Tin oxide based dye sensitized solar cells

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TEH JUN JIE

2014

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**TIN OXIDE BASED
DYE-SENSITIZED SOLAR CELLS**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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the requirement of the degree of
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2014

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List of Abbreviations

Chemical Names

AgCl	Silver chloride
FTO	Fluorine doped tin oxide
HCl	Hydrochloric acid
ITO	Tin doped indium oxide
I ⁻	Iodide ion
I ₂	Iodine
I ₃ ⁻	Triiodide ion
LiI	Lithium iodide
Pt	Platinum
SnO ₂	Tin oxide
Si	Silicon
TiCl ₄	Titanium tetrachloride
TiO ₂	Titanium dioxide
ZnO	Zinc oxide

Physical Variables

E _C	Conduction band edge
E _F	Fermi energy level
E _{gap}	Bandgap
FF	Fill factor
IPCE	Incident photon to electron conversion efficiency
J _{sc}	Short circuit current density
PCE	Power conversion efficiency
R ₁	Interface charge transfer resistance at photoelectrode
R _{pt}	Interface charge transfer resistance at counter electrode
R _s	Series resistance
V _{fb}	Flat-band potential
V _{oc}	Open circuit voltage
Z	Impedance
λ	Wavelength
τ _n	Electron life time

Abbreviations

AC	Alternating current
ASnO ₂	Anodized tin oxide
CNT	Carbon nanotube
CPV	Concentrator photovoltaic
CVD	Chemical vapor deposition
DI	De-ionized
DSSCs	Dye sensitized solar cells
FESEM	Field emission scanning electron microscopy
Ga-SnO ₂ -NC	Gallium doped tin oxide nano-cuboids
HOMO	Highest occupied molecular orbital
HR-TEM	High resolution transmission electron microscopy
LUMO	Lowest unoccupied molecular orbital
Mo,Ga-SnO ₂ -NC	Molybdenum, Gallium co-doped tin oxide nano-cuboids
MWCNT	Multi-walled carbon nanotube
NHE	Normal hydrogen electrode
NP	Nanoparticle
PV	Photovoltaic
SWCNT	Single-walled carbon nanotube
TCO	Transparent conductive oxide
1-D	One-dimension
2-D	Two-dimension
3-D	Three-dimension

Abstract

Dye sensitized solar cells (DSSCs) have been drawing much of the attention over the globe and extensive research has been carried out to achieve high power conversion efficiency and yet low cost of fabrication. Photoanode in DSSC is the heart of the device in which it governing all the importance charge transfer and transport processes. However, commonly used titanium dioxide based photoanode has low electron mobility which causes high charge transfer resistance. Thus, tin oxide which has much higher electron mobility has been proposed in this project and its performance can be further improved by material and nanoscale engineering. The aim of PhD project is to design and fabricate tin oxide nanomaterials with desired physical and electrical property to enhance the performance of DSSC. Besides, insightful study of the enhanced properties are done to enhance fundamental knowledge on DSSC.

A sieve-like SnO_2 nanoporous sheets (ASnO_2) obtained through anodization of tin foil in aqueous ammonia solution was employed in photoanode in DSSC. It was found that the well-interconnected SnO_2 sieve walls achieved better charge transportation and successfully suppressed the charge recombination. Thus, ASnO_2 exhibits higher V_{oc} and short circuit current compared to ordinary SnO_2 nanoparticles. Further study shows that this closely packed pore arrangement of the tin oxide sheets provides higher charge injection rate, suppressed charge recombination and reduced charge transfer resistance, thus better photocurrent and enhanced device performance were obtained.

To tailor the conduction band edge of tin oxide to increase open circuit voltage of DSSCs, gallium doped SnO_2 nano-cuboids ($\text{Ga-SnO}_2\text{-NC}$) was synthesised by hydrothermal method with the aid of commercially available SnO_2 nanoparticles ($\text{SnO}_2\text{-NP}$) as the growth seeds. Even though Ga-doping wasn't found any changes in

morphology and crystallinity, however it successfully increased the band edge of SnO₂, in which it is capable of suppressing photoelectron backflow and achieving a higher open circuit voltage ($V_{oc} \sim 0.74$ V). To the best of our known, this high V_{oc} is the highest among SnO₂ based electrodes without TiO₂ knowledge. Besides, common problem of low fill factor (FF) in tin oxide based DSSC has been solved through gallium doping. Optimum gallium doping which moderate up-shift of tin oxide band edge results in better charge injection from dye to electrode and impedes electron from recombination with electrolyte, which in turn to increase V_{oc} and power conversion efficiency.

Despite high V_{oc} and FF were achieved through gallium doping, short circuit current (J_{sc}) remained relatively low compared to TiO₂ based DSSC. As a result, we have found a way to increase J_{sc} while maintaining high V_{oc} and FF of Ga-SnO₂-NC, which is through further doping of molybdenum (Mo) into Ga-SnO₂-NC. Optimum Mo doping had significantly increased the J_{sc} by 73% while keeping V_{oc} and FF of Ga-SnO₂-NC relatively unchanged. The enhancement mechanism was studied under electrochemical impedance spectroscopy (EIS) and was found mainly due to the increase in conductivity across mesoporous Mo, Ga-SnO₂-NC layer where it significantly reduces the series resistance of the DSSC device and thus increases the short circuit current. With all the parameters such as V_{oc} , J_{sc} and FF were all increased through simple doping of gallium and molybdenum, tin oxide has the utmost potential to be the alternative to TiO₂ as mesoporous semiconducting material in photoanode.

With the aim of constructing a solar cell with low cost of fabrication and high efficiency. We have developed a simple CNT-Si solar cell which is capable of generating photo-current in both directions (front and back). The device consists of a filtered multi-walled CNT attached on thin n-type Si sandwiched by two indium

doped tin oxide electrodes. Besides advantage of ease of fabrication, it has the effective area much bigger compare to typical CNT-Si cell because employ of ITO avoided opaque electrodes which used much of the area. The basic operating principles also provide insightful understanding of this new CNT-Si cell; while other treatments were also tested to improve the solar cell conversion efficiency.

In summary, this interdisciplinary research project extended into novel material and device engineering, photovoltaic design and fabrication, electrochemical analysis to achieve the objective of creating a low cost and high power conversion efficiency solar cell. Furthermore, insightful studies on nano-composites and nano-structure advanced the fundamental knowledge in energy harvesting.

Chapter 1 Introduction

1.1 Background and history of dye sensitized

Energy is the basic building block to support all the living things in the world and we all know the importance of it. Energy can be in the form of electrical, chemical, mechanical, etc. and we are harvesting it in all sort of form. Mankind over the globe has marked an enormous increase in energy consumption over last century. The dramatic increment mainly due to growing of global industrialization and mass product; and to enhance mankind secure and comfort level. Thus, energy consumption per inhabitant per year was 5800 kWh in 1890, increased to 20200 kWh in 1970 and maintained at this level till present; the world energy consumption now is around 5.33×10^{20} J.^[1] The dominant energy sources of energy are from fossil fuels such as coal, oil and gas; and they accounted more than 80% of the total energy supply^[2]. However, with the world energy consumption is expected to grow further, solely reliance of fossil fuels is just insufficient. Furthermore, massive consumption of fossil fuels has caused negative impact on our environment, and the deterioration has limited mankind progress. As a result, we are turning our attention towards renewable energy where it can support our needs of energy without compromising the ability of future generation to their own needs. Renewable energy such as hydroelectric, biomass, wind energy, solar energy, etc. are gaining increasing attention.^[3-6] Solar energy has appeared to be particularly attractive as it considered inexhaustible to human civilization and we just merely require 0.02% of 1.2×10^{14} of solar energy delivered on the earth to support our present energy consumption.

Since solar energy was targeted as the next source of energy, solar cell or photovoltaic (PV) cell has undergo intensive research and widely been used. Many

type of solar cell has been developed such as thin film, multi-junction, monocrystalline silicon, small molecule, polymer solar cell, etc.^[7-11] To date, highest achievable power conversion efficiency (PCE) is 44.7% which was jointly developed by Fraunhofer Institute for Solar Energy Systems ISE, Soitec, CEA-Leti and the Helmholtz Center Berlin.^[12] It is III-V multi-junction solar cells used in concentrator photovoltaics (CPV) which can achieve more than double the efficiency of conventional PV cell in sun-rich locations. However, the cost of manufacturing of this type of solar cell is extremely high due to high cost of III-V compound and complication of manufacturing thus is not viable for mass production and the typical PV cell that commercially available are having only 15-25% PCE.^[13-15] As a result, researcher has been putting much of their effort in search of a new type of PV cell which has high PCE, ease of production, low manufacturing cost as well as environmental friendly. One of the latest type of PV cell which fulfil the above criteria is named Dye Sensitized Solar Cell (DSSC).^[16, 17]

DSSC was spurred the interest of researcher after the publication of a seminar paper by O'regan and Gratzel in 1991.^[18] The reported DSSC performance recorded a PCE of up to 12% for a cell and 9% for mini-module, moreover, stability has been tested for 1000 h at 80 °C with incredible PCE sustained at 8-9 %. Besides, the prospect of extreme low cost of manufacturing and ease of fabrication have open up the opportunity and possibility to design a solar cell with high flexibility of colour, shape and transparency.^[19, 20]

The typical device configuration of DSSC is as follow: At the heart of the device is the mesoporous oxide layer typically TiO₂ or ZnO nanoparticles (size 10-30 nm and film thickness of ~ 10 μ m) of that have been sintered together to establish electronic conduction.^[21, 22] The porosity is 50-60%.^[23, 24] The mesoporous layer is

then deposited on a transparent conductive oxide (commonly used FTO or ITO) on a glass or plastic substrate. Attached to the surface of the nanocrystalline film is a monolayer of the charge-transfer dye to complete as a photoanode.^[25, 26] A liquid electrolyte containing I^-/I_3^- redox couple is sandwiched between photoanode and a platinized counter electrode to form a complete DSSC.^[21, 27, 28]

The working principle of DSSCs is shown in Figure 1 where it started from photo-excitation of dye results in the injection of an electron into the conduction band of the oxide, leaving the dye in its oxidized state.^[29] The dye is restored to its ground state by electron transfer from the electrolyte, usually an organic solvent containing the iodide/triiodide redox system.^[30] The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The I_3^- ions formed by oxidation of I^- diffuse a short distance ($<50\ \mu\text{m}$) through the electrolyte to the cathode, which is coated with a thin layer of platinum catalyst, where the regenerative cycle is completed by electron transfer to reduce I_3^- to I^- .^[21, 29, 31] Performance of DSSCs can be further improved by various enhancement in fabrication and dye molecule modification.

Figure 1 Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell.^[29] Copyright 2012 with permission from American Chemical Society.

With the initial work in early 90's, enormous of DSSC components and configurations have been developed. With the concept of diversity and alternative for future success of DSSC, several thousand of dyes have been developed; hundreds of electrolyte have been tested as well as numerous alternative semiconducting material and morphology have been investigated as mesoporous films. Thus such technologies are expected to progress rapidly through new material and design based on fundamental insights of DSSC.

1.2 Motivations

Despite intensive research on DSSC has been undergoing, DSSC performance still inferior to silicon based PV. As a result, much work need to be done to make DSSC a device which capable of replacing current silicon based PV. There are several factors that limit the performance of DSSC and cost of manufacturing: despite platinum (Pt) is superior and commonly been employed as the catalytic component to catalyse the reduction process of I_3^- to I^- at the counter electrode of DSSC, the cost of Pt is the major stumbling block to attain a low cost and long term production sustainability for mass production. Besides, low electron diffusion rate with diffusion rate constant of 10^9 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ across electrolyte also limit the overall performance of DSSC.^[31] The major hurdle so far is on the photoelectrode where the relatively high charge transport resistance across mesoporous metal-oxide semiconductor has causes severe charge recombination during photoelectron injection, electron transfer and transport. As far, mesoporous TiO_2 exhibit the highest power conversion efficiency.^[17] However, its nature of having low electron mobility which causes the high charge transport resistance has led researcher to search for other metal oxides such as ZnO , Nb_2O_3 and SnO_2 as a potential substitute for TiO_2 .^[32-34]

SnO₂ is a promising material to be employed in photoelectrode, as it has some superior characteristic over TiO₂ such as n type semiconductor with wide bandgap of $E_G=3.5\text{eV}$ and high electron mobility ($\sim 100\text{-}200\text{ cm}^2\text{ V}^{-1}\text{s}^{-1}$).^[35, 36] However, SnO₂ has weak interfacial adhesion between particles which become charge recombination spot during electrons transport process. Besides, the open circuit voltage (V_{oc}) for SnO₂ nanoparticle-based DSSCs were found to be between 0.3-0.4V, this is due to high recombination kinetics with the electrolyte and SnO₂ has a conduction band edge E_c , of about 0.3 eV lower than that of anatase TiO₂.^[37, 38]

Thus we capitalise the high electron mobility of SnO₂ and make it a good alternative or substitution of TiO₂ as the main semiconducting material in DSSC photoanode. As a result, the main motivation behind this PhD project is to study and enhance the power conversion efficiency of SnO₂ based DSSC by improving the interconnectivity between particles based on the fundamental understanding of electron transport mechanism in mesoporous semiconductor in DSSC, and engineering SnO₂ to has a higher conduction band edge. Besides, study, explore and engineer of SnO₂ nanostructured composites based DSSC to enhance the overall PCE.

