

Single-Walled Carbon Nanotube electrodes for all-plastic, electronic device applications

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Declaration

I declare that this thesis

Single-Walled Carbon Nanotube electrodes for all-plastic, electronic device applications

is entirely my own research under the supervision of Dr. John. C. de Mello and Dr. Xuhua, Wang. The research was carried out in the Department of Chemistry at Imperial College London. All published and unpublished material used in this thesis has been given full acknowledgement. None of this work has been previously submitted to this or any other academic institution for a degree or diploma, or any other qualification.

Sung Soo Kim

September, 2010

Abstract

In this thesis, new mechanically robust, high performance transparent conducting films of commercially sourced arc-made Single-Walled Carbon Nanotubes (SWCNTs) on both glass and flexible substrates were produced using spin-coating or spray deposition, interlayer or stencil patterning methods and used for fabricating efficient, flexible polymer-fullerene bulk hetero-junction solar cells.

After carefully optimizing the dispersion process of SWCNTs with H₂O:SDS (up to 0.03 wt.%) and developing an efficient surfactant removal/p-doping procedure with nitric acid, highly conductive and smooth SWCNT thin films (ca. 30 nm) were obtained with more than 6,500 Scm⁻¹ at > 69 % transmittance and 7 nm (r.m.s.) roughness. In particular, SWCNT films spray coated from H₂O:SDS exhibited electrical conductivities of up to 7694 ± 800 Scm⁻¹. To our knowledge, these values are the highest so far reported for SWCNT electrodes. Peak values for the ratio of the dc conductivity to the optical conductivity (σ_{dc}/σ_{op}) were obtained as up to 24, which is quite similar to state of the art SWCNT films so far reported.

In addition, two patterning methods were developed to define electrode patterns of SWCNT thin films for electronic device applications. Interlayer lithography provided a fast and high resolution patterning procedure for SWCNT thin films at micron and sub-micron length scales, which is important for the fabrication of high-speed transistors requiring short channel lengths, and offers an attractive route to fabricating high-density integrated circuits. In addition, stencil patterning provides a simple and fast method, which is well suited for low resolution electronic device applications such as organic solar cells.

The patterned highly conductive SWCNT electrodes were incorporated into P3HT:PCBM bulk heterojunction solar cell applications, obtaining the best device performance of 3.6 %, which is the best result so far reported in the literature.

Finally, to break through the limited performance ($\sigma_{dc}/\sigma_{op} < 25$) of SWCNT thin films, layered hybrid thin films of SWCNTs on reduced Graphene-Oxide were fabricated by a simple spray coating method and the optimised hybrid films were incorporated into relatively efficient organic solar cells (2 % efficiency).

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To Jaekyung, Juyoung, Inyoung

Thanks a lot forever

List of Publications and Awards

1. S.S. Kim et al., Advanced Functional Materials, *2010*, **20**, 1-7
2. D-S Leem & S.S Kim et al., Small, *2010*, **6**, 971
3. S.S. Kim et al., Chemical Science (Submitted)
4. Best poster prize, Cambridge CNT symposium, 2008
5. Best poster prize, SID Organic Electronics 2009,2009

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Chapter 1 Introduction

1.1 Overview of plastic electronics

Organic semiconductors are attracting increasing interest from researchers due to their large area and low cost roll to roll manufacturing capabilities, which derive in large part from their excellent mechanical flexibility.¹ These features are virtually unique to organic materials, because the inorganic materials widely used for conventional electronics are normally brittle and require complex and high cost processing techniques.² Lightweight and flexible circuits with organic materials can lead to the successful development of new bendable devices such as flexible displays, including electronic papers, smart windows, wearable computers, and conformable polymer solar cells, as shown in Figure 1.1.



Figure 1.1 Photographs of printed electronic devices; from left to right, Flexible Display (SAMSUNG), Flexible Electrochromic window (SIEMENS), Polymer solar cell (KORNAKA)

Polymeric semiconductors are known to have several advantages: (a) low-cost synthesis,³ (b) easy manufacturing of thin film devices by solution processing and reel to reel printing,³ (c) high absorption coefficients exceeding 10^5 cm^{-1} ,⁴ (d) chemically tuneable electronic band gaps.⁵

Organic semiconductors have a delocalised, conjugated and weak π electron system, and therefore their lowest electronic excitations are π - π^* transitions with an energy gap between 1.4 eV and 3 eV, leading to the light absorption or emission in the visible spectral range. Their energy gap can be tuned by changing the degree of conjugation in a molecule, chemical design, and functionalisation.⁶

However, their conductivities are limited by the low mobilities ($\sim 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)⁷ and by the small number of charge carriers, due to the large energy gap. In this context, various chemical doping, photochemical and electrochemical techniques can be used to induce additional charge carriers in organic semiconductors.⁸

In addition, due to the weak electronic localisation, the optical excitations of semiconducting polymers are localised on a molecule or single conjugate unit, resulting in a considerable binding energy of 0.5 - 1 eV. Such excitations are classified as Frenkel excitons, in contrast to the Mott Wannier excitons for inorganic semiconductors, which are more localised and therefore less tightly bound with weaker binding energies of below 0.01 eV. The larger binding energy of Frenkel excitons hinders spontaneous charge pair (positive and negative charge carriers) generation from excitons at room temperature (under which conditions the available thermal energy K_{BT} is 25 m eV), and it must be overcome for photovoltaic applications.

Figure 1.2 shows that donor and acceptor type bilayer structures of two organic semiconductors with offset frontier orbital can generate free charge carriers under optical excitation and therefore function as a p-n junction.³

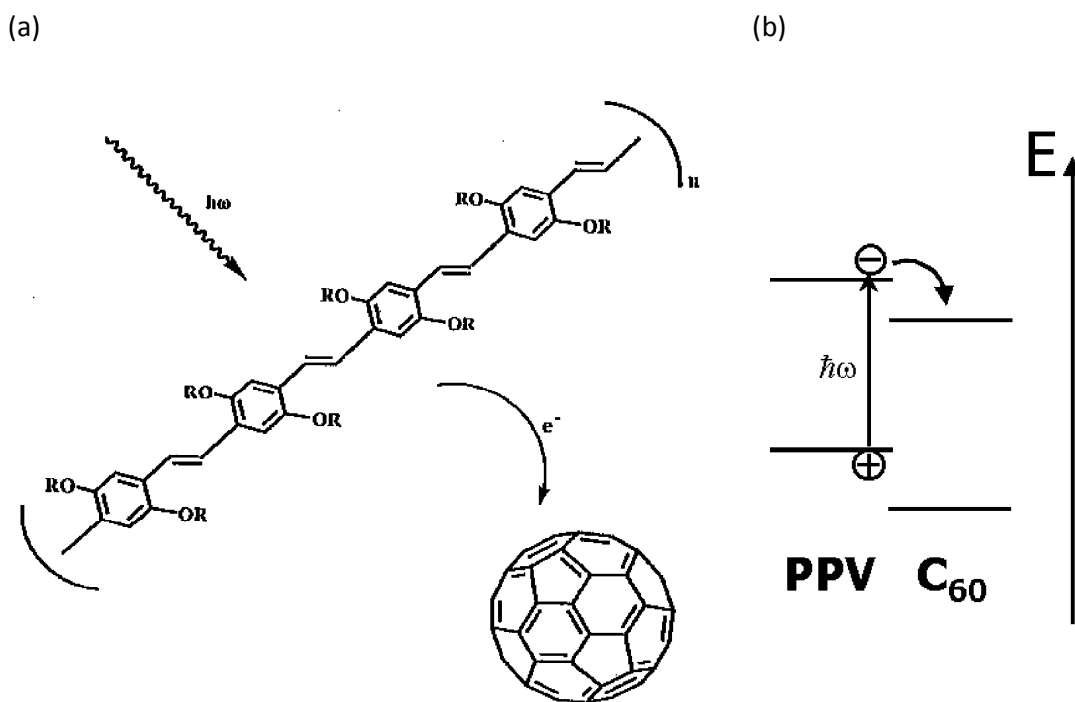


Figure 1.2 Illustration of the photo-induced charge transfer, (a) After photo-excitation in the poly(p-phenylenevinylene) (PPV) polymer, the electron is transferred to the C₆₀, (b) The energy level diagram for the PPV:C₆₀ system. (Taken from reference 3)

Organic semiconductors can therefore absorb sunlight, create excitons (strongly bounded electron-hole pair), split the excitons at heterojunctions, and transport these charge carriers. Derivatives of phenylene vinylenes such as poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene) (MDMO-PPV), and derivatives of thiophenes such as poly(3-hexylthiophene) (P3HT) have been widely used as hole-conducting and electron-donating semiconducting polymers.³

One effective and widely used electron acceptor for vacuum deposited devices is a buckminsterfullerene (C_{60}), however, the solubility of C_{60} is generally poor and it cannot be used directly for solution processed devices.⁹ Allemand et al.⁹ therefore synthesized a soluble derivative of C_{60} , (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6] C_{61}) (PCBM), which is now widely used in polymer/fullerene solar cells. Many other solubilised fullerenes are now being studied.¹⁰ Small molecules such as phtaocyanine, pentaxene, perylene derivatives were also used to fabricate molecular solar cells by vacuum deposition of electron donor and acceptor thin layers successively. However, they normally require high cost and intricate vacuum sublimation process, which may not be compatible with large area, printable electronics. The organic semiconductors used for organic solar cell applications are shown in Figure 1.3.

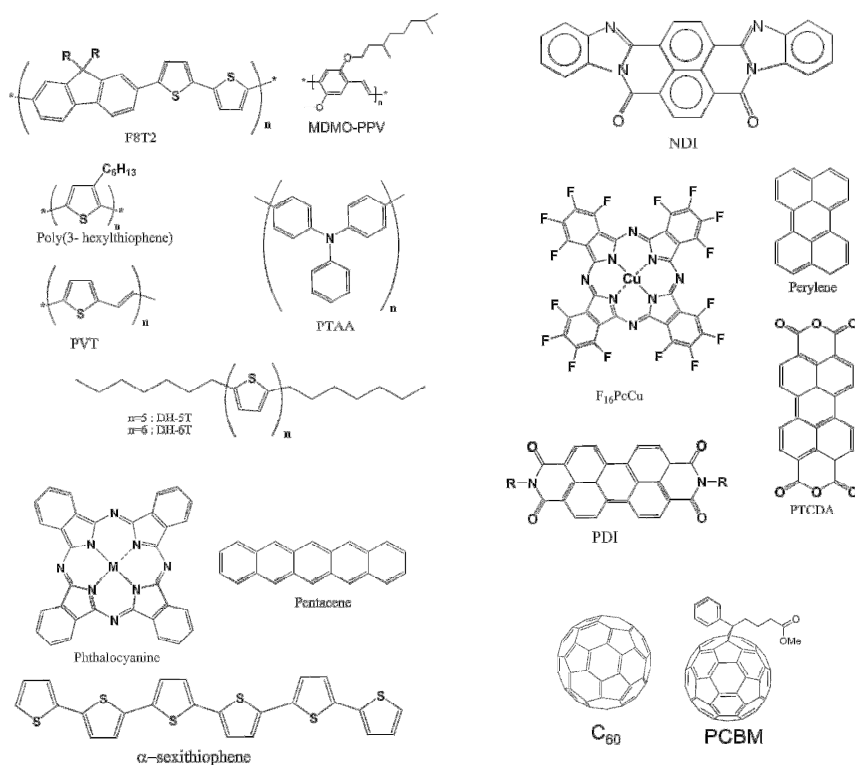


Figure 1.3 Typical organic semiconducting materials used for organic solar cells. (Taken from reference 8)

To summarize, the important difference of organic semiconductors to their inorganic counterparts lies in the orders of magnitude lower charge carrier mobility, which is partly compensated by their strong absorption coefficients that allow thin films (~ 100 nm) to be employed for the active layer. Another difference to crystalline, inorganic semiconductors is the relatively small diffusion length of excitons (10 - 20 nm) in these amorphous and disordered organic materials. These differences have a major effect on the design and efficiency of organic semiconductor devices.³

1.2 Plastic solar cells

Since the discovery of the photovoltaic effect by Edmund Becquerel in 1839, photovoltaic cells have been mainly made with inorganic solid-state materials such as silicon and other compound semiconductors such as GaAs, CdS, CdTe. These materials can provide high power conversion efficiency (15 - 25 %), but their high production cost and sophisticated processing requirements, in addition to the large environmental cost of using toxic materials, have hindered their ability to compete with other energy sources.¹¹

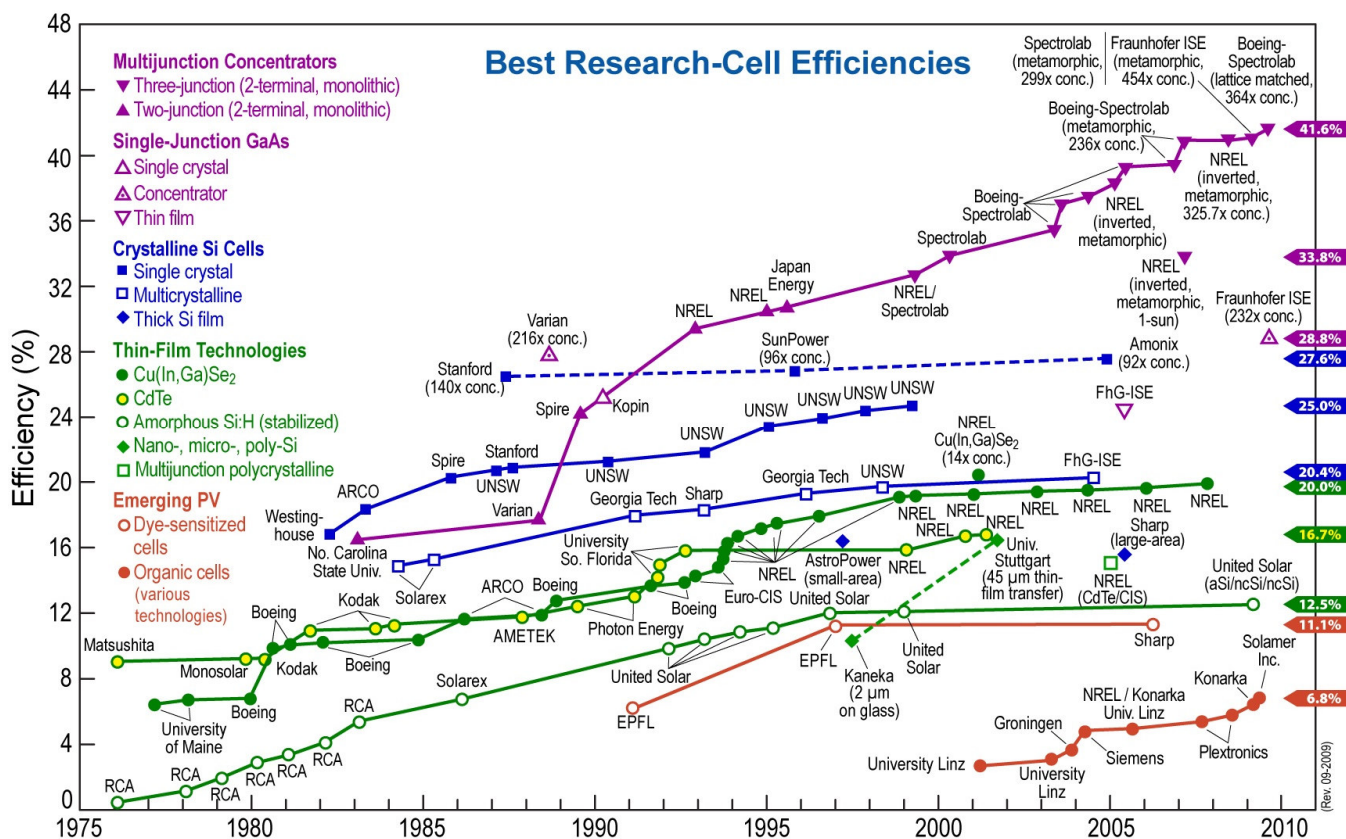


Figure 1.4 Timeline showing the highest reported device efficiencies for various types of solar cells. (Taken from National Renewable Energy Lab (NREL))

After the oil crisis in the 1970s, solar cells started to attract more interest and low cost materials capable of delivering competitive device efficiencies were intensively sought. Polycrystalline silicon, amorphous silicon, other thin film materials and organic semiconductors were the main candidates and significant progress has been made with all these materials systems, as shown in Figure 1.4.

For higher efficiency, new device structures were designed including inverted solar cells,¹² tandem solar cells,¹³ and multiple junction solar cells.¹⁴ King et al.¹⁴ made 3 junction solar cells with a structure of GaInP/GaAs/Ge and achieved a device performance of 41.6 %.

Recently, thin film solar cells using CdTe/CdS have been successfully commercialised with a module efficiency of 11 %, low cost (1.08 US \$ per watt), and long term stability (20 years).

However, their mass production is accelerating demand of the constituent materials (Te) and their rising price and scarcity are serious problems. (see Figure 1.5) Toxicity of Cd is also an issue with many countries heavily regulating its use.

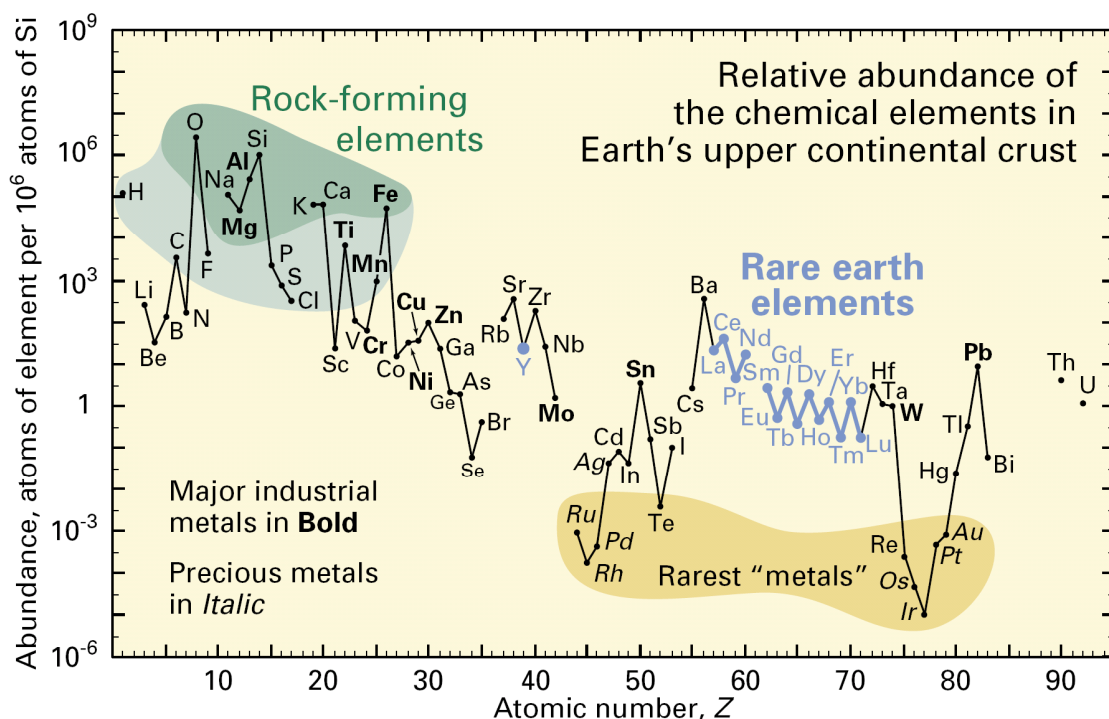


Figure 1.5 The relative abundance of materials compared to Si. (Taken from U.S. Geological Survey Fact Sheet 087-02)

In this context, due to the urgent needs for sufficient supplies of renewable energy from carbon neutral sources, organic photovoltaic technologies have emerged as a promising alternative technology.¹⁵

The basic working mechanism of organic solar cells can be explained by four consecutive steps; (1) absorption of a photon leading to the formation of an excited state: the electron-hole pair or “exciton”, (2) exciton diffusion to a dissociation site, (3) charge separation at the dissociation site, (4) transport of the separated electron and hole within the organic semiconductor to their respective electrodes, as shown in Figure 1.6.¹⁶

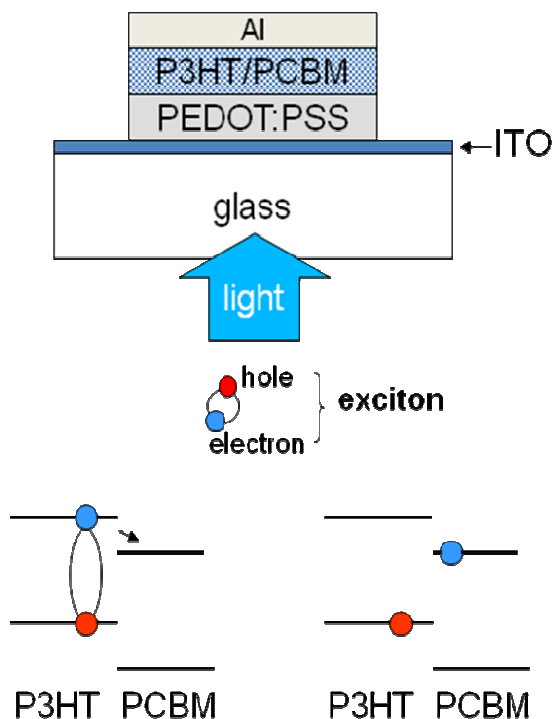


Figure 1.6 The working principles for a blended polythiophene/fullerene solar cell

Because of the fairly large band gap in typical semiconducting polymers (> 2.0 eV), only about 30 % of the incident solar light can be absorbed. The photo-excitations in organic materials lead to the generation of excitons as coulombically bounded electron-hole pairs.⁸ The electron and hole are tightly bound in organic semiconductors, so much higher energy input than the thermal energy is required to dissociate these excitons. The electric field provided by the asymmetric work functions of the electrodes is not sufficient to separate these excitons. Blending conjugated polymers with electron acceptors, e.g. fullerenes, has been widely reported as an efficient way to separate excitons at their interfaces into free charge carriers, due to different electron affinities of two materials.¹⁷

The electron will be accepted by the material with the larger electron affinity and the hole will be accepted by the material with the lower ionization potential. For efficient photovoltaic devices, the created charges should be transported to the respective electrode within their life time.³

Poly(3-hexylthiophene):1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁ (P3HT:PCBM) bulk hetero-junction solar cells have been intensively studied for the last decade.⁶ The morphology of the blended active layer has a strong impact on the overall device efficiency, affecting both the exciton dissociation probability and the ease of charge transport to the electrodes. In this context, many works on device annealing,¹⁸ controlling the donor polymer's regioregularity,¹⁹ and using additives such as oleic acids and alkylthiols^{20, 21} have been reported to optimize the morphology of the active layer.

P3HT can only absorb photons with wavelength smaller than 675nm due to its band gap energy (1.85 eV) and PCBM is known to be a poor light absorber.²² In addition, due to the energy band offset of donor and acceptor materials, higher open circuit voltages than 0.7 V cannot be expected, calculated from the equation, " $V_{OC} = \frac{1}{e}(|E_{HOMO}^{P3HT}| - |E_{LUMO}^{PCBM}|) - 0.3$ ", as shown in Figure 1.7.²³ Voc is proportional to the difference between the HOMO level of the donor material and the LUMO level of the acceptor compound. However, due to the strong exciton binding energy in the donor-acceptor blend, the minimum energy offset (~ 0.3 eV) is required.²³

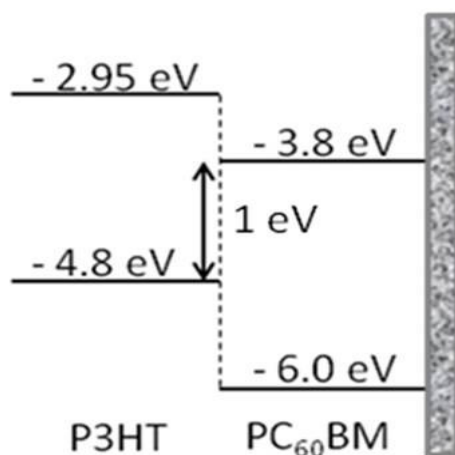


Figure 1.7 The energy band diagram for P3HT and PC₆₀BM.

The maximum short circuit current is normally determined by the optical band gap of the donor polymer, since fullerenes tend to be only weakly absorbing. The open circuit voltage is related to the difference between the highest occupied molecular orbital (HOMO) level of the donor polymer and the lowest unoccupied molecular orbital (LUMO) of the acceptor. Because PCBM is the unbeaten acceptor so far, the donor energy level has been mainly modulated to maximize the short circuit current and the open circuit voltage. Donors with smaller band gaps and higher HOMO levels will lead to more absorption of light but less open circuit voltage. Therefore there is a compromise between the two values. In this context, low band-gap polymers to ideally match with the energy level of PC₆₀BM or PC₇₁BM have been recently studied, leading to the highest reported device efficiency of 7.4 %.^{21, 24}

Dennler et al.²³ calculated the maximum obtainable power conversion efficiency with blended polymer solar cells as shown in Figure 1.8. External quantum efficiencies of 65 % and fill factors of 65 % were assumed. As a result, by developing a donor with an ideal optical band gap of 1.4 eV, polymer solar cells with 10 % power conversion efficiency are expected to be realized soon. However, it should be noted that all the parameter values that they assumed for their calculations, could in principle be improved upon and in many cases already have been, meaning efficiencies higher than 10 % may be achievable.

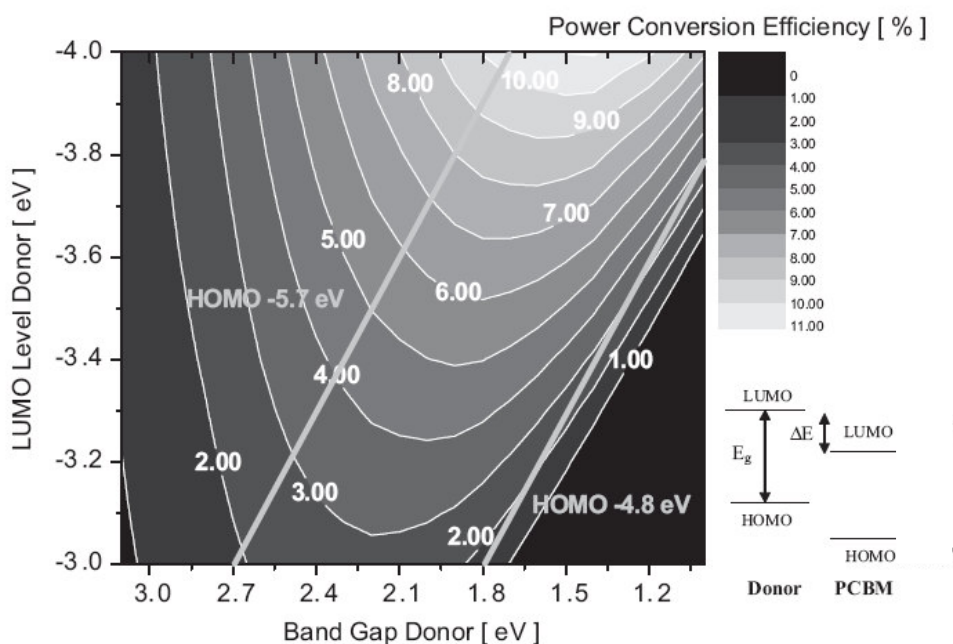


Figure 1.8 The calculated efficiency under 1 sun illumination for single junction devices based on the donor with a variable band gap (E_g) and LUMO level (ΔE), and an acceptor with a variable LUMO level. (Taken from reference 23)

1.3 Overview of transparent conducting films (TCFs)

One of the biggest challenges to the commercialization of organic electronic devices is the lack of high performance transparent conducting films (TCFs), which can be used as flexible electrodes. Transparent conducting films are an essential technology used in many optoelectronic device applications, including solar cells, light emitting diodes, thin film transistors, and smart windows.^{25, 26} Even though different transparent conducting materials are needed for specific applications, there are common metrics to be considered for selecting transparent conducting film including: high electrical conductivity, high optical transparency in the visible and infrared region, a suitable work function, surface uniformity and low cost fabrication.^{26, 27}

To date Indium Tin-Oxide (ITO) is the only anode material which has been shown to exhibit the necessary balance of good conductivity, smooth surface and strong adhesion (on glass substrates).²⁸ However, ITO has severe drawbacks; Indium is a rare material and its supply is limited. Sputtering techniques to attach ITO on top of rigid substrates require very expensive and intricate experimental conditions, which are not readily adaptable to roll to roll mass production. In addition, ITO tends to crack when repeatedly flexed, resulting in irreversible drops in the electrical conductivity.²⁹

There are a limited number of materials for making alternative transparent conductors to ITO; (1) thin metallic foils,³⁰ (2) metal nanowire meshes,³¹ (3) intrinsically conducting polymers,³² (4) carbon nanotubes,^{33, 34} and (5) graphenes.³⁵

As shown in Table 1.1, conducting polymers have problems of comparatively low conductivity at the similar transmission to other competitors and susceptibility to property changes during thermal and wet chemical processing. Nanowires of silver exhibit low sheet resistances at high transmittance but their high materials cost and high surface roughness in a film due to their relatively large diameters (~ 50 nm) are significant issues. Graphene is one of the most promising TCF materials but the development of viable large area production techniques that can provide adequate macroscopic conductivities is still a long way off.

Table 1.1 Comparison of transparent conducting materials: single walled carbon nanotubes (SWCNTs), ITO, nanowires, conducting polymers. (Rewritten from EIKOS (2006))

	SWCNTs dispersion	Graphene	Sputtered ITO	Metal Nanowire meshes	Intrinsically Conducting Polymers dispersion
Transparency	√	√	√√	√	√
Conductivity	√√	√√ or √	√√	√√	√
Cost	√√	√√	×	√	√
Colour	√√	√√	√	√	√
Printing capability	√√	√ or ×	×	√√	√√
Flexibility/Durability	√√	√√	×	√√	√√
Environmental stability	√√	√√	√√	√	×

√√ Good √ OK × Bad

Although each electronic device applications has its own unique requirements for the transparent conducting film, a target of 90% of transmittance at 550 nm and less than 100 Ω/sq of sheet resistance has been recognized as a sensible technological target for alternative transparent conducting films to ITO.³⁶

1.4 Single Walled Carbon Nanotubes (SWCNTs) and their applications in plastic electronics

Since their discovery in 1993, carbon nanotubes (CNTs) have attracted intensive interest from researchers due to their unique structural, electrical, thermal, chemical, and mechanical properties.^{37, 38}

Carbon nanotubes are nanomaterials composed of rolled-up graphite sheets with diameters between 0.5 nm and 2 nm and lengths of up to several μm . As shown in Figure 1.9, the roll-up vector (m, n) , which is the folding vector of the base graphene lattice, determines the tube diameter and chirality; either of metallic ($n - m = 3k$, k is an integer) or semiconducting (otherwise).³⁹

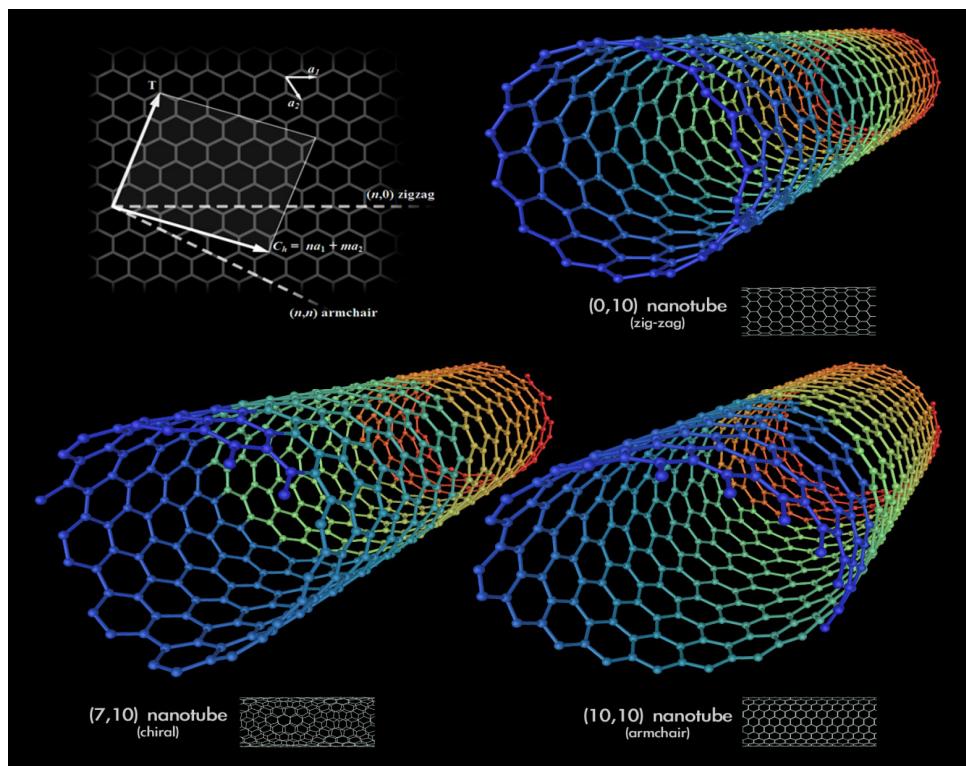


Figure 1.9 The folding vector from a graphite sheet to form carbon nanotubes. (Taken from reference 40)⁴⁰

Among different types of carbon nanotubes [such as single-walled, thin multi-walled, and multi-walled], single walled carbon nanotubes (SWCNTs) in a film are known to have the highest electrical conductivity ($> 6,000 \text{ S cm}^{-1}$) at the acceptable optical transmission ($> 80\%$), due to their smaller diameter ($\sim 1 \text{ nm}$), and high achievable purity levels (80 - 90 wt %).^{41, 42}

In addition, due to their novel 1-D nanostructure for well-known quantum confinement of electrons, SWCNTs have been reported to have high intrinsic carrier mobilities ($10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),⁴³ high intrinsic conductivities ($400,000 \text{ Scm}^{-1}$),⁴³ high intrinsic mechanical strength (50 - 100 G Pa),⁴⁴ large intrinsic thermal conductivity ($6,000 \text{ WmK}^{-1}$),⁴⁵ and tube-diameter dependent band-gaps for semiconducting nanotubes ($E_{\text{gap}} \approx 1/R_{\text{tube}}$).⁴⁶

SWCNTs have been synthesized by three major methods: arc-discharge, laser-ablation, and chemical vapour deposition. Recently, HiPCO (high-pressure carbon monoxide disproportionation) method was also developed for the mass production of SWCNTs by Smalley's group.⁴⁷ Although different production methods lead to varying material parameters, laser ablation and arc-made SWCNTs have been reported to have the best TCF performance due to their longer length (5 - 20 μm), lower defects and larger diameter ($\sim 1.4 \text{ nm}$), as shown in Figure 1.10.^{33, 48} However, laser-ablation SWCNTs have a drawback of extremely high production cost, which will hinder the commercial use.

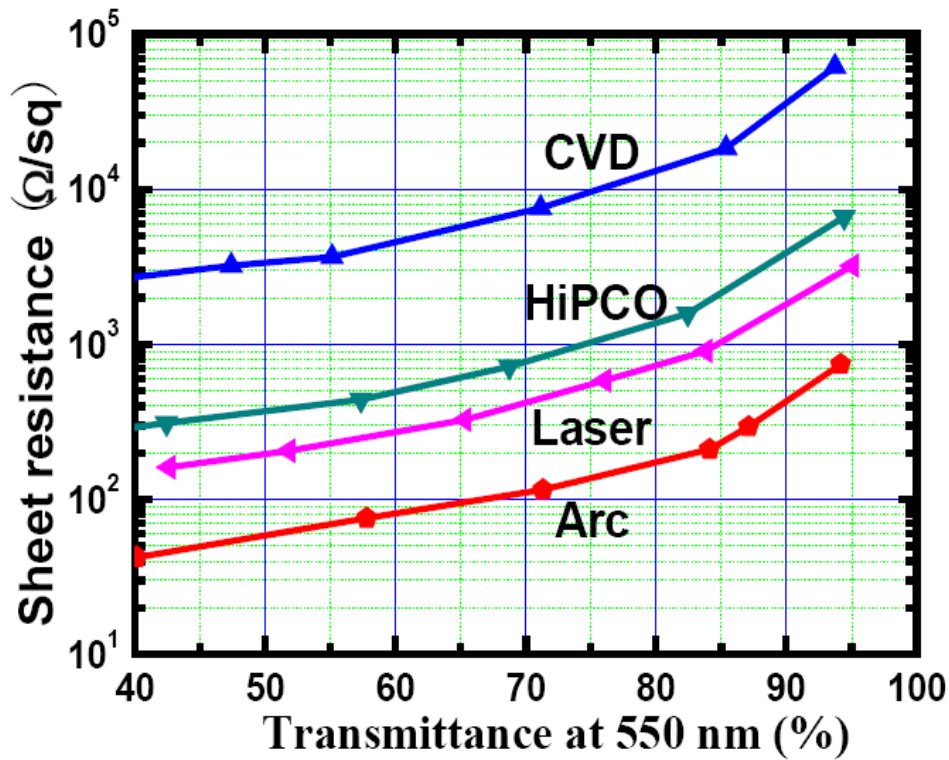


Figure 1.10 Transmittance versus sheet resistance characteristics for SWCNTs made with different production methods. (Taken from reference 48)

Recently, the integration of SWCNTs into organic electronics has attracted increasing attention.³³ Thin film networks of randomly distributed SWCNTs in particular can provide unique and novel optoelectronic properties, which may lead to the enhanced device performance and compatibility with flexible and stretchable devices.⁴²

Because of the random mixture of metallic (1/3) and semiconducting (2/3) tubes, SWCNT thin films have a semiconductor-metal transition as the film thickness approaches 8 - 10 nm and the percolation of the metallic tubes is attained.³³ The semiconductor behaviour just below the percolation threshold can be ideal for the active layer in thin film transistors and sensors.^{38, 49} SWCNT thin films with thickness from 10 to 100 nm can be used as TCFs to replace ITO, due to their high electrical conductivity at moderate transmission.^{34, 50} Micron thick (non-transparent) SWCNT films can be used as electrodes for supercapacitors, fuel cells, and batteries, due to their high current carrying capability and high electrochemical stability.⁵¹

1.5 Outline for this thesis

This thesis covers the essential issues associated with SWCNT thin films as alternative TCFs to ITO for organic device applications, mainly polymer solar cells. Rather than direct growth methods for SWCNT thin film deposition, solution-based coating methods are selected due to their compatibility with large scale, printable electronics.

Chapter 2 presents a literature review on solution based fabrication methods for SWCNT electrodes and their electrical, optical, and mechanical properties. Chapter 3 describes a variety of analytical techniques used to measure the properties of thin film SWCNTs and their performance in electronic devices, especially solar cells.

For successful commercialization of SWCNT thin films as TCFs, there are several problems to be solved. Firstly, SWCNTs have extremely high molecular weight, typically up to 10^5 - 10^6 , and tend to interact with each other by strong van der Waals interactions. As a result, individual SWCNTs aggregate to form bundle structures, resulting in extremely poor solubility in both aqueous solvent and many organic solutions. Therefore, it is necessary to enhance solubility by using various dispersion agents.^{33, 42}

Appropriate deposition and patterning methods should be also identified to ensure low sheet resistance, high transmittance, and low roughness of SWCNT thin films. Removal of dispersion aids and effective doping to enhance conductivity must also be tackled.³⁶

Chapter 4 compares various surfactants for preparing well dispersed SWCNT solutions and assesses the effectiveness of different deposition methods as judged by the electrical, optical, and morphological properties of the final films. Chapter 5 presents two newly developed patterning methods to fabricate SWCNT electrodes for device applications and compares their effectiveness with standard photolithography and plasma etching: (1) interlayer lithography for high resolution patterns, and (2) in-situ spray patterning for medium and low resolution patterns.

Chapter 6 describes the application of various SWCNT electrodes to organic solar cells, using a variety of dispersing aids and various patterning methods to prepare the SWCNT films, as described in chapters 4 and 5. The use of SWCNT films in organic device applications presents various challenges and appropriate solutions were developed in the course of this work. The wetting ability of SWCNT thin films was first enhanced with simple water-miscible alcohol treatments and the influence of other device fabrication conditions such as annealing temperatures, and film thicknesses were investigated for optimisation with the SWCNT electrodes. Flexible devices on plastic substrates with SWCNT films were also demonstrated to show the feasibility of fabricating the all-flexible electronic devices with highly conductive SWCNT thin films.

Chapter 7 presents the electrical, optical, and mechanical properties of double-layered SWCNT-reduced Graphene-Oxide hybrid films for the purpose of breaking through the performance limits of SWCNT-only or reduced Graphene-Oxide-only films. Their application in organic solar cells as transparent electrodes was also demonstrated with promising preliminary results. Chapter 8 concludes this thesis and mentions future works.

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Chapter 2 Literature Review

2.1 Introduction

This thesis mainly focuses on the fabrication of thin film SWCNTs and their application to organic solar cells. SWCNTs are known to have a work function comparable to that of ITO and high current carrying capacity, and to be flexible but mechanically strong.¹ However, thin film properties such as optical transmission, electrical conductivity, and mechanical flexibility depend sensitively on the choice of SWCNT type, solvent, dispersant (if any), deposition method and post-deposition treatment. In this chapter, I review the existing literature relating to these issues.

First, the current methods to disperse SWCNTs in aqueous and organic solvents are discussed. Various SWCNT thin film coating and patterning methods are then reviewed. Due to the presence of semiconducting SWCNTs (at a two thirds number fraction) in a random SWCNT sample, the doping of as-deposited SWCNT thin films is essential to improve their electrical performance. The efficacy of different doping methodologies is reviewed below. The electronic, optical and mechanical properties of SWCNT thin films are then discussed, and finally relevant figures of merits for characterising the overall quality of SWCNT thin films as transparent conducting films are introduced.

2.2 CNTs dispersion

Solution based coating techniques have several benefits compared to direct growth methods for film deposition. Their low temperature processing requirements (typically < 100 °C) are compatible with plastic substrates and the ability to process under ambient conditions offers a viable route to low cost, large area production. For this reason, solution processing has been intensively studied as a means of preparing thin film SWCNTs.

To achieve high quality SWCNT films, effective and stable dispersion of the SWCNTs is crucial.² However, SWCNTs have extremely high molecular weights (10^5 - 10^6), and tend to aggregate into large ropes or bundles as a result of strong attractive van der Waals interactions. Bundle properties are known to be inferior to those of isolated SWCNTs, and bundle formation causes very poor solubility in organic or aqueous solvents.^{3, 4}

Generally, SWCNTs are dispersed in solvents with the aid of mild ultrasonication followed by high speed centrifugation. The sonication facilitates the break up of the initial nanotube powder into smaller aggregates and then accelerates the exfoliation of individual nanotubes from these bundles.⁵ Figure 2.1 shows the typical “unzipping” mechanism of SWCNTs using a surfactant.⁵ The “unzipping” process normally takes place within a few seconds or less depending on the surfactant adsorption rate, the SWCNT length, and the effective area of the surfactant headgroup.⁶ However, sonication generally heats up the solution, which can affect the dynamics of the ultrasonic process. Therefore, temperature control during the sonication process is important, especially when using strong probe-type ultrasonic systems.

