Solution-processible carbon nanotubes-based thin films as counter electrodes in dye sensitized solar cells

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NANYANG
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**SOLUTION-PROCESSIBLE CARBON NANOTUBES-
BASED THIN FILMS AS COUNTER ELECTRODES IN
DYE SENSITIZED SOLAR CELLS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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BASED THIN FILMS AS COUNTER ELECTRODES IN
DYE SENSITIZED SOLAR CELLS**

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ABSTRACT

Platinum (Pt) and fluorine-doped tin oxide (FTO) are commonly used as counter electrodes (CEs) in dye sensitized solar cells (DSSC), but the high processing temperature of Pt and brittle behavior of FTO makes them unsuitable for application in flexible, bifacial DSSC. Carbon nanotubes (CNT) is a possible alternative as Pt- and/or FTO-free CEs, as the conducting and catalytic properties can be tuned by altering its physical aspects (e.g. tube length, surface defects, functionalization). Thin pristine single-walled CNT films (with 3-5% surface carboxylate side groups) of similar optical transmittance (80-85% @ 550 nm) to Pt/FTO gave comparable DSSC performance only when illuminated under low light intensity (1% Sun), as high CE-to-electrolyte charge transfer resistance (R_{CT}) caused charge recombination to dominate with brighter illumination intensities.

To improve R_{CT} and sheet resistances (R_S), chemical modification by nitric acid (HNO_3) was carried out. R_S was reduced, resulting in an increase in the short circuit current density (J_{SC}) of the DSSCs when both FTO and Pt were replaced. However, fill factors (FF) remained low and the V_{OC} increment phenomenon persisted. This indicated that the decrease in R_S from HNO_3 treatment was not sufficient for thin CNT films as CE. Hence, surface modification of CNT was explored with the formation of Au or Pt nanoparticle clusters on CNT surfaces by spontaneous electroless chemical bath deposition. Au exhibited charge transfer mechanism with CNT and increased the work function from 4.85 eV to 5.12 eV. However, poor Au precursor wetting led to the formation of sparse dendritic Au clusters of up to 150 nm in diameter. This decreased Au-CNT system's potential to create charge transfer complexes with CNT to improve DSSC performance. Both R_S and R_{CT} were found to decrease leading to a small

decrease in series resistance of the DSSC and an increase in J_{SC} , improving efficiency from 0.22% to 0.25% under 100% Sun illumination. In the case of Pt decoration, Pt properties were preserved as indicated by the negligible changes in R_{CT} values and the close proximity of oxidation peak onsets of Pt-CNT and pristine Pt from cyclic voltammetry measurements. J_{SC} was most significantly improved (13.7 mA/cm² to 14.2 mA/cm² with 100% Sun, and 147 μ A/cm² to 158 μ A/cm² with 1% Sun), giving promising DSSC efficiencies of 3.8% and 5.6% respectively.

CoS or NiS were also investigated as Pt alternatives. Unlike NiS, CoS is semiconducting, but better wetting led to a more homogeneous deposition on CNT and a higher DSSC efficiency. The excellent catalytic properties of both sulfides further increased J_{SC} , but FF were low due to limited contact area between the nanoparticles and CNT surfaces. By altering the synthesis method to preform CoS-CNT nanocomposite, at low concentration, both FF and optical transmittance were improved and DSSC efficiency reached 5.78% when illuminated at 100% Sun from the photo anode side, and 2.22% from the CE side. Incident light on both sides of the DSSC may thus be utilised in transparent photovoltaic applications such as power-producing windows.

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LIST OF ABBREVIATIONS

CE – counter electrode

CNT – carbon nanotube

DNH2 – commercially available dye from Dyesol; commonly known as Z907 in literature

DSSC – dye sensitized solar cell

FESEM – field emission scanning electron microscopy / microscope

FF – fill factor

FTO – fluorine-doped tin oxide

I_{SC} – short circuit current

J_{SC} – short circuit current density

NADH – nicotinamide adenine dinucleotide ($C_{21}H_{27}N_7O_{14}P_2$)

PCE – percentage conversion efficiency

PEN – polyethylene naphthalate

PET – polyethylene terephthalate

R_{CT} – charge transfer resistance

R_{Diff} – diffusion resistance

R_s – sheet resistance

R_{Series} – series resistance

V_{OC} – open circuit voltage

T_g – glass transition temperature

1. INTRODUCTION

1.1. BACKGROUND

1.1.1. INTRODUCTION TO SOLAR CELLS

The combination of dwindling fuel resource and global warming resulting from high CO₂ emission has led to a pressing need for alternative sustainable energy sources, such as wind power, hydropower, geothermal power and solar power. Of these, solar power is most readily available in Singapore. Solar cells (or photovoltaics) are devices that harvest and convert sunlight into electrical energy, and this technology can be classified into 3 generations: (1G) Si monocrystalline solar cells, GaAs; (2G) thin film polycrystalline, e.g. amorphous Si solar cells, Cadmium Indium Gallium Sulfide (CIGS), Cadmium Telluride (CdTe); and (3G) organic / multijunction / tandem solar cells.

Single crystal Si cells have high average conversion efficiencies at 24.7% for single junction solar cells ¹. Its good stability and good conversion efficiencies make them highly suited for converting solar power on rooftops and buildings, but these cells are costly due to stringent material requirements and high fabrication cost. In comparison, due to the disordered or less ordered structure of amorphous and multi-crystalline Si, 2G cells generally have lower efficiencies, but are more affordable than single crystal Si cells. In order to avoid the use of Si and to reduce the cost-per-watt, the active materials can be made up of organic molecules (3G cells). Most of these materials are solution processible and hence reduces the fabrication cost of cells. Two examples of 3G solar cells are shown in Fig. 1.1. They are the organic bulk heterojunction cell (BHJ) ² and the dye sensitized solar cell (DSSC) ³.

FIGURE 1.1. SCHEMATIC DIAGRAMS OF AN ORGANIC BHJ CELL (LEFT) ² AND A DSSC (RIGHT).

1.2. DYE SENSITIZED SOLAR CELLS

The DSSC is an electrochemical photovoltaic cell that can harvest light efficiently at both high and low light intensities ³. Hence, DSSC is practical for both indoor and outdoor applications. The standard counter electrode (CE) material used in DSSC is platinum (Pt) which is normally processed either by sputter-coating from a Pt disc or thermally drying a coating of precursor solution to obtain a few hundred nanometers thick layer of Pt. Both methods employ expensive Pt sources and are therefore impractical for large scale device fabrication. Also, due to the brittle nature of the fluorine-doped tin oxide (FTO) film on which Pt is deposited, this film is unsuitable to be used on flexible substrates as multiple bending cycles will result in cracks and fatigue failure. Therefore for flexible DSSCs application, an alternative has to be found the standard CE.

1.2.1. CARBON NANOTUBES BASED COUNTER ELECTRODE FOR DSSCs

Carbon based materials such as carbon black, graphene and carbon nanotubes (CNT) are promising alternatives and each of these has their advantages and

disadvantages. Carbon black has high surface area which is useful for catalysis but a thick layer is required for effective charge conduction and hence it is usually opaque^{4,5}. Graphene has excellent charge conduction along the plane but it is a poor catalytic material⁶⁻⁸. CNT is structurally similar to graphene but both its catalysis and conduction properties may change with physical aspects such as tube length and surface functionalization. In the case of single-walled CNT, an antagonistic effect between conductivity and catalysis may be expected as the latter can be improved by introducing CNT surface defects through ozone treatment⁹. These defects may also lower activation energies required for interaction with other nanomaterials (e.g. acids, metals and their compounds) to form nanocomposites with adjustable electrical properties.

1.3. PROBLEM STATEMENT

Many groups have reported the use of CNT as an effective replacement for Pt while retaining FTO as the conducting substrate⁹⁻¹³; thicknesses of these thin films (10 μm)⁴ could be reduced to below 1 μm and would allow most light to pass through for dye excitation in the DSSC⁹. CNT has also been used directly on glass to replace FTO; however, much thicker films ($\geq 5 \mu\text{m}$) were required to achieve comparable device performance using standard CE (Pt/FTO)¹⁰. This would result in black and opaque CEs. To date there are very few reports on the use of thin CNT films to replace Pt and FTO, largely due to the issue of higher sheet resistance (an order of magnitude higher) which affects the charge distribution within the device. However, coupling CNT thin films with nanoparticles or chemical modifications may remove this limitation and improve their performance as CEs in DSSCs.

The main concerns for the application of CNT in DSSC CEs are therefore: 1) fabricating CNT networks that have high light transmittance and have conductivity comparable to FTO, 2) ensuring these CNT networks do not antagonize other concurrent chemical reactions within the solar cell (e.g. speeding up the backward reaction such that it competes against charge separation and collection in DSSCs), and 3) understanding and altering CNT properties so that such thin film electrodes can be optimized for application with multiple material combinations.

1.4. OBJECTIVES

1.4.1. INVESTIGATION OF A NEW ARCHITECTURE FOR SOLUTION-PROCESSIBLE, FLEXIBLE BI-FACIAL DSSC

Using CNT to replace FTO and Pt in a conventional DSSC architecture means that low temperatures of no more than 150 °C are necessary during device fabrication, and making flexible devices is possible. As replacement of FTO and Pt at the CE with thick CNT films has been demonstrated, the challenge here is to use thin CNT films at the CE, with optical transmittances that allow for bifacial DSSC behavior. The aims are therefore:

- to investigate the feasibility of using solution-processed CNT networks to replace FTO and catalytic layers
- to investigate the feasibility of using CNT networks in flexible DSSC devices

1.4.2. INVESTIGATING THE ROLE OF NANOMATERIALS IN THE ENHANCEMENT OF THE PERFORMANCE OF CNT NETWORKS

The alteration of CNT properties such as work function and sheet resistance is possible either by n- or p- doping of thin film CNTs via chemical solutions, or by energy level shifting / creating charge transfer complexes via metal nanoparticle decorations. The primary goals are:

- to treat CNT networks with chemical solutions and investigate their impact on work function modification
- to prepare metal and metal oxide nanoparticle decorations on CNT and investigate their effect on work function modification, conductivity, light transparency and scattering, and possible charge recombination in DSSC, using techniques such as Kelvin probe spectroscopy, conducting atomic force microscopy (cAFM) and Raman spectroscopy.

1.4.3. FUNDAMENTAL STUDIES ON THE CONTRIBUTION OF NANOPARTICLES IN DSSCs WITH CNT-BASED CEs

Effective replacement of both FTO and catalytic layers require an optimum balance of conductivity and catalytic properties of CNT. Metal and metal oxide nanoparticle-CNT systems need to be better understood for their role in the DSSC. The main objectives are:

- to understand the relationship between the type of conducting / catalytic layer(s) with device performance
- to understand the contribution of the abovementioned materials on device performance using analysis methods such as impedance spectroscopy, cyclic voltammetry and Tafel plots.

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2. LITERATURE REVIEW

2.1. CARBON NANOSTRUCTURES

The abundance and ubiquity of carbon is known but often undermined, as it is present in all known life forms, as well as in the Sun, cosmic stars, and planetary atmospheres. Different allotropes of carbon have different physical properties, such as hardness, phase stability, electrical conductivity and thermal conductivity. As a single atom it is non-metallic, but its tetravalence allows a wide variety of compounds to form with other elements to change this property. This is the case even for pure carbon allotropes – for example, diamond is one of the hardest known materials with very poor electrical conductivity ¹, while graphite (commonly known as “pencil lead”) is soft and a good conductor of electricity ². Other than diamond and graphite, there are other forms of nanostructured carbon, including graphene, amorphous carbon, fullerenes and carbon nanotubes.

Graphene’s structure is made of single-layer two-dimensional graphite. It absorbs only 2.3% of incident white light and is highly transparent ³. It has high planar conductivity of around 550 S/cm (1250S/cm for polycrystalline graphite) and an optical transmittance of above 70% over the spectral range of 1000–3000 nm ⁴. However, due to its low surface area to volume ratio, graphene has poor catalytic activity ^{4,5}. Graphene nanoribbons (GNRs) of zigzag or armchair configurations (see Fig. 2.1) have different metallicity. The zigzag configuration gives metallic GNRs, while armchair configurations can result in either metallic or semiconducting GNRs ⁶. In addition, the energy bandgap of armchair GNRs can be adjusted as it is inversely correlated to the nanoribbon width.

FIGURE 2.1. SCHEMATIC DIAGRAM SHOWING INTERLINKED C-C BONDS OF A GRAPHENE SHEET / UNROLLED SINGLE-WALLED CARBON NANOTUBE (SWNT), WITH HIGHLIGHTED ZIGZAG (IN RED), ARMCHAIR (IN BLUE) AND CHIRAL (IN GREEN; SWNT-ONLY) CONFIGURATIONS ⁷.

Amorphous carbon (a-C) may not be fully amorphous as its name suggests, but have a range of sp^2 - sp^3 carbon atom ratios, and thus can appear fully amorphous or with the inclusion of diamond crystallites depending on its structure. An example of carbon that falls within this category is carbon black, which has a high surface area-to-volume ratio and is thermally conductive and catalytically active. Although undoped a-C is poorly photoconductive and shows weak p-type semiconductor properties, the possibility of changing its conductivity makes it a viable material for optoelectronic applications. For example, a-C/Si hetero-junctions have been made possible by n-doping with phosphorous and nitrogen, and p-type by doping with boron. In addition, a thick, compact layer of carbon black has been shown as an effective counter electrode for the dye sensitized solar cell, albeit fully opaque and lacking in film stability ^{8,9}.

Fullerenes have become the most preferred material for electron acceptance and transport in organic photovoltaic devices, ever since the buckminsterfullerene (C_{60}) was discovered in 1985 at Rice University¹⁰. It is capable of ultra-fast photo-induced electron transfer; the high electric mobility is attributed to their closely packed face-centered cubic (FCC) structure. Theoretical predictions and experimental findings have suggested direct bandgap n-type semiconductor behavior of crystallized C_{60} ¹¹. C_{60} is typically used either as a thin photoactive layer in bilayer heterojunction organic solar cells, or as a polymer blend with an electron-donor material (e.g. poly(3-hexylthiophene) (P3HT)) in bulk heterojunction organic solar cells for best device efficiencies.

Since S. Iijima's discovery in 1991¹², carbon nanotubes (CNT) have been studied and applied in various applications such as composites¹³, sensors^{14,15}, transistors^{16,17}, supercapacitors^{18,19} and solar cells²⁰. The most common CNT forms used are the single-walled CNT (SWNT) and multi-walled CNT (MWNT), but depending on the synthesis method, other variants such as the double-walled CNT (DWNT), nanohorns, nanocups and nanoflowers also exist. Each "wall" or shell of the CNT is akin to a rolled up sheet of graphene and is therefore capable of 1-dimensional ballistic transport with electrical conductivity 1000 times greater than a copper wire, as well as a high elastic modulus to withstand stress and strain^{21,22}. A random network of CNT forms a flexible, mesh-like conducting film that can function as an effective DSSC counter electrode. Although CNT is more conductive but less catalytically active than carbon black, Trancik *et al.* has shown that ozone treatment of CNT films may used to improve catalytic activity²³.

2.2. PROPERTIES OF PRISTINE CNT

CNTs have nanoscale cylindrical structures and attracted much research interest due to its unique mechanical and electronic properties combined with chemical stability. Depending on the arrangement of the carbon honeycomb structure, CNTs can have either metallic or semiconducting properties. CNTs were observed to be p-type with a high-predicted mobility²⁴. CNTs have a direct bandgap that is inversely related to the nanotube diameter. In addition, the energy bandgap of metallic nanotubes is zero, while semiconducting nanotubes have an energy bandgap in the order of about 0.5 eV. The multiple bands of a single CNT can contribute optoelectronically to cover a wide range of energies. In other words, the use of CNTs of different diameters and chiralities together (i.e. a combination of different bandgaps) should be able to result in a continuous response over a wide spectral range.

CNT-based heterojunctions are able to offer unique geometry on top of good electronic, thermal and mechanical behaviour. Incident photons cause the excitation of free electron-hole pairs, which are then separated by an externally applied voltage or internal electric fields (e.g. at Schottky barriers, p–n junctions, defect sites) to generate photocurrent. Studies on photocurrent transport at CNT junctions by Zhu *et al.* revealed band-to-band transitions and photon-assisted tunneling. This applies to not only individual CNT but to CNT bundles and films⁶.

MWNT and SWNT are two types of CNT structures available. MWNTs are composed of closed and concentric graphene nanotubes (i.e. each of them a rolled-up graphene sheet), often with diameters up to 25 nm. A SWNT in contrast is made up of a single graphite sheet rolled seamlessly, with a diameter of 1-2 nm. SWNTs are usually observed to be in bundles of parallel nanotubes that are in contact with one

other.

As the CNT structure is closely related to graphene sheet, nanotubes are labeled with the graphene lattice unit vectors a_1 and a_2 , as well as the circumferential or chiral vector (C_h), which is also known as the vector that links two crystallographically equivalent sites on a sheet of graphene. The chiral vector of the geometry of SWNT is unique for nanotubes of different chirality, and is defined as:

$$C_h = na_1 + ma_2$$

where n and m are chiral indices. The diameter of nanotube, d , can be predicted by the equation

$$d = \left| \frac{C_h}{\pi} \right| = \frac{\sqrt{(3a_{c-c})}}{\pi} \sqrt{(n^2 + n \cdot m + m^2)}$$

where a_{c-c} is the length of the C–C bond. The chiral angle θ , or the angle between C_h and a_1 , defines the tilt angle of the hexagonal motif with respect to the nanotube's axis direction. It is calculated as:

$$\theta = \tan^{-1} \left[\frac{\sqrt{3}m}{m + 2n} \right]$$

The hexagonal symmetry of graphene's lattice indicates that the value of θ is $0 \leq \theta \leq 30^\circ$. m and $2n$ are parameters of the zone-folding model of nanotubes: nanotubes with $\text{mod} [(m + 2n), 3] = 1$ or 2 are semiconducting (type 1 or type 2), while those having $\text{mod} [(m + 2n), 3] = 0$ are metallic²⁵.

2.3. CNT FILM FABRICATION: A COMPARISON OF METHODS

For optical characterization of the SWNTs samples, a method for debundling and separating each SWNT is needed. Ultrasonication in water or surfactant solutions is used to separate the nanotubes bundles, followed by filtration and / or centrifugation to remove large residual bundles and impurities. Larger impurities can be removed by filtration, followed by an ultracentrifugation process that allows the separation of individual nanotubes and small bundles from large residual bundles (see [Appendix 1](#)). Pristine CNT without defects are hydrophobic and can only be solution processed in water with the help of surfactants. Surfactant molecules encapsulate individual CNT and prevent aggregation to reoccur, resulting in greater suspension stability ²⁵. Other choices of solvents that do not require the use of surfactants include organic solvents such as N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), but these are toxic and not environmentally friendly. Although surfactant molecules help in the formation of stable CNT suspensions in water, they are electrically insulating and optically absorbing, and would increase R_s and light absorbance if left in the CNT film. Hence they are removed either by post treating films in nitric acid or by thermal annealing them under an inert environment.

A completely water-based CNT suspension is ideal, as this avoids the incomplete removal of trapped residual surfactants in the CNT film. This is possible with commercially available CNT that have been modified with 3-5% carboxylic side groups along the surface or ends (e.g. P3-SWNT, Carbon Solutions Inc.). Carboxylic side groups are hydrophilic and contribute to the formation and stability of CNT suspension without the need for surfactants. Each carboxylate site is akin to a defect site – it is antagonistic to nanotube conductivity, but may also function as a site for

nanomaterial functionalization to confer catalytic properties, in addition to improving the stability of the suspension in water. The potential of using defect sites for catalysis offers the possibility of Pt replacement, especially since thermal deposition of Pt occurs at temperature above 400 °C and is not possible for flexible substrates.

Depositing CNT on substrates can be done by the following methods: spin coating²⁶, dip coating²⁷, vacuum pump filtration²⁸ and spray coating²⁹. Unlike brittle cracking or fracturing that come with the flexing of ITO or FTO films, the resulting CNT films when deposited on flexible substrates showed stable conductivity under repeated bending^{27,30}. Among these deposition methods, spin coating and dip coating form thinner smoother films, and allows great control of the film thickness and transparency since the process is repeated to reach sufficient thickness; however these are time-consuming processes^{26,27}. In contrast, the vacuum pump filtration method first forms the CNT film on top of the filter before it is pressure-transfer printed to the substrate manually. This not only makes it difficult to control film transparency, but also poses the problem of non-uniform film adhesion during the transfer process. Spray coating utilizes an air brush technique, which is a straightforward and fast method that allows easy adjustment of the transparency of CNT films, although the films generally have higher surface roughness than those fabricated by spin and dip coating methods²⁹. Compared to the thermal deposition of Pt, the deposition temperature of CNT spray coating is low enough (125 °C) to allow for solvent evaporation. This is close to or below the glass transition temperatures (T_g) of flexible substrates (100-200 °C, depending on molecular structure and density of polymer), and allows for CNT film deposition on flexible substrates with higher T_g .

2.4. MODIFICATION AND FUNCTIONALIZATION OF CNT

2.4.1. CHEMICAL MODIFICATION OF CNT

CNT conductivity and work function can be tuned by p-doping or n-doping after exposure to chemicals, such as HNO_3 ³¹⁻⁴³, NADH⁴⁴ and viologens⁴⁵. N-doping of CNT happens when surface adsorbed NADH and viologens donate electrons to CNT. For viologens, according to first principles calculations, it is estimated that the Fermi level of CNT may be upshifted by a maximum of 0.3 eV⁴⁵. However, environmental oxidation causes the n-doping of CNT using either drop-coated NADH or viologens to be unstable and reversible (after 100 days for NADH and 80 days for viologens) under ambient conditions. If CNT films were NADH-treated, the n-doping was recoverable upon thermal annealing the CNT film or device at 150 °C⁴⁴. This annealing process would not be feasible for the DSSC as the dye degrades at temperatures above 60 – 80 °C.

CNT can be p-doped upon treatment with the Brønsted acids H_2SO_4 , HNO_3 or HCl . Graupner *et al.* immersed buckypaper for 20 min in 4 M of each acid, and observed that only H_2SO_4 caused structural damage. The structural damage done to CNT as a result of H_2SO_4 treatment adversely affects nanotube and film resistances. In addition, X-ray photoelectron (XPS) spectra revealed the highest binding energy for H_2SO_4 (+0.5 eV), followed by HNO_3 (+0.2 eV) and HCl (+0.1 eV)³¹.