1.3 Overall objectives

The overall objective of this research is focusing on synthesis and characterizing of SnO₂ nanomaterials with unique structures and properties to suit the transport mechanism of SnO₂ based DSSC. Besides, studies of the effect of the modifications towards electrochemical reactions in DSSC.

1.3.1 Synthesis and study of a well-connected SnO₂ nanostructure to suppress charge recombination during electron transportation

SnO₂ nanoparticle-based DSSCs exhibit lower open circuit and fill factor due to poor interconnectivity between particles that results in high recombination losses as compared to the conventional TiO₂-based DSSCs. As a result, the main purpose of this project is to explore a well-interconnected nanostructured SnO₂ to achieve better charge transportation to suppress charge recombination events. Structural and electrochemical effects were investigated to better understand the enhancement mechanism based on fundamental knowledge.

1.3.2 Synthesis and the effect of SnO₂ composite nanostructure in shifting conduction band edge of SnO₂ to enhance overall PCE

The major drawback for SnO₂ to be employed in photoanode of DSSC is due to its lower conduction band edge (E_c) which cause fast backflow of photoelectrons to the electrolyte and a negative shift of the electron quasi-Fermi level (E_{F-n}), leading to further reduction of open circuit voltage (V_{oc}). Thus, SnO₂ with higher Fermi Level

need to be engineered to serve as a blocking layer to obtain high V_{oc} and suppress backflow of photoelectrons. SnO_2 with higher Fermi Level is explored through doping of some group III elements. Moreover, the underlying mechanism for enhanced solar energy harvesting due to shifting of Fermi level is also investigated.

1.3.3 Synthesis and the effect of SnO_2 composite nanostructure in increasing conductivity or electron mobility of SnO_2

Although Fermi level shifting can increase V_{oc} and fill factor of SnO_2 based DSSC, further effort is needed to enhance short circuit current (J_{sc}) to make SnO_2 a better alternative compare to TiO_2 as a photoanode material. To solve this puzzle, synthesis of SnO_2 with doping of some big atoms with large valence electrons to increase the number of free electrons and electron mobility to ultimately increases the J_{sc} . With enhanced charge transport along photoanode, specially designed DSSC to identify the influences of the foreign atom towards the overall PCE of DSSC.

1.4 Organization

This research project examines and engineer the tin oxide based photoanode in nanoscales to improve its power conversion efficiency of DSSC through enhancement of charge transport and transfer mechanism, suppression of charge recombination. This research extended to design and develop a cost effective and efficient silicon-carbon nanotube solar cell. Chapter 1 introduces the history of solar cell and the emerging of DSSC. Overview of the motivations and objective for this research project on DSSC are included. Chapter 2 reviews on recently research and development on the advancement of every components in DSSC. Chapters 3 state the experiment procedure, chemicals and characterization equipment used in this research project. Chapter 4 describes the synthesis procedure and the effect of well-connected sieve-like SnO_2 structure as photoanode in DSSC. Chapter 5 describe the investigation of the effect of gallium doping in tin oxide nano-structure towards the performance of conversion efficiency of DSSC. Chapter 6 discusses on the effect of further doping of molybdenum in gallium doped tin oxide in search for higher short circuit current. Lastly, chapter 7 provides a general conclusion for all the chapters and recommendation for future research work.

Chapter 2 Literature Review

This chapter we will discuss the key components of DSSCs and their functions in more details, such as photo-electrode, the sensitizer and the counter electrode. The charge transfer dynamics across the various interfaces in DSSCs and current research direction in achieving higher PCE will be reviewed in details.

2.1 Fundamental of DSSC

2.1.1 Differences of DSSC with conventional Si-based PV cell

Photovoltaics (PV) utilize the properties of semiconductor to harvest light and convert it into electricity. A conventional PV cell, semiconductor is the major component to absorb light and transport charges, thus type of semiconductor differentiates type of PV cell. There are all sorts of semiconductor being used in PV cell such as gallium arsenide, cadmium telluride, amorphous silicon, etc, however the commonly used semiconductor in commercial is crystalline silicon cell due to low cost and mature fabrication technology.^[12, 39-42]

A PV cell consists of two types of semiconductors named P-type and N-type. N-type and P-type are the negative and positive carriers respectively which distributed evenly over the material. When both types of semiconductor are brought together, a junction named depletion region is formed. The positive and negative carriers are attracted and migrated to each other, the charges are counterbalanced by the electric field across the depletion region that is formed. Thus, depletion region provide the ability to convert light into electricity.^[43, 44]

Silicon was chosen mainly due to its bandgap (E_{gap}) of 1.4eV which just good to absorb most of the sunlight. During excitation, electron from valence band is excited to conduction band, forming an electron-hole pair in the semiconductor. However,

excited electron formed in the depletion region only will contribute to photocurrent, the rest of it will recombine with the hole created in the valence band.^[43] This is because electric field formed across depletion region will separate the electron-hole pair generated and force the electron and hole to flow in a desired direction to create a photocurrent.

Figure 2.1 (a) Cross-section and (b) Energy band diagram for Si-based PV cell.

However, DSSC is designed to using low cost material and ease of fabrication method. Despite its ease of fabrication, the mechanism of converting solar energy to electrical energy is not direct as we have discussed in previous chapter. It consists of several process such as charge transfer and transport, redox reaction of mediator, oxidation and reduction of chemical reaction in both electrode.^[29, 31] Typical DSSC has the configuration shown in figure 2.1, where photoelectrode consists of metal oxide and dye, counter electrode is a catalyst of reduction of redox reaction such as platinum, while in between is the redox mediator.^[21] During energy harvesting, each dye molecule absorbs a photon once per second and the electrons in valence band of dye are excited then inject the electron into the conduction band of the oxide, leaving the dye in its oxidized state. After which, the electrons are transported across the metal oxide and collected by transparent conductive oxide (TCO). The dyes in the oxidized state are restored to its ground state by electron transfer from the electrolyte,

usually an organic solvent containing the iodide/triiodide redox system.^[45] The I_3^- ions formed from oxidation of I^- diffuse across the two electrode to the cathode which is coated with a thin layer of platinum as a catalyst of reduction process, in which the regenerative cycle is completed by electron transfer to reduce I_3^- to I^- .^[46]

In comparison of both silicon based PV cell and DSSC, there are several distinct differences and have some advantage over each other. PV cell has widely been used, however its cost of production is extremely high mainly due to fabrication processes are very costly, but DSSC is extremely low cost in fabrication. Electron-hole separation in Si-based PV cell is mainly driven by the electric field whereas kinetic transfer of electron is occurred in DSSC, as such length of depletion region determine the amount of excited electron contribute to the photocurrent. In Si-based PV cell, charge carrier are transport in both semiconductor and all the carrier (majority and minority) are coexist in the bulk semiconductor, thus slight impurities will result in high charge recombination rate. On the other hand, electron transport in DSSC mainly occur in semiconductor layer in which supported by regeneration of electrolyte, thus the recombination process mainly occur in the interface. Lastly, voltage generated in Si-based PV cell is determine by E_{gap} of the intrinsic semiconductor, while it is determine by the difference between Fermi level (E_F) of the semiconductor oxide and redox reaction of electrolyte in DSSC.^[47, 48]

Table 2.1 Comparison of PV cells and DSSCs

	PV Cells	DSSCs
	- Depletion region absorb light - Electron hole pair separate by electric field	- Dye absorb light - Electron hole pair separate by kinetic transfer
Pros	- High power conversion efficiency	- Ease of fabrication - Low material cost
Cons	- Prone to impurity - High cost of manufacturing - High material cost	- Relatively low power conversion efficiency

2.1.2 Physics of electron transfer and recombination process in photoanode

Figure 2.2 Schematics of processes and typical time constants under working conditions in DSSCs under 1 Sun condition.^[31] Copyright 2010 with permission from American Chemical Society.

Table 2.2 Summary of electron transport, transfer processes and the rate of occurring in DSSC under working condition

	Process	Process name	Time Frame (s)	Equation Number
(1)	$D / \text{TiO}_2 + h\nu \rightarrow D^*_{\text{LUMO}} / \text{TiO}_2$	Excitation	10^{-13}	(2.1)
(2)	$D^*_{\text{LUMO}} / \text{TiO}_2 \rightarrow D^+ / \text{TiO}_2 + e_{\text{cb}}^-$	Injection	10^{-13} - 10^{-11}	(2.2)
(3)	$e_{\text{cb}}^- / \text{TiO}_2 \rightarrow e_{\text{cb}}^- / \text{TCO}$	Percolation	10^{-3}	(2.3)
(4)	$D^+ / \text{TiO}_2 \rightarrow D / \text{TiO}_2$	Relaxation	10^{-8}	(2.4)
(5)	$D^+ / \text{TiO}_2 + e_{\text{cb}}^- / \text{TiO}_2 \rightarrow D / \text{TiO}_2$	Recombination	10^{-4}	(2.5)
(6)	$I_3^- + e_{\text{cb}}^- / \text{TiO}_2 \rightarrow 3I^-$	Recombination	10^{-2}	(2.6)
(7)	$D^+ / \text{TiO}_2 + 3I^- \rightarrow I_3^- + D / \text{TiO}_2$	Regeneration	10^{-6}	(2.7)

Although the detail of DSSC energetic and kinetics of charge transfer and transport mechanism is still under debate and extensive research, it is widely been accepted and agreed with the basic mechanism proposed in figure 2.2. In the figure 2.2 shown above is the basis kinetics that occurs at oxide/dye/electrolyte in DSSC under working condition and details are summarized in table 2.1. First of all, photon excitation (Eq 2.1) occur when dye absorbed photon and electron from excited dye are injected into conduction band of semiconductor or TiO_2 . Excited charge separation occurs at π orbitals of the organic ligand of Ru-complex to the acceptor state of TiO_2 . Femtosecond transient absorption spectroscopy are normally employed in study of the injection process. One of the most astounding finding is that the ultrafast injection of electron in typical Ru-complexes is occurred in femtosecond. Despite the mechanism of ultrafast injection is still under debate and extensive research, it is generally understand that is due to direct adhesion of the dye or sensitizer to the semiconductor oxide surface which in turn to have a direct transfer of electron.^[49, 50] Injection process is often compete with relaxation process (Eq 2.4) in which the excited dye is relaxed to its ground state. It is reported that the lifetime of the typical excited Ru-complex dye is 20-60 ns.^[51] Thus, a much faster injection rate over relaxation of excited dye has enabling DSSC obtaining a high charge injection efficiency (ϕ_{inj}).

$$\phi_{inj} = \frac{k_{inj}}{k_{inj} + k_{decay}} \quad (2.8)$$

where k_{inj} is the rate constant for charge injection while k_{decay} is decay constant of the excited dye.

For DSSCs device performance, the time scales of the injection process should be compared with decay of the excited state of the dye to the ground state. It was found

that electron injection rate is well faster than the excited state decay as a result successfully competing against the deactivation of the excited dye molecule and the dye cation radical is formed with a yield of nearly 100 %. In order to obtain high ϕ_{inj} to have better PCE of DSSC, we need to achieve significant k_{inj} over k_{decay} (roughly 100 times) based on the equation above, however large k_{inj} may cause kinetic redundancy.^[52, 53] Thus it may be wise to sacrifice slightly on fast injection by increase conduction band edge which in turn will lead to higher V_{oc} . As a result, in developing new dye molecule, matching the dye with a suitable oxide is crucial to optimize ϕ_{inj} and V_{oc} .

Unlike injection process, transportation or percolation (Eq 2.3) across mesoporous semiconductor occur relatively very slow, typically in milliseconds.^[54-56] TiO_2 nanoparticles (NP) is wide used as the mesoporous semiconductor layer, however crystalline TiO_2 NP is very much different from that of its compact analogues. First, low conductivity of mesoporous TiO_2 NP does not inherit conductivity of the film or compact analogues.^[57, 58] Next, its NP does not have built-in electrical field. Thus the transport mechanism can be view in which electrons percolate through hopping from one crystalline particles to another. Photoelectron transferred from dye to conduction band of mesoporous semiconductor is mainly driven by the gradient in electron concentration for transportation or usually named ‘diffusion’.^[59, 60] This is because semiconductor NP do not have internal electrical field and do not show any significant band banding as it is not electronically doped and is surround by electrolyte. The electron diffusion process is being described by the ambipolar diffusion model:^[61]

$$D_{amb} = \frac{n+p}{\left(\frac{n}{D_p}\right) + \left(\frac{p}{D_n}\right)} \quad (2.9)$$

Where D_{amb} is the ambipolar diffusion coefficient, n and p are charge concentration of negative and positive carrier respectively. D_p and D_n correspond to diffusion coefficients of positive and negative carrier.