Strong sonication can damage nanotubes by causing defects on SWCNTs and even cutting the tubes, and these defects and shortened tubes can lead to decreased electrical conductivity in the final film.⁷ Hence it is preferable to use mild sonication over longer periods of time to disperse SWCNTs. The optimal sonication time depends on the SWCNT purity, adsorbed functional groups, the surfactant and solvent choice, SWCNT and/or surfactant concentration, the sonication power and frequency, solution volume and temperature, and pH value.⁸

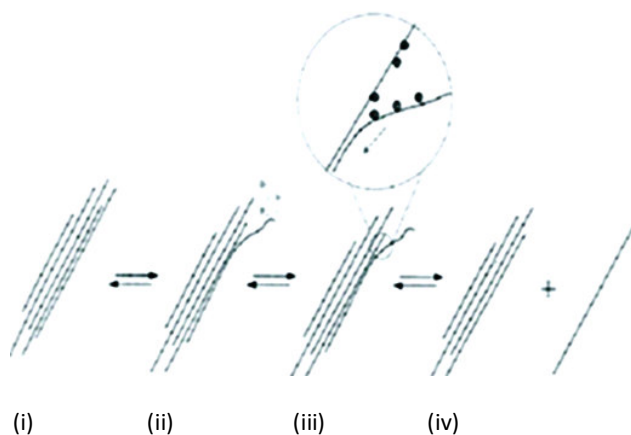


Figure 2.1 The mechanism of SWCNT isolation from bundles using a surfactant (i) Ultrasonic processing opens the bundle end, (ii) which then becomes a site for additional surfactant adsorption, (iii) release of an isolated, surfactant-coated SWCNT into solution (iv). (Taken from reference 5)

Centrifugation can remove the remaining large aggregates and either the SWCNT concentration remaining after centrifugation or the quantity of aggregates can be used to assess the ability of the specific solvent/surfactant system to disperse SWCNTs.⁹

The dispersion of SWCNTs in common organic solvents has been reported by many research groups. Due to the non-polarity of pristine SWCNTs, initially N-Methylpyrrolidone (NMP) and Dimethylformamide (DMF)

were investigated as potential nanotube solvents due to their strong polarity and low tendency for hydrogen bond donation.¹⁰ Bergin et al.¹¹ reported that the enthalpy of mixing SWCNTs in N-Methylpyrrolidone (NMP) is negative and NMP has better nanotube dispersability compared to Dimethylformamide (DMF). Landi et al.¹² quantified the dispersing capability for SWCNTs with various alkyl amide solvents, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N,N-diethylacetamide (DEA), and N,N-dimethylpropanamide (DMP). However, final SWCNT concentrations with all alkyl amide solvents were fairly low ($< 6.25 \mu\text{g/ml}$). (See Figure 2.2)

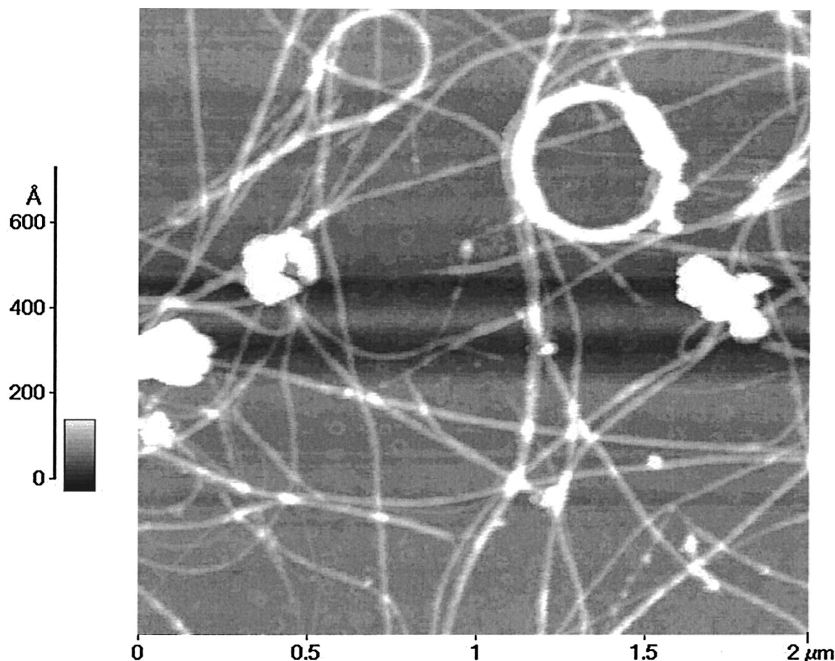


Figure 2.2 The AFM image of SWCNTs dispersed in DMF (Taken from reference 11)

Bahr et al.¹³ found by using UV/VIS absorption spectroscopy that the most appropriate organic medium for dispersing SWCNTs is 1, 2-dichlorobenzene (DCB) ($\approx 0.1 \text{ mg/ml}$) compared with Chloroform, NMP, Pyridine, Acetone, DMF, Trimethylbenzene, Dimethylbenzene, Ethanol, Toluene. Niyogi et al.¹⁴ also showed that DCB is a better solvent than DMF by using UV/VIS/NIR spectroscopy. However, S. B. Fagan et al.¹⁵ reported there to be only a weak interaction of DCB molecules with SWCNTs using resonant Raman spectroscopy, indicating imperfect dispersion of nanotubes in DCB. In addition, chlorinated solvents tend to heavily functionalise SWCNTs when sonicated and can consequently degrade their electronic properties.⁴

Recently, Bergin et al.¹⁶ tested a wide range of 64 organic solvents and reported that the concentration of nanotubes remaining after centrifugation for cyclohexyl-pyrrolidone (CHP) is up to 3.4 mg/ml . However, most of these organic solvents are restricted in use due to their toxicity and limited solubility (≈ 0.05

mg/ml). In addition, the stability of SWCNTs in organic solvents is very sensitive to any water take-up that may occur, as this leads to significant aggregation.¹⁷

To overcome the limited solubility in organic solvents, several approaches to functionalising SWCNTs have been employed. Covalent attachment of functional groups to SWCNTs has been widely used to prepare exfoliated SWCNTs in both aqueous and organic solvents.¹⁸ The functionalised nanotubes tend to form a stable colloidal suspension, sterically stabilised by osmotic pressure or electrostatic interaction induced from adjacent functional groups. In some cases, the interaction between a functional group and a solvent can lower the enthalpy of mixing and increase solvent configurational effects, resulting in better dispersion of SWCNTs in solvents.¹⁹ However, covalent functionalisation is known to significantly alter the structural and electronic properties of pristine SWCNTs, which can be problematic.²

Non-covalent strategies for dispersing SWCNTs in aqueous solutions by using extreme acids can facilitate dispersion but the formation of numerous defects during the functionalisation process normally deteriorates their intrinsic electronic properties.²⁰

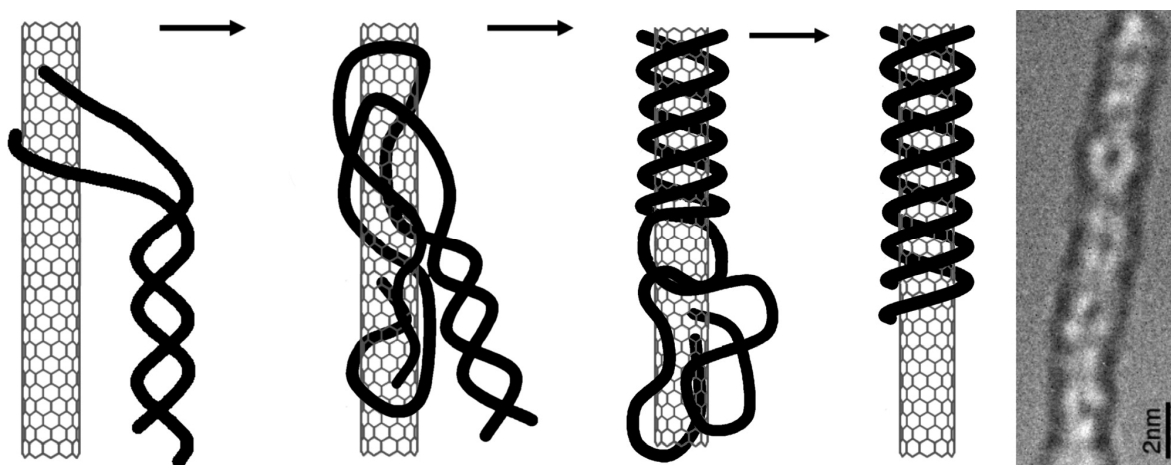


Figure 2.3 The mechanism of ordered DNA wrapping of CNTs and an HRTEM image of a 32-day-old sample. (Taken from reference 21)²¹

The use of dispersing aids such as hydrophilic polymers or bio-molecules (DNA, peptides) is also known to aid exfoliation of CNT bundles in aqueous solutions, but they are not suitable for the solubilisation of SWCNTs in organic solvents.^{3, 4, 22} DI water as a solvent has various merits of being environmental friendly, safe, and readily available. Polymer wrapping is commonly used for CNT dispersion in DI water, especially for CNT-polymer composite applications.²³ However, in terms of making high quality SWCNT thin films for electronic applications, polymer-wrapped dispersions are problematic due to the large size of polymers and the difficulty of removing them from the final film.

DNA²⁴ and proteins²⁵ for biological applications and Nafion²⁶ for fuel cell applications also have been shown to have an excellent ability to disperse SWCNTs in water. These materials can bind onto the SWCNTs non-covalently, while preserving the CNTs' intrinsic electrical and optical properties. (See Figure 2.3) However, all these non-covalent strategies normally use large quantities of dispersing aids to achieve the targeted solubility, which will cause undesirable intermolecular interaction between the adsorbed insulating dispersant molecules and the SWCNTs. Therefore their use inevitably requires additional and challenging removal steps, which may induce defects on the SWCNTs due to strong acid or high temperature treatment steps.^{1, 2} Harsh removal processes are especially problematic for flexible device application using plastic substrates.

Therefore the best strategy for dispersing SWCNTs for thin film electronic applications will be to select the most effective dispersing agents with a maximum solubility of SWCNTs in water and, once dispersed, remove them thoroughly using a mild method that does not induce any potential tube defects.

The simple and most common method to disperse SWCNTs for thin film fabrication is the use of surfactants as interfacial stabilizers in water, due to their ability to individualize CNTs at high concentrations (~ 20 mg/ml).²⁷ Surfactants have also advantages of interacting noncovalently with SWCNTs and being readily rinsed off in subsequent washing steps.

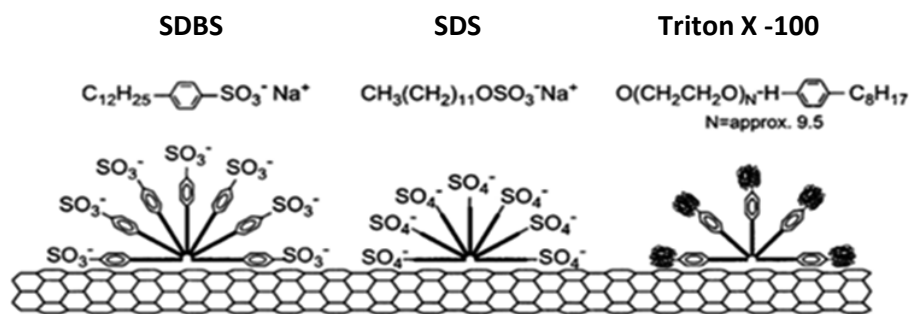


Figure 2.4 The schematic view of surfactant adsorption onto the SWCNT surfaces. (Taken from reference 27)

As shown in Figure 2.4, the hydrophobic end of a surfactant attaches to the bundled SWCNTs, while the hydrophilic end helps pull the CNTs into water. The headgroup, chain length, and surfactant weight are found to affect the dispersion ability of the surfactant.²⁸ Sodium dodecyl sulfate (SDS), and sodium dodecylbenzene sulfonate (SDBS), and Triton X-100 have been the most widely studied surfactants.²⁷

SDBS is known to completely exfoliate SWCNTs in DI water up to 20 mg/ml and its suspension can be stable over months at ambient conditions without significant aggregation or bundling.²⁷ Residual surfactants can also be removed from the deposited films with relatively mild post acid treatments to ensure the maximum electrical conductivity.²⁹ However, after surfactant removal, voids between SWCNTs can induce substantial morphological disorder. Hence surfactants with smaller molecular weights are preferred for obtaining smooth films.

2.3 SWCNT thin film deposition

Once a stable and well dispersed SWCNT suspension has been obtained, the next challenge is to uniformly deposit the SWCNT solution without causing significant aggregation of the tubes.² Various solution-based deposition methods have been used to fabricate thin film SWCNTs on glass or plastic substrates. Useful techniques must provide control over the tube density (D), which is defined as the number of the tubes per unit area of random network films and the overall uniform porosity of the SWCNTs.³⁰

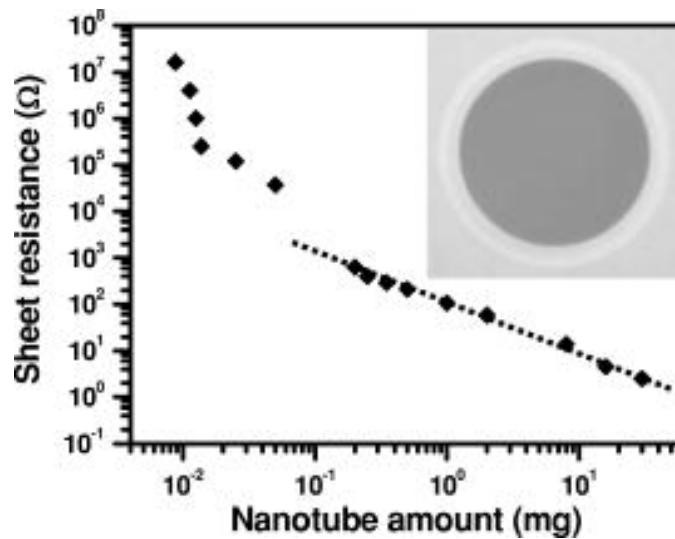


Figure 2.5 Sheet resistance of thin film SWCNTs versus the mass of deposited material. The inset shows a photo image of a uniform two-inch diameter carbon nanotube film (dark region) on a filter. (Taken from reference 30)

Wu et al.³¹ reported a vacuum-filtration method with laser-ablation SWCNTs for preparing thin films on a filter via vacuum-filtering of a dilute surfactant (Triton X-100) based suspension of purified SWCNTs in water. The filtration membrane was dissolved using a solvent after transferring the films to a target substrate. 50 nm thick SWCNT films produced in this way had a sheet resistance of 30 Ω /sq and optical

transmittance of over 70% in the visible spectrum. By using a porous membrane filter with a pore size of 20 - 200 nm³², the vacuum filtration method ensured comparatively uniform and extremely precise control over the tube density as shown in Figure 2.5. However, due to the undesirable use of a filter substrate, an additional transfer process to the target substrate is necessary.

Ozel et al.³³ and Zhou et al.³⁴ combined a polydimethylsiloxane (PDMS) based transfer-printing technique with vacuum filtration, which allowed controlled deposition and patterning together, as shown in Figure 2.6. McGehee et al.³⁵ vacuum-filtered a SWCNT solution dispersed with Triton X -100 over a porous alumina membrane, and the SWCNT thin films were lifted off with a PDMS stamp and transferred to a flexible PET substrate by contact printing. Their 125- μ m-thick polyethylene terephthalate (PET) substrates coated with a 30 nm thick SWCNT film had a transmittance of 85% at 550 nm and a sheet resistance of 200 Ω /sq. However, the deposition technique using a vacuum filtration is limited by the area of the filters and cannot ensure consistent transfer of high quality SWCNT films to the substrate.

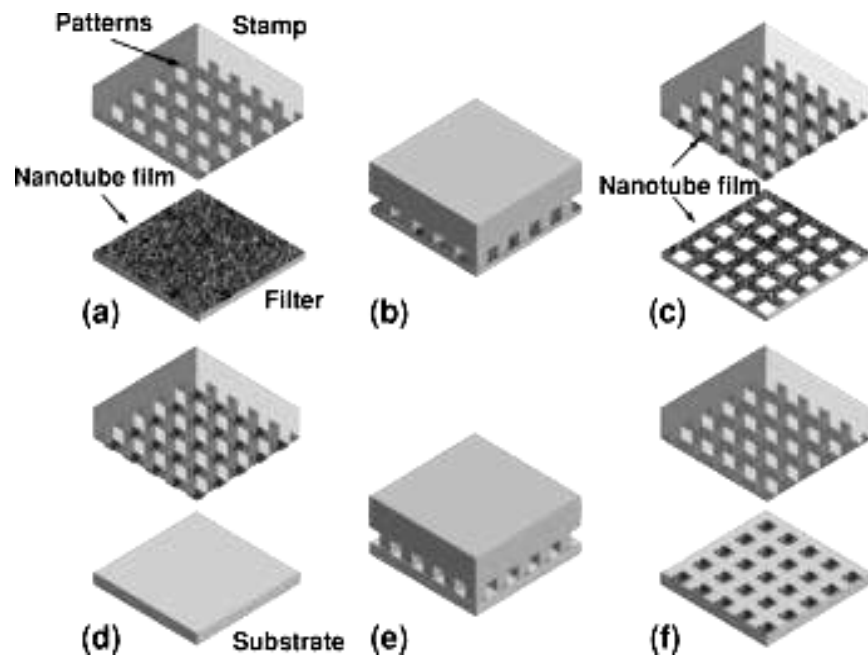


Figure 2.6 Schematic illustrating vacuum filtration and PDMS transfer printing for CNT films. (a), (b) Conformal contact between PDMS stamp and nanotube films on the filter. (c) PDMS stamp is removed from the filter. Patterns of nanotube films are transferred onto the PDMS stamp. (d), (e) PDMS stamp with patterned nanotube films makes contact with a flat receiving substrate. (e) PDMS stamp is removed from the substrate after mild heating. (Taken from reference 34)

Ng et al.³⁶ used dip coating to make thin film SWCNTs on various substrates. Their polyethylene terephthalate (PET) substrates coated with around 100 nm of SWCNTs had a transmittance of 69% at 550 nm and a sheet resistance of 130 Ω /sq. Dip coating is a simple and scalable technique for large area production but due to the unavoidable coating of both sides of the substrate, its applications can be limited.

The most popular and simple solution based method for thin film deposition is spin-coating, which ensures a uniform surface coverage with high controllability over film thickness.^{37, 38} Yim et al.³⁷ made transparent single wall carbon nanotube (SWCNT) films on PET by spin coating SWCNTs dispersed in dichloroethane (DCE). After post-acid processing, the so-formed SWCNT films had a visible-range transmittance of 80 % and a sheet resistance of 85 Ω /sq. However, due to the dilute nature of the SWCNT suspension, multiple repetitions are needed to achieve appreciable film thickness ($\sim$ 20 nm). In addition, spin-coating is not viable for large area production due to the fixed area of a spin-coater chuck and excessive materials wastage.

Drop-casting is an easy and rapid method to deposit SWCNT films, which is also applicable to large area deposition.³⁹ However, the resultant films are relatively rough with over 10 nm (r.m.s) roughness. In particular, drop-casting is less appropriate for thin film fabrication due to the poor controllability over the tube density and film thickness.

Langmuir-Blodgett (LB) deposition based on the hydrophobic SWCNTs has been also reported as a means of fabricating monolayer films.⁴⁰ However, using the process to make 10 - 100 nm SWCNT films as needed for electrode applications is very slow and the control of the thin layer on water is often tricky.

Electrophoretic deposition has been used to make SWCNT thin films on conductive substrates by applying a DC electric field.⁴¹ The technique uses an electrochemical procedure to attach negatively charged SWCNT particles on a metal deposited electrode. As shown in Figure 2.17, it is a simple and fast technique with an uniform film morphology.

Compared with drop casting (DC), spray coating (SC), and filter/transfer (FT), electrophoretic deposition (EPD) was reported to have the lowest roughness ($\sim$ 5 nm) followed by DC (10 nm), FT (45 nm), and SC (55 nm).⁴² However, the post removal process for the remaining oxidized alumina particles can be challenging.

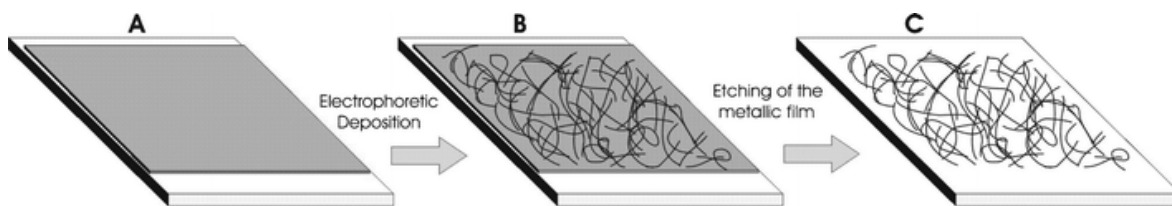


Figure 2.7 Schematic diagram of the electrophoretic deposition. (a) Thermal deposition of the metallic layer, (b) Electrophoretic deposition of SWCNTs and oxidation of the metallic layer, (c) etching of the metallic film. (Taken from reference 41)

The practical challenge for solution deposition methods is the low solubility of SWCNTs and their strong intertube interactions, which often lead to non-uniform and largely bundled SWCNT films.¹ Concentrated SWCNT solution cannot be easily wetted onto the target substrates as well. Continuous spray coating with a diluted SWCNT ink on a heated substrate is an attractive method to tackle these issues. Although the resultant films can be inhomogeneous and slightly rough due to the micrometer size of SWCNT droplets exiting from an air-pressured spray nozzle, spray coating is a fast and handy method to make highly conductive SWCNT thin films, especially with surfactant based inks.⁴³ Careful process optimisation, moreover, can yield adequate film quality for electronic applications.

Hu et al.⁴⁴ used a surfactant (SDS) containing aqueous dispersion of arc-discharge SWCNTs to coat glass and plastic substrates with a simple air-brush. The resultant films had sheet resistances of 100 Ω/sq on glass and 300 ohm/square on PET with around 80 % of transmittance at 550 nm. Geng et al.²⁹ also fabricated thin films on PET by spray-deposition from sodium dodecyl sulfate (SDS) assisted single-walled carbon nanotube solutions. After nitric acid treatment, SWCNT films with a sheet resistance of 70 Ω/sq and a transmittance of 80 % were obtained.

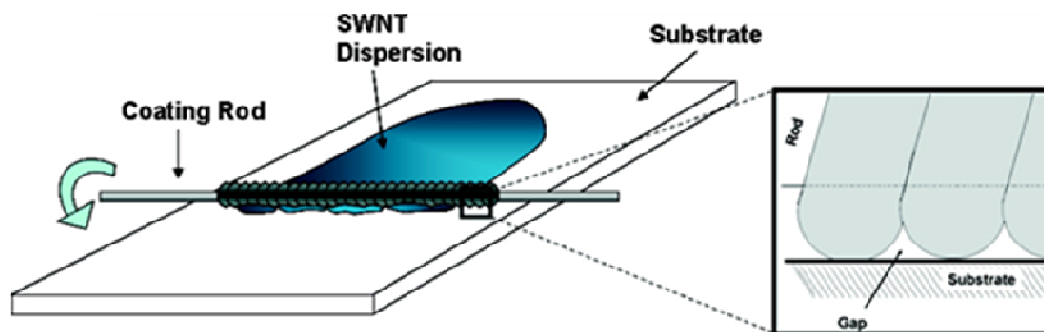


Figure 2.8 Schematic illustration of a rod coater. (Taken from reference 45)

Dan et al.⁴⁵ used a wire bar coating method to make uniform and scalable SWCNT films as shown in Figure 2.8. After acid treatment, SWCNT films with a sheet resistance of 140 Ω/sq and a transmittance of 70 % were obtained. However, achieving adequate control over the surface tension and the ink/surface interaction can be often challenging with wire bar coating, making it difficult to control film uniformity.

Ink-jet printing is one of the most promising deposition methods, which has attracted intensive interests from industry due to its fast nature, high controllability and compatibility with large area, mass production. However, the intricate procedure to prepare the concentrated ink and the need to avoid aggregation during the printing process is challenging. In addition, controlling the tube density of the deposited films is not easy for thin film applications.^{46, 47}

Controlled large-area deposition of highly conductive carbon nanotube films from solution with high homogeneity is still a challenging task. Each deposition method has its own merits and disadvantages. LB and spin coating can be effective for making films that are a few monolayers in thickness. However their ability to scale up is extremely limited. Spray, filtration/transfer, and electrophoretic methods provide good control over the coating process, and spray coating in particular is appropriate for large scale, thin film applications, with the main challenge being to ensure homogeneous film deposition. Rod and inkjet coating can be useful for large area, thick film applications. However, they place strict requirements on the preparation of the inks and target surfaces.

2.4 SWCNT thin film patterning

For transparent electrode applications, appropriate patterning techniques must be developed. There are several commonly used techniques for patterning SWCNT films prepared from solution, such as inkjet printing,⁴⁷ micro-contact printing,^{48, 49} photolithography or E-beam lithography with (or without) plasma etching,⁵⁰ lift-off photolithography,^{2, 51} PDMS based stamping,⁵² and laser ablation.⁵³

Ink-jet printing is an ideal patterning method, which enables large area deposition and relatively high resolution patterning in a single process. However, the interaction between an ink and a printing nozzle is often complicated and thin film deposition below 50 nm thickness is also challenging.⁴⁶

Rogers et al.⁴⁹ developed a micro-contact printing method as shown in Figure 2.9, by using a PDMS based micro-fluidic channel to control the flow of CNT solution, which led to the formation of high resolution patterns (height 50 μm $\times$ width 250 μm) of SWCNTs. Through the accurate control of fluid dynamics,

complex patterns of SWCNT films were obtained. However, scaling up this technique for the large area applications could be highly problematic.

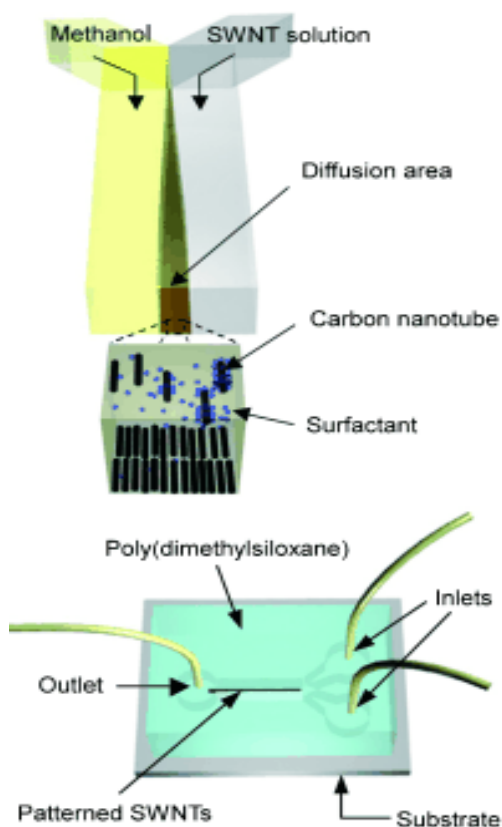


Figure 2.9 A micro-fluidic patterning device built with poly(dimethylsiloxane) (Reprinted with permission from reference 49b)

There are also subtractive patterning methods for as-deposited SWCNT films. Hu et al.⁵¹ used wet photolithography combined with dry plasma etching to define the fine patterns for spray deposited SWCNT thin films. As shown in Figure 2.10a, after spin-coating micron thick photoresist (PR) layers on top of the deposited SWCNT films, exposing, and developing in the usual way to form a patterned film of cross-linked photoresist, gas plasma within a reactive ion etcher (RIE) system was used to remove the exposed SWCNTs. For higher resolution patterns with features down to 100 nm, e-beam lithography was successfully used.⁵⁰ However, there can be potential defects or oxidation of SWCNTs in imperfectly protected areas during the patterning process due to the use of harsh chemicals and plasma treatments.

Alternatively, Hu et al.⁵¹ employed lift-off lithography to pattern SWCNT films. This technique has the merit of avoiding chemically induced degradation of the SWCNT films as the photoresist is patterned before spray coating the SWCNTs, as shown in Figure 2.10b.

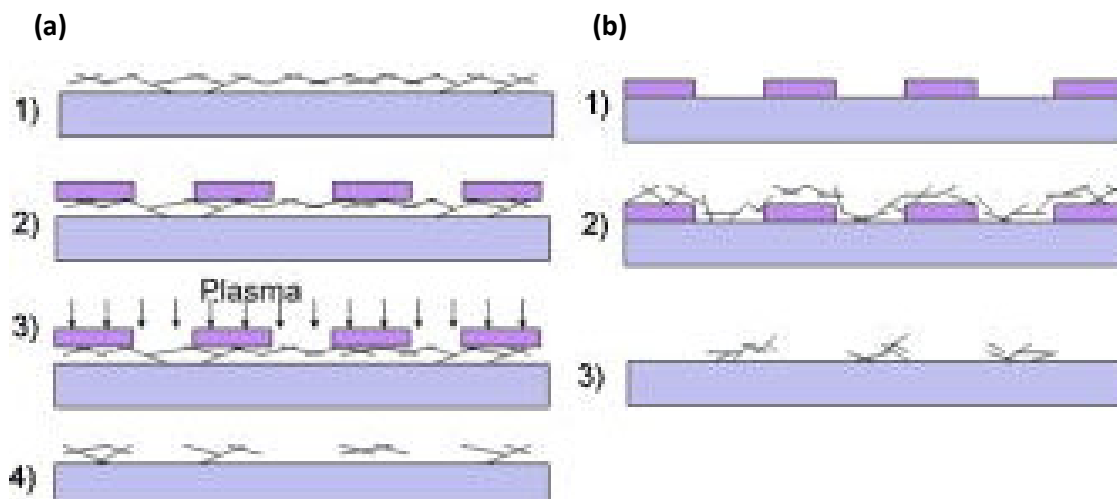


Figure 2.10 (a) Photolithography/plasma etching process. (1) Transparent substrate is treated with silane and nanotubes are spray-deposited on top of it, (2) PR is spin-coated and patterned by exposure and development, (3) Thin film SWCNTs are plasma etched, and (4) PR is removed with acetone. (b) Alternative lift-off lithography process. (1) PR is patterned, (2) Substrate is treated with silane, followed by spray deposition of SWCNTs, and (3) PR is removed. (Taken from reference 51)

Polydimethylsiloxane (PDMS) based transfer patterning combined with vacuum filtration deposition has been intensively used for patterning SWCNT films, although its practicality in a mass production environment is highly questionable.⁵⁴ Direct laser methods can also be used to pattern SWCNT films, and are compatible with roll to roll manufacturing.⁵⁵ However, its unavoidable focused thermal emission is an issue for plastic substrates.

Appropriate patterning methods for each device application should be chosen based on the requirements for target resolution, materials sensitivity, substrates (rigid or plastic), and cost.² To ensure highly conductive and transparent SWCNT films, non-destructive methods are strongly preferred. In addition, for large scale device applications, simple and rapid techniques are desired. Finally, for flexible device applications on plastic substrates, low temperature patterning methods are essential.

2.5 SWCNT thin film doping

Due to the presence of semiconducting SWCNTs in thin films prepared from unsorted SWCNTs, doping is essential to achieve optimum conductivity. In films of pure metallic SWCNTs, since boundaries between tubes or bundles have minor effects, the conduction mechanism is mainly derived by ballistic quantum

transport.⁵⁶ However random networks of SWCNTs exhibit temperature dependent resistance, with the resistance decreasing at higher temperatures. This behaviour can be explained by variable range hopping (VRH) models that assume strong localization of electrons at tube junctions between the bundles, due to the existence of semiconducting SWCNTs,^{57, 58} as shown in Figure 2.11.

Semiconducting SWCNTs have Coulomb-gap-type conduction, due to Coulomb interactions between localized electrons, which introduces severe hopping barriers that significantly reduce the electrical conductivity.⁵⁸ Chemical doping of nanotube random networks have been reported to change these conduction mechanisms dramatically by increasing charge carrier numbers through charge transfer between dopants and SWCNTs.⁵⁹

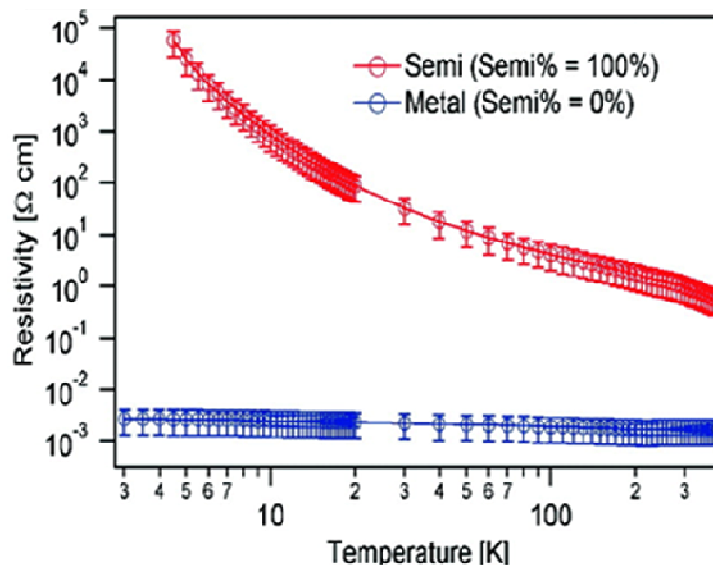


Figure 2.11 Sheet resistivity of pure metallic (Metal, Semi% = 0%) and semiconducting (Semi, Semi% = 100%) SWCNT films with increasing temperature. (Taken from reference 59b)

For thin film applications, p-type hole doping of SWCNT films with electron withdrawing materials such as HNO_3 , O_2 , NO_2 , Br_2 , SOCl_2 , F_4TCNQ , and transition metals is effective at enhancing electrical conductivity. The doping is performed by simply dipping SWCNT thin films into the dopant solutions for several hours and then drying thoroughly. Normally electrical conductivity increases by a factor of 5 or so after the doping process, while causing only minor changes in optical transmission in the visible range.

However, the exposure time is a critical consideration: Excessive exposure to oxidizing agents may produce no significant enhancements in conductivity, but substantially increase the risk of possible defects on the SWCNTs.²⁹ Parekh et al.⁶⁰ reported a decrease in the sheet resistance of SWCNT thin films by a factor of 5

after exposure to HNO_3 for 3 hours followed by SOCl_2 for 3 hours. Smalley et al.⁶¹ reported that Br_2 and K doping increased the CNT film conductivity by a factor of 15.

As shown in Figure 2.12, Geng et al.²⁹ reported that SWCNT film conductivity was enhanced by a factor of 4 with 12 M of HNO_3 doping for 1 - 2 hours, which was attributed to the doping process itself together with surfactant removals and the densification of the film by 25% to improve the cross-junction connectivity between SWCNTs

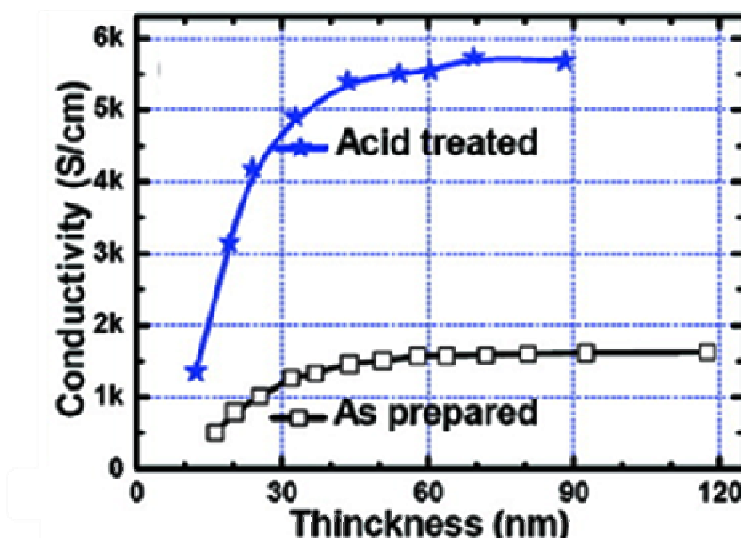


Figure 2.12 Conductivity as a function of film thickness before and after acid treatment. (Taken from reference 29)

There are also gas dopants for SWCNT thin films, however, they typically undergo weak binding to SWCNTs and so can be easily dedoped.⁶² In order to use doped SWCNT thin films in electronic applications, the dopants on tubes should be stable under normal device fabrication conditions, such as thermal annealing, wet chemical processing, and storage/usage conditions.² A top coating of PEDOT:PSS has previously been reported to slow the desorption process, allowing the conductivity of doped SWCNT films to be maintained over 250 hours.⁶³ Elsewhere, spin coating a thin PEDOT:PSS layer on top of SWCNT films has been reported to significantly decrease the surface roughness of the top surface²⁸ and to decrease the total sheet resistance by 20 % more than would be expected from geometric considerations alone. It is probably due to enhanced adhesion and closer packing of the two layers.³⁵

It is clear from the above discussion that the principal challenge is to find a stable and effective doping method to enhance SWCNT thin film performance. In addition, compatibility with elevated temperature processing and common organic solvents is a challenging prerequisite for device applications.⁶⁰

2.6 Properties of SWCNT thin films

Thin films prepared from unsorted SWCNTs have a two dimensional structure comprising a mixture of semiconducting (2/3) and metallic (1/3) tubes, and therefore show the collective behaviour of the individual tubes with additional electrostatic screening characteristics at the tube-tube junctions.⁶⁴

2.6.1 Electronic properties

The electronic band structure of individual SWCNTs has been reported to mainly depend on their chirality and tube diameters, as shown in Figure 2.13.⁶⁵⁻⁶⁷ Kane et al.⁶⁷ calculated that the semiconducting tubes have band gaps of around 0.5 - 0.6 eV, while metallic tubes ($n \neq m$) have small gap values (~ 0.01 eV).

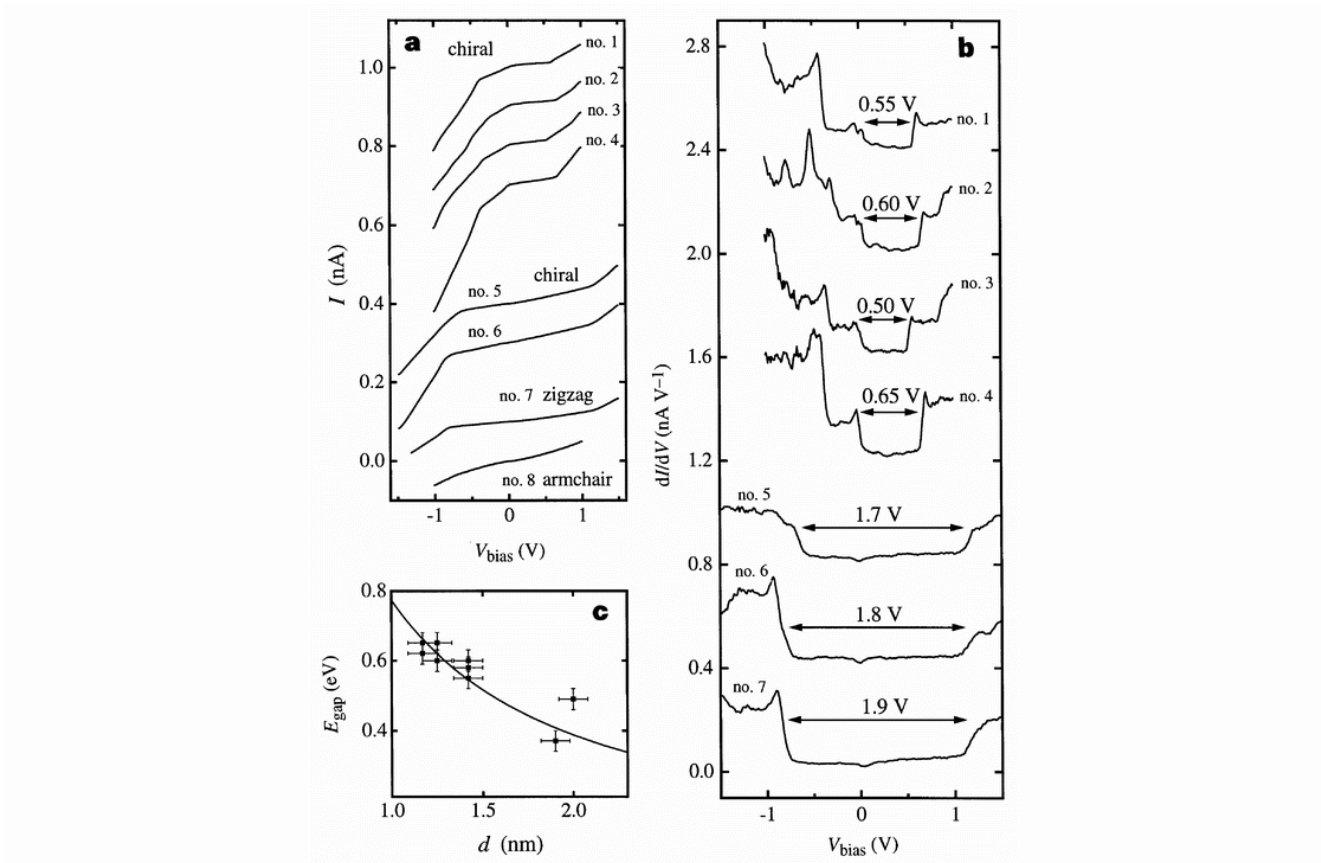


Figure 2.13 (a) Current–voltage characteristics of various individual nanotubes measured with tunneling spectroscopy. Nos.1–6 are chiral, no.7 is zigzag and no. 8 is armchair, (b) The differential conductance (dI/dV) versus applied bias. Here dI/dV is considered to be proportional to the density of states of the tube. (c) Energy band gap (E_{gap}) versus diameter (d) for semiconducting chiral tubes. (Taken from reference 60c)

However, Smalley et al.^{60c} found that for semiconducting (chiral) SWCNTs, the band gap varied with diameter as $E_{\text{gap}} \approx 1/d - 0.6/d$ (eV), and for metallic SWCNTs ($n \neq m$), a large secondary band gap varied with diameter as $E_{\text{gap}} \approx 1/d^2$ (eV) was observed.^{66, 68} This is known as a curvature effect for small diameter

nanotubes (1 – 2 nm), which displaces the electronic states significantly away from the intrinsic Fermi energy and therefore opens up a gap by mainly distorting the conduction band.⁶⁸

The work function of SWCNT thin films is also very important for their potential use as electrodes in displays, solar cells and other optoelectronic applications. Various methods have been used to measure the work functions of SWCNT films including Kelvin probe,⁶⁹ ultraviolet photoelectron spectroscopy,⁷⁰ photoelectron emission,⁷¹ and most studies have found that the collective work function of SWCNT films is around 4.6 - 5.0 eV.

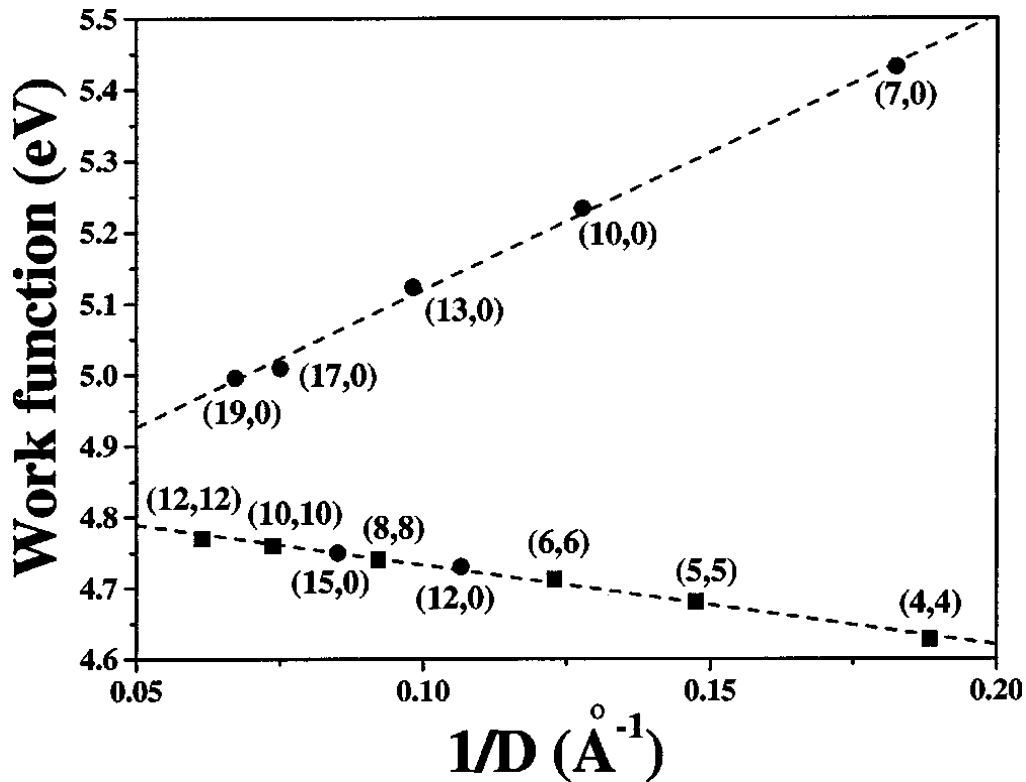


Figure 2.14 Work functions of individual metallic and semiconducting SWCNTs versus the inverse tube diameter ($1/D$). Squares are armchair SWCNTs (metallic) and dots are zigzag SWCNTs. (metallic or semiconducting) (Taken from reference 67)

However, individual SWCNT chirality, length and diameter, the bundle size can also affect the work function. As shown in Figure 2.14, Zhao et al.⁷² calculated that the work function of metallic tubes is around 4.7 eV and show minor increases with tube diameters, while semiconducting tubes have a work function larger than 4.91 eV, which decreases significantly with a tube diameter. They also calculated the work function of SWCNT bundles to be around 5.0 eV and not significantly dependent on the tube size or chirality.

For electrode applications in OLEDs or organic solar cells, higher work function facilitates hole injection or extraction. Several groups have reported techniques for modifying the work function of SWCNT films by using acid oxidation ($\text{HNO}_3/\text{H}_2\text{SO}_4$),⁷³ alkali metals,⁷² and plasma treatments.⁷² However, stabilising the modified work function is challenging. Jackson et al.⁷⁴ showed that within 2 hours, the work function of acid modified CNT films returns to that of undoped CNT film, probably due to exposure to moisture.