HNO_3 is commonly used for refluxing CNTs to create surface carboxylate groups, although at an expense of nanotube conductivity since they are CNT surface defects³²⁻³⁴. As mentioned earlier, carboxylate groups improve the compatibility between CNT and water and also act as active sites for functionalization. A less harsh method was to expose CNT films to concentrated HNO_3 vapor, which reduces sheet

resistances (R_S) without changing the film thickness, but this requires very high concentrations (above 12 M) of HNO_3 . Instead of introducing defects, HNO_3 molecules are believed to intercalate within the CNT film and extract electrons from adjacent nanotubes^{35,36}.

2.4.2. NANOPARTICLE DECORATIONS OF CNT

Many metallic nanoparticles are able to form in close proximity to CNT surfaces, such as Au, Ti, Al, Ni, Pd, Fe, Ag, Pt and Pb⁴⁶⁻⁵⁰. As a result, CNT can be used as a sacrificial scaffold structure for the synthesis of metal nanowire interconnects, and metallic nanoparticle-decorated CNT may be used for gas sensing. Using electron beam deposition, Zhang & Dai observed that the strength of interaction between the metal and CNT differs from metal to metal. They noted that Au, Al, Pb and Fe have weak interaction with CNT surface⁴⁶, while Zhang *et al.* reported strong interaction with CNT for Ti, Ni and Pd⁴⁷. Density functional calculations of CNT adsorption profiles of various metal elements by Park *et al.* have also suggested that Al, Au, Pt, Pd and Ti have increasing binding energies with CNT in that order. Interfacial wetting improvement also follows the same sequence, and increases the possibility of metal-carbon bond formation while decreasing the risk of metal oxidation⁴⁸. The strength of the interaction between the metal and CNT determines its nucleation density and nanoparticle size; weaker interactions exhibit lower nucleation densities and bigger average particle sizes.

Besides electron beam deposition^{46,47}, the decoration of CNT surfaces with metallic nanoparticles is possible with chemical bath deposition methods such as ethanol-assisted electroless spontaneous reduction⁵¹ or electrodeposition^{52,53}. A

variety of metallic nanoparticle sizes and CNT surface coverage can be obtained by optimizing the chemical deposition parameters, such as metal salt precursor concentration, reaction time & temperature. Chemical bath deposition has a high degree of penetration into porous materials such as CNT films, and therefore allows nanoparticle deposition throughout the film. Since the chemical bath deposition method does not require high temperatures for reaction, it is also feasible to use plastic substrates for this method.

The main difference between the electroless reduction and electrodeposition methods is the additional supply of optimized applied voltage bias as nucleation potential for the latter. An example of electrodeposition on CNT films was done by Day *et al.*, who were able to obtain CNT with a high density of Pt nanoparticles by using an applied bias of -0.4 V over 30 s⁵³. Electrodeposition requires a highly conducting supporting substrate to act as the cathode (e.g. FTO, ITO or metallic substrates) in order to obtain a uniform deposition; the use of plastic substrates is therefore not possible. In contrast, electroless deposition negates the use of an additional applied voltage bias, provided that the metal deposited has a higher work function (i.e. higher electrochemical potential) than the material on which it is deposited. In other words, the choice and range of metal deposition would be smaller if the work function of the deposited substrate is higher. With this method, Choi *et al.* successfully decorated CNT (work function: 4.8 eV) with Pt and Au (work function: 6.3 eV and 5.1 eV) within seconds of reaction⁵¹.

Other than metal^{46,53} and metal oxides^{54,55}, metal sulfides such as CoS, NiS and WS₂ have shown catalytic activity that is either on par with or better than Pt on FTO substrates in DSSC⁵⁶⁻⁶⁰. Direct deposition of these metal sulfide nanoparticles on

conducting oxide substrates was typically achieved using electrodeposition⁵⁶⁻⁵⁸. Other deposition methods, such as spray coating of hydrothermally preformed metal sulfide nanoparticles⁵⁹ and heat annealing of drop coated metal sulfide precursor solutions⁶¹, were also reported to give similar results. The excellent catalytic activity and high surface area of these nanoparticles yielded charge transfer resistances that were on par or lower than that of Pt. However, the key issue with using these metal sulfide CEs in DSSCs is high diffusion resistance across the electrolyte, as a result of unwanted complex formation of sulfide with the electrolyte redox species. This results in low limiting current densities and a compromised overall percentage conversion efficiency (*PCE*, or η).

A possible reason for high diffusion resistance is additional reaction between the metal sulfide and iodide/triiodide species in the electrolyte. In lithium-sulfur (Li-S) batteries, researchers have discovered that sulfide ions that diffuse in the electrolyte during battery cycling can react irreversibly with Li to form the insoluble insulator dilithium sulfide (Li_2S), and decrease battery life⁶¹. As the iodide/triiodide species in DSSC electrolyte is Li-based, a similar situation is likely to occur to DSSCs with metal sulfide CEs. The stability of these catalytic metal sulfide nanoparticles in electrolyte can be improved by binding the nanoparticles preferentially onto the CE, so as to decrease the diffusion resistance. By using MWNT at the CE as a scaffold for CoS deposition, Lin *et al.* showed that not only was the CoS electrochemically stable in the electrolyte, but catalytic activity and device efficiency (*PCE* = 6.96%) of the DSSC with this nanocomposite CE were improved as compared to devices that had either only MWNT (η = 2.91%) or only CoS (η = 5.86%) as CEs (in both cases, FTO were used as the substrate)⁵⁷.

2.5. INTERPRETATION OF DSSC PERFORMANCE

In order to determine the solar cell performance, there are several parameters that must be considered including fill factor (FF), short circuit current (I_{SC}) or short circuit current density (J_{SC}), open circuit voltage (V_{OC}) and PCE . FF , which is determined by V_{OC} and I_{SC} , measures the squareness of the current to voltage (I - V) curve, as shown in Fig. 2.2.

FIGURE 2.2. A TYPICAL I - V CURVE, SHOWING V_{OC} AND I_{SC} . P_{MAX} , I_{MAX} AND V_{MAX} REFER TO THE MAXIMUM OBTAINABLE POWER, CURRENT AND VOLTAGE RESPECTIVELY ⁶².

The FF is defined as the ratio of the maximum obtainable power to the theoretical power,

$$FF = \frac{I_{max} \times V_{max}}{V_{OC} \times I_{SC}},$$

where I_{max} is the maximum obtainable current, V_{max} is the maximum obtainable voltage, V_{OC} is the potential built up due to flow of minority carriers, and I_{SC} is the light-generated current from minority carrier flow. The most important key parameter

in measuring the photovoltaic (PV) performance is the *PCE*, or power density generated by a PV cell as a fraction of incident light power density.

$$PCE = \frac{I_{sc} \times V_{oc} \times FF}{P_s \times A} ,$$

where *FF* is the fill factor, P_s is the incident light power density and *A* is the area of a PV cell.

2.6. APPLICATIONS OF CARBON NANOTUBES IN DYE SENSITIZED SOLAR CELLS

There is much interest in incorporating CNT in DSSC, either as an alternative replacement material or as an additional component to improve device behavior due to improved charge transfer and / or catalysis. The effect of adding CNT to different parts of the DSSC – the anode, electrolyte and counter electrode – has been investigated by other researchers⁶³⁻⁷⁵. The addition of CNT to Ru-based dyes was not reported in literature, as the hydrophilic dyes have poor wetting on the relatively hydrophobic CNT surface, which would likely result in phase separation⁶³.

Similarly, there is a challenge in incorporating CNT into the electrolyte to improve DSSC performance – more so with SWNT than MWNT – as rebundling or aggregation due to van der Waals attraction of CNT surfaces can occur in the electrolyte, affecting suspension stability and DSSC stability over time. Nonetheless, CNT in electrolyte can act as effective electron transfer channels from the CE to dye, as reported by Lee *et al.*, whose DSSCs with either SWNT or MWNT in the electrolyte

gave slight improvements in J_{SC} (+0.9 mA/cm² and +2.1 mA/cm² respectively) as compared to the standard DSSC's (8.11 mA/cm²)⁶⁴.

As for the use of CNT in DSSC photo anode, there are two main approaches: 1) as a physical mixture with TiO₂ to provide electron transport channels connecting the TiO₂ nanoparticles, or 2) as an electron collector layer between FTO and TiO₂⁶⁵⁻⁶⁹. The first approach simply requires a homogeneous blend of a very small amount of CNT (less than 1 wt%) in the mesoporous TiO₂ layer to boost DSSC efficiency⁶⁵. The risk of charge recombination increases with higher amounts of CNT as they may also act as a catalyst for triiodide reduction. This is the same reason why the second approach is more difficult.

CNT surfaces at the photo anode need to be shielded from the electrolyte for the DSSC to work, and this can be done using a layer of TiO₂. The thickness of the blocking layer must be optimised to allow electron tunneling from TiO₂ to CNT. Brown *et al.* directly deposited a layer of TiO₂ on top of the CNT anode, and found that V_{OC} and FF decreased due to the lack of blocking layer on CNT surface, while J_{SC} improved due to more efficient charge separation and transport, leading to a slightly decreased DSSC efficiency⁶⁶. Others have suggested the use of sol-gel synthesis to form TiO₂ nanoparticles on the CNT surfaces to improve V_{OC} and FF , although the increase in charge transfer resistance as a result of TiO₂ coverage may compromise the J_{SC} and result in no increase in the PCE ^{67,68}. Another possible alternative to the sol-gel technique is atomic layer deposition, which allows a high degree of CNT surface coverage and control of TiO₂ thickness, but forms amorphous TiO₂ and is also too slow a process to adopt for DSSC anode fabrication⁶⁹.

The application of CNT films as DSSC counter electrodes has been demonstrated within the last decade. Films that were a few micrometers thick effectively replaced either Pt only⁷⁰, or both FTO and Pt⁷¹. Studies on the stability of CNT in electrolyte by Koo *et al.* showed that the DSSC efficiency remained stable over 5 days when CNT was used, whereas this decreased by more than 50% after 3 days when either sputtered or electrodeposited Pt was used⁷². Using CNT in place of Pt therefore has the benefit of increasing the lifespan of DSSC, although the thick CNT films used would cause their appearance to be black and opaque, making them unsuitable for bifacial DSSCs.

However, scaling down the film thickness such that the optical transmittance becomes comparable to Pt/FTO substrates will result in high R_s (CNT: $\sim 500 \Omega/\text{sq}$, Pt/FTO: $\sim 15\text{-}30 \Omega/\text{sq}$, with 80-85% transmittance @ 550 nm)^{73,74}, which can reduce the DSSC performance. The issue of high R_s of pristine, thin CNT films makes them unfavourable as DSSC CEs. As such, the first demonstration of using thin CNT films to replace both FTO and Pt in DSSCs was not reported until recently by Aitola *et al.*. Using thin CNT films with 27% optical transmittance @ 550 nm and an average R_s of $60 \Omega/\text{sq}$ as counter electrodes, the DSSCs were found to suffer from very low FF as well as decreased J_{sc} under 1 Sun illumination, and as a result the overall efficiency ($PCE = 0.74\%$) was just 17% of a standard DSSC⁷⁵.

The application of thin CNT films as transparent DSSC CE for bifacial application has been largely unexplored to date. However, the ability to alter properties of CNT by structural or surface modification through a variety of methods makes it possible for such an application, for example, the use of ozone treatment to improve CNT's catalytic activity as mentioned earlier²³. More details of the properties of CNT

that can be modified will be explained in the next section. The effects of different CNT modifications on film and DSSC properties need to be studied and understood for effective application of thin CNT films as CE.

2.7. EXISTING CONCERNS AND CHALLENGES

One of the advantages in some of the third generation cells is the possibility of making flexible solar cell devices. In both third generation solar cells shown in Fig. 1.1, transparent conducting oxides (TCOs) such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO) are commonly employed as electrode materials. These thin films boast high conductance and light transmittance, but are expensive ⁷⁶ and suffer from brittle cracking ⁷⁷ when bent, drastically lowering the conductivity in flexible devices.

A suitable replacement material is CNT. The excellent conductivity and structural compliance of CNT makes it an ideal candidate as a conducting electrode in solar cells, where light-induced electrical charge is collected. CNT in its defect-free form is an excellent conductor, but the formation of core-filled hybrids and surface decorations from bulk and surface interactions with other materials can change its material properties to either improve the performance of electrical devices (biosensors (catalytic effect), nanoFET (semiconductor), and supercapacitors (conductor)), or effectively replace unfavorable materials in the manufacturing process.

Various approaches have been adopted to modify CNT based electrode properties: CNT selection (metallic/semiconducting, single-/double-/multi-walled), growth method, morphology/alignment in bulk, physical/chemical alteration of tubes

for WF tuning (surfactant, metal nanoparticles, plasma, dangling chains e.g. COOH, charge doping). At 4.8-4.9 eV, the work function (WF) of carboxylated CNT is also comparable to ITO's (Φ : 4.9-5.0 eV), ensuring minimal interfacial charge transfer barrier. Although this does not match the WF of FTO (Φ : 4.2-4.4 eV), it can be tuned by modifying the CNT surface through physical or chemical methods⁷⁷. By controlling the extent of WF increase or decrease, CNT thin films can be adapted to any WF requirement for use in other systems besides solar cells. Hence in order to effectively control CNT WF, the focus would be to understand and predict the interactions between CNT and its modifier.

Besides the good electrical conductivity of CNT, its catalytic property is also an advantage as an electrode (e.g. replacing both Pt nanoparticles and ITO in a DSSC). However, obtaining CNT that is both conducting and catalytic is difficult. This is because CNT surface defect sites offer lower activation energies for catalytic reactions, but decrease axial conductivity along the nanotube. In other words, the antagonistic effect of conductivity on catalytic activity implies a compromised point where these two properties are optimal. As such, pristine CNT requires modification – chemically or by formation of nanocomposites – to push beyond this limit. The possibilities of CNT modification are abundant and only limited by CNT's interaction with the choice of modifier. The work reported in Chapters 3 to 6 will provide a detailed analysis of CNT interaction with a few modifiers, namely, HNO₃, Au, Pt, CoS and NiS, and how each of these in turn affect CNT film properties and behavior as DSSC CEs.

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3. PRISTINE CNT NETWORKS IN DSSC

3.1. INTRODUCTION

In the DSSC, transparent conductive oxide (TCO) films coated on glass substrates are typically used as electrodes. Commercially available substrates have an average sheet resistance (R_s) of 15-30 Ωsq^{-1} and optical transmittance of 80-85% at 550 nm. Platinum (Pt) is used as the counter electrode (CE) material to catalyse the reduction of triiodide species in the electrolyte, and it is commonly processed either by sputter-coating from a Pt disc or thermally drying a coating of precursor solution above the TCO film to obtain a layer of a few hundred nanometers in thickness.

The standard TCO material for the DSSC is fluorine-doped tin oxide (FTO), but other alternative oxides such as tin-doped indium oxide (ITO), zinc oxide and aluminum zinc oxide (AZO) have also been proposed in literature¹⁻³. However, ITO is less cost-effective due to the use of indium as a main component, while zinc oxide-based films have lower levels of optical transparency despite having comparable electronic properties with FTO. Moreover, the deposition of these materials on glass has to be carried out in high vacuum condition for all these TCO films and hence the manufacturing process is time consuming. Most importantly, all these TCO films have a common shortcoming – they are inherently brittle and vulnerable to cracks and fatigue failure on flexible substrates, making them incompatible for the development of flexible photovoltaic devices.

To overcome this limitation, other materials have been suggested as flexible alternatives of transparent conducting films, including the conductive polymer mixture PEDOT:PSS, and carbon-based nanomaterials such as graphene and carbon nanotubes

(CNT). PEDOT:PSS is soluble in water and forms highly transparent films by a simple and fast spin-coating process, although the average R_s of these films are at least ten times more than that of TCO films of the same optical transmittance⁴. As mentioned in Section 1.1.1, graphene is highly transparent and has excellent planar conductivity⁵, but the synthesis of large scale conductive pristine graphene sheets for deposition on flexible substrates remains a challenge, as film conductivity is highly sensitive to the presence of unreduced oxides and other structural defects⁶.

CNT can be solution processed in both its pristine form in water (with the help of surfactants) or in toxic organic solvents such as N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). The use of surfactants is necessary to form stable pristine CNT suspensions in water, but surfactants molecules are electrically insulating, and must be removed either by post-treating CNT films in nitric acid or thermally annealing them under an inert environment, as residual surfactant molecules increase CNT film R_s and optical absorbance.

However, incomplete removal or trapped residual surfactants in the CNT film is common, and hence a completely water-based CNT suspension is desired. This is achievable with commercially available CNT that have been modified with 3-5% carboxylic side groups along the surface or ends (e.g. P3-SWNT, Carbon Solutions Inc.). Carboxylic side groups aid the formation and stability of CNT suspension without the need for surfactants. Each carboxylate site is akin to a site of defect that is antagonistic to nanotube conductivity, but may also be used as a site for nanomaterial functionalization, to confer catalytic properties, and to improve the stability of suspension in water. The potential of using defect sites for catalysis offers the possibility of Pt replacement, especially since thermal deposition ($> 400\text{ }^{\circ}\text{C}$) is not

possible for flexible substrates. Unlike graphene, a CNT film is made of a random network of nanotubes with axial conductivity (and not planar), hence the CNT film conductivity is relatively more tolerant to the presence of defects.

CNT is commonly present in 2 forms, the single-walled CNT (SWNT) which is structurally similar to a single rolled up sheet of graphene, and the multi-walled CNT (MWNT) which is analogous to several concentric layers of SWNT of different diameters. SWNT thin films confer higher conductivity than multi-walled CNT (MWNT) thin films of the same transparency, because the nanotube conductivity reduces as the outer diameter of an MWNT increases, and the sonication process required for preparing MWNT suspensions are more likely to introduce defects that further decrease conductivity due to abrasion between the adjacent concentric nanotubes that are present within a single MWNT. It is due to these properties of CNT that P3-SWNT has been chosen for this work.

CNT deposition on substrates can be achieved by a variety of methods, such as spin coating ⁷, dip coating ⁸, vacuum pump filtration ⁹ and spray coating ¹⁰. The resulting CNT films when deposited on flexible substrates showed stability of conductivity under repeated bending ^{8,11}. Among these deposition methods, spin coating and dip coating form thinner smoother films that can be repeated to allow for greater control of film thickness and transparency, but are otherwise time-consuming processes. The vacuum pump filtration method forms the CNT film first before pressure-transfer printing it to the substrate, which makes it difficult to control film transparency, and poses the problem of non-uniform film adhesion during the transfer process.

In this work, a thin film of CNT is deposited using spray coating, which utilizes

an air brush technique. This is a straightforward and fast method that allows easy adjustment of the transparency of CNT film¹⁰. As mentioned earlier, in contrast to the thermal reduction of Pt precursor coatings at above 400 °C, the deposition temperature of CNT spray coating is relatively lower at 125 °C for solvent evaporation. This is close to or above the glass transition temperatures of flexible substrates (approx. 100-200 °C, depending on molecular structure and density of polymer) and allows for CNT film deposition on flexible substrates.

Unlike other methods such as transfer printing or layer-by-layer dip coating, spray coating does not require strong chemical bonding to control adhesion of CNTs on the substrate, hence chemical pretreatment of substrates is not crucial. Also, unlike other photovoltaic applications where smooth flat electrode surfaces are necessary to prevent device shorting, the lower surface roughness of films obtainable using spin coating and dip coating methods were not required for CEs in DSSC. In fact, as DSSC electrodes, surface roughness actually improves catalytic activity instead.

As the optimization of variables for obtaining highly conductive, well-suspended CNT is itself a comprehensive study, therefore this work only focused on the process steps involved in centrifugation and suspension preparation. A study was previously done by Hecht *et al.*¹² to show the relationship between the conductivity of SWNT network and its bundle length. An experiment was carried out by fabricating SWNT networks of different bundle lengths; the network resistance was found to reduce with increasing bundle length due to the decrease in charge transfer reactions across nanotube junctions.

Various SWNT bundle lengths were obtained by varying probe sonication time in a separate study, which showed a decrease in bundle lengths with longer sonication

durations ¹³. Although the study showed that sonication is necessary for the de-bundling of nanotubes in suspension leading to improvement in film conductivity, long sonication durations reduce the length of the nanotubes and decrease film conductivity. This antagonistic effect therefore suggests that an optimum sonication duration leading to maximum conductivity may be found. However, the optimum duration of sonication itself depends on a few factors, such as sonication power (supply of kinetic energy), temperature (supply of heat) and initial CNT concentration (distribution of total energy received), which have yet to be considered as a combination.

A more comprehensive study of effect of sonication therefore involves an investigation on the effect of sonication power and concentration of CNT suspension on the R_s and transmittance of the final CNT film. This serves as the focus in the first part of the discussion in this chapter. Some of the factors listed above were fixed, such as centrifugation speed and duration, sonication duration and source of CNT nanopowder (P3-SWNT). The optimization of R_s and optical transmittance of CNT films based on suspension preparation in the first part of this chapter were done using glass substrates. The best film with a R_s of $300 \Omega\text{sq}^{-1}$ at 80% optical transmittance (at 550 nm) was obtained with sonication power of 400 W and an initial CNT concentration of 0.3 mg/mL.

The criteria to determine if pristine CNT films can be used to effectively replace both FTO and Pt layers are conductivity and catalytic activity respectively, while allowing sufficient light transmittance for bifacial purposes. As mentioned earlier, the R_s of FTO-glass used in a standard DSSC typically falls in the range of 15-30 Ωsq^{-1} , with light transmittances of 80-85%. As this R_s range is 10-20 times lower than the R_s of the optimized CNT films in this study, the device efficiency of our

DSSC is not expected to match that of a standard cell. Indeed, Aitola *et al.* found that the use of thin CNT films with 27% optical transmittance on PET substrates give reasonable device efficiencies at low light intensities, but suffer from poor fill factors (FF) under 1 Sun illumination¹⁴. However, Wu *et al.* reported that high purity CNT continuous films could be competent alternative electrodes with resistance and transparency matching those of ITO films, which have similar R_s and transmittances as FTO¹⁵.

It is therefore of interest to study how our CNT films fare against standard Pt/FTO CEs. Following the optimization of CNT film fabrication process, CNT films were fabricated not only on glass but also on the plastic substrates polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), and tested in DSSC as CE without further modification. These are subsequently referred to as pristine, or control, CNT thin films. The later part of the results in this chapter therefore demonstrates and analyses the effect of CNT replacement of both FTO and Pt on DSSC device behavior and performance in comparison with those of a standard DSSC.