There are several factors affect the rate of diffusion in mesoporous layer. First of all, density of traps in the nanoparticles, grain boundaries and oxide/electrolyte interface is the main factor that lead to decrease of charge diffusion coefficient.^[60] It was found that increase in particles size or reduce in surface roughness leads to decrease in trap density and increases in electron diffusion coefficient. There are experiments point the importance of grain boundaries towards electron transportation. It was reported that mesoporous TiO_2 NP has preferential orientation of their crystal faces which attribute to higher degree of ordering and decrease number of grain boundaries has leads to faster electron transportation. Chemical diffusion coefficient (D_n) affect by traps density is derived using small-modulation methods in MT model as below:^[61]

$$D_n = (1 + \frac{\partial n_t}{\partial n_v})^{-1} D_o \quad (2.10)$$

Where D_o is the diffusion coefficient in conduction band, n_t and n_c are density of trapped electrons and total electrons in the conduction band. Network geometry of mesoporous film also affect the charge transport. Benkstein et al. carried an experiments with different porosities of mesoporous TiO_2 NP with coordination number of particles decreases with increasing porosity. It was found that electrons become tortuous and longer diffusion path in more porous films, which in turn to have slower charge transport. The percolation threshold was found to be at 76% porosity.^[62]

After photo-induced excitation of dye and electron injection from dye to mesoporous TiO_2 , the dye is in oxidized state and it needs to be regenerated through reduction by electron donor (Eq 2.7). The commonly used electron donor or

electrolyte in DSSC is iodide with concentration $> 0.1\text{M}$ so as to ensure the lower limit for regeneration time. The details regeneration of oxidized sensitizer (D^+) by iodide is believed to have the mechanism below:

In Eq 2.11, there is most likely of a single electron transfer between D^+ and I^- . However, iodide is unlikely to form iodine radical ($\text{I}^{\cdot}$) due to its higher electropositivity than most of the dyes used in DSSC. As a result, iodine radical bound to dye ($\text{D}\cdots\text{I}$) is more likely and it is less positive in potential. Subsequently, addition of another iodide leads to the formation of $(\text{D}\cdots\text{I}_2^{\cdot-})$ in Eq 2.12, which dissociate the dye to its ground state and left $\text{I}_2^{\cdot-}$ in Eq 2.13. Finally, $\text{I}_2^{\cdot-}$ dissociate into triiodide and iodide in Eq 2.14 due to its highly unstable condition.^[63-65] It was suggested that 0.5 to 0.6 eV of driving force (ΔG) between oxidation state of dye and redox potential of iodide/triiodide electrolyte is needed to ensure fast regeneration of dye. It was found that half time ($t_{1/2}$) of the typical dye regeneration is around 1 to 10 μs , however with ΔG of more than 0.5 eV, a rapid regeneration kinetics was observed.^[66-68] Presence of cations such as Li^+ also promote rapid regeneration of the oxidized dye because the cation absorbed on the surface of the oxide attracted higher concentration of I^- . Besides, bromide is a superior candidate to iodide as it provide sufficient positive of oxidation potential of the dye, other materials such as cobalt(II)-bis [2,6-bis(1-butylbenzimidazol-2-yl)pyridine] and 2,2,7,7-tetrakis-(N,N-di-p-methoxyphenyl-

amine)-9,9-spirobifluorene also being explored for rapid dye regeneration, further will be discussed. ^[16, 69, 70]

Slow charge transportation as discussed previously has lead to possible charge recombination of electron in semiconductor to either oxidized dye (Eq 2.5) or acceptor in electrolyte (Eq 2.6). The kinetics of back flow of electrons from conduction band in semiconductor to oxidized dye occurring in microsecond to millisecond time frame and depends on the electron concentration in the semiconductor.^[66, 71] On the other hand, recombination of electron with electrolyte is observed to be relatively less severe as electron lifetime with I/I_3^- was found to be relatively longer (1-20ms). The back flow of electron is mainly due to weak overlap of semiconductor conduction band and d-orbital of ruthenium dye molecule in which recombination is accelerated with thermal activation and thus decreases the transfer rate constant.^[72] Next, recombination encounter diffusion-limited between conduction band edge and dye molecule.^[73, 74] Oxidized dye are expected to be regenerated in a very fast rate, recombination with oxidized dye is expected to be unlikely, thus recombination are expected mainly from electron in semiconductor to acceptor in the electrolyte or mediator. Recombination of electrons in semiconductor with acceptor in electrolyte is studied in actual devices by measuring transient response of the open circuit potential (V_{oc}). This recombination process only occur in semiconductor/electrolyte interfaces where dye fail to effectively cover the semiconductor and it can be suppressed by introducing a compact metal oxide to act as a blocking layer on top of the mesoporous semiconductor. ^[75]

In a nut shell, there are many factors affecting the whole transport and transfer mechanism in the photoanode such as concentration of trap in semiconductor oxide, concentration of acceptor and coverage of dye molecule on semiconductor surface etc.

2.1.3 Reduction reactions at counter electrode and transport of mediator

Redox mediator employed in between two electrodes is mainly driven by diffusion and has high conductivity and ionic strength to prevent the influence of electric field and transport by migration. Concentration of the redox mediator and distance between the electrodes affect the diffusion impedance in which act as a series resistance in the device.^[76] Viscous electrolyte with low diffusion coefficients and lengthy diffusion length have which limits the large flux of redox component thus limit the photocurrent. To achieve diffusion resistance of as low as $0.7 \Omega \text{ cm}^2$ minimizing the distance between two electrodes to less than $10 \mu\text{m}$ is necessary.

At counter electrode, triiodide is reduced to iodide as shown below:

Counter electrode for DSC with iodide electrolyte can be easily prepared by having a thin layer of platinum (Pt) deposited on TCO. Pt which has charge transfer resistance of less than $1 \Omega \text{ cm}^2$ has the best performance in term of stability and PCE.^[77] Pt is used as a catalyst for the reaction in Eq 2.15, triiodide dissociates to iodine ions upon receiving electrons. Charge transfer resistance cause by charges exchange in counter electrode can be define as:^[78]

$$R_{CT} = \frac{\eta}{J} = \frac{RT}{nFJ_o} \quad (2.16)$$

Where η is the overpotential for reaction Eq 2.15, J is current density, J_o is the exchange current density. The ideal RCT should be $< 1 \Omega \text{ cm}^2$ to avoid significant losses where high losses may cause significant lower in fill factor and V_{oc} .

2.1.4 Modelling of DSSC

DSSC has been further explored and studied through several modelling methods over past few years.^[79-81] Since DSSC photo-electrochemical is a complicated electrochemical reaction, thus modelling and simulation of DSSC is a powerful tools to evaluate its performance. First of all, classic mechanics modelling has been employed in DSSC in which charges injection into semiconductor are assume to behave like a classical particles when study of the transportation of the charges across the semiconductor.^[82, 83]

Next, optical modelling used to examine the light scattering path ways across the semiconductor oxide layer.^[84, 85] It helps in guiding to design an effective semiconductor layer to maximize the light absorption to increase the PCE of DSSC.

Lastly, the most useful widely used model in DSSC is the electrical modelling in which DSSC is being represented by an equivalent circuit consisting of several electrical components.^[86-89] As shown in Figure 2.3 below, DSSC is being represented in impedance form where it signify the charge transport and transfer across several interfaces. R_s is attributed by the overall series resistance across the two electrode of the device, which may be affected by the distance of the two electrode, viscosity of the electrolyte etc. R_1 and R_{pt} represent the charge transfer resistance across the photoelectrode/ electrolyte and electrolyte/counter electrode interface respectively, while CPE is the constant phase elements for their respective interfaces.^[90] The respective value can be obtained by simulation fitting of the data obtained in Electrochemical Impedance Spectroscopy (EIS) with the equivalent circuit.

Figure 2.3 Equivalent circuit model of DSSC

2.2 Photo-electrode semiconductor materials

Photo-electrode is the heart of the DSSC device where it consists of a mesoporous semiconductor oxide which typically has a thickness of 10 μ m and porosity of 50-60%. Mesoporous layer is deposited on top of TCO, where fluorine-doped tin oxide (FTO) is commonly used due to its high optical transmittance, good conductivity and thermal stability for electron collection.^[91-93] On top of the mesoporous layer is coated with a monolayer of dye. Mesoporous structure is used in DSSC to enhance the absorption of light by maximizing the surface area and number of dye attached to the surface.

TiO₂ has been widely used in photoanode in DSSC due to some of its natural properties such as non-toxic, low cost etc and will be further discussed in the following section.^[94-96] Besides, some other attempt to increase PCE of DSSC will also be reviewed.

2.2.1 Titanium dioxide, TiO₂

The key to the breakthrough for DSSC in 1991 was the use of a mesoporous electrode, with a high internal surface area to support high loading of monolayer of a sensitizer or dye.^[18] The high efficiency of charge transport was the puzzling phenomenon when DSSCs were first unveiled. Mesoporous electrodes are very much different characteristic as compared to their compact analogs because (i) the inherent conductivity of the film is very low; (ii) the small size of the nanocrystalline particles does not support a built-in electrical field; and (iii) the electrolyte penetrates the porous film all the way to the back-contact making the semiconductor/ electrolyte

interface essentially three-dimensional. Charge transport in mesoporous systems is under keen debate today and several interpretations based on the Montrol Scher model for random displacement of charge carriers in disordered solids have been advanced.^[97] Currently, TiO₂ nanoparticles (10-20nm) has been favored as the material for photoanode due to its stability, non-toxic, wide bandgap of 3.2eV and high reflective index ($n=2.4-2.5$).^[98-100] Anatase TiO₂ is preferred structure in used in DSSC, because it has a larger bandgap and a higher conduction band edge energy, E_c . This leads to a higher Fermi level and V_{oc} in DSSCs for the same conduction band electron concentration. Some facts about TiO₂ in DSSC have been discovered by O'Regan and Durrant:^[101]

- >90% of electrons in TiO₂ are trapped while only <10% in CB
- A TiO₂ particles (18nm) has roughly 600 dye molecules on surface
- Electron injection into TiO₂ particles is $\sim 600 \text{ s}^{-1}$
- 1 dye per 150 TiO₂ particles is in oxidized state
- There are $\sim 1000 \text{ I}^-$ and 200 I_3^- ions around TiO₂ particles

Figure 2.4 SEM image of (a) cross-sectional images (b) Enlarged image from the cross-section of TiO₂ photo-electrode films.^[102] Copyright 201 with permission from Nature.

The most common technique used to prepare TiO₂ nanoparticles is the hydrolysis of titanium precursor such as titanium butoxide with base or acid, and subsequently undergo hydrothermal growth and crystallization.^[103-105] TiO₂ NP grow under acidic condition has crystalline anatase form and exposing <101> face. Rutile and anatase based DSSC was studied by Park et al, and it was found that V_{oc} are similar for both device, despite anatase has higher conduction band edge of 0.1-0.2 eV.^[106] However, rutile TiO₂ exhibit lower photocurrent by 30% which was ascribed by the large particle size and low surface area of the rutile electrode.^[107] Sintering of the film in 450°C in air is also essential to remove organic components in the paste and also enhance the electronic connectivity between particles, thus improving the mechanical stability and electrical conductivity of the TiO₂ film.^[108, 109] To further improve the performance of DSSC, TiCl₄ treatment has been employed.^[110, 111] This treatment deposited an ultrapure TiO₂ shell on the mesoporous layer which can improve the injection efficiency and electron lifetime significantly. Besides, it can also increase dye absorption, this is mainly due to increase of surface roughness thus higher surface area.

Charge transport across mesoporous semiconductor often limited by trap where the random distributed trap hindered electron transport across the semiconductor. As a result, one-dimensional nanostructure approach such as nanotube and nanowire can improve the charge transport process by increasing electron diffusion length and reduce defects which may cause surface traps.^[112, 113] Well-ordered and vertically orientated TiO₂ nanotubes shown in Figure 2.5 can be grown by anodization of titanium foil in fluoride-based electrolyte. The nanotubes obtained has a dimension of <1000µm, wall thickness of 5-30nm and pore diameter of 12-240nm.^[114] The nanotubes is in amorphous phase right after anodization and crystallize upon sintering

in air at 500°C. The TiO₂ nanotube based DSSC on titanium substrate exhibit PCE of 6.9%, with light illuminated through counter electrode, however there are absorption losses through counter electrode and electrolyte. On the other hand, nanotube grown on FTO substrate with thickness of 1.1 μm with TiCl₄ treatment achieves PCE of 4.4% with strong absorbing dye.

Figure 2.5 (a) Schematic diagram of TiO₂ nanotube array in DSSC. (b) SEM image (top view) of TiO₂ nanotubes.^[114] Copyright 2006, with permission from Elsevier.

2.2.2 Zinc oxide, ZnO

The use of ZnO as photoelectrode material in DSSC has increased dramatically in terms of publication only second to TiO₂. This is due to some of its superior property over TiO₂ (Table 2.2) such as higher electron mobility which favor electron transportation, similar bandgap and conduction band edge with TiO₂.^[115] Despite ZnO is superior in terms of inherit properties, PCE of typical ZnO based DSSC (5-6%) is still much lower as compared to TiO₂ based DSSC (~11%). Besides, its poor chemical stability towards acidic and basic condition is the major drawback.^[116] However, the main attribute that attract intensive research is its ease of synthesizing in a highly crystalline ZnO with various morphologies such as nanoparticles, nanowires, nano-rods, nanotubes, etc. ^[117-120]

Table 2.3 Comparison of physical properties of ZnO and TiO₂^[115]

	ZnO	TiO₂	SnO₂
Crystal structure	Rocksalt, zinc blende and wurtzite	Rutile, anatase and brookite	Rutile tetragonal
Energy band gap (eV)	3.2-3.3	3.0-3.2	3.5
Electron mobility in bulk (cm² V s⁻¹)	200	0.1-4	250
Refractive index	2.0	2.5	2.0
Electron effective mass	0.26	9	0.2-0.3
Relative dielectric constant	8.5	170	13

Figure 2.6 SEM images of nanostructured ZnO films: a) Dispersed nanosheets. b) Nanosheet-assembled spheres. c) Nanobelt array. Reproduced with permission from [115]. d) A ZnO tetrapod formed in a three-dimensional structure with four arms extending from a common core. e) Networked film with interconnected ZnO tetrapods.^[115] Copyright 2009 with permission from Wiley-VCH.