2.6.2 Transport properties

SWCNTs have extremely high intrinsic mobilities ($> 100,000 \text{ cm}^2/(\text{V}\cdot\text{s})$) and ballistic current carrying capacity. However, due to the statistical composition of semiconducting (2/3) and metallic (1/3) SWCNTs in a random network, the electrical transport of SWCNT thin films with many tube-tube junctions is governed by percolation and tube-to-tube hopping rates.⁴⁴

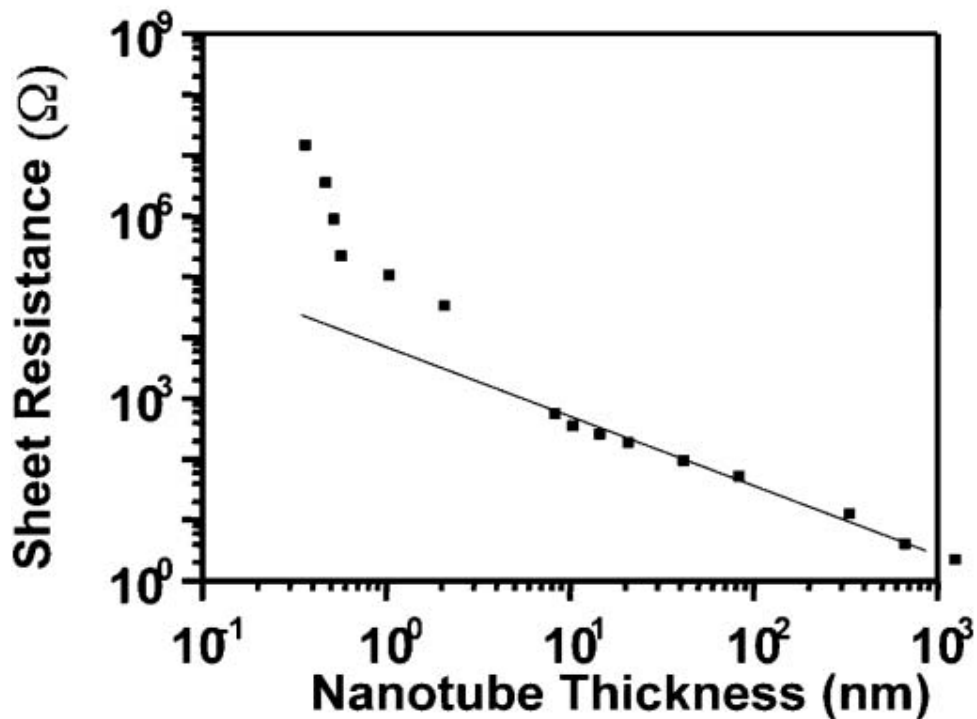


Figure 2.15 Sheet resistances versus SWCNT film thickness. (Taken from reference 44)

As shown in Figure 2.15, at high tube thicknesses, above the so-called percolation threshold, the electrical conductivity is weakly temperature dependent, implying the conduction mechanism is dominated by metallic tubes, whereas at low tube thicknesses, the strong temperature dependence implies that it is dominated by the (majority) semiconducting tubes.⁴³

For metallic enriched SWCNT random networks with medium and high tube density, Gruner et al.⁴⁴ approximated the dependence of sheet resistance (R_s) on tube density (D) by the following equation.

$$R_s = k(D - N_c)^\alpha L_s^\beta \quad (2-1)$$

where k is a fitting constant, N_c is the percolation threshold, L_s is the average tube length, α is a parameter given by the spatial arrangement of SWCNTs in the film, and β is a parameter determined by the tube-tube junction resistance and SWCNT conductivity. For the infinite 2D network, N_c can be expressed by

$$L_s \sqrt{\pi N_c} = 4.236 \quad (2-2)$$

For SWCNT films with low D , the conductivity is dominated by semiconducting channels, because the probability of metallic percolation is so low that the conductance is limited by the Schottky barriers.⁷⁵ This semiconducting behaviour can be useful for transistor operation. However, for transparent conductive film applications, longer SWCNTs are preferred to minimize the role of tube-tube junctions in transport.⁷⁶ Metal-rich SWCNT films would be preferable, but the cost and low yield of current sorting techniques make them commercially unviable at present.

2.6.3 Optical and mechanical properties

Irrespective of the small band gaps of SWCNTs, SWCNT thin films are highly transparent especially in the visible part of the spectrum, due to their small diameter and high aspect ratio, low reflectivity,^{77, 78} and their intrinsically high charge carrier mobility.⁴³ The optical absorption of the network is mainly dependent on tube density of the random network and SWCNT diameter but is also affected by factors such as tube-tube junction resistances, SWCNT length, and even doping.⁴³

From various optical measurements,^{78, 79} optical characteristics of SWCNT thin films such as transmission, reflection, and absorption for a given wavelength were extracted,⁸⁰ as shown in figure 2.16a. While ITO (120 nm) is known to have a relatively low average reflection of 20 %, SWCNT films (25 nm) have an even lower average reflection of below 10 % over the range of 200 - 2500 nm wavelength.⁸⁰

Figure 2.16b compares transmission characteristics of SWCNT thin films (25 nm) with a range of other transparent electrodes of optimised thickness, such as, ITO (120 nm), Ag grid (10 nm), graphene (10 nm), and PEDOT:PSS (50 nm). SWCNT films and graphene in particular surpassed other competitors in the far-infrared region, implying their potential as IR compatible electronic devices.

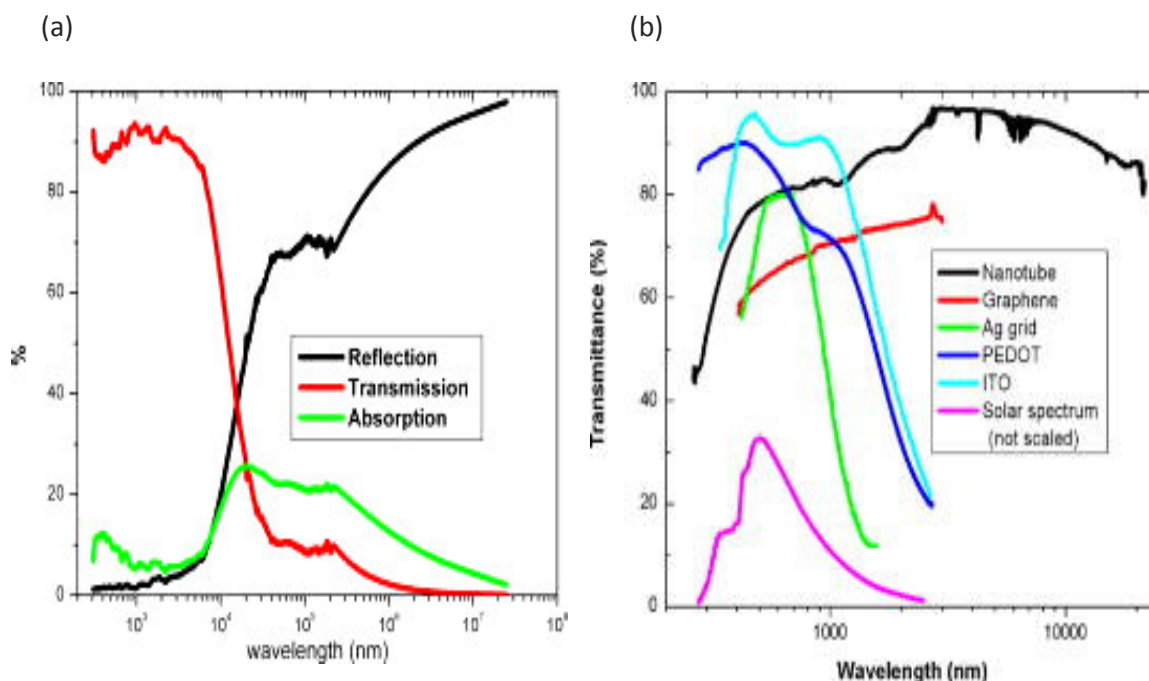


Figure 2.16 (a) Reflection, transmission, and absorption of a 25 nm SWCNT film in a wavelength range from 400 nm to 2 cm. (b) Transmission spectra for various transparent conducting materials as thin films including SWCNTs (25 nm), graphene (10nm), Ag nanowires (10nm), PEDOT:PSS (50nm), and ITO (120 nm). (Taken from reference 80)

SWCNT thin films can provide outstanding mechanical flexibility, stretchability, and foldability due to the intrinsically superior mechanical properties of SWCNTs such as high elastic moduli and fracture stress.⁸¹ The electrical properties of SWCNT thin films have been shown to vary by just 14 % under high tensile strains (18 %), while ITO typically cracks at just 2% tensile strain, as shown in figure 2.17.⁸²

Importantly, the failure of SWCNT films was attributed to the cracking of the substrate, not due to the SWCNT films.²⁸ However, the adhesion of SWCNTs on substrates is generally poor and therefore, for the large area flexible device applications, an adhesion promoter such as aminopropyltriethoxysilane (APTES)⁵¹ or perylene-c⁸³ is deposited underneath the SWCNT films to ensure resilience against the repeated tensile bending.

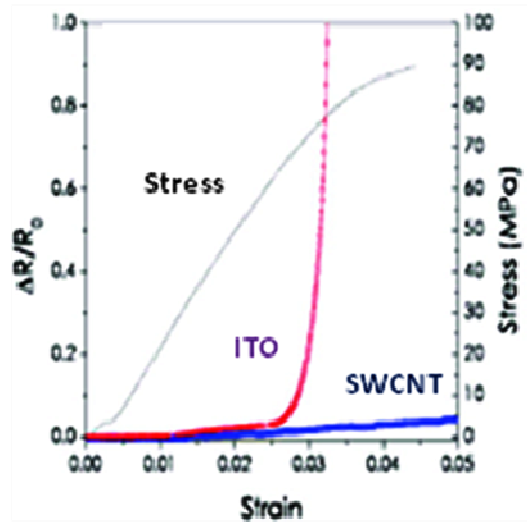


Figure 2.17 Tensile tension test for SWCNT films spray coated on PET and ITO deposited on PET, showing fractional change in sheet resistance versus strain. (Taken from reference 80)

Because the mechanical properties of SWCNT films are mainly affected by the intrinsic strength of SWCNTs, their length scale also affects their mechanical properties. As shown in Figure 2.18. De et al.⁸⁴ showed that longer length SWCNTs (Iljin) result in better mechanical properties than shorter SWCNTs (Hipco) when used in polymer composites.

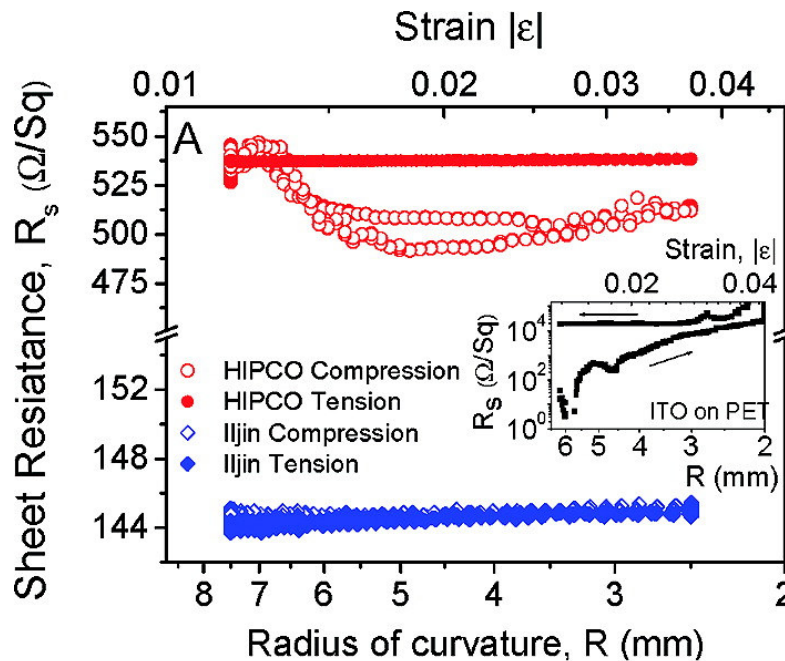


Figure 2.18 Sheet resistance versus number of bending cycles for SWCNT-PEDOT:PSS composites with thickness of 50 nm and M_f (mass fraction) = 55 % (Hipco) and M_f (mass fraction) = 60 % (Iljin) both in compression and in tension. Inset: Results for a film of ITO on PET. (Taken from reference 84)

2.6.4 Figure of merits for evaluating SWCNT thin films in the optoelectronic properties

Many research groups have reported the transmittance versus sheet resistance characteristics of their SWCNT thin films normally with values of transmission at 550 nm, as shown in Figure 2.19. There is typically a trade off between the transparency and conductivity for transparent electrodes with thicker films providing lower sheet resistances but lower transmittances.⁴³ In order to compare their properties in a practical way, various efforts for making the appropriate figure of merits (FoMs) to represent optoelectronic properties of different transparent conducting films have been made.^{44, 45, 85-87}

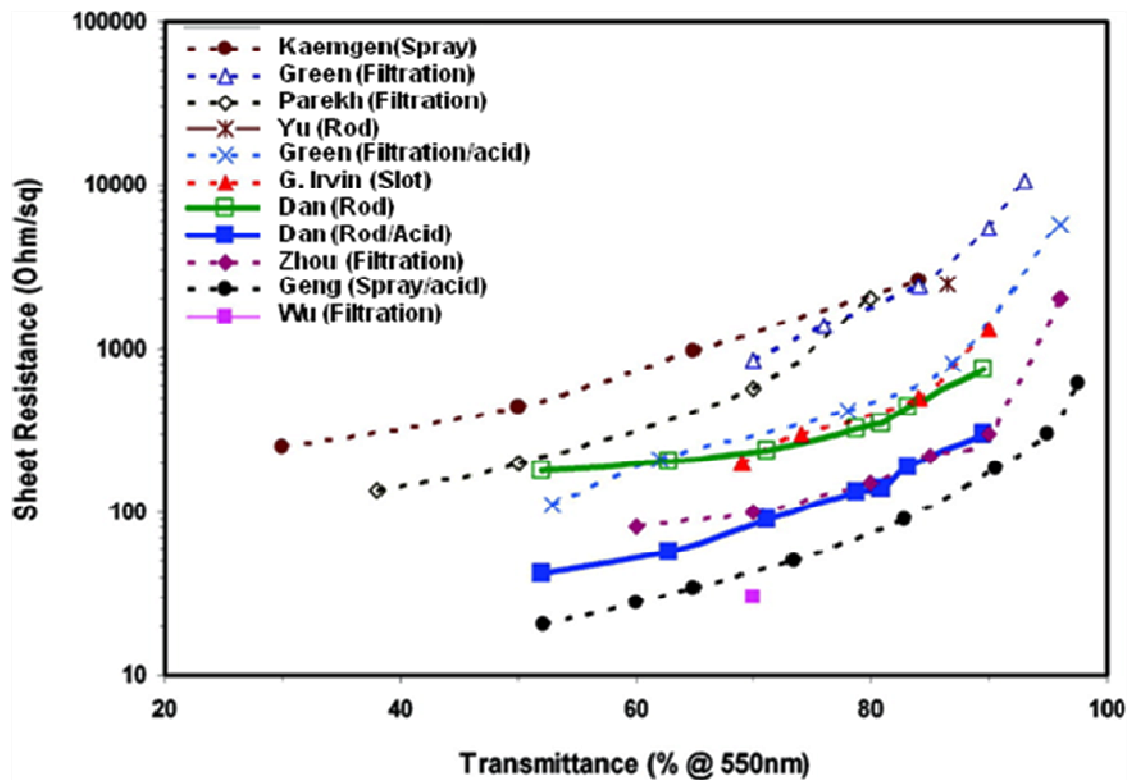


Figure 2.19 Transmittance versus sheet resistance trade-off characteristics for reported SWCNT films. These are classified into films prepared by spray coating, vacuum filtration, rod-coating, slot-coating. (Taken from reference 43)

Following earlier works, Fraser et al.⁸⁵ used a FoM for metallic thin films as $F_{TC} = T/R_s$. However, Haacke⁸⁶ found that F_{TC} overemphasizes the value of the sheet resistance and proposed a new FoM as $\Phi_{tc} = T^x/R_s$ ($x \sim 10$), using the fixed thickness at which maxima of Φ_{tc} occurs. These FoMs can occasionally be useful to find a usable thickness of TCFs, but in reality, figures of merits of this nature are somewhat arbitrary.

For the direct comparison among other TCFs from different materials, other FoMs, which are independent from the film thickness, have been sought.^{44, 88} Electrical conductivity (dc conductivity, σ_{dc}) is generally defined as $\sigma_{dc} = 1/(R_s \cdot t)$, here t is the film thickness and R_s is the sheet resistance. Dressel et al.⁸⁹ empirically derived that the transmittance for thin film SWCNTs is dependent on the optical conductivity (σ_{op}) using the so-called Tinkham formula as follows, assuming the interference effects within the film to be neglected.

$$T = (1 + \frac{Z_0}{2} \sigma_{op} t)^{-2} \quad (2-3)$$

where Z_0 is the impedance of free space (376.73 Ω), assuming that the film thickness (10 ~ 50nm) is much less than the light wavelength (550 nm). Although Equation (2-3) is valid only for free-standing films, it is commonly applied in an empirical sense to substrate-supported films.

The sheet resistance (R_s) is related to the film thickness (t) and the electrical conductivity (σ_{dc}), expressed by

$$R_s = 1/(\sigma_{dc} \cdot t) \quad (2-4)$$

Hence Equation (2-3) can be rewritten by

$$T = (1 + \frac{Z_0}{2R_s} \frac{\sigma_{op}}{\sigma_{dc}})^{-2} \quad (2-5)$$

From which we obtain σ_{dc}/σ_{op} as a new dimensionless FoM. Higher values of σ_{dc}/σ_{op} imply transparent conducting films with high electrical conductivity and high transmittance.

The minimum industry standard for transparent electrodes is considered to be $R_s = 100 \Omega/\text{sq}$ and $T = 90\%$, which corresponds to $\sigma_{dc}/\sigma_{op} = 35$.²⁹ Doherty et al.⁹⁰ calculated the maximum potential values of σ_{dc}/σ_{op} for potential alternative TCFs using best-case literature data. They obtained values of 35 for SWCNT films,³¹ 330 for graphene films,⁹⁰ and 450 for silver nanowire films, while a best-case ITO has a value of 223.⁹¹ Figure 2.20 shows the transmittance versus sheet resistance for reported papers on graphene films with their theoretical limits.

Here, graphene was calculated for the best case figure of merit (330) in its highly doped state, but so far the best graphene film have reached only ~ 2.6.⁹⁰ Silver nanowires in thin film networks are known to suffer from stability, adhesion, and very rough surfaces problems, which hinder their applications as transparent electrodes in organic electronic devices.⁹⁰ In contrast, SWCNT thin films have medium figure of

merit (~ 25), low surface roughness ($\sim$ (r.m.s.) 6 nm), high mechanical strength, and good stability in their optical and electrical properties, making them still attractive as transparent electrodes for flexible electronic device applications.

Further improvements of SWCNT thin film properties are expected by combining SWCNTs with other materials such as graphene,⁹² polymers,⁸⁴ in order to become viable transparent conducting electrodes to replace ITO.

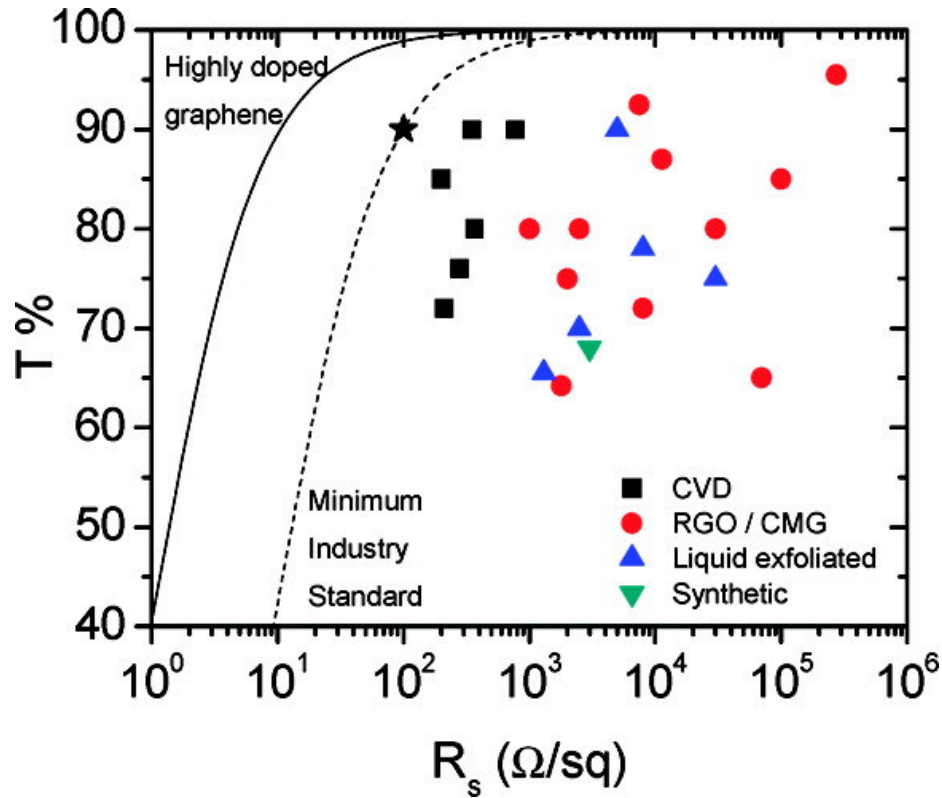


Figure 2.20 Transmittance versus sheet resistance characteristics for reported graphene films. These are classified into graphene films prepared by CVD, reduced graphene oxide or chemically modified graphene, pristine exfoliated graphene, or chemically synthesized graphene. The star and dashed line illustrates the set of data consistent with $\sigma_{dc}/\sigma_{op} = 35$. The solid line corresponds to the calculated case of highly doped graphene ($\sigma_{dc}/\sigma_{op} = 330$). (Taken from reference 90)

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Chapter 3 Analytical Techniques and Preliminary Experiments

3. 1 Introduction

In the work reported here, SWCNT films were used as transparent conducting electrodes for plastic electronic devices. A variety of commonly used techniques for characterizing SWCNT thin film electrodes and solar cells were employed.

SWCNT thin films were made from SWCNT suspensions in a liquid which often contained a dispersant aid to enable the dissolution of CNTs at relatively high loadings. Several techniques were used to provide comprehensive and relative information about the SWCNT films such as the dispersability of SWCNTs¹ and the efficacy of surfactant removal.² Although there have been many reports on obtaining reliable information about the SWCNT films in the presence of background such as substrates and impurities, it is still a challenging task.

In order to make transparent and highly conductive SWCNT thin film electrodes for organic electronics applications, a smooth surface, low sheet resistance, high optical transparency in the visible and IR spectral ranges, suitable work function, and good wetting on the substrate must be ensured.³ Therefore, the techniques such as a four-point probe conductivity measurements, surface profilometry, UV-VIS-NIR spectrometry, Kelvin probe analysis, and contact angle measurements were adopted. To characterize the structure, morphology, purity, doping and defects levels, and to obtain additional information about crystal disorder, nanotube diameter, chirality and the metallic and semiconducting behaviour of SWCNTs, Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FE-SEM), and Raman spectroscopy were also employed.

In addition, organic photovoltaic devices fabricated with SWCNT thin films were characterized with a solar simulator under AM1.5 one sun illumination and an external quantum efficiency measurement rig. Finally, as preliminary experiments, the effect of the annealing temperature was investigated to achieve better device efficiencies for P3HT:PCBM bulk heterojunction solar cells.

3. 2 Characterization of SWCNT thin films

3.2.1 Atomic Force Microscopy and Scanning Electron Microscopy

Atomic Force Microscopy (AFM) was used for characterising the surface morphology of the SWCNT films at the nanometre level. AFM can provide a 3D surface profile and reveal the diameter and lengths of individual SWCNTs. Moreover, samples viewed by AFM do not require any special treatments such as metal/carbon coatings that would irreversibly modify or damage the sample.⁴

In AFM measurements, a sample is mounted on a piezoelectric element that can move in three dimensions. When the probe tip is brought into proximity with the sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law, in which a material body is deformed (the strains) in linear proportion to the force causing the deformation (the stress). The deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes.⁵

If the tip was scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. AFM operating modes can be classified as static (contact) or dynamic (tapping). For this research, mostly tapping mode AFM was used to avoid damaging the delicate SWCNT samples.

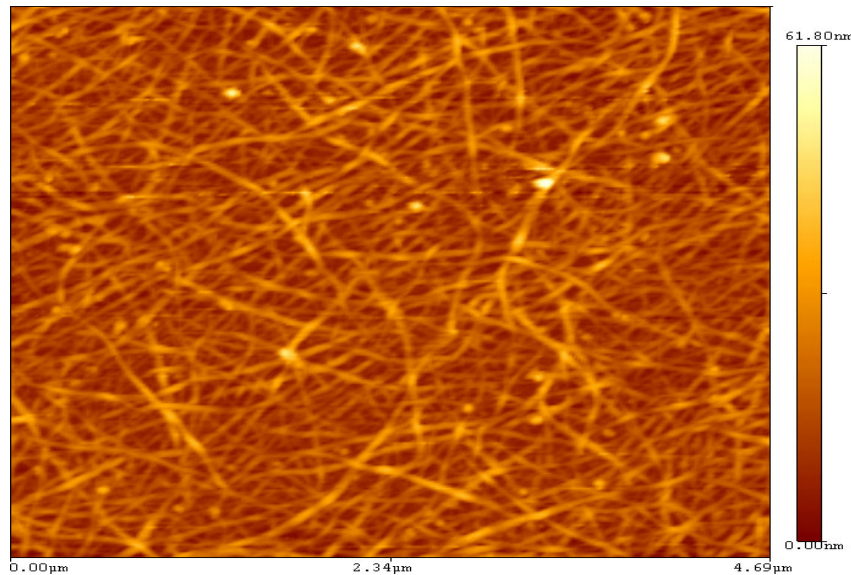


Figure 3.1 4.7 μm x 4.7 μm Atomic Force Micrograph for thin-film SWCNTs.

A Pacific Nanotechnology Inc. Nano-I (TM) AFM was used in this research with a scan rate of 0.5 Hz and 1024 sample lines to produce surface images of the kind shown in Figure 3.1. Most of SWCNT samples were spin or spray coated on glass substrates of size 12 mm × 12mm. In the case of SWCNT samples on plastic substrates, the film was immobilised on a metal puck using double sided sellotape.

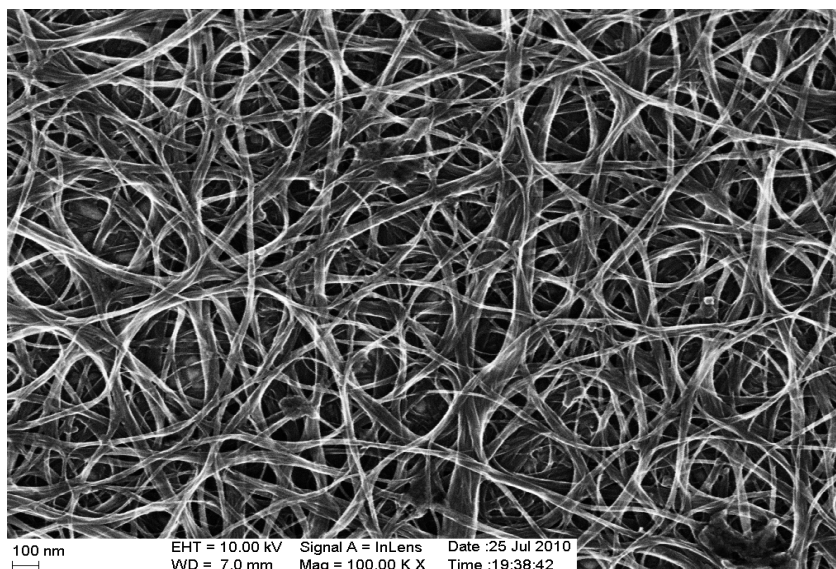


Figure 3.2 Field Emission Scanning Electron Micrograph of a SWCNT thin-film.

Field Emission Scanning Electron Microscopy (FE-SEM) was also used to characterise the surface of the SWCNT films and to identify potential defects such as voids in the films. A high-energy beam of electrons scanned across the surface of the sample in a raster scan pattern generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen, from which it is possible to extract information about surface topography and composition. FE-SEM can produce very high-resolution images on a 1 to 5 nm scale,⁶ as shown in Figure 3.2. All SEM images were taken using a LEO Gemini 1525 FEGSEM with the SWCNT samples deposited on glass or plastic substrates.

3.2.2 Raman Spectroscopy

Raman spectroscopy is one of the essential tools for characterising SWCNTs as it provides important information about chemical purity, doping, defects, nanotube diameter, chirality and metallic/semiconducting behaviour.⁷⁻⁹

When a material is illuminated, light will be scattered, reflected or transmitted. A very small part (1 in every 10^7 photons) is scattered inelastically and the resulting radiation is called Raman scatter. A typical Raman spectrum for arc-made SWCNT films on a glass substrate is shown in Figure 3.3.

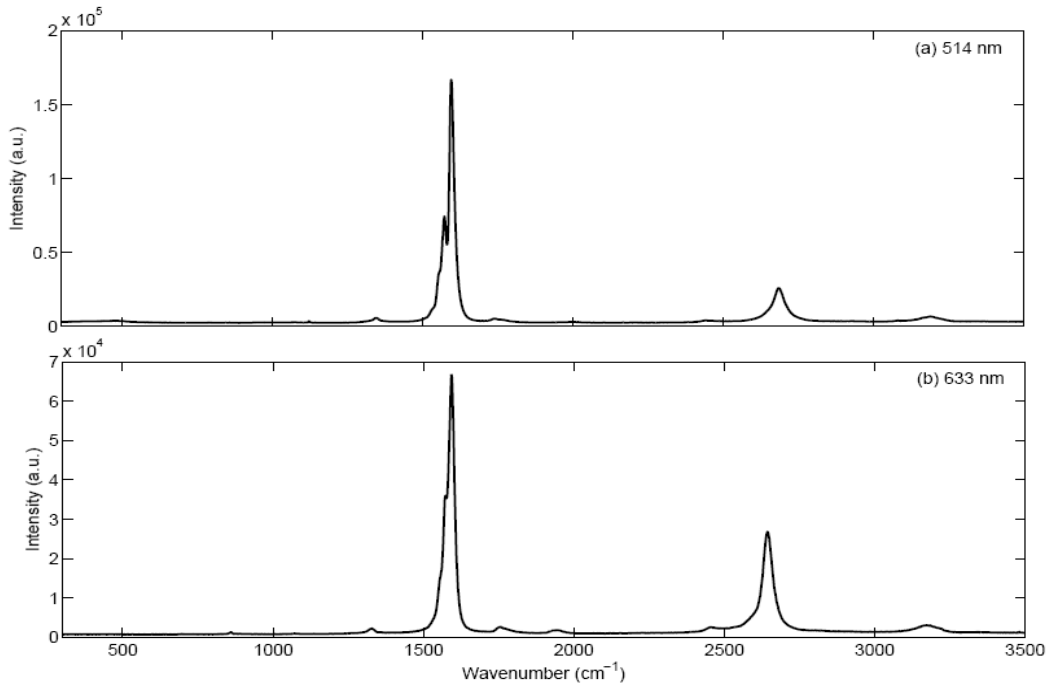


Figure 3.3 Raman spectra for arc-made SWCNTs excited by a laser with wavelength of (a) 514nm and (b) 633nm

During a Raman scattering, a photon excites the sample molecule from the ground state to a virtual energy state and when the molecule relaxes, it emits a Raman photon, returning to a different vibrational state. The difference in energy between the original state and this new state leads to a Raman shift in the emitted photon's frequency away from the excitation wavelength, as shown in Figure 3.4.⁸

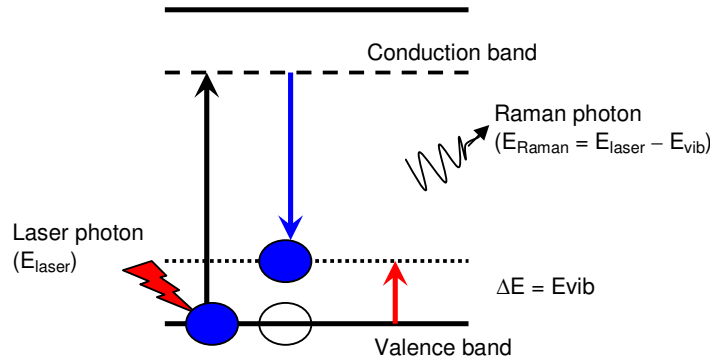


Figure 3.4 Raman scattering process for CNTs.

The Radial Breathing Mode (RBM) of a SWCNT can normally be seen between 75 and 300 cm^{-1} , and is associated with the symmetric sp^2 in-phase displacement of the carbon atoms in the radial direction. This usually allows the diameter of the single walled carbon nanotubes to be extracted, since the RBM peak frequency (ω_{RBM}) is inversely proportional to diameter (d). Many research groups have fitted their

experimental data on the size dependence of the radial breathing mode frequency using the relation of $\omega_{\text{RBM}} = A/d + B$. For water-assisted chemical vapour deposition (CVD) growth samples, values of $A = 227.0 \pm 0.3 \text{ (nm}\cdot\text{cm}^{-1})$ and $B = 0.3 \pm 0.2 \text{ (cm}^{-1})$ are obtained. However, most reported values of ω_{RBM} in the literatures are up-shifted from these values of A and B, due to various environmental effects.⁹ For typical SWCNT bundles in the diameter range of 1.3 - 1.7 nm, more typical values of A and B are $A = 234 \text{ cm}^{-1}$ and $B = 10 \text{ cm}^{-1}$ giving;⁸

$$\omega_{\text{RBM}} = 234/d + 10 \quad (3-1)$$

The Defect mode (D) is located between 1330 and 1360 cm^{-1} and is normally associated with disorder of the hexagonal sp^2 bonded lattices for carbon nanotubes. It is therefore associated with both the defects on the SWCNTs and graphitic impurities in the as-made SWCNT films. The level of disorder in SWCNTs is frequently characterised in terms of the $I_{\text{D}}/I_{\text{G}}$ intensity ratio between the disorder-induced D-band and the in-plane vibration induced G band within the graphite layer.⁹ As an indication, a value of $I_{\text{D}}/I_{\text{G}} = 0.1$ is considered low.

The G mode is the most intense Raman mode located around 1580 cm^{-1} and is due to the in-plane stretching of the C-C bond in SWCNTs. When the bond lengths and angles of rolled graphene are changed by strain, possibly caused by the interaction with a substrate or other external perturbations, the hexagonal symmetry of graphene is broken. Therefore the G-band is highly sensitive to strain effects and can be used to probe any modification on the surface morphology of SWCNTs.⁹

The G-band can also provide information about the level of doping of the SWCNTs due to its strong dependence on the varying coupling between the electron and phonon energies depending on the position of the Fermi level and the temperature. The G-band frequency and the spectral width of metallic SWCNTs are strongly affected by a phonon excitation process. In addition, their G-band shape can be fitted to a non-symmetrical Breit-Wigner-Fano (BWF) line, which is observed only when the electronic density of states at the Fermi level has a finite value. However, semiconducting SWCNTs are only weakly affected by the phonon excitation and so do not undergo any change in the G-line width.⁹

In this work, Raman spectra were obtained using an inVia Raman microscope (Renishaw) with excitation lasers of 514 nm or 633 nm at low power (below 10 %) with 50 times optical magnification in a spot area of 1 micron diameter. Each spectrum was taken using 2 repeats of 10 second detection times.

3.2.3 Sheet resistance and dc conductivity

The sheet resistance and electrical conductivity of the SWCNT thin films were evaluated by a home-made four-point probe station equipped with a KEITHLEY 2400 source-measure unit and a KEITHLEY 2000 multimeter. The schematic diagram of the probe positioning is shown in Figure 3.5. In a four-point probe, a chosen constant current (typically 1 μA to 100 μA) is injected into a conducting film through the two outer probes, and a voltage is measured between the two inner probes. The high impedance of the voltmeter minimizes the current flow through it and there is no potential drop across the contact resistance associated with the sensing probes. Therefore the resistance associated with the thin film can be accurately measured with a four-point probe, even when the sample has a comparable resistance to the probes.

The thin film thickness (l) was measured with a Dektak surface profiler at a scan length of 400 μm . If probes with uniform spacing (d) are placed on a practically infinite slab material, then the surface resistivity, ρ , is given by¹⁰

$$\rho = 2\pi d V/I \text{ } \mu\text{Ohm-Centimeters for } l \gg d \text{ or} \quad (3-2)$$

$$\rho = (\pi l / \ln 2) V/I \text{ } \mu\text{Ohm-Centimeters for } d \gg l$$

Here, l is the thickness of the thin film.

For thin SWCNT films, the second equation gives the sheet resistance as

$$R_s = \rho/l = (\pi / \ln 2) V/I \approx 4.532 V/I \text{ (Ohm/sq) for } d \gg l \quad (3-3)$$

The electrical (dc) conductivity is then calculated from the below equation

$$\sigma \text{ [S/m]} = 1/\rho \text{ [Ohm-Meter]} = 1/(R_s \cdot l) \quad (3-4)$$

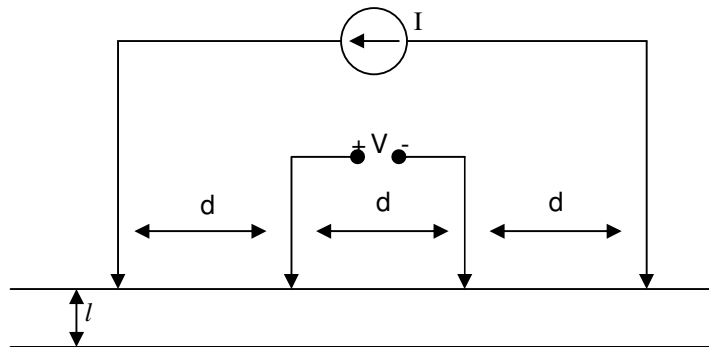


Figure 3.5 Schematic view of a 4-point probe station

3.2.4 Optical transmittance

For transparent electrodes, the optical transmittance is clearly an important value to be measured. Due to the one dimensional nature of the carbon nanotube quantum wires, the SWCNT network can form a loose mesh that is highly transparent in the visible and infrared ranges. Transmission is mainly determined by the optical absorption of the SWCNT network. Since photon absorption is due to the local excitation of the individual carbon nanotubes, the transmittance is inversely proportional to the density of the SWCNT network.¹¹

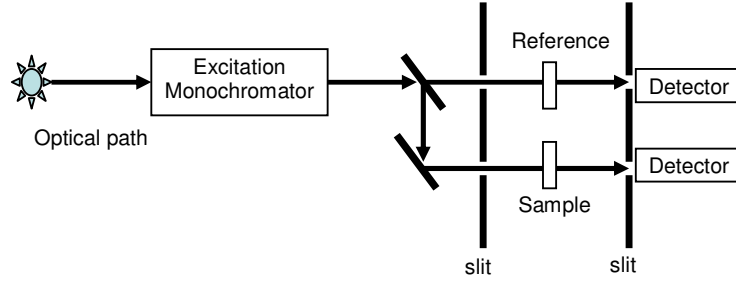


Figure 3.6 Schematic view of a UV-VIS-NIR spectrometer

A UV-VIS-NIR optical spectroscopy (Shimadzu, UV-1601) was used for measuring transmittance over the wavelength range of 200 - 1,000 nm. (A schematic diagram is shown in figure 3.6) A reference of a bare glass substrate was used because the transmittance of the substrate cannot be neglected when measuring highly transmissive films. The maximum detectable optical density (absorbance) was 3 and spectral resolution was 1-2 nm.

Transmittance (T) is the ratio of (I/I_{in}), where I is the light intensity after it passes through sample and I_{in} is the incident light intensity. According to the Beer-Lambert law, T can be rewritten as $T = 10^{-\alpha \cdot l}$, where α is absorption coefficient, which determines how far into a material light of a particular wavelength can penetrate before it is substantially absorbed and l (cm) is the optical path length.¹²

Absorbance (A) can be calculated from transmittance (T) as follows.

$$A = -\log_{10}(T) = \log_{10}(T_{reference}/T_{sample}) \quad (3-5)$$

Absorbance (A) can therefore be rewritten as follows, where ϵ is the molar absorptivity of a absorber and c is the concentration of the absorbing species¹²;

$$A = \alpha \cdot l = \epsilon \cdot c \cdot l \quad (3-6)$$

3.2.5 Kelvin probe

The work function is the energy needed to release electrons from a material's surface, and is an extremely sensitive indicator of surface condition. It is normally affected by adsorbed or evaporated layers, surface reconstruction, surface charging, oxide layer imperfections, surface and bulk contamination.¹³ In this work, a Kelvin probe system manufactured by Besocke Delta Phi GmbH (Julich, Germany) was used to measure the work function of the as-deposited SWCNT films. The probe, a 2.5 mm diameter gold mesh disk, is attached to an electrically driven piezoelement, which vibrates at a frequency of 170 Hz. The distance to the sample surface should be in the range of 0.5 mm – 1 mm. Freshly cleaved highly oriented pyrolytic graphite (HOPG) was used as a reference sample, which is considered to have a work function of 4.6 eV.¹⁴

The Kelvin probe is a non-contact, non-destructive measurement device based on a vibrating capacitor and measures the work function difference, or the surface potential difference, between a conducting specimen and a vibrating tip. The Kelvin probe method is a relative rather than absolute method to measure work function and its precision is therefore heavily dependent on the stability of the work functions of both the probe and the reference sample. The gold probe is relatively inert and its work function remains stable in a constant environment. The reference of freshly cleaved highly oriented pyrolytic graphite (HOPG) is also known to be reasonably independent of ambient atmosphere.¹⁵

A lock-in amplifier with a high gain current voltage preamplifier was used to detect the AC current, while the electric potential was applied between to the tip and sample, consisting of a DC-bias V_{DC} and an AC-voltage $V_{AC} = \sin(\omega_0 t)$ at the mechanical resonance frequency of the tip (ω_0).

When two materials with different work functions are brought together, electrons in the material with the lower work function flow to the one with the higher work function until the Fermi levels are aligned. The potential is called the contact potential difference denoted generally as V_{CPD} . Here, the potential difference is equivalent to the difference in work functions. This contact potential difference can be measured by applying a variable external backing potential to the parallel plate capacitor, formed by the sample and probe. When the surface charges disappear, at that point the backing potential will equal the contact potential as below equation.¹⁶

$$V = (V_{DC} - V_{CPD}) + V_{AC} \sin(\omega_0 t) \quad (3-7)$$

3.2.6 Contact angle

A contact angle measurement is a useful tool for evaluating the wetting property of thin film surfaces (hydrophobic or hydrophilic) in order to make multilayer thin film structures. In this work, it was necessary to deposit a layer of PEDOT: PSS from an aqueous solution on top of the SWCNT films as part of the device fabrication procedure, so a hydrophilic top surface of the SWCNT films was preferred, whereas SWCNT films are normally hydrophobic.

Therefore, various surface treatments were evaluated for changing the wetting behaviour of the target SWCNT film and a contact angle measurement rig (Kruss drop shape analysis system (DSA 10)) was used to evaluate the efficacy of the various treatments.

Contact angle is defined as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. If the angle is less than 90° , the water is generally considered as wetting the target film; otherwise, it is said to be non-wetting.¹⁷ Figure 3.7 illustrates a surface profile of a contact angle on a film.

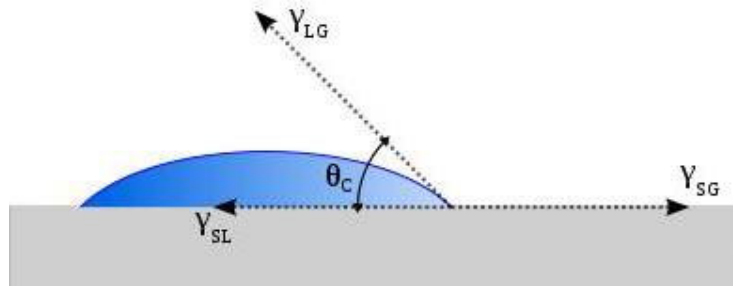


Figure 3.7 An illustration of the sessile drop technique with a liquid droplet partially wetting a solid substrate; θ_c is the contact angle, and γ_{SG} , γ_{LG} , γ_{SL} represent the solid-gas, gas-liquid, and liquid-solid interfaces, respectively

The contact angle is determined by the intermolecular bonds or cohesive forces between the molecules of a liquid, which lead to a surface tension. When the liquid encounters another substance, there is usually an attraction between the two materials. The adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to another material will tend to spread over the material. Liquids with strong cohesive bonds and weaker adhesive forces will tend to form a droplet when in contact with another material.¹⁷

For a hydrophilic liquid to spread over the surface of a target electrode, two conditions must be met. First, the surface energy of the SWCNT/air interface must be greater than the combined surface energies of the liquid/air and the SWCNT/liquid interfaces. Second, the surface energy of the SWCNT/air interface must exceed the surface energy of the SWCNT/liquid interface.