The CNT films used in this work were more transparent, yet had better DSSC performance than similar devices made by Aitola *et al.* regardless of incident light intensity, which highlights the importance of optimization of CNT film fabrication. However, poor FF and J_{SC} under the maximum 1 Sun illumination were also observed for all devices reported in the results, and to lesser extents with decreasing illumination intensities, which mirrored the case of Aitola *et al.*. High charge transfer resistance at the CE to electrolyte interface was revealed by impedance analyses as the main reason for this observation, which needs further film modification to significantly decrease it, as well as improve catalytic activity.

As highly catalytic CNT films with low charge transfer resistances are required to improve DSSC performance, the subject of CNT film treatment / modification will therefore be addressed in upcoming chapters. In this chapter, the optimization and application of pristine thin CNT films deposited on glass and plastic substrates as CEs of DSSC are demonstrated, and serve as a reference for subsequent studies. Issues and phenomenon are discussed in detail when analysing changes in device behavior.

3.2. METHODS

As-received carboxylated SWNT (P3-SWNT, Carbon Solution Inc.) nanopowder was dispersed at different concentrations (0.05 – 0.3 mg/mL) in 40 mL of deionized (DI) water and bath sonicated for 30 min. To improve dispersion, the bottle containing this suspension was then immersed in an ice bath, and probe sonicated at different powers (100 – 400 W; Vibra-cell VCX500 with 13 mm dia. probe tip, Sonics) for 20 min, followed by centrifugation at 14000 rpm for 70 min, after which the supernatant was extracted and stored for subsequent use.

Glass substrates for optical and resistivity studies were bath sonicated in absolute ethanol and DI water for 15 min each and blow-dried with compressed air. The substrates were exposed to air plasma for 3 min and then heated at 125 °C for 10 min. For the application in DSSC, glass, PET and PEN substrates were prepared similarly, except that the initial CNT concentration was fixed at 0.3 mg/mL and sonication power was fixed at 400 W, (i.e. the optimized variables). Keeping the temperature at 125 °C, CNT suspension was spray coated onto the substrates in a sweeping motion using an air brush (Grafo T1, Harder & Steenbeck) and a piston-based compressor (Hymair). Finished samples were air cooled and kept in petri dishes

at ambient conditions (25 °C, 1 atm). Transmittances of incident light were measured with UV-vis spectrophotometer (UV-3200, Shimadzu); all CNT films had at least 60%T @ 550 nm. R_s measurements were recorded using a 4-point probe system (Keithley 2400 SourceMeter).

CNT films deposited on glass, PET and PEN, as well as FTO glass ($15 \Omega\text{sq}^{-1}$; Asahi) were employed as base substrates for CEs. These films had optical transmittances of 80%T – 85%T @ 550 nm. A hole was drilled in each of them for the subsequent filling of electrolyte. The Pt precursor, chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$; Aldrich) was prepared as a 5 mM solution in absolute ethanol, drop casted onto the FTO surface and heated at 450 °C for 15 min to form a layer of Pt particles (i.e. Pt/FTO). All working electrodes were made of FTO glass and a double layer of 8 μm mesoporous TiO_2 (DSL 18NR-T, Dyesol) + 5 μm thick scattering TiO_2 (DSL 18NR-AO, Dyesol) sintered at 500 °C. Dye soaking (DNH2, Dyesol) was done for 16 h to ensure sufficient dye uptake by TiO_2 before assembly with the CE, where a ring spacer (SX1170-25, Solaronix) held them together (110 °C, 20 s) and sealed off the cell active volume. This volume was then filled with either electrolyte MPN-50 (Solaronix) or the electrolyte coded Z946 (1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.15 M I_2 , 0.5 M N-butylbenzimidazole (NBB), and 0.1 M guanidine thiocyanate (GNCS) in methoxypropionitrile (MPN), from EPFL). The hole was finally covered with the same spacer and an optically-clear glass coverslip above it. The cross-sectional cell architectures of DSSC and CEs tested are shown in Fig. 3.1. Current density to voltage (J - V) measurements were taken under dark condition and light condition (AM1.5, Newport solar simulator) at 100% Sun (1 Sun or $100 \text{ mW}\cdot\text{cm}^{-2}$), 50% Sun and 1% Sun. Both the Nyquist and Bode plots were obtained through impedance spectroscopy under dark condition (Autolab 302N / FRA, Eco Chemie B.V.).

FIGURE 3.1. CROSS-SECTIONAL ARCHITECTURES OF DSSC WITH DIFFERENT COUNTER ELECTRODES: (A) STANDARD CELL ARCHITECTURE WITH Pt/FTO CE, (B) GLASS/CNT CE, AND (C) PLASTIC/CNT CE. THE ARCHITECTURE FOR THE PHOTO ANODE WAS KEPT THE SAME FOR ALL DEVICES.

3.3. RESULTS AND DISCUSSION

3.3.1. CORRELATION STUDIES OF CNT FILMS – OPTICAL TRANSMITTANCE AND RESISTIVITY

Both the transmittance and the R_s of CNT films are strongly affected by the CNT dispersion conditions such as probe sonication and centrifugation process (for removal of impurities and large aggregates). In order to understand the correlation between transmittance and R_s , a series of different probe sonication powers were used to prepare the suspensions with a low initial CNT concentration of 0.1 mg/mL. It is expected that by increasing the probe sonication power, CNT would be better dispersed, although the nanotube lengths may be reduced at high sonication powers. The effect of sonication power can be seen in Fig. 3.2.

In general, increasing the thickness of CNT films decreases the optical transmittance, but decrease R_s due to an improvement in charge percolation. The charge percolation threshold is known to be reached at film thicknesses close to the average CNT length in the film ¹⁶, which explains the gradual convergence of R_s obtained from all sonication powers as transmittance decreased to 60%T. When transmittances were higher than 60%T, the projected R_s of CNT films was lowest when prepared using 100 W, and R_s increased with increasing sonication power. Hence 100 W is an ideal sonication power to prepare films with low R_s at all transmittances. This low sonication power is related to the CNT concentration used. As the CNT concentration is fairly low (0.1 mg/mL), minimum energy is required to cause the debundling of the nanotubes, therefore a low sonication power of 100 W was sufficient. R_s is observed to increase as probe sonication power increases, due to the reduction in the nanotube lengths at a high sonication power (400 W). These shorter nanotubes will result in higher intertube resistance that can be observed from the higher R_s .

However, when sonication power increased from 100 W to 400 W, the slopes of best-fit curve for each of the tested sonication powers in Fig. 3.2 were observed to decrease in steepness. For the films prepared using all four conditions with 60-65% transmittance, the R_s converged at 200-260 Ωsq^{-1} . This suggests that the effect of sonication power on R_s would be more significant for thinner, more transparent films. Ideally, the CNT films should have similar optical transmittances as the standard FTO films in standard DSSCs (i.e. 80-85%T). Therefore based on the initial CNT concentration used (0.1 mg/mL), using lowest sonication power (100 W) will result in a CNT film with the lowest R_s . In practice however, higher CNT concentrations are preferred for shorter spray coating durations.

FIGURE 3.2. TRANSMITTANCE VERSUS SHEET RESISTANCE FOR COMPARISON BETWEEN DIFFERENT CNT SONICATION POWERS AT AN INITIAL CNT CONCENTRATION OF 0.1 MG/ML.

FIGURE 3.3. TRANSMITTANCE VERSUS SHEET RESISTANCE FOR COMPARISON BETWEEN DIFFERENT CNT SONICATION POWERS AT AN INITIAL CNT CONCENTRATION OF 0.2 MG/ML.

When the CNT concentration was higher (0.2 mg/mL) and sonicated at either 100 W or 400 W, it was found that the effect of sonication powers was different from

the previous observation. In Fig. 3.3, although R_s also decreases when transmittance decreases, the R_s values decrease when probe sonication power increases from 100 W to 400 W. This is because more energy is required to debundle the CNT when a higher concentration is used, and a more debundled CNT network resulted in a lower R_s .

Since using a high sonication power to process a higher CNT concentration is better for obtaining highly transparent CNT films with lower R_s , an ideal CNT suspension should have as high a concentration as possible, while maintaining suspension stability. The effect of increasing CNT concentration while keeping sonication power at 400 W was therefore investigated. The concentrations tested were 0.05, 0.1, 0.2 and 0.3 mg/mL, and the results are shown in Fig. 3.4. The highest sonication power tested was 400 W due to equipment limitation. Also, the maximum CNT concentration was kept at 0.3 mg/mL as suspensions with higher CNT concentrations were no longer stable.

For each of these concentrations, the R_s values were observed to decrease when transmittance decreases. In addition, an increase in R_s is observed as the CNT concentration decreases – at 80% transmittance, R_s increased from 300 Ωsq^{-1} with 0.3 mg/mL to 825 Ωsq^{-1} with 0.05 mg/mL. This is because debundling (which decreases R_s) is dominant over nanotube scission (which increases R_s) at higher CNT concentrations, while the reverse is true for low CNT concentrations¹⁷. Hence, an optimum combination of sonication power and CNT concentration is required to obtain the best R_s at 80%T. Fig. 3.5 suggests that the decrease in R_s with increasing CNT concentration follows a power-law relation – an observation that has been reported in other papers^{18,19}. The lowest R_s at 80%T that can be achieved is 300 Ωsq^{-1} , and this for a CNT film prepared using 0.3 mg/mL CNT solution probe sonicated at 400 W.

This is a 60% improvement as compared to that of 0.05 mg/ml CNT solution ($R_S = 825 \Omega\text{sq}^{-1}$ at 80%T).

FIGURE 3.4. TRANSMITTANCE VERSUS SHEET RESISTANCE FOR COMPARISON BETWEEN DIFFERENT CNT CONCENTRATIONS AT SONICATION POWER OF 400 W.

FIGURE 3.5. SHEET RESISTANCE (80% TRANSMITTANCE @ 550 nm) VS. CONCENTRATION OF CNT SUSPENSION, USING PROBE SONICATION POWER OF 400 W, WITH DATA POINTS OBSERVING A POWER-LAW RELATION.

The optimum probe sonication power required to sonicate CNT suspensions in order to obtain the lowest possible R_s in the resulting thin film is also dependent on the initial CNT concentration. A higher CNT concentration will require higher sonication power to debundle the nanotubes effectively. If the power is too high, it would be detrimental to the film conductivity as the excess energy contributes to nanotube scission and result in an increase in surface defects.

From this study, the best CNT film with lowest R_s of $300 \Omega\text{sq}^{-1}$ at 80%T was obtained with a sonication power of 400 W and an initial CNT concentration of 0.3 mg/mL. To study the effect of different substrates, pristine CNT films were prepared on glass, PET and PEN substrates using the optimized processing conditions, and subsequently tested as CEs in DSSC to study and understand the differences in device behavior as compared to a standard DSSC that uses Pt/FTO as the CE.

3.3.2. DEVICE PERFORMANCE

DSSC cells with various CEs (see Fig. 3.1) were studied under different light intensities in order to study its effect on the cell behaviour. Fig. 3.6 shows the device performance at lowest illumination intensity of 1% Sun, and Table 3.1 summarizes the device parameters for the different CEs: V_{OC} , J_{SC} , FF and PCE .

FIGURE 3.6. *J-V* GRAPHS OF ALL DSSCs AT 1% SUN ILLUMINATION.

TABLE 3.1. COMPARISON OF DEVICE PERFORMANCE AT 1% SUN ILLUMINATION.

Device @ 1% Sun	V_{OC} (mV)	J_{SC} ($\mu A/cm^2$)	FF	PCE (%)
Standard	507.4	146.4	0.768	5.62
glass/CNT CE	554.7	159.5	0.553	4.74
PEN/CNT CE	579.2	152.1	0.555	4.81
PET/CNT CE	586.1	155.9	0.553	4.97

From Table 3.1, it can be observed that in general, higher J_{SC} values but lower fill factors were obtained for the CNT-based CE as compared to the standard Pt/FTO CE. Since CNT does not generate charges under illumination, the J_{SC} improvement suggests that CNT is able to collect more charges than Pt at its interface with the electrolyte. This improvement in J_{SC} may be due to the increase in catalytic activity resulting from the use of carboxylated CNT. Carboxylate sites on CNT surfaces are

able to act as catalytic sites to increase the overall catalytic activity of the film, which may be a reason behind the J_{SC} improvement. The lower fill factors appear to be a result of higher series resistance (R_{Series}) – observed as a decrease in slope of J - V curve after the point of maximum obtainable power (P_{max} , see Fig. 2.2)²⁰ – indicating that there might be a higher concentration of charge traps and that the R_s of the CNT-based CE is higher compared to standard CE. Even with more efficient charge collection (indicated by the higher J_{SC}), due to higher R_{Series} in the cell, FF appears to be reduced and hence CNT based devices performed worse than a standard cell.

Higher R_{Series} values caused a higher potential to be required to induce a stronger electric field for the charges to overcome the energy barrier of the charge trapping site. Otherwise, back reaction occurs and results in charge loss. The higher chance of back reaction is likely due to a mismatch in R_{Series} of electrode materials, i.e. between FTO at the photo anode and CNT film at the CE. The significantly higher R_{Series} of the CNT film would very likely cause a higher charge injection resistance from the film to the electrolyte, lowering the rate of electron injection for triiodide reduction, and consequently delaying the rate of electron extraction at the FTO/TiO₂ interface at the photo anode. A buildup of electrons within the bulk TiO₂, causes an imbalance in the electron distribution across the DSSC and increases the chances of back reaction; this phenomenon will be discussed in detail in the later part of this section.

As for the observed increase in V_{OC} , it has been reported that a V_{OC} improvement may result from decreased electron transfer resistance at the photo anode's TiO₂ / FTO interface, due to the presence of an additional compact TiO₂ interlayer, which “favours the accumulation of electrons at the interface of FTO

resulting in a more negative Fermi level and thus a larger V_{OC} ”²¹. A similar situation may apply in this case: while the above describes nonhomogeneous charge density distribution due to lower electron transfer resistance at the photo anode, the same skewed charge distribution observed in our work is likely due to the *higher* electron transfer resistance at the counter electrode (i.e. making the electron transfer resistance of the photo anode relatively *lower*). In both cases, there is no net charge in the device, but a charge density distribution inhomogeneity is nonetheless present due to differences in resistances of the two electrodes.

When the light intensity increased to 50% Sun, the charge trapping issues became more severe. This can be seen from the change in the slope of the $J-V$ curves in Fig. 3.7 and drastically decreased FF values in Table 3.2. At 50% Sun, the increase in light intensity resulted in an increase in current generated for all devices. All CNT-based CE devices have lower J_{SC} and fill factor values as compared to the standard device, although the J_{SC} of the devices with plastic/CNT CE are close to that of the standard. Looking at the $J-V$ response curve, the change in the shape of the curve implies a decrease in shunt resistance and an increase in R_{Series} . The result of this is a lower FF at a higher light intensity. With decreasing applied potential, charges build up at the CE-electrolyte interface, and back reaction becomes more dominant over tri-iodide reduction. This is most likely the cause for the drastic decrease in FF , which in turn led to the decrease in the J_{SC} as shown in the $J-V$ graphs.

FIGURE 3.7. *J-V* GRAPHS OF ALL DSSC PERFORMANCES AT 50% SUN ILLUMINATION.

TABLE 3.2. COMPARISON OF DEVICE PERFORMANCE AT 50% SUN ILLUMINATION.

Device @ 50% Sun	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)
Standard	643.0	7.5	0.743	6.92
glass/CNT CE	666.7	6.0	0.176	1.37
PEN/CNT CE	683.2	7.3	0.197	1.94
PET/CNT CE	691.8	7.2	0.176	1.71

FIGURE 3.8. J - V GRAPHS OF ALL CELL PERFORMANCES AT 100% SUN ILLUMINATION.

TABLE 3.3. COMPARISON OF DEVICE PERFORMANCE AT 100% SUN ILLUMINATION.

Device @ 100% Sun	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)
Standard	661.7	14.1	0.717	6.73
glass/CNT CE	678.6	7.3	0.171	0.85
PEN/CNT CE	695.5	11.9	0.159	1.33
PET/CNT CE	704.7	10.0	0.156	1.11

When illumination increases to 100% Sun, J_{SC} increases for all devices (see Table 3.3), but poorer J_{SC} and FF values are more apparent in these J - V graphs (see Fig. 3.8). No saturation plateau was observed for any DSSC with CNT-based CE at 0V, which implies that the maximum current could have been higher than J_{SC} if measurements were extended to negative bias voltage. This is similar to the behaviour of the DSSC with glass/CNT CE when measured at 50% Sun. One possible reason for

this observation is that there is greater extent of charge buildup within the TiO_2 layer with higher illumination intensity. Such charge buildup can be expected since an increase in light intensity corresponds to an increase in the number of charges generated, whereas R_s of an electrode is an intrinsic material property independent of illumination. It implies that the charge collection effectiveness of pristine, thin CNT films is limited by the film thickness and therefore CNT CE functioned well under low illumination intensities, but beyond a certain illumination intensity, charge buildup and loss become significant and detrimental to device performance. This may explain why thicker CNT films have been used in literature for comparable performance with standard devices under high illumination intensities ^{10,11,14,15}. To investigate whether charge buildup and recombination are critical with the use of thin CNT films, impedance analysis and cyclic voltammetry characteristics are essential and the results will be discussed later (see related discussion on Fig. 3.11 and Table 3.4).

Similar for all the illumination conditions, there was an increase in V_{OC} when FTO was not used in the CE. In general, when a thin film of CNT deposited on FTO glass was used as the CE, a decrease in V_{OC} is observed compared to standard Pt/FTO CEs, resulting from a positive shift of the Fermi level of TiO_2 ²². However, in our case, under 1 Sun illumination, DSSCs with CNT on glass, PEN and PET CE showed increase in V_{OC} by more than 0.04V instead. The reason for this difference may be due to the absence of FTO in the CE. This results in non-homogeneous voltage and current distributions due to differences in the anodic and cathodic (i.e. CE) R_s ²³.

FIGURE 3.9. CROSS SECTIONAL ARCHITECTURE (TOP) AND SCHEMATIC PROFILES OF CURRENT DENSITY AND VOLTAGE DISTRIBUTIONS (BOTTOM) FOR A STANDARD DSSC (LEFT) VS. OUR DSSC DEVICES EMPLOYING CNT ON GLASS OR PET AS COUNTER ELECTRODES (RIGHT).

FIGURE 3.10. ENERGY BAND DIAGRAM OF DSSC COMPONENTS, SHOWING QUASI-FERMI LEVELS (QFL) OF TiO_2 UPON ILLUMINATION, AND AN UPWARD SHIFT IN QFL OF ELECTRONS RESULTING IN AN INCREASE IN THE OPEN CIRCUIT VOLTAGE (V_{OC}) AS A RESULT OF USING CNT INSTEAD OF Pt/FTO. THE V_{OC} IS DEFINED BY THE DIFFERENCE BETWEEN THE ELECTRON QFL OF THE SENSITIZER (TiO_2) AND THE REDOX POTENTIAL OF THE ELECTROLYTE (I_3^- / I^-).

Since the photo anode uses FTO but the CE only relies on CNT for conduction, the difference in R_s causes current distribution to skew to the CNT side and voltage distribution to the FTO side (see Fig. 3.9). V_{OC} in liquid-electrolyte-based DSSC is defined by the difference between the quasi-Fermi level (qFL) of electrons in the

sensitizer on TiO_2 and the redox potential of electrolyte ($\text{I}_3^- / \text{I}^-$). As the mesoporous TiO_2 at the photo anode is slightly negatively charged with respect to the CE, this has the effect of raising the qFL of electrons of TiO_2 and therefore increasing V_{OC} ²⁴; Fig. 3.10 illustrates how this raising of qFL changes the V_{OC} .

As compared to the use of FTO in the CE, there is an increase in the overpotential with CNT CEs; a larger potential difference is required to overcome the charge transfer resistance from the CNT CE to the electrolyte to complete the circuit faster than the rate of back reaction ($\tau \approx 1 \mu\text{s}$). When the potential difference shifts closer to zero (i.e. voltage bias approaches V_{OC}), the reverse saturation current increases and the J - V curve slopes off. The onset of this slope occurs at a lower voltage for devices with CNT CEs, which lead to poor fill factors and device efficiencies. Since the abovementioned issues can be attributed to the difference in conductivity of the two electrodes, they are not expected to show up if both anode and cathode are made of CNT films (i.e. same material). However, the need to prevent exposure of CNT surfaces to the electrolyte while maintaining charge conductivity with TiO_2 remains a challenge to date; further discussion is available in a reference elsewhere²².

The FF values for CNT CEs at various light intensities are generally poor, arising partly from non-optimal cell resistances that overshadow the relatively more efficient charge collection of CNT. This is particularly serious at higher light intensities when the R_{Series} becomes the bottleneck. The device impedance analyses were carried out to look into the effect of different CE architectures on the cell resistances.

FIGURE 3.11. NYQUIST PLOTS OF CNT-BASED CE DEVICES (BEST-FIT CURVE SHOWN FOR PEN/CNT AS DOTTED BLUE LINE, ABOVE) VS. STANDARD CELL (BELOW). ω_{max} AND ω_{max2} ARE MAXIMUM RADIAL FREQUENCIES (OBTAINED FROM CORRESPONDING BODE PLOTS NOT SHOWN HERE) GIVING PEAK Z'' VALUES FOR THE 1ST AND 2ND SEMICIRCLES, WHILE R_a AND R_b CORRESPOND TO R_{sh} AND R_1 IN FIG. 3.12.

FIGURE 3.12. EQUIVALENT CIRCUIT OF ALL DEVICES: R_h = FTO OR CNT SHEET RESISTANCE, R_1 & C_1 = CE/ELECTROLYTE CHARGE TRANSFER RESISTANCE AND CAPACITANCE, R_3 & C_3 = RESISTANCE AND CAPACITANCE OF TRI-IODIDE DIFFUSION IN ELECTROLYTE, R_{sh} = SHUNT RESISTANCE, Z_2 = RESISTANCE AT ELECTROLYTE/DYE/TiO₂ INTERFACE. ²⁵

For a standard device, the R_{Series} is the sum of 3 resistances: sheet resistance of the electrode material (R_s), charge transfer resistance at the CE/electrolyte interface (R_1), and tri-iodide diffusion resistance in the electrolyte (R_3) ²⁶. This is summarized in the formula below:

$$R_{Series} = R_s + R_1(\text{Pt/electrolyte}) + R_3 \quad (4-1)$$

However, for CNT-based CE devices, CNT replaces both FTO and Pt, hence the formula translates into:

$$R_{Series} = R_{CNT} + R_1(\text{CNT/electrolyte}) + R_3 \quad (4-2)$$

As the electrolyte/dye/TiO₂ is kept constant, R_3 is assumed to be the same for all devices tested. Using the Nyquist plots, the first two resistance contributions can be derived from the two x-intercepts respectively (R_a and $R_a + R_b$) from the first semicircle. ω_{max} and ω_{max2} are maximum radial frequencies obtained from the peak height of the

first 2 semicircles. The inverse of these values can be related to transport time across the CE/electrolyte interface and carrier lifetime (τ_0) respectively ^{27,28}.

$$\omega_{\max} = \tau_0^{-1} \quad (4-3)$$

Table 3.4 shows the R_a and R_b values obtained from Fig. 3.11.