Due to its ease of synthesis and crystallization, ZnO nanostructure with various morphologies has been reported with the aim of increasing the surface area for higher dye loading and better connectivity for faster charge transportation. Figure 2.6 (a) shows ZnO nanosheets employed as mesoporous oxide in photoanode, in which it exhibit low PCE of 1.55%.^[121] However ZnO nanosheet shperes (Figure 2.6 (b)) prepared by hydrothermal shows remarkable enhancement in terms of PCE to 2.61%.^[122] The enhancement is believed to attribute by high degree of crystallinity and porosity which in turn to have low resistance for electron transport. ZnO nanobelt

with high degree of orientation and porosity shown in Figure 2.6 (c) was fabricated through electrodeposition method and studied for DSSC.^[123] ZnO nanobelt with thickness 5nm, surface area of $70 \text{ m}^2 \text{ g}^{-1}$, shows a PCE of 2.6% as well. Last but not least, ZnO tetrapod which consists of a 3-D structure with four arms shown in Figure 2.6 (d) achieved PCE as high as 3.27%. ^[124]ZnO tetrapod connected with each other to form a large porosity film (Figure 2.6 (e)) with high surface area for higher dye loading. Besides, incorporation of ZnO NP in ZnO tetrapod can further increases the internal surface area of the film.^[125]

Furthermore, ZnO can act as a blocking layer to prevent charge recombination of electron in conduction band of TiO_2 to electrolyte (Figure 2.7).^[126] The core shell structure of TiO_2 -ZnO was synthesized through hydrothermal method and it demonstrated an improvement of PCE of TiO_2 DSSC from 4.76% to 6.55% after ZnO modification.

Figure 2.7 Schematic diagram of the energy levels of a core-shell-structured (TiO_2 -ZnO) photoelectrode in DSCs. Reproduced with permission from.^[126] Copyright 2006, American Institute of Physics.

2.2.3 Tin oxide, SnO₂

Tin dioxide (SnO₂) has recently been considered as a promising alternative due to its wider bandgap (3.5 eV) than both TiO₂ and ZnO which benefits for the long-term stability of DSSCs against UV degradation, and high electron mobility (~100-200 cm² V⁻¹s⁻¹) which reduces charge recombination.^[35, 60] In addition, it is able to form homo-junction with FTO substrate, therefore, negate the issue of high contact resistance originated from the hetero-junction between TiO₂ and FTO. But SnO₂-based DSSCs critically suffer from the problem of low conduction band edge (E_c which is ~0.3 eV lower than that of anatase TiO₂), which causes fast backflow of photoelectrons to the electrolyte (a form of charge recombination) and thus reduction of open circuit voltage (V_{oc}).^[127] To tackle this issue, a thin layer of metal oxide with higher conduction band edge (e.g., Al₂O₃, Cr₂O₃, TiO₂, CdO, CuO, ZnO, MgO) has been coated onto SnO₂.^[128-132] Ternary oxides (Zn₂SnO₄ and BaSnO₂) have also been synthesized to favourably shift the band structure.^[133-137] Besides, SnO₂ is a chemically stable oxide that has a conduction band edge E_c about 0.5 eV lower than that of TiO₂ (anatase). It can therefore be used in combination with dyes with low-lying LUMOs that inject poorly into TiO₂, such as some perylene sensitizers.

Figure 2.8 PCE of SnO₂ NP based coated with various semiconductor divalent metal oxides.

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Besides, different SnO₂ nanostructures had been investigated such as nanowires prepared by sol gel ^[138], nanorods prepared by hydrothermal method^[139] and nanoparticles prepared by thermal evaporation. Despite various attempt has been conducted to improve the power conversion efficiency of SnO₂ based DSSCs, none of them is comparable or superior than TiO₂ based DSSC. This is mainly due to poor adhesion between dye^[128] and SnO₂ nanoparticles and occurrence of trap states under conduction band of SnO₂ lead to drastic recombination and the occurrence of the trap state mainly due to incomplete coordination of Sn on SnO₂ nanoparticles.^[140] In order to increase the efficiency of SnO₂ based DSSC, common practice of TiCl₄ treatment on SnO₂ nanoparticle surface shows significant improvement on the device performance.^[141] As formation of thin TiO₂ layer on SnO₂ nanoparticles enhanced dye loading on photoelectrode, thus improve light harvesting efficiency.

2.3 Counter electrode

Counter electrode is an important component used to complete the electrical circuit of the device by returning the redox mediator to its reduced state. Maximum voltage of DSSC is determined by the difference of Fermi level of semiconducting oxide and redox potential at counter electrode. However under working condition with light illumination, counter electrode mostly affected by over-potential at the electrode surface.^[142, 143] Thus, to reduce the over-potential caused by mass transport and electrocatalytic reduction of mediator, a catalyst is needed to accelerate the reduction of oxidized mediator.

2.3.1 Platinized Conducting Glass

Counter electrodes for DSSCs with I^-/I_3^- electrolytes can be easily prepared by deposition of a thin Pt onto a TCO substrate.^[144-146] Without platinum, TCO substrate such as FTO is a poor counter electrode due to its high charge transfer resistance, more than $10^6 \Omega \text{ cm}^2$ towards I^-/I_3^- electrolytes. A thin layer of catalytic platinum on TCO can be prepared through various methods such as electrodeposition, spray pyrolysis, sputtering, thermal-deposition and physical vapor deposition.^[147-150] However, Pt film prepared through electro deposition and vapor deposition tends to dissolve in I^-/I_3^- electrolytes, therefore not suitable for commercial use where long term stability is needed. Best performance and long-term stability has been achieved with nanoscale Pt clusters prepared by thermal decomposition of platinum chloride compounds where charge transfer resistances of less than $1 \Omega \text{ cm}^2$ is achieved and very low Pt-loadings ($5 \mu\text{g cm}^{-2}$) are needed, as a result counter electrode remains transparent.^[151, 152]

2.3.2 Carbon based catalytic counter electrode

As an indispensable component in DSSC, in which performance of counter electrode (CE) governing the PCE of the entire cell. However Pt is too costly to be used in mass production, thus a low cost and easily printable material has been extensively researched. Carbon materials was found to be a good alternative for reduction of I_3^- . In 2010, Aksay's group found that the oxygen containing functional groups on functionalized graphene sheets (FGSs) contribute to catalytic performance towards I_3^-/I^- redox reaction. DSSC device with FGS as CE achieve a PCE of 4.99% with that of Pt (5.48%).^[153] Further study shows that C/O ratio of FGS affect the efficiency of DSSC by modulating the charge transfer resistance (R_{ct}), conductivity and morphology of counter electrode. The optimum C/O ratio is slightly more than 7, lower than that has proven to be non-conductive which suppress the charge transferring rate.

Xu et al. fabricated a new counter electrode by layer-by-layer compositing GO with PDDA followed by electrochemical reduction (ER).^[143] With Ru complex C106TBA as dye, DSSC with PDDA@ERGO counter electrode exhibits high PCE of 9.5% in conjunction with low volatility electrolytes. The superior performance was mainly due to synergistic effect of oxygen containing functional groups on ERGO and positively charged N groups in PDDA. Furthermore, it has extreme stability where the PCE retention of 82% after 1000h of light soaking in 1 sun condition. In addition to GO (or reduced-GO), other heteroatom doped graphene such as B and N which inherit the intrinsic properties of graphene and also exhibit superior catalytic property. Dai's group found that the N doped graphene with doping level up to 7.6 at % achieve comparable PCE with that of Pt (7.07%).^[154] The N doping process induced high

porosity, good hydrophilicity, large surface and higher free electron density which result in higher J_{sc} , V_{oc} and fill factor. Another group investigated the influence of N content on the electrocatalytic activity of N doped reduced graphene oxide nanosheets (N-GNSs) synthesized by ammonia annealing. It was found that the R_{ct} values of prepared samples and peak position values (ΔE_p) of I_3^-/I^- decreased with the increase of annealing temperature which indicated the decrease of electro-catalytic activity of N-GNSs. The decrease amount of doped N from 7.31 at% of N-GNS 600 to 3.91 at% of N-GNS 900. DSSC measurements showed a high PCE of 8.03%, larger than of Pt (7.33%). In contrast to Cui's report, Hou et al. found that the nitrogen bonding states played a main role for the catalytic activity of N-doped Graphene. Despite extremely high N content of 18 at% was achieved through annealing GO under cyanamide at 700 °C, however maximum PCE of 5.4% was achieved upon sintering at 900 °C where N content only 7.4 at%. Further analysis shows the overall catalytic activity in fact depended on total content of pyridinic and graphitic N.

Besides, N doped graphene nanoplatelets (NGnPs) with doping level of 2.79 at% was electrostatically sprayed on FTO/glass substrate (Fig 2.11(a)) and employed as CE in conjunction with $Co(bpy)_3^{3+/2+}$ as a redox couple was reported by Kim et al.^[155] The optimized NGnP electrode exhibited significantly lower R_{ct} of 1.73 Ω/cm^2 compared with Pt (3.15 Ω/cm^2), thus result in higher FF (74.2%) and PCE (9.05%) performance than that of Pt (FF 70.6% and PCE 8.43%). Similar results was reported by Jeon et al., using NGnPs prepared by ball milling method as CE material where the performance of NGnPs based DSSC also outperform that of Pt with every performance parameters of J_{sc} , V_{oc} , FF and PCE (14.162 mA/cm², 890 mV, 74.1% and 9.34%, respectively) triumph that of Pt (14.113 mA/cm², 886 mV, 70.8%, and PCE 8.85%).^[156] Das et al. reported a noticeable enhancement of electro-catalytic

activity of large-scale graphene towards I_3^-/I^- when treated with CF_4 reactive-ion plasma. During the plasma process, the produced F^- is proved to form covalent and possible semi-ionic bonds with C atoms in graphene, which led to an electrochemically active surface with large amount of active edge-plane sites. This promoted the electrode-electrolyte interfacial charge transfer activity towards I_3^- redox species, which is supported by the increased exchange-current density and decreased charge-transfer resistance.

Figure 2.9 (a) Schematic diagram of an e-spray setup and the SEM image of NGnP coat on FTO crystal. (b) I-V characteristics of the DSSCs with CE of Pt vs NGnP under 1 sun illumination.^[155]

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2.3.3 Metal sulphide based CE

It was reported that electrodeposited CoS as suitable catalyst for the iodide/triiodide redox couple.^[157-159] Deposited on a flexible substrate (ITO/PEN) it outperforms Pt on the same substrate, with a charge transfer resistance down to $1.8 \Omega \text{ cm}^2$, while thermal Pt on FTO gave $1.3 \Omega \text{ cm}^2$ using the same ionic liquid electrolyte. Besides, nickel sulphide (NiS) deposited through electrodeposition has found to have better optical and catalytic property towards I^{3-} reduction which in turn improve the device performance with comparable performance with Pt of 6.8% PCE.^[160] Furthermore, MoS_2 and WS_2 were introduced into DSSC device as a CE. The results show that the two sulfides exhibit excellent catalytic activities for regeneration of both the conventional redox couple (I_3^-/I^-) and new organic redox couple (T_2/T^-). WS_2 CE achieved PCE of 7.59% which comparable to Pt, while MoS_2 achieved a PCE of 7.73% which is superior to Pt.^[161]

Figure 2.10 SEM image of (a) MoS_2 and (b) WS_2 .^[161] Copyright 2011 with permission, Royal Society of Chemistry.

2.3.4 Conducting polymer based CE

Counter electrodes with low cost of manufacturing which consist of conducting polymers have also been researched. Novel conducting polymer such as Poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted much of the attention as it has good conductivity, high flexibility, remarkable stability, and low cost. Furthermore it was found that, it has the catalytic capability to catalyze I_3^-/I^- reaction. PEDOT has a molecular structure shown in Figure 2.13 below:^[162]

Figure 2.11 PEDOT molecular structure^[162]

Despite its excellent conductivity, PEDOT solubility in solvent is an issue to be employed as CE of DSSC. However, the issue was solved by introducing water-soluble polyelectrolyte to counter balance the charge dopant during polymerization. Polyelectrolyte used such as poly(styrene sulfonic acid) (PSS) and P-toluenesulfonate (TsO) to form PEDOT:PSS and PEDOT:TsO.^[162] Both have been tested in as CE material and was found that PEDOT:TsO achieved comparable performance, PCE (4.6%) with that of Pt (4.67%), however PEDOT:PSS can only manage to achieve PCE of 2.1% mainly due to low fill factor. The low fill factor of PEDOT:PSS may due to its lower conductivity than PEDOT:TsO, and PSS⁻ molecule which consists of negative charge that causes repulsion and hindered I_3^- molecule from contacting the active sites of PEDOT chain, which in turn causing the increase in overpotential. Imidazole (Im) has a remarkably ability to increase kinetics of oxidative

polymerization, thus Lee et al exploited Im to increase conductivity of PEDOT which grown on FTO as CE of DSSC. It was found that DSSC with CE made up of PEDOT with Im/3,4-ethylenedioxythiophene (molar ratio of 2, where optimum ratio is needed to have a balanced roughness vs conductivity shown in Figure 2.14) demonstrate a PCE of 7.44% which is very much compared to sputter Pt (7.77%).^[163] Studies have shown that the high efficiency was mainly attributed by its high conductivity and large surface area, which resulting a good electrocatalytic activity towards I_3^- reaction.