3.2.7 Current - Voltage characteristics of a solar cell

A photovoltaic device was tested using a computerised KEITHLEY 236 source-measure unit to obtain the current-voltage (J-V) characteristics under 1 sun, AM 1.5 illumination (100 mW cm^{-2} at 25°C) with a xenon lamp solar simulator, as shown in Figure 3.8. The sample was kept in a home-made sample holder sealed with quartz glass window under nitrogen atmosphere.¹⁸ The photovoltaic cell produces power in the voltage range from 0 to V_{oc} (open circuit voltage). The cell power density is given by $P = JV$. P reaches a maximum P_M at the voltage of V_M and the current density of J_M , known as the maximum power point.¹⁹

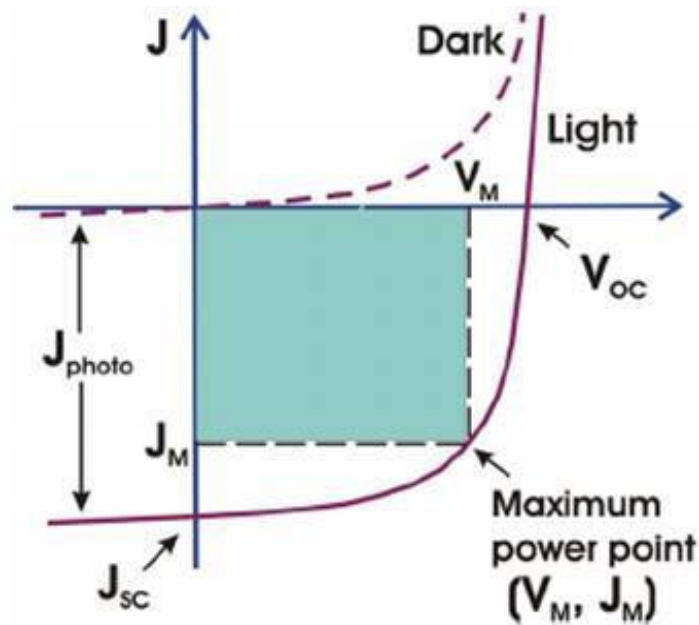


Figure 3.8 Current (J) versus Voltage (V) characteristics for solar cells with the key parameters (V_{oc} , J_{sc}).

The short circuit current (J_{sc}) is mainly determined by the product of the incident spectral photon flux density ($b_s(E)$) and quantum efficiency (QE), which is the probability that an incident photon of energy E will deliver one electron to the external circuit.²⁰ J_{sc} can then be expressed by the following equation.

$$J_{sc} = q \int b_s(E)QE(E)dE \quad (3-8)$$

Here $b_s(E)$ is the incident spectral photon flux density, the number of photons of energy in the range from E to $E + dE$, which are incident on unit area in unit time, and q is the electronic charge.

Quantum efficiency (QE) generally depends on (1) the absorption coefficient of the solar cell material, (2) the efficiency of charge separation and (3) the efficiency of charge collection in the device.¹⁹

Besides electrodes and interfacial effects, short circuit current (J_{sc}) is dependent on the photo-induced charge carrier density and the charge carrier mobility within the organic semiconductors. So it can be rewritten as follows.

$$J_{sc} = ne\mu E \quad (3-9)$$

Where n is the density of charge carriers, e is the elementary charge, μ is the mobility, and E is the electric field. Semiconducting polymers have comparatively low charge carrier mobilities, whose absolute values are sensitive to the composition and nanomorphology of the solid films. Solvent type, solvent evaporation time and the deposition temperature can affect the nanomorphology. In addition, the short circuit current increases with temperature in the polymer/fullerene bulk heterojunction devices, which indicates a thermally activated hopping transport in these disordered systems.²⁰

The open circuit voltage (V_{oc}) is determined by the difference of the quasi Fermi levels of the two charge carriers. In organic solar cells, it was reported to be linearly dependent on the HOMO level of the electron donor such as P3HT and the LUMO level of the electron acceptor such as PC₆₁BM.²¹ The open circuit voltage is lowered by charge carrier losses at electrodes and is also affected by the nanomorphology of the active layer in the polymer-fullerene based bulk heterojunction solar cells.

In addition, interfacial effects at the metal/organic semiconductor interface, such as oxide formation, can lead to changes in the effective work function of the electrodes and influence the open-circuit voltage. Overall, the open circuit voltage is sensitive to the energy level of the used materials as well as their interfaces.²⁰

The fill factor (FF) characterises the “squareness” of the J-V curve as shown in the following equation.

$$FF = \frac{J_M V_M}{J_{sc} V_{oc}} \quad (3-10)$$

The fill factor (FF) is related to the fraction of the photo-generated charge carriers that actually reach the electrodes, when the built-in potential is lowered toward the open circuit voltage. However, there is a trade-off between charge carrier recombination and transport. Hence the product of the lifetime τ and the mobility μ determines the distance d that charge carriers can drift under a certain electric field E .²⁰ This can be expressed as follows.

$$d = \tau \times \mu \times E \quad (3-11)$$

To achieve the larger FF ($> 50\%$), the product $\tau \times \mu$ should be maximized. For a fixed active layer thickness ($\sim d$), higher electric fields can lead to higher FF . Furthermore the series resistances of the electrodes can directly influence the FF significantly. Finally the device should be free of shorts to maximize the parallel shunt resistance, which prefers smoother electrodes.²²

The power conversion efficiency (PCE) of the cell is defined as the power density delivered at operating point as a fraction of the incident light power density (P_{in}) as shown the following equation.

$$PCE = \frac{J_M V_M}{P_{in}} = \frac{J_{sc} V_{oc} FF}{P_{in}} \quad (3-12)$$

3.2.8 External quantum efficiency

The spectral response of a photodiode (a solar cell) can be measured using the monochromated output of a Xenon lamp, referencing the measured photocurrent against a calibrated silicon photodiode. The photocurrent was measured here using a computerised KEITHLEY 236 source-measure unit. The schematic diagram is shown in Figure 3.9.

The photocurrent density of a sample, $J_{sc}(\lambda)$, and photocurrent density of a calibrated silicon photodiode $J_{sc}^{si}(\lambda)$ are obtained at a particular wavelength. The intensity of the light source, $P(\lambda)$, is calculated as function of wavelength using the spectral response, $SR_{si}(\lambda)$ and photocurrent spectra of the silicon photodiode at the wavelength λ , which is expressed as $P(\lambda) = \frac{J_{sc}^{si}(\lambda)}{SR_{si}(\lambda)}$. The external quantum efficiency is then calculated by using the following equation.²⁰

$$EQE(\lambda) = J_{sc}(\lambda) / P(\lambda) \cdot hc/e\lambda \quad (3-13)$$

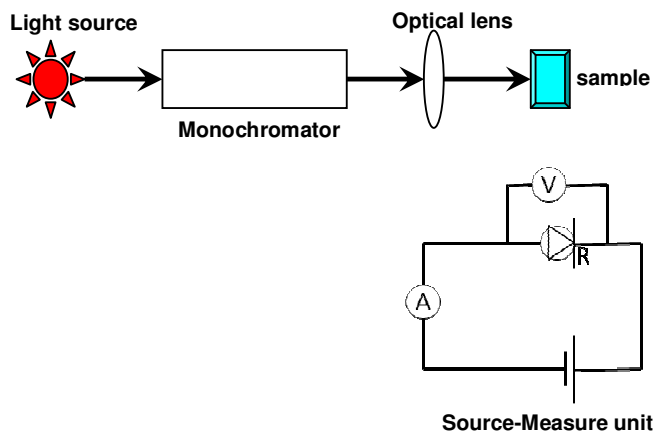


Figure 3.9 A schematic diagram of the external quantum efficiency measurement.

3.2.9 The effect of annealing temperature on organic solar cells

As preliminary experiments, P3HT:PCBM bulk heterojunction solar cells were optimized by measuring the final device characteristics obtained at different annealing temperatures.

P3HT:PCBM bulk-heterojunction solar cells were fabricated by spin-coating onto ITO electrode a 35 ~ 40 nm layer of PEDOT: PSS (Baytron P). A 175 nm layer of regioregular poly(3-hexylthiophene) (P3HT, Merck Chemicals Ltd.) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{61} (PCBM, API Services, Inc.) was then deposited by spin-coating from a 1:0.7 blend of the two components in chlorobenzene. The devices were completed by thermal deposition of Al (100 nm), and were finally annealed for 30 minutes inside a nitrogen filled glove box (oxygen and moisture level is below 0.1 ppm) by changing annealing temperatures from 20 °C (room temperature) to 150 °C, an upper limit for compatibility with standard plastic substrates. The current-voltage characteristics of the devices at AM 1.5 illumination was obtained using a tungsten-halogen lamp solar simulator.

As shown in Figures 3.10 and 3.11, the device annealing at higher temperature led to an increase in the open circuit voltage and the fill factor over all temperatures, but a slight decrease in the short circuit current above 110 °C. There was a continuous increase in device efficiency with increasing temperature up to 150 °C therefore was proportionally increased, attributable to improved vertical phase segregation and better electrical contact between the Al cathode and the active layer.^{23, 24}

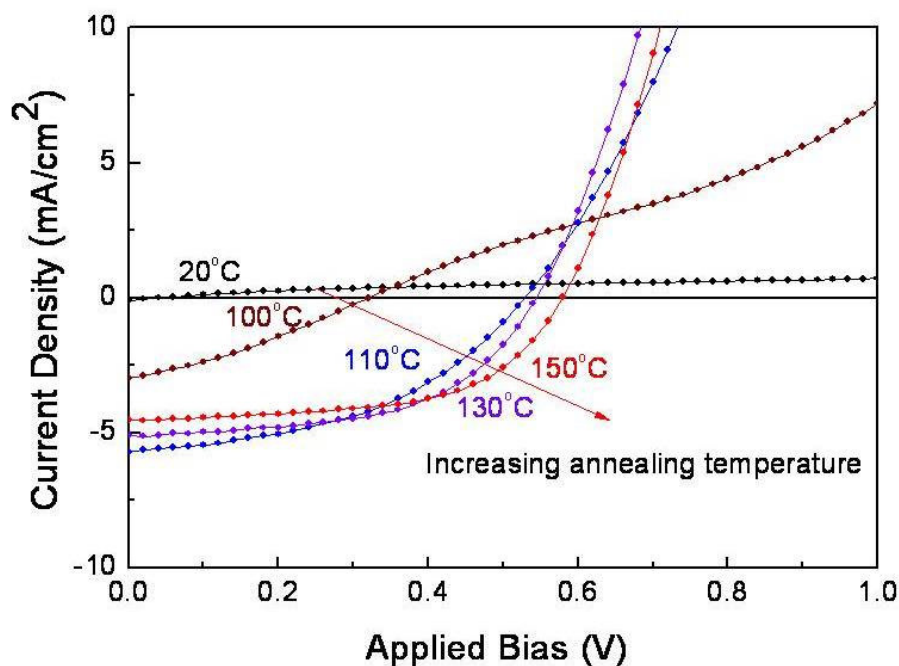


Figure 3.10 The effect of annealing temperature on the current-voltage characteristics under one-sun illumination for P3HT:PCBM bulk-heterojunction solar cells based on ITO-coated glass ($15 \Omega/\text{sq.}$) with the general structure of ITO/PEDOT:PSS(40nm)/ P3HT:PCBM(100nm)/Al(100nm).

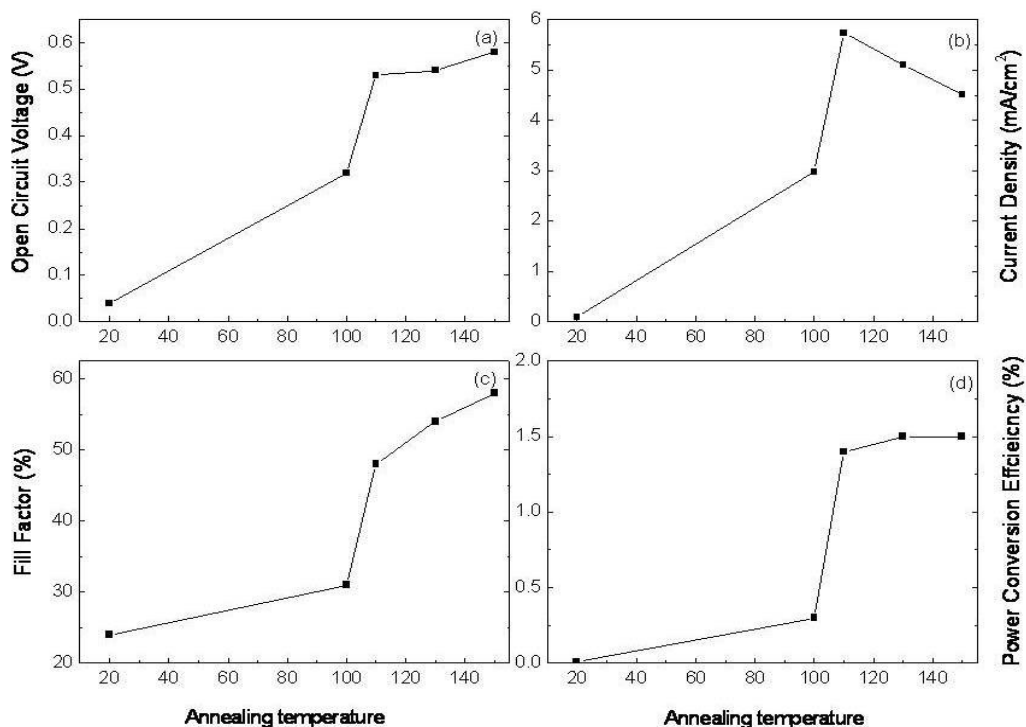


Figure 3.11 Effect of annealing temperature on (a) open circuit voltage, (b) short circuit current, (c) fill factor, and (d) power conversion efficiency under one-sun illumination for the same P3HT:PCBM bulk-heterojunction solar cells

The best device performance was obtained with the device annealed at 150 °C, even though the value is fairly lower than the previously reported works,^{20, 24} probably due to both the specific batch of P3HT (Merck Chemicals Ltd.) and Al single cathode employed for this work. P3HT with higher regio-regularity is favourable for higher optical absorption and charge transport, caused from the better molecular packing of P3HT.²⁴

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Chapter 4 Single Walled Carbon Nanotube thin films

4.1 Introduction

Ambient solution-processable single-wall carbon nanotube (SWCNT) thin film electrodes provide a good balance of transparency, conductivity and work-function that compares favourably with ITO. However, because of their large aspect ratio, SWCNTs are subject to large van der Waals forces, which cause them to bundle together as ropes.¹ In this context, one of the challenges in making SWCNT films is to exfoliate the CNTs without using covalent chemistry or other harsh experimental conditions, which could worsen the electrical conductivity.

Many research groups have tested various CNT dispersion methods, including the use of surfactants as dispersing aids^{2,3}, polymers as dispersion aids⁴, direct dispersion of pristine or functionalized SWCNTs in organic solvents or water^{5,6}, and other dispersion aids such as DNA, protein and starch.⁷ The use of dispersants has the advantage of allowing higher SWCNT loadings in the SWCNT solutions, thereby reducing solvent usage, although effective post-deposition treatments are required to eliminate the surfactant from the final film.

There were also other research groups who used organic solvents to eliminate the need for a surfactant removal step.^{6,8} These pure organic solvents allow for the direct solvation of SWCNTs without recourse to surfactants, but almost all are restricted-use chemicals. In addition, the best suspension phase of SWCNTs in these organic solvents can only last a few hours before further ultrasonication is needed, which hinders the deposition process.

In addition, to minimise variations in the inherent electrical, chemical, and mechanical properties of SWCNTs, surface functionalisation through chemical bonds is not desirable. Wrapping SWCNTs with polymer, DNA, protein has attracted many researchers due to potentially enhanced morphology of deposited SWCNT thin films, but dispersants of this kind are ill-suited to electrode fabrication due to their difficulty of removal. Polyvinylpyrrolidone (PVP) (often in combination with other surfactants) has been intensively investigated as a dispersant due to its potential use in large area printing.⁹

The best strategy to make highly conductive SWCNT thin films is to choose the best dispersive surfactant for SWCNTs, which can later be easily removed without significantly disrupting the network of SWCNTs.

There are three types of surfactants: anionic (negative charge in water), cationic (positive charge in water), and non-ionic (neutrally charged in water). The headgroup, chain length, and surfactant molecular weight are known to affect the dispersion ability of a surfactant.¹ Anionic surfactants, such as sodium dodecyl benzene sulfonate (SDBS), are known to have better ability to disperse SWCNTs compared to cationic or non-ionic classes.^{3, 10, 11} Nonionic surfactants are also very difficult to remove from a cast SWCNT/surfactant film, which limits the film's electrical conductivity.¹² The following table 4.1 lists the dispersability of SWCNTs in deionised water with each surfactant of different types.

Table 4.1 Different types of surfactants for dispersing SWCNTs in DI water, which concerns their maximum solubility (the author's experimental results are combined with a selected reference³)

Surfactants	SWCNT equivalent solubility in water (mg ml ⁻¹)	Type
Sodium Dodecyl Benzene Sulfonate (SDBS)	20 (CH ₃ (CH ₂) ₁₁ C ₆ H ₄ SO ₃ Na)	Anionic
Sodium Dodecyl Sulphate (SDS)	0.3 (NaC ₁₂ H ₂₅ SO ₄)	Anionic
Sodium Carboxymethyl Cellulose (CMC)	0.3 (Na-CMC)	Anionic
Didodecyl dimethyl ammonium bromide (DTAB)	≤ 0.1 (C ₁₂ H ₂₅) ₂ (CH ₃) ₂ NBr)	Cationic
Triton X-100	≤ 0.5 (C ₁₄ H ₂₂ O(C ₂ H ₄ O) _n (n = 9-10))	Nonionic

A key challenge in SWCNT thin film preparation is to ensure the inherent optoelectronic properties of SWCNTs survive the solution based deposition process used to prepare the SWCNT thin films. Many research groups have tried numerous deposition methods, as discussed below.

Wu et al.¹³ reported the use of the vacuum filtration method to process laser-ablation-made SWCNTs for making transparent conductive CNT films. They formed CNT films on a filtration membrane by vacuum-filtering a dilute surfactant-based suspension of purified SWCNTs, and the filtration membrane was dissolved using a solvent after transferring CNT films to the desired substrate. Their as-prepared 50 nm CNT films had a sheet resistance of 30 Ω/sq and a transmittance greater than 70 % over the visible range of the spectrum.

Rowell et al.¹⁴ used a stamp contact printing method to fabricate SWCNT transparent anodes. After vacuum filtering well dispersed and stable solutions of arc-discharge SWCNTs with surfactants over a porous alumina membrane, the SWCNT films were lifted off with a PDMS stamp and transferred to a flexible polyester (PET) substrate by printing. Their 30 nm SWCNT films on 125µm thick PET flexible substrates showed 85 % transmittance at 550 nm and 200 Ω/sq sheet resistance.

The filter/transfer (FT) approach has the benefit of yielding loosely bundled films that permit easy removal of insulating surfactants. Anodes based on FT-derived films can accordingly exhibit high conductivities of up to 6700 S/cm.¹⁵ However, the limited scalability of the FT technique is problematic for large scale production.

Hu et al.¹⁶ coated surfactant-assisted aqueous dispersions of arc-discharge SWCNTs on PET with an air-brush. The PET surface was modified by soaking into 1 wt % 3-aminopropyltriethoxysilane for 5 min beforehand to assist film adhesion. The sheet resistances of the resultant films were 300 Ω/sq on PET substrates with 80 % transmittance at 550 nm.

H. Z. Geng et al.¹⁷ used a spray method to fabricate SWCNT transparent anodes on a PET substrate from a sodium dodecyl sulfate (SDS) assisted single-walled carbon nanotube solution. After acid treatment, sheet resistances of 40 Ω/sq and 70 Ω/sq at the corresponding transmittances of 70 % and 80% were obtained.

Tenent et al.¹¹ have reported ultrasonic spray-coating to be one of the preferable techniques for fabricating large area SWCNT electrodes. They obtained their best results by using an aqueous stock solution of laser-vaporised SWCNTs using carboxymethyl cellulose (CMC) as the dispersant. This is due to its ability to yield high quality dispersions with modest sonication. They noted that standard surfactants such as sodium dodecyl sulphate [SDS, NaC₁₂H₂₅SO₄] required more intense sonication – with a higher risk of tube-cutting and shortening – and had a tendency to yield non-uniform hazy films. Their 40 nm SWCNT films showed sheet resistances of 60 Ω/sq at transmittances of 68 % after nitric acid treatment.

However, CMC-derived films require delicate handling compared to those prepared using SDS and other common surfactants such as sodium dodecyl benzene sulphonate [SDBS, CH₃(CH₂)₁₁C₆H₄SO₃Na]. For instance, routine acid treatment can cause them to delaminate from the underlying substrate, especially when rinsed, which complicates their handling in a manufacturing environment.

In this chapter, I focus on spray coated SWCNT thin films, prepared from aqueous dispersions of SWCNTs using various anionic surfactants such as SDS, SDBS, CMC and SDBS/PVP, and compare the performance of the resultant films with surfactant-free reference films prepared by spin-deposition from pure dichloroethane (DCE). DCE is a very good organic solvent to disperse SWCNTs and has a low boiling point of 78 °C, which makes the spin-coating process easier than other typically used organic solvents for SWCNT dispersion. (boiling point: ~200 °C).

4.2 Experimental Details

In this work, arc-made SWCNTs were used to make solution based thin films by the following procedure. (see Figure 4.1) SWCNTs were purchased from Iljin Nanotech, Korea with a quoted purity, diameter and length of 60 - 70 wt%, 1.0 - 1.2 nm, and 5 - 20 μm , respectively. The as-received CNTs were placed in a vacuum oven overnight at 100 °C and then used without further purification.

To prepare the dispersion solution for the spin-coated films, the dried SWCNTs were first added in excess at approximately 10^{-3} wt.% to DCE solvent, and subjected to mild ultrasonication at 100 W overnight. The resultant solution was centrifuged (15,000 rpm), and the upper 50 % of the supernatant was retained. Films were deposited on to clean glass substrates by a process of repetitive spin-coating, with the number of repetitions controlling the thickness of the final film. Spin-coating from surfactant-free solutions typically yields smoother SWCNT films than other deposition techniques but, due to the apolarity and dilute nature of the SWCNT solutions, several hundred repetitions are typically needed to prepare films of appreciable thickness (> 20 nm).

To prepare the solutions for the spray-coated films, the dried SWCNTs were normally dispersed at approximately 0.03 wt.% in water containing 0.3 wt.% of pre-dissolved SDS, SDBS, CMC or SDBS with polyvinylpyrrolidone (denoted $\text{H}_2\text{O}:\text{SDS}$, $\text{H}_2\text{O}:\text{SDBS}$, $\text{H}_2\text{O}:\text{CMC}$ or $\text{H}_2\text{O}:\text{SDBS/PVP}$, respectively in the ensuing discussion). For higher loading content of SWCNTs in deionised water, 0.1 wt.% of SWCNTs was dispersed with approximately 1 wt.% of pre-dissolved SDBS or SDBS/PVP. After the same process of ultrasonic agitation, high-speed centrifugation, and decanting, the well dispersed SWCNT solution was deposited onto a heated glass substrate at 90 °C using a simple pressure-driven airbrush that was repeatedly swept backwards and forwards over the substrate to ensure a uniform coverage. The film thickness was controlled by holding the spray conditions constant and varying the amount of deposited material.

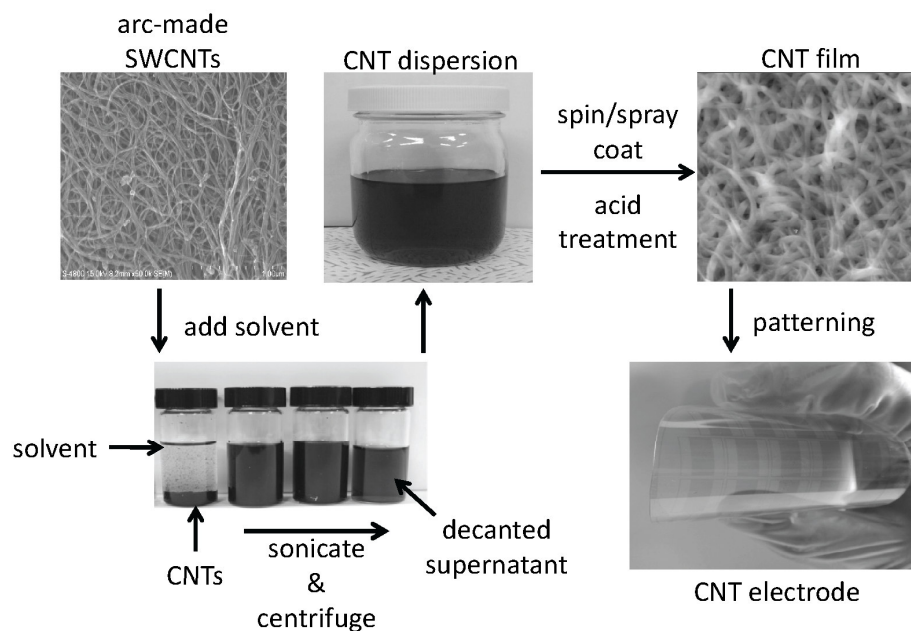


Figure 4.1 Schematic illustrating the process of SWCNT electrode fabrication, which involves the following key steps: dry arc-made SWCNTs are added to a solvent and subjected to high speed centrifugation; the upper 50 % of the supernatant is retained; SWCNT films are deposited by spin-coating (DCE) or spray-coating ($\text{H}_2\text{O}:\text{SDS}$, $\text{H}_2\text{O}:\text{SDBS}$, etc) and patterned by selective oxygen plasma treatment, photolithography or in-situ spray patterning.

Spray-coating is a simple on-demand deposition technique that ensures efficient materials usage, whilst yielding films that are somewhat rougher than those obtained through spin-coating. In pressure-driven systems, a fast-moving stream of compressed gas creates a localised reduction in pressure above the nozzle outlet of a reservoir containing the SWCNT solution at atmospheric pressure. The solution nebulises as it exits the nozzle and, on emerging into the gas-stream, is further dispersed into a fine mist of minute droplets that are propelled towards the substrate where they are deposited. In ultrasonic spray deposition (as used by Tenent et al.), a high frequency piezoelectric disc provides the driving force for atomisation, removing the need for a fast-moving carrier gas, and so enabling a ‘softer’ lower velocity spray to be obtained. This results in somewhat smoother films and provides superior control over film thickness, albeit at the expense of reduced throughput and a more costly spray-head.

All SWCNT films were subjected to a combination of thermal annealing at below $100\text{ }^{\circ}\text{C}$ and nitric acid treatments as described below to oxidatively dope the SWCNTs and remove surfactants and other organic contaminants, in order to obtain highly conductive SWCNT thin films.¹⁸

4.3 Results and discussions

In this section, various properties of the deposited SWCNT thin films such as film morphology, electrical conductivity, variation of sheet resistance under repetitive mechanical bending, work function, and optical transmission were studied for solutions prepared with a variety of different dispersing aids. The results are presented in the following sections.

4.3.1 Spin and spray coated SWCNT thin films from different dispersants

Figure 4.2 shows $4\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ AFM images for three SWCNT thin films of comparable thickness ($\sim 25\text{ nm}$), obtained by spin-coating from DCE and by spray-coating from $\text{H}_2\text{O}:\text{SDS}$ and $\text{H}_2\text{O}:\text{SDBS}$. The chemical structures of DCE, SDS, and SDBS are also included in the figure. The spin-coated film had a thickness of 24 nm and was the smoothest of the three with a root-mean-square (r.m.s.) roughness of 2.0 nm ; the $\text{H}_2\text{O}:\text{SDS}$ sample had a mean thickness of 26 nm and an intermediate roughness of 11 nm ; while the $\text{H}_2\text{O}:\text{SDBS}$ sample had a mean thickness of 28 nm and a high roughness of 17.5 nm .

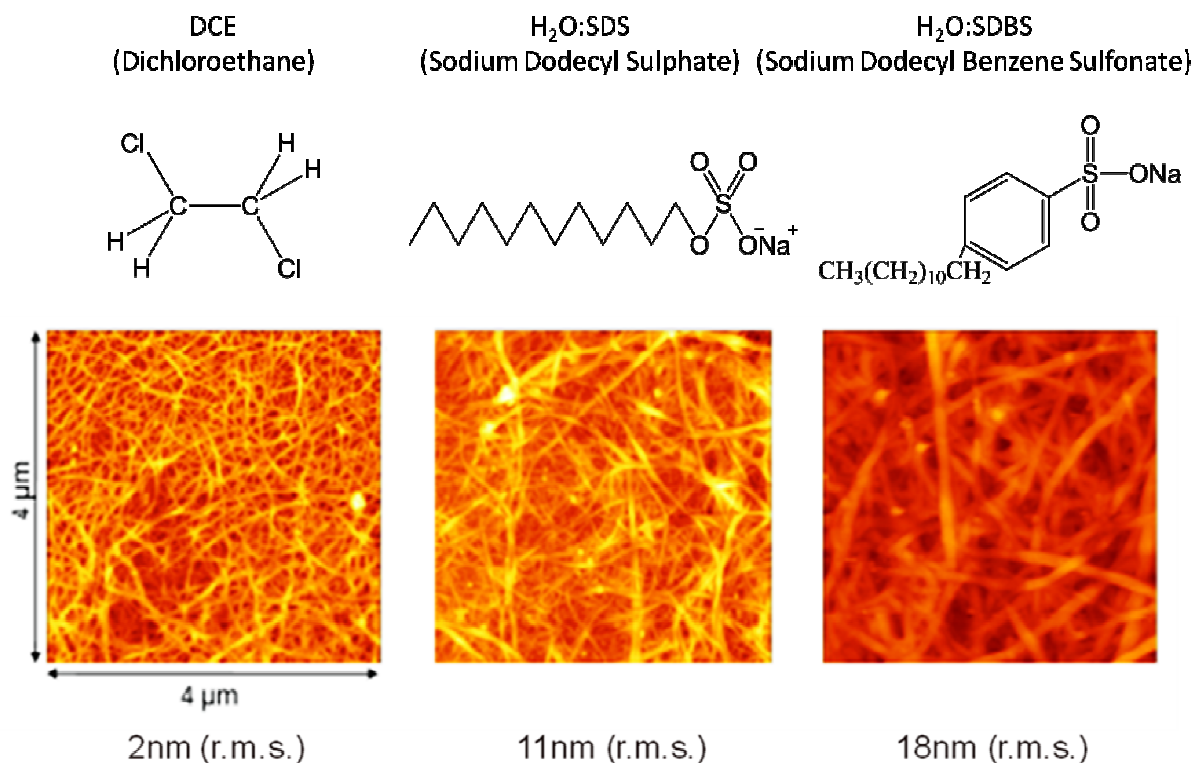


Figure 4.2 $4\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ Atomic Force Micrographs for thin-film SWCNTs spin-coated from DCE (24 nm) and spray-coated from $\text{H}_2\text{O}:\text{SDS}$ (26 nm) and $\text{H}_2\text{O}:\text{SDBS}$ (28 nm).

In the latest work, I have managed to reduce the roughness of my SWCNT films to ≤ 6 nm by reducing the flow-rate of the carrier gas. This latter value is somewhat better than that routinely achievable by the FT method (≤ 10 nm),¹⁹ but is a little worse than that obtained by Tenent et al.²⁰ using ultrasonic spray deposition (≥ 3 nm).

All the Films prepared using DCE, H₂O:SDS and H₂O:SDBS were mechanically robust and were found to expel surfactant readily when treated with acid.²¹ They showed no tendency to delaminate from the underlying substrate during the routine handling either before or after acid treatment. In fact, similar films on flexible polyester (PET) substrates have proven to be extremely resilient, showing no tendency to fracture or wear even when flexed repeatedly to a radius < 5 mm. The variation of sheet resistance with the number of bending cycles is shown in Figure. 4.3. For comparison purpose, SWCNT films prepared using DCE or H₂O:SDS were used for the bending test.

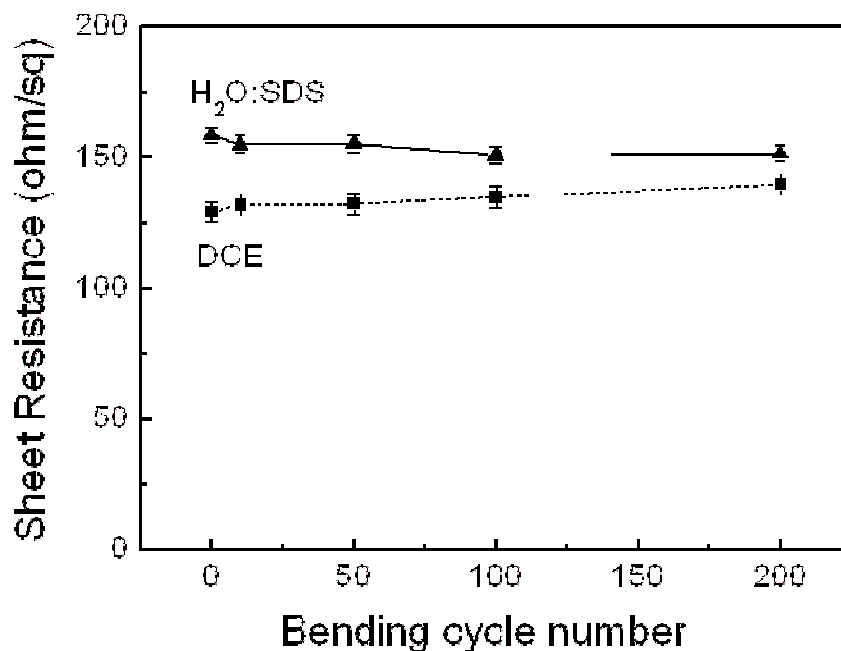


Figure 4.3 The influence of repetitive flexing on the sheet resistance of two SWCNT electrodes on PET - spin-coated from DCE and spray-coated from H₂O:SDS. A bending radius of 5 mm was used for the measurements.

The sheet resistance, transmittance and electrical conductivity versus the SWCNT thin film thickness are shown for the different dispersants in Figure 4.4. Figure 4.4a shows the transmission T at 550 nm as a

function of the film thickness l over the approximate range $0 < l < 100$ nm, where for each film l has been determined using surface profilometry over a scan length of 400 μm . (UV/VIS transmission spectra for the films are provided in Figure 4.5). The transmission of light through CNT films has previously been analysed using Tinkham's formula, which takes into account optical interference effects in self-standing films of optical conductivity σ_{op} :

$$T = \left(1 + \frac{Z_0}{2} \sigma_{op} l\right)^{-2} \quad (4-1)$$

Where $Z_0 = 377 \Omega$ is the impedance of free space. Although Equation (4-1) is valid only for free-standing films, it is commonly applied in an empirical sense to substrate-supported films.²² The transmission versus thickness curves in Fig. 4.4a fit well to Tinkham's formula, yielding (effective) optical conductivities at 550 nm of 133 ± 4 , 480 ± 2 and $315 \pm 16 \text{ Scm}^{-1}$ for films deposited from DCE, $\text{H}_2\text{O}:\text{SDS}$ and $\text{H}_2\text{O}:\text{SDBS}$, respectively.

The optical conductivity of the spin-coated films lies slightly below the usual range of 150 to 200 S cm^{-1} for state-of-the-art CNT films, indicating unusually good transmission characteristics – a fact we attribute to the high uniformity and weak consequent scattering of the spin-coated films. The relatively high optical conductivities of the other two films are consistent with the hard-impact nature of the spray-coating process, which yields dense rough films that are more strongly absorbing and scattering.

Fig. 4.4b shows the sheet resistance $\mathcal{R}$ determined using the four-point probe method as a function of film thickness l for the three sets of samples. In each case, there was a monotonic reduction in sheet resistance with film thickness: for the spin-coated films, $\mathcal{R}$ decreased from a value of $3045 \pm 650 \Omega/\text{sq}$ at 2.3 nm to $85 \pm 5 \Omega/\text{sq}$ at 40 nm; for the spray-coated films from $\text{H}_2\text{O}:\text{SDS}$, $\mathcal{R}$ decreased from a value of $1412 \pm 40 \Omega/\text{sq}$ at 7.3 nm to $25 \pm 1 \Omega/\text{sq}$ at 58 nm; and for the spray-coated films from $\text{H}_2\text{O}:\text{SDBS}$, $\mathcal{R}$ decreased from a value of $399 \pm 10 \Omega/\text{sq}$ at 8.7 nm to $53 \pm 7 \Omega/\text{sq}$ at 47 nm. Above 10 nm, the sheet resistance of the spray-coated films was substantially lower than the spin-coated films of equivalent thickness, presumably because the higher film density allowed for better electrical connectivity between individual nanotubes.

Fig. 4.4c shows for the same three sets of samples the conductivity $\sigma_{dc} = 1/(\mathcal{R}l)$ as a function of film thickness. Numerous factors influence the conductivity of the films, including the ratio of conducting to

semiconducting tubes in the initial dispersion, the length, alignment and connectivity of the tubes, the nature and weight fraction of any residual surfactant, and the efficacy of the acid treatment.²³

There are significant differences between the three data sets but, in common with previous reports, in all cases the thinnest films exhibited the lowest conductivities, consistent with a loss of percolation as previously discussed by Doherty et al.²⁰

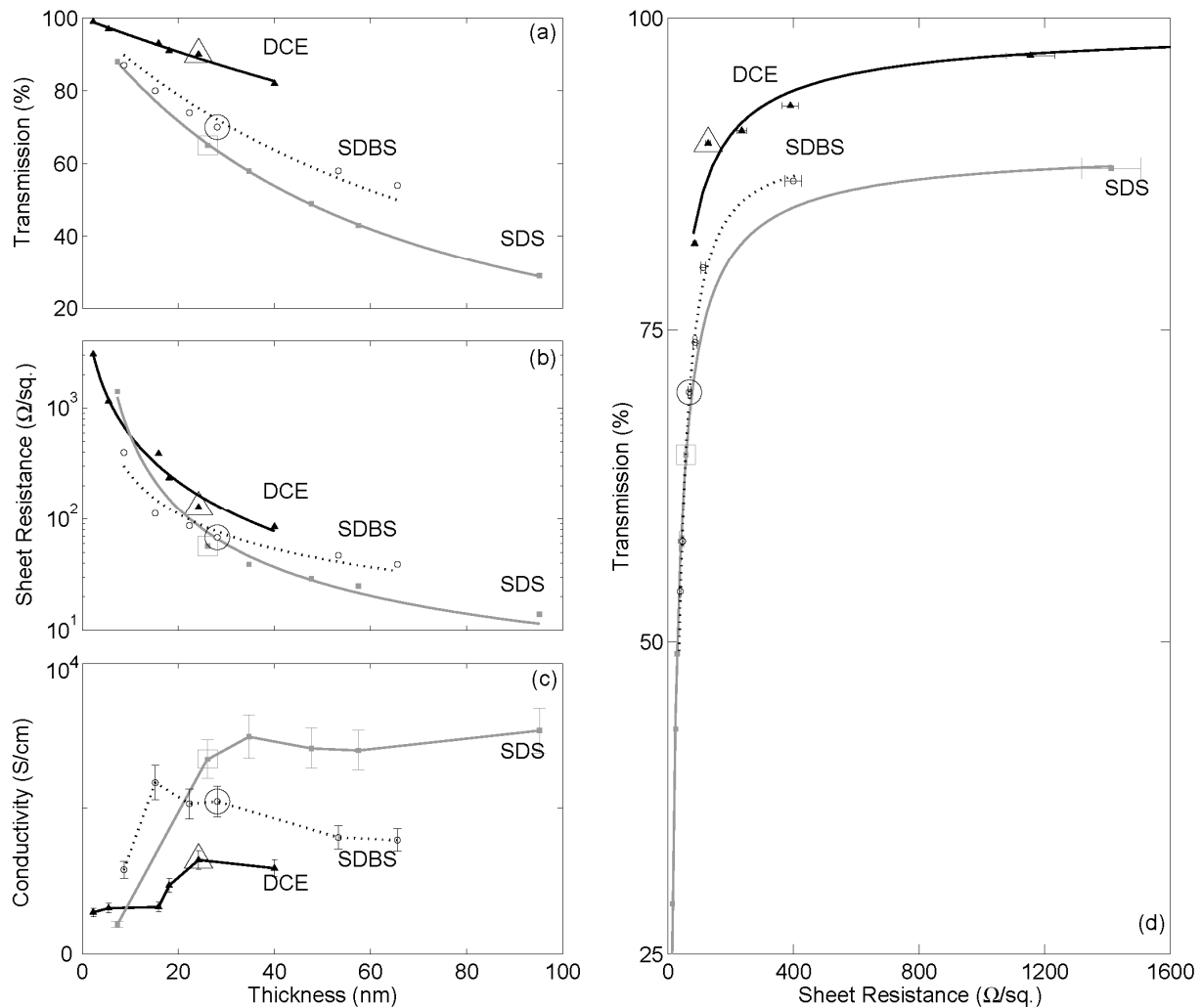


Figure 4.4 Thickness dependence of (a) the transmission, (b) the sheet-resistance, and (c) the conductivity of thin-film SWCNTs spin-coated from DCE and spray-coated from $\text{H}_2\text{O}:\text{SDS}$ or $\text{H}_2\text{O}:\text{SDBS}$. The mean thickness l of each film was determined using surface profilometry. (d) Transmission versus sheet-resistance “trade-off” characteristics for the same films using data extracted from (a) and (b). The lines in (a) are numerical fits to Tinkham’s formula, Equation (4-1); all other lines are “guides to the eye”. The circled data points indicate films used for device fabrication in chapter 6.

The highest conductivities were obtained for films spray-coated from H₂O:SDS with $l > 34$ nm, all of which exhibited conductivities greater than 7000 Scm⁻¹ (with the highest value of 7694 ± 800 Scm⁻¹ being obtained at 95 nm). These are extremely high values for spray-coated films that to our knowledge represent the highest reported to date, exceeding even those of filter/transfer-made films - a fact we attribute to the gentle processing conditions employed (which lessen tube-cutting and shortening), the high film densities obtained using pressure-driven spray-deposition, and efficient surfactant elimination and doping by nitric acid.

The data in Figure 4.4a-b illustrates the usual trade-off between sheet resistance and transmission, with an increase in film-thickness leading to a beneficial reduction in sheet resistance at the expense of an unfavourable drop in transmission. A clearer understanding of this trade-off can be obtained by plotting the transmission versus the sheet resistance for the three SWCNT films, see Figure 4.4d. Evidently, for any given sheet resistance in the range 100 to 400 Ω /sq, the highest transmission was obtained for spin-coated films from DCE, followed by spray-coated films from H₂O:SDBS, and lastly spray-coated films from H₂O:SDS, as shown in Figure 4.5.

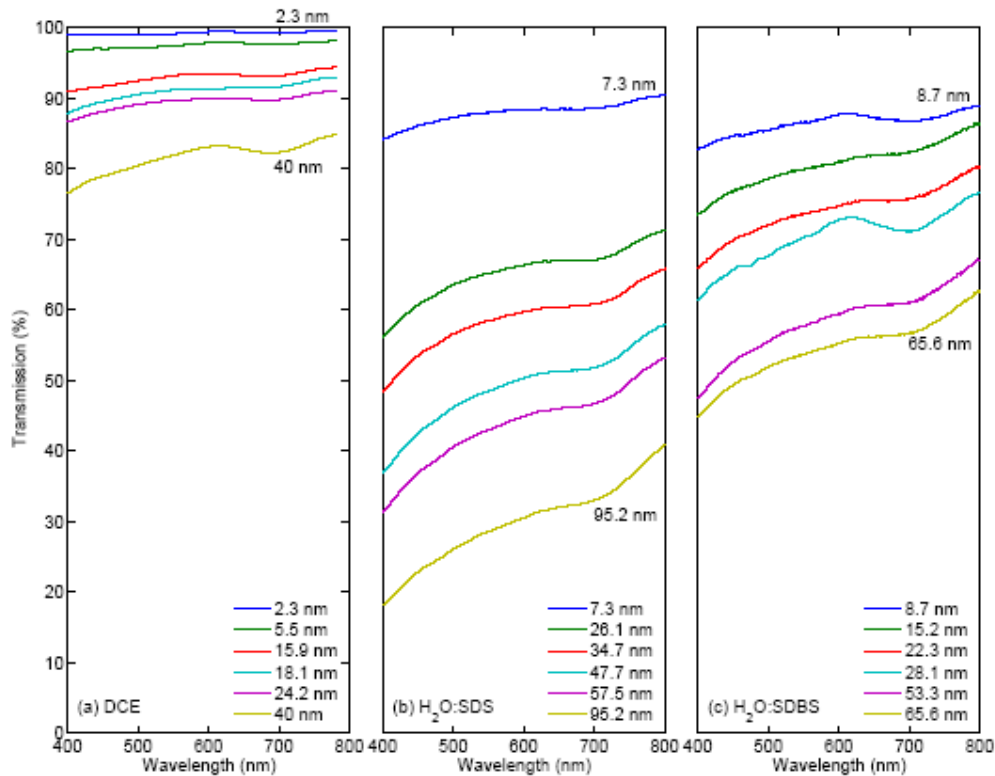


Figure 4.5 Transmission spectra for CNT films (a) spin-coated from DCE, (b) spray-coated from H₂O:SDS; and (c) spray-coated from H₂O:SDBS.

