

Fabrication of carbon nanotube based transparent conductive thin films using layer-by-layer technology

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Abstract

This paper presents a simple and convenient process for the fabrication of carbon nanotube based optically transparent and electrically conductive thin films. Single-walled carbon nanotubes (SWNTs) are chemically treated to introduce negatively charged carboxylic groups on their surfaces, so that a stable SWNT aqueous dispersion can be obtained without any surfactant. The substrate surface is modified by a layer-by-layer nanoassembly technique, in which a positively charged hydrophilic polymer molecular layer is formed on the top of the substrate. This helps the SWNT dispersion to be cast onto the substrate using convenient wet coating techniques and increases the bonding force between the thin films and the substrates. Using the developed process, large sizes of conductive pure SWNT thin films that are uniform and highly transparent have been fabricated.

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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 (3000–6000 S/cm) and high optical transparency, indium tin oxide (ITO) thin films are often used in these applications [1,2]. Typically, ITO thin films need to be deposited or post-annealed at high temperatures; otherwise its electrical and optical properties will be compensated [3]. Another shortcoming of ITO films prepared by conventional methods is their brittleness, a 2% strain will make the films crack and thus lose conductivity [4]. Recently investigated wet coating techniques can provide ATO/polymer films with excellent flexibility [5] (ATO, antimony tin oxide, is a material similar to ITO), but compared to ITO films 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-styrenesulfonate) (PEDOT:PSS) which is a conductive polymer material. With PEDOT:PSS, flexible

films can be made that can continue to conduct beyond 60% strain [6]. However, the low transparency and conductivity (~ 1 S/cm) [7] of PEDOT:PSS restricts its suitability for many applications.

Single-walled carbon nanotubes (SWNTs) have also been recently investigated for fabricating transparent conductive thin films/coatings. SWNTs have a high conductivity (in the order of $10^3 \sim 10^4$ S/cm [8]) and high aspect ratio (> 100). However, it is difficult to uniformly coat SWNT thin films on substrates due to the aggregation of SWNTs. One approach is to add carbon nanotubes into a polymer matrix, such as polyimide [9], the resulting polymeric composites have good mechanical properties but low conductivity (10^{-9} S/cm). Therefore, they are suitable for those applications that do not require high electrical conductivity such as electrostatic charge mitigation. To fabricate transparent thin film transistors from CNTs, Hines et al. have successfully transferred printed carbon nanotube (CNT) networks using an imprinter [10]. Cao et al. grew CNT networks using the chemical vapor deposition (CVD) method and used transfer printing for device assembly [11]. However, these processes are difficult to be scaled up to large area thin films, for example electrodes of LCD displays. Zhang et al. developed another dry-state process by spinning of 5 nm

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MWNT sheet from the sidewalls of a MWNT forest (vertically oriented) [12], which yields a highly strong, transparent and conductive CNT sheet. This process need a well-grow MWNT (or SWNT) forest and the draw process does not work for all MWNT forests. Another approach is to disperse SWNTs in aqueous dispersion with the help of a surfactant (such as Triton X-100 and sodium dodecyl sulfate (SDS)) — thin films can then be made by wet coating techniques [13,14], or a filtration method [15–18]. Since the surfactant adsorbed on the surface of SWNTs can greatly affect electrical properties, the process will be followed by a rinsing step to wash away the surfactant, which may wash away some parts of the SWNT thin films as well. Moreover, even though this process can reduce the amount of surfactant on the surface, there is still some surfactant stuck inside the SWNT thin films which will affect conductivity. This motivates the need for developing a simpler fabrication processes for fabricating large uniform CNT thin films with improved electrical and optical transmission properties.

In this paper, we develop a simple and convenient process to fabricate transparent conductive SWNT thin films. Briefly, the process is comprised of three steps: (i) Oxidizing SWNTs with a mixture of sulfuric acid and nitric acid for an adequate length of time. The negatively charged carboxylic groups introduced on the SWNT surfaces help SWNTs to be stably dispersed in water even without any surfactant. (ii) Modifying the surface of the substrate using layer-by-layer (LBL) nanoassembly. Eventually, a positively charged and hydrophilic poly(diallyldimethylammonium chloride) (PDDA) molecular layer is deposited on top of substrate surface; and (iii) Coating pure SWNT thin films on to modified substrate surfaces using wet coating techniques, including wire-wound rod coating.

