTs.

Field-emission gun scanning electron microscope (FEG-SEM) (JEOL 6500) was employed to examine the SWNT powders and coatings. The energy dispersive spectrometer (EDS) associated with the FEG-SEM system was utilized to examine the approximated chemical compounds for the carbon nanotubes before and after the acid treatments. Film thickness was measured by a profilometer (Tencor P-10). The surface resistivity was measured with four-point probe apparatus, and the light transmission spectra were obtained from UV-vis spectrometer (Cary 50).
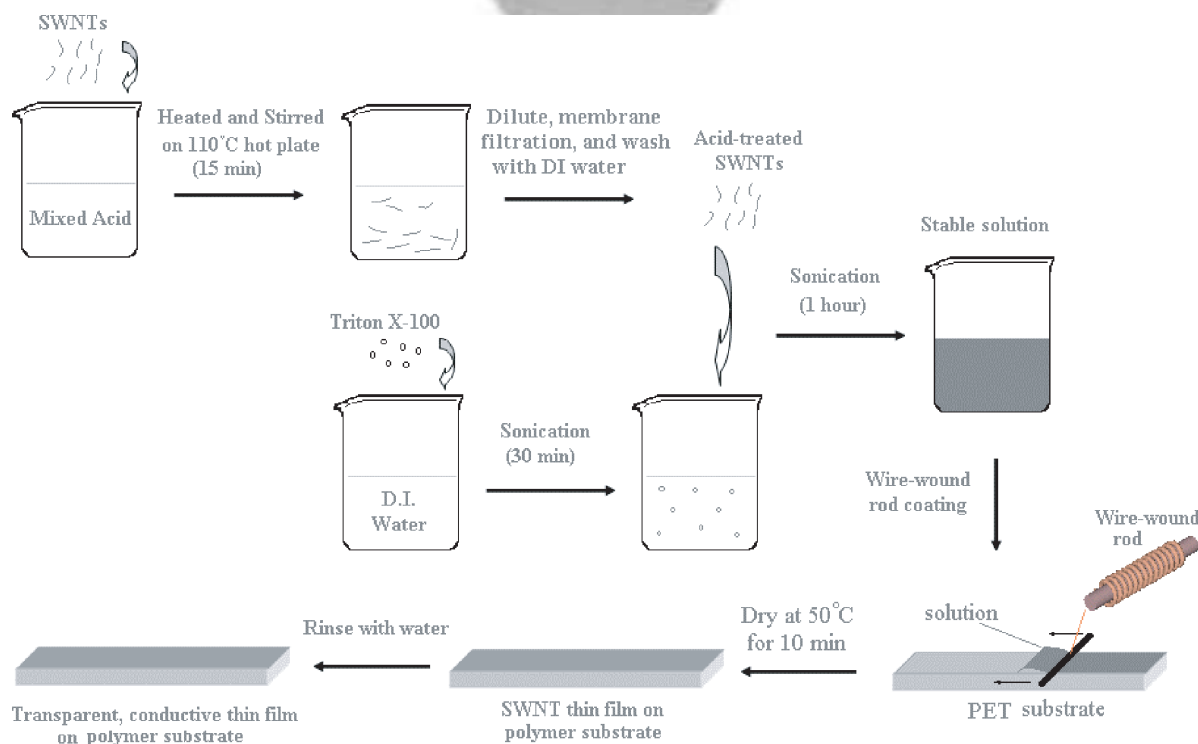
Fig. 1. Schematic diagram of the fabrication process of SWNT thin films.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 and Figure 3 show the SEM images of the SWNT powders before and after acid treatment respectively. As can been seen in Figure 2, only few nanotubes are exfoliated out of the bulk—most un-treated SWNTs tend to aggregate together due to the van der Waals force, while much more nanotubes are exfoliated off the aggregation after being treated with acid mixture. This exfoliation can make the SWNTs easier to be dispersed into water, which will be a topic of detailed discussion later. It was also noted that the volume increased by more than five times after the acid treatment. The changes of element percentages before and after the acid-treatment is shown in Table I, which indicates that in addition to the increase of O from the introduced carboxylic acid groups (–COOH), some S and Si were also introduced to the nanotube powders from the H_2SO_4 and the glassware during the acid treatment. Note that H can not be detected by EDS element analysis equipment due to its low atomic weight.

A picture of the transparent conductive film on a PET substrate fabricated from the acid treated SWNT solution is shown in Figure 4(a). The visible light transmission spectrum of this SWNT thin film is shown in Figure 4(b), which indicated an average transmittance of 88%. The film thickness profile is measured by a profilometer (Tencor P-10), in which the transverse displacement of a computer controlled stylus was recorded when the stylus moved along a path on the surface of an object while a small and constant force is applied to "keep in touch" (Tencor P-10 profilometer has the capable of 1 Å resolution). The measured results for a stepped thin film are shown in Figure 5. As can be seen, there is a height jump at around 45 micrometer location, the thin film surface is not very smooth and the average thickness is about 100 nm.