In situations where the dc conductivity is invariant with thickness, Eq. (1) can be re-expressed in the form

$$T = \left[1 + \frac{(Z_0 / 2\Re)}{(\sigma_{dc} / \sigma_{op})}\right]^{-2} = \left[1 + \frac{(Z_0 / 2\Re)}{\gamma}\right]^{-2} \quad (4-2)$$

Where $\Re = 1/l\sigma_{dc}$ and $\gamma = \sigma_{dc}/\sigma_{op}$ determine the fall-off rate for the transmission as the sheet resistance diminishes. γ is a widely used figure of merit for transparent conductors, with higher values of γ being preferred as they yield a higher transmission for a given sheet resistance. For reference, industry targets of $R_s = 100 \Omega/\text{sq}$ and $T = 90 \%$ correspond to γ values greater than 35.

The films reported here exhibited thickness-dependent conductivities, and so the complete data sets did not fit well to Equation (4-2). However, dividing the optical conductivities obtained from Figure 4.3a by the individual dc conductivities shown in Figure 4.3c, we obtained peak γ values of 24.3 ± 3 , 15.6 ± 1.6 and 17.5 ± 3 for DCE, H₂O:SDS, and H₂O:SDBS, respectively.

Although these are lower than the industry target of 35, they are quite reasonable values for CNT films with the spin-coated films being close to the state-of-the art. In practice, all three deposition methods allowed sheet resistances of around $100 \Omega/\text{sq}$. to be obtained from $\sim 25 \text{ nm}$ films with reasonable transmission, e.g. $\Re = 128 \pm 2 \Omega/\text{sq}$. at $T = 90 \%$ for spin-coated films from DCE, $\Re = 57 \pm 3 \Omega/\text{sq}$ at $T = 65 \%$ for spray-coated films from H₂O:SDS, and $\Re = 68 \pm 5 \Omega/\text{sq}$. at $T = 70 \%$ transmission for spray-coated films from H₂O:SDBS (see circled data in Fig. 4.3).

Work function measured with a Kelvin probe ranged between 4.7 and 4.9 eV for spray-coated SWCNT films from H₂O:SDS and H₂O:SDBS, while for comparison ITO has a work function of around 4.7 eV, as shown in Figure 4.6. SWCNT films prepared using DCE had around 4.9 eV. There was no obvious trend with increasing surface coverage of spray-coated SWCNTs and the slight variations probably came from slightly different degrees of oxidation during the film preparation procedure. All SWCNT films had adequate work functions for use as anodes in organic electronic devices.

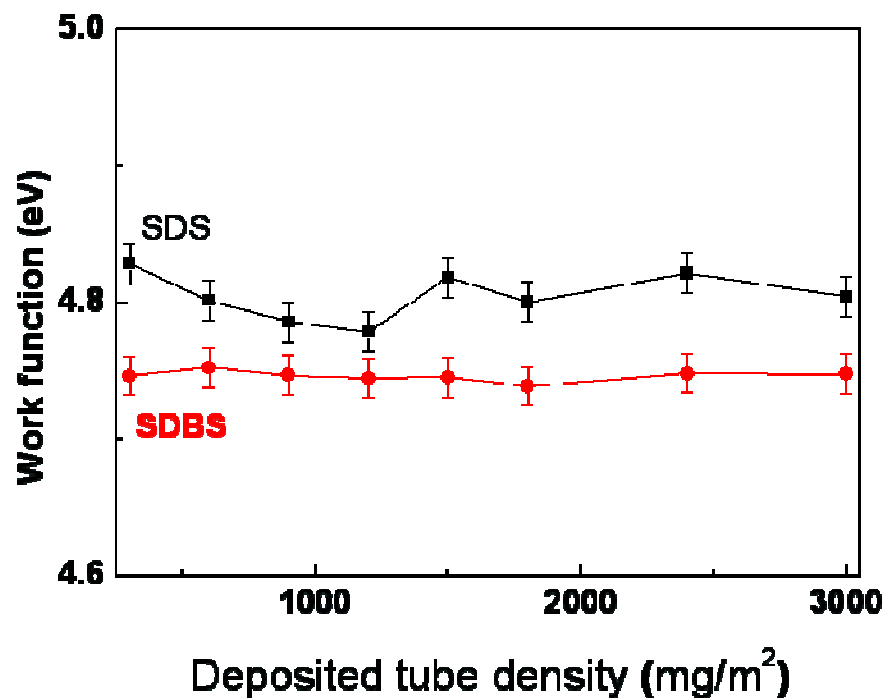


Figure 4.6 Variation of the work function with surface coverage of spray-coated SWCNTs on top of glass substrates. SWCNTs were dispersed in DI water using SDS or SDBS and the work function was measured with a Kelvin probe.

4.3.2 Spray coated SWCNT thin films using different surfactants

We then compared the anionic surfactant SDS with CMC - the preferred anionic surfactant of Tenent et al. For this work 0.03 wt.% of SWCNTs were dispersed in DI water using 0.3 wt.% surfactant and the morphological, optical, and electrical properties of the resultant films on glass were compared.

Figure 4.7 compare the electrical conductivity, sheet resistance (Ω) and transmittance (T) at 550 nm of the two sets of samples. In each case, there was a monotonic reduction in sheet resistance with film thickness. However, above 10 nm of film thickness, for the spray-coated films from H₂O:SDS, the dc conductivity was more than twice that of the spray-coated films from H₂O:CMC. It is probably due to the higher film density for the spray-coated films from H₂O:SDS as evident from Figure 4.7a, which would be expected to provide the better electrical connectivity between individual nanotubes.

The work function measured with a Kelvin probe for the spray coated SWCNT films from H₂O:CMC was around 5.0 eV, which is slightly higher than that of the spray coated SWCNT films from H₂O:SDS (~ 4.8 eV).

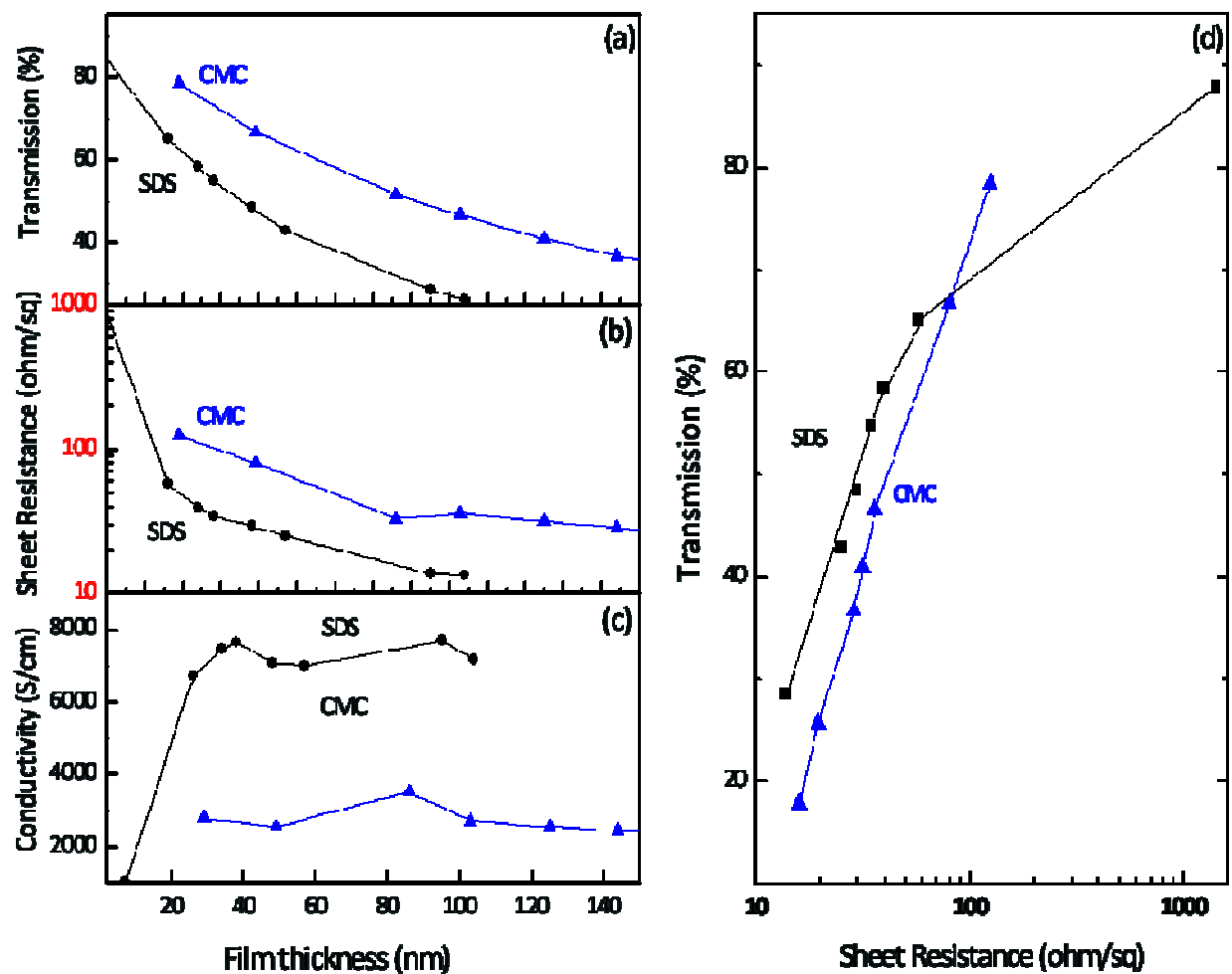


Figure 4.7 Thickness dependence of (a) the transmittance, (b) the sheet-resistance, and (c) the dc conductivity of thin-film SWCNTs spray-coated from H₂O:SDS or H₂O:CMC. (d) Transmittance versus sheet resistance for the SWCNT films spray-coated from H₂O:SDS or H₂O:CMC. The mean thickness l of each film was determined using surface profilometry.

The optical conductivity (determined by fitting the above data to a Tinkham's formula) for the spray coated SWCNT films from H₂O:CMC was $240 \pm 1 \text{ S cm}^{-1}$, which was much lower (better) than that of SWCNT films from H₂O:SDS ($489 \pm 5 \text{ S cm}^{-1}$). However, dividing the optical conductivities by the individual dc conductivities shown in Fig. 4.7c, we obtained peak γ values of 11 ± 1.6 for H₂O:CMC, which is significantly lower than 15.6 ± 1.6 for H₂O:SDS. Typical SWCNT films from H₂O:CMC with 29 nm thickness had a sheet resistance of $\mathcal{R} = 124 \pm 3 \text{ } \Omega/\text{sq}$ at a transmission of $T = 78 \%$.

However, with loosened bundles of SWCNTs, the spray-coated films from H₂O:CMC had better morphology, confirmed with a AFM. Figure 4.8 shows 4 μm $\times$ 4 μm AFM images for two films of comparable thickness (~ 30 nm), obtained by spray-coating from H₂O:SDS and H₂O:CMC. The spray-coated film from H₂O:CMC had a thickness of 25 nm and was the smoother of the two with a (r.m.s.) roughness of 7.0 nm; the H₂O:SDS sample had a mean thickness of 30 nm and an higher roughness of 10 nm.

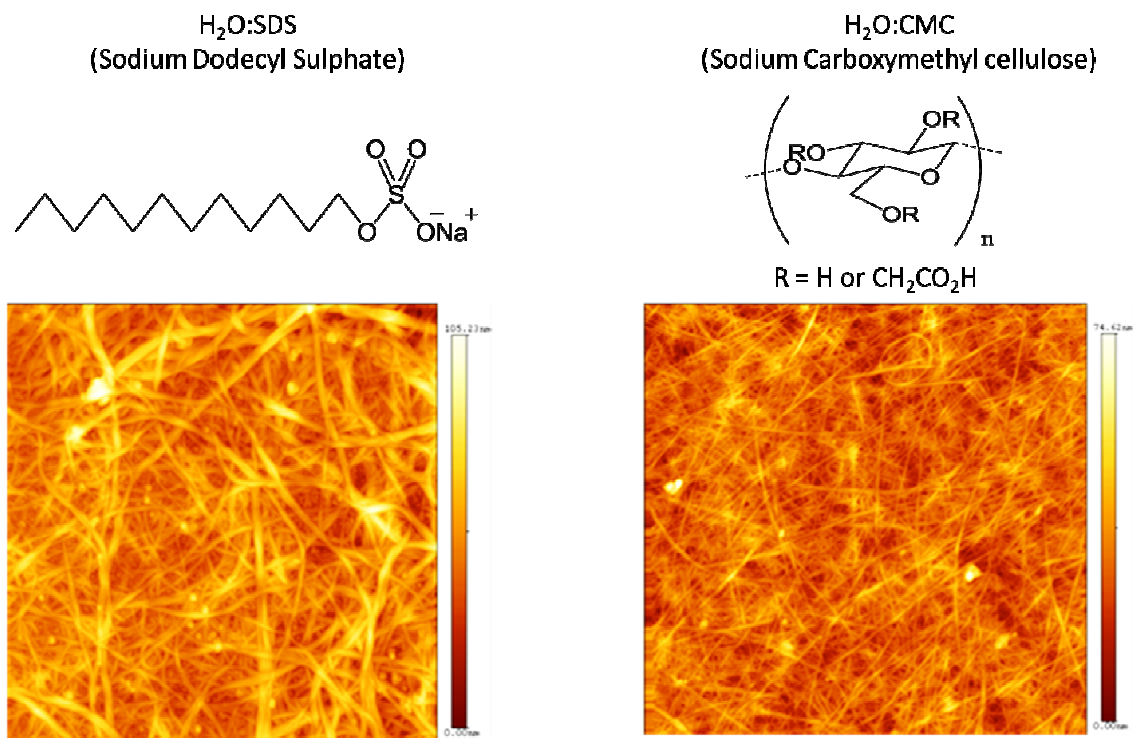


Figure 4.8 4 μm $\times$ 4 μm Atomic Force Micrographs for thin-film SWCNTs spray-coated from H₂O:SDS (30 nm) and spray-coated from H₂O:CMC (25 nm).

4.3.3 Spray coated SWCNT thin films using a high concentration of SWCNT solution

We then tested whether higher concentrations of SWCNTs in the initial dispersion could affect the as-deposited thin film characteristics. For this work, we used the anionic surfactant SDBS both on its own SDBS and also combined with Polyvinylpyrrolidone (PVP), due to its surface planarising effect.

100 mg of SWCNTs was dispersed in 100 ml of DI water with either SDBS (100 mg) or SDBS (40 mg) together with PVP (80 mg). In both cases, dispersions with up to 0.1 wt% of SWCNTs in DI water could be achieved with a mild ultrasonication overnight without any sediment, which will be beneficial for large area printing methods such as inkjet printing or gravure printing.

The spray-coated films from H₂O:SDBS had a electrical conductivity of $4103 \pm 319 \text{ S cm}^{-1}$, which was higher than for the spray-coated films from H₂O:SDBS/PVP ($3155 \pm 520 \text{ S cm}^{-1}$), as shown in Figure 4.9. It is probably due to imperfect removal of PVP from the films, which can be confirmed from Figure 4.10.

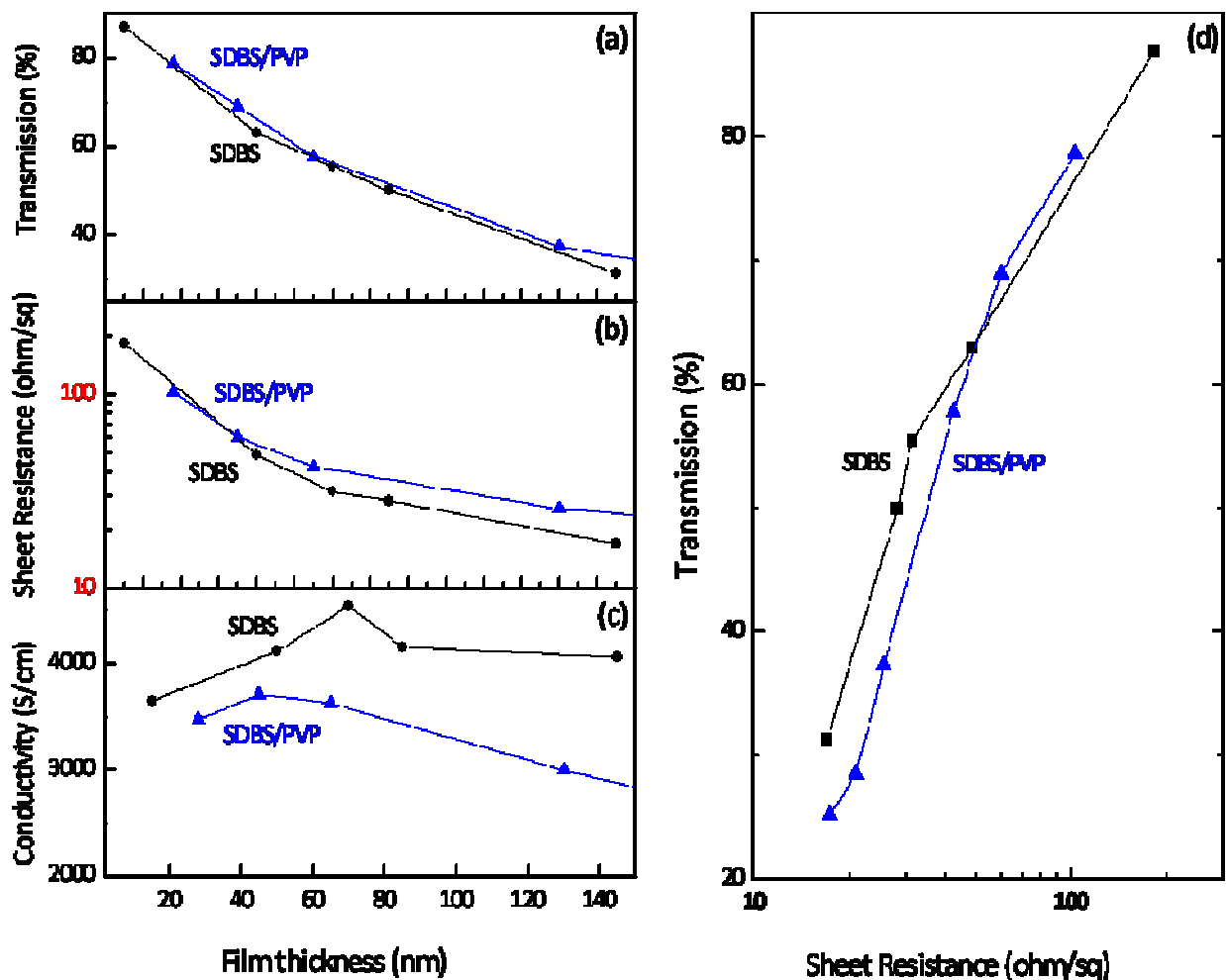


Figure 4.9 Thickness dependence of (a) the transmittance, (b) the sheet-resistance, and (c) the dc conductivity of thin-film SWCNTs spray-coated from H₂O:SDBS or H₂O:SDBS/PVP. (d) Transmittance versus sheet resistance for the SWCNT films spray-coated from H₂O:SDBS or H₂O:SDBS/PVP. The mean thickness / of each film was determined using surface profilometry.

The optical conductivity fitted the data with a Tinkham's formula for the spray coated SWCNT films from H₂O:SDBS/PVP was $245 \pm 9 \text{ S cm}^{-1}$, while the SWCNT films spray coated from H₂O:SDBS had $267 \pm 14 \text{ S cm}^{-1}$. The value for H₂O:SDBS/PVP SWCNT films were comparatively low (good), probably due to the ordered arrays of SWCNTs wrapped with PVPs.

By dividing the optical conductivities by the individual dc conductivities shown in Fig. 4.9c, we obtained peak γ values of 13 ± 2 for H₂O:SDBS/PVP compared to 15.4 ± 1.4 for H₂O:SDBS. Typical SWCNT films from H₂O:SDBS/PVP with 28 nm thickness had a sheet resistance (R_s) of $103 \pm 1.7 \text{ } \Omega/\text{sq}$ at a transmittance (T) of 79 %.

However, with loosened bundles of SWCNTs, the spray-coated films from H₂O:SDBS/PVP were smoother than previously imaged SWCNT films from H₂O:SDBS, confirmed with a AFM. (Also see Figure 4.2) Figure 4.10 shows a $4 \text{ } \mu\text{m} \times 4 \text{ } \mu\text{m}$ AFM image for the SWCNT film of 28 nm thickness, spray-coated from SDBS/PVP. It had a (r.m.s.) roughness of 10.6 nm, compared to 18 nm for the SWCNT film spray-coated from SDBS.

H₂O:SDBS/PVP
(Sodium Dodecyl Benzene Sulfonate/Polyvinylpyrrolidone)

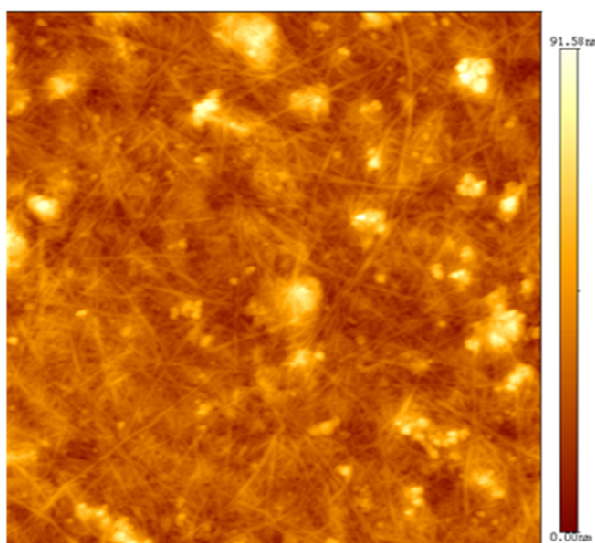
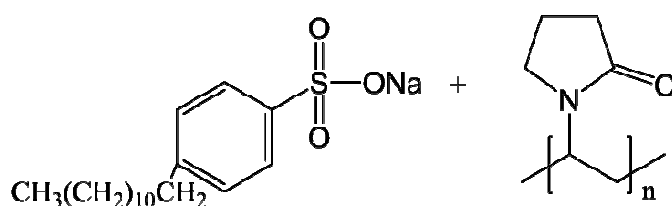


Figure 4.10 $4 \text{ } \mu\text{m} \times 4 \text{ } \mu\text{m}$ Atomic Force Micrographs for thin-film SWCNTs spray-coated from H₂O:SDBS/PVP (28 nm).

The work function measured with a Kelvin probe for the spray coated SWCNT films from H₂O:SDBS/PVP was around 5.0 eV, which was slightly higher than the spray coated SWCNT films from H₂O:SDBS (~ 4.8 eV) and is similar to that of the spray coated SWCNT films from H₂O:CMC.

4.3.4 Influence of SWCNTs loading

Here, we note that by using SDBS for higher loading SWCNTs in DI water (0.1 wt.%), we couldn't find any significant increase in the peak γ values with 15.4 ± 1.4 by varying thickness and concentration over 0.03 wt.% of SWCNTs in DI water ($\gamma = 17.5 \pm 3$), as shown in Figure 4.11. This is probably due to no significant change in the tube density of the final film by varying initial loading SWCNTs in DI water. Here, note that the SWCNT film (dc) conductivity is mainly derived from the effectively deposited tube density.

Since using an air-brush spray coating technique with higher loading SWCNTs did not lead to an increase in the tube density of the resultant film, electrical/optical properties of the thin film SWCNTs deposited from high concentration of SWCNT suspensions are expected to improve more by using other printing techniques such as gravure or inkjet printing to effectively deposit denser SWCNTs in a unit area. However, essential removal steps of dispersing aids can be more challenging to ensure highly conductive SWCNT films as well. All these works remain as future works.

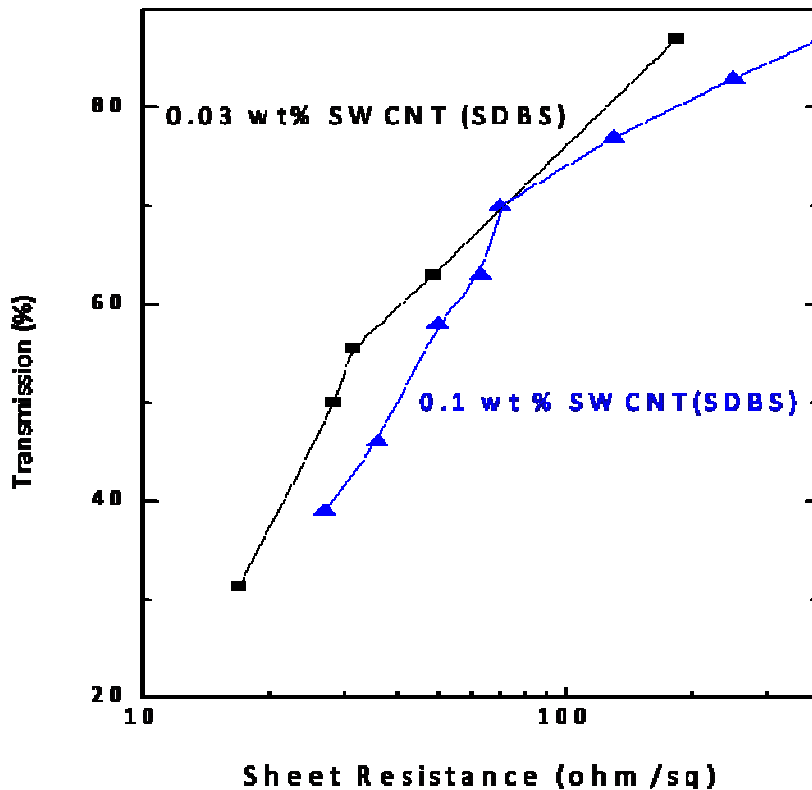


Figure 4.11 Transmittance versus sheet resistance for the SWCNT films spray-coated from H₂O:SDBS by varying initial concentration of SWCNTs. (0.1 wt % versus 0.03 wt %)

4.4 Conclusion

We have fabricated and evaluated SWCNT thin-films as beneficial means for replacing the conventional transparent electrode of ITO. SWCNT films made from different dispersants and different deposition methods were investigated. These include spin-coated SWCNT films from dichloroethane, and films deposited by pressure-driven spray-coating from deionized water using SDS, SDBS, CMC, SDBS/PVP as the dispersive agent. All of the SWCNT films were found to be mechanically robust, with no tendency to delaminate from the underlying substrate during handling.

Whilst all the above surfactants can be used to prepare mechanically robust spray-coated SWCNT films, we find here that SDS yields moderately smooth electrodes with the most favourable transmission versus sheet resistance characteristics. For instance, using SDS, we obtain sheet resistances of $57 \text{ } \Omega/\text{sq}$ at 65 % transmittance and conductivities in excess of 6700 S cm^{-1} – values that compare favourably with surfactant-free films. Post acid treatment with HNO_3 yielded high conductivities $> 1000 \text{ S cm}^{-1}$ for all of the SWCNT films, with values of up to $7694 \pm 800 \text{ S cm}^{-1}$ being obtained when using SDS as the surfactant.

To our knowledge, these values are the highest so far reported for SWCNT electrodes, and are higher even than the values of 6667 S cm^{-1} previously obtained using vacuum filtration and membrane transfer. The SWCNT films exhibited sheet resistances around $100 \text{ } \Omega/\text{sq}$ at reasonable transmission, for example, $128 \pm 2 \text{ } \Omega/\text{sq}$ at 90% for DCE; $57 \pm 3 \text{ } \Omega/\text{sq}$ at 65% for $\text{H}_2\text{O}:\text{SDS}$; $68 \pm 5 \text{ } \Omega/\text{sq}$ at 70% for $\text{H}_2\text{O}:\text{SDBS}$, $124 \pm 3 \text{ } \Omega/\text{sq}$ at $T = 78 \%$ for $\text{H}_2\text{O}:\text{CMC}$, and $103 \pm 1.7 \text{ } \Omega/\text{sq}$ at $T = 79 \%$ for $\text{H}_2\text{O}:\text{SDBS/PVP}$.

Peak values for the ratio of the dc conductivity to the optical conductivity were obtained as follows: 24.3 ± 3 for DCE; 15.6 ± 1.6 for $\text{H}_2\text{O}:\text{SDS}$; 17.5 ± 3 for $\text{H}_2\text{O}:\text{SDBS}$; 11 ± 1.6 for $\text{H}_2\text{O}:\text{CMC}$; and 13 ± 2 for $\text{H}_2\text{O}:\text{SDBS/PVP}$. All the results are summarized in Table 4.2.

Table 4.2 Physical characteristics of SWCNT thin films made with different dispersants.

	$R_s \text{ [}\Omega/\text{sq}]$	$T \text{ [%]}$	$\sigma_{\text{Op}} \text{ [S cm}^{-1}]$	$\sigma_{\text{dc}} \text{ [S cm}^{-1}]$	$\sigma_{\text{dc}} / \sigma_{\text{Op}}$
DCE	128 ± 2	90	133 ± 4	3228 ± 300	24.3 ± 3
$\text{H}_2\text{O}:\text{SDS}$	57 ± 3	65	480 ± 2	7694 ± 800	15.6 ± 1.6
$\text{H}_2\text{O}:\text{SDBS}$	68 ± 5	70	335 ± 30	5875 ± 600	17.5 ± 3
$\text{H}_2\text{O}:\text{CMC}$	124 ± 3	78	240 ± 1	2781 ± 67	11 ± 1.6
$\text{H}_2\text{O}:\text{SDBS/PVP}$	103 ± 1.7	79	245 ± 9	2411 ± 56	13 ± 2

The work function for spin- or spray-coated SWCNT films ranged between 4.7 ± 0.05 eV and 5.0 ± 0.05 eV, which are suitable for use as anodes in organic electronic device applications such as organic solar cells, organic light emitting diodes and transparent organic transistors.

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Chapter 5 Patterning Methods for SWCNT Films

5.1 Introduction

Thin-film single-wall carbon nanotubes (SWNTs) have been successfully used as high performance, transparent and conducting electrodes in many optoelectronic devices application, including organic light-emitting diodes,¹ solar cells,² thin film transistors,³ and stretchable actuators.⁴ Their suitability for large area, solution processing at ambient conditions combined with very high mechanical strength makes them attractive for transparent, flexible electronic devices where they can be used in place of Indium Tin Oxide (ITO), which has drawbacks of both high volatility in Indium prices and its brittleness, which causes an irreversible electrical conductivity drop when it is repeatedly bent.⁵

So far, researchers have reported many different patterning methods for SWCNT electrodes such as transfer contact printing,^{1b, 6} dry plasma-etching,⁷ photolithography,⁸ selective electrochemical deposition,⁹ and ink-jet printing.¹⁰ However, these techniques generally lack in either scalability to larger substrates or low cost, simple processing protocols.^{1b, 5b, 6-7, 9-10}

From the perspective of electronic device applications with SWCNT films, organic photovoltaics with blends of regioregular poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) have been reported with around 3% power conversion efficiency (PCE).^{2a-c} However, due to their use of a very delicately handled surfactants such as sodium carboxymethyl cellulose (CMC) or vacuum filter/transfer patterning techniques (with both limited size of filters and fairly high final film roughness), their industrial viability for large area, mass production is limited.

A critical challenge for making SWCNT electrodes is to develop scalable large area deposition and patterning techniques for various electronic applications, while preserving the highest electrical conductivity at high optical transparency.^{5b, 11} In chapter 4, the author reported the scalable fabrication of SWCNT films (with both the highest dc conductivity reported to date and reasonable uniformity) by pressure driven spray-coating from deionized water using sodium dodecyl sulphate (SDS) as a surfactant.^{2d}

In this chapter, we demonstrate that a recently developed patterning technique known as interlayer lithography allows for the rapid patterning of SWCNT films at the micron and sub-micron levels with a minimum of processing steps.¹² The interlayer technique involves the use of an intermediate layer of photoresist located between the substrate and the target film. The resist layer is exposed through a photo mask either before or after deposition of the target material, rendering selective parts of the resist soluble in an appropriate developer. Immersion in the developer removes the soluble parts of the resist layer together with the overlying parts of the target layer, leaving a thin patterned film of the target material over a likewise patterned film of the resist. The resist and the target material are in effect patterned simultaneously in a single expose/develop step (without the need for etching or other harsh process steps), which both reduces the number of processing steps and minimizes the risk of damage to the target material.

The interlayer method can be applied to many thin-film materials on a wide variety of substrates but, in the specific case of SWCNTs, the method has two noteworthy advantages: firstly, the nanotubes form a loose open network that is easily penetrated by the developer, allowing for fast dissolution of the resist (and hence patterning) in a matter of seconds; and, secondly, the resist material (if chosen carefully) can be made to serve also as an adhesion layer in place of commonly employed siloxanes. In practice, since adhesion layers are virtually always needed to obtain robust SWCNT films and prevent delamination from the underlying substrate, preparing SWCNT films for interlayer patterning is no more difficult than preparing standard (non-patternable) films.

Finally, a simple in-situ patterning method was developed using spray coating via a metal mask (stencil) to directly pattern the SWCNT films on the target substrates. This in-situ spray patterning method has the merit over conventional photolithography of not requiring subsequent removal of the photoresist (PR) and avoiding a number of harsh chemical process steps that may adversely affect the electrical properties of the targeted SWCNT films.^{7b, 12} Therefore this patterning method when combined with optimised acid treatments can ensure the potentially highest conductivity of thin film SWCNTs and is ideally suited to organic solar cell applications, where high resolution patterning is not required.

5.2 Experimental Details

Experimental details will be mentioned in Sections 5.3.1 and 5.3.2 with results and discussions.

5.3 Results and Discussions

5.3.1 Interlayer patterning

In this section, for rapid and high resolution patterning of SWCNT thin films, interlayer patterning method was developed. Conventional photolithography and interlayer lithography were employed to pattern as-deposited single-walled carbon nanotube films, as shown in Figure 5.1. For a conventional photolithography, the substrate was firstly treated with 1 wt % of silane (3-aminopropyltriethoxysilane, APTES) solution in DI water to improve the adhesion of CNT films onto the substrates. The SWCNT films dispersed in DI water with SDS were then spray-coated on to the substrates at 90 °C on a hot plate and the negative photoresist (PR) of SU-8 2 was then spin-coated on top of it at 4000 rpm for 40 seconds. The resist layer above the SWCNT film was next exposed through a mask by a UV light-source, initiating a cross-linking reaction that rendered the exposed regions insoluble. The PR/SWCNT substrate was then immersed in a SU 8 developer and subjected to mild ultrasonic agitation (Decon FS100b) for 30 seconds to dissolve the unexposed resist to leave a patterned layer of the cross-linked SU-8 2 on top of SWCNT film. After photolithography, oxygen plasma (100 W for 5 minutes) was employed to remove the nanotubes in the uncovered areas with a PR layer. Finally the PR was stripped off by acetone and the sample was rinsed in isopropyl alcohol (IPA), then de-ionized (DI) water and finally blown with nitrogen gas to dry.

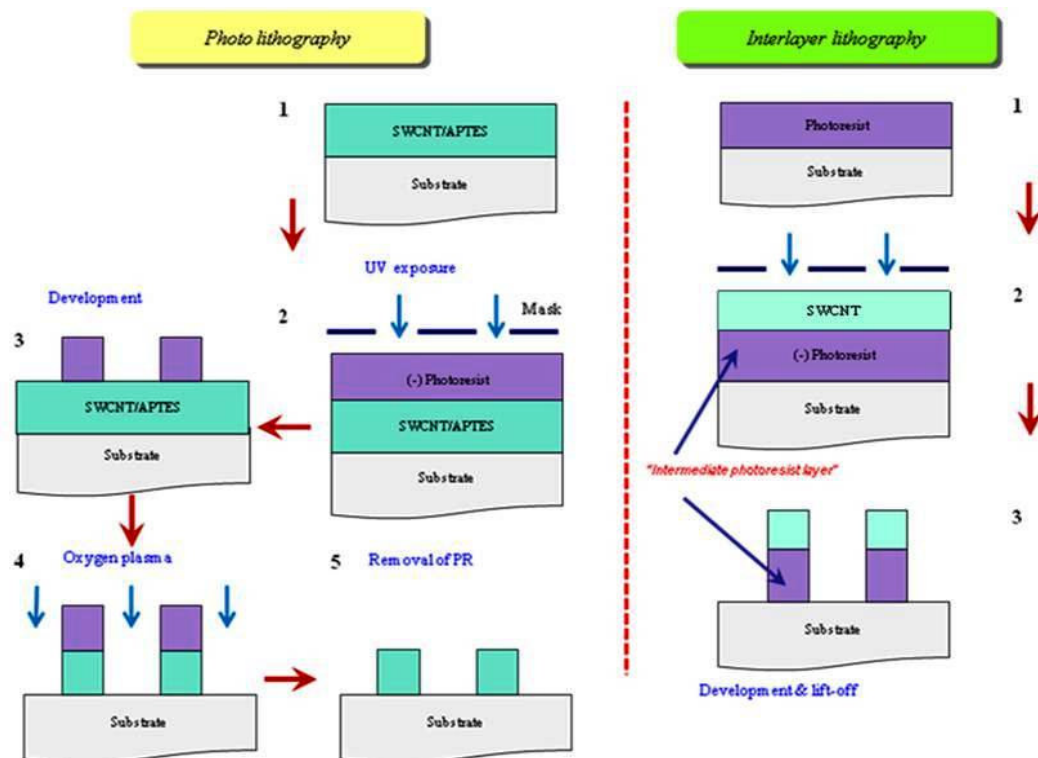


Figure 5.1 The Illustration of patterning by photolithography followed by plasma etching or interlayer lithography, as applied to spray-coated SWCNT thin films using a negative resist

A patterned thin film SWCNTs on a plastic substrate that has been prepared in this way is shown in below Figure 5.2.

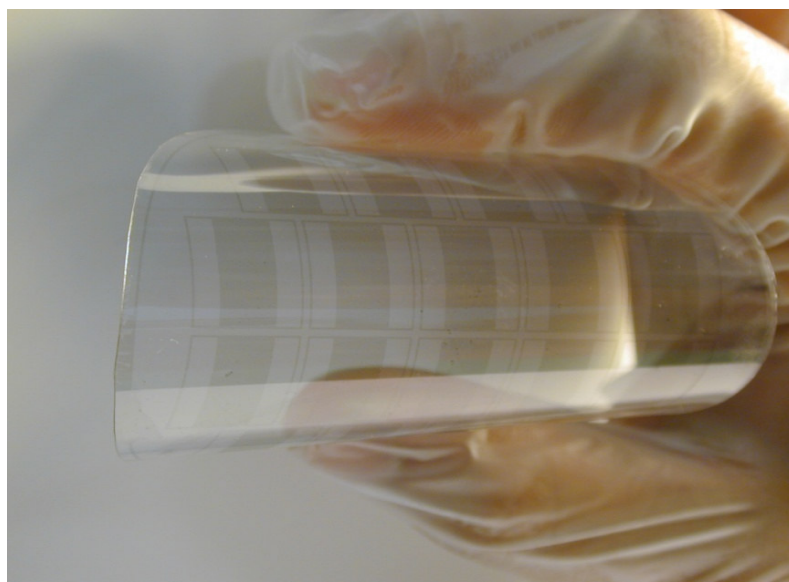


Figure 5.2 Patterned SWCNT film (spray-coated from $\text{H}_2\text{O}:\text{SDS}$) by a photolithography

Figure 5.1 also provides a schematic illustration of the interlayer method as developed at Imperial college London to pattern SWCNTs, using the negative resist SU-8 2. The resist – prediluted with an SU-8 thinner in a 1:5 weight ratio – was spin-coated on to the substrate and soft-baked at 95 °C for 1 minute, producing a resist thickness of 135 ± 10 nm. The resist layer was next exposed through a mask by a UV light-source, initiating a cross-linking reaction that rendered the exposed regions insoluble, and the substrate was then transferred to a hot-plate for a 3 minute post-exposure bake at 95 °C to complete the cross-linking of the resist. Then, 0.02 wt% solution of SWCNTs in de-ionised water containing 0.3 wt% sodium dodecyl sulfate was spray-deposited on top of the UV-exposed resist layer at 80 °C. The coated substrate was immersed in SU 8 developer and subjected to mild ultrasonic agitation (Decon FS100b) for 30 seconds to dissolve the unexposed resist and simultaneously remove the SWCNTs above, leaving a patterned layer of SWCNTs on top of an identically patterned layer of the cross-linked SU-8 2.

Finally, the patterned films were rinsed with de-ionised water to remove any residual surfactant and, for high conductivity electrode applications, they were immersed in 4 M HNO_3 overnight and soaked in 15.5 M HNO_3 for 30 minutes to oxidatively dope the SWCNTs. The acid treatment carried out here was somewhat weaker than usual so as to avoid marring the SU-8 interlayer. The films were then rinsed with de-ionised water and finally dried in a hot oven (80 °C).

Figures 5.3a and b show the interlayer patterned large area ($2.5\text{ cm} \times 2.5\text{ cm}$) arrays of lines of individual width $650\text{ }\mu\text{m}$ on glass and polyethylene naphthalate (PEN). Figure 5.3c shows an enlarged image of one of the line arrays on glass. The edges of the pattern are sharply demarcated from the exposed glass substrate, with the dark regions corresponding to the patterned SWCNTs. The total thickness of the patterned film was measured to be $165 \pm 10\text{ nm}$, implying an overall SWCNT film thickness (t) of ca. 30 nm .

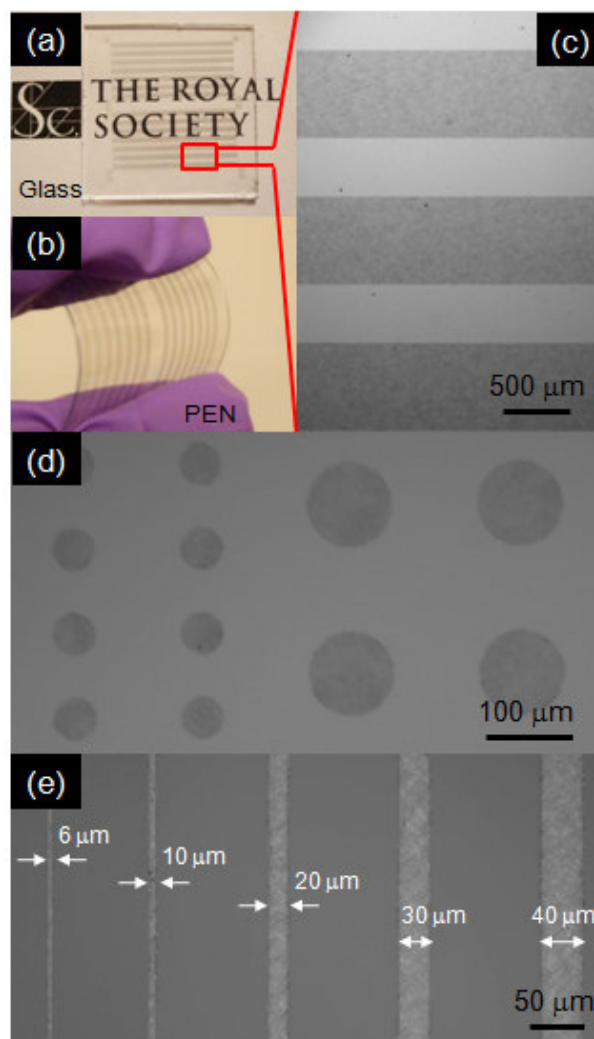


Figure 5.3 Illustration for large area ($2.5\text{ cm} \times 2.5\text{ cm}$) patterning of spray-coated SWCNTs using SU-8 2 negative resist on (a) glass and (b) PEN. Optical micrographs of (c) lines of width $650\text{ }\mu\text{m}$, (d) dots of diameter 50 and $100\text{ }\mu\text{m}$, and (e) lines of width 6 , 10 , 20 , 30 , $40\text{ }\mu\text{m}$ (all on glass substrates)

Figure 5.3d shows a series of SWCNT dots of diameters 50 and $100\text{ }\mu\text{m}$, and Figure 5.3e shows a series of lines of widths 6 , 10 , 20 , 30 , and $40\text{ }\mu\text{m}$ from left to right (all on glass). The evident ability to pattern at the micron length-scale is important for multiple applications in optoelectronics, including the fabrication of high resolution displays and image sensors.^{1b, 13}

The interlayer patterned SWCNT electrodes exhibited good optical characteristics, e.g. for $t = 30$ nm, the transmittance was found to vary between 76 to 84 % over the visible wavelength range 400 - 800 nm, as shown in Figure 5.4. The transmittance of the (uncoated) SU-8 2 interlayer was > 97 % over the same wavelength range, indicating that the presence of the interlayer had virtually no effect on the transparency of the final SWCNT electrode. The root-mean square roughness was determined using AFM microscopy to be 8 nm (inset of Figure 5. 4), which is fairly better than the pristine interlayer-free SWCNTs as described in chapter 4.