Figure 2.12 root mean square roughness and conductivity of PEDOT films versus Im/3,4-ethylenedioxythiophene molar ratios. ^[163] Copyright 2006, with permission from Elsevier

Besides its great conductivity and catalytic property, conducting polymer based CE has the advantage of making flexible device. TiC/PEDOT:PSS has been explored by Yeh et.al., where TiC NPs were incorporated with PEDOT:PSS on a flexible ITO substrate to fabricate a flexible CE as shown in Figure 2.15.^[164] The DSSC with CE of TiC/PEDOT:PSS exhibit a PCE of 6.5% which is very much close to the performance of Pt (6.84%).

Figure 2.13 Flexible counter electrode (fabricated with PEDOT:PSS/ TiC-nanoparticles composite film on ITO–PEN substrate).^[164] Copyright 2006, with permission from IOP Publishing

Besides PEDOT, polyaniline (PANI) is also a novel material with high electrical conductivity. Electrochemically deposited PANI as a counter electrode for DSSCs shows good electrochemical activity. Synthesis of PANI by electrochemically polymerization method can be done through CV scanning under several cycles such as 3, 6, 10, and 20 cycles, the growth is shown in figure 2.16. The optimized PANI CE (6 cycles deposition) shows better PCE (6.85%) than that of Pt (6.44%), and high fill factor of 63.8% as well as V_{oc} of 0.844V. This is mainly due to its extreme low charge transfer resistance of only $0.5\Omega\text{ cm}^2$ while conventional Pt electrode hold a charge transfer resistance of $1.8\Omega\text{ cm}^2$.^[165]

Figure 2.16 Electrochemically deposit of PANI under (a)3, (b)6, (c)10 (d) 20 cycle of CV scanning.^[165] copyright 2006, with permission from Elsevier

Moreover, PANI nanoparticles at the compact and scattering layers increases the reactive surface, it also results in higher electron transport resistance across the polymer film. Under optimal condition, DSSC with such PANI based CE recorded 11.6 % improvement in the photocurrent as compared to conventional Pt counter electrode.

2.4 Electrolyte

2.4.1 Liquid electrolyte

Electrolyte is used to ensure continuous operation of DSSC as well as regenerate the oxidized dye which undergoes excitation by incoming photons. A good liquid redox electrolyte need to be chemically stable, low viscosity to minimized charge diffusion rate, good solvent for redox couple component and need to avoid dissolution of adsorbed dye and even semiconducting material.

Figure 2.15 Gerischer diagram of the dye-sensitized solar cell with iodide/triiodide electrolyte.^[31]

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The most commonly used mediator is I^-/I_3^- redox couple.^[166] Standard $E(I_3^-/I^-)$ for iodide redox couple is at around +0.35 vs NHE while oxidation potential of sensitizer ($E(S^*/S)$) is believe to be at +1.1V vs NHE which is much lower compare to $E(I_3^-/I^-)$.^[167] Thus, this indicate that there is a large driving force of up to 0.75 V for reduction of oxidized dye as a result, reduction of dye in I^-/I_3^- system is extremely fast. To further enhance the regeneration rate, a high concentration of I^- ions should be present and the transportation of I_3^- ions to the counter electrode needs to be fast too.

I^-/I_3^- redox couple is the preferred redox mediator for DSSC mainly due to its stability and efficiency. Many iodide salts have been studied in liquid electrolyte in DSSC. Redmond and Fitzmaurice found Li^+ and Mg^{2+} adhere on mesoporous TiO_2 where it shifted the conduction band position.^[168] Moreover, it was found that V_{oc} of DSSC increases with the presents of cation in the order of $Li^+ < Na^+ < K^+ < Rb^+$.^[169]

Other alternative of redox mediator such as bromide has also been successfully tested with positive result where extreme high V_{oc} of 0.94V and PCE of 5.22% was achieved. This is mainly due to higher HOMO level of bromide than that of the redox potential, thus a significant driving force existed to dye regeneration.^[170]

Besides, selenocyanate ($SeCN^-$) and thiocyanate(SCN^-) have also been used as alternative to iodide electrolyte.^[171, 172] Despite poor performance of $SeCN^-/(SeCN)_3^-$ was initially reported, Gratzel et al has dramatically improved the performance by mixing 1-ethyl-3-methylimidazolium with $SeCN^-/(SeCN)_3^-$ to achieve a PCE of 7.5% with good stability over 2 months.

2.4.2 Quasi-solid state electrolyte

Liquid electrolyte has widely been used in research, however its liquid state become a big issue when it is come to mass production for commercial use for a period of more 5 years. As constant cyclical expend and contact under daytime and nighttime may cause leakage of the liquid electrolyte. As a result, quasi-solid state of electrolyte is being proposed. Quasi-solid state electrolytes show PCE which is slightly lower than its compatriot liquid electrolyte, it is likely to its limited mobility of redox ions in the quasi-solid electrolyte.^[173-175] Quasi-solid state DSSC with acceptable PCE of 6% were obtained by gelating a 3-methoxypropionitrile (MPN)

based electrolyte using 5 wt% poly(vinylidene fluoride-*co*-hexafluoropropylene), yielding thermally stable DSCs exhibiting comparably low losses in charge transport efficiency.^[176]

2.5 Sensitizer or Dye

Dye is the sensitizer that plays a crucial role in harvesting incident photon in DSSC.

Photo-sensitizer usually has the characteristic as follow:

- Broad absorption spectrum which covers the whole visible region and even the part of the near-infrared.
- Consist of anchoring groups (-COOH, -H₂PO₃, -SO₃H...) to graft firmly onto the oxide surface via physi- or chemi-sorption.
- The excited state level of the photosensitizer should be higher in energy than the conduction band edge of n-type semiconductor of DSSC
- Oxidized state of the photosensitizer should be more positive than the redox potential of electrolyte for higher driving force of dye regeneration
- Avoid dye aggregation on the semiconductor surface

2.5.1 Metal complex dye

Among the metal complexes, Ru complexes based dye have widely been used due to its broad absorption spectrum, suitable excited and ground state energy levels, relatively long excited-state lifetime and good (electro)chemical stability. Metal complex in the dye usually surrounded by ancillary ligands which having at least one anchoring group, while double or triple anchoring group is drawing attention of

researchers. Ancillary ligands such as bipyridines and terpyridines tuned with different substituents are employed to enhance the electrochemical property and metal to ligand charge transfer process of dye to increase PCE of DSSC. Molecular structure of commonly used Ru complexes as shown in Figure 2.18 below:

Figure 2.16 commonly used Ru-complex dye (N3, N719 and Z907).^[31] Copyright 2010

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Gratzel et.al. synthesized a mononuclear Ru complexes in 1993 coded as N3 (Figure 2.18 (a)), chemically named as cis-(SCN)₂bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II).^[18, 177] N3 dye has shown some promising property such as high photon to electron conversion efficiency (IPCE), broader light absorption spectrum than previously available sensitizer, long excited state lifetime of around 20 ns and good adhesion towards TiO₂ semiconductor surface. Thus, DSSC with the incorporation of N3 dye achieved PCE over 10% for first time.

While investigating the effect of proton content in N3 dye on DSSC performance, Nazeeruddin et al. created doubly protonated dye named N719,Z907 (Figure 2.18(b)), (Bu₄N)₂[Ru(dcbpyH)₂(NCS)₂].^[178] DSSC with N719 dye exhibit higher PCE than that of N3 due to introduction of carboxylic acid which shifted the dye

oxidation/reduction potential to more negative, which in turn to have higher driving force for electron injection from dye to semiconducting oxide.

Next, Gratzel and co-workers attempted to minimize the problem of dye aggregation on semiconductor oxide by testing different substituents in ancillary ligand to increase molar extinction coefficient, and a yet another promising dye is created and named Z907 (Figure 2.18(c)).^[179] Z907 is an amphiphilic heteroleptic molecule, which shows high thermal stability where it maintained 7% of PCE under long term thermal stress. Besides, to further improve dye Z907, 3-methoxystyryl was introduced into ancillary ligand which can extend the π conjugation of bipyridine and increase the absorption of light. As a result, this novel dye coded as Z910 demonstrate PCE of 10.2% with outstanding stability.

2.5.2 Organic dyes

Organic dyes have some superior property over commonly used Ru metal complex dye such as

- Ease of design and synthesis as organic dyes are in diverse form
- Environmental friendly and low cost of production
- Higher molar extinction coefficient
- Exhibit higher PCE in p-type DSSC

Organic dye has a general structure of donor- π -acceptor. Under light condition, electrons undergo intramolecular charge transfer from donor to acceptor through π bridge for typical n-type DSSC. As a result, design of new dye base on the basic building blocks above is easy by adjusting HOMO and LUMO of all the component to ensure unblocked intermolecular charge transfer. There are hundreds of type of

organic dye synthesized for DSSC including coumarin dyes, indoline dyes, tiarylamine dyes, carozole dyes, etc. ^[180-183]

Indoline dye with molecular structure shown in Figure 2.19 is one of the most promising organic dye. Indoline dye 103 reported by Horiuchi, Uchida and co-workers used simple synthesis procedure, low cost and the dye exhibit a good efficiencies of 6.1% in 2003.^[182] With much afford had been done in extending the absorption spectrum, dye 104 was created and it shows PCE of 9.0% with optimization on TiO₂ semiconducting oxide by Gratzel et. at.. The outperform indoline dye from the list shown in Figure 2.19, is the dye 105 where n-octyl substitute the ordinary rhodanine to minimize π - π stacking which cause dye aggregation on semiconducting oxide surface. The maximum PCE obtain by dye 105 is 9.5%.

Figure 2.17 Molecular structures of Indoline dyes. ^[31] Copyright 2010 with permission, American

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Chapter 3 Experimental Approaches

This chapter discusses the fabrication process for DSSC and the various instrumentation methods adopted in this project. Details about solar cell performance characterization are also elaborated.

3.1 Materials and reagents

Dye sensitizer [RuL₂(NCS)₂ : 2 TBA] (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, TBA = tetrabutylammonium), or commonly known as the N719 dye, was acquired from Solaronix SA. Liquid electrolyte (HL-HPE) were purchased from Dyesol Co. The liquid electrolyte contains a mixture of inorganic iodide salt, organic iodide salt, and pyridine derivative dissolved in acetonitrile and valeronitrile solution. Acetonitrile, tert-butanol, acetic acid, hydrochloric acid, ammonium hydroxide (25-30% NH₃) and Tin foils were purchased from Sigma-Aldrich, while gallium nitrate was purchased from Alfa Aesar. All chemicals were of reagent grade and all solutions were prepared in deionized water (milliQ). Conducting FTO coated glass substrate (12-13 $\Omega \square^{-1}$) was purchased from Nippon Glass Sheet Co.

3.2 Fabrication of DSSC

In this session, process of fabricating device will be reviewed. However, metal oxide paste fabrication will only be discussed in the Chapter 4 due to different fabrication method for each project.

3.2.1 Preparation of photo-electrode and counter electrode

First, FTO was washed with decon90 (1:10, decon90 to water ratio) under sonication for 30min, follow by another cycle of cleaning in DI water under sonication. After cleaning, FTO was dried with air. To prepare the photo-electrode, an active region was first defined on the FTO coated glass substrate by a masking layer. The masking layer used was 3M adhesive tape. The unwanted regions were then covered by the adhesive tape and the active region remains exposed, the active region was controlled at 0.12 cm². After which, the masked FTO glass was then coated with a mesoporous SnO₂ layer by means of doctor blading. The overall thickness of the SnO₂ film was controlled by number of cycle of doctor blading; typically thickness for 2 cycles of doctor blading was approximately 8μm. After doctor blading, adhesive tape was removed. Subsequently, a temperature program consisting of heat ramps and isotherms was employed to anneal the printed film. This was done to separate the combustion of the additives such as ethanol and terpineol and sintering of SnO₂ particles in time, so as to avoid contamination due to carbon inclusions. The upper sintering temperature and duration is capped at 450 °C for 30 min. The annealing atmosphere was also found to affect the integrity of the SnO₂. For instance, ramping rate can affect the morphology of the oxide particles such a way that high ramping rate would cause agglomeration of particles due to rapid dehydration. Agglomeration of particles reduces the surface area of the film and hence degrades the performance of the device. The optimum ramping rate was found to be around 5°C min⁻¹. In this project, no scattering particles were added to the SnO₂ paste and the resulted film was highly transparent. Next, the SnO₂ photo-electrode was immersed into 0.3 mM N719 solution (50:50 mixture of acetonitrile and tert-butanol by volume) for 16 hr. As for the counter electrode, FTO was drilled with two holes within the area of 0.12 cm² and

then was sputtering a layer of Pt on predrilled FTO glass at an applied current of 20 mA for 80 seconds using JFC-1600 fine coater (JOEL Ltd, Japan).

3.2.2 Assembly of device

Well sealed cell structure was adopted to assemble the DSSC. After removing the photo-electrode from the dye solution, it was washed with ethanol and dried under a nitrogen flow. Parafilm was used to cover up the non-active region and then the platinized counter electrode was then placed on top of the dye-loaded SnO_2 film, the two electrodes were hold firmly together and place on top of a hotplate at 70°C for sealing followed by an injection of the liquid electrolyte through the two holes. A summary of the fabrication process for the DSSC developed in this project is illustrated in Figure 3.1.