Oxidizing carbon nanotubes with a mixture of sulfuric acid and nitric acid is a well-known chemical treatment for nanotubes. By oxidizing carbon atoms at the caps, defects and side walls of the carbon nanotubes, this oxidation method has been used to cut SWNTs into short tubes [19], and amide or noncovalent functionalization for SWNTs [20,21]. After our research in reference [13], we found that, with adequate acid treatment time, the introduced carboxylic groups (–COOH) on SWNT surfaces

can also help SWNTs to be stably dispersed in water even without any surfactant. 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 dispersion. With a long enough acid treatment time, stable SWNT dispersion can be obtained without the need for a surfactant.

In order to uniformly cast the SWNT/water dispersion on the top of substrate surfaces, hydrophobic substrate surfaces need to be modified. Layer-by-layer (LBL) nanoassembly surface modification is utilized in our study, which is a versatile and simple technique that fabricates ultrathin films by alternately adsorbing oppositely charged materials on the substrate. Materials used for this purpose include polyelectrolytes, proteins, and DNA [22]. This process could be used to fabricate multilayered composites and to modify substrate surface. When being used as a surface modification method, this process has several important advantages over other surface modification techniques such as plasma treatment and corona discharge: 1) The outermost surface could be deposited with a material that has desired properties such as positively or negatively charged, hydrophilic or hydrophobic. 2) The substrate could be any size and shape. 3) The process is low cost.

Both the acid treatment and LBL nanoassembly processes are essential to this new SWNT thin film fabrication process. The acid treatment removes the need for a surfactant in the films which greatly enhances the conductivity while retaining excellent optical properties, while the positively charged and hydrophilic surface helps to make a large sized uniform SWNT thin film and increases the bonding force between SWNTs and the substrate.

2. Thin film fabrication

The high purity SWNTs (>95%) for this study were supplied by Timesnanoweb (Chengdu, China), and had been synthesized using chemical vapor deposition (CVD) techniques.

A schematic of the fabrication process is shown in Fig. 1. In the acid treatment procedure, 100 mg nanotubes were added to

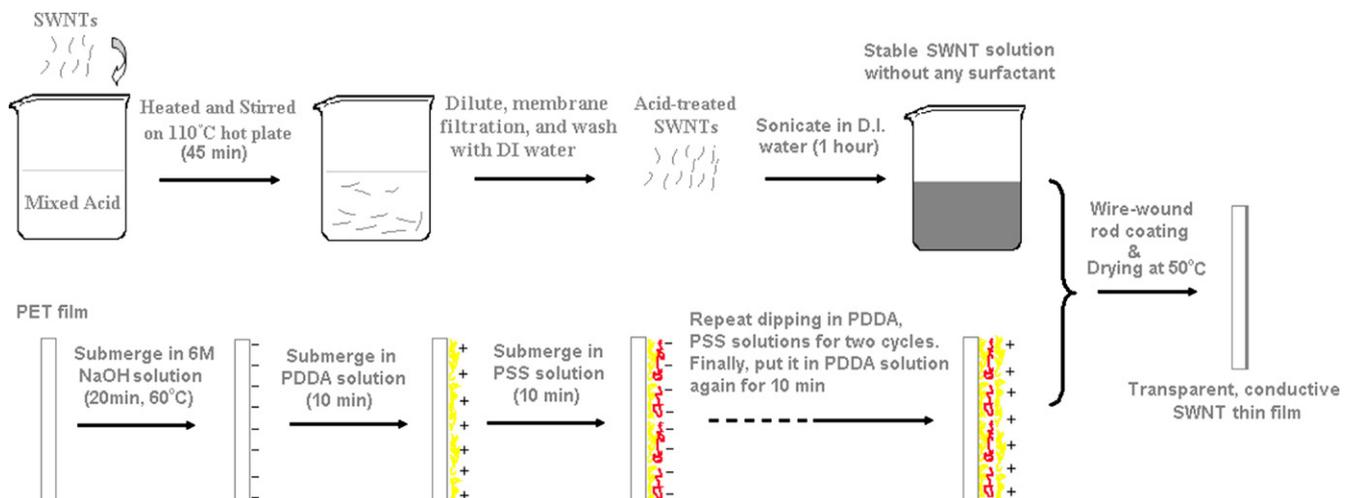


Fig. 1. Schematic diagram of the fabrication process of SWNT thin films.