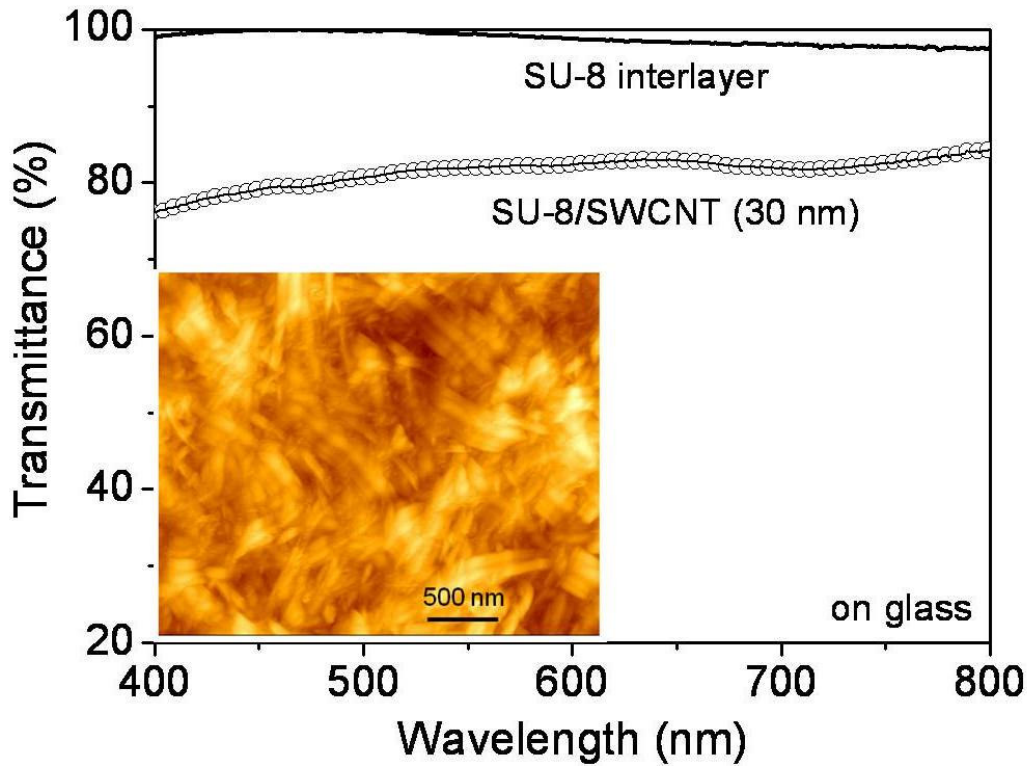


Figure 5.4 The optical transmittance of a ca. 30 nm spray-coated SWCNT film and SU-8 2 interlayer alone on glass substrates, patterned by interlayer lithography using the negative resist SU-8 2. The inset shows an AFM image of the patterned film.

The transmittance (T) and sheet resistance ($\mathcal{R}$) of the interlayer-patterned SWCNT films (8 mm x 12 mm) were investigated as a function of film thicknesses, and were both found to decay monotonically with thickness in accordance with expectation (see Figure 5.5). For example, we obtained values of $T = 95.5\%$ (at a reference wavelength of 550 nm) and $\mathcal{R} = 6,464 \pm 230 \Omega/\text{sq}$ for $t = 7$ nm, falling to $T = 69\%$ and $\mathcal{R} = 76 \pm 2 \Omega/\text{sq}$ for $t = 59$ nm. The 7 nm film exhibited a relatively low dc conductivity (σ_{dc}) of $221 \pm 8 \text{ Scm}^{-1}$ consistent with incomplete percolation,^{5d, 8} while the remaining films exhibited dc conductivities in excess of 700 Scm^{-1} , with a highest conductivity of $2,593 \pm 66 \text{ Scm}^{-1}$ being obtained for the 30 nm film.

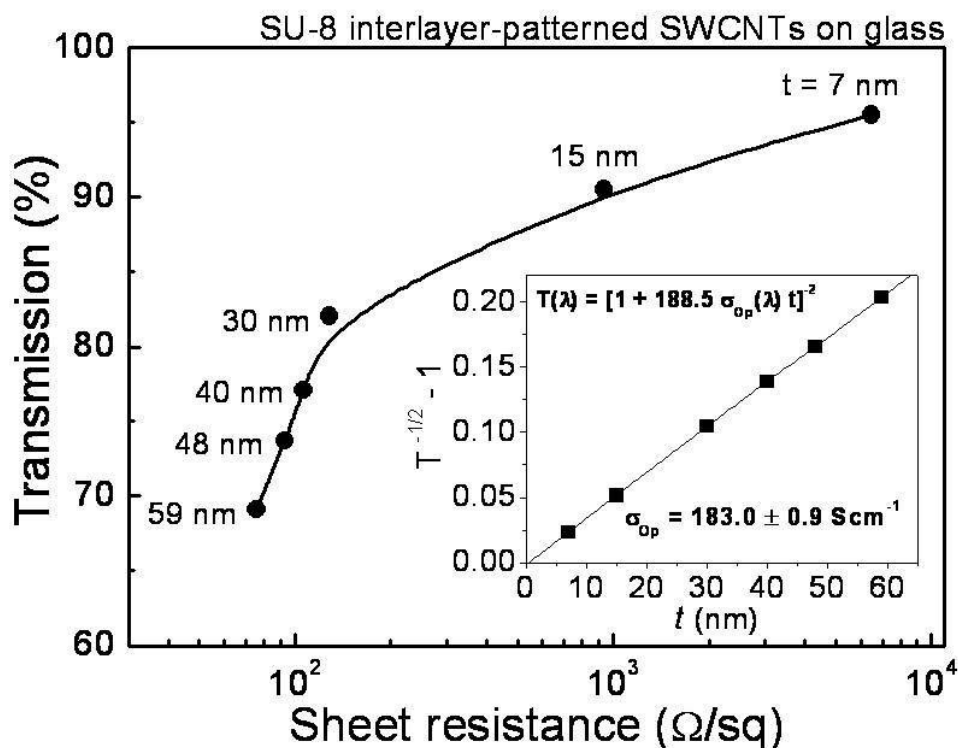


Figure 5.5 Transmittance versus sheet resistance characteristics for spray-coated SWCNT films of varying thickness – all patterned by interlayer lithography using SU-8. Inset: Transmittance versus thickness plot for the extraction of the optical conductivity; the data has been linearised in accordance with Tinkham’s formula (shown).

These dc conductivity values are slightly lower than the those for the unpatterned SWCNT films we reported in chapter 4, probably due to the reduced tube density and the gentler acid treatment that was used here to avoid damaging the interlayer.^{2d} The optical conductivity (σ_{op}), obtained by fitting the transmission versus sheet-resistance data to Tinkham’s formula, was determined to be $183 \pm 0.9 \text{ S cm}^{-1}$ for our interlayer-patterned SWCNT films, which lies inside the desirable range of 130 to 200 S cm^{-1} for highly transmissive CNT films and substantially lower (i.e. better) than the value of $480 \pm 2 \text{ S cm}^{-1}$ that we obtained for the interlayer-free SWCNT films prepared in chapter 4.^{2b, 5d, 6}

The result was attributed to the planarising effect of the SU-8 interlayer and the consequent reduction in optical scattering. The ratio of the dc to optical conductivity (σ_{dc}/σ_{op}) was in the range 10 - 14, which is considered reasonably good (but not remarkable) characteristics for SWCNT films. (Higher values are better).

The negative resist SU-8 can be used to pattern SWCNT films with feature sizes down to a few microns. To achieve sub-micron resolution, however, it is generally necessary to use a positive resist. Here, we used AZ 7220, which is widely used for high resolution patterning of silicon. The interlayer patterning procedure was carried out as follows: (i) The positive photoresist AZ 7220 (Clariant, as received), was spin-coated on a Si substrate at 4000 rpm for 40 seconds and soft-baked at 110 °C for 90 seconds; (ii) The SWCNT layer was then spray-coated on the exposed resist as before (the post-exposure bake was omitted since this step is not required for a positive resist); (iii) The films were exposed to 119 mJ cm⁻² of 365 nm radiation using a Karl Suss MA/BA 6 mask aligner patterning; and (iv) The films were developed by 120 seconds immersion in MIF 300 developer with intermittent ultrasonication. (every 30 seconds)

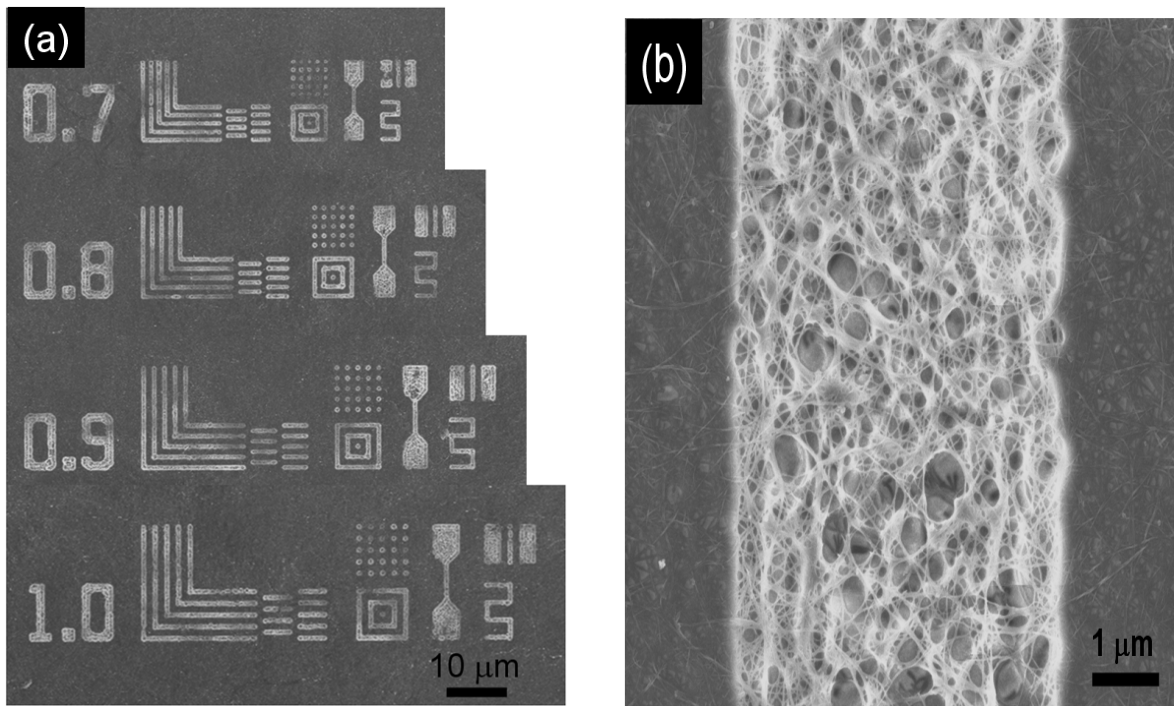


Figure 5.6 SEM images of spray-coated SWCNTs on Si, patterned by a interlayer lithography using the positive resist AZ 7220, showing (a) various features of width 0.7 to 1.0 μm and (b) a line of width 5 μm .

Figure 5.6 shows SEM images of spray-coated SWCNTs ($t = 30$ nm) patterned using AZ 7220 on a Si substrate, using a series of mask patterns with progressively decreasing feature sizes (from bottom to top). The minimum feature size in each image is indicated in microns by the digit on the left hand side, and it is evidently possible to obtain high resolution patterns down to sub-micron length scales (~ 0.7 μm) due to the enhanced resolution of the positive resist and associated equipment.

In Figure 5.6b, we show a high resolution SEM image of a thin line of width $5\mu\text{m}$, which revealed the structure of the SWCNT network on the resist layer and showed the clear demarcation of the SWCNTs from the adjacent regions of uncoated substrate. Although there was a small amount of residual *debris* in the uncoated regions, this was due to imperfect removal of unwanted material by the intermittent ultrasonic treatment, and should be easily avoidable by use of an alternative resist material. The ability to pattern at micron and sub-micron length scales is important for the fabrication of high-speed transistors requiring short channel lengths, and offers an attractive route to fabricating high density integrated circuits.¹³⁻¹⁴

Interlayer patterned SWCNT films were mechanically robust and were found to expel surfactant readily when treated with acid.¹⁵ They showed no tendency to delaminate from the underlying substrate during routine handling either before or after acid treatment. In fact, similar films on flexible polyester (PET) substrates have proven to be extremely resilient, showing no tendency to fracture or wear even when flexed repeatedly to a radius $< 5\text{ mm}$, as shown in Figure 5.7.

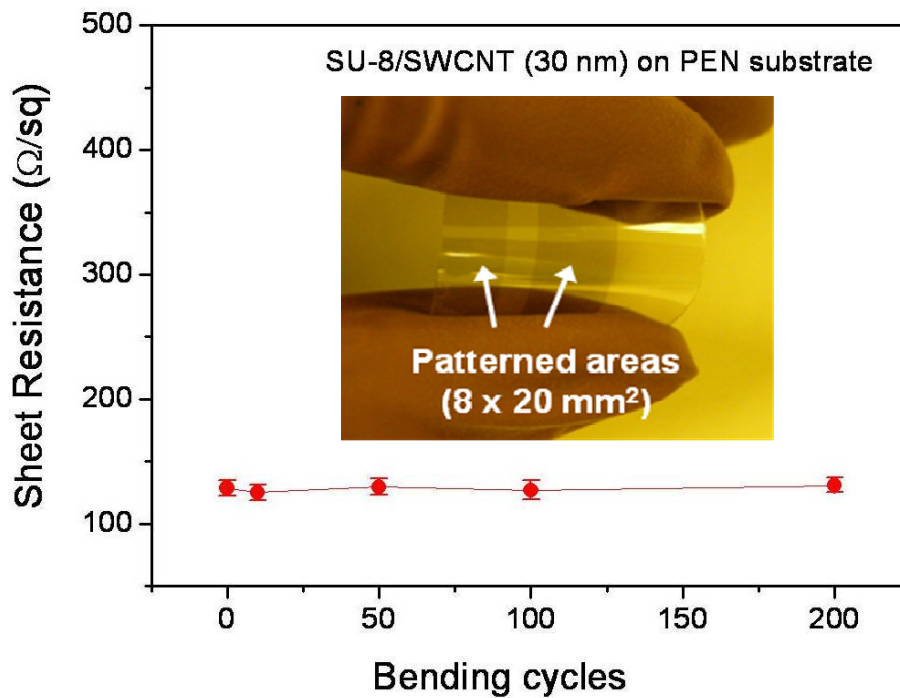


Figure 5.7 Influence of repetitive flexing on the sheet resistance of a interlayer patterned SWCNT electrode on PET. A bending radius of 5 mm was used for the measurements.

Overall, we have found interlayer lithography to be an effective method for the high resolution patterning of thin film SWCNTs on glass, silicon and PEN substrates. Using a 135 nm layer of the negative resist SU-8 2 coated with a 30 nm layer of SWCNTs, we were able to achieve patterns with a minimum feature size of

6 μm , suitable for a variety of optoelectronic devices, including light-emitting diodes, solar cells, and transistors. Switching to the positive resist AZ 7220 on Si allowed for the patterning of submicron features.

5.3.2 In-situ spray patterning

For feature sizes of several hundred microns and above, deposition through a contact stencil (placed directly above the substrate) can provide a simple and faster method for patterning SWCNT thin films. Here, in-situ spray patterning of thin film SWCNTs via a metal mask was compared with a combination of conventional photolithography and plasma dry etching. In both cases, the 2-step nitric acid treatment was used to remove the residual surfactant and induce a p-doping effect to maximize the electrical conductivity.

Figure 5.8 illustrates an in-situ spray coating/patterning method with a pattern mask to fabricate SWCNT electrodes. The SWCNT solution was directly spray coated through the pattern mask onto clean glass substrates. The in-situ patterned SWCNT films beneficially avoid any contact with potential organic contaminants such as photoresists or other wet etching chemicals. Such patterned films can therefore potentially lead to a higher electrical conductivity via more efficient nitric acid doping than patterned SWCNT films prepared by wet lithographic etching.

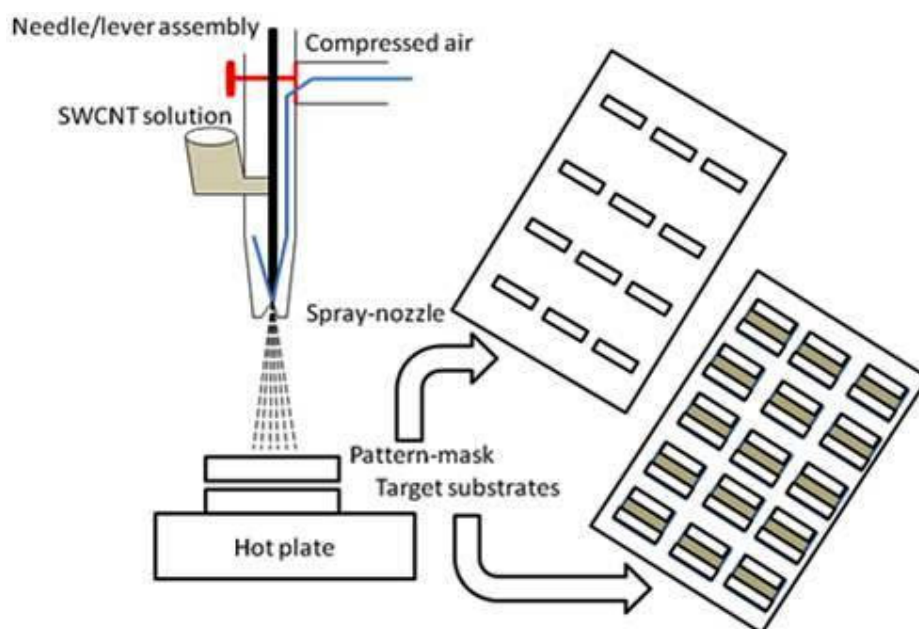


Figure 5.8 A schematic diagram of the process for the in-situ spray patterning technique.

The details of preparing the spray-patterned SWCNT films are as follows: Commercially sourced arc-made SWCNTs (Hanhwa Nanotech., purity of 60 - 70 wt%, diameter of 1.0 - 1.2 nm and length of 5 - 20 μm) were dispersed at approximately 0.03 wt.% in water containing 0.3 wt.% of pre-dissolved SDS (denoted $\text{H}_2\text{O}:\text{SDS}$). The SWCNT solution was then deposited onto heated glass substrates at 90 °C using a simple pressure-driven airbrush through a pattern mask. The film thickness was controlled by holding the spray conditions constant and varying the amount of deposited material. The patterned SWCNT films were immersed in 4 M HNO_3 overnight, rinsed with de-ionised water, immersed again in 15.5 M HNO_3 for 2 hours, and rinsed thoroughly with de-ionised water before being dried with a nitrogen gun at room temperature.

The optical and electrical characteristics of in-situ patterned films were then compared with the properties of photolithography patterned films. Both types of films were made from the same batch of SWCNT solution. Stencil- and lithographically-patterned films of varying thickness were characterised by AFM to have similar root mean square roughnesses of ~ 7 nm – fairly good for pressure-driven spray deposition. Figure 5.9 shows SEM images of an in-situ spray patterned film and a photolithography patterned film after acid treatments.

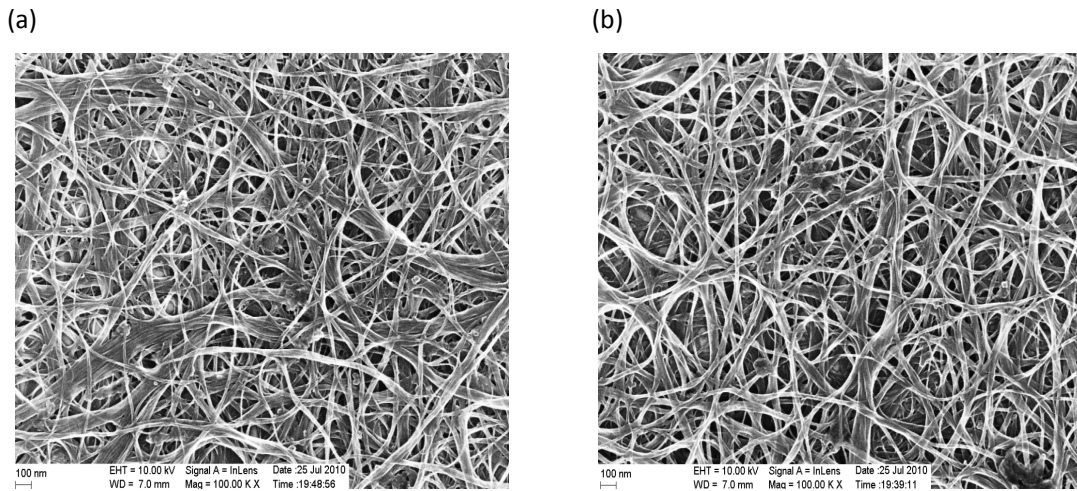


Figure 5.9 Field-Emission SEM images for films, (a) in-situ spray-patterned from $\text{H}_2\text{O}:\text{SDS}$ (51 Ω/sq), (b) photo-lithography/plasma etching patterned from $\text{H}_2\text{O}:\text{SDS}$ (58 Ω/sq).

Figure 5.10a shows the transmittance (T) versus sheet-resistance (R_s) trade-off characteristics for the two sets of films. The trade-off characteristics were similar in both cases, with for instance the stencil patterned films showing $T = 69\%$ at $R_s = 51\ \Omega/\text{sq}$ and the lithographically patterned films showing $T = 71\%$ at $R_s = 58\ \Omega/\text{sq}$.

However, further examination by Raman spectroscopy revealed a clear difference in the defect densities. Figure 5.10b shows normalised 633 nm Raman spectra for the 51 Ω/sq stencil-patterned film and the 58 Ω/sq lithographically patterned film. The two spectra have a similar overall appearance, although the ratio of the defect mode (D) peak intensity to the tangential shear mode (G) peak intensity is approximately forty percent higher for the lithographically patterned films, indicating a higher degree of process-induced damage to the crystalline quality.¹⁶ (see Table 5.1) Hence, stencil-patterning appears to be a preferable patterning method for lower resolution applications.

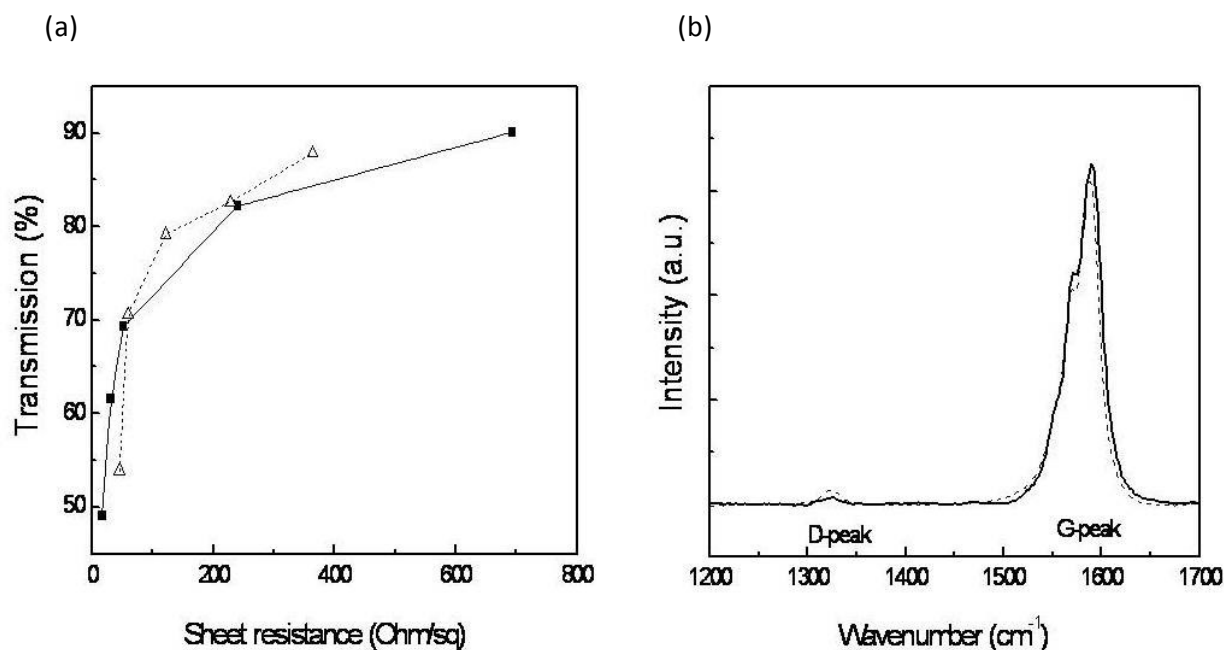


Figure 5.10 (a) Transmission versus sheet resistance “trade- off” characteristics for thin-film SWCNTs spray-coated from $\text{H}_2\text{O}:\text{SDS}$ and patterned from an in-situ spray pattern mask (line) versus a photolithography/plasma etching (dashed), (b) Raman spectra for SWCNT films spray patterned with a metal mask (line, 51 Ω/sq) versus films patterned via photolithography/plasma etching (dashed, 58 Ω/sq)

Table 5.1 Raman spectra of SWCNT films patterned by in-situ spray and photolithography

	D peak	G peak	I(d) / I(g)
In-situ spray	1322.6 cm^{-1}	1590.3 cm^{-1}	2.7 %
Photolithography	1322.6 cm^{-1}	1588.6 cm^{-1}	5.0 %

We then optimised the in-situ spary patterned SWCNT electrodes as shown in Figure 5.11. With around 30 nm thick SWCNT films, we could obtain a sheet resistance of $51 \pm 0.1 \Omega/\text{sq}$ at 69% transmission, corresponding to a dc conductivity of $6,532 \pm 15 \text{ S}\cdot\text{cm}^{-1}$. The ratio of the dc to optical conductivity (σ_{dc}/σ_{op}) was in the range 18 - 24 depending on film thickness, being considered state of the art characteristics for SWCNT films.

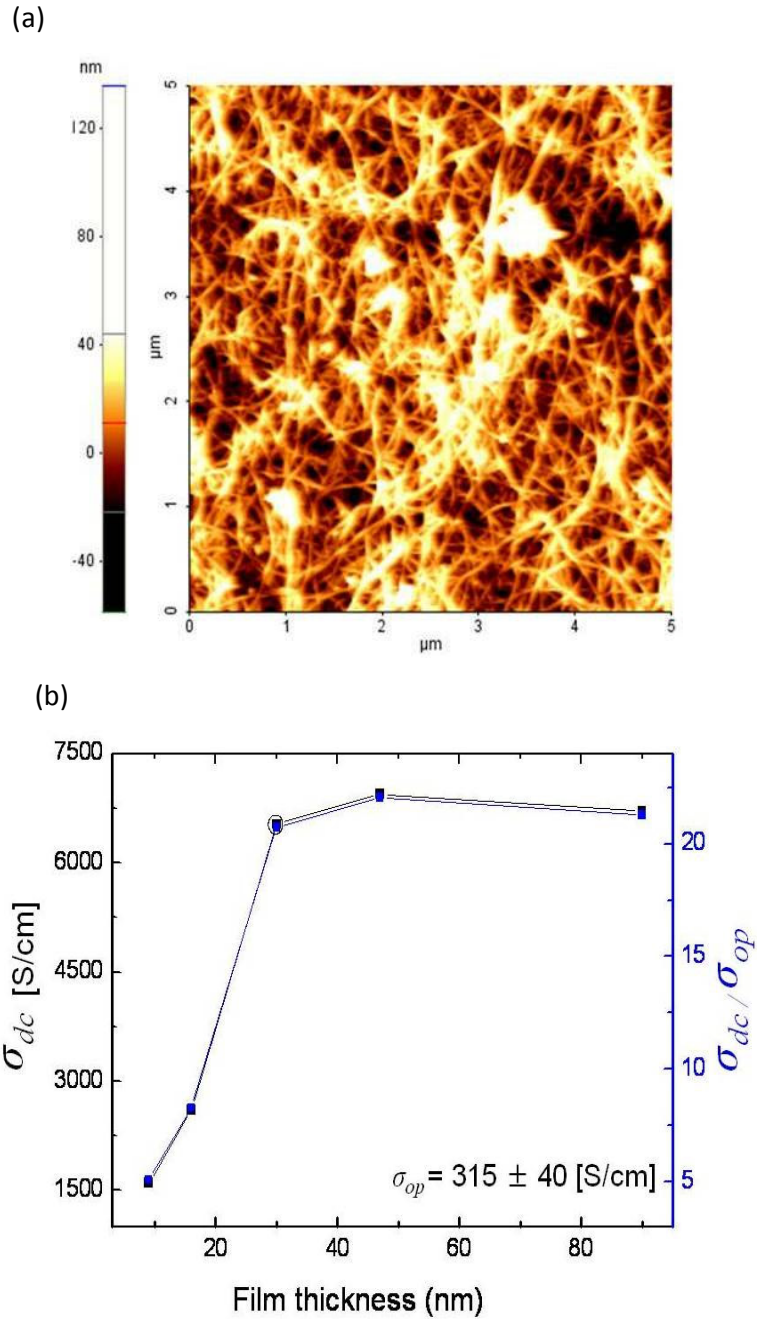


Fig. 5.11 (a) $4 \mu\text{m} \times 4 \mu\text{m}$ Atomic Force Micrographs for thin-film SWCNTs stencil patterned from $\text{H}_2\text{O}:\text{SDS}$ (30 nm) on glass, (b) Thickness dependence of electrical conductivity for thin-film SWCNTs in-situ spray-patterned from $\text{H}_2\text{O}:\text{SDS}$. (A 30 nm thick film is circled. This film was selected for the OPV device applications in chapter 6)

Finally, using the in-situ spray patterning method with a pattern mask of 10 μm channel length, SWCNT films with source-drain patterns for thin film transistor applications were demonstrated as shown in Figure 5.12. High resolution optimisation for device applications remains as a further task.

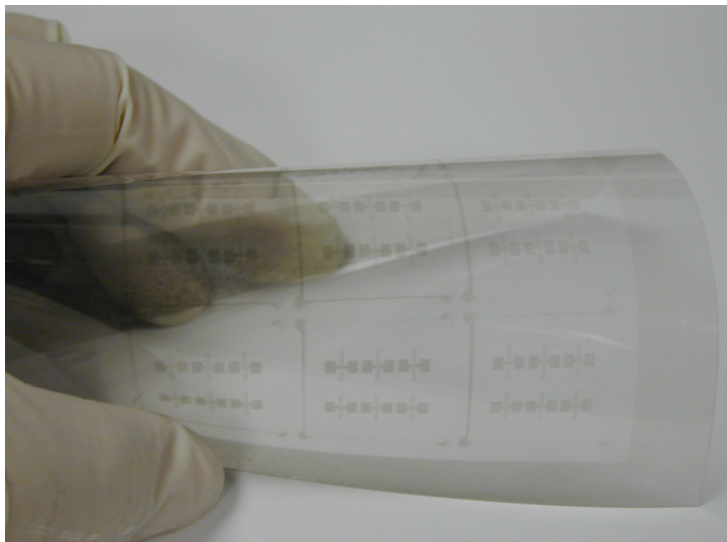


Figure 5.12 The optical image for in-situ spray patterned SWCNT films (10 cm $\times$ 10 cm) with 10 μm channel length

5.4 Conclusion

In conclusion, Interlayer lithography provides a fast and high resolution pattern for SWCNT thin films at micron and sub-micron length scales, which is important for the fabrication of high-speed transistors requiring short channel lengths, and offers an attractive route to fabricating high-density integrated circuits. The patterned SWCNT films (ca. 30 nm) on [SU-8 2] exhibited good transparency in the visible ($> 77\%$ at 550 nm), and a moderate dc conductivity of $2,860 \text{ Scm}^{-1}$.

In-situ spray patterning gives a simple and fast method and is well suited for low resolution electronic device applications such as organic solar cells. Highly conductive and smoothly patterned SWCNT thin films (ca. 30 nm) were easily obtained with more than $6,500 \text{ Scm}^{-1}$ at $> 69\%$ transmittance using the in-situ spray patterning method.

These two patterning methods can be used to prepare mechanically robust spray-coated SWCNT films. In addition, we further find that interlayer method yields rapid, high resolution patterning for SWCNT thin

films, while in-situ spray patterning can lead to the simple, faster, and medium-low resolution patterning suitable for organic solar cells applications.

All the patterned SWCNT films exhibited sheet resistances of around 100 Ω/sq at reasonable transmission, for example, $128 \pm 3 \Omega/\text{sq}$ at 82% for interlayer patterning, $51 \pm 0.1 \Omega/\text{sq}$ at 69% for in-situ spray patterning, compared to $58 \pm 2 \Omega/\text{sq}$ at 71% for photolithography and oxygen plasma etching.

Peak values for the ratio of the dc conductivity to the optical conductivity ($\sigma_{\text{dc}}/\sigma_{\text{op}}$) were obtained as follows: 14 ± 0.7 for interlayer patterning, 20.7 ± 3 for in-situ spray patterning, and 12.6 ± 2.8 for photolithography and oxygen plasma etching. We should note that for interlayer patterning, the gentler post-acid treatment was used to avoid damaging the interlayer, which led to the lowered value of $\sigma_{\text{dc}}/\sigma_{\text{op}}$. The results are summarized in Table 5.2.

Table 5.2 The optimised results for SWCNT films made with different patterning methods.

	$R_s [\Omega/\text{sq}]$	$T [\%]$	$\sigma_{\text{op}} [\text{Scm}^{-1}]$	$\sigma_{\text{dc}} [\text{Scm}^{-1}]$	$\sigma_{\text{dc}} / \sigma_{\text{op}}$
Interlayer patterning	128 ± 3	82	183 ± 0.9	2593 ± 66	14.0 ± 0.7
In-situ spray patterning	51 ± 0.1	69	315 ± 40	6532 ± 15	20.7 ± 3
Photolithography/ plasma etching	58 ± 2	71	302 ± 44	3805 ± 187	12.6 ± 2.8

5.5 References

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Chapter 6 Organic solar cells with SWCNT electrodes

6.1 Introduction

Organic solar cells offer a promising route to low cost sustainable electricity generation due to their potential for high volume manufacturing on flexible plastic substrates.¹ A key obstacle to successful commercialisation, however, is the absence of high performance flexible electrodes that can be processed at plastic-compatible temperatures ($< 150\text{ }^{\circ}\text{C}$).² For rigid applications, indium tin oxide (ITO) is the transparent conductor of choice, but its high cost, tendency to crack when flexed, and need for high temperature processing ($> 350\text{ }^{\circ}\text{C}$) are problematic for large area solar applications.³

Due to their high work function (4.7 - 5.0 eV), solution processability in ambient environments and mechanical flexibility, SWCNT thin films have been intensively investigated as a potential replacement for ITO in organic photovoltaic (OPV) devices, with the most promising results to date having been achieved using films prepared by spray-coating or a combination of vacuum filtration and transfer printing.⁴

Anodes based on filter/transfer (FT)-derived SWCNT films with high conductivities of up to 6700 S/cm ,⁵ have been reported to give power conversion efficiencies (PCEs) as high as 2.5 % in polythiophene/fullerene OPV devices, compared to 3 % for ITO-based reference devices.⁶ But the limited scalability of the FT technique is problematic for large area solar applications.

Tenent et al. have reported spray-coating to be a preferable technique for fabricating large area SWCNT electrodes.⁷ They obtained their best results using electrodes spray-coated ultrasonically from an aqueous stock solution of laser-vaporised SWCNTs, using carboxymethyl cellulose (CMC) as the dispersant. Polythiophene/fullerene devices based on CMC-derived anodes gave high PCEs of 3.1 %, compared to 3.6 % for equivalent ITO-based reference devices. However, the use of CMC as a surfactant complicates their handling in a manufacturing environment.

In this chapter, we used the dispersion, deposition, and patterning methods for making SWCNT electrodes, reported in chapters 4 and 5, and fabricated bulk-heterojunction polymer solar cells to evaluate their suitability as methods for preparing high quality devices.

To enable the successful use of SWCNT electrodes in polymer solar cell applications, several problems were tackled in advance. The wetting of the hydrophobic SWCNT films was enhanced to enable the spin-coating of a PEDOT:PSS layer, which is needed to planarize the rough surface of the SWCNT electrodes, and so reduce the risk of electrical shorting.⁸ (The use of PEDOT:PSS has also been reported to decrease the sheet resistance by 20 % due to the provision of additional conduction paths from the PEDOT:PSS layer and a potential p-doping effect by PSS on the SWCNT films.⁹) The device fabrication conditions were also optimised to the SWCNT electrode. The film thicknesses for the PEDOT:PSS and P3HT:PCBM layers were optimized to extract the maximum current, and the optimal annealing temperature to achieve a better morphology of the polythiophene/fullerene layer for enhanced charge separation was found, as described in chapter 3.^{1b, 10} A flexible solar cell made with SWCNT films on a plastic substrate was finally demonstrated, although further work remains to be done in the optimisation of device fabrication for (plastic) compatible low temperature processing.

6.2 Experimental Details

6.2.1 Deposition, Patterning of the SWCNT thin films and Fabrication of organic solar cells therewith

The SWCNT suspension was prepared as described in chapter 4. The cleaned substrates (glass or plastics) were then coated with SWCNT solutions in one of two ways: (i) repetitive spin-coating from DCE at room temperature; or (ii) spray-coating on to a heated substrate at 90°C from H₂O:surfactant mixtures using an air brush [Graphics Direct Ltd] with a 0.4 µm nozzle. Figures 6.1 shows uniformly deposited SWCNT films with little aggregation obtained by spin-coating from surfactant-free DCE.

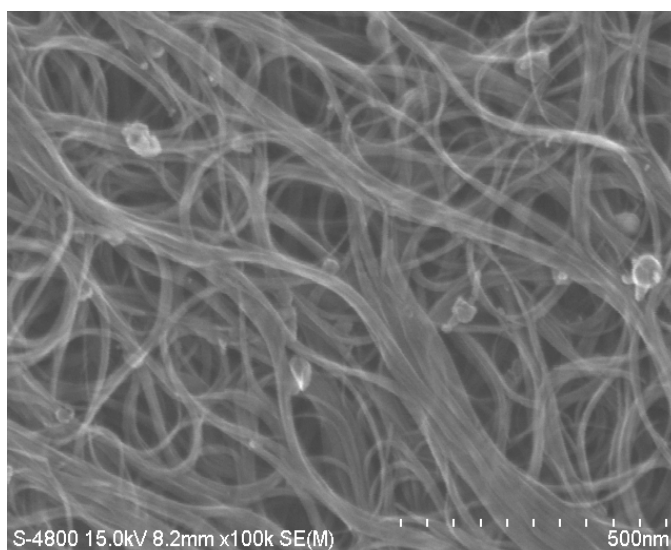


Figure 6.1 The Field-Emission SEM image of a 25 nm SWCNT film, spin-coated from DCE.

To pattern the SWCNT films for OPV devices, (i) conventional photolithography in combination with plasma etching, (ii) interlayer-lithography, and (iii) in-situ spray patterning methods were employed, as described in chapter 5. The patterned SWCNT films were immersed in 4 M HNO_3 overnight and soaked in 15.5 M HNO_3 for 30 minutes to 2 hours, rinsed thoroughly with de-ionised water, and finally dried with a nitrogen gun.

P3HT:PCBM bulk-heterojunction solar cells were fabricated by spin-coating onto each electrode a 35 - 40 nm layer of PEDOT: PSS (Baytron P). A 175 - 260 nm layer of regioregular poly(3-hexylthiophene) (P3HT, Merck Chemicals Ltd.) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{60} (PCBM, API Services, Inc.) was then deposited by spin-coating from a 1:0.7 blend of the two components in chlorobenzene. The devices were completed by thermal deposition of LiF (1 nm) capped with a thick layer of Al (100 nm), and they were finally annealed in a dry N_2 atmosphere at 140 - 150 $^\circ\text{C}$ for 30 minutes, as shown in Figure 6.2.

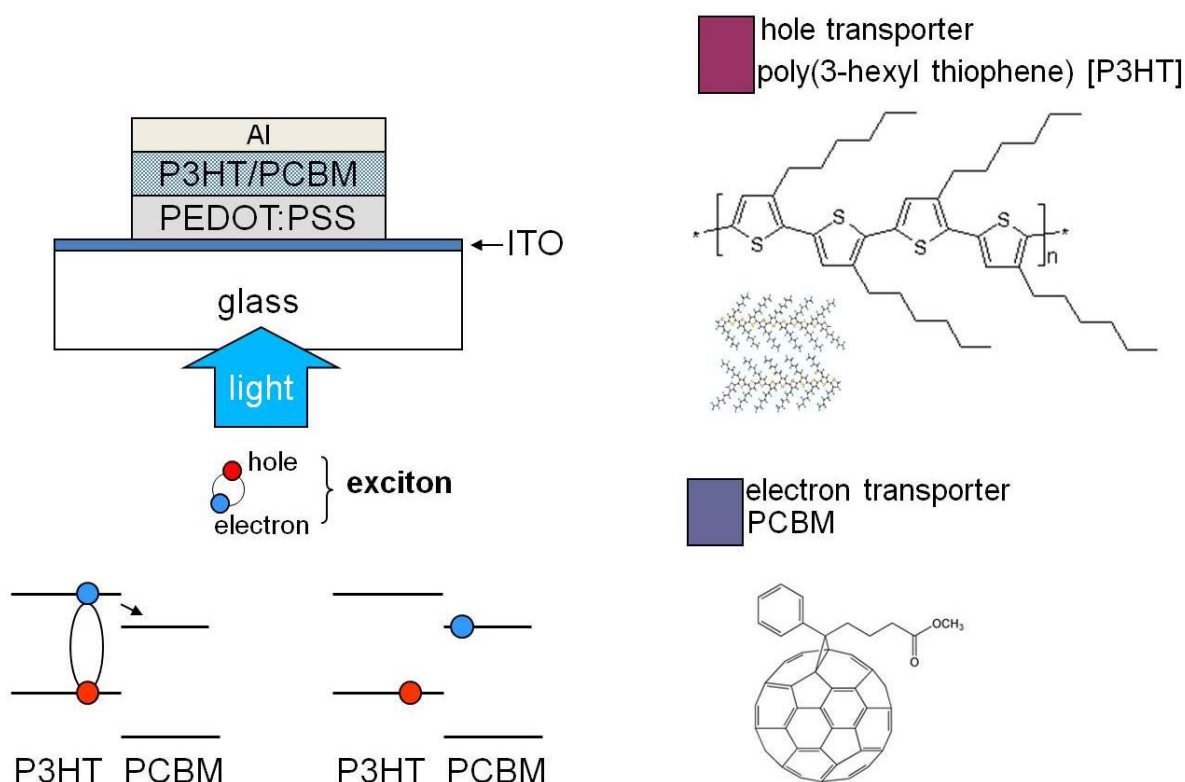


Figure 6.2 The device structure for the bulk-heterojunction organic solar cells.

Contact angle measurements were undertaken using a Kruss Drop Shape Analysis System, DSA 10 with a 40 μl droplet of HPLC-grade water. A tungsten-halogen lamp solar simulator was used to obtain the current-voltage characteristics of the devices at AM 1.5 illumination.¹¹ Action spectra were obtained using the monochromated output of a Xenon lamp, referencing the measured photocurrent against that obtained with a calibrated silicon photodiode.

6.3 Results and Discussions

6.3.1 The improved wetting characteristics of the SWCNT electrodes

In our initial studies, we compared SWCNT films spin-coated from DCE with films spray-coated from $\text{H}_2\text{O}:\text{SDS}$ and $\text{H}_2\text{O}:\text{SDBS}$. However, the fabrication of organic solar cells was complicated by the extreme hydrophobicity of SWCNT films,¹² which makes it difficult to deposit a uniform surface-coating of poly(3,4-ethylenedioxythiophene): polystyrene:sulphonate [PEDOT:PSS].^{3a} PEDOT:PSS is widely used as a current spreading layer on top of transparent conductors to ameliorate the effects of asperities in the underlying material and to increase the effective work function and conductivity.



Figure 6.3 The wetting characteristics of the SWCNT films before (left) and after (right) spin-treatment with ethanol. In all cases there is a substantial reduction in contact angle after treatment, indicating improved wetting which is essential for subsequent deposition of PEDOT:PSS. The wetting characteristics for a water droplet on untreated ITO-coated glass are also shown for comparison.