Figure 3.1 Schematic of DSSC fabrication process

3.3 Solar cell performance characterization

The current-voltage (I-V) curve, as shown in Figure 3.2, is one of the most important data used to characterize the performance of a PV cell. The primary parameters of the curve used to define the cell performance include: the short-circuit current density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (FF) and the power conversion efficiency (η_{PCE}). The J_{sc} is measured at an applied potential of zero volt and is a function of the illumination intensity. The V_{oc} corresponds to the potential difference between the two terminals of the solar cell when there is no external load connected and the current within the cell is zero. The FF is defined as the ratio of the maximum power point (P_{max}) to the product of J_{sc} and V_{oc} (Eq. 3.1) and indicates the deflection of the I-V characteristics from a square like curve. To achieve high fill factors, the parallel shunt resistance within the cell needs to be as high as possible while series resistance has to be as small as possible. Lastly, the η_{PCE} is represented as the ratio of P_{max} obtainable to the incident radiation power (P_{in}) on the device surface (Eq. 3.2).

$$FF = \frac{J_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}} \quad (3.1)$$

$$\eta_{PCE} = \frac{P_{max}}{P_{in}} = \frac{FF \cdot J_{sc} \cdot V_{oc}}{P_{in}} \quad (3.2)$$

Figure 3.2. A typical current-voltage curve for light current in a PV cell.

The current-voltage characteristics of the dye-sensitized test cells were measured with a Keithley model 2420 source meter under one sun condition using a solar light simulator (Abet Technologies S2000 with a 550 W xenon lamp and an AM 1.5 filter, 100 mW cm^{-2}). Prior all measurements, a black mask with an exposed region of 0.25 cm^2 was placed over each device to define the active area and eliminate any refracted and reflected light from outside this area. The incident photon-to-electron conversion efficiency (IPCE) was also recorded with the Keithley source meter. During the measurement, light from the 150 W xenon lamp situated in Newport 67005 research arc lamp housing was focused through a Newport 74125 Oriel 260 1/4 m monochromator onto the surface of the DSSC under test. If not specified otherwise, the IPCE was measured under short circuit conditions. Additionally, the IPCE is defined as the ratio of the number of charge carriers ($n_{\text{electron}}(\lambda)$) collected in the solar cell to the number of photons of a given energy ($n_{\text{photon}}(\lambda)$) incident on the active surface of the device, and could be represented by the following equation,

$$\text{IPCE}(\lambda) = \frac{n_{\text{electron}}(\lambda)}{n_{\text{photon}}(\lambda)} = \frac{I(\lambda)/e}{P_{\text{in}}(\lambda)/h\nu} = \frac{I(\lambda)}{P_{\text{in}}(\lambda)} \cdot \frac{h\nu}{e\lambda} \quad (3.3)$$

where $I(\lambda)$ is the photocurrent measured under monochromatic illumination at a given wavelength λ with an irradiation power intensity of $P_{\text{in}}(\lambda)$.

Flat band potential measured using Mott-Schottky equation

Poission's equation can be solved by employing Boltzmann distribution of electron in space charge and Gauss's law of electric field in the interface of charge within the region. It gives to the Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_D} (V - V_{fb} - \frac{k_B T}{e}) \quad (3.4)$$

Where C is the interfacial capacitance, A is the area, N_D the number of donors, V the applied voltage, k_B is Boltzmann's constant, T the absolute temperature, and e is the electronic charge.

As a result from the equation, plotting of $\frac{1}{C^2}$ vs V should provide a linear line, in which V_{fb} can be obtained from interception with x-axis with $\frac{k_B T}{e}$ as constant, as shown in the figure. Thus any shift intersect indicate change in flat band potential. Besides, N_D can be easily obtained from the slope with a known ϵ and A .

Figure 3.3 A typical Mott-Schottky plot

3.4 Other characterization techniques

There are some other characterization techniques employed in this project to further study the mechanism of DSSC. They are summarized as follow:

- (1) The optical transmittance and absorbance spectra between the wavelengths of 200 nm and 800 nm were calibrated using a UV-visible spectrophotometer (Shimadzu UV-2450, Japan) with 3.5 ml of quartz cuvette. Measurements were conducted with reference to optical transmittance of air.
- (2) Interfacial impedance of assembled DSSC was analyzed with the aid of electrochemical impedance spectroscopy (EIS) (Solartron Analytical 1260 Impedance/Gain-phase Analyzer in conjunction with the 1294 Impedance Interface measuring unit, United Kingdom). The EIS were recorded under open circuit voltage conditions over a frequency range of 0.1 to 10^5 Hz with applied alternating current amplitude of 10-15 mV.

- (3) The morphologies of the fabricated films and materials were obtained using field emission scanning electron microscopy (FESEM) (JEOL JSM-6700F, Japan) and transmission electron microscopy (TEM) (JEOL JEM-2010, Japan).
- (4) X-ray diffraction (XRD) (Siemens D5008) was used to determine the crystallinity and crystal structure of the materials.
- (5) Energy dispersive spectroscopy (EDS) (Oxford Instrument EDS model 6587 coupled with a SEM JEOL JSM5600LV and Oxford Instrument Link ISIS system software).

Chapter 4 Nanoporous Tin Oxide Photoelectrode Prepared by Electrochemical Anodization in Aqueous Ammonia to Improve Performance of Dye Sensitized Solar Cell

4.1 Introduction

Dye-sensitized solar cell (DSSC) has been intensively researched over the last few decades due to its low fabrication cost and potential high power conversion efficiency.^[18, 160, 184] To date, the most researched DSSCs are based on TiO₂ nanoparticle photoanode which could achieve power conversion efficiency, PCE~12%. However, n-type tin oxide (SnO₂) has attracted great interest as the photoelectrode material in DSSC due to its favourable properties over TiO₂ such as wider bandgap (3.5eV) which makes fewer oxidative holes in the valance band and benefits for the long-term stability of DSSC, high electron mobility (~100-200 cm² V⁻¹s⁻¹) which suggests a faster diffusion transport of photo-induced electrons.^[35] Besides SnO₂ deposited onto FTO can negate interfacial effects due to the homo-junction with respect to F-doped SnO₂ substrate. Recently, composite photoanode such as TiO₂/SnO₂ nanotube, nanosheet and ZnO/SnO₂ nanoparticles have been demonstrated to be more efficient materials in photo-conversion efficiency than that of TiO₂ nanoparticles.

Reproduced in part from Teh, J.J.;Ting, S.L.;Leong, K.C.;Li, J.;Chen, P., Teh, J.J.;Guai, G.H.;Wang, X.;Leong, K.C.;Li, C.M.;Chen, P., Nanoporous tin oxide photoelectrode prepared by electrochemical anodization in aqueous ammonia to improve performance of dye sensitized solar cell, Journal of Renewable and Sustainable Energy **2013**, 5, 023120-8. Copyright (2013) with permission from American Institute of Physics.

However, unmodified SnO₂ nanoparticle-based DSSCs exhibit lower open circuit voltage (V_{oc} , typically between 0.3-0.4 V) due to poor interconnectivity between particles that results in high recombination losses and low fill factor, as compared to the conventional TiO₂-based DSSCs (0.7-0.8 V) .^[185-188] Such small V_{oc} is attributed to the lower conduction band edge E_c of SnO₂ (by ~0.3 eV) than that of anatase TiO₂. SnO₂ also has a low charge recombination resistance which ensures fast backflow of photoelectrons to the electrolyte and a negative shift of the electron quasi-Fermi level (E_{F-n}), leading to further reduction of V_{oc} .^[127] To overcome these issues, this study develops a photoelectrode based on sieve-like SnO₂ nanoporous sheets formed through anodization of tin foil in aqueous ammonia solution. Similar to the recent application of orderly one-dimensional SnO₂ nanostructures such as nanowires and nanotubes, the well-interconnected SnO₂ sieve walls were found to achieve better charge transportation to suppress charge recombination events.^[189, 190] As the result, DSSC with anodized sieve-liked SnO₂ sheet (ASnO₂) based photoelectrode achieves higher V_{oc} (0.61V) than that based on SnO₂ nanoparticles (0.51V) with TiCl₄ treatment. The closely packed pore arrangement of the metal oxide sheets also provides higher charge injection rate, which in turn leads to better photocurrent and enhanced device performance.

4.2. Experiment synthesis

4.2.1 Synthesis of anodized SnO₂.

High purity of tin foils (0.126 mm thick, 99.9% purity, Sigma-Aldrich) with dimensions of 2 cm × 1 cm were cleaned in ethanol and DI water under sonication before it was being used as the working electrode in anodization. Platinum foil with the same dimensions was used as the counter electrode. At room temperature, a constant voltage (40 to 60V) was applied to the electrodes in an electrolyte of 0.5M NH₄OH (Sigma-Aldrich) for anodization. As prepared ASnO₂ on tin foil was immersed into DI water and put under sonication for 10 minutes to detach nanoporous tin oxide from tin substrate. This was repeated for several times to obtain significant amount of nanoporous tin oxide. Nanoporous tin oxide suspended in DI water was then tip-sonicated for 30 times with 2s sonication and 2s pause. The solution was filtered using membrane filter with pore size of 0.22 μm and then dried at 70°C.

4.2.2 Synthesis of SnO₂ nanoparticle.

1.2 g of anhydrous SnCl₂ (Sigma-Aldrich, 99.9%) was added into 60 mL of distilled water with stirring, and formation of white precipitate was observed. Subsequently, 1 mL of 40% HCl was added to dissolve the precipitate. The solution was then refluxed at 90°C for 5 hr under continuous stirring. During the reaction, the solution gradually turned opaque. After synthesis, SnO₂ nanoparticles were collected by centrifugation and rinsed with DI water and ethanol, followed by drying at 70 °C in air.

4.2.3 Electrode preparation and DSSC fabrication.

ASnO₂ or SnO₂ nanoparticle powder was made into paste, following the standard procedure for making TiO₂ paste for DSSCs.^[191] The photoelectrode was made by blading the paste on the conductive substrate (fluorine-doped SnO₂ glass, FTO), with an active area of 0.12 cm². The electrode was annealed at 450 °C for 1 hr to obtain higher crystallinity, followed by immersion into TiCl₄ solution (20 mM) for 30 min at 70°C. It was subsequently sintered at 450 °C for 30 min in air. Finally, the photoelectrode was soaked in a mixture solution of equal amount of tert-butanol and acetonitrile containing 0.5 mM N719 dye for 16 hr at room temperature and then washed with ethanol. Platinum sputtered FTO was used as the counter electrode. 50 mM tri-iodide in acetonitrile (AN-50, Solaronix) was used as the low viscosity electrolyte.

4.3 Material Characterization

Figure 4.1 SEM images of (a) ASnO₂ sheet (top view), (b) ASnO₂ sheets (cross-section), (c) ASnO₂ coated on photoelectrode, (d) SnO₂ nanoparticles

Figure 4.1(a) shows the SEM image (top view) of the ASnO₂ sheets formed after anodization of a tin foil at 60 V. Unlike anodization of TiO₂ which form nanotube array, ASnO₂ has a sieve-like nanoporous structure with an average pore size ~40 nm, which is in good agreement with the previously reported works.^[192-195] Figure 4.1(b) depicts the cross-section of ASnO₂, in which multiple sheets of sieve-like ASnO₂ are formed during the anodization process due to internal cracking of the anodized oxide caused by gases generated from hydrolysis of water.^[193] The thickness of each ASnO₂ sheet is ~150 nm. ASnO₂ sheets were harvested from the tin substrate by sonication and made into paste in order to be coated on the photoelectrode as a thin-film. As

revealed by SEM (Figure 4.1(c)), the ASnO_2 sheets on photoelectrode form aggregates while retaining its nanoporous structure to pose a large surface area. SnO_2 nanoparticles (~ 100 nm in diameter) (Figure 4.1(d)) was also synthesized as the comparison material for photoelectrodes.

Figure 4.2 (a) XRD spectrum, (b) infrared spectrum, (c) UV-vis absorbance spectra and (d) optical bandgap calculation of ASnO_2 annealed at 450°C .

As shown in Figure 4.2(a), XRD spectrum of ASnO_2 exhibits prominent diffraction angles at 26.5° , 34° and 52° , corresponding well to the tetragonal SnO_2 (JCPDS, 41-1445). The presence of such sharp peaks signifies that the ASnO_2 sheets exhibit high crystallinity with the grain size of 4.8 nm, as estimated by Scherer's formula: $D =$

$K\lambda/(\beta\cos\theta)$, where D is the grain size, K is Scherer constant (usually taken as 0.94) and β is the full-width-at-half-maximum (FWHM) for the peak centered at 0.463 radians.^[196] In the spectrum of Fourier transform infrared spectroscopy (FTIR) shown in Figure 4.2(b), the vibration absorption peak of the Sn-O bond in SnO₂ is detected at 593 cm⁻¹, while that of Sn-OH bond is absent at 530 cm⁻¹.^[197] This confirms that A-SnO₂ consists only of the stannic oxide and not a mixture of both oxide and hydroxide. The stretching adsorption peak of O-H is located at 3390 cm⁻¹ while the peak at 1640 cm⁻¹ could be attributed to the adsorption of moisture on the metal oxide. A-SnO₂ was also found to have a strong light adsorption at 394 nm, which indicates an optical bandgap of 3.15 eV (Figure 4.2(d)). This bandgap is slightly lower than that of reported 3.6eV.^[198]

4.4 A-SnO₂ based DSSC device performance

Figure 4.3 (a) Photocurrent density-voltage curves measured under simulated sunlight power of 100 mW cm⁻² and (b) dark currents of the DSSCs equipped with A-SnO₂ or SnO₂ nanoparticles

Figure 4.3(a) shows the characteristic current density-voltage (J-V) curves of DSSCs based on TiCl₄-treated A-SnO₂ photoelectrodes with different film thickness. Their corresponding photovoltaic parameters are summarized in Table 4.1. The

commonly used DSSCs based on TiCl_4 -treated SnO_2 -nanoparticle-coated photoelectrodes were also prepared as a comparison (control). As shown in Table 4.1, with identical film thickness (8 μm), the ASnO_2 photoelectrode significantly outperforms the SnO_2 nanoparticle electrode in terms of short-circuit photocurrent density (J_{sc} : 6.85 vs. 3.64 mA/cm^2) and open circuit voltage (V_{oc} : 0.56 vs. 0.51 V). While the thickness of ASnO_2 film increasing from 5 μm to 10 μm , the dye loading increases from 0.10 to $0.63 \times 10^{-7} \text{ mol}/\text{cm}^2$ and the photocurrent is improved from 4.44 to 7.60 mA/cm^2 . Although both V_{oc} and fill factor (FF) decrease with thicker oxide film, the large enhancement in photocurrent leads to significant improvement in the overall power conversion efficiency (PCE) (from 1.29% with 5 μm film to 1.71% with 10 μm film).