TABLE 3.4. R_a AND R_b VALUES OF DEVICES OBTAINED FROM THEIR RESPECTIVE NYQUIST PLOTS.

Device	$R_a (R_s, \Omega)$	$R_b (R_1, \Omega)$	$\omega_{\max} (\text{Hz})$	$\omega_{\max 2} (\text{Hz})$
Standard	30.1	43.4	1389.5	26.8
Glass/CNT CE	37.1	103.6	4453.6	1.4
PEN/CNT CE	305.3	3561.0	100.0	2.0
PET/CNT CE	137.5	2642.8	4.4	2.0

Comparing the R_a (R_s) values, the R_s of CNT CE are higher than that of FTO, due to CNT surface defects from the presence of covalently-bonded COOH groups, which also act as the catalytic sites. Among all CNT CE, glass/CNT has the lowest R_s at 37.1 Ω , which is comparable to FTO at 30.1 Ω . R_s of PET/CNT and PEN/CNT trail at 137.5 Ω and 305.3 Ω respectively. This observed difference in R_s may be related to the possibility of warping and the low glass transition temperatures (T_g) of plastic supporting substrates. After prolonged heating at 120 °C or higher, the plastic substrates tend to warp, and a non-flat surface influences the thickness and density uniformity in the CNT film, causing the observed difference in R_s values.

While the standard device charge transfer resistance, R_b , is 1.4 times its R_a value, the R_b values of glass/-, PEN/- and PET/CNT CE devices are 2.8, 11.7 and 19.2 times higher than their R_a values. Hence, the reaction that limits device performance in CNT-based CE DSSCs is the charge transfer between CNT and the electrolyte. Slow charge transfer slows down tri-iodide reduction and this can result in charge buildup at the CE/electrolyte interface, which will increase the probability of recombination (back reaction) to occur at the photo anode, and a decrease in shunt resistance is observed. To avoid this issue, the R_1 needs to be lowered for efficient tri-iodide reduction. Some possible reasons for high charge transfer resistance may be: i) porosity and roughness of CNT thin film, which is better described as a mesh than a compact layer, and forms a fractal interface with its own impedance that increases at low frequencies and changes the equivalent circuit (see Fig. 3.13)²⁹, ii) the electrolyte may react with or bind to CNT surface and these compounds formed may alter the charge transfer properties.

FIGURE 3.13. MODEL OF FRACTAL ELECTRODE-ELECTROLYTE INTERFACE (LEFT), AND THE EQUIVALENT CIRCUIT MODELING THE DOUBLE-LAYER CHARGING BEHAVIOUR (RIGHT).

Comparing the relative electron transport times across CE/electrolyte interface (based on decreasing $\omega_{\max}$ values), glass/CNT < standard < PEN/CNT < PET/CNT, whereas for electron lifetimes (based on decreasing $\omega_{\max 2}$ values), standard < PEN/CNT = PET/CNT < glass/CNT. To maximize charge collection, the electron transport time should be kept small (i.e. large $\omega_{\max}$ for faster transport times) and the electron lifetime extended (i.e. small $\omega_{\max 2}$ for lowering chances of recombination). In order to reduce the transport time, catalytic activity of the film must be improved, whereas electron recombination can be suppressed by reducing the R_s of the film. One possible method to do this is to decorate CNT with Pt nanoparticles, which may not only aid in catalysis, but also improve the intertube resistance within the CNT thin film network; the investigation and analysis of experiments related to CNT decoration with metal nanoparticles (either Au or Pt) will be discussed in Chapter 5.

3.4. SUMMARY AND CONCLUSION

Thin pristine single-walled CNT films (with 3-5% surface carboxylate side groups) of similar optical transmittance (80-85% @ 550 nm) to Pt/FTO were shown to have comparable DSSC performance only when illuminated under low light intensity (1% Sun), as high CE-to-electrolyte charge transfer resistance (R_{CT}) caused charge recombination to dominate with brighter illumination intensities. Since more charges are generated at higher illumination intensities but the rate of electron transfer at the CE does not increase, the extent of both the electron buildup at the photoanode and triiodide ions waiting to be reduced scales up with illumination intensity. As a result, CNT-based devices do not fare as well as standard DSSC, especially at 50% Sun illumination or higher, where lower J_{SC} and/or FF were obtained. However, there is an

improvement in V_{OC} values due to non-homogeneous current and voltage distributions, as FTO is still used at the photo anode. Although none of the devices were short-circuited, CNT CE suffered from high charge transfer resistance at the CE/electrolyte interface despite being able to catalyze the redox reaction.

In other words, CNT film conductivity and catalytic activity needs to be further enhanced to improve charge transfer for effective replacement of the standard CE. Modification of films after fabrication is necessary as pristine CNT films are unable to match the standard CE performance. Subsequent chapters will focus on CNT film modification to enhance conductivity and/or catalytic activity of DSSC CEs, which in turn should lead to an improvement in device efficiencies.

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4. CHEMICAL TREATMENT OF CNT NETWORKS IN DSSC

4.1. INTRODUCTION

From Chapter 3 it is evident that the conductivity and catalytic activity of pristine CNT films need to be improved so as to lower the high charge transfer resistance at the CE-electrolyte interface. Several methods to modify CNT have been reported in literature to improve the conductivity and to tune the work function. These include surface functionalization ^{1,2}, core-filling with metal-based nanoparticles ³, and p- or n- doping by chemical treatments such as HNO₃ ⁴⁻¹⁶, NADH ¹⁷ and viologens ¹⁸. N-doping of CNTs is effected by the donation of electrons from surface adsorbed NADH and viologens. For viologens, first principles calculations estimated a maximum upshift in the Fermi level of CNT by 0.3 eV. However, due to environmental oxidation, the n-doping of CNT using drop-coated NADH or viologens is unstable and reversible (after 100 days and 80 days respectively) under ambient conditions. For the NADH method, n-doping was recoverable by heat annealing the CNT film or device at 150 °C. This would not be feasible for the DSSC, as the dye degrades at temperatures above 60 – 80 °C.

P-doping of CNTs can be done using the Brønsted acids H₂SO₄, HNO₃ and HCl. Graupner *et al.* immersed buckypaper for 20 min in 4 M for each of these acids, and observed that only H₂SO₄ caused structural damage. Based on XPS spectra, H₂SO₄ also had the highest binding energy (+0.5 eV), followed by HNO₃ (+0.2 eV) and HCl (+0.1 eV) ⁴. As H₂SO₄ treatment caused structural damage to CNT, this adversely affects nanotube and film resistances. Hence, H₂SO₄ is unsuitable for treatment of

CNT films for DSSC application. Between the other two acids, HNO_3 gave a greater binding affinity and is therefore preferred for treating CNT films.

Albeit antagonistic to sheet conductivity ⁵, HNO_3 is commonly used for refluxing CNTs to create surface carboxylate groups ^{6,7} which will improve the compatibility between CNT and the polar solvents and also act as active sites for functionalization. To reduce the extent of structural damage to CNT, immersion is a better treatment method for CNT films for DSSC applications. Another less harsh method was to expose CNT films to concentrated HNO_3 vapor, which reduces sheet resistances without changing the film thickness, but requires very high concentrations (above 12 M) of HNO_3 ^{8,9}.

In order to have a better control of the treatment, a slightly different approach was adopted in this work. CNT thin film is deposited on a substrate before completely immersing the substrate with CNT film into HNO_3 solution. This acid-treated film is then used as the CE for DSSCs. Various concentrations of HNO_3 solutions were used for immersing the CNT films for different durations. This treatment provides the advantage of using of pristine CNT films with minimum modifications and other than the CNT, no new material is introduced in the DSSC system. A detailed understanding on how the acid concentration and immersion duration affects the CNT films in terms of conductivity and catalytic activity and hence the DSSC device performance is studied for the first time. In particular, the effect of acid concentration and immersion time on film morphology, optical transmittance, sheet resistance, work function, Raman spectra and DSSC behavior will be analysed and discussed in the following sections.

4.2. METHODS

CNT films were fabricated using the same spray coating method as described in Section 3.2. Optical transmittances at 550 nm of the resulting CNT films were found to be $75 \pm 6.5\%$ (UV-vis spectrophotometer UV-3200, Shimadzu). Surface profiler (Alpha-Step IQ, KLA-Tencor) showed the average thickness of CNT films to be about 120 nm. These films were immersed in HNO_3 solutions of varying concentrations (0.5 M, 1 M, 2 M, 4 M, 6 M, 8 M and 10 M) for different durations (15 min, 30 min, 1 h, 2 h, 4 h and 8 h). Acid immersion was carried out in the dark as HNO_3 is a light-sensitive solvent. After the treatment, the films were briefly immersed in DI water to stop the acidic reaction and then dried with a stream of nitrogen gas. Looking at the field emission scanning electron microscope (FESEM) images of these films, random network of CNT bundles can be observed and changes in the morphology due to different conditions were also observed (JSM-7600F, JEOL). Sheet resistance changes were measured using a 4-probe system (Series 2400 SourceMeter, Keithley). Kelvin probe force microscopy (KPFM) measurement was done using an Asylum Research MF3PD atomic force microscope (AFM) system with the Pt-coated Si cantilever (Olympus AC240 TM, resonant frequency ~ 70 KHz, spring constant of 2 N/m, tip height 14 μm and tip radius ~ 30 nm). KPFM images of the sample were taken with the tip biased at 1 V and applying a scan rate of 1 Hz on a typical scan area of $1 \mu\text{m} \times 1 \mu\text{m}$. Average surface potential value from the imaged area was then extracted from the histogram distribution of the surface potential (refer to [Appendix 2\(c\)](#)). The measured local surface potential difference is derived from

$$\Delta SP = (\varphi_{tip} - \varphi_s) / e \quad (1),$$

where φ_{tip} is the work function of the conducting tip, φ_s is the work function of the measured sample, and e is the electronic charge ¹⁹. The CNT films in this study showed an initial work function of 4.6 ± 0.1 eV. All the Raman spectra were taken using an excitation wavelength of 488 nm (Alpha300 SR, Witec).

For the device fabrication, photo anodes were made of FTO glass with either: i) a screen printed layer of 12 μm mesoporous TiO_2 (average particle size: 25 nm), or ii) 8 μm mesoporous TiO_2 + 5 μm scattering TiO_2 (average particle size: 400 nm), both sintered at 500 °C, and soaked in dye (Ruthenium-based dye, Z907) for 16 h to ensure sufficient dye uptake by TiO_2 . A ring spacer (SX1170-25, Solaronix) sealed off the cell active volume between the photo anode and CE. This volume was filled with a methoxypropionitrile-based electrolyte (R-50, Solaronix) through the pre-drilled CE. The hole was finally covered with the same spacer and an optically-clear glass coverslip above it. J - V characteristics of the cells were obtained under 1 Sun, AM1.5 (100% Sun or 100mW cm^{-2} ; Newport solar simulator) illumination and under room lighting (0.2% Sun equivalent).

4.3. RESULTS AND DISCUSSION

4.3.1. EFFECT OF ACID TREATMENT ON SHEET RESISTANCE

The sheet resistances of the as-deposited, HNO_3 -treated CNT films were measured using 4-probe setup. Fig. 4.1(a) shows the sheet resistances of CNT thin films deposited on glass and PET substrate after treatment with HNO_3 solutions of different molarity, as well as their corresponding surface potential changes in Fig. 4.1(b). The average sheet resistances of CNT films before treatment were $211 \Omega/\text{sq}$

and 315 Ω/sq on glass and PET substrates respectively. Each data point is an average of 10 measurements on different regions in the film. The change in sheet resistance as a function of immersion time at 4 M of HNO_3 can be seen in Fig. 4.2. The values were found to stabilize after 1 h or more.

FIGURE 4.1. (A) 4-PROBE SHEET RESISTANCE MEASUREMENTS OF HNO_3 -TREATED CNT THIN FILMS ON GLASS AND PET SUBSTRATES AS A FUNCTION OF HNO_3 CONCENTRATION, SHOWING A GENERAL DECREASE IN SHEET RESISTANCE FOR ALL SAMPLES. (B) SURFACE POTENTIAL (SP) VALUES OF HNO_3 TREATED CNT SAMPLES DEPOSITED ON GLASS AND PET SUBSTRATES, AND THEIR CORRESPONDING WORK FUNCTION VALUES (INSET) AS DERIVED FROM EQUATION (1). (C) FESEM IMAGE OF A TYPICAL HNO_3 -TREATED CNT FILM, SHOWING A NETWORK OF RANDOMLY ALIGNED CARBON NANOTUBE BUNDLES.

FIGURE 4.2. 4-PROBE SHEET RESISTANCE MEASUREMENTS OF CNT THIN FILMS DEPOSITED ON (A) GLASS AND (B) PET SUBSTRATES AS A FUNCTION OF 4 M HNO_3 IMMERSION TIME (15 MIN, 30 MIN, 60 MIN, 120 MIN, 240 MIN OR 480 MIN). SHEET RESISTANCE VALUES STABILIZED AFTER A MINIMUM IMMERSION TIME OF 60 MIN.

Although all the CNT thin films were spray coated using the same method, initial sheet resistances of the PET samples (250-363 Ω/sq) were higher than the glass samples (140-246 Ω/sq). Since FESEM images showed similar film morphology for both substrates, the difference in the sheet resistance is most probably not due to differences in the wetting properties of the substrates (see Fig. 4.3). The other possible reason is that the substrate was altered during spray coating process. During spray coating, the substrates are exposed to 120 °C for extended time and this may cause PET (glass transition temperature (T_g) $\approx$ 150°C) to undergo softening and warp when cooled to room temperature. The effect of the warping on the device performance will be discussed later.

As evident from Fig. 4.1(a), a substantial reduction in the sheet resistance is observed for all samples with HNO_3 treatment, suggesting that the CNT surfaces are cleaned of impurities and residual metal catalyst particles after the treatment²⁰⁻²². The extent of reduction in sheet resistance increased with HNO_3 molarity until the maximum reduction occurred at 4 M for both glass and PET samples, beyond this concentration, the trend of sheet resistance reduction did not extend predictably, although the sheet resistance values did not decrease any further (refer to Fig. 4.4).

Surface potential (SP) values of the pristine and HNO_3 treated CNT films on PET and on glass substrates as a function of molarity are shown in Fig. 4.1(b). Fig. 4.1(c) shows the network morphology of the CNT film comprised of bundles of randomly aligned CNTs. The decrease in SP upon acid treatment with higher molarity solution corresponds to an increase in the work function of the sample (Fig. 4.1(b), inset)¹⁹. Beyond 4 M, the SP of the film saturates. The decrease in surface potential is larger for CNT films on glass substrates, which we attributed to its lower oxygen permeability²³ and thus better retention of HNO_3 p-doping effect.

4.3.2. STRUCTURAL EFFECT OF ACID TREATMENT

Structural damage is known to occur during acid refluxing of CNT^{6,7}. Although immersion is fast and relatively less harsh, there is still a small likelihood that damage can occur. There is a possibility that CNT exposure to higher HNO_3 concentrations could cause the debundling²² and / or structural damage of CNT^{15,22,25}, therefore there is an optimal molarity where there is a maximum reduction in sheet resistance without damaging the CNT. To investigate whether the CNT bundles have been damaged by HNO_3 exposure and to determine the reason behind this increase in work function, Raman spectra of the acid treated samples were analysed (see Fig. 4.5).

FIGURE 4.3. FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM) IMAGES SHOWING SIMILAR MORPHOLOGY OF AS-DEPOSITED CNT THIN FILMS ON (A) GLASS AND (B) PET SUBSTRATES AT 10,000X MAGNIFICATION.

FIGURE 4.4. CHANGES IN SHEET RESISTANCE VALUES OF CNT THIN FILMS DEPOSITED ON GLASS AND PET SUBSTRATES AS A FUNCTION OF HNO₃ MOLARITY. THE MAXIMUM DECREASE IN SHEET RESISTANCE VALUES OCCURRED AT 4 M IN BOTH CASES.

FIGURE 4.5. RAMAN SPECTRA (EXCITATION WAVELENGTH = 488 NM) OF CNT THIN FILMS DEPOSITED ON GLASS SUBSTRATES AND IMMERSSED IN HNO₃ OF VARIOUS CONCENTRATIONS. THERE IS AN UPSHIFT OF THE WAVENUMBERS REGARDLESS OF ACID CONCENTRATION USED FOR THE TANGENTIAL MODES (A) G BAND (1585 cm⁻¹ TO 1594 cm⁻¹) AND (B) G' BAND (2681 cm⁻¹ TO 2691 cm⁻¹). THE DISORDERED MODE D BAND PEAK POSITION EXPERIENCED A LESS SIGNIFICANT UPSHIFT FOR ALL NON-PRISTINE SAMPLES (1351 cm⁻¹ ~ 1355 cm⁻¹). PEAK POSITIONS BEFORE UPSHIFTING ARE INDICATED WITH AN ARROW (↕).

FIGURE 4.6. RAMAN SPECTRA (EXCITATION WAVELENGTH = 488 NM) OF RADIAL BREATHING MODES (RBM; $160\text{ cm}^{-1} \sim 230\text{ cm}^{-1}$) OF THE CNT SAMPLE LABELED “4 M” IN FIG 5, (A) BEFORE AND (B) AFTER NITRIC ACID TREATMENT FOR 1H. TWO SIGNIFICANT DECONVOLUTED PEAKS AT 170 cm^{-1} AND 182 cm^{-1} WERE RIGHT-SHIFTED TO 176 cm^{-1} AND 187 cm^{-1} RESPECTIVELY, AS WELL AS AN INCREASE IN RELATIVE PEAK INTENSITY FOR THE LATTER. THE SIMULTANEOUS OCCURRENCE OF BOTH OBSERVATIONS LENDS SUPPORT TO THE THEORY OF CNT LATTICE SHRINKAGE.

Many authors have proposed using the D/G ^{20-22,24-27} and D/G' ^{28,29} relative band ratios to assess CNT defect density and the extent of disorder in its graphitic structure after HNO_3 refluxing and in these cases, the objectives are contaminant removal and CNT sidewall / open ends functionalization with $-\text{COOH}$ groups ²⁷. As a result of the carboxylation, the D band peak intensity is typically observed to increase with the increase in structural defect concentration, the G band peak intensity decreases with more broken 6-carbon hexagonal rings, and the G' band intensity is a D band overtone arising from a secondary phonon effect which is independent of defect concentration ³⁰. In all our measurements, neither D/G nor D/G' band ratios showed any significant changes, therefore eliminating carboxylation as the main consequence of our acid treatment method. The part of spectrum typically observed at $1500\sim 1600\text{ cm}^{-1}$ is made up of convoluted peaks contributed by pristine CNT of various diameters. The height and shape of this profile was similar for all samples, indicating that the CNT's are mostly intact without damage.

Fig. 4.5 shows that these peaks consistently right shifted: D (+4 cm^{-1}), G (+9 cm^{-1}) and G' (+10 cm^{-1}) bands for all acid-treated samples, regardless of concentration. Nitric acid p-dopes CNT (increased CNT work function) by a charge transfer mechanism that occurs via electron withdrawal from the sp^2 orbital in the CNT lattice, causing an increment in the work function. In addition, the loss of electrons leads to a contraction of the C-C bond, and the lattice hardening can be translated to a right-shift in the tangential peaks^{15,16,20}. Peaks in the radial breathing modes (RBM) also experienced a similar right-shifting, as seen in Fig. 4.6. The RBM corresponds to a set of convoluted peaks, caused by the excitation of individual CNT tubes of different diameters^{24,31-34}. Deconvolution of RBM spectra obtained for the pristine sample resulted in two prominent peaks at 170 cm^{-1} and 180 cm^{-1} , which were subsequently right shifted to 176 cm^{-1} and 187 cm^{-1} respectively after 4M treatment. The magnitude of the right shift was consistent (± 1 cm^{-1}) across the whole range of acid concentrations. Furthermore, the intensity of the peak at 176 cm^{-1} decreased relative to the peak at 187 cm^{-1} , which also supports the theory of lattice hardening. Since peaks in the RBM are diameter dependent and higher wavenumbers within the RBM correspond to smaller tube diameters³⁵, the peak ratio difference is linked to the charge transfer effect of nitric acid that caused some CNT to shrink in diameter. All RBM, disordered, and tangential mode peaks were upshifted non-selectively after CNT treatment with all acid concentrations, strongly suggesting intercalation as the primary effect of our nitric acid treatment.

4.3.3. DEVICE PERFORMANCE

To analyse the effect of nitric acid treatment on device behavior, the device performance were compared for DSSC using CEs made from CNT films on FTO

substrates at various nitric acid concentrations – 0.5 M, 4 M and 8 M. We used photo anodes with 8 μm mesoporous TiO_2 + 5 μm scattering TiO_2 . The control sample used a CE that was unexposed to nitric acid. All devices were tested under 1 Sun illumination on either side and under room lighting (0.2% Sun), and short circuit current (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and percentage conversion efficiency (η or PCE) are summarized in Table 4.1.

TABLE 4.1. SUMMARY OF DSSC PERFORMANCE WHEN FTO-GLASS SUBSTRATES WERE USED FOR THE CE; J_{SC} IMPROVEMENT WAS MOST SIGNIFICANT FOR ACIDIC CONCENTRATION OF 0.5 M.