The high hydrophobicity of the SWCNT films is apparent from the left-hand side of Figure 6.3, which shows the wetting characteristics of water droplets on pristine spin- and spray-coated SWCNT films: for the spin-coated film from DCE, the contact angle (θ_c) was $98^\circ \pm 2^\circ$; for the spray-coated film from $\text{H}_2\text{O}:\text{SDS}$, θ_c was $105^\circ \pm 2^\circ$; and for the spray-coated film from $\text{H}_2\text{O}:\text{SDBS}$, θ_c was $110^\circ \pm 7^\circ$. The wetting characteristics on typical ITO-coated glass are also shown, for which the contact angle was just $38^\circ \pm 3^\circ$, indicating much better wetting than for any of the SWCNT films.

Treatment with water-miscible short-chain alcohols has previously been shown to induce significant chemical and physical changes in the surface properties of SWCNT films, leading to improved wetting characteristics.¹³ The right-hand side of Figure 6.4 shows the wetting characteristics for the same SWCNT films after a simple spin-treatment with ethanol at 1500 rpm for one minute. For the spin-coated film from DCE, θ_c was reduced by about 15° to $83^\circ \pm 2^\circ$; for the spray-coated film from $\text{H}_2\text{O}:\text{SDS}$, θ_c was reduced by about 23° to $82^\circ \pm 1^\circ$; and, for the spray-coated film from $\text{H}_2\text{O}:\text{SDBS}$, θ_c was reduced by about 35° to $75^\circ \pm 1^\circ$. In all cases, the spin-treatment improved the wetting sufficiently to allow smooth films of PEDOT:PSS to be deposited on top of the SWCNTs by simple spin-coating.

6.3.2 Spin and spray coated SWCNT electrodes for OPV applications

Spin-coated SWCNT films from DCE and spray-coated films from $\text{H}_2\text{O}:\text{SDS}$ and $\text{H}_2\text{O}:\text{SDBS}$, as shown in Table 6.1, were used as transparent anodes for bulk-heterojunction solar cells comprising an active layer of poly(3-hexylthiophene) (P3HT) and phenyl- C_{61} -butyric acid methyl ester (PCBM), and LiF/Al cathode. Control devices using ITO anodes were also fabricated.

Table 6.1 Physical characteristics of ITO and SWCNT electrodes for device fabrication

Anode	Thickness [nm]	Sheet Resistance [$\Omega/\text{sq.}$]	Conductivity [S cm^{-1}]	Transmission at 550 nm [%]	Work function [eV]
ITO/glass	150	15	4444	97	4.8
SWCNT/glass (DCE)	24	128	4629	90	4.9
SWCNT/glass ($\text{H}_2\text{O}:\text{SDS}$)	26	57	6704	65	4.8
SWCNT/glass ($\text{H}_2\text{O}:\text{SDBS}$)	28	68	5230	70	4.8

Following the spin-treatment of the SWCNT films with ethanol, P3HT:PCBM bulk-heterojunction solar cells were fabricated by spin-coating onto each electrode a 40 nm layer of PEDOT:PSS (Baytron P), followed by a ~175 nm layer of P3HT(Merck Chemicals Ltd.):PCBM(API Services, Inc.) from a 1:0.7 blend by weight of the two components in chlorobenzene.

The devices were completed by thermal deposition of a LiF(1nm)/ Al(100nm) cathode, and were finally annealed in a dry N₂ atmosphere at 150 °C for 30 minutes. The pixel size defined by the spatial overlap of the SWCNT anode and the LiF/Al cathode was 0.045 cm².

Figure 6.4a shows the current-voltage characteristics (under one-sun solar illumination) of solar cells fabricated using the anodes in Table 6.1. Figure 6.4b, shows the spectral response curves under low intensity illumination for the devices. The device with an anode spray-coated from H₂O:SDS had an open-circuit voltage of 0.59 V, while the other three devices had virtually identical open-circuit voltages of ~0.55 V. Strikingly, the highest short-circuit current of 9.9 mA/cm² was obtained for the device with a SWCNT anode spin-coated from DCE, around 18 % higher than the equivalent device with an ITO anode (8.4 mA/cm²) despite its poorer transmission and sheet resistance characteristics. The devices with spray-coated SWCNT anodes had lower short-circuit currents of 7.3 and 6.7 mA/cm² for H₂O:SDS and H₂O:SDBS, respectively. The lower values are partly attributable to their poorer transmission characteristics: 65 % and 70 % at 550 nm for the devices deposited from H₂O:SDS and H₂O:SDBS, respectively, compared with 90 % for the device deposited from DCE, as shown in Table 6.2.

The device with a spin-coated SWCNT anode had a fill-factor of 43 % compared to 50 % for the ITO device, resulting (coincidentally) in the same overall power conversion efficiency of 2.3 % at the maximum power point. The observed maximum power conversion efficiency of 2.3 % is fairly low for an ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al device, which is mainly due to the specific batch of P3HT (Merck Chemical Ltd.) employed for this work. The devices with spray-coated anodes had fill-factors of 46 and 31 % for H₂O:SDS and H₂O:SDBS, yielding maximum power conversion efficiencies of 2.2 and 1.2 %, respectively. The first of these efficiency values is especially encouraging, being at virtual parity with the ITO-based device despite the SWCNT film having been deposited by a scalable ambient process. The substantially lower PCE of the SDBS device is consistent with the markedly lower slope of its current-voltage curve in the range of $V > V_{oc}$, which indicates significantly higher electrode series resistance. This is in turn consistent with the high surface roughness of the spray-coated film from H₂O:SDBS, which would be expected to result in relatively poor contact with the adjacent PEDOT:PSS layer, hindering the extraction of holes.

The dark J-V curve also indicates that the device fabricated with the rougher SWCNT films had higher dark currents, with lower shunt resistance and poor rectification. Their devices made with a spray-coated film from H₂O:SDBS had an extremely poor rectification ratio of ~ 10 (± 1 V), whereas the other devices had a rectification ratio of $\sim 10^2$.¹⁴ (see Figure 6.4c)

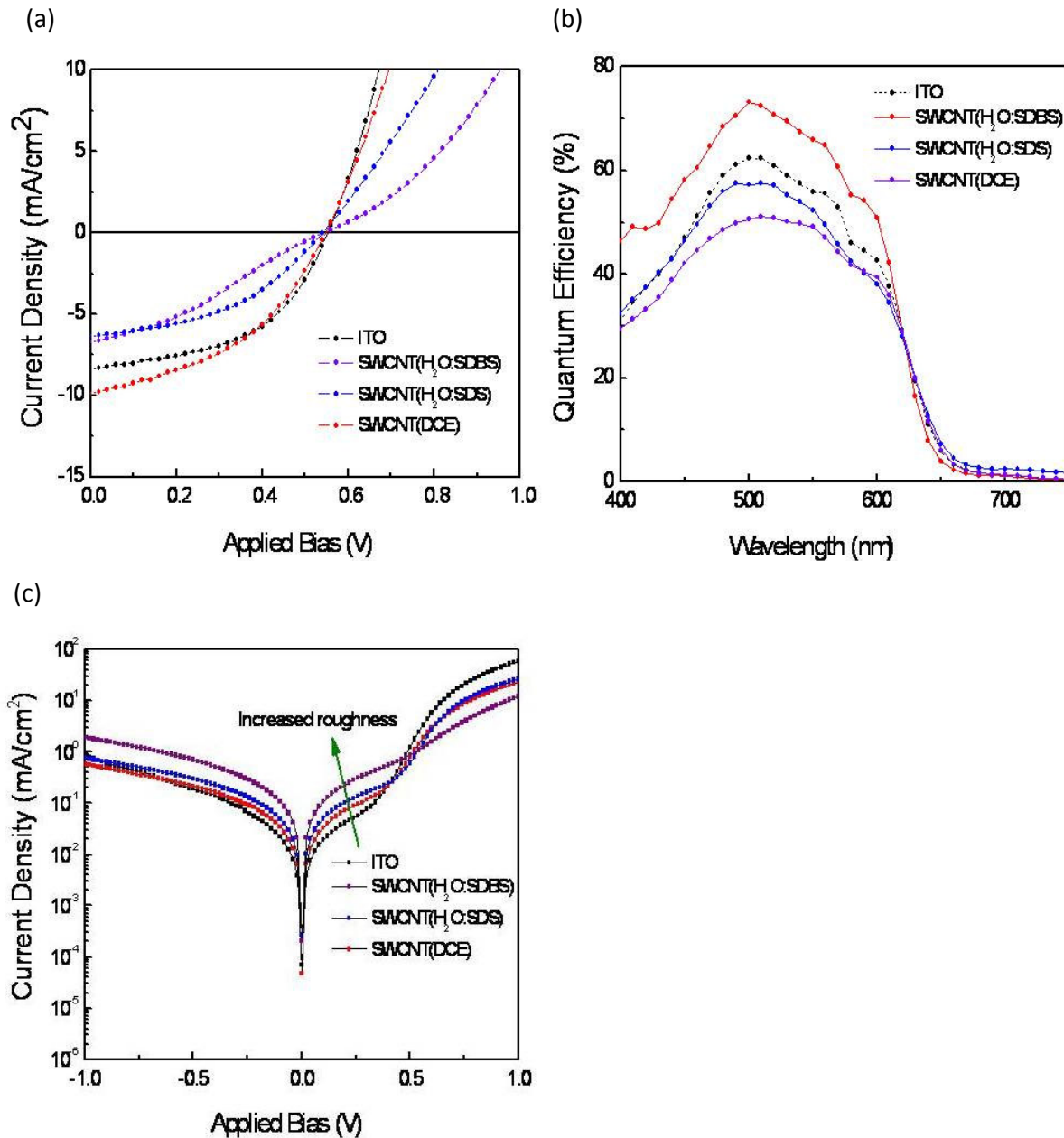


Figure 6.4 (a) Current-voltage characteristics under one-sun illumination (100 mW cm⁻²) for P3HT:PCBM bulk-heterojunction solar cells based on the SWCNT anodes from Table 6.1, and with the general structure SWCNT(24-28nm)/PEDOT:PSS(40nm)/P3HT:PCBM(175nm)/LiF(1nm)/Al(100nm). The current-voltage characteristics of an equivalent device fabricated on ITO-coated glass (15 Ω /sq.) are also shown for comparison, (b) External quantum efficiency, and (c) Dark current-voltage characteristics for the same devices.

Table 6.2 Device characteristics of OPVs fabricated using ITO and SWCNT electrodes

Anode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
ITO/glass	0.55	8.4	50.0	2.3
SWCNT/glass (DCE)	0.55	9.9	43.1	2.3
SWCNT/glass (H_2O :SDS)	0.59	7.3	46.4	2.2
SWCNT/glass (H_2O :SDBS)	0.55	6.7	31.3	1.2

6.3.3 Spray coated SWCNT electrodes from H_2O :CMC for OPV applications

The effect of the surface roughness of the SWCNT electrodes on the OPV performance was further investigated by comparing the SWCNT films spray-coated from different anionic surfactants. Spray coated SWCNT films from H_2O :SDS and H_2O :CMC were prepared, as shown in Table 6.3. As mentioned in chapter 4, the spray coated SWCNT films from H_2O :CMC have an especially low (r.m.s.) roughness of ~ 5 nm compared to SWCNT films from H_2O :SDS with a (r.m.s.) roughness of ~ 12 nm. P3HT:PCBM bulk-heterojunction solar cells using SWCNT electrodes prepared from both surfactant systems were then fabricated with the same process conditions mentioned in Section 6.3.2.

Table 6.3 Physical characteristics of SWCNT electrodes prepared from H_2O :SDS and H_2O :CMC

Anode	Thickness [nm]	Sheet Resistance [$\Omega/\text{sq.}$]	Conductivity [S cm^{-1}]	Transmission at 550 nm [%]	Work function [eV]
SWCNT/ glass (H_2O :SDS)	30	57	5847	65	4.8
SWCNT/glass (H_2O :CMC)	25	125	3200	70	5.0

Figures 6.5a-c show the device characteristics of the solar cells fabricated using the SWCNT thin films, whose characteristics are shown in Table 6.3, together with an ITO reference device. The device with the SWCNT electrode spray-coated from H_2O :CMC had an open-circuit voltage of 0.55 V, while the device with a SWCNT film spray-coated from H_2O :SDS had a slightly lower open-circuit voltage of 0.53 V, probably due to the better energy alignment of the Fermi level of the CMC-derived SWCNT film with the HOMO of P3HT, caused from a higher work function (5.0 eV).

The higher short-circuit current of 7.7 mA/cm^2 was obtained for the device with a SWCNT anode, spray-coated from $\text{H}_2\text{O}:\text{CMC}$, whilst the device with a spray-coated SWCNT anode from $\text{H}_2\text{O}:\text{SDS}$ had a short circuit current of 7.1 mA/cm^2 . This is partly attributable to the different transmission characteristics: 70 % and 65 % at 550 nm for the SWCNT films deposited from $\text{H}_2\text{O}:\text{CMC}$ and $\text{H}_2\text{O}:\text{SDS}$, respectively.

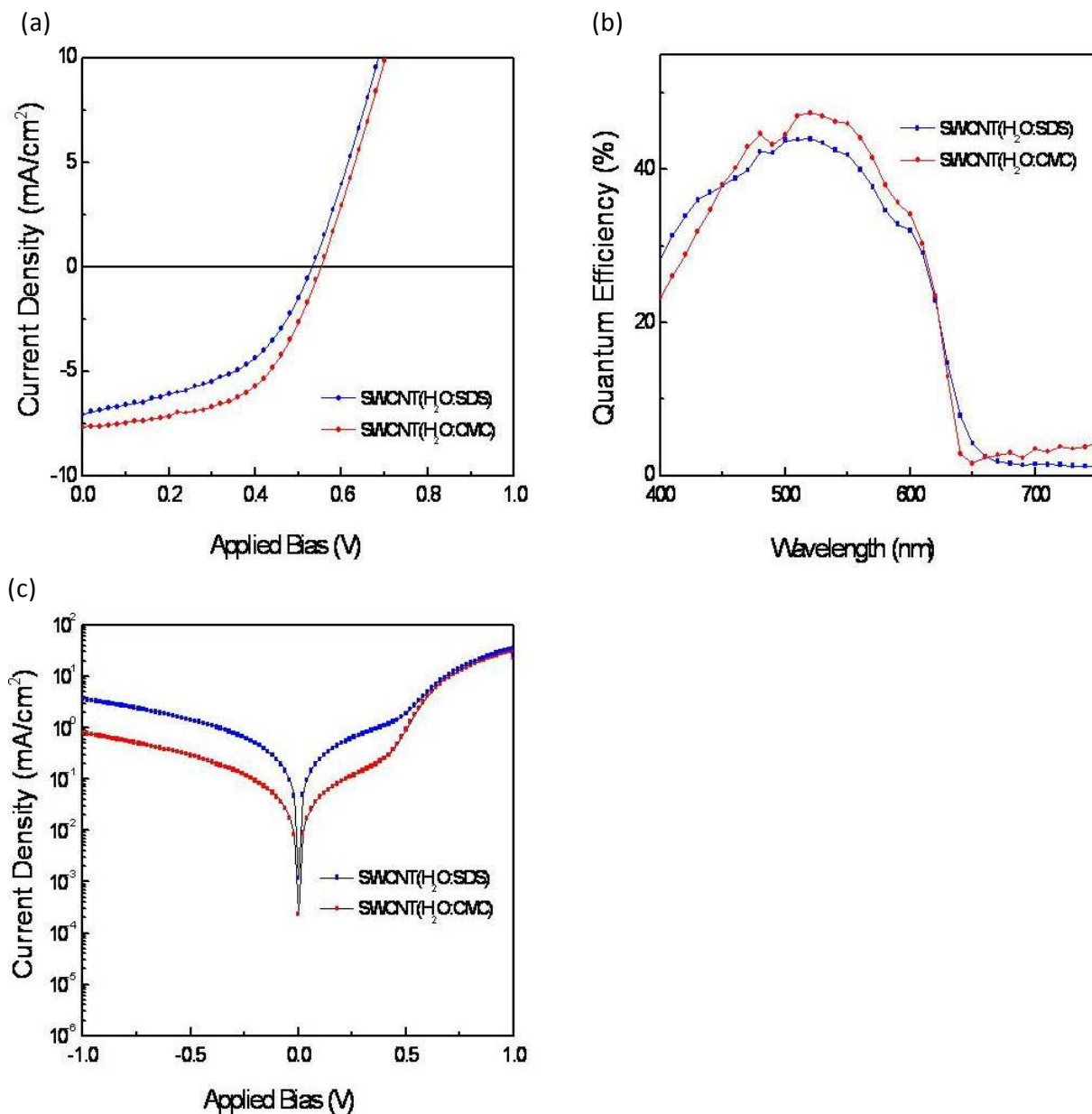


Figure 6.5 (a) Current-voltage characteristics under one-sun illumination for P3HT:PCBM bulk-heterojunction solar cells based on SWCNT anodes, prepared by spraying from $\text{H}_2\text{O}:\text{SDS}$ and $\text{H}_2\text{O}:\text{CMC}$. (see Table 6.3), and with the general structure Anode/PEDOT:PSS/P3HT:PCBM/LiF/Al, (b) External quantum efficiency, and (c) Dark current-voltage characteristics.

The device with a spray-coated anode from H₂O:CMC had a fill-factor of 54 % compared to 47 % for H₂O:SDS, yielding maximum power conversion efficiencies of 2.3 and 1.8 %, respectively. Here note that the H₂O:SDS device efficiency (1.8 %) is lower than the value reported for the H₂O:SDS device (2.2 %) described in section 6.3.2, due to the specific batch of P3HT (Merck Chemical Ltd.). However, two devices with SWCNT anodes from H₂O:CMC and H₂O:SDS were made at the same time and therefore their device performances are comparable.

The lower PCE of the H₂O:SDS device is consistent with the significantly larger leakage current and lower rectification ratio ($\pm 1V$), confirmed from Figure 6.7c, which is attributable to the higher density of shunts in the rougher SWCNT films. Table 6.4 summarises the key performance characteristics for the two devices.

Table 6.4 Device characteristics of OPVs fabricated using ITO and SWCNT electrodes

Anode	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%]
SWCNT/ glass (H ₂ O:SDS)	0.53	7.1	47.3	1.8
SWCNT/glass (H ₂ O:CMC)	0.55	7.7	53.9	2.3

6.3.4 Spray coated SWCNT electrodes via different patterning methods for OPV applications

In chapter 5, we reported three different patterning methods for SWCNT films: photolithography followed by plasma etching, interlayer lithography, and stencil patterning. Here we investigate the performance of the differently patterned films in organic solar cell applications.

6.3.4.1 Spray coated SWCNT electrodes via interlayer patterning for OPV applications

The Interlayer patterned SWCNT film with a 30 nm thickness was selected for making organic solar cells, due to its highest dc conductivity (see Section 5.3.1), whilst the photolithography patterned SWCNT film with the same thickness and standard ITO were employed for the purpose of comparison, as shown in Table 6.5.

Organic solar cells were fabricated using spray-coated SWNT electrodes on glass patterned by either conventional photolithography or interlayer lithography using an SU-8 2 resist as follows: a 35 nm layer of PEDOT:PSS (Baytron P) was spin-coated onto the SWNT electrode and then annealed at 140 °C for 30 minutes; a 210 nm blended layer of P3HT (Merck Chemicals Ltd.) and PCBM (API Services Inc.) was spin-coated onto the PEDOT:PSS from a 1:0.7 blend of the two components in chlorobenzene; and a LiF

(1nm)/Al (100nm) cathode was deposited on the P3HT:PCBM by thermal evaporation under high vacuum (10^{-6} mbar) through a shadow mask; the devices were post-annealed at 150 °C for 30 min in a dry-nitrogen environment. ITO control devices were also fabricated in the same way.

Table 6.5 Physical characteristics of ITO and SWCNT electrodes for device fabrication

Anode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
ITO/glass	0.55	8.4	50.0	2.3
Photolithography patterned SWCNT/ glass ($\text{H}_2\text{O}:\text{SDS}$)	0.59	7.3	46.4	2.2
Interlayer patterned SWCNT/glass ($\text{H}_2\text{O}:\text{SDS}$)	0.56	9.2	50.3	2.4

The device with an interlayer patterned SWCNT thin film had a short-circuit current of 9.2 mA/cm^2 , an open-circuit voltage of 0.56 V, and a fill-factor of 50.3%, as shown in Figure 6.8. These values correspond to a reasonable power conversion efficiency (PCE) of 2.4%, which is slightly better than the value of 2.2%, obtained for a device using a SWCNT electrode patterned by conventional photolithography. This is probably due to the higher transmittance ($T > 75\%$) and lower surface roughness ($< 8 \text{ nm}$) of the interlayer patterned SWCNT electrode compared with the photolithographically patterned film ($T > 65\%$ and surface roughness $> 12 \text{ nm}$). This is supported by the dark J-V characteristics in Figure 6.8c, where it is evident that the device using an Interlayer-lithography patterned SWCNT electrode had a strikingly lower leakage current and significantly larger rectification ratio of 1.4×10^2 ($\pm 1\text{V}$), which is broadly comparable to the ITO device (2.2×10^2), illustrating the importance of the surface uniformity for SWCNT electrodes. Table 6.6 shows the key device characteristics for each anode.

Anode	Thickness [nm]	Sheet Resistance [$\Omega/\text{sq.}$]	Conductivity [S cm^{-1}]	Transmission at 550 nm [%]	Work Function [eV]
ITO/glass	150	15	4444	97	4.8
SWCNT/glass (Photo-lithography)	30	57	5847	65	4.8
SWCNT/glass (Interlayer-lithography)	30	128	2860	75	4.8

Table 6.6 Device characteristics of OPVs fabricated using ITO and SWCNT electrodes

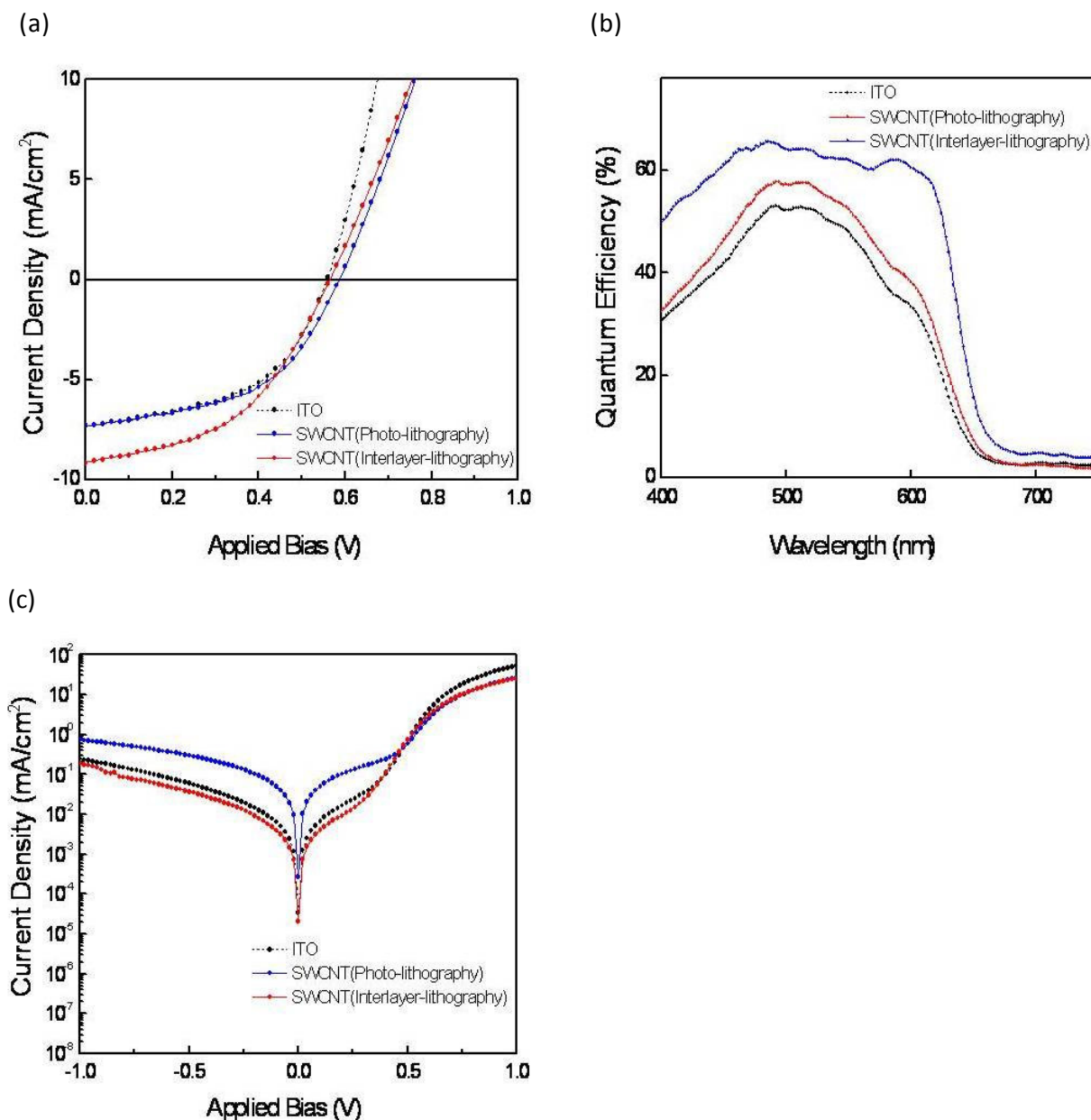


Figure 6.6 (a) Current-voltage characteristics under one-sun illumination for P3HT:PCBM bulk-heterojunction solar cells based on the anodes from Table 6.5, and with the general structure Anode/PEDOT:PSS/P3HT:PCBM/LiF/Al, (b) External quantum efficiency, and (c) Dark current-voltage characteristics.

6.3.4.2 Spray coated SWCNT electrodes via stencil patterning for OPV applications

In chapter 5, we found that electrodes patterned by conventional photolithography combined with dry plasma etching had more tube defects and therefore less electrical conductivity than stencil patterned SWCNT films, due to the harsh chemical treatments, which would be expected to worsen their performance in electronic devices.

Here, we used the stencil patterned SWCNT films from an initial SWCNT suspension in H₂O:SDS. (see Section 5.3.2) The resultant SWCNT electrode was then subjected to the standard surfactant removal and p-doping procedure with nitric acid described in Section 5.2, yielding highly conductive and smooth film with $\sigma_{dc} > 6,500 \text{ Scm}^{-1}$ at $T > 69\%$, as shown in Table 6.7.

Table 6.7 Physical characteristics of ITO and stencil patterned SWCNT electrodes for device fabrication

Anode	Thickness [nm]	Sheet Resistance [$\Omega/\text{sq.}$]	Conductivity [S cm^{-1}]	Transmission at 550 nm [%]	Work function [eV]
ITO/glass	150	15	4444	97	4.8
Stencil patterned SWCNT/ glass (H ₂ O:SDS)	30	51	6532	69	4.8

The author then made OPV devices with a structure of stencil patterned SWCNT thin film (30nm)/PEDOT:PSS(35nm)/P3HT:PCBM(250-260nm)/LiF(1nm)/Al(100nm). A reference ITO device was also made for comparison. The SWCNT device had a power conversion efficiency of 3.6%, which to our knowledge is the best performance for organic solar cells with a blended P3HT(Rieke Metals Inc.):PCBM(API Services Inc.) active layer using a SWCNT thin film anode. Note that all the devices were made with a low temperature process ($< 150^\circ\text{C}$), which is compatible with plastic substrates.

The excellent J-V characteristics of the stencil patterned SWCNT device under 1 sun illumination are shown in Figure 6.7, together with those of the ITO control device. The good device performance is attributable to the highly conductive and smooth SWCNT electrodes ((r.m.s.) 7nm roughness), and the chemically non-damaging stencil patterning process, followed by the standard post acid treatment to maximize electrical conductivity.

Enhanced SWCNT electrode properties combined with the thicker active layer (175nm $\rightarrow$ 260nm) led to the significant increases of device performance compared to the devices reported in Section 6.3.2, yielding a short circuit current of 11.2 mA/cm^2 , an open circuit voltage of 0.59 V, a fill factor of 54.2 %, and an overall power conversion efficiency of 3.6 %. These characteristics were significantly better than the ITO control device, which had a short circuit current of 11.9 mA/cm^2 , an open circuit voltage of 0.58 V, a fill factor of 43.8 %, and an overall power conversion efficiency of 3.0 %. The dark J-V characteristic confirms that the highly conductive and smooth SWCNT electrode contributed to the significantly lowered leakage current and the fairly high rectification ratio of $3.8 \times 10^2 (\pm 1\text{V})$.

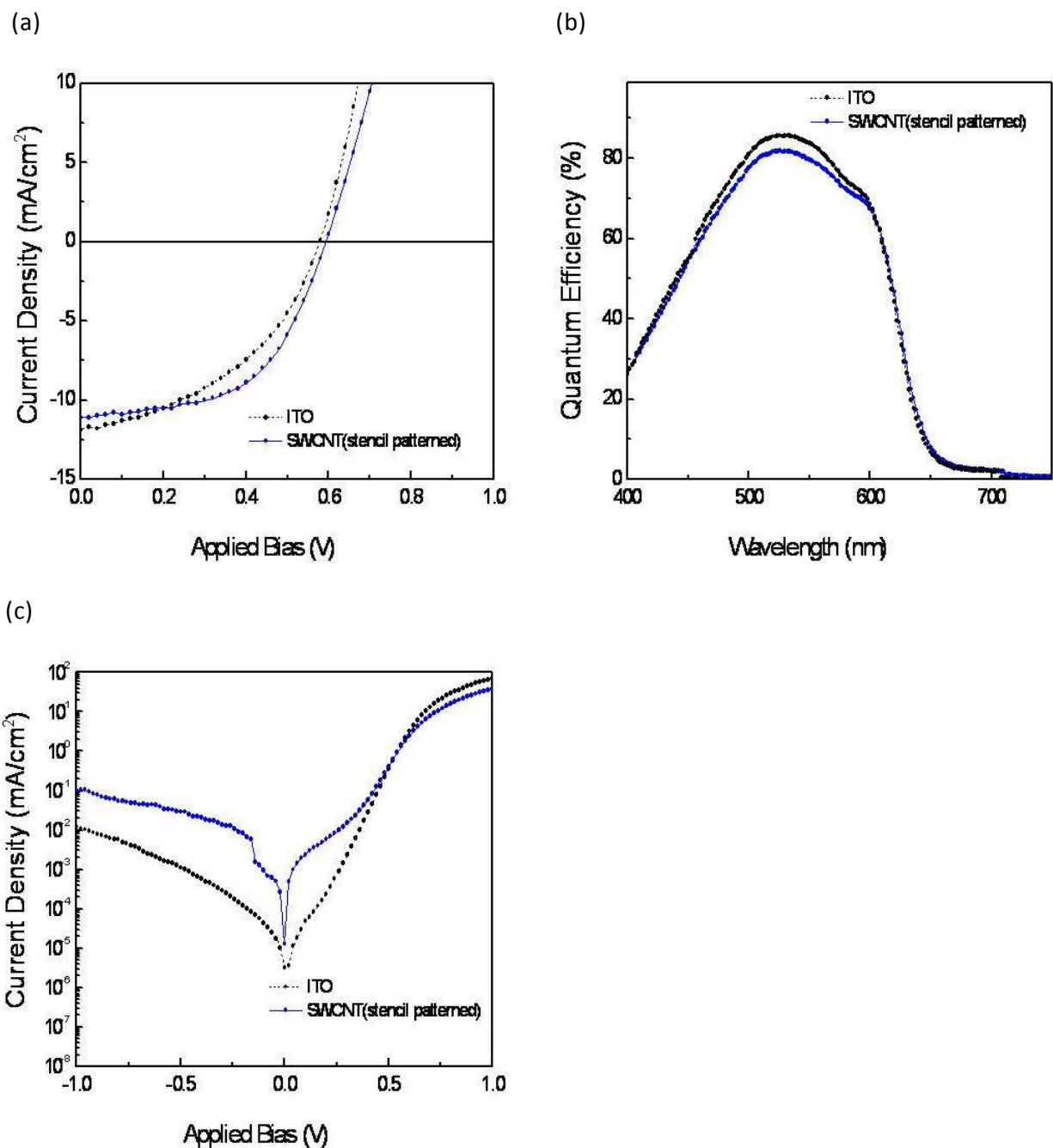


Figure 6.7 (a) Current-voltage characteristics under one-sun illumination for P3HT:PCBM bulk-heterojunction solar cells based on the anodes from Table 6.7, and with the general structure anode/PEDOT:PSS/P3HT:PCBM/LiF/Al, (b) External quantum efficiency, and (c) Dark J-V characteristic.

Table 6.8 summarises the key values for the OPV device performance. Applying a specific batch of a low band gap polymer:PC₇₀BM active layer instead of the current P3HT: PC₆₁BM active layer, would be expected to improve device performance further, but this remains as a planned task for the future.¹⁵

Table 6.8 Device characteristics of fabricated P3HT:PCBM solar cells

Anode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
ITO/glass	0.58	11.9	43.8	3.0
SWCNT/glass (spray patterned)	0.59	11.1	54.2	3.6

6.3.5 Flexible OPVs with an in-situ spray patterned SWCNT electrodes

SWCNT thin films have great potential for flexible and stretchable devices due to their mechanical strength and stable electrical property even when they are repeatedly bent. For the purpose of demonstrating this feature, the author made an organic solar cell with a structure of SWCNT thin film (30nm) on PET/PEDOT:PSS(35nm)/P3HT:PCBM(250-260nm)/LiF(1nm)/Al(100nm). The SWCNT electrode was prepared using the stencil patterning method for spray deposited SWCNT thin films from H_2O :SDS. The same procedure was used to fabricate devices on PET plastic, except the annealing temperature was reduced to 120 °C to avoid damaging the substrate.

Whilst the reduced temperature was not expected to affect the performance of the SWCNT electrode itself, a reduction in the overall device performance was observed due to the non-optimal processing conditions of the P3HT:PCBM active layer. Nevertheless, as shown in Figure 6.8, it was possible to prepare moderately efficient devices on plastic in this way with PCEs of up to 2.6 % due to the use of a lower annealing temperature for the active layer. It was comparable to a control device fabricated using ITO coated glass (2.9 %). Interestingly, a SWCNT/PET device had a slightly higher open circuit voltage of $V_{oc} = 0.58$ V but a significantly lower short circuit current of $J_{sc} = 9.8 \text{ mA/cm}^2$, compared to the reference ITO device. ($V_{oc} = 0.54$ V, $J_{sc} = 12.3 \text{ mA/cm}^2$). This is mainly due to the difference in thermal conductivities between a PET for SWCNTs and a glass substrate for ITO, which led to the effectively different annealing temperatures for devices, fabricated using those two electrodes. The results reported here indicate the viability of SWCNT electrodes as low cost ambient-processable electrodes for plastic electronic devices.

Table 6.9 summarises the device characteristics of organic solar cells using stencil patterned SWCNTs on PET and ITO on glass substrates.

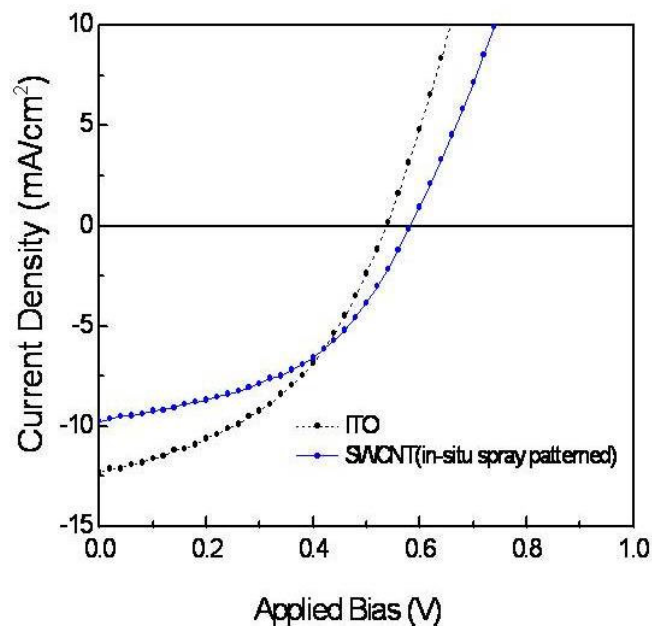


Figure 6.8 Current-voltage characteristics under one-sun illumination for flexible P3HT:PCBM bulk-heterojunction solar cells using the in-situ spray patterned SWCNT (30nm) on PET with the general structure anode/PEDOT:PSS/P3HT:PCBM/LiF/Al. An ITO control device is also shown for comparison.

Table 6.9 Device characteristics of fabricated P3HT:PCBM solar cells

Anode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
ITO/glass	0.54	12.3	43.3	2.9
SWCNT/PET (stencil patterned)	0.58	9.8	46.3	2.6

6.4 Conclusion

In conclusion, we have fabricated bulk heterojunction solar cells using thin-film SWCNT anodes in place of conventional ITO. Various types of SWCNT films were prepared: spin-coated SWCNT films from dichloroethane, and films deposited by pressure-driven spray-coating from deionised water using SDS, SDBS, or CMC as a surfactant. Different patterning methods such as the conventional photolithography followed by plasma etching, interlayer-lithography and stencil patterning were also compared.

The as-prepared films were highly hydrophobic, but a simple spin-treatment with ethanol was found to improve the wetting characteristics sufficiently to allow for the subsequent deposition of uniform PEDOT:PSS films. Using the SWCNT electrodes, organic bulk heterojunction solar cells with the general structure SWCNT($\sim 30\text{nm}$)/PEDOT:PSS($35\sim 40\text{nm}$)/P3HT:PCBM($175\sim 260\text{nm}$)/ LiF(1nm)/Al (100nm) were fabricated. The devices with SWCNT electrodes patterned by photolithography/plasma etching had respective PCEs of 2.3, 2.2 and 1.2 % for DCE, H_2O :SDS and H_2O :SDBS, with the first two being at virtual parity with reference devices using ITO-coated glass as the anode (2.3 %).

By employing interlayer-lithography to pattern the SWCNT films or using a CMC surfactant as a dispersing aid, we could significantly lower the surface roughness of the resultant SWCNT electrodes from (r.m.s.) 12nm to $5 \sim 8\text{nm}$, resulting in the lower leakage current and a higher rectification ratio. These results show the importance of uniform SWCNT film deposition for OPV applications to minimise shunts and electrical shorts.

However, wet etching based patterning techniques could induce tube defects and therefore yield less conductive SWCNT films. By using a simple and scalable stencil patterning technique and by increasing the thickness of the active layer from 175 nm to 260 nm, we obtained a power conversion efficiency of 3.6 %, which to our knowledge is the highest reported to date. The highly conductive ($\sigma_{\text{dc}} > 6,500 \text{ S cm}^{-1}$ at $T > 69\%$) and smooth SWCNT electrode ((r.m.s.) roughness $< 7\text{nm}$) led to a significantly lower leakage current ($\sim 10^{-2} \text{ mA/cm}^2$) and an increased rectification ratio of $5.9 \times 10^3 (\pm 1\text{V})$, and therefore higher device efficiency (3.6 %).

Finally, a flexible device fabricated with a stencil patterned SWCNT electrode on a PET substrate was demonstrated using process temperatures below 120°C . The device efficiency with a flexible SWCNT electrode was 2.6 %, which is comparable to 2.9 % for the reference ITO/glass device processed under identical conditions.

All the results show that highly conductive and transparent SWCNT electrodes are promising materials for organic solar cell applications, particularly in flexible devices. ITO-free OPV devices using SWCNT electrodes prepared by low temperature all-solution processes may be an important corner-stone for printable, roll to roll based organic electronic device applications. Further enhancements in device performance with SWCNT electrodes are expected by switching to a superior active layer system comprising a suitable low band gap polymer and PC₇₀BM, due to the better light absorption and charge transport.

6.5 References

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Chapter 7 SWCNT-Graphene(r-GO) electrodes for organic solar cells

7.1 Introduction

In previous chapters, I optimized SWCNT electrodes to make highly efficient organic solar cells in lieu of ITO anodes. However, our SWCNT thin films had limited performance ($\sigma_{dc}/\sigma_{op} \sim 24$) that, whilst close to the state of the art ($\sigma_{dc}/\sigma_{op} \sim 25$), are still some way behind (unflexed) ITO on glass substrates ($\sigma_{dc}/\sigma_{op} \sim 223$).¹ Hence further improvements are needed for SWCNT thin films to become viable transparent conducting electrodes.

Graphene and thin film networks of silver nanowires have been intensively investigated as potential competitors to SWCNTs.² Silver nanowires in thin film networks were reported to have great potential as electrodes due to ballistic quantum transport ($\sigma_{dc}/\sigma_{op} \sim 450$),³ but, they are known to suffer from stability and adhesion problems.² More importantly, due to the relatively large diameters of silver nanowires (~ 50 nm), the resultant thin films tend to have very rough surfaces, which complicates device fabrication.

As shown in Figure 7.1, Graphene, a single sheet of graphite, is a zero-band gap semiconductor with extremely high carrier mobility.⁴ It is also known to have high mechanical strength and electrical stability.⁵ However, it has comparatively high optical absorption/reflection (2.3 % per layer in the visible wavelength range), and it is difficult to reproduce high quality graphene films over a large area.⁶ Recently, graphene has been calculated to have a theoretical best case figure of merit (σ_{dc}/σ_{op}) of 330 in its highly doped state, but so far the best graphene film has exhibited merit values of only ~ 2.6 .²

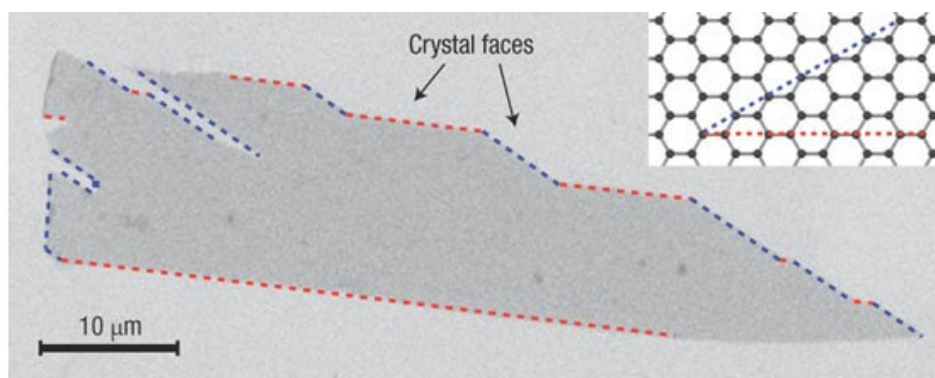


Figure 7.1 Scanning electron microscopy image of a graphene crystal, which shows that most of the crystal's faces are zigzag and armchair edges as indicated by blue and red lines and illustrated in the inset. (Taken from reference 4).⁴

Recently, there have been many reports on improving the thin film properties of a SWCNT network by combining with graphene in two different ways: casting a single layer from a solution of the two components,^{7,8} or casting a layer of SWCNTs on top of a layer of graphene.⁹⁻¹¹ Yang et al.⁷ made composite films from SWCNT/reduced graphene oxide solution, with a sheet resistance of 636 Ω/sq at 88 % transmission. Note that reduced graphene oxide is often denoted as graphene. They then fabricated a bulk-heterojunction organic solar cell (P3HT:PCBM) using the hybrid film and obtained a power conversion efficiency of 0.85 %. However, the use of chemically damaging hydrazine, as a reducing agent, is a significant problem, as it can cause tube defects and is hazardous.

Coleman et al.⁸ then demonstrated the feasibility of water based solution processing to prepare mixed solution of SWCNTs and graphene by using surfactants. They showed that the addition of a small quantity (3 wt%) of graphene (relative to the SWCNTs) to a SWCNT suspension could enhance the thin film properties by 40 % in terms of $\sigma_{\text{dc}}/\sigma_{\text{op}}$ ($12.5 \rightarrow 18$). They attributed it to the junction resistance between nanotubes and graphene being lower than the junction resistance between two tubes. However, the hybrid solution approaches commonly rely on liquid phase self assembly of the two components and it can therefore be difficult to control the surface morphology of the resultant films, which is a disadvantage for device applications.

On the other hand, solution based layer by layer (LBL) methods can provide nanometer scale control over the thin film composition, thickness and morphology.¹² Moreover they are simple, low cost, and scalable.⁹ Kim et al.⁹ made a LBL hybrid film by dip-coating graphite oxide films in an aminated MWCNT solution, followed by hydrazine reduction. Hong et al.¹¹ spin-coated a MWCNT solution onto graphite oxide, followed by chemical reduction and high temperature annealing ($\sim 1000^\circ\text{C}$). However, the post-reduction process with strong chemical treatments used in both cases again risks inducing tube defects, and so reducing the film electrical conductivity. Ideally the reduction process for graphite oxide should be done before the SWCNT thin films are deposited on top of reduced-graphene oxide.