Table 4.1 Photovoltaic parameters for DSSCs with 5 μm , 8 μm and 10 μm ASnO_2 film and 8 μm SnO_2 nanoparticle film.

Film	Surface Area (m^2/g)	Dye loading ($\times 10^{-7} \text{ mol}/\text{cm}^2$)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
8μm SnO_2 nanoparticles	166.7	0.45	0.51 ± 0.00	3.64 ± 0.05	55.0 ± 2.4	1.02 ± 0.02
5μm ASnO_2	72.5	0.10	0.61 ± 0.01	4.44 ± 0.11	47.5 ± 1.7	1.29 ± 0.03
8μm ASnO_2	-	0.36	0.56 ± 0.02	6.85 ± 0.25	43.2 ± 1.8	1.66 ± 0.04
10μm ASnO_2	-	0.63	0.53 ± 0.00	7.60 ± 0.07	40.0 ± 1.6	1.71 ± 0.02

Interestingly, although the 8 μm thick ASnO_2 photoelectrode has lower dye loading as compared to the SnO_2 nanoparticle based photoelectrode of the same film thickness, its performance is superior. To better understand the enhancement mechanism for

ASnO₂ based DSSC, the dark currents were measured (Figure 4.3(b)). Since the dark current of a DSSC represents the backflow of electrons from the photoelectrode to the redox electrolyte, the higher onset potential of ASnO₂ electrode suggests that it has a lower charge recombination rate as compared to SnO₂ nanoparticle electrode.^[199, 200] It is also noted from Figure 4.3(b) that the recombination rate undesirably increases with the increasing thickness of ASnO₂ film, as evidenced by the decreasing onset potential. This explains the drop of V_{oc} and FF with a thicker film.

4.5 Open-circuit voltage decay analysis

Figure 4.4 Open-circuit voltage-decay (OCVD) curves (a) and electron lifetime as a function of V_{oc} for DSSCs using ASnO₂ photoelectrodes with different film thicknesses.

To further investigate the effects of increasing ASnO₂ thickness on charge recombination, open-circuit voltage-decay (OCVD) technique was employed in which the decrease in V_{oc} is continuously monitored while turning off the light shone on the device (Figure 4.4 (a)). The electron lifetime is given by $\tau_n = -(kT/e)(dV_{oc}/dt)^{-1}$, where kT is the thermal energy, e is the positive elementary charge, and dV_{oc}/dt is the decaying rate of V_{oc} .^[201] As shown in Fig. 4b, a thicker ASnO₂ photoelectrode has a

shorter electron life time, which implies a higher charge recombination rate.^[202] The dependence of τ_n on V_{oc} is linear shown in Figure 4.4(b), indicating the absence of surface traps which could cause recombination of electrons with the redox electrolyte through tunnelling.^[203]

4.6 Electrochemical analysis of $ASnO_2$ DSSC

Figure 4.5 Nyquist plots (a) and their zoom-in views in high-frequency region (b) of the $ASnO_2$ and SnO_2 nanoparticles based DSSCs.

Electrochemical Impedance Spectroscopy (EIS) measurements were also employed to provide further understanding of charge transport and transfer properties of the $ASnO_2$ based DSSC.^[204-207] In Figure 4.5 (a) shows the Nyquist plots of DSSCs with SnO_2 nanoparticle electrode and $ASnO_2$ electrode with different film thickness, measured under 100mWcm^{-2} light illumination. In each plot, the smaller (preceding) semicircle at the high-frequency region represents the redox reaction of I^-/I_3^- at the Pt(counter electrode)/electrolyte interface (enlarged view shown in Figure 4.5 (b)), while the larger semicircle at the low-frequency region is ascribed to the combined effect of charge transfer and/or recombination across the oxide/dye/redox electrolyte

interface. The equivalent circuit of the DSSC device is depicted in Figure 4.5 (b) (inset), where R_s is the series resistance; R_1 and R_{pt} represent the interfacial charge transfer resistances at the photoelectrode and counter electrode, respectively.^[208-210] The fitted values of R_s , R_1 and R_{pt} are summarized in Table 4.2. As shown, R_1 (162.6 Ω) of the $ASnO_2$ photoelectrode (8 μm thick film) is much smaller than that of the SnO_2 nanoparticle based electrode of the same film thickness (366.9 Ω). Such reduction in the interfacial charge transfer resistance implies a faster electron injection rate, therefore, an improved photocurrent. This is likely attributed to the interconnected sieve-like structure of $ASnO_2$ which provides a large porous and conductive surface for rapid transfer of electrons from photo-excited dye molecules. When the thickness of the $ASnO_2$ film is increased to 10 μm , R_1 is further reduced to 87.1 Ω which in turn contributes to the even better device performance.

Table 4.2 The series resistance (R_s) and interfacial charge transfer resistance (R_1 at photoelectrode and R_{pt} at counter electrode)

	R_s / Ω	R_1 / Ω	R_{pt} / Ω
8μm SnO_2 nanoparticles	35.26	366.9	5.20
5μm $ASnO_2$	31.16	201.9	1.85
8μm $ASnO_2$	33.05	162.6	2.02
10μm $ASnO_2$	37.64	87.1	5.58

4.7 Conclusion

In summary, nanoporous sieve-like SnO₂ sheets were synthesized by anodization in aqueous ammonia solution (ASnO₂). DSSCs equipped with 8 μm of ASnO₂ based photoelectrode were found to outperform DSSCs equipped with same thickness of SnO₂ nanoparticle based photoelectrode in terms of open circuit voltage (0.56V over 0.51), short circuit current (6.85mA/cm² over 3.64mA/cm²) and power conversion efficiency (1.66% over 1.02%). The enhancements were found due to suppressed charge recombination and reduced charge transfer resistance. This study further corroborates the potentials of SnO₂ in the solar cell applications and suggests that the performance of SnO₂ based DSSCs could be improved by engineering the interconnectivity of SnO₂ structure.

Chapter 5 Gallium-doped Tin Oxide Nano-cuboids for Improved Dye Sensitized Solar Cell

5.1 Introduction

Dye-sensitized solar cells (DSSCs) are promising green energy devices with low-cost which typically consist of a photoanode made by coating mesoporous metal-oxide semiconductor film on fluorine-doped tin oxide (FTO) glass, a platinum coated FTO counter electrode, dye molecules incorporated onto photoanode, and electrolyte.^[29, 184] But the practical use of current DSSCs is limited by their low power conversion efficiency.

The semiconducting metal-oxide material used is the key component governing the device performance, including photoelectron injection, electron transfer and transport, dye loading capacity, and charge recombination.^[211, 212] Thus far, titanium oxide (TiO₂) is the most popular choice. The conversion efficiency of TiO₂ based DSSCs, however, is largely limited by its low conductivity which, in turn, leads to undesired charge recombination. Tin oxide (SnO₂) has recently been considered as a promising alternative due to its wider bandgap (3.5 eV) which benefits for the long-term stability of DSSCs against UV degradation, and high electron mobility (~100-200 cm² V⁻¹s⁻¹) which reduces charge recombination between injected electrons and holes in valence band.^[35, 60] In addition, SnO₂ is able to form homo-junction with FTO substrate, therefore, negate the issue of high contact resistance originated from the hetero-junction between TiO₂ and FTO.^[213]

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But SnO₂-based DSSCs critically suffer from the problem of low conduction band edge (E_c is ~0.3 eV lower than that of anatase TiO₂), which causes fast backflow of photoelectrons to the electrolyte (a form of charge recombination) and thus reduction of open circuit voltage (V_{oc}).^[127, 185, 186, 214] To tackle this issue, a thin layer of metal oxide with higher conduction band edge (e.g., Al₂O₃, Cr₂O₃, TiO₂, CdO, CuO, ZnO, MgO) has been coated onto SnO₂.^[128-131] Alternatively, ternary oxides (Zn₂SnO₄ and BaSnO₂) have been synthesized to favorably shift the band structure.^[134-137, 215] However, the achieved improvement is still limited.

Herein we report the synthesis of gallium (Ga) doped SnO₂ nano-cuboids (Ga-SnO₂-NC) using the commercially available SnO₂ nanoparticles (SnO₂-NP) as the growth seeds under hydrothermal condition. We demonstrate that Ga-doping increases the band edge of SnO₂ whereby suppressing photoelectron backflow thus achieving a higher open circuit voltage ($V_{oc} \sim 0.74$ V). This value is comparable to that of TiO₂-NP based photoanodes and, to the best of our knowledge, the highest for SnO₂ based electrodes without TiO₂ coating. With a high V_{oc} as well as a high fill factor (FF $\sim 73.7\%$), the DSSCs equipped with Ga-SnO₂-NC photoanode are able to achieve a power conversion efficiency up to $\sim 4.05\%$ ($\sim 185\%$ improvement as compared to the use of commercial SnO₂ nanoparticles). Finally, the underlying mechanism of such enhancement is proposed.

5.2 Synthesis of Ga-SnO₂-NC

All chemicals were purchased from Sigma-Aldrich except gallium nitrate hydrate from Alfa Aesar and absolute ethanol from Merck.

Ga-SnO₂-NCs were synthesized by a hydrothermal method with SnO₂ NP of size ~15nm as a seed layer for the growth of nanocuboid (Figure 5.1). Specifically, 1 mmol of tin (IV) chloride pentahydrate, predetermined gallium nitrate hydrate (0, 1, 3, 5% molar ratio to tin chloride) and 15 mmol of sodium hydroxide were dissolved in 25ml DI water. After continuous stirring for 10 min, 60 mg of tin oxide nanoparticles was added and tip-sonicated for 50 cycles (2s sonication and 2s pause for each cycle). The suspension was then transferred into 40 ml Teflon-lined autoclave and reacted hydrothermally at 180°C for 24 hr. After cooling down to the room temperature, the products were centrifuged, rinsed thoroughly with distilled water for several times, and finally dried at 70 °C.

Figure 5.1 Grow of Ga-SnO₂-NC from SnO₂ NP as seed

5.3 Electrode Fabrication

Ga-SnO₂-NC powder was made into paste using the standard procedure for DSSC electrode fabrication.^[191] The photoanode was fabricated by doctor-blading the paste on fluorine-doped SnO₂ glass (FTO), with an active area of ~0.12 cm² and thickness

of $\sim 8\mu\text{m}$. It was subsequently sintered at $450\text{ }^{\circ}\text{C}$ for 30 min in air. Finally, the photoanode was soaked in a mixture solution of equal amount of tert-butanol and acetonitrile containing 0.475 mM N719 dye and 0.025 mM D149 dye for 16 hr at room temperature, followed by washing with ethanol. Platinum sputtered FTO was used as the counter electrode. 50 mM tri-iodide in acetonitrile (AN-50, Solaronix) was used as the low viscosity electrolyte.

5.4 Characterization of physical property of Ga-SnO₂-NC

The crystallinity of the nanostructures was investigated using Siemens D5008 X-ray diffractometer with Cu K α radiation ($\lambda=1.5406\text{ \AA}$) at 40 kV and 40 mA, scanning from $2\theta=20^{\circ}$ to 70° with a scan rate of 2° per minute. The morphology was observed using FESEM (JEOL JSM-6700) and TEM (JEOL 2010). UV-vis absorbance spectra were measured by Shimadzu 3600 UV-vis Spectrophotometers. XPS measurement was obtained from a ESCALAB MK-II system. The current-voltage tests of DSSCs were performed under one sun condition using a solar light simulator (Abet Technologies S2000 with 550W xenon lamp and an AM 1.5 filter, 100 mW/cm^2). Electrochemical impedance spectroscopy (EIS) was performed under illumination of a solar light simulator and the cell was biased at the V_{OC} induced by the illumination with the frequency range of 0.1 Hz to 0.1 MHz. The flat-band potential (V_{fb}) was calculated from the Mott-Schottky plots. To obtain the Mott-Schottky plot, the Ga-SnO₂-NC film was soaked in a 0.5M Na₂SO₄ aqueous solution and the impedance was measured as a function of the applied AC voltage (500 Hz, 10mV).

Ga-doped SnO₂ nano-cuboids (Ga-SnO₂-NC) were hydrothermally grown using the commercial SnO₂-NPs as the seeds with the doping level controlled by the molar ratio between Ga and Sn precursors (1, 3, or 5%). FESEM image shows that the sizes

of the SnO₂-NP range from 10-100 nm (Figure 5.2(a)). After hydrothermal deposition, aggregates of nano-cuboids (20-50 nm) are obtained (Figure 5.2(b)). Figure 5.2(c) and 5.2(d) shows high resolution TEM reveals that the inter-planar spacing of the nano-cuboid crystal is ~0.45 nm corresponding to the distance of the neighboring (100) planes in tetragonal rutile SnO₂ structure.

Figure 5.2 (a) FESEM image of SnO₂-NP, (b) FESEM image of Ga-SnO₂-NC, (c, d) HR-TEM of Ga-SnO₂-NC.

XPS shows that Ga 2p_{2/3} peak (at 1117.1 eV) arises commensurate with the used dose of Ga precursor (Figure 5.3(a)), indicating the success of Ga doping. With 1% Ga precursor, the trace amount of Ga is not detectable by XPS. While the use of 3% (or 5%) Ga precursor gives the ratio of Ga to Sn to 0.024 (or 0.035) in the obtained Ga-SnO₂-NCs. Consistently, the peaks of Sn 3d_{5/2} and Sn 3d_{3/2} in XPS spectrum left-shift with increasing Ga doping level resulting from the defects and charge imbalance induced by the dopants (Figure 5.3(b)).^[216, 217] The symmetric and narrow peaks (FWHM $\approx$ 1.35 $\pm$ 0.05 eV) suggest the oxidation state of Sn to be 4+.^[218, 219] On the

other hand, Ga-doping does not alter the XRD spectrum of Ga-SnO₂-NC (Figure 5.3(c)) which exhibits prominent diffraction angles at 26.6°, 33.9° and 51.8°, corresponding well to the rutile tetragonal SnO₂ (JCPDS, 41-1445). This suggests that the dopants are well-dispersed and do not cause significant change in the SnO₂ lattice structure. The sharp XRD peaks indicates that Ga-SnO₂-NCs exhibit high crystallinity with the grain size of ~42.2 nm (similar to the size of nano-cuboid) which is estimated by Scherer's formula: $D = K\lambda/(\beta\cos\theta)$, where D is the grain size, K is Scherer constant (usually taken as 0.94) and β is the full-width-at-half-maximum (FWHM) for the peak centered at 0.464 radians.^[89] Thus, individual nano-cuboids are essentially single crystals.

Figure 5.3 XPS spectra (a and b), XRD patterns (c), and Mott-Schottky plots of Ga-SnO₂-NCs with different doping levels (black, red, blue, green curves correspond to the use of 0, 1, 3, 5% of Ga-precursor during synthesis, respectively). In the y-axis of Mott-Schottky plot, C refers to interfacial capacitance.

The difference between the Fermi level of the active semiconducting material in a DSSC and the oxidation potential of the electrolyte determines the V_{oc} of DSSC. In order to ascertain the effect of Ga-doping towards the band edge or Fermi level, flat-band potentials (V_{fb}) of Ga-SnO₂-NC based photoanode were determined from Mott-Schottky plots (Figure 5.3(d)).^[220, 221] According to the Mott-Schottky theory, $V_{fb} = E - kT/e$ where E is interpolated from the linear fitting of the transition region of Mott-Schottky plots with x-axis; k is the Boltzman constant; T is the temperature; e is the elementary charge. As shown in Figure 5.3(d), V_{fb} left-shifts with increasing Ga-doping (from -0.34 with 0% Ga to -0.81 V with 5% Ga precursor), indicating that Ga-doping causes increase of Fermi-level which promises a higher V_{oc} and a higher fill-factor due to enhanced impedance to the backflow of photoelectrons to the electrolyte.

5.5 Optical property of Ga-SnO₂-NC

UV-vis absorption of various doping of Ga-SnO₂-NC was measured and plotted in Figure 5.4 to determine its optical bandgap. The direct optical band gap (E_g) was determined using equation below:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (5.1)$$

where $h\nu$ is the Photon energy, B is a constant related to the material, α is the absorption and n takes the value of 2, 3, 1/2 and 3/2 depending on the nature of the material. n=1/2 has been employed as SnO₂ has the nature of direct band gap.

Figure 5.4 Optical band gap calculated from UV-vis absorption

E_g obtained by extrapolating the straight line in the $(\alpha h\nu)^2$ vs $h\nu$ graph at $(\alpha h\nu)^2 = 0$. We may observe that the optical bandgap increases slightly from 3.15eV to 3.2eV as the doping concentration increases from 0% to 5%. UV-vis absorption measurements suggest that Ga-doping leads to up-shift of band edge instead of widening the band gap of SnO_2 .

5.6 Ga-SnO₂-NC based DSSC device performance

To make the photoanode, the commercial SnO_2 -NPs or the prepared Ga-SnO₂-NCs were doctor-bladed onto FTO substrate followed by immersion into a mixture of dye D149 and N719. Dye 149 adheres well with Ga-SnO₂-NC whereas N719 absorbs short-wavelength light more efficiently (desirable for high V_{oc}). Using D149 alone provides high short circuit current density (J_{sc}) but low open circuit voltage (V_{oc}) while using N719 alone does the opposite. We found that the ratio of 1:19 between D149 and N719 gives the highest power conversion efficiency due to the synergistic combination of the two dyes. This ratio is thus used for all the following experiments.

The fabricated DSSCs using a platinum counter electrode were then evaluated under the illumination of one sun condition (100 mW cm^{-2}). Figure 5.5(a) depicts the current density-voltage (J-V) curves of DSSCs equipped with SnO_2 -NP based anode or Ga- SnO_2 -NC based anodes. As shown in Table 5.1, a remarkable enhancement (61%) of power conversion efficiency (PCE) is observed with SnO_2 -NCs (without doping) as compared with SnO_2 -NPs. This is attributable to the improved interconnectivity between SnO_2 nano-cuboids as compared with that of SnO_2 nanoparticles. With Ga-doping (3% Ga precursor), PCE is further boosted by 124% to 4.05%. Higher Ga-doping (5%) achieves high V_{oc} (0.75V) and fill factor (FF, 74.6%) due to elevation of band edge. These values outperform that of all previously reported SnO_2 based DSSCs without TiO_2 coating. But, on the other hand, such high Ga-doping leads to decrease of J_{sc} because too high a band edge impedes injection of photoelectrons thereby degrades PCE.

Figure 5.5. (a) Photocurrent density vs. voltage measured under the simulated sunlight (100 mW cm^{-2}). (b) Dark currents of the DSSCs equipped with SnO_2 -NP or Ga- SnO_2 -NC based photoanode. Black, red, blue, green curves correspond to the use of 0, 1, 3, 5% of Ga-precursor during synthesis, respectively.

The dark current of a DSSC represents the backflow of electrons from the photoanode to the redox electrolyte and dye. Hence the higher onset potential to turn on the dark current suggests a lower charge recombination rate.^[199, 200] As observed from Figure 5.5(b), DSSCs equipped with SnO₂-NP, SnO₂-NC, or slightly-doped Ga-SnO₂-NC (1% Ga precursor) based photoanode exhibit similar charge recombination rate. Nevertheless the recombination rate decreases desirably when Ga-SnO₂-NCs are doped to a higher level (3 or 5 % Ga precursor) because significantly elevated band edge leads to high resistance for electron back-flow to the electrolyte (Figure 5.6).

Figure 5.6 Illustration of band structures and electron transfers

Table 5.1 Comparison of photovoltaic parameters for DSSCs with a SnO₂-NP or Ga-SnO₂-NC based photoanode. The percentage values indicate the concentration of Ga-precursor used in the synthesis.

Sample (n = 5)	V _{oc} (V)	J _{sc} (mA/cm ²)	$FF = \frac{P_{max}}{J_{sc}V_{oc}}$ (%)	$PCE = \frac{J_{sc}V_{oc}FF}{P_{in}}$ (%)
SnO₂-NP	0.59±0.017	7.00±0.110	34.4±4.14	1.42±0.326
0% Ga-SnO₂-NC	0.62±0.000	7.56±0.176	48.9±2.42	2.29±0.120
1% Ga-SnO₂-NC	0.62±0.006	7.51±0.350	55.6±1.40	2.59±0.068
3% Ga-SnO₂-NC	0.74±0.012	7.41±0.085	73.7±1.10	4.05±0.135
5% Ga-SnO₂-NC	0.75±0.006	6.30±0.143	74.6±0.57	3.52±0.070

5.7 Electrochemical analysis of Ga-SnO₂-NC based DSSC

Electrochemical impedance spectroscopy (EIS) was employed to further investigate the effect of Ga-doping on the charge transport and transfer properties of the DSSC. Figure 5.7 shows the Nyquist plots of DSSCs using SnO₂-NC photoanode with different Ga-doping levels, measured under 100mWcm⁻² light illumination, with frequencies ranging from 0.1 to 100 kHz and an alternating current amplitude of 10 mV. The curves are fitted with the equivalent circuit illustrated in the inset where R_s is the series resistance; R_a or R_{pt} represents the interfacial charge transfer resistances at the photoanode or counter electrode; CPE1 and CPE2 are the Helmholtz capacitance at respective electrodes.^[222] In the Nyquist plot, the size of the smaller semicircle at high frequency range corresponds to the total charge transfer impedance at the counter electrode (R_{pt} in parallel with CPE2) while the larger semicircle at low frequency range corresponds to that of photoanode (R_a in parallel with CPE1). The ease of electron transfer from excited sensitizer (dye) molecules to electrode and the

difficulty of electron backflow to electrolyte lead to a small R_a . All the EIS fitted parameters are listed in Table 5.2. The EIS measurements reveal that R_a of photoanode largely drops from 89.3 to 53.9 Ω when Ga-doping increases to 3% (precursor concentration). This is because 1) Ga-SnO₂-NC, with an elevated conduction band approaching that of the sensitizer, serves as a bridge to facilitate electron transfer from the sensitizer to the underlying SnO₂-NP and subsequently the electrode or to the electrode directly; 2) increased difference between the elevated conduction band and the oxidation potential of the electrolyte also impedes the electron backflow to electrolyte (Figure 5.6). Reduced R_a leads to improved V_{oc} and FF (Table 5.2).

However, further doping (5% Ga-precursor) causes increase of R_a because an over-boosted conduction band of Ga-SnO₂-NC (greater than that of sensitizer) by a high doping level increases electron injection resistance. This explains the observed reduction in short-circuit current (J_{sc}) at this doping level (Table 5.2). Therefore, doping with 3% Ga-precursor is optimal to achieve high PCE.

Figure 5.7 Nyquist plots of DSSCs equipped with a Ga-SnO₂-NC based photoanode. The percentage values indicate the concentration of Ga-precursor used in synthesis. Inset shows the equivalent circuit.

Table 5.2 Fitted parameters for EIS spectrum of Ga-SnO₂-NC DSSC

Sample	R_s (Ω)	R₁(Ω)	R_{pt}(Ω)
0% GSO-NCA	60.1	89.3	4.95
1% GSO-NCA	59.7	77.4	1.8
3% GSO-NCA	33.8	53.9	5.56
5% GSO-NCA	41.9	56.3	8.15

5.8 Conclusion

In summary, we have demonstrated a DSSC with a Ga-SnO₂-NC photoanode, which achieves high open-circuit potential, fill-factor, and photo conversion efficiency. The improved performance is resulted from moderate up-shift of the band edge by Ga-doping which increases open circuit voltage, facilitates electron injection from the sensitizer to the electrode, and impedes electron recombination with the electrolyte. This study shows that the performance of SnO₂-based DSSCs can be improved by engineering the band structure of SnO₂.

Chapter 6 Molybdenum, Gallium co-doped Tin Oxide for enhanced photoelectrode of DSSC

6.1 Introduction

Dye-sensitized solar cells (DSSC) has increased much of the attention of researcher mainly due to its low-cost of fabrication where a photoanode and counter electrode made from mesoporous metal-oxide semiconductor film coated on fluorine-doped tin oxide (FTO) glass and sputtered platinum on FTO electrode respectively. The improvement of DSSC performance has been slowing down where the most recent record of highest power conversion efficiency is 15% in 2013, with the employment of inorganic-organic composite as dye, TiO_2 as mesoporous oxide material and an organic hole transport material. Despite the record high PCE, the issue of high charge transport resistance of TiO_2 which causes significant charge recombination has not been solved.^[177] Mesoporous oxide is the heart of DSSC which governing the whole DSSC performance, where most of the process such as excited electron injection, electron transfer and transport, dye loading capacity and charge recombination occurred in the oxide layer. However commonly used TiO_2 has low electron mobility which in turn causes high charge transport resistance. As a result, a material with higher electron mobility is needed to further improve the PCE of DSSC. In search of better and more efficient charge transport, ZnO and SnO_2 which have higher electron mobility were often been used as an alternative to TiO_2 .^[37, 118] SnO_2 has the highest electron mobility of $\sim 100\text{-}200 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ over the other two oxide, besides it has wider bandgap of 3.5 eV that prevent UV degradation and sustain long term stability.^[35, 60]

Despite SnO_2 has high electron mobility, SnO_2 based DSSC performed poorly in terms of PCE. This is mainly due to its lower conduction band edge than TiO_2 and ZnO (~ 0.3 eV lower) which causes electron backflow to electrolyte, thus causing the device to have low open circuit voltage (V_{oc}) and fill factor (