Sample	% Intensity	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η (%)
Ctrl	100 (front)	7.765	0.550	24.1	1.017
0.5M		10.031	0.554	19.9	1.095
4M		9.069	0.576	19.1	0.988
8M		8.018	0.584	22.4	1.039
Ctrl	100 (back)	2.098	0.561	36.6	0.427
0.5M		2.883	0.524	32.1	0.479
4M		2.877	0.542	32.9	0.509
8M		2.311	0.535	34.9	0.427
Ctrl	0.2	0.018	0.418	73.4	2.794
0.5M		0.027	0.377	59.1	3.024
4M		0.022	0.433	74.4	3.428
8M		0.020	0.404	68.1	2.733

When illuminated, regardless of the direction and intensity, an improvement in J_{SC} was observed for all HNO_3 treated samples, indicating the effectiveness of the acid in lowering the series resistance. Since nitric acid is able to remove contaminants and cause charge transfer in CNT by intercalation, this could explain the highest J_{SC} from samples treated with 0.5 M HNO_3 . However, although intercalation is the dominant mechanism, a higher acid concentration may have induced some surface defects in CNT bundles via carboxylation that was not significant to show up in the Raman spectra, but will still modify the conductivity of individual tubes. These traps act as recombination centers for the photogenerated carriers and account for the lowest J_{SC} for 8 M-treated samples. For all the devices tested, FF was low ($< 40\%$) under 1 Sun illumination due to low catalytic activity of such thin CNT films, but this was improved at 0.2% Sun (indoor / room lighting conditions) because charge transport efficiency increased when less charge was generated. FF improvement was also observed to a smaller extent with 1 Sun back illumination for the same reason due to light scattering from the 400nm TiO_2 particles. On FTO substrates, 4 M nitric acid treatment resulted in the most significant improvements in device performance at 0.2% Sun and back illumination at 1 Sun. Therefore, this concentration was used for the treatment of CNT films on glass and PET for FTO-free CE substrates and the results are shown in [Table 4.2](#).

TABLE 4.2. SUMMARY OF DSSC PERFORMANCE WHEN GLASS AND PET SUBSTRATES WERE USED FOR THE CE; J_{sc} SIGNIFICANTLY IMPROVED FOR 4 M WITH GLASS SUBSTRATES UNDER ALL ILLUMINATION CONDITIONS, BUT WITH PET SUBSTRATES THIS ONLY IMPROVED UNDER 100% SUN FRONT ILLUMINATION, POSSIBLY DUE TO WARPING OF THE SUBSTRATE AS A RESULT OF PROLONGED HEATING AT 120 °C DURING THE CNT SPRAY COATING PROCESS. NOTE THAT V_{oc} INCREASED FOR ALL SAMPLES WITH FTO REMOVED FROM CES.

		<i>Glass</i>				<i>PET</i>			
Sample	% Intensity	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Ctrl	100	1.587	0.636	17.9	0.179	1.689	0.636	17.9	0.191
4M	(front)	2.582	0.603	18.5	0.285	2.079	0.670	18.3	0.252
Ctrl	100	1.539	0.632	17.8	0.172	1.956	0.726	16.2	0.228
4M	(back)	2.427	0.569	21.1	0.288	1.784	0.703	19.0	0.236
Ctrl	0.2	0.00847	0.449	66.8	1.257	0.00955	0.392	63.4	1.176
4M		0.0112	0.445	69.1	1.706	0.00664	0.400	65.8	0.865

Comparing the device performance of DSSC with CNT on glass and CNT on PET (without any acid treatment condition) under 1 Sun illumination, the J_{sc} values were found to be comparable, due to the high optical transmittance of thin CNT films and substrates. For the device using glass substrate, 4 M HNO₃ treatment improved all the device parameters except V_{oc} . However with PET substrates, it is worthwhile to note that significant device improvement is only seen under 1 Sun front illumination. The J_{sc} values decreased under both room light and back illumination. Although the PET substrates have a glass transition temperature of about 150 °C, there is slight warping of the PET substrate after extended heating at 120 °C during the CNT film

spray coating process, which lead to an uneven planar profile. This could have brought about significant variation in the incident light intensity (and hence charge concentration) across the CNT film and increase the possibility of back reaction on a smaller scale when an area of CNT film come into close contact with TiO_2 . An alternative flexible substrate (e.g. polyethylene naphthalate, PEN) may be considered to avoid the issue of warping and thus improve J_{sc} and overall PCE . Rather than employing a harsh acid refluxing method for the treatment of CNT, a short 1 h immersion in 4 M nitric acid was adequate for improving device behavior regardless of FTO presence.

The phenomenon of V_{OC} increase when FTO was not used in the CE was again observed by comparing V_{OC} values from [Tables 4.1 & 4.2](#). In this case, DSSC with CEs on glass and on PET showed an average V_{OC} increase of 0.1V instead under 1 Sun illumination. The FTO source used here had a sheet resistance value of 15 Ω/sq , but CNT on glass and on PET had sheet resistances of 120 Ω/sq and 180 Ω/sq respectively after 4 M HNO_3 treatment, hence the difference in sheet resistances between CNT and FTO is about ten times on average. Further reduction in CNT sheet resistance cannot be achieved using this acid treatment method, hence the incorporation of additional materials that are more conducting and/or catalytic to form CNT-nanocomposites can be more effective in CNT modification and will be discussed in the next two chapters.

4.4. SUMMARY AND CONCLUSION

The results have demonstrated that immersion of thin pristine CNT films in 4 M HNO_3 solution prior to device fabrication provides the following advantages: i) structurally non-destructive, ii) most effective to decrease SP / increase work function,

iii) creates p-doping via a charge transfer reaction through intercalation, iv) gives the maximum sheet resistance reduction, and v) capable of improving J_{SC} in device performance even when FTO was not used. The phenomenon of V_{OC} increase, which was observed in the absence of FTO on the CE, was attributed to inhomogeneous voltage and charge density distributions stemming from sheet resistance differences between anode and cathode materials. As flexible bifacial devices require optically transmitting, yet sufficiently conducting and catalytic CEs, HNO_3 pretreatment method will help to improve the CNT thin film quality for such an application. However, as film conductivity and catalytic activity are still not on par with the standard Pt/FTO, nanocomposite formation with other materials may be necessary, as this is likely to yield a synergistic combination of material properties. Therefore the choice and optimization of materials to interact with CNT films is crucial, and will be the main focus for the next two chapters.

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5. METAL NANOPARTICLE DECORATION OF CNT NETWORKS IN DSSC

5.1. INTRODUCTION

As seen in Chapters 3 and 4, the main issue with using thin CNT films as counter electrodes (CEs) in DSSC is that the transport of electrons across the electrode/electrolyte interface is slower compared to the conventional Pt/FTO CE, and the probability for recombination is higher. In order to improve the conductivity and/or catalytic activity of CNT films as CEs in DSSC while trying to preserve their optical transparency, one option was to use metal nanoparticles-CNT composites. In general, the intertube conductivity can be aided by the presence of these metallic nanoparticles, and the catalytic activity can also be improved with the correct choice of metal.

There are many metallic nanoparticles that can form in close proximity to CNT surfaces, such as Au, Ti, Al, Ni, Pd, Fe, Ag, Pt and Pb ¹⁻⁵. The decoration of CNT surfaces with metallic nanoparticles using various methods of synthesis has been reported ^{1,2,6-8}. The purpose of these experiments was to use CNT as a sacrificial scaffold structure for the synthesis of metal nanowire interconnects, and metallic nanoparticle-decorated CNT was also used for gas sensing.

The strength of interaction between the metal and CNT differs from metal to metal. For example, using electron beam deposition, Zhang & Dai observed that Au, Al, Pb and Fe have weak interaction with CNT surface ¹, and Zhang *et al.* reported the opposite for Ti, Ni and Pd ². Density functional calculations of CNT adsorption profiles of various metal elements by Park *et al.* have also suggested that Al, Au, Pt,

Pd and Ti have increasing binding energies with CNT in that order. Interfacial wetting improvement also follows the same sequence and likewise for the possibility of metal-carbon bond formation while decreasing the risk of metal oxidation³. The strength of the interaction between the metal and CNT will determine its nucleation density and nanoparticle size. Weaker interactions exhibit lower nucleation densities and bigger average particle sizes, as shown in Fig. 5.1. However, the line-of-sight deposition of metal nanoparticles renders the electron beam deposition method unsuitable for our CNT films, as CNT surfaces within the mesh network cannot be fully utilized for metallic nanoparticle synthesis.

Besides electron beam deposition, these metallic nanoparticle-CNT systems can also be achieved using chemical bath deposition methods such as ethanol-assisted electroless spontaneous reduction⁶ or electrodeposition^{7,8}. The most significant benefit of chemical bath deposition over electron beam deposition is its high degree of penetration in porous materials such as the CNT films, allowing nanoparticle deposition throughout the film. Various metallic nanoparticle sizes and CNT surface coverage can be obtained by controlling the chemical deposition parameters, such as metal salt concentration, reaction time & temperature. As the chemical bath deposition method does not require high temperatures for reaction, it is also feasible to use plastic substrates for this method.

The main difference between the electroless reduction and electrodeposition methods is the need to supply an optimized applied voltage bias as nucleation potential for the latter. Day *et al.* was able to obtain CNT with a high density of Pt nanoparticles by electrodeposition using an applied bias of -0.4 V over 30 s⁸. As CNT thin films are not sufficiently conducting, in order to obtain a uniform deposition, electrodeposition

of Pt on CNT requires a highly conducting supporting substrate to act as the cathode (e.g. FTO, ITO or metallic substrates). The use of plastic substrates is therefore not possible. In contrast, electroless deposition negates the use of an additional applied voltage bias, provided that the metal deposited has a higher work function (i.e. higher electrochemical potential) than CNT ⁶. The range of metallic nanoparticles that can be deposited is therefore limited to high work function metals such as Au and Pt, which is ideal for this work, as both metals are suitable to be used as CE materials in DSSC.

FIGURE 5.1. TEM IMAGES OF: (A) TI, (B) NI, (C) PD, (D) AU, (E) AL, AND (F) FE. BIGGER PARTICLE SIZES AND LOWER NUCLEATION DENSITIES INDICATES A WEAKER INTERACTION WITH CNT SURFACE ².

Since a blend of material properties can be expected from a composite metal nanoparticle-CNT system, the choice of metal nanoparticles should be such that the limitations in pristine CNT are compensated. Therefore, the nanoparticles should ideally be sufficiently conducting and catalytic. By decorating these nanoparticles on CNT, a more effective CE that will improve device efficiency can be obtained. These

metallic nanoparticles should also be chemically resistant to the electrolyte ions and does not oxidise readily in air.

Taking these criteria into consideration, the choice of metal nanoparticle-CNT systems for use as CE in DSSC can be narrowed down to two combinations, Au-CNT and Pt-CNT. Both Au and Pt are noble elements that are commonly used on their own as CE in DSSC. As Au has a weaker interaction with CNT compared to Pt¹, it is interesting to study how this affects the nanoparticle formation on CNT and its impact on device behavior. Kim *et al.* has previously published findings on CNT films spin coated with various concentrations of Au precursor solutions, noting a steady increase in work function and decrease in sheet resistance (R_s) with increasing Au concentrations from 0.5 mM to 80 mM. In addition, the Raman spectrum of Au-CNT showed a 16 cm^{-1} right shifting of the G band peak with their 80 mM sample when compared to a pristine CNT sample, which provides the evidence for charge transfer taking place. However, the CNT used in their experiments was non-carboxylated, and no high-resolution electron images were taken to analyse Au particle formation. They suggested the nature of deposition to be physisorption followed by reduction to form neutral Au particles. Since in their work, no further steps were taken to remove residual Au precursors after the deposition, there is an assumption that any excess precursors did not contribute to Au deposition or growth over time⁹.

To address some of the above issues, as well as investigate the interaction of Au with carboxylated CNT, morphological analysis was done for CNT films exposed to Au precursor solution by chemical bath immersion for various durations, but at a fixed concentration of 5 mM. This is similar to the method reported by Choi *et al.*⁶. These films were rinsed with water and ethanol immediately after the immersion

process to prevent the possibility of extended reaction due to the presence of excess Au precursor. For the Au-CNT system, by varying the duration of CNT film immersion, changes in CNT film characteristics were analysed and the performance of DSSCs made using the different electrodes were compared. Poor wetting resulted in a low density of Au clusters, but charge transfer at the Au-CNT interface increased the work function and film conductivity. A slight improvement in device efficiency was obtained at 1 Sun illumination as a result of decreased series resistance.

Besides Au, Pt is a suitable candidate for improving the CNT thin films for the application as CEs in DSSCs. There are a few reasons for choosing the Pt-CNT system. It is similar to Au in that it has a higher electrochemical potential than CNT and hence can be reduced relatively easily on CNT surfaces by the same ethanol-assisted method. It is also highly catalytic and used very commonly in standard DSSCs. Since Pt is known to have a stronger interaction with CNT¹, this will affect the morphology of the Pt nanoparticles on CNT. Good wetting caused a dense coverage of Pt nanoparticles on CNT surfaces, but negligible differences in charge transfer resistances suggested that no charge transfer complex was formed between them. Cyclic voltammetry results indicated the preservation of catalytic property of Pt in the Pt-CNT system. Under 1% Sun and 1 Sun illumination, due to a corresponding increase in J_{SC} the DSSCs had improvement in device efficiencies, reaching 3.8% and 5.6% respectively.

Although generally, Pt-CNT conferred better device behavior than Au-CNT, the electrode is FTO-free but not Pt-free, hence the evaluation of suitable Pt alternatives by means of metal sulfides-based CNT nanocomposites will be covered in Chapter 6.

5.2. METHODS

CNT films were fabricated on glass substrates by the same spray-coating method as described in Section 3.2. Compared to CNT films used in Chapter 3, the average optical transmittance and R_s of these films were lower, ranging from 47% to 50% at 550 nm and $150 \Omega \cdot \text{sq}^{-1}$ for Au-CNT films, and 32% and $86 \Omega \cdot \text{sq}^{-1}$ for Pt-CNT films. Au and Pt were deposited using the method described by Choi *et al.*⁶. Au precursor solution was made by first dissolving chloroauric acid (HAuCl_4) in DI water (10 mM) before diluting to half the concentration (5 mM) with an equal volume of absolute ethanol just before the deposition. Pt precursor solution was made by first dissolving sodium tetrachloroplatinate hydrate ($\text{Na}_2\text{PtCl}_4 \cdot x\text{H}_2\text{O}$) in DI water (10 mM) before diluting to half the concentration (5 mM) with an equal volume of absolute ethanol prior to the deposition. For Au-CNT, the CNT films were immersed in Au precursor solution for various durations (1 s – 3 min), and immediately rinsed with copious amounts of water to prevent further reaction, followed by rinsing with ethanol and dried in air. For Pt-CNT, the CNT films were immersed in Pt precursor solution for various durations (1 s – 60 s), and immediately rinsed with copious amounts of water to prevent further reaction, followed by rinsing with ethanol and dried in air. The changes in morphology, work function, R_s and impedance of the resulting CNT films were studied. DSSCs were fabricated, and their testing and analysis were carried out as described in Sections 3.2 and 4.2.

5.3. RESULTS AND DISCUSSION

5.3.1. AU-CNT FILMS AS DSSC COUNTER ELECTRODES

As discussed earlier, weak interaction between Au and CNT may have an effect on the formation process and hence may result in large particles on CNT. Using chemical bath deposition, Au nanoparticles can form on the CNTs. The morphology of Au nanoparticles formed on CNT changed with changing reaction time as seen in [Fig. 5.2](#). During the first 60s of immersing CNT films in Au precursor solution, a small number of Au globular clusters (dia. < 100 nm) was observed. This is an indication of low nucleation density under these conditions. From the FESEM images of films immersed for 2 s and 5 s, it can be seen that the Au clusters appeared to have also grown from underneath the CNT film towards the surface. This showed that the Au precursor solution penetrates the CNT network, resulting in the possibility of trapped Au clusters scattered and hidden within the CNT film.

Due to the weak Au-CNT interaction mentioned earlier, particle growth is dominant over nucleation. Clusters underwent a rapid increase in diameter in the first 20 s, reaching an average diameter of 120 nm. Globular Au clusters started growing into a spiky dendritic form from around 20 s, and this morphology remained unchanged up to 60 s. After 60 s the average cluster diameter increased to 150 nm. Comparing the two cluster morphologies, the spiky dendritic form is more desirable as it would have a larger surface area exposed to the DSSC electrolyte. The X-ray diffraction spectrum of an Au-CNT film that was immersed for 60 s confirmed the presence of Au (please refer to [Appendix 3](#)).

FIGURE 5.2. SECONDARY ELECTRON MICROSCOPE IMAGES OF AU NANOPARTICLES / CLUSTERS FORMED ON CNT FILMS IMMERSIED IN AU PRECURSOR SOLUTION FOR 2 s, 5 s, 10 s, 20 s, 30 s AND 60 s. BESIDES AN INCREASE IN SIZE OF CLUSTERS, NO OTHER APPRECIABLE DIFFERENCE WAS OBSERVED BEYOND IMMERSION TIME OF 60 s.

The work function of the CNT films was altered as a result of the Au nanoparticles decoration. There is a strong correlation between work function changes and precursor solution immersion time. This can be seen in Fig. 5.3 where the work function of pristine CNT films is shown to increase almost linearly from 4.85 eV to 5.0 eV after 20 s of immersion, and approaches the limit at 60 s (5.12 eV) and does not

further increase from 60 s to 180 s. This value is close to the work function of pristine Au (5.1 eV – 5.2 eV); hence the work function for Au-CNT composite lies between the work functions of Au and CNT. Two properties may be inferred: 1) charge transfer occurs at the Au-CNT interface to cause an increase in work function, and 2) the similarity of the maximum work function of Au-CNT with the work function of Au suggest that the Au nanoclusters are neutral and in close proximity to CNT surfaces.

Raman spectroscopy was done on the samples to study the nature of interaction, however no differences in spectra were observable. This was because the low concentration of Au precursor led to undetectable right-shifting of the G band. Kim *et al.* predicted this value to be lower than the resolution of our Raman equipment (minimum resolution: 4 cm^{-1}) – a 5 cm^{-1} right-shifting was observed for their 10 mM sample⁹.

The R_S and optical transmittances of the films were measured and the results are shown in Table 5.1. The R_S of CNT films remained unchanged up to 60 s of immersion. A 10% decrease in R_S was obtained when the immersion time was increased to 60 s. This suggests that a minimum duration of 60 s immersion is necessary for the formation and growth of Au clusters such that the conductivity of the CNT film is improved. The optical transmittances of all the films had negligible changes with immersion time, indicating that the Au clusters in the CNT films had minimum interference with light transmittance properties of the films.

FIGURE 5.3. EFFECT OF AU PRECURSOR IMMERSION TIME ON THE WORK FUNCTION OF CNT FILM, SHOWING AN ALMOST LINEAR INCREASE IN WORK FUNCTION, SATURATING AT ≈ 5.12 eV AT AROUND 60 s.

TABLE 5.1. SHEET RESISTANCES (R_s) AND OPTICAL TRANSMITTANCES (T%, @ 550 nm) OF CNT FILMS BEFORE AND AFTER IMMERSION IN 5 mM AU PRECURSOR SOLUTION FOR 5 s, 10 s, 30 s AND 60 s.

Immersion Time (s)		5	10	30	60
R_s	Before	137.1	154.2	146.9	146.1
	After	143.6	160.6	151.4	130.4
	% Difference	4.7	4.2	3.0	-10.7
T%	Before	47.6	49.9	48.7	49.1
	After	48.0	50.5	49.2	49.6
	Difference	0.4	0.6	0.5	0.5

Since the work function increased due to the presence of more Au particles on the CNT film with increasing immersion time, and also R_s decreased with 60 s immersion time, the charge transfer resistances (R_{CT}) of the Au-CNT films may be changed as well. As seen earlier, Raman spectra failed to show the charge transfer interaction, hence impedance analysis may be able to provide some insight to this change.

EIS measurements of symmetrical half cells were carried out across a voltage range of 0.5 V – 0.8 V. The effect of immersion time on the R_{CT} of the films is shown in Fig. 5.4. A decrease in R_{CT} was generally observed for all immersion times, indicating that the presence of Au on the CNT film improves the charge transfer at the electrode / electrolyte interface. However, the decrease in R_{CT} for 5 s, 10 s and 30 s appeared to be similar. After 60 s, R_{CT} was distinctly lowered. This observation is similar the R_s changes as shown in Table 5.1, which suggests that a minimum immersion time of between 30 s and 60 s is required to improve the electrical properties of the CNT films. An increase in Au cluster size and number may contribute to this improvement; it is during this time that the Au to CNT charge transfer interaction contributes significantly to cause an improvement of CNT film conductivity.

Au cluster size, shape and distribution are factors that may affect the Au-CNT interaction. As spiky dendritic forms of Au clusters were formed within 20 s of immersion time, the trendlines for 5 s, 10 s and 30 s immersion imply that Au cluster morphology alone may not be the deciding factor for improving film conductivity, but that these clusters need to reach a critical size (≈ 150 nm @ 60 s) to cause significant change to the R_{CT} . On top of this, density of the clusters is also an important

consideration, but since cluster densities are low for all the Au-CNT samples, the significance of cluster size is dominant. Although the hidden Au clusters within the CNT film cannot be comprehensively analysed by FESEM, the distribution within the film is assumed to be sparse (similar to surface analysis) due to poor wetting of the CNT surface. This means that the improvement such CEs can achieve so as to improve DSSC device performance may be limited.

FIGURE 5.4. LOGARITHMIC GRAPH OF CHARGE TRANSFER RESISTANCES (R_{CT}) OF SYMMETRICAL HALF CELLS MADE FROM CNT FILMS BEFORE AND AFTER IMMERSION IN 5 mM AU PRECURSOR SOLUTION FOR 5 s, 10 s, 30 s AND 60 s, MEASURED UNDER A VOLTAGE RANGE OF 0.5 V – 0.8 V. THE REFERENCE CELL IS MADE FROM PRISTINE CNT FILMS AND LABELED “CONTROL”.

Nonetheless, as seen from the changes in R_s and R_{CT} , the hypothesis is that using an Au-CNT film with an immersion time of 60 s as the CE in a DSSC would show an improvement in the device behavior. DSSC performance of two cells with different electrodes (pristine CNT and Au-CNT after 60 s immersion in precursor solution) were compared under 0.2% and 100% Sun illumination. The J - V curves and summary of measured DSSC data are shown in Fig. 5.5 and Table 5.2 respectively.

FIGURE 5.5. J - V GRAPHS OF DSSCs WITH DIFFERENT COUNTER ELECTRODES OF EITHER AU-CNT FILM IMMERSERD FOR 60 s (AU-CNT) OR PRISTINE CNT FILM (CNT-ONLY), UNDER ILLUMINATION INTENSITIES OF (LEFT) 0.2% SUN AND (RIGHT) 100% SUN.

TABLE 5.2. SUMMARY OF DSSC PERFORMANCE WHEN CNT OR AU-CNT FILMS WERE USED FOR THE COUNTER ELECTRODE.