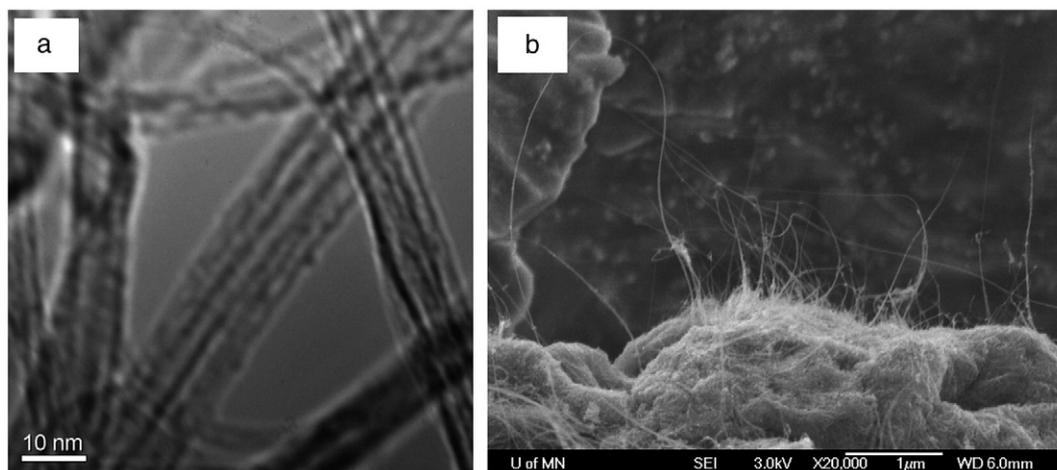


Fig. 2. (A) TEM image of the as-received SWNTs and (B) SEM image of the as-received SWNTs.

40 ml of an acid mixture of sulfuric acid (98 wt.%) and nitric acid (69 wt.%) in a ratio of 3:1, and stirred for 45 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) were added into 10 ml of DI water and bath ultrasonicated for 1 h to get stable SWNT aqueous dispersion.

The substrate, poly(ethylene terephthalate) (PET) film, was firstly hydrolyzed with 6 M NaOH aqueous solution for 20 min at 60 °C, which introduced negatively charged carboxylic and alcohol functional groups on the PET surface [23]. After rinsing with DI water, the PET film was immersed in 1.5 wt.% poly (diallyldimethylammonium chloride) PDDA dispersion (with 0.5 M NaCl) for 15 min at room temperature, followed by rinsing with DI water. The PET film was then dipped into 0.3 wt.% poly (sodium styrenesulfonate) (PSS) (with 0.5 M NaCl) for 15 min and rinsed. The PDDA/PSS adsorption treatment was repeated for two cycles and finally treated with PDDA dispersion again. The outer most surface layer is thus a positively charged PDDA molecular layer. Here PDDA is chosen for its high hydrophilicity among common polycations [24].

The SWNT/water dispersion were applied to the substrates by wire-wound rod coating and dried at 50 °C. After drying, additional SWNT layers could be coated above the initial SWNT layer to achieve a desired combination of electrical and optical properties.

3. Characterization of SWNTs before and after acid treatment

In this study, transmission electron microscope (TEM) (FEI Tecnai T12) and field-emission gun scanning electron microscope (FEG-SEM) (JEOL 6500) were employed to examine the SWNT powders and coatings. Fourier transform infrared spectrometer (FTIR) (Nicolet Magna-IR 750) was utilized to analyze the structure of SWNTs. 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.

Figs. 2 and 3 show TEM and SEM images of the SWNT powders before and after acid treatment respectively. As can be seen from Fig. 2(A), most un-treated SWNTs tend to aggregate together as bundles due to the van der Waals force,