Figure 6 is the SEM image of the SWNT film, which shows a randomly ordered network formed on the surface
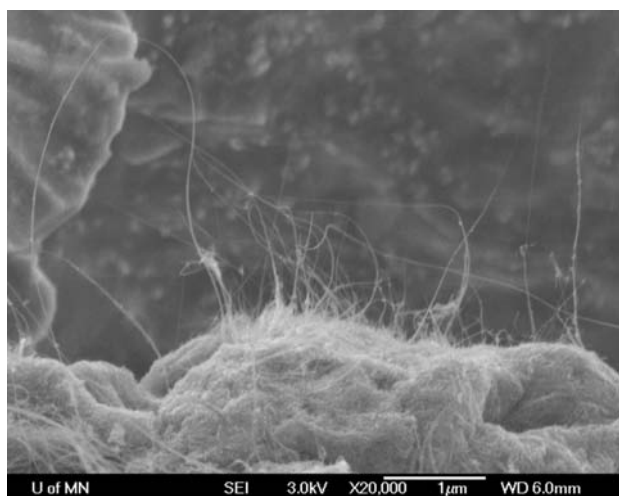

Fig. 3. SEM image of SWNTs treated with H_2SO_4/HNO_3 acid mixture.

(there are some impurities from the nanotubes and substrate also shown in the SEM picture). This random network lets the SWNT bundles contact each other, thus make the film conductive. The measured surface resistivity is about 6 k$\Omega/\square$. Therefore, the conductivity of the film is 16.6 S/cm (calculated as 1/(surface resistivity $*$ film thickness in cm)). A comparison of the electrical properties of some transparent conductive thin films is listed in Table II. As will be discussed in the next paragraph, the acid-treatment can increase the conductivity of SWNT thin films by three times for the solution wet-coating approach. Although worse than the filtration fabricated pure SWNT films and sputtered ITO films, the conductivity of our films are much higher than the commercial BAYTRON® P PEDOT:PSS (about 1 S/cm) and polymer/SWNT composites. In addition, this CNT thin film also has a better transparency than the PEDOT:PSS coating and filtration fabricated SWNT films. Note that different carbon nanotubes synthesized by different methods can lead to different thin film properties even using the same fabrication process. For example, the conductivity of the films in Ref. [10] is higher than our films for the same approach, which is due to the different SWNTs being used (as indicated in their paper, their pulsed-laser ablation synthesized SWNTs have better results than other kinds of SWNTs). However, laser-SWNTs are not commercially available due to the low production yield, while the CVD-SWNTs have been large scale synthesized at a much lower cost. Therefore, CVD-SWNTs were used in this study to reduce cost.

Fig. 2. SEM image of the as-received SWNTs.

Table I. Weight percentages of different elements in as-received SWNTs and acid-treated SWNTs.

	C	Co	Cl	O	S	Si
As-received SWNTs	98.29	1.23	0.48	—	—	—
Acid-treated SWNTs	88.86	1.08	0.13	9.07	0.38	0.48

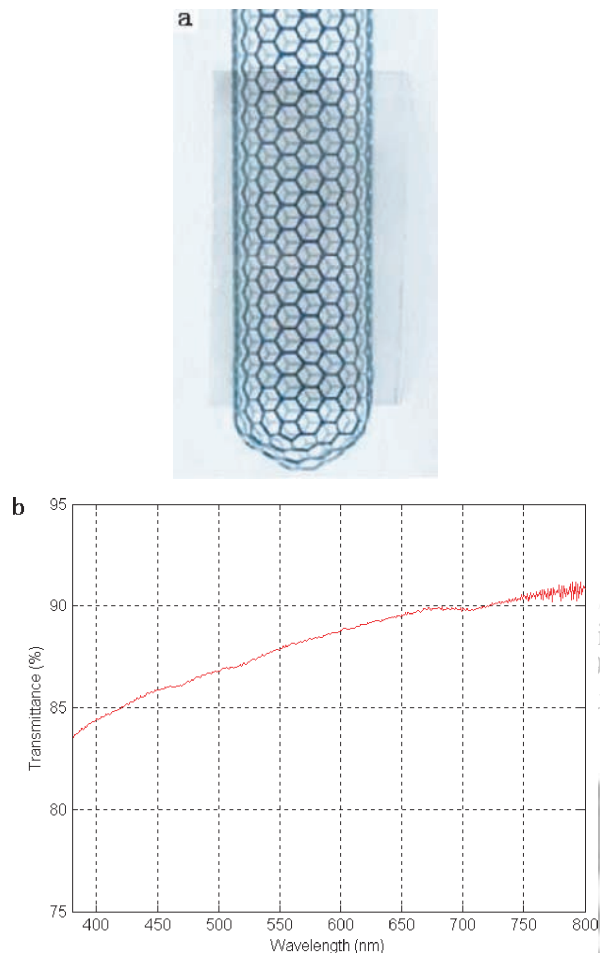**Fig. 6.** SEM image of the SWNT network of the CNT conductive film.