Cell	% Intensity	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	η (%)
CNT	100	2.173	0.540	19.0	0.219
Au-CNT (60 s)	100	2.690	0.531	17.0	0.245
CNT	0.2	0.0244	0.419	62.0	3.134
Au-CNT (60 s)	0.2	0.0222	0.411	65.0	2.910

Under 0.2% Sun illumination, the J - V curves of both DSSCs overlapped with each other and share similar J_{SC} , V_{OC} , and FF values, with an overall efficiency of 3.1% for the DSSC with pristine CNT and 2.9% for the DSSC with Au-CNT (Table 5.2). The former has a slightly better efficiency. Pristine CNT films have been shown to function efficiently as CEs in DSSC under low intensity (indoor lighting) as they are

able to effectively conduct the low number of charges generated (see Sections 3.3.2 and 4.3.3). Slightly thicker CNT films with optical transmittances of 47-50% and an average R_s of $150 \Omega \cdot \text{sq}^{-1}$ were used for these devices, as this improves charge percolation and collection (refer to explanation in Section 3.1). Comparing the two DSSCs, the slightly lower efficiency of Au-CNT device under this low light condition is due to its lower J_{SC} and V_{OC} , which in turn gave rise to a better FF . However, the J - V curves of both devices are similar as shown in Fig. 5.5, suggesting that there is no appreciable benefit for having Au clusters in CNT films under such low light intensity.

As seen in Section 3.3.2, the issue of poor device performance when using CNT thin films as CEs becomes obvious with light intensities of at least 50% Sun. The advantage of using Au-CNT as CE compared to pristine CNT therefore becomes obvious when testing the devices under 100% illumination. As expected, under 100% Sun illumination, the DSSC with pristine CNT film CE suffered poor J_{SC} and FF , showing an overall efficiency of only 0.22%. With the inclusion of Au clusters, the DSSC with Au-CNT film CE had a slightly improved efficiency of 0.25%, which was due to a 24% improvement in J_{SC} .

A closer look at the corresponding J - V curves showed a steeper slope of curve for the DSSC with Au-CNT, indicating a lower series resistance. It is noted that the slight decrease in FF in this case is due to the fact that the current do not reach saturation at $V = 0V$ for both devices. If the current for both devices saturates at $V = 0V$, the steeper slope of curve from Au-CNT would have been translated to a better FF instead. Since the series resistance is defined as the sum of R_s , R_{CT} and diffusion resistance in the electrolyte (R_{DIFF}), the decrease in series resistance can be attributed to the improvement in R_s and R_{CT} seen in Table 5.1 and Fig. 5.4. Device performance

under high light intensity illumination is thus improved with the Au-CNT system. Nonetheless, the J_{SC} and FF values are still far from those of a standard DSSC, and another alternative to Au should be chosen to improve the CE performance.

Although the Au-CNT system has the potential to improve the FF of a DSSC with pristine CNT CE (by decreasing R_s , if the saturation current can be reached), poor precursor wetting on CNT surface due to low binding energy limit the extent of interfacial interaction to a significant extent. An improvement in CNT surface wetting is therefore critical for the Au-CNT system, and may be achieved by optimizing the synthesis method, e.g. using other organic solvents for precursor immersion. As DSSC performance still fares poorly as compared to a standard DSSC, Pt was chosen as the alternative to Au and evaluated as a possible means to boost device performance. Pt-CNT CEs were prepared using the same synthesis method as that of Au-CNT.

5.3.2. PT-CNT FILMS AS DSSC COUNTER ELECTRODES

Looking at Fig. 5.6, Pt nanoparticles (less than 50 nm in diameter) decoration appears to be homogeneous (inset, Fig. 5.6 (right)), and the pores in the CNT mesh become much smaller due to the presence of these nanoparticles. Unlike Au, which forms large scattered clusters on the CNT film, the Pt clusters are densely packed and form a conformal coverage on the CNT surfaces, suggesting a relatively stronger interaction between the Pt precursors and CNT.

FIGURE 5.6. FESEM IMAGES OF CNT ONLY (LEFT) WITH SMOOTH POROUS MORPHOLOGY, VS. PT-CNT (RIGHT) WITH INCREASED ROUGHNESS AND PRESENCE OF ≤ 50 NM DIA. NANOPARTICLE CLUSTERS ¹⁰. REPRODUCED BY PERMISSION OF THE PCCP OWNER SOCIETIES.

FIGURE 5.7. RAMAN SPECTRA OF CNT-ONLY (TOP) VS. PT-CNT (BOTTOM) FILMS ON GLASS, SHOWING CHANGES IN THE RATIO OF SHOULDER PEAKS OF THE G BAND (1580 cm^{-1}) AS A RESULT OF PT NANOPARTICLES DECORATION.

In order to determine the nature of interaction, Raman spectra were collected from films with and without Pt. The Raman spectra shown in Fig. 5.7 reveal the nature of Pt nanoparticles interaction with CNT. Comparing samples with and without Pt, peak shifts were not observed, suggesting non-covalent interaction between Pt and CNT. No Raman peaks were observed for Pt nanoparticles on glass. The peak ratios between the D band ($\sim 1340\text{ cm}^{-1}$; attributed to nanotube defects and amorphous carbon) and the carbonyl band ($\sim 1739\text{ cm}^{-1}$) is lower for Pt-CNT ($C/D_{\text{Pt}} = 0.768$) compared to CNT-only samples ($C/D_{\text{thick}} = 0.413$, $C/D_{\text{thin}} = 0.409$) ¹¹. These

differences in ratios suggest that Pt nanoparticles deposit preferably at the intrinsic defect sites on the CNT (e.g. Stone-Wales defects, pentagon and heptagon rings) rather than interacting with the carboxylate groups, which in turn suggests that the former may enable lower activation energy for Pt reduction¹².

To investigate how the Pt precursor immersion time may affect the R_{CT} , impedance measurements of symmetrical half cells were tested in the same way as that for Au-CNT. Prior to this impedance measurement, the CNT films were immersed in Pt precursors solution for a range of immersion times (5 s – 60 s). The results are summarized in Fig. 5.8. Unlike Au-CNT where R_{CT} significantly decreased after 30 s immersion time, the R_{CT} values for all half cells of Pt-CNT were similar to those of the control device which used pristine CNT. Therefore, the series resistances of the resulting DSSCs are not expected to improve with Pt-CNT. This was shown to be the case when the DSSCs were tested under illumination, as the slopes of J - V plots in Fig. 5.9 have similar gradient.

FIGURE 5.8. LOGARITHMIC GRAPH OF CHARGE TRANSFER RESISTANCES (R_{CT}) OF SYMMETRICAL HALF CELLS MADE FROM CNT FILMS BEFORE AND AFTER IMMERSION IN 5 MM PT PRECURSOR SOLUTION FOR 5 s, 10 s, 30 s AND 60 s, MEASURED UNDER A VOLTAGE RANGE OF 0.5 V – 0.8 V. THE REFERENCE CELL IS MADE FROM PRISTINE CNT FILMS AND LABELED “CONTROL”.

FIGURE 5.9. GRAPHS OF PERFORMANCE OF DSSC WITH DIFFERENT COUNTER ELECTRODES AT 1% SUN (LEFT) AND 100% SUN (RIGHT). IN BOTH CASES, AS COMPARED TO FIG. 5.5, INCREASING THE THICKNESS OF CNT IMPROVED THE FF (AND V_{OC} FOR 1% SUN), WHEREAS THE PRESENCE OF PT IMPROVED THE J_{SC} . “PT-CNT” DENOTES CNT DECORATED WITH PT NANOPARTICLES.

To study the effect of light intensity on the device behavior, DSSCs with the two types of CEs were measured at 1% and 100% Sun respectively. The results are shown in Fig. 5.9 and Table 5.3. The thicknesses of the CNT films used in the Pt-CNT study (optical transmittance: 32%, average R_S : $86 \Omega \cdot \text{sq}^{-1}$) are higher than that of the films in the Au-CNT study (optical transmittance: 47-50%, average R_S : $150 \Omega \cdot \text{sq}^{-1}$). As compared to the control device in the previous Au-CNT experiment, the benefits of using a thicker and more conductive CNT-only film as CE resulted in an increase in J_{SC} and V_{OC} , and improved FF . With these more conductive films, current saturation can be achieved at 100% Sun. Since film conductivity is the only variable, and the net rate of electron extraction by the TiO_2 is balanced by the net rate of triiodide reduction at the CE – electrolyte interface¹³, recombination reaction caused by the buildup of electrons in TiO_2 was more effectively suppressed. The results prove that a sufficiently thick CNT film is able to function as a suitable alternative CE material to Pt, albeit having a much lower light transmittance of 32% @ 550 nm.

TABLE 5.3. SUMMARY OF DEVICE PERFORMANCE FOR DSSC WITH DIFFERENT COUNTER ELECTRODES WHEN ILLUMINATED AT 1% AND 100% SUN.

Cell	% Intensity	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	η (%)
CNT	100	13.712	0.678	40.8	3.83
Pt-CNT (60 s)	100	14.244	0.682	38.7	3.81
CNT	1	0.147	0.545	65.1	5.14
Pt-CNT (60 s)	1	0.158	0.554	64.9	5.62

With the introduction of Pt nanoparticles, PCE increased from 5.14% to 5.62% at 1% Sun, mainly due to the 7.5% improvement in J_{SC} . Since the addition of Pt nanoparticles improves J_{SC} and PCE , thinner CNT films that are decorated with Pt nanoparticles with this method can therefore be used instead of thicker pristine CNT films to achieve similar device performances, and at the same time increase light transmittance, hence making this suitable for bifacial application. Although J_{SC} also improved at 100% Sun, the slope of the curve closely followed that of the DSSC with the thicker CNT film CE. This suggests similar series resistance values, as inferred from the similarity of R_{CT} values in Fig. 5.8, and this indicates that Pt nanoparticles confer a faster catalytic rate to the CE with negligible effect on the film conductivity. Cyclic voltammetry measurements in Fig. 5.10 show that this improvement can be attributed to an improvement in catalysis.

FIGURE 5.10. CYCLIC VOLTAMMETRY MEASUREMENTS (SCAN RATE = 10 mV/s) COMPARING 3 DIFFERENT SAMPLES ON FTO-GLASS WORKING ELECTRODES: PT-ONLY, CNT-ONLY AND PT-CNT, USING PT COUNTER ELECTRODE AND AG / AGCL REFERENCE ELECTRODE (SILVER CHLORIDE ELECTRODE; SCE), IN AN ELECTROLYTE COMPOSITION OF 10 mM LiI + 0.1 M LiClO₄ + 1 mM I₂ IN ACRYLONITRILE ¹⁰. REPRODUCED BY PERMISSION OF THE PCCP OWNER SOCIETIES.

Relative differences in catalytic activity can be seen by comparing the current densities (marked by area under the curves) and the onset of the oxidation peaks for the different samples. As CNT has significant capacitance properties, a scan rate of 10 mV/s was chosen to minimize capacitive effects on total current densities, so that the latter reflects Faradaic contribution more accurately. From Fig. 5.10, it was observed that the current densities (i.e. areas under the curves) of all three samples are comparable, which was expected as the samples with an area of 1 cm² each were prepared similarly.

The reduction trough at +100 mV was not present in CNT-only, as the carboxylated CNT thin film used was p-type (hole conducting) in nature. As the CE only plays the role of reduction of triiodide, the lack of this trough is not a concern for this application, but gives more insight on Pt interaction with CNT. The presence of

this trough in Pt-CNT indicates that the redox nature of Pt has been largely preserved – which agrees well with non-covalent interaction inferred from Raman spectroscopy.

There is a slight positive shift in the oxidation potentials away from the origin. From -0.4 V ~ -0.2 V, the trend is similar between Pt-CNT and CNT-only which is typical of resistor behavior, showing that the CNT film conductivity is not compromised in Pt-CNT. The onset of first oxidation peaks occurs first for Pt-only and followed closely by Pt-CNT; that of CNT-only required an additional +0.3 V. The trend of onset of second oxidation peaks was also Pt-only < Pt-CNT < CNT-only. The first oxidation peak occurs when the CE material releases an electron for the reduction of triiodide (I_3^-) ions; the I^-/I_3^- species has a redox potential of +0.035 V, hence the closer these 2 values are, the smaller is the loss of potential energy and better suppression of current loss from back reactions at the working electrode of the DSSC.

As observed, Pt-CNT has a potential slightly more positive than that of Pt-only, which can be attributed to the p-type nature of the CNT used in this work. This small effect also implies that the catalytic nature of Pt is dominant over CNT, which can be expected due to the dense surface coverage of Pt on CNT (Fig. 5.6). This supports the hypothesis that the presence of Pt nanoparticles improves the catalytic rate of CNT thin film, accounting for the 7.5% improvement in J_{SC} from our device characteristics at 100% Sun. Using both CNT and Pt nanoparticles as the CE therefore leads to a synergistic effect where catalytic rate is improved without compromising the conductivity of CNT film to bring about an enhancement in the device performance.

5.4. SUMMARY AND CONCLUSION

Ethanol-assisted spontaneous reduction of Au precursor on CNT films formed low density clusters of Au dendrites that are up to 150 nm in diameter. The small number of large Au clusters is a direct result of the poor wetting of Au on CNT surface. In the presence of Au clusters, the optical transmittances did not change significantly, while the work function increased from 4.85 eV to a maximum of 5.12 eV in 60 s, which is similar to the work function of Au (5.1-5.2 eV). The increase in work function is indicative of a charge transfer mechanism, although at a low immersion concentration of 5 mM, changes in Raman peaks were predicted to be smaller than the imaging resolution of our Raman spectrometer. The presence of charge transfer effect can be shown through impedance measurement since the changes in R_S and R_{CT} can be detected. R_S and R_{CT} were found to decrease most significantly for films that were immersed for 60 s, which led to a decrease in series resistance of the DSSC and increased J_{SC} , and the result is a slight improvement in the efficiency from 0.22% to 0.25% under 100% Sun illumination. As poor Au precursor wetting decreased the Au-CNT system's potential to create charge transfer complexes with CNT and improve DSSC performance, an improvement in CNT surface wetting is therefore necessary by optimizing the synthesis method.

Unlike the case of Au-CNT, Pt nanoparticle clusters of less than 50 nm were formed by spontaneous reduction from precursor solution, randomly and homogeneously on the CNT thin film. Raman tests reveal the nanoparticle-CNT interaction to be non-covalent (observed as the absence of peak shifting when comparing the Raman spectra of CNT against that of Pt-CNT). The shoulder peaks of the G band (G: 1580 cm^{-1}) – the D band (D: 1340 cm^{-1} ; corresponding to defects) and

carbonyl band (C: 1739 cm^{-1} ; corresponding to carboxylate groups) – showed a change in relative ratio (C/D) from 0.4 to 0.8, suggesting preferential Pt deposition on CNT intrinsic defect sites (such as pentagon-heptagon kinks) over surface carboxylate groups. This shows that intrinsic defect sites of CNT may offer lower energy of activation for Pt reduction, and should therefore be able to form nanoparticles on pristine non-carboxylated CNT as well.

R_{CT} values were found to be comparable for all Pt precursor immersion times, which suggests the lack of charge transfer reaction. This observation, as well as the non-covalent interaction inferred from Raman analysis, indicated possible preservation of Pt properties in the Pt-CNT system. This was further shown by the close proximity of oxidation peak onsets of Pt-CNT and pristine Pt from cyclic voltammetry measurements. While the Au-CNT system had decreased series resistance in the corresponding DSSC, the Pt-CNT system gave an improvement in catalytic activity, appearing in cyclic voltammetry curves as shifts in oxidation peak onsets that indicated a decrease in potential energy loss. When tested under 100% and 1% Sun illumination, the DSSC series resistance, which is observed from the slope of J - V curve, was found to be similar for DSSCs that employed either CNT only, or Pt-CNT. The only significant improvement resulting from the use of Pt nanoparticles was an increase in J_{SC} for both illumination intensities, which was attributed to the improved catalytic activity of the Pt-CNT film. With Pt, the J_{SC} increased from 13.7 mA/cm^2 to 14.2 mA/cm^2 under 100% Sun illumination, and from $147\text{ }\mu\text{A/cm}^2$ to $158\text{ }\mu\text{A/cm}^2$ under 1% Sun illumination. Device efficiencies reached 3.8% and 5.6% respectively, greatly improving the results obtained with Au-CNT.

The good conducting and catalytic properties of Pt-CNT meant that it can serve effectively as the CE for a fully flexible DSSC suitable for both indoor and outdoor applications. However, this type of CE is FTO-free but Pt is still present. A Pt alternative still needs to be found for this application. Chapter 6 will explore and discuss the effectiveness of replacing Pt with metal sulfides and CNT nanocomposites and their potential as CEs in DSSC.

5.5. REFERENCES

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6. METAL SULFIDE NANOPARTICLE DECORATION OF CNT NETWORKS IN DSSC

6.1. INTRODUCTION

Although Pt-CNT has been shown to be a competent alternative counter electrode (CE) in DSSC under both high and low illumination intensities, only FTO was replaced, and Pt was still present to catalyze the reduction of triiodide ions. Besides metal and metal oxides ^{1,2}, metal sulfides such as CoS, NiS and WS₂ were shown to have catalytic activity on par with (if not better than) Pt on FTO substrates in DSSC ³⁻⁷. Direct deposition of these metal sulfide nanoparticles on conducting oxide substrates was mainly achieved using electrodeposition ³⁻⁵, while other deposition methods, such as spray coating of hydrothermally preformed metal sulfide nanoparticles ⁶, and heat annealing of drop coated metal sulfide precursor solutions, were also reported ⁷. A combination of excellent catalytic activity and high surface area yielded charge transfer resistances that were either on par or even lower than that of Pt. However, high diffusion resistances is the main issue with these metal sulfide CEs, causing low limiting current densities and the overall device efficiency to be compromised. A possible reason for high diffusion resistance is additional reaction between the metal sulfide and iodide/triiodide species in the electrolyte.

The stability of these catalytic metal sulfide nanoparticles in electrolyte should be improved to decrease the diffusion resistance, and this stability can be improved by binding the nanoparticles preferentially onto the CE. This is achievable with using CNT in the CE as the scaffold for deposition, similar in concept to the metal nanoparticle depositions discussed in Chapter 5. Lin *et al.* showed that not only was

MWNT electrodeposited with CoS electrochemically stable in electrolyte, but catalytic activity and device efficiency ($\eta = 6.96\%$) of the DSSC with this nanocomposite CE were enhanced as compared to devices that had either only MWNT ($\eta = 2.91\%$) or only CoS ($\eta = 5.86\%$) as CEs (in both cases, FTO were used as the substrate)⁴. The structural similarity of MWNT and SWNT strongly suggests the applicability of CoS-SWNT nanocomposites as DSSC CEs, although this has not yet been reported. As discussed before in Section 3.1, SWNT is more suitable than MWNT for application as DSSC CE, as the ultrasonication of CNT suspension introduces more defects (and decreases conductivity) due to the abrasion of adjacent concentric nanotubes within individual MWNT. Hence the synthesis of metal sulfide-SWNT nanocomposites and the investigation on the effect of such alternative DSSC CEs on device behaviour is carried out in this work.

In this chapter, a simple, solution-processable method is reported to obtain working DSSC with a bilayer CE structure of thin CNT film with CoS or NiS (i.e. FTO- and Pt-free). Results show that CoS outperformed NiS as an alternative CE catalyst material in a DSSC (giving higher J_{sc}), which was likely due to better and more uniform coverage of nanoparticles on CNT surfaces. The importance of surface coverage for interfacial interaction is very clearly demonstrated in this study, because though NiS has better conductivity as inferred from Tafel plots, poorer surface coverage still limits its performance as CE. However, both NiS/CNT and CoS/CNT device efficiencies were affected by the very low $FF (\leq 0.30)$, and R_{CT} and R_{Diff} were high, suggesting that the bilayer configuration was not ideal for contact and interaction with CNT. Moreover, such bilayer films require separate synthesis steps for each layer.

To ensure maximum surface interaction, a one-step synthesis method was

adopted for easier and possibly more homogeneous film fabrication. Sulfide precursors were introduced into a solution of suspended CNT. CoS/CNT was prepared using this modification since its morphology on CNT is more homogeneous as compared to NiS/CNT. To differentiate the nanocomposite prepared using the different methods of synthesis, all samples and their data (using the mixture-in-solution method) were referred to as “CoS-CNT”. As metal sulfides nanoparticles are light absorbing, the precursor concentrations could also be varied and optimized for light transmittance and device performance. Since the focus of the latter part of this study is to investigate the effect of CoS concentration on the catalytic behaviour of CoS-CNT composites in DSSC CEs, the conductivity of the base substrate was kept constant by using FTO glass. The 0.04 mM solution resulted in CoS-CNT composites that gave optimal DSSC efficiencies of 5.78% when illuminated under 1 Sun from the photo anode side, and 2.22% from the CE side. This is comparable to that of a standard Pt CE-based DSSC (5.83% and 3.34% respectively).

6.2. METHODS

Microscope glass (soda-lime silica) was used as FTO-free substrates for the CEs with metal sulfide / CNT bilayer architecture. FTO-glass was used in the fabrication of metal sulfide-CNT monolayer films. The substrates were pre-drilled for the subsequent filling of the electrolyte. They were rinsed in absolute ethanol and deionized water (Milli-Q, 18 MΩ.cm), and exposed to ozone plasma for 3 min. Purified carboxylated single-walled carbon nanotubes with semiconducting to a metallic ratio of 2 : 1 (P3-SWNT, Carbon Solutions, Inc.) suspended in deionized water (0.3 mg/mL) after sonication and centrifugation (14 000 rpm, 70 min) were

spray-coated onto the glass substrates and held at 120 °C to remove the water thoroughly. The film obtained has a final optical transmittance of 70% at 550 nm (UV-vis spectrophotometer UV-3200, Shimadzu). Using a surface profiler (Alpha-Step IQ, KLA-Tencor), the average thickness of CNT films is found to be about 150 nm. 1 mL of CoS and NiS precursor solutions (1 : 4 molar ratio of $\text{CoCl}_2/\text{C}_4\text{H}_6\text{NiO}_4$: $\text{C}_2\text{H}_5\text{NS}$, Sigma-Aldrich) in acetone were then sprayed onto the CNT films, dried and annealed at 350 °C for 30 min in an Ar environment to prevent the formation of oxides. These bilayer films are referred to as CoS/CNT and NiS/CNT. Details of the precursor solution synthesis have been reported previously⁷.