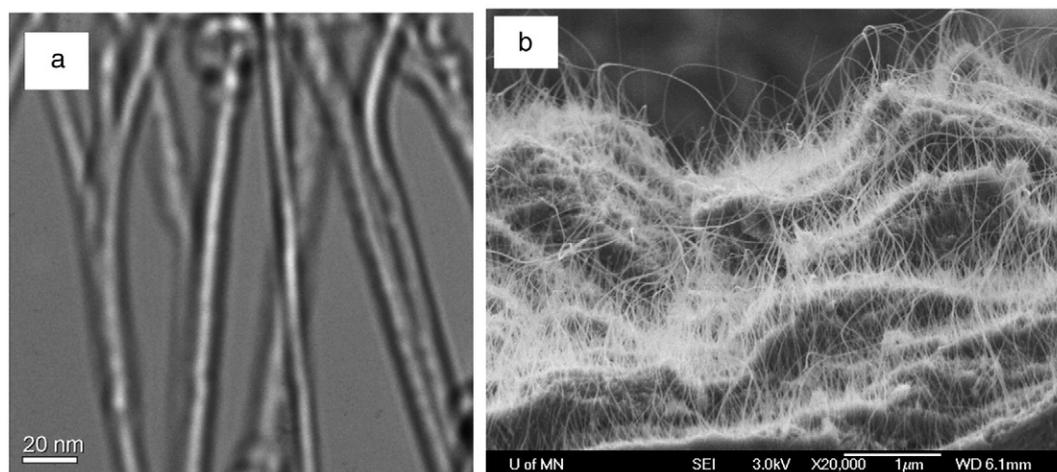


Fig. 3. (A) TEM image of SWNTs treated with H₂SO₄/HNO₃ acid mixture and (B) SEM image of SWNTs treated with H₂SO₄/HNO₃ acid mixture.

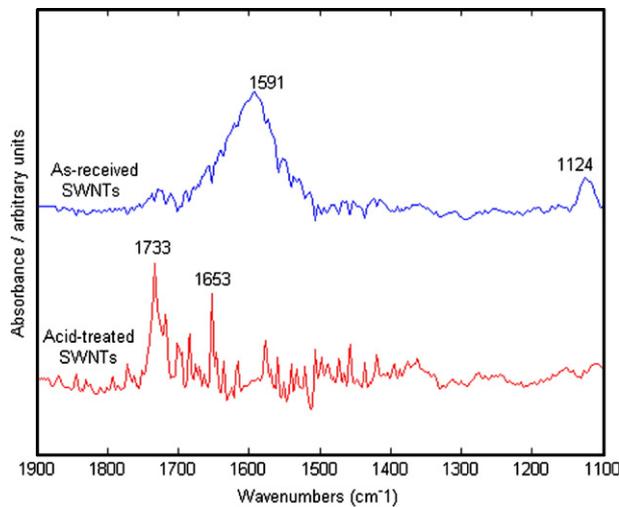


Fig. 4. FTIR spectrum of the as-received SWNTs and acid-treated SWNTs.

with 4–8 nanotubes in most bundles. After being treated with acid mixture, the treated SWNTs more like to be individual nanotubes, or at most 2 or 3 tubes aggregate together (Fig. 3 (A)). SEM picture of the acid-treated SWNTs also shows that most nanotubes are exfoliated off the aggregation. It was also noted that the volume increased by more than five times after the acid treatment. Another found difference for the SWNTs before and after the acid treatment is the average diameters of the SWNTs. From TEM images, it shows that the as-received SWNT is about 1–2 nm in diameter, but the acid-treated SWNT samples have only large diameter SWNTs (3~5 nm). This is probably because the small SWNTs are more easily attacked and destroyed by the acid mixture, thus are cut into short tubes. Small and/or short SWNTs are then more like to be washed away during the SWNT sample collection step that is performed after the acid treatment step.

Fourier transform infrared spectrometer (FTIR, Nicolet Magna-IR 750) is utilized to analyze the structures of SWNTs. Fig. 4 shows the FTIR spectra for the as-received SWNTs and acid-treated SWNTs. After being treated with acid, one peak at 1733 cm^{-1} appeared in the spectrum, which is associated with $\text{C}=\text{O}$ of $-\text{COOH}$ groups [25,26]. This indicates the introduction of carboxylic groups to the ends and/or side walls of SWNTs by the acid treatment. It was also found that the peak at 1591 cm^{-1} that associated with $\text{C}-\text{C}$ groups of the as-received SWNTs was shifted to 1653 cm^{-1} , which indicated possible structure changes in SWNTs [25].

The changes of element percentages for SWNTs before and after the acid treatment were analyzed with an energy dispersive spectrometer (EDS) associated with the SEM

Table 1
Weight percentages of different elements in as-received SWNTs and acid-treated SWNTs

	C	Co	Cl	O	S	Si
As-received SWNTs	98.3	1.2	0.5	–	–	–
Acid-treated SWNTs	85.1	1.6	–	12.9	0.3	0.1

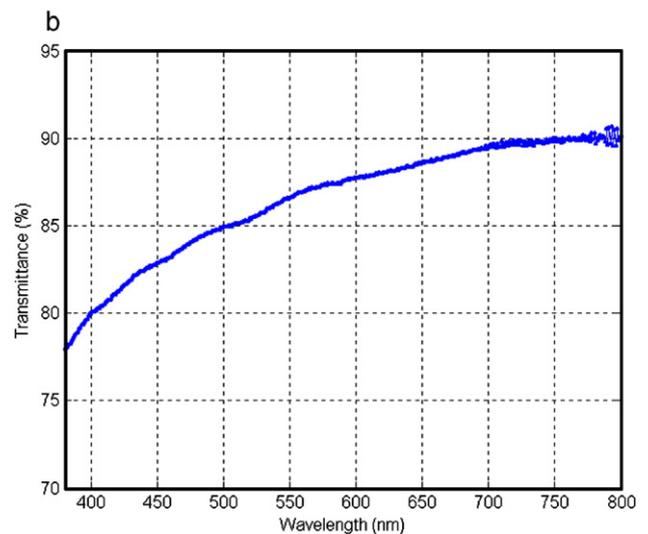
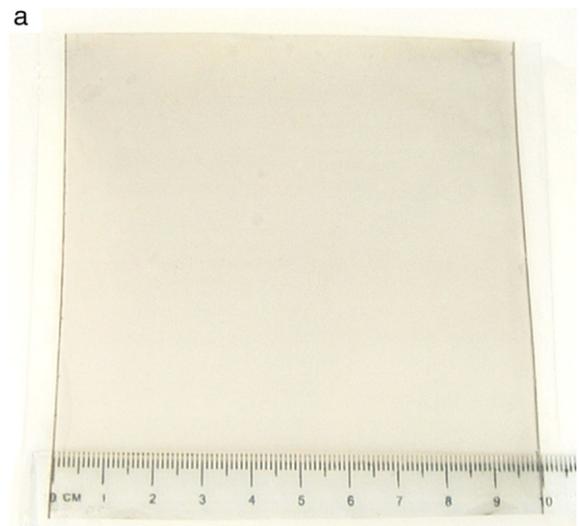


Fig. 5. (a) A picture of the transparent conductive film on a PET substrate (the ruler is behind the film) and (b) the light transmission spectrum of the CNT film on the visible light range.

system. The results are shown in Table 1, which indicated that the significant increase of O from the introduced carboxylic acid groups ($-\text{COOH}$), some S and Si were also introduced to the nanotube powders from the H_2SO_4 and the glassware

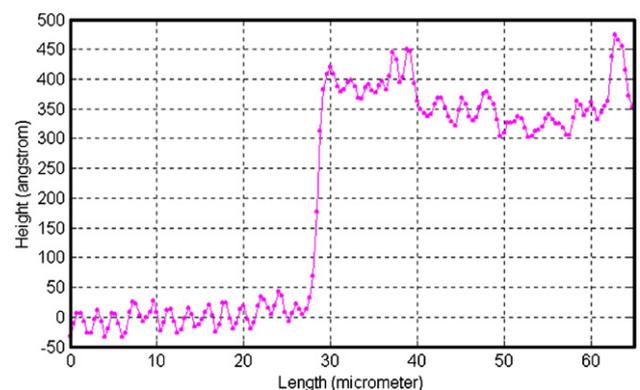


Fig. 6. Thickness profile of the CNT film (average thickness is about 37 nm).

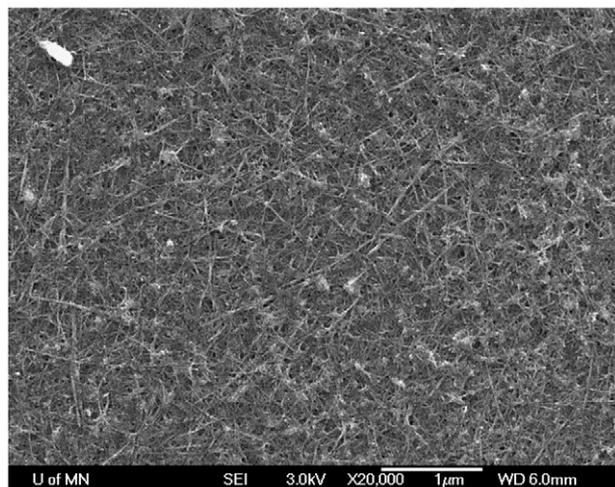


Fig. 7. SEM image of the SWNT network of the SWNT conductive thin film.

during the acid treatment. Note that H can not be detected by EDS element analysis equipment due to its low atomic weight.

4. Results and discussion

A picture of a 100 mm × 100 mm transparent conductive film on a PET substrate is shown in Fig. 5(a). The layer-by-layer (LBL) nanoassembly introduces a positively charged and hydrophilic PDDA molecular layer on top of substrate surface. The hydrophilic property of PDDA (advancing contact angle $\theta_A \approx 35^\circ$ [24]) enables the SWNT dispersion to be spread out. The positive charge confines the negatively charged SWNTs and prevents their aggregation during the drying process. In addition, this increases the bonding force between SWNTs and the substrate. Due to the nature of the fabrication process, the film can be readily scaled up; the only limit is the size of coating apparatus.

The visible light transmission spectrum of this SWNT thin film is shown in Fig. 5(b), which indicates an average transmittance of 86.5% (measured by a Cary 50 UV–vis spectrometer). The film thickness profile measured by a profilometer (Tencor P-10, 1 Å vertical resolution) is shown in Fig. 6 (the average thickness is about 37 nm.).

Fig. 7 is a SEM image of the SWNT film, which shows a randomly ordered tight SWNT network. Since there are no surfactant in the SWNT thin film, the SWNTs contact each other directly, which greatly enhances the conductivity. The measured surface resistivity is about $2.5 \text{ k}\Omega/\square$. Therefore, the conductivity of the film is 108 S/cm (calculated as $1/(\text{surface resistivity} \times \text{film thickness in cm})$). The electrical properties of the pure SWNT thin films from this new process is much better than the SWNT thin films fabricated from the surfactant-assisted wet-coating approach (conductivity of 17 S/cm) with the same batch of SWNTs [13] (note: the properties of SWNTs made from different synthesis methods might be slightly different and might have different purity and metallic SWNT concentration, here we use the same batch of SWNTs from the same company for better comparison). This improvement in electrical properties is due to the improvement of contact between SWNTs by removing surfactants in the final SWNT thin film.

However, the electrical properties of the SWNT thin film will be affected by two adverse effects brought to the SWNTs during the acid treatment in this fabrication process. The first adverse effect is, as discussed before, the SWNTs being cut into shorter tubes by the acid [19], thus the aspect ratio will be decreased. Second, the conductivity of the bulky SWNTs will also be slightly decreased by the acid oxidation with the introduction of $-\text{COOH}$ groups [27,28]. In a summary, Table 2 lists the advantages and disadvantages of current methods of fabricating CNT thin films.

5. Conclusions

Large size, uniform, and flexible transparent conductive thin films have been prepared in a novel and convenient process, which consists of acid treatment for SWNTs and LBL nanoassembly surface modification for the substrates. The carboxylic acid groups introduced from the acid treatment can render SWNTs to be stably dispersed in water without any surfactant. The LBL nanoassembly introduces a positively charged and hydrophilic PDDA molecular layer on the top of the substrate surface. The hydrophilic property of PDDA enabled the SWNT dispersion to spread out, while the positive charge confined the negatively charged SWNTs and prevented

Table 2
Comparison of different methods for fabricating CNT transparent conductive thin films

Method		Advantages	Disadvantages
LBL wet coating SWNT thin film (this research)		Simple, convenient Easy to scale up No need for expensive equipment	Medium electrical conductivity
CNT films fabricated from surfactant-assisted CNT dispersion	Wet coating and surfactant washing [13,14]	Simple, convenient Easy to scale up No need for expensive equipment	Low to medium electrical conductivity CNT film might break during the washing process
	Filtration and surfactant washing [15–18]	High film conductivity	Difficult to scale up CNT film might break if the film is to be transferred to a substrate
Dry-state process (transfer printing, imprinting, forest spinning) [10–12] SWNT/polymer composite [9]		High film conductivity	Difficult to scale up Need expensive equipment
		Could be simple Easy to scale up	Very low conductivity

their aggregation during the drying process. Although the electrical property of the SWNT thin film is worse than some other CNT thin films reported in literature, this proposed fabrication method is simple and easy to be scaled up for large films, which is one of the key issues for applying this technology to commercial applications. This fabrication process also has the advantages of being low cost with no need for expensive equipment.

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