Besides Yang et al.,⁷ there have been several other reports of fabricating organic solar cells with graphene films as the transparent electrode. Goki et al.¹³ used a 14 nm thick, reduced graphene oxide film with a sheet resistance of 40 K Ω/sq at 64 % transmission for making P3HT:PCBM solar cells with 0.1 % efficiency. Wang et al.¹⁴ also employed 30 nm thick transparent graphene films with a sheet resistance of 1.6 K Ω/sq to make P3HT:PCBM solar cells with 0.4 % efficiency. Gomez et al.¹⁵ used graphene films synthesized by chemical vapour deposition method, which had a sheet resistance of 3.5 K ohm/sq at 89 % transmission. They then made CuPc/C₆₀ solar cells with a device efficiency of 1.18 %.

However, for all cases, the device performance with graphene electrodes was fairly low compared to control devices using ITO or SWCNT electrodes (3 - 5 %), due to the low electrical conductivity (at comparable transparency) of the graphene films.

In this chapter, the author spray-coated a well dispersed and comparatively dilute SWCNT solution on top of a reduced Graphene-Oxide(r-GO) thin film, while varying SWCNT film thickness and/or the number of r-GO layers in order to find the optimum condition for maximising the electrical conductivity at comparatively high transmission (~90 %) of the LBL hybrid film. Results obtained with the hybrid films were compared to SWCNT only thin films. The optimised SWCNT/r-GO films as anodes were successfully implemented into OPV devices based on P3HT:PCBM and demonstrated to show high performance, compared with the devices using SWCNT only thin films or r-GO only films.^{13, 16, 17}

7.2 Experimental Details

Graphene(r-GO) films used in this chapter were made by Dr. Eda Goki in the Materials department at Imperial College London, using the following common procedures, as shown in Figure 7.2.

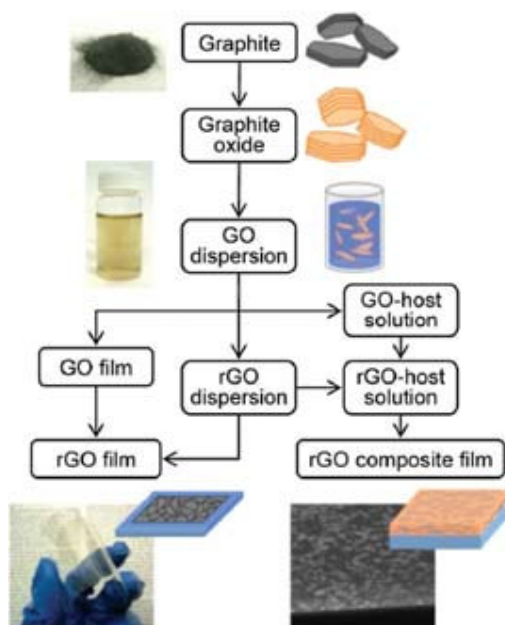


Figure 7.2 A schematic diagram for fabricating reduced graphene oxide thin film. The gray and the orange sheets represent unoxidized and oxidized graphene sheets, respectively. (Taken from reference 18)¹⁸

A slurry of graphene oxide (GO) was obtained from SP-1 graphite (Bay Carbon) using the modified Hummers method.¹⁹ The slurry was diluted in a mixture of water (< 20 wt.%) and methanol and sonicated to achieve exfoliated sheets of GO. A Langmuir–Blodgett (L–B) technique was used to uniformly deposit GO

films. GO sheets were carefully laid at the water/air interface, and the floating GO films were deposited on a target substrate (glass or PET), as it was slowly raised out of the solution. The GO film was then allowed to dry and adhere to the substrate at room temperature under a 1 kg weight for at least 10 h. The films were then rinsed with methanol and dried by blowing with a nitrogen gun. The reduction process of the GO films was carried out by thermal annealing in NH_3 atmosphere above 300 °C.

The SWCNT suspension was then prepared with 0.01 wt% of arc-made SWCNTs (Hanhwa) in $\text{H}_2\text{O}:\text{SDS}$, as shown in the chapter 4. The SWCNT solution was then spray-coated onto the heated r-GO film at 90 °C through a pattern mask using an air brush [Graphics Direct Ltd] with a 0.4 μm nozzle. The r-GO layer underneath was then scratched out to define an electrode pattern. The patterned SWCNT/ r-GO hybrid films were immersed in 4 M HNO_3 overnight and soaked in 15.5 M HNO_3 for 2 hours, rinsed thoroughly with de-ionised water, and finally dried with a nitrogen gun. By comparing the electrical conductivity of r-GO-only films before and after the nitric acid treatments, we found a slight increase ($\sim 10\%$) of the electrical property by the doping process.

P3HT:PCBM bulk-heterojunction solar cells were then fabricated by spin-coating onto the hybrid films a 50 nm layer of PEDOT: PSS (Baytron P). A 260 nm layer of regioregular poly(3-hexylthiophene) (P3HT, Rieke Metals) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{60} (PCBM, API Services, Inc.) was then deposited by spin-coating from a 1:0.7 blend of the two components in chlorobenzene. The devices were completed by thermal deposition of LiF (1 nm) capped with a thick layer of Al (100 nm), and were finally annealed in a dry N_2 atmosphere at 150 °C for 30 minutes.

7.3 Results and Discussions

Firstly, the adhesive interaction of SWCNTs with r-GO was investigated, since the adhesion of the hybrid films on the substrate significantly determines their viability as flexible electrodes and influences the permissible processing conditions. Three different surface treatments on glass were tested for comparison: an adhesion promoter (APTES 1 wt.% in water) on glass, a r-GO monolayer deposited on glass, and bare glass. The SWCNT suspension was spray-coated and post-acid treated, rinsed with DI water, and finally dried with a N_2 gun for each substrate. The adhesive ability was assessed by measuring the change in transmission versus the amount of material emitted from the spray head.

As shown in Figures 7.3a-b, the r-GO monolayer had a comparable adhesive ability to the adhesion promoter (APTES) by depositing over 300 mg/m^2 of SWCNTs, while bare glass showed the very poor

adhesion. Here, film thicknesses were estimated from the Tinkham equation (see Chapter 4), assuming the optical conductivity for SWCNT films to be 250 S cm^{-1} from previous results in chapter 4. However, it should be stressed that the optical conductivity of thin film SWCNTs varies according to the concentration of SWCNT suspension, the surface energy of target substrates, and other experimental conditions such as humidity. So the thicknesses plotted are approximate. Figure 7.3c shows the different morphologies of the deposited SWCNT films on each substrate. Here tube density indicates the amount of SWCNT solution emitted from the spray head at a distance of 30 cm.

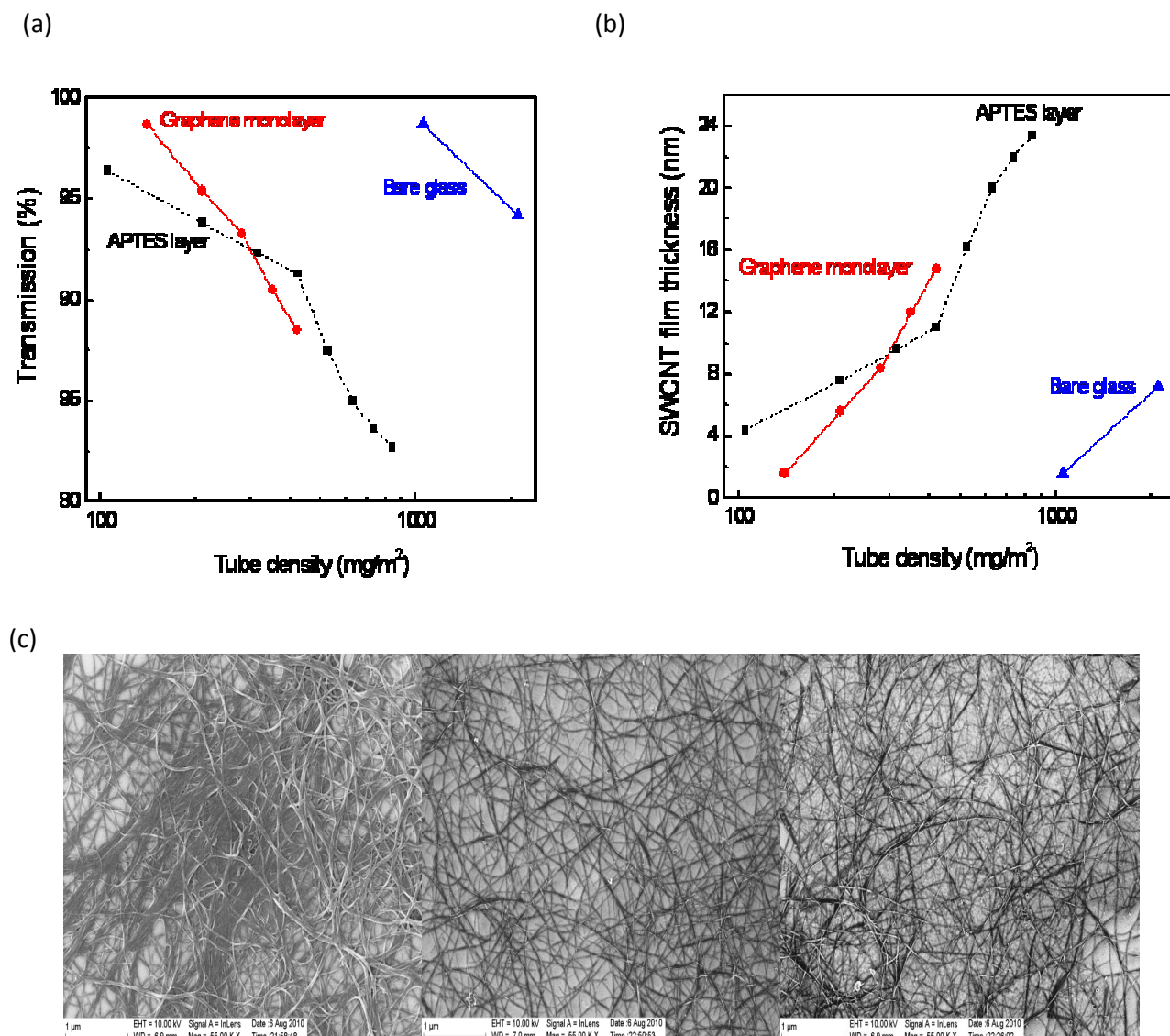
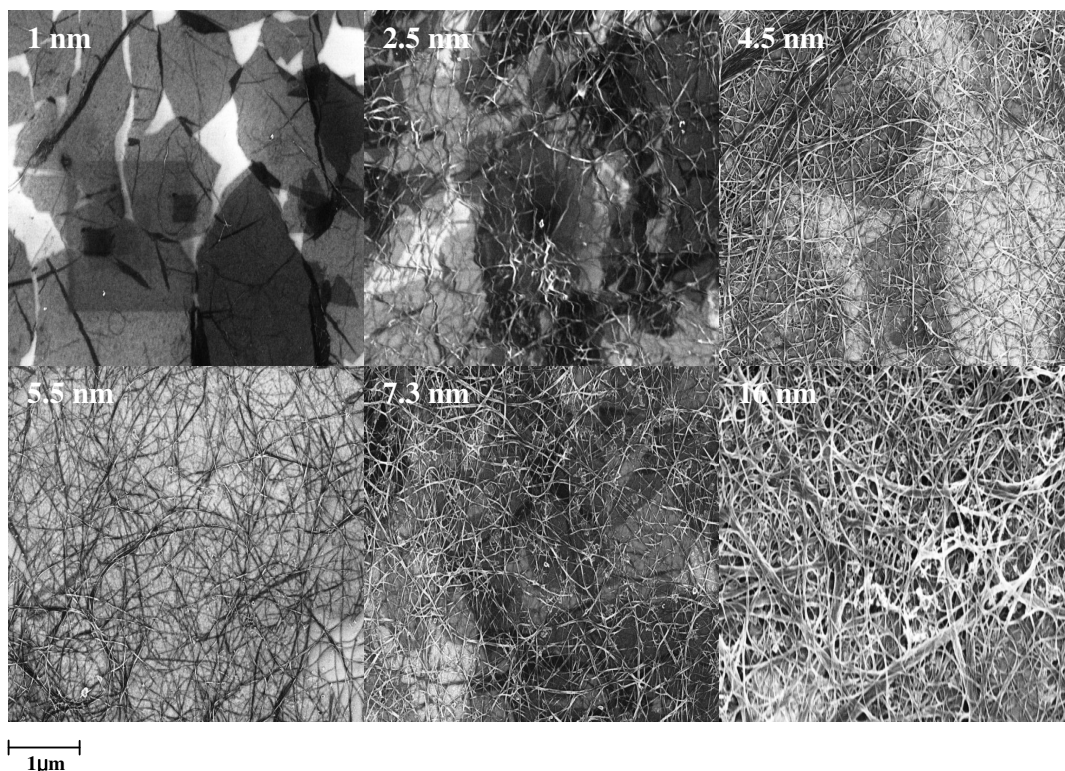


Figure 7.3 (a) Transmission versus tube density on glass, adhesion promoter (APTES), reduced graphene oxide. (b) Nominal thickness versus tube density, and (c) Scanning Electron Microscopy images for tubes deposited on glass, APTES, reduced graphene oxide. (from left to right) Here tube density indicates the amount of SWCNT solution emitted from the spray head at a distance of 30 cm.

Figure 7.4 shows Scanning Electron Microscopy images for SWCNT films on r-GO monolayer/glass substrates with different film thicknesses from 1 nm to 16 nm and also SWCNT films on APTES treated glass substrates with film thicknesses of 3.5 nm, 4.5 nm, and 6 nm. It is evident from the SEM images that the SWCNT conducting network is well ordered on the r-GO monolayer, and similar in structure to the SWCNT network on APTES. Interestingly, the thinnest bundles of tubes were formed on the r-GO layer to connect discrete r-GO islands, while slightly thicker bundles tubes were obtained on APTES. A high degree of tube aggregation was observed with a bare glass substrate.

(a)



(b)

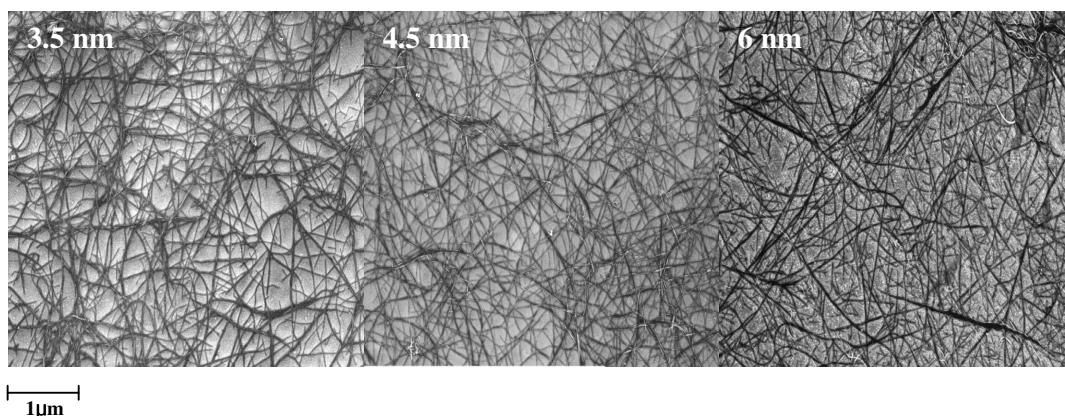


Figure 7.4 (a) Scanning Electron Microscopy (SEM) images for SWCNT films on the r-GO monolayer coated glass substrates for films of varying thickness: 1 nm, 2.5 nm, 4.5 nm, 5.5 nm, 7.3 nm, 16nm, (b) SEM images for SWCNT films on a APTES treated glass substrates for films of varying thickness: 3.5 nm, 4.5 nm, 6 nm.

A reasonable hypothesis is that the r-GO layer interacts more strongly with SWCNTs, due to the strong interaction of the carbon atoms from the two materials, while APTES is selectively reacting with hydrophilic tails of surfactants attached to SWCNTs, resulting in slightly larger bundles. In the case of glass, only the biggest and heaviest bundles remain on the substrate, with the remainder “bouncing”. It is encouraging to find that r-GO can function as a better adhesion promoter than APTES and that it can even decrease tube aggregations and so potentially provide better electrical conductivity.

With increasing SWCNT film thickness on r-GO, absorption spectra of the hybrid films are increasingly dominated by the metallic tubes in the SWCNT layer, as shown in Figure 7.5.

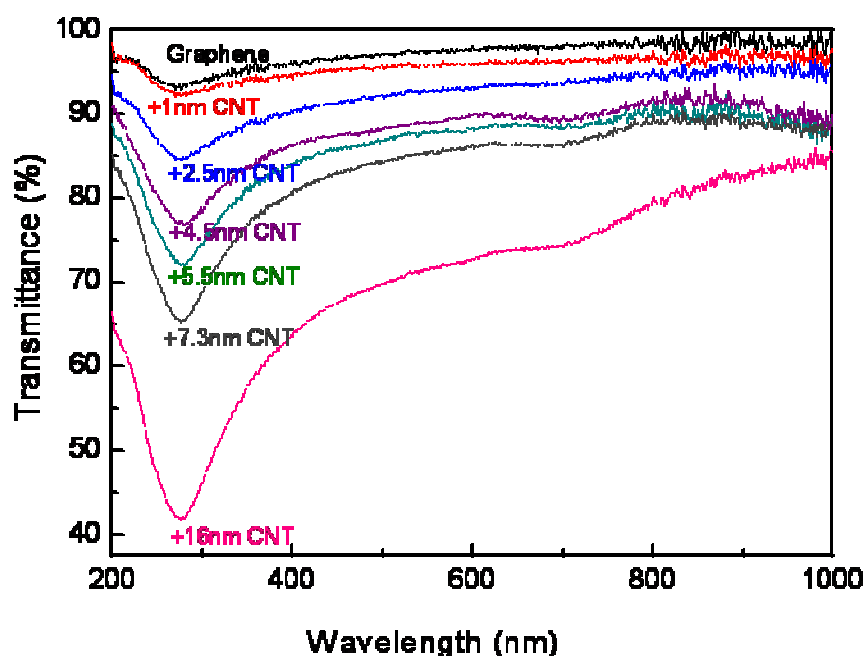


Figure 7.5 Transmission spectra for SWCNT thin films of varying thickness on a r-GO monolayer.

The hybrid films were mechanically robust and the surfactants were readily removed with standard post-acid treatments. The r-GO/SWCNT films showed strong adhesion to the glass substrate, and did not delaminate during routine handling either before or after acid treatment. In addition, when deposited on flexible PEN substrates, they showed no significant tendency to fracture or wear even when flexed repeatedly to a radius < 5 mm. The variation of sheet resistance with the number of tensile bending cycles is shown in Figure 7.6. There was only a slight increase in resistance with bending cycle numbers up to 150, beyond which the sheet resistance started to increase more quickly with bending cycle number.

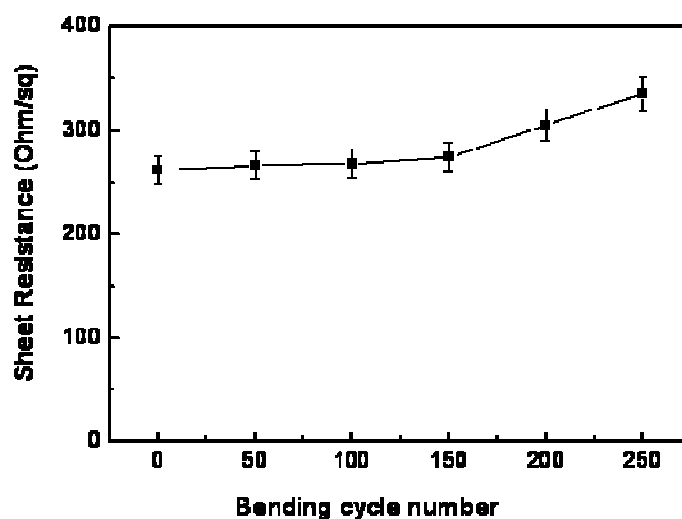


Figure 7.6 The influence of repetitive flexing on the sheet resistance of the hybrid film on PEN

The work function measured with a Kelvin probe ranged between 4.9 eV and 4.95 eV for spray-coated SWCNT films on the r-GO monolayer which is reasonable for use as anodes in organic electronic devices, as shown in Figure 7.7. Reduced graphene oxide films have a comparatively high work function of 5.0 eV. The hybrid films show an intermediate work function of around 4.9 eV between that of the SWCNTs (4.8 eV) and r-GO (5.0 eV).

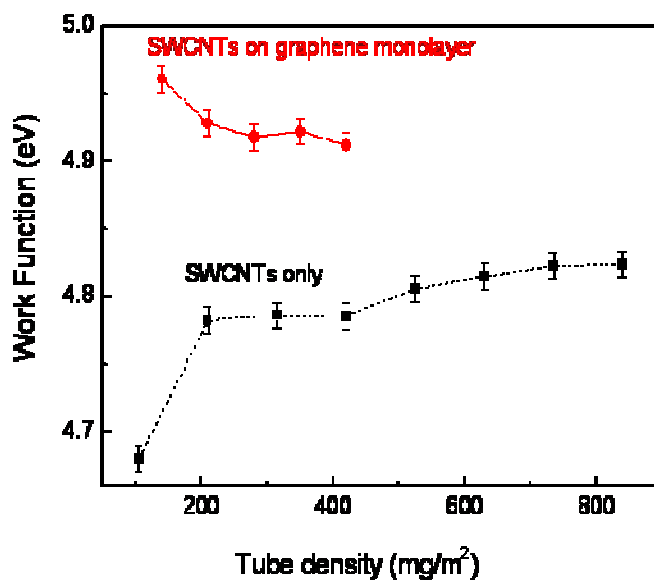


Figure 7.7 Work functions versus tube density on top of APTES (black) and r-GO monolayer (red). SWCNTs were dispersed in DI water with SDS and the work function was measured with a Kelvin probe.

Figure 7.8 compares the transmittance at 550 nm, the sheet resistance, and the figure of merit (FoM) for the two sets of samples: thin-film SWCNTs on either r-GO monolayer/glass or APTES treated glass. Here, due to the difficulty of measuring accurate film thickness below 10 nm, which may include substantial errors, the FoM of σ_{dc}/σ_{op} was used as the principal means of comparison, because it can be calculated independently of the film thickness. In each case, there was also a monotonic reduction in sheet resistance with film thickness.

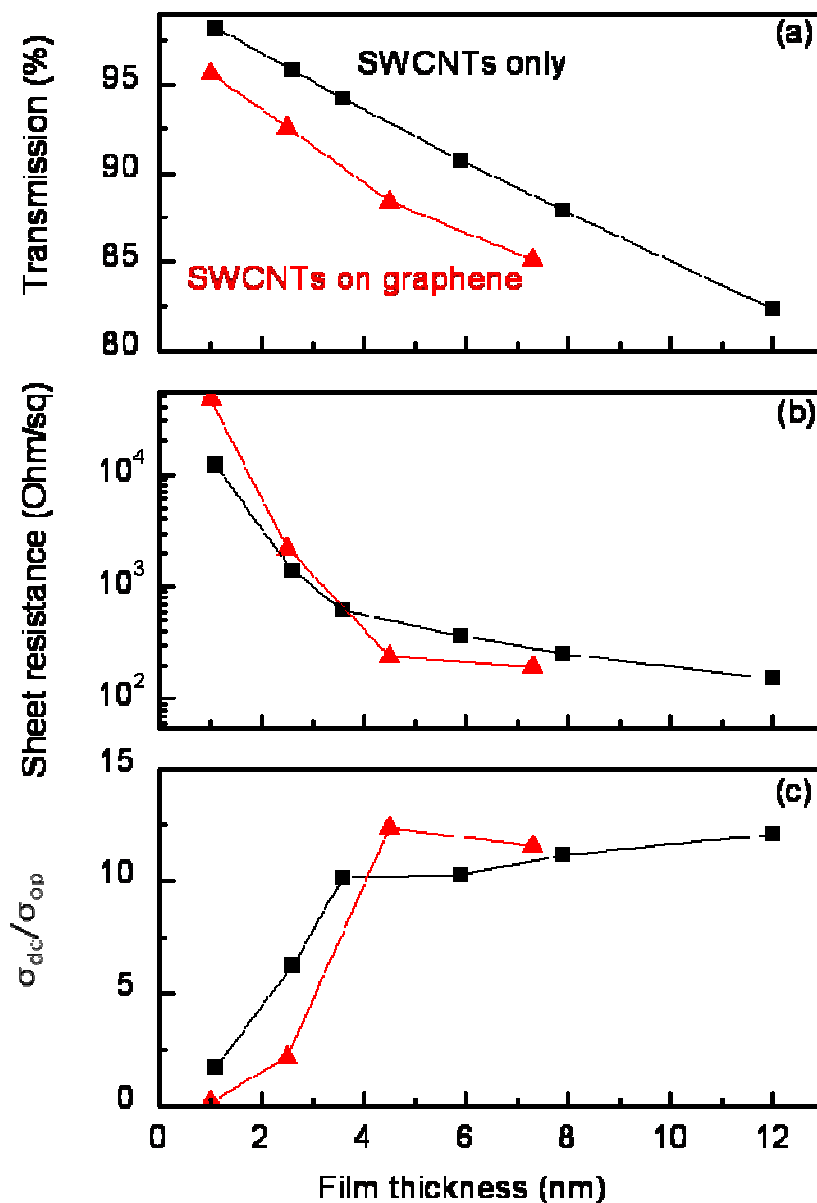


Figure 7.8 Thickness dependence of (a) the transmittance, (b) the sheet resistance, and (c) the figure of merit (σ_{dc}/σ_{op}) for thin-film SWCNTs on either r-GO monolayer/glass or APTES treated glass. The mean thickness l of each film was determined using a surface profilometry

Interestingly, from 4 to 8 nm of SWCNT film thickness, below the metallic percolation threshold,²⁰ the spray-coated SWCNT films on r-GO had better FoMs than the SWCNT-only films at the similar transmission, even though each r-GO layer had around 2.5 % light absorption/reflection and a poor electrical conductivity of 1 - 2 M Ω /sq. The superior performance is probably due to the formation of the thinner bundles of SWCNTs on r-GO than APTES. Thin bundles are just as effective at transporting charge as thicker bundles but are substantially more transmissive. While r-GO-SWCNT junctions were the dominant conducting pathways with the highly porous SWCNT films on r-GO, by increasing the SWCNT film thickness, tube-tube junctions took over the main role in forming electrical highways. The lower barrier height of tube- r-GO junctions than tube-tube junctions, as explained by Coleman et al.,⁸ may also contribute to the better performance.

Figure 7.9 shows that around 4.5 nm SWCNT thin films on a r-GO monolayer had optimal trade-offs between the sheet resistances of $220 \pm 20 \Omega/\text{sq}$ at $88 \pm 2 \%$ transmission compared to SWCNT only films, whilst over 8 nm of SWCNTs on r-GO showed almost similar properties to SWCNTs only films.

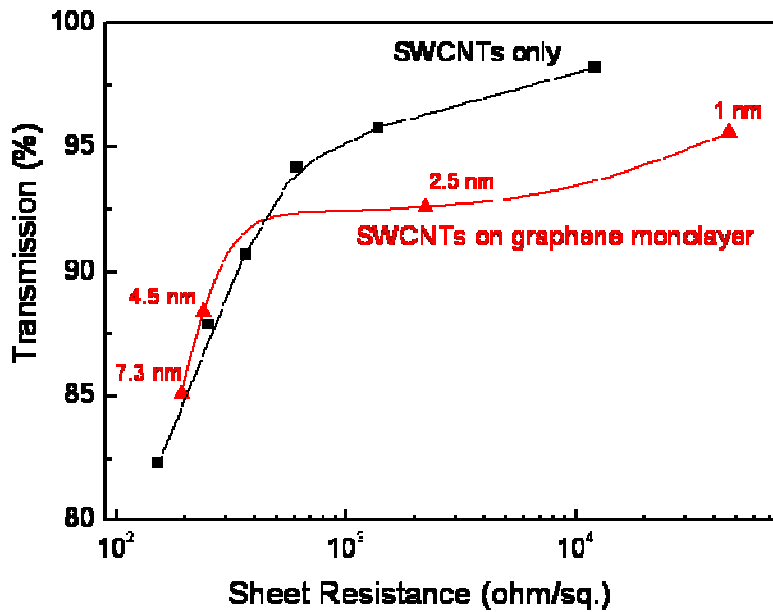


Figure 7.9 Transmittance versus sheet resistance for the SWCNT films spray-coated on either r-GO monolayer/glass (red) or APTES treated glass (black).

We then used these optimised hybrid films as transparent anodes for making bulk-heterojunction solar cells with an active layer of poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁-butyric acid methyl ester (PCBM). Reference devices with SWCNT-only anodes were also made for comparison purposes. Table 7.1 shows the measured properties of various anodes used for device fabrication.

Table 7.1 Physical characteristics of SWCNT/r-GO and SWCNT-only electrodes.

Anode	Thickness [nm]	Sheet Resistance [Ω/sq]	Conductivity [S cm^{-1}]	Transmission at 550 nm [%]	Work function [eV]
SWCNTs only	2.2	1495	3040	96	~4.8
SWCNTs only	4.8	541	3851	92	~4.8
SWCNTs only	8.0	220	5682	88	~4.8
SWCNTs/graphene(1)	2.5	746	5362	94	~4.9
SWCNTs/graphene(1)	4.5	240	9259	88	~4.9
SWCNTs/graphene(1)	6.0	200	8333	85	~4.9
SWCNTs/graphene(2)	3.8	500	5263	88	~4.9
SWCNTs/graphene(4)	4.0	750	3333	85	~4.9

*The number in graphene () indicates the number of r-GO monolayer.

Following the previously mentioned spin-treatment of the SWCNT films with ethanol, P3HT:PCBM bulk-heterojunction solar cells were fabricated with a pixel size (defined by the spatial overlap of the SWCNT/r-GO or SWCNT anodes and the LiF/Al cathode) of 0.045 cm^2 .

Figures 7.10a-c show the current-voltage characteristics (under one-sun solar illumination) for solar cells fabricated using the anodes in Table 7.1. Figure 7.10d shows the dark current-voltage characteristics for selected devices. The devices made with thin film SWCNTs on r-GO monolayer anodes had slightly better device performance than devices fabricated with SWCNT-only anodes, whilst devices fabricated with SWCNT thin films on double or 4 layers of r-GOs had worsened device performance, probably due to the significant reduction in light transmission caused by the higher number of (almost insulating) r-GO layers.

Increasing the SWCNT film thickness caused the open circuit voltage to increase up to 0.56 V for SWCNT/ r-GO devices and up to 0.60 V for SWCNT-only devices, while the highest short circuit current of 10.4 mA/cm^2 was obtained for the device made with a 4.5 nm SWCNT film on a r-GO monolayer. These results are consistent with the FoM values in Figure 7.8. Fill factors for devices using SWCNT-only films or SWCNTs on r-GO films were low compared to results reported elsewhere in this thesis, probably due to higher surface roughness, which is consistent with relatively high leakage currents, evident in Figure 7.10d.

The power conversion efficiency of 2.0 % for devices made with 4.5 nm SWCNTs on a r-GO monolayer is fairly high, compared to the organic solar cells using graphene electrodes reported elsewhere in the literature,^{7, 13, 15, 16} but slightly lower than the polymer solar cells using SWCNT electrodes.

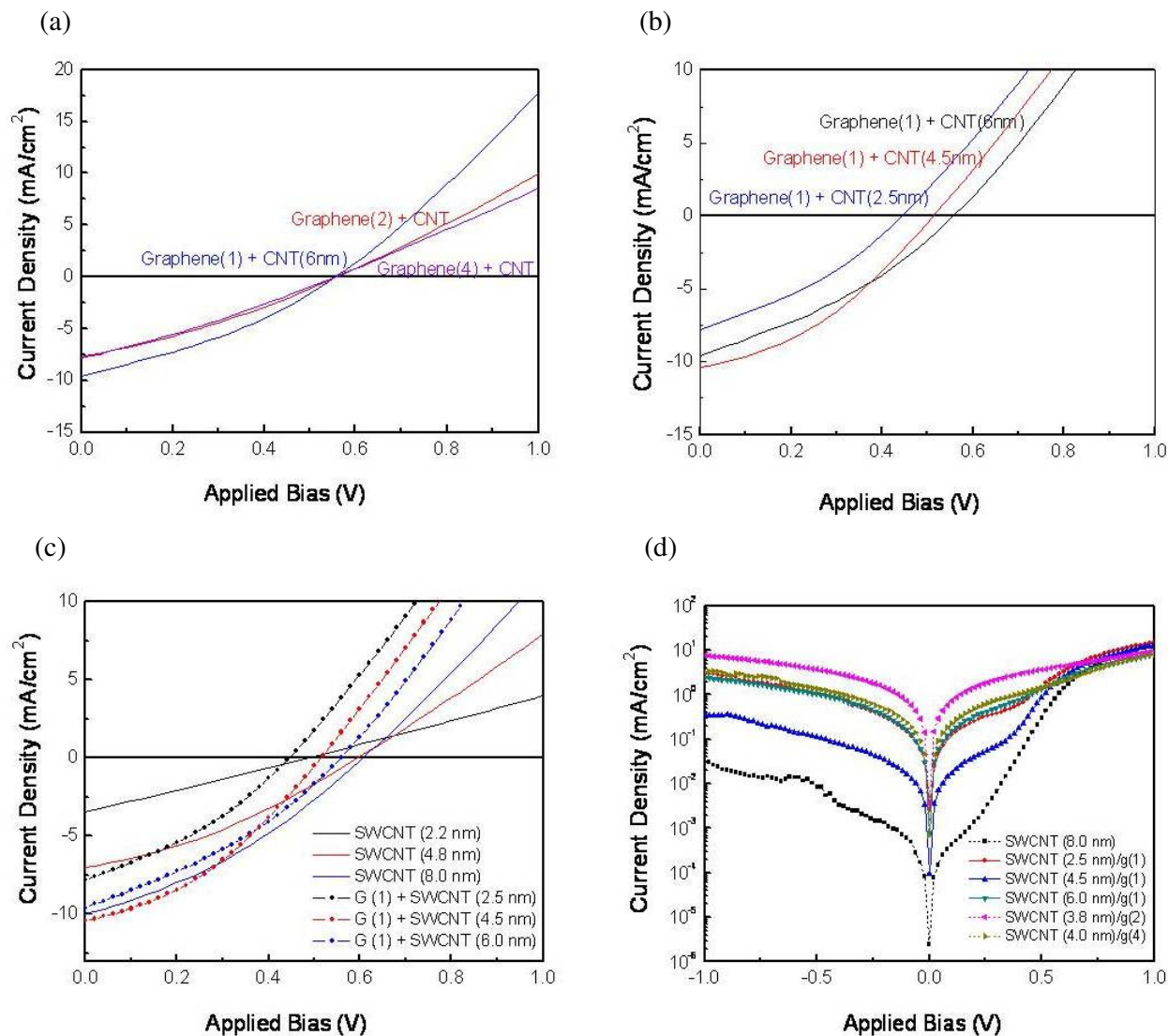


Figure 7.10 (a),(b),(c) Current-voltage characteristics under one-sun illumination (100 mW cm⁻²) for P3HT:PCBM bulk-heterojunction solar cells based on SWCNT/r-GO or SWCNT-only anodes from Table 7.1, with the general structure anode/PEDOT:PSS(50nm)/P3HT:PCBM(260nm)/LiF(1nm)/Al(100nm), and (d) Dark current-voltage characteristics.

Table 7.2 summarises the device characteristics for organic solar cells fabricated using SWCNT/r-GO hybrid films and SWCNT-only films as transparent electrodes.

Table 7.2 Device characteristics of OPVs fabricated using SWCNTs/ r-GOs and SWCNTs electrodes

Anode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
SWCNTs only (2.2 nm)	0.49	3.4	25.6	0.4
SWCNTs only (4.8 nm)	0.59	7.0	33.1	1.4
SWCNTs only (8.0 nm)	0.60	10.0	33.3	2.0
SWCNTs(2.5 nm)/graphene(1)	0.44	7.8	34.4	1.2
SWCNTs(4.5 nm)/graphene(1)	0.51	10.4	36.5	2.0
SWCNTs(6.0 nm)/graphene(1)	0.56	9.6	33.1	1.8
SWCNTs(3.8 nm)/graphene(2)	0.56	7.9	30.2	1.3
SWCNTs(4.0 nm)/graphene(4)	0.56	7.8	29.1	1.3

*The number in graphene () indicates the number of r-GO monolayer.

7.4 Conclusion

In conclusion, we have made layered hybrid thin films of SWCNTs on r-GOs by a simple spray coating method and showed that they can surpass SWCNTs-only or r-GO-only films in their electrical and optical properties. In particular, the 4.5 nm SWCNT networks on a r-GO monolayer resulted in the optimum thin film properties, yielding a sheet resistance of $220 \pm 20 \Omega/\text{sq}$ at $88 \pm 2 \%$ transmission.

From 4 to 8 nm of SWCNT film thickness, the spray-coated SWCNT films on r-GO had better FoMs than the SWCNT-only films at comparable transmission, even though each r-GO layer with around 97.5 % transmittance had a poor electrical conductivity of $1 - 2 \text{ M } \Omega/\text{sq}$. Interestingly, we found that the SWCNTs formed thinner bundles on r-GO than on the APTES treated glass, which may facilitate performance by minimising SWCNTs absorption without sacrificing conductivity. Since tube-tube junction resistances dominate the overall resistance and there is more contact area in larger bundles than in smaller bundles, the conductivity of SWCNT networks will decrease with the bundle diameter.²¹

The hybrid films were mechanically robust and showed strong adhesion on glass or plastic substrates, with no tendency to delaminate from the underlying substrate during the routine handling either before or after acid treatment. In addition, the double layered films on flexible PEN substrates showed relatively

little change in their sheet resistance even when flexed repeatedly. The work function for the hybrid films was 4.9 ± 0.05 eV, which is favourable for use as anodes in organic electronic device applications.

We also fabricated relatively efficient organic solar cells with 2% efficiency using the optimised hybrid SWCNT/r-GO. Their device performance compared to the devices made with SWCNT only films at the similar thickness, were slightly enhanced, mainly due to the better electrode performance of the hybrid films.

By using both more conductive graphene films (by efficient doping) and controlled deposition methods for SWNCTs such as spin-coating and ultrasonic spraying, further enhancements in electrode performance are to be expected.

7.5 References

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Chapter 8 Conclusion and Future works

8.1 Conclusion

Plastic Electronics is of widespread interest due to its potential for low cost manufacturing and high volume roll-to-roll production on flexible substrates. Device fabrication on plastic substrates requires the use of flexible electrode materials. The key requirements of such electrodes are high conductivity, high transparency, mechanical flexibility and good thermal stability. The most widely used electrode material, Indium Tin Oxide (ITO), is becoming more and more expensive due to the increasing scarcity of Indium and highly intricate production process. In addition, it is brittle and cracks when repeatedly flexed.

In this context, new mechanically robust, high performance transparent conducting films of commercially sourced arc-made SWCNTs on both glass and flexible substrates were produced using spray deposition, interlayer or stencil patterning methods. The main achievements in this thesis were as follows.

First, SWCNT films were prepared from various dispersants and deposition methods: spin-coated SWCNT films from dichloroethane (DCE), and films deposited by pressure-driven spray-coating from deionized water using a variety of anionic surfactants as the dispersive agent. (SDS, SDBS, CMC, SDBS/PVP) All of the SWCNT films were found to be mechanically robust, with no tendency to delaminate from the underlying substrate during handling. SWCNT thin films showed no significant change in their sheet resistance even when flexed repeatedly, confirming their compatibility with flexible device fabrications on plastic substrates.

After carefully optimizing the dispersion process of SWCNTs with H₂O:SDS (up to 0.03 wt.%) and developing an efficient surfactant removal/p-doping procedure with nitric acid, highly conductive and smooth SWCNT thin films (ca. 30 nm) were obtained with more than 6,500 Scm⁻¹ at > 69 % transmittance and 7 nm (r.m.s.) roughness.

In particular, SWCNT films spray coated from H₂O:SDS exhibited electrical conductivities of up to 7694 ± 800 Scm⁻¹. To our knowledge, these values are the highest so far reported for SWCNT electrodes. Peak values for the ratio of the dc conductivity to the optical conductivity (σ_{dc}/σ_{op}) were obtained as up to 24, which is quite similar to state of the art SWCNT films so far reported.

Second, two patterning methods were developed to define electrode patterns of SWCNT thin films for electronic device applications. Interlayer lithography provided a fast and high resolution patterning procedure for SWCNT thin films at micron and sub-micron length scales, which is important for the fabrication of high-speed transistors requiring short channel lengths, and offers an attractive route to fabricating high-density integrated circuits. In addition, stencil patterning provides a simple and fast method, which is well suited for low resolution electronic device applications such as organic solar cells.

Third, the patterned highly conductive SWCNT electrodes were incorporated into P3HT:PCBM bulk heterojunction solar cell applications. The wetting characteristics of SWCNT electrodes were improved with a simple spin-treatment with ethanol, which permitted the subsequent deposition of uniform PEDOT:PSS films.

By using a simple and scalable stencil patterning technique and by increasing the thickness of the active layer to 260 nm, we obtained the best device performance of 3.6 %, which is the best result so far reported in the literature. In addition, a flexible device fabricated with a stencil patterned SWCNT electrode on a PET substrate was demonstrated using process temperatures below 120 °C. The device efficiency was 2.6 %, which is comparable to 2.9 % for the reference ITO/glass device processed under identical conditions.

Finally, to break through the limited performance ($\sigma_{dc}/\sigma_{op} < 25$) of SWCNT thin films, layered hybrid thin films of SWCNTs on Graphene-Oxide (r-GO) were fabricated by a simple spray coating method. Interestingly, we found that the SWCNTs formed thinner bundles on r-GO than on the APTES treated glasses, which may facilitate their performance as transparent electrodes by minimising SWCNTs absorption without sacrificing conductivity. The 4.5 nm SWCNT networks on a r-GO monolayer resulted in the optimum thin film properties, yielding a sheet resistance of $220 \pm 20 \Omega/\text{sq}$ at $88 \pm 2 \%$ transmission.

Importantly the spray-coated SWCNT films on r-GO had slightly better FoMs (σ_{dc}/σ_{op}) of up to 12 compared to SWCNT-only films at comparable transmission, even though each r-GO layer was only 97.5 % transmissive and had a poor electrical conductivity of 1 - 2 M Ω/sq . We then fabricated relatively efficient organic solar cells (2 % efficiency) using the optimised hybrid SWCNT/r-GO film.

8.2 Future work

The minimum industry standard for transparent electrodes is considered to be $R_s = 100 \Omega/\text{sq}$ and $T = 90 \%$, which corresponds to $\sigma_{dc}/\sigma_{op} = 35$. Our SWCNT thin films had good performance ($\sigma_{dc}/\sigma_{op} \sim 24$) close to the

state of the art, but are still some way behind (unflexed) ITO on glass substrates ($\sigma_{dc}/\sigma_{op} \sim 223$). Hence further improvements are needed for SWCNT thin films to become viable transparent conducting electrodes, remaining those works as future tasks.

First, by using pure metal or metal-enriched SWCNTs instead of unsorted SWCNTs, SWCNT thin films properties are expected to be enhanced in terms of much higher conductivity at comparable transmission. Different surfactants in dispersing SWCNTs¹ or specific interlaying thin films beneath SWCNTs² can lead to more selective interaction with metallic or semiconducting SWCNTs.

Second, with unsorted SWCNTs, careful purification process and efficient doping methods to ensure maximum electrical conductivity of SWCNT thin films must be developed not to induce any potential tube defects. Since covalent chemical method to purify SWCNTs such as liquid-phase or gas-phase oxidation induces tube cutting or defects, non-covalent physical methods such as filtration, centrifugation, use of different surfactants in dispersion process (or combination of them) will be preferred.³ Doping with SOCl_2 or new polymers such as tetracyanoquinodimethane (TCNQ) after HNO_3 treatments can be investigated for further enhancement in electrical conductivity.⁴

Third, for using large area printing techniques such as inkjet, gravure, higher loading techniques (> 1 mg/ml) of (finally remained) SWCNTs in DI water must be developed. Combination of different surfactants, surfactant/polymer such as SDBS/PVP can be investigated for their increased dispersing ability.

Fourth, making highly conductive hybrid electrodes by combining SWCNTs with other noble materials such as graphene or conducting polymers, may lead to more enhancements in thin film electrode properties. High quality of graphene sheets or conducting polymers must be employed to ensure better thin film properties.

Fifth, a specific batch of a low band gap polymer:PC₇₀BM active layer, instead of the current P3HT: PC₆₁BM active layer, for organic solar cell applications of SWCNT electrodes could be straightforwardly used to improve device performance further.

In addition, to make highly efficient ITO-free OPV devices using SWCNT electrodes, processing conditions at low temperature must be optimised as a corner stone to printable, roll to roll based organic electronic device applications.

8.3 References

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