CoS-CNT films were also prepared by dissolving the CoS precursors (1 : 4 molar ratio of $\text{CoCl}_2/\text{C}_4\text{H}_6\text{NiO}_4$: $\text{C}_2\text{H}_5\text{NS}$, Sigma-Aldrich) in water separately before adding the various concentrations (0.0013 mM – 20 mM) into the CNT suspension and ultrasonicated for 60s. The CoS-CNT suspensions were then spray-coated onto the FTO-glass substrates and held at 120 °C to evaporate the solvent; care was taken to ensure the same volume of *pristine* CNT suspension was deposited per substrate. Annealing was also done at 350 °C for 30 min in an Ar environment to prevent the formation of oxides. Field Emission Scanning Electron Microscope (FESEM, JEOL JSM-7600F) images were collected to study the morphology of all CNT films before and after functionalization. Cyclic voltammetry plots were obtained using the three-electrode system immersed in an electrolyte composed of 10 mM LiI + 0.1 M LiClO_4 + 1 mM I_2 in acrylonitrile and the measurements were collected using a potentiostat (Autolab 302N, Eco Chemie B.V.).

For device fabrication, the photo anodes were made of FTO glass and a double layer of 8 mm mesoporous TiO_2 (average particle size: 25 nm) +5 mm thick scattering

TiO₂ (average particle size: 400 nm), and sintered at 500 °C. Dye (ruthenium-based dye, Z907) soaking was done for 16 h to ensure sufficient dye uptake by TiO₂ before assembly with the CE, and a ring spacer (SX1170-25, Solaronix) held them together and sealed off the cell active volume. This volume was then subsequently filled with the commercially available methoxypropionitrile-based electrolyte R-50 (Solaronix). The hole was finally covered with the same spacer and an optically-clear glass coverslip above it. J - V measurements for all the fabricated DSSC were collected at AM1.5 light intensity (1 Sun or 100 mW/cm²; Newport solar simulator). Symmetrical half cells, with a second identical CE in place of the photo anode, were fabricated similarly for electrochemical and impedance measurements (Autolab 302N, Eco Chemie B.V.).

6.3. RESULTS AND DISCUSSION

6.3.1. BILAYER COUNTER ELECTRODES – NiS/CNT AND CoS/CNT

XRD spectra showed that the compounds synthesized are Co_{8.4}S₈ and Ni₃S₂ (see Fig. 6.1); these will be known as CoS and NiS henceforth. Both spectra match those obtained from sulfides synthesized by Mulmudi *et al.* using the same method ⁷, indicating that the presence of CNT does not promote any phase transformation of the metal sulfides.

FIGURE 6.1. LEFT: X-RAY DIFFRACTION (XRD) SPECTRA OF $\text{Co}_{8.4}\text{S}_8$ AND $\text{Co}_{8.4}\text{S}_8$ ON CNT: (I) UNDETECTED $\text{Co}_{8.4}\text{S}_8$ PEAK IN $\text{Co}_{8.4}\text{S}_8$ SPECTRA, AND (II) PEAK OF CNT (101). RIGHT: XRD SPECTRA OF Ni_3S_2 WITH (ABOVE) AND WITHOUT (BELOW) CNT FILM AS A BASE LAYER: * INDICATES PRESENCE OF AMORPHOUS CARBON ⁸. REPRODUCED BY PERMISSION OF THE PCCP

OWNER SOCIETIES.

The morphology of CoS and NiS decoration on CNT is shown in Fig. 6.2. Just like Pt/CNT (Fig. 5.6), CoS was present in similar nanocluster sizes of ≤ 50 nm. However, CoS appeared to be less conformal on CNT surfaces compared to Pt/CNT. The formation of NiS nanoclusters on CNT surfaces was similar to that of CoS, although the average nanoparticle size is larger. When observed under high magnification, a dense layer of polydisperse spherical clusters (≤ 100 nm) covered the CNT film surface. NiS has similar particle sizes as CoS, but fused clusters in the foreground appear to be much larger. The coverage of NiS on CNT is poorer, and the large size of the clusters suggests that contact with the CNT film surface may be poor. A wider area image (see Fig. 6.2(b), low magnification) also showed non-homogeneous distribution of NiS, with islands of NiS nanoclusters among patches of pristine CNT bundles.

FIGURE 6.2. TOP VIEW FESEM IMAGES OF (A) CoS/CNT AND (B) NiS/CNT NANOCOMPOSITE THIN FILMS AT LOW MAGNIFICATION (50 000X) AND HIGH MAGNIFICATION (150 000X; INSET) ⁸. REPRODUCED BY PERMISSION OF THE PCCP OWNER SOCIETIES.

FIGURE 6.3. (A) TAFEL PLOTS OF SYMMETRICAL HALF-CELLS OF CoS/CNT AND NiS/CNT AND (B) THEIR CORRESPONDING CYCLIC VOLTAMMETRY PLOTS, WITH Pt/CNT SHOWN AS REFERENCE ⁸. REPRODUCED BY PERMISSION OF THE PCCP OWNER SOCIETIES.

The Tafel and cyclic voltammetry plots in Fig. 6.3 give some information on the electrochemical activity of the CNT–metal sulfide nanocomposites. Looking at Fig. 6.3(a), CoS/CNT is found to have a gentler Tafel slope compared to NiS/CNT. Since the steeper the Tafel slope is, the lower the overpotential, one would expect the opposite based on the better CNT surface coverage of CoS. However, because CoS is semiconducting in nature ⁹ while NiS (specifically Ni₃S₂) is electrically conductive ¹⁰, CoS is likely to introduce a Schottky barrier at its interface with CNT and contribute to

Chapter Six – Metal Sulfide Nanoparticle Decoration of CNT Networks in DSSC interfacial resistance. The gradient of the Tafel curve at voltage higher than 0.2 V is non-zero, indicating that maximum current densities were not reached for both CoS/CNT and NiS/CNT. In general, gentle Tafel curve is an indication that FF is low for both CoS/CNT and NiS/CNT. Since maximum current densities were not reached, there is likely a high diffusion resistance for electrodes when applied in DSSCs.

In the cyclic voltammetry plot (Fig. 6.3(b)), as compared to Pt/CNT (230 mV, 675 mV, from Fig. 5.10), significant right-shifting of oxidation peaks were observed for both CNT–sulfide nanocomposites (CoS: 350 mV, 700 mV; NiS: 300 mV, 715 mV). It is suspected that the right-shifting may be correlated with high charge transfer resistances, and this will be discussed next together with the device behaviour. Nonetheless, all CNT–sulfide peak onsets lie between that of Pt and CNT (cf. Fig. 5.10), indicating that a faster catalytic response of CNT is still achievable with these nanocomposites, albeit only a slight increase due to their relative proximity to CNT.

TABLE 6.1. SUMMARY OF DEVICE CHARACTERISTICS OF DSSC EMPLOYING DIFFERENT COUNTER ELECTRODES, AND THEIR RESPECTIVE SYMMETRICAL HALF CELL IMPEDANCE

DATA ⁸ • REPRODUCED BY PERMISSION OF THE PCCP OWNER SOCIETIES.

		Device Parameters				Impedance		
		Illumination: 1 Sun				(with FTO substrates)		
	Counter Electrode	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)	R_S (Ω)	R_{CT} (Ω)	R_{Diff} (Ω)
Standard	Pt/FTO	12.87	0.73	0.55	5.13	15.8	56.9	21.0
FTO-free	Pt/CNT	14.24	0.75	0.35	3.76	14.0	59.1	122.7
FTO- & Pt-free	CoS/CNT	15.16	0.70	0.30	3.13	15.0	686.0	1126.4
	NiS/CNT	12.85	0.72	0.28	2.57	15.5	230.5	250.5

FIGURE 6.4. CURRENT DENSITY–VOLTAGE PROFILES OF DSSC WITH CNT/NANOCOMPOSITES OR STANDARD Pt/FTO COUNTER ELECTRODES, UNDER 1 SUN INCIDENT LIGHT INTENSITY ⁸ • REPRODUCED BY PERMISSION OF THE PCCP OWNER SOCIETIES.

The current density–voltage (J–V) behavior of DSSC under 1 Sun illumination using metal sulfide decoration on CNT as the CE is shown in Fig. 6.4, and device performance is summarized in Table 6.1, with Pt/FTO being the standard cell for comparison. All DSSC CEs were FTO-free except for Pt/FTO. To investigate the interaction between the decorated CNT and electrolyte within the DSSC, impedances of symmetrical half cells were measured, and electrode–electrolyte charge transfer resistance (R_{CT}) and bulk diffusion resistance (R_{Diff}) data were extracted from Nyquist plots (Table 6.1). The former is calculated from the width of the first semicircle occurring at high frequency range of 100 kHz–100 Hz, and the latter from the width of the second (overlapping) semicircle occurring at frequencies below 100 Hz ^{6,7,11}. Sheet resistances (R_S) for all devices were in the range of 14.0–15.8 Ω /sq because FTO was retained for all impedance measurements. Otherwise, R_{Diff} could not be determined if the series resistance (R_{Series}) is too high.

The trend for R_{CT} and R_{Diff} , $CoS/CNT > NiS/CNT$, agrees well with the catalytic activity trend determined from the Tafel plot. Nonetheless, Pt/CNT has the lowest charge transfer resistance among all CNT-based CEs due to the good wetting and coverage of Pt on CNT. The higher R_{Diff} compared to Pt/FTO is likely due to undesired (i.e. competing) reaction of sulfide with LiI redox species. This may contribute to the back reaction, since triiodide reduction is then expected to occur at a slower rate across the electrolyte. Indeed, from Fig. 6.4, it is clear that only Pt/FTO and Pt/CNT have reached the maximum experimental current densities at short-circuit conditions (i.e. $V = 0$ V), with Pt/FTO giving the highest FF among all tested devices.

The graph for Pt/CNT has a kink near V_{OC} that significantly decreased the FF ; since the only thing that is different between the two devices is the replacement of FTO with CNT, the phenomenon may be attributed to the difference in R_S of FTO ($\sim 15 \Omega/sq$) and CNT thin film ($\geq 200 \Omega/sq$): distribution of charges within the cell is non-homogeneous as a result, and the kink is caused by the energy barrier needed to overcome for effective return of electrons from the CNT film¹². In fact, this kink also showed up for the corresponding DSSC discussed in the previous chapter (Fig. 5.9, right), but the effect was less noticeable due to the lower R_S of the CNT film ($86 \Omega/sq$). Nonetheless, there is a substantial improvement in J_{SC} ($+1.37 \text{ mA/cm}^2$) and V_{OC} ($+0.02$ V) for the Pt/CNT device over the standard cell, giving a promising final conversion efficiency (η) of 3.76%, or 73.3% of that of the standard cell.

As for the devices with CNT–sulfide nanocomposite CEs, none of the maximum experimental current densities were reached at J_{SC} due to poor FF (gentle slopes of curve as V approaches V_{OC}). Small gradient of slopes is indicative of high R_{Series} , which are a combination of sheet, charge transfer and diffusion resistances.

Adding up these resistance values in Table 6.1, one can observe that CoS/CNT has the highest R_{Series} , but not the lowest J_{SC} and η . Although the R_{Series} of NiS/CNT is much lower than that of CoS/CNT, the latter's device behavior outperforms the former, particularly in J_{SC} (15.16 mA/cm² vs. 12.85 mA/cm²) and PCE (3.13% vs. 2.57%). From the characterization of FTO- and Pt-free CEs, despite being more catalytic and conducting, the device behavior of NiS/CNT paled in comparison to CoS/CNT. While one would expect NiS/CNT to outperform CoS/CNT as a CE based on the impedance measurements and Tafel plot, it appears that the low density, patchy coverage of NiS clusters on CNT outweighed the benefit of its relatively low interfacial charge transfer resistance. Poor coverage (see Fig. 6.2(b)) resulted in a significant decrease in overall surface area of catalyst exposed to the electrolyte, as well as slower catalytic activity of the nanocomposite film, since the CNT with its higher oxidation peak onsets is least catalytic compared to any of the nanocomposites (see 6.3(b)).

In this work, all the CNT films did not undergo treatment or modification before the deposition of metal sulfides. One way to improve the coverage of NiS on CNT films is to treat the films chemically or physically before deposition of the NiS precursor (e.g. brief ozone plasma treatment, surface coating with conducting polymer, etc.). This approach may be extended to the other metal sulfides to improve the FF . In fact, despite a R_{Series} of more than ten times that of Pt/FTO, CoS/CNT has the highest J_{SC} among all tested devices (15.16 mA/cm²); despite poor surface coverage of NiS on CNT, the J_{SC} of NiS/CNT (12.85 mA/cm²) is on par with that of Pt/FTO (12.87 mA/cm²) — both J_{SC} which have not reached the maximum value possible — highlighting the excellent catalytic properties of CoS and NiS, and suggesting that device performance could be pushed even higher if FF can be improved.

The enhanced feasibility of thin CNT films functionalized with metal/metal sulfides in FTO-free CE of DSSC is evident from an improvement of catalytic activity when CoS or NiS nanoparticles are deposited on CNT surfaces. CoS/CNT appeared to give the best photovoltaic performance despite having poorer catalytic activity and conductivity compared to NiS/CNT. This can be attributed to the more homogeneous deposition of CoS compared to NiS. For both sulfides/CNT CE, the J_{SC} values were higher than or comparable to that of Pt/FTO. This study shows that CNT–metal sulfide nanocomposites has the potential to replace FTO and Pt in DSSC CEs if uniform, large scale precursor deposition can be achieved to result in a more homogeneous nanocomposite. This is likely to improve the charge transfer properties of the nanocomposite. Thus the synthesis method should ideally be modified so as to obtain a single uniform film of nanocomposite – with controllable degrees of light transmittance – instead of the bilayer films used here.

The next section will discuss the results obtained when different concentrations of CoS precursors were added to CNT suspensions before spray coating and annealing on FTO-glass to form CoS-CNT films. Increasing CoS concentration result in films that were more light absorbing (refer to [Appendix 6](#)), and the effect of CoS concentration on other film properties and DSSC behaviour will also be presented.

6.3.2. CoS-CNT FILMS AS DSSC COUNTER ELECTRODE CATALYSTS

A comparison of XRD spectra in [Fig. 6.5](#) indicates that the nanocomposite formed is similar to that in the bilayer configuration, although a few characteristic peaks either did not appear or had diminished peak heights due to the much lower concentrations of CoS in the new samples. The XRD spectra of nanocomposites with

different CoS concentrations appeared similar, hence the chemical composition is independent of CoS concentrations from 0.0013 mM to 20 mM. Using a range of CoS concentrations of 20, 5, 2.5, 0.4, 0.04 and 0.0013 mM, different morphologies of CoS-CNT film on FTO glass can be obtained and they are shown in Fig. 6.6. Pristine CoS on FTO glass (refer to Appendix 4) appeared as highly fused patches of nanoparticle clusters, while pristine CNT on FTO glass show a network of tubes over a layer of FTO particles. Even at a concentration as low as 20 mM, the CoS precursors were in excess and resulted in an additional layer of interconnected CoS nanoparticle clusters above the CoS-CNT thin film (i.e. FTO / CoS-CNT / CoS structure); the appearance of these nanoclusters were similar to those obtained from the CoS/CNT bilayer film seen in Fig. 6.2(a). CoS concentration was therefore reduced to prevent the formation of this additional layer.

FIGURE 6.5. X-RAY DIFFRACTION (XRD) SPECTRA OF $\text{Co}_{8.4}\text{S}_8$ AND $\text{Co}_{8.4}\text{S}_8$ ON CNT: (*) COMMON PEAK DETECTED IN ALL SAMPLES, (i) UNDETECTED $\text{Co}_{8.4}\text{S}_8$ PEAK IN $\text{Co}_{8.4}\text{S}_8$ SPECTRA, AND (ii) PEAK OF CNT (101).

FIGURE 6.6. TOP VIEW FESEM IMAGES OF CoS-CNT NANOCOMPOSITE THIN FILMS ON FTO GLASS AT 100 000X MAGNIFICATION. CoS CONCENTRATIONS ARE INDICATED ON EACH IMAGE IN mM. PRISTINE CNT IS THE CONTROL SAMPLE WITHOUT CoS, WHICH SHOWS A NETWORK OF CNT ABOVE A CONTINUOUS LAYER OF FUSED FTO PARTICLES.

At 5 mM CoS, the additional CoS layer can be prevented and the nanoclusters formed were well-dispersed, although the size distribution varied from 10 nm to 50 nm in diameter. Homogeneity of CoS dispersion was preserved when the concentration decreased from 5 mM to 0.04 mM. There is a reduction in the size of the nanoparticles, down to about 10 nm (≤ 2.5 mM), and following that a decrease in nucleation density (≤ 0.4 mM). CoS nanoparticles were no longer observed at 0.0013 mM (refer to

Appendix 5), but the subsequent characterization of the CoS-CNT film and DSSC behavior improvement suggested the presence of CoS (see Fig. 6.7, Fig. 6.8 and Table 6.2, 6.3). The most likely explanation for this observation, is that this concentration is too low for CoS nucleation and growth during annealing, but nonetheless allowed the formation of stable complexes with CNT while in solution.

The Tafel plots in Fig. 6.7 showed the electrochemical activity behavior of symmetrical half cells, except for the cell made using 20 mM CoS. A film prepared using 20mM CoS will have an additional CoS layer that would not allow for fair comparison with the other samples. The gradient of the Tafel plots for the CoS-CNT samples increases with increasing CoS concentrations up to 2.5 mM. Since nanoparticle size and distribution remained uniform, this trend was expected, since more CoS nanoparticles should improve the catalytic activity of the films. Also, all CoS-CNT Tafel slopes were steeper than that of CNT only. The Tafel slope for 5 mM CoS-CNT almost exactly overlapped that of the 2.5 mM CoS-CNT sample, suggesting that a decrease in surface area-to-volume ratio for the larger clusters / particles was detrimental to the catalytic effect even though twice the concentration of CoS was present. The slope of Tafel plot for 0.4 mM CoS-CNT cell is similar to the Pt-only cell, and those for 2.5 mM and 5 mM CoS had steeper Tafel slopes. This indicates that a minimum of 0.4 mM CoS is necessary for CoS-CNT to match the catalytic activity of Pt.

The cyclic voltammetry graphs for CoS-CNT cells are shown in Fig. 6.7(b). All the CoS-CNT samples had onset potentials for oxidation higher than Pt, but lower than CNT. There was a slight variation in both oxidation peak onsets for all CoS-CNT samples, at $+545 \pm 50$ mV and $+785 \pm 50$ mV, which was possibly due to grounding

issues. Nonetheless, the relative onsets of oxidation peaks were not expected to change for all the CoS-CNT samples, because the CNT is decorated with the same material – CoS nanoparticles / clusters – and only the CoS concentration were varied.

FIGURE 6.7. (A) TAFEL PLOTS OF SYMMETRICAL HALF-CELLS OF CoS-CNT WITH VARIOUS CoS CONCENTRATIONS, WITH CNT AND Pt SHOWN AS REFERENCES. (B) CORRESPONDING CYCLIC VOLTAMMETRY PLOTS, WITH Pt SHOWN AS REFERENCE.

FIGURE 6.8. CURRENT DENSITY–VOLTAGE PROFILES OF DSSC UNDER 1 SUN INCIDENT LIGHT INTENSITY, WITH VARIOUS CONCENTRATIONS OF CoS-CNT, PRISTINE CNT OR STANDARD Pt AS COUNTER ELECTRODES.

TABLE 6.2. SUMMARY OF DEVICE CHARACTERISTICS OF DSSC EMPLOYING DIFFERENT COUNTER ELECTRODES, AND THEIR RESPECTIVE SYMMETRICAL HALF CELL IMPEDANCE DATA. THE DATA VALUE DENOTED “N.A.” INDICATES THAT THE R_{DIFF} SEMICIRCLE WAS OVERLAPPED BY THE MUCH LARGER R_{CT} SEMICIRCLE SUCH THAT CURVE FITTING WAS NOT POSSIBLE.

		Illumination: 1 Sun				Impedance (with FTO substrates)		
	Counter Electrode	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	η (%)	R_{S} (Ω)	R_{CT} (Ω)	R_{Diff} (Ω)
Standard	Pt/FTO	14.702	0.719	55.2	5.83	12.045	5.53	4.532
Pt-free	CNT/FTO	13.488	0.636	15.2	1.30	17.580	1152.8	N.A.
CoS-CNT/FTO	5 mM	11.533	0.707	67.5	5.03	13.852	17.799	14.977
	2.5 mM	13.306	0.707	66.6	6.27	13.382	69.873	44.291
	0.4 mM	14.111	0.715	58.1	5.86	15.344	32.999	13.131
	0.04 mM	13.911	0.722	57.6	5.78	15.346	34.791	15.649
	0.0013 mM	13.834	0.711	37.0	3.64	14.797	27.037	14.750

At 1 Sun illumination, the J – V behavior of DSSCs with CE prepared at various concentrations of CoS-CNT are shown in Fig. 6.8, and the device performance are summarized in Table 6.2. As expected, due to the very high R_{CT} value, the DSSC with CNT only gave a very low FF of 15.2% despite having a high J_{SC} value of 13.5 mA/cm². It was not possible to determine the R_{Diff} due to the R_{CT} semicircle overlapping with that of the R_{Diff} . Since FTO was used at both photo anode and CEs, the difference in R_{S} has become negligible (anode: ~15 Ω /sq; CE: 17.58 Ω /sq), and hence its V_{OC} value at 0.636 V was lower than that of the standard Pt cell (0.719 V).

The problems of low V_{OC} and FF were greatly improved for all the CoS-CNT

devices, regardless of the CoS concentration. V_{OC} values were in the range of 0.707 V $\sim$ 0.722 V, comparable to that of Pt, and this improvement may be attributed to the significant decreases in R_{CT} by more than an order of magnitude (1152.8 Ω to $< 70 \Omega$). For CoS-CNT devices, R_{CT} increased with increasing CoS concentration up to 2.5 mM, possibly due to the contribution of contact resistance at the CoS/CNT interface which increases with CNT surface coverage. The increase in CoS size distribution (10 – 50 nm), as well as less homogeneous CNT surface coverage, may have caused the sharp decrease in R_{CT} with 5 mM CoS (see Fig. 6.6). Although R_{CT} and R_{Diff} values are much lower than those of CNT, they are still at least 3x higher than those of Pt, but the differences did not affect the device behaviour much under 1 Sun illumination. J_{SC} values (11.5 $\sim$ 14.1 mA/cm²) were slightly lower than that of Pt (14.7 mA/cm²), except for the cells with the CE prepared at 0.0013 mM (37.0%). FF was improved (57.6 $\sim$ 67.5% vs. 55.2% for Pt). Since FF is inversely related to the extent of overpotential in the DSSC, a quick comparison with the Tafel results reveal that the trend agrees well with the observed FF changes with varying CoS concentrations. In other words, with increasing CoS concentration, overpotential decreased and FF increased. Therefore, it is also expected that the J - V slope steepness will decrease if the CoS concentration is further decreased to below 0.0013 mM, and approach the slope of CNT-only (i.e. no CoS).