Fig. 4. (a) A picture of the transparent conductive film on a PET substrate (the background is a SWNT model printed on a paper) and (b) the light transmission spectrum of the CNT film on the visible light range.

Similar discrepancy of surface resistivity was also found in CNT thin films of Ref. [11] and Ref. [15], both of which use the same fabrication filtration process but different SWNTs.
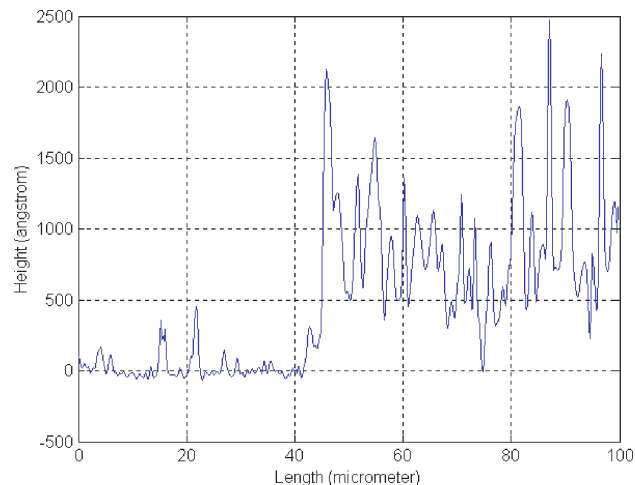

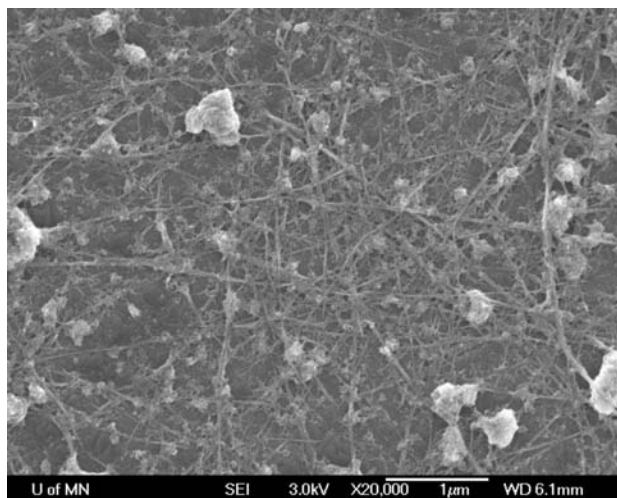**Fig. 5.** Thickness profile of the CNT film (average thickness is about 100 nm).

The comparison of the CNT films from acid-treated SWNTs and as-received SWNTs is shown in Figure 7. To obtain a film with the same surface resistivity as the film from acid-treated SWNTs, a much thicker coating has to be applied for the as-received SWNTs, resulting in a much less transparency. In other words, if we want to keep the similar light transmittance, the film from as-received SWNTs will have higher surface resistivity than the film from acid-treated SWNTs. Experimental results show that the conductivity of the film from acid-treated SWNTs is about three times of the film from as-received SWNTs. We believe that the increase of film properties is attributed to the better nanotube dispersion and less adsorbed surfactant on the SWNT surfaces, both of these two reasons are attributed to the carboxylic groups introduced from the acid treatment.

It is well known that the H_2SO_4/HNO_3 mixture is a strong oxidizing acid mixture that will attack the end caps, defects, and side walls of carbon nanotubes, and cover these sites with carboxylic groups.[16] When nanotubes are dispersed in water, the introduced carboxylic groups induce negative charges on those attacked sites of nanotubes. As a result, the electrostatic repulsion between the negative charges of nanotubes can dramatically increase the stability of aqueous solutions. For MWNTs, because much more carboxylic groups can be created, stable solutions could be obtained even without surfactant[17] (MWNTs are not used in this study because of their low conductivity). As for SWNTs, with fewer carboxylic groups, it still needs surfactant[12] or covalent functionalization[13] to make stable solutions. However, much less surfactant will be needed compared to the SWNTs without acid treatment, which can be explained by the interaction mechanism between surfactant and carbon nanotubes. Take our surfactant Triton X-100 as an example. Typically, the hydrophobic part of Triton X-100 is absorbed on the surface of nanotubes, while hydrophilic PEG unit makes the

Table II. The comparison of conductivity and transmittance of some transparent conductive films.

Transparent conductive films		Surface resistivity (Ohms/□)	Conductivity (S/cm)	Average visible light transmittance
SWNT films fabricated from the surfactant-assisted wet-coating approach	Using acid-treated CVD-SWNTs (this study)	6 k	16.6	88%
	Using as-received CVD-SWNTs (this study)	18 k	5.5	85%
	Using laser-SWNTs[10]	1 k	50	85%
Filtrated pure SWNT thin films	HPCo SWNTs[15]	1 ~ 1.5 k	N/A	85%
	Laser-SWNTs[11]	30	6600	70%
SWNT/ASTAA polymer composite[9]		10^6	$1 * 10^{-9}$	About 60%
PEDOT:PSS[6]		N/A	1 ~ 5 S/cm	80%
ATO/polymer nanocomposite[4]		N/A	0.01 S/cm	85%
Sputtered ITO films[1, 2]		about 50	3000 ~ 4500	85%

nanotubes soluble in water.[18] On those sites covered with carboxylic groups, the hydrophobic part of Triton can not be adsorbed, thus less surfactant will be adsorbed on the surface of SWNTs. Our experiments also verified that less surfactant will be needed to disperse acid-treated SWNTs. We need only 0.5% Triton-X 100 to fully disperse 0.1% acid-treated SWNTs but need 1% Triton-X 100 to fully disperse 0.1% as-received SWNTs. This better nanotube dispersion can lead to better thin film SWNT network forming from the solution.

Another reason for the increase of conductivity by acid-treatment for SWNTs is that less surfactant will be adsorbed on the SWNT surfaces. It is very obvious that the electrical contact between two Triton-X coated sites will be very poor. In our experiments, before the dried CNT thin film was rinsed with water, the surface resistivity is in the order of MΩ/□. After rinsing with water, the surface resistivity dramatically decreases to the order of KΩ/□, which indicated the inverse effect of the Triton-X connections. Less Triton-X connections inside the SWNT thin film thus definitely will be beneficial to the thin film electrical property. As explain before, the acid-treated SWNTs adsorb much less Triton-X 100 surfactant than the as-received SWNTs, which will lead to much less Triton-X connections in the thin film thus increase the conductivity. It is noted that the longer the acid treatment time, the more carboxylic groups will be created.[16] However, the SWNTs will be cut into shorter tubes with the increasing acid treatment time,[12] thus the aspect ratio will be decreased. The conductivity of the bulky SWNTs will also be decreased to some extend with the acid oxidation.[19, 20] Both of these two phenomena have adverse effects on the conductivity of CNT thin films. Therefore, the acid treatment time is a trade-off between the quantity of carboxylic groups and those adverse effects.

4. CONCLUSIONS

Flexible transparent conductive thin films have been prepared from acid-treated SWNTs aqueous solutions using wet coating techniques. The carboxylic acid groups (–COOH) introduced from the chemical acid treatment can enhance the stability of SWNT solutions. By adsorbing less surfactant on the surface of acid-treated SWNTs, the electronic connection between nanotubes was improved. The conductivity of SWNT thin films was increased thereby. Experimental results showed that the conductivity of SWNT films from the acid-treated SWNTs was three times of that of as-received SWNTs.

Fig. 7. Comparison of the films made from acid-treated SWNTs and as-received SWNTs, both films have the same surface resistivity.

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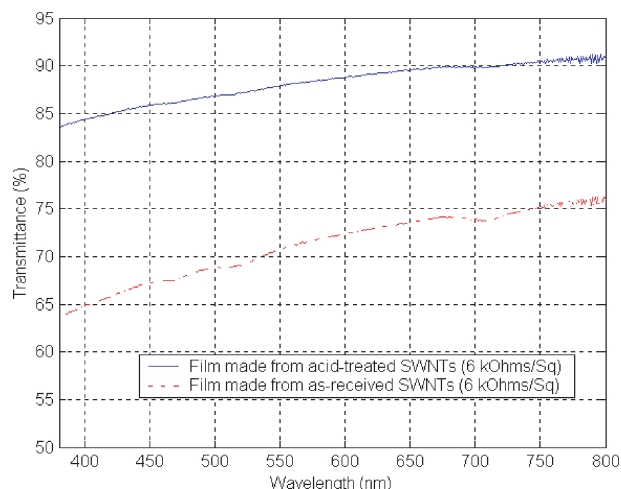
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