It is noted that the DSSC with 5 mM CoS-CNT CE has a significantly lower J_{SC} than other devices. This could be due to an excess of sulfide ions (S_x^{2-}) as suggested by the presence of larger nanoparticles (> 10 nm diameter) that are available to react with Li-ions to form LiS_2 charge complexes (see page 17, 2nd paragraph). Whereas for the bilayer CoS-CNT CE configuration there was a greatly decreased fill factor due to high diffusion resistance, the improved CoS coverage on CNT improved

the fill factor, but competition (for Li ions) against LiI redox shuttle complexes remains, and is likely to decrease the maximum current density obtainable and decrease device performance as a result. Among the other devices, the DSSC with CE prepared using 2.5 mM CoS gave the best *PCE* of 6.27%. This is 7.5% higher than the *PCE* of the standard Pt DSSC (5.83%) and would be the ideal concentration to adopt if the cell is only illuminated from the anode side. To improve optical transmittance and have the possibility of bifacial application, lower CoS concentrations would be preferred. To demonstrate the possibility of bifacial operation of these DSSC, all devices were tested under 1 Sun illumination from the CE side (i.e. back illumination). The results are summarized in [Table 6.3](#).

TABLE 6.3. SUMMARY OF DEVICE CHARACTERISTICS OF DSSC EMPLOYING DIFFERENT COUNTER ELECTRODES WHEN TESTED UNDER 1 SUN ILLUMINATION, EITHER FROM THE FRONT (ANODE) OR BACK (CE).

Counter Electrode	Illumination side	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	η (%)	Normalized back <i>PCE</i> (of Front <i>PCE</i>) %	Combined % <i>PCE</i>
Pt/FTO	Front	14.702	0.719	55.2	5.83	57.29	9.17
	Back	6.649	0.707	70.9	3.34		
CNT/FTO	Front	13.488	0.636	15.2	1.30	73.08	2.25
	Back	5.662	0.685	24.4	0.95		
5 mM	Front	11.533	0.707	67.5	5.03	8.75	5.47
	Back	0.892	0.647	76.6	0.44		
2.5 mM	Front	13.306	0.707	66.6	6.27	23.92	7.77
	Back	2.744	0.704	77.5	1.50		

0.4 mM	Front	14.111	0.715	58.1	5.86	28.33	7.52
	Back	3.540	0.681	68.9	1.66		
0.04 mM	Front	13.911	0.722	57.6	5.78	38.41	8.00
	Back	4.432	0.692	72.3	2.22		
0.0013 mM	Front	13.834	0.711	37.0	3.64	48.08	5.39
	Back	4.736	0.692	53.4	1.75		

From the normalized back *PCE* values, it is obvious that while 2.5 mM gave the best *PCE* for front illumination, back illumination only resulted in device performance that is 23.92% of this, whereas the same normalized back *PCE* values increased with decreasing CoS concentration. This is largely influenced by the J_{SC} values that showed similar trend due to the increasing amount of light transmitted through the CE. The light absorbing property of CoS (see [Appendix 6](#)) is evident from the significant reduction in J_{SC} with the addition of 0.0013 mM CoS to CNT, which significantly decreased the normalized back *PCE* value from 73% to 48%.

For the evaluation of the possibility of bifacial application of these DSSCs, the front and back *PCE* values for each device were combined. 0.04 mM CoS is the most optimal CE for bifacial DSSC as it gives the best combined efficiency of 8%. J_{SC} of this device under back illumination is 33% lower than the standard device, and this can be accounted for by the slightly higher light absorbance of the CoS-CNT CE, causing less transmitted light and hence decreased number of charges generated. As seen from the results discussed so far, CoS-CNT CE has good potential to replace Pt-FTO CE. To improved the device performance further, it is recommended that the CoS nanoparticle size be decreased in order to decrease the light absorbance during back illumination.

6.4. SUMMARY AND CONCLUSION

The deposition of CoS or NiS nanoparticles as a separate layer on CNT films for use as FTO-free CE of DSSC has been shown to improve the catalytic activity of pristine CNT films. Both of the sulfide-based devices had J_{SC} values that were higher than or comparable to that of Pt/FTO. Despite showing poorer catalytic activity and conductivity, CoS/CNT gave a better photovoltaic performance than NiS/CNT, and this was attributed to the better homogeneity of CoS nanoparticle size and distribution. However, the FF of both devices were low, which was likely to be due to the bilayer configuration of these CE that limited the contact / interaction area between the nanoparticles and the CNT surfaces.

Modifying the synthesis method from bilayer to mixture-in-solution allowed the deposition of a single uniform film of CoS-CNT nanocomposite on FTO-glass substrates, and by decreasing the CoS concentration, the light transmittance through the films could be increased. CoS-CNT composite has been demonstrated as an effective replacement of Pt in DSSCs, and the ratio of the amount of CNT-to-CoS has also been optimised. At 0.04mM CoS concentration, the efficiency reached 5.78% when illuminated under 1 Sun from the photo anode side, and 2.22% from the CE side, comparable to that of a standard Pt CE-based DSSC (5.83% and 3.34% respectively). Furthermore, unlike the bilayer configuration of the CoS/CNT CE, the optical transmittance of this CoS-CNT CE is high enough to utilise incident light on both sides of the DSSC for light absorption, enhancing its potential for higher efficiencies and their use in transparent photovoltaic applications such as power-producing windows.

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7. SUMMARY OF MAIN FINDINGS AND CONCLUSION

High charge transfer resistances between the CE and electrolyte, as well as poor catalytic activity, are the main challenges for the use of pristine, thin CNT films as CEs in DSSC. In [Chapter 3](#), CNT films (from carboxylated SWNT) with high optical transparency (80-85% @ 550 nm) replaced FTO and Pt as CEs in DSSCs, and were tested under 1%, 50% and 100% Sun illumination. The DSSCs performed well only under 1% Sun illumination, but suffered from poorer *FF* with increasing light intensity. This is because the number of charges generated increases with light intensity, and if the charge collection is limited by the film thickness, there will be an increase in charge buildup and recombination, and this decreases the *FF*.

CE/electrolyte charge transfer resistance was identified to be the process that limits the device performance based on impedance analysis. The significantly higher sheet resistance of the CNT film causes a higher charge injection resistance from the film to the electrolyte, lowering the rate of electron injection for triiodide reduction, and consequently delaying the rate of electron extraction at the FTO/TiO₂ interface at the photo anode. A buildup of electrons within the bulk TiO₂ causes an imbalance in the electron distribution across the DSSC and increases the chances of back reaction. V_{OC} was observed to increase for all devices with CNT CE (FTO-free), which was due to the mismatch in sheet resistances of the photo anode and CE, causing non-homogeneous current and voltage distributions, with the slightly negatively-charged photo anode raising the electron qFL of TiO₂.

A similar observation was observed in the DSSCs studied in [Chapter 4](#), except with smaller V_{OC} increments, due to decreased sheet resistances when CNT films were

pretreated with 4 M HNO_3 prior to DSSC fabrication and testing. This chemical treatment method was structurally non-destructive, able to increase the work function by p-doping the CNTs via a charge transfer reaction through intercalation, and able to improve the J_{SC} of the DSSCs when replacing both FTO and Pt. However, overall device efficiencies were still far from a standard device with Pt/FTO CE, as charge transfer resistances are still high. Hence the intrinsic conductivity and catalytic activity of thin CNT films are not sufficient to meet the requirement of a standard CE, and tapping on these properties of other materials by forming nanocomposites may be a more effective solution.

In Chapter 5, the formation of CNT nanocomposites with two common DSSC CE catalytic metals, Au or Pt, achieved by spontaneous electroless chemical bath deposition, was presented. Wetting of CNT was poor for Au (sparse dendritic clusters of ≤ 150 nm) but good for Pt (homogeneous dense particles of ≤ 50 nm). This difference in wetting corresponds well with the relative binding energies derived from first principles calculations by Park *et al.*¹. Although the right-shifting of peaks in Raman spectra of Au-CNT showed the formation of charge transfer complex, causing a maximum increase in work function and decrease in charge transfer resistance with 60s of reaction time, the poor morphological interaction led to an insignificant decrease in R_{Series} , resulting in minimal improvement in DSSC efficiency. In contrast, no charge transfer mechanism was observed in Pt-CNT, and similar oxidation peak onsets from cyclic voltammetry tests revealed that the catalytic activity of Pt was preserved in the nanocomposite. Raman spectra revealed non-covalent interaction, as well as preferential deposition at intrinsic CNT defect sites over carboxylate sites. As the charge transfer resistance was not decreased with Pt-CNT, the R_{Series} remained unchanged, with only J_{SC} improvement contributing to an increase in DSSC efficiency.

At 3.8% and 5.6% with 100% and 1% Sun illumination respectively, Pt-CNT can serve effectively as the CE for a fully flexible DSSC suitable for both indoor and outdoor applications, even though only FTO is replaced.

It must be highlighted here that the same synthesis conditions did not produce the same interaction behavior, since charge transfer mechanism was significant for Au but not Pt. The morphology of nanoparticle / nanocluster formation is also crucial to the effectiveness of the nanocomposite, as the charge transfer property of Au suggests that this nanocomposite can potentially decrease the counter electrode impedance should the wetting be improved. Pt has excellent CNT surface coverage, but otherwise retains its intrinsic properties and relies on the CNT network frame to build a well-connected conducting and catalytic FTO-free film.

The effectiveness of metal sulfide – CNT nanocomposites as both FTO-free and Pt-free CEs was discussed in [Chapter 6](#). CoS or NiS was deposited as a catalytic layer (replacing Pt) on top of CNT films (replacing FTO) and used as DSSC CEs. CoS showed better wetting, more homogeneous deposition and smaller particle size distribution than NiS, but both were highly catalytic as J_{SC} values of the corresponding DSSCs were similar (for NiS) or higher (for CoS) than that of the standard device. However, CoS is semiconducting (NiS is metallic) and likely to introduce a Schottky barrier at the CoS-CNT interface, evident from the gentler Tafel slope (higher overpotential) and lower FF in DSSCs. Both nanocomposites also had much higher R_{Diff} than Pt/FTO (with CoS $\gg$ NiS), suggesting that the stability of the metal sulfide nanoparticles in this bilayer CE configuration is low. The importance of the morphology of nanocomposite to the DSSC performance was again reflected in the higher J_{SC} obtained with CoS under identical fabrication and test conditions.

As the morphology of nanoparticles is crucial to the improvement of conductivity and catalytic activity of the nanocomposite CE, CoS deposition was further optimized by reacting the precursors with CNT before film fabrication, and the effect of CoS concentration on CNT film and DSSC properties was studied. Good wetting and improved interface interaction were achieved by changing the synthesis method. Similar to the case of Pt-CNT, cyclic voltammetry measurements showed that the catalytic property of CoS was preserved; this was the same regardless of concentration, although the extent of catalytic behavior was linked to the density of CoS nanoparticles (i.e. surface area exposed to electrolyte decreased with lower CoS concentration, and the nanocomposite film becomes less catalytic with decreased FF). Due to the Schottky barrier described earlier, with increasing CoS concentration (up to 2.5 mM), the density of CoS nanoparticles deposited on CNT surfaces increased, resulting in increases in charge transfer resistance. Further increasing the CoS concentration increased the nanoparticle size and widened the size distribution, and this decreased the CoS-CNT interface area and lowered the charge transfer resistance. 0.04 mM CoS was optimal for bifacial DSSC application – PCE was comparable to a standard DSSC when illuminated from the photo anode, and 33% lower when illuminated from the CE because CoS is optically absorbing. By controlling the nanoparticle size, distribution and density, CoS/CNT has great potential as a Pt-free and FTO-free CE.

In conclusion, the “ideal” counter electrode should efficiently drive the return of electrons for triiodide reduction so as to minimize the occurrence of back reaction (charge loss) at the photo anode. For that to happen, the series resistance should be as low as possible, which comprises of sheet resistance, R_{CT} and R_{Diff} . A defect-free counter electrode would be ideal in lowering sheet resistance as it maximizes charge

transport within the material, but for a CNT film it would not be sufficiently catalytic unless made significantly thick and black. On the other hand, thinning the CNT film increases sheet resistance and R_{CT} , hence defects are necessary and function as nucleation sites to form nanocomposites with additives that can rectify these shortcomings. Although the general idea of achieving smaller nanoparticles with dense, homogeneous CNT surface coverage was the goal behind each nanocomposite synthesis method (so as to allow bifacial DSSC behavior), the nature of electronic interaction of the additive was also crucial in determining the ideal morphology for lowering charge transfer resistance (e.g. Au required larger dendritic clusters due to poor wetting of CNT surfaces). In addition, the stability of such nanocomposites in the electrolyte medium may affect not only the device performance but device stability or lifespan as well. The choice of dye and electrolyte should be considered together with the choice of nanocomposite additive, so as to prevent undesirable competitive reactions with the dye or redox species. As such, there is no best material choice *per se*, but a synergistic interaction of materials in a DSSC that makes an ideal device.

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8. FUTURE WORK

The importance of good precursor wetting on CNT surface has been highlighted in the case of Au-CNT in Section 5.3.1, and again with NiS/CNT in Section 6.3.1. Modification to the CNT surface may be necessary to improve the wetting of Au and NiS precursors, but the possibilities were not explored in this work. The introduction of additional changes to CNT (e.g. structural alteration, nanocomposite formation with 2 other materials) can also be pursued as a separate area of study. CNT films may be subjected to oxidation prior to nanocomposite formation, so as to introduce more surface defects as sites of reduction. This may be done with exposure to ozone, but at the expense of film conductivity. CNT surfaces may also be modified with ligands to improve precursor wetting, e.g. the use of silane-based ligands is known to increase surface hydrophilicity, although also at the expense of axial electrical conductivity ^{1,2}. Changes to the synthesis method that employs such surface modifications will require optimization to achieve sufficient wetting and conductivity for application as DSSC CE.

As suggested at the end of Section 5.3.1, other organic solvents may be used for the precursor immersion process, such as substituting ethanol in DI water with the stronger reducing agent sodium borohydride (NaBH_4), or adding dilute hydrogen peroxide (H_2O_2) to increase Au precursor solubility and aid the oxidation of the CNT film. However, introducing both ethanol and H_2O_2 in the same reaction setup in the reduction of Au requires optimization, as esterification of ethanol occurs as a competing reaction, is exothermic, and may produce unwanted side products (contaminants) such as acetaldehyde or acetic acid. Also, as Au cluster growth likely occurred with a preferred direction, TEM studies will aid in identifying what this is,

and whether the presence of CNT (or other nanomaterials of choice) will cause any changes to this direction.

To further improve the DSSC performance with 0.04 mM CoS-CNT CE, it is recommended that the CoS nanoparticle size be decreased in order to decrease the light absorbance during back illumination. Nanoparticle sizes of less than 10 nm may be obtained by further optimising the CoS concentration such that it falls between 0.04 mM (average nanoparticle size: 10 nm; see Fig. 6.6) and 0.0013 mM (undetected from FESEM; see Appendix 5), without compromising on DSSC efficiency when illuminated from either electrode. In order to better understand the interface and near-surface interactions between CNT and adjacent nanoparticles in a metal / metal sulfide – CNT nanocomposite system, TEM analyses and other electrical behaviour studies should be done to determine the extent of physical proximity and electron cloud distribution, and how these affect the nanocomposite film's conductivity.

Transient photocurrent measurements may also be pursued as future work to further understand the role of defects as charge traps in the CNT-based counter electrodes. For TiO_2 , the origin of traps and how they affect the recombination have been discussed in literature; the density of trap states are influenced by nanoparticles' surface area-to-volume ratio and can be tuned to reduce charge recombination with TiCl_4 treatment³. While photo anodes have been much studied (charge transport after charge injection from the dye), this is not so for the counter electrode. Should electron return to the electrolyte via the counter electrode be slow enough to hamper charge transfer at the photo anode – something not observed with standard Pt-FTO counter electrodes – then the study of CE charge trapping becomes more crucial.

Besides the use of pristine CNT, a combination with graphene may be adopted to improve on the CE's conductivity and catalytic activity. For example, an additional thin film of graphene may be integrated as a planar conducting layer so that the CNT thin film can focus on catalysis. As graphene can be considered the 2D structural equivalent of CNT, a bilayer structure with reduced graphene oxide (rGO) replacing FTO and CNT replacing Pt (see Fig. 8.1) may change the equivalent circuit to compare with that of a standard DSSC. A decrease in R_{Series} and an increase in FF may be obtained by controlling the R_s of the rGO film.

FIGURE 8.1. **DIAGRAM OF CROSS-SECTIONAL VIEW OF COUNTER ELECTRODES, SHOWING THIN FILMS OF REDUCED GRAPHENE OXIDE AND CNT (LEFT) IN RELATION TO FTO AND Pt LAYERS RESPECTIVELY (RIGHT).**

Alternatively, graphene may be incorporated in CNT films for use as DSSC CE. A recent study by King *et al.* reports that a mere 3 wt % of rGO flakes in CNT thin films lowers the sheet resistance, possibly by sitting between adjacent nanotubes and acting as an inter-nanotube charge transport promoter (see Fig. 8.2), while higher concentrations of graphene exert an antagonistic effect by swelling the CNT network instead; however these CNT-graphene thin films have yet to be tested on any device⁴.

FIGURE 8.2. SCHEMATIC OF USING RGO RANDOMLY PLACED WITHIN THE CNT THIN FILM MATRIX FOR IMPROVING THE LATTER'S INTERTUBE CHARGE TRANSPORT.

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CONTRIBUTIONS OF THESIS AND LIST OF PUBLICATIONS

The contributions of this thesis are listed as follows:

- Elucidating the origin of V_{OC} increment in the presence of FTO-free CNT CE – a significant mismatch of R_s of both electrodes cause an imbalance in current and voltage distribution, raising qFL of TiO_2 .
- Understanding the different nature of interaction of metal nanoparticles Au and Pt with CNT – under the same synthesis conditions, charge transfer mechanism was significant for Au but not Pt, and Au has potential to decrease the counter electrode impedance if wetting is improved. Pt has excellent CNT surface coverage, but otherwise retains its intrinsic properties and relies on the CNT network frame to build a well-connected conducting and catalytic FTO-free film.
- First demonstration of CoS/CNT and NiS/CNT bilayer films on FTO-free and Pt-free substrates. The importance of good CNT surface coverage of CoS was revealed in DSSC performance, which despite a Schottky barrier at the CoS-CNT interface fared better than NiS/CNT.
- The synthesis of CoS-CNT hybrid system and its application as CE in bifacial DSSC are yet to be reported. This CoS-CNT hybrid is shown to be an effective Pt/FTO replacement (with 0.04 mM CoS) due to the lowered charge transfer resistance, as a result of excellent wetting and CNT surface coverage, and a high surface area of exposure to electrolyte.

The list of publications are listed as follows:

1. L. Zhang, H. K. Mulmudi, S. K. Batabyal, Y. M. Lam, S. G. Mhaisalkar, **Metal / Metal Sulfide Nanoparticles-decorated Single-walled Carbon Nanotubes Networks as FTO-free Counter Electrodes in Dye-sensitized Solar Cells**, *ICMAT 2013* (Symposium G5.1-6), presented.
2. L. Zhang, H. K. Mulmudi, S. K. Batabyal, Y. M. Lam, S. G. Mhaisalkar, **Metal / Metal Sulfides Functionalized Single-walled Carbon Nanotubes: FTO-free Counter Electrodes for Dye Sensitized Solar Cells**, *Phys. Chem. Chem. Phys.* **14** (2012), 9906 – 9911.
3. L. Zhang, M. Rao, J. Kochupurackal, N. Mathews, Y. M. Lam, S. G. Mhaisalkar, **Effect of Nitric Acid Concentration on Doping of Thin Film Single-walled Carbon Nanotubes for Electrode Application in Transparent, Flexible Dye Sensitized Solar Cells**, *MRS Proceedings* **1436** (2012).
4. L. Zhang, E. Y. K. Png, S. G. Mhaisalkar, Y. M. Lam, **Metal Nanoparticles-decoration of Single-walled Carbon Nanotubes for Transparent, Flexible Electrodes in Bifacial Solar Cells**, *ICMAT 2011* (Symposium Q8-4), presented.
5. L. Zhang, J. Kochupurackal, Y. M. Lam, S. G. Mhaisalkar, **Ultrathin Layers of Metal Oxides on Carbon Nanotubes for Photo Anodes in Flexible Dye Sensitized Solar Cells**, *ICMAT 2011*, poster.

6. L. Zhang, M. Rao, J. Kochupurackal, Y. M. Lam, S. G. Mhaisalkar, **HNO₃ Intercalation of Single-walled Carbon Nanotubes Counter Electrodes – Towards Bifacial, Flexible Dye-Sensitized Solar Cells**, submitted.
7. L. Zhang, L. Z. Teo, S. K. Batabyal, Y. M. Lam, S. G. Mhaisalkar, **Catalytic and Transparent Single-walled Carbon Nanotubes – Cobalt Sulfide Nanocomposite Films as Effective Counter Electrodes in Dye Sensitized Solar Cells**, in preparation for submission.

APPENDIX

Appendix 1. Various forms of SWNT obtainable from debundling and dispersion: (L to R) from powdered form to suspensions after sonication and /or centrifugation.

Appendix 2. (a) Atomic Force Microscope and (b) Kelvin Probe Force Microscope (KPFM) images (scanned size: 1 μm²) of a HNO₃ treated CNT film, showing surface roughness of bundled nanotubes and the mesh-like network from their random alignment. All the HNO₃ treated CNT films exhibited a similar topography. (c) Under KPFM, the histogram distribution of actual values of surface potential (SP) observe a Gaussian fit, and the recorded SP value is obtained as the average of all SP values obtained at full width half maximum (FWHM).

Appendix 3. X-ray diffraction spectrum of Au-CNT film on an FTO substrate, after 3 min reaction time in Au precursor solution. Lines in green and red correspond to FTO and Au respectively. The labeled red lines match the peaks found in the spectra, confirming the presence of Au in the film.

Appendix 4. Topographical FESEM image of pristine CoS showing the formation of dense, highly fused patches of CoS nanoparticle clusters on top of an FTO glass substrate.

Appendix 5. Topographical FESEM image of CNT film with 0.0013mM CoS. Although the formation of CoS nanoparticles were not observable, DSSC results showed a slight improvement in device performance as compared to the use of a pristine CNT film.

Appendix 6. Symmetrical half-cells with electrodes of different composition. (L-R): Pt/FTO, 0.0013 mM, 0.04 mM, 0.4 mM, 2.5 mM and 5 mM CoS-CNT. The 0.04 mM sample's slightly lower light transmittance than Pt accounts for the lower J_{SC} of the corresponding device under back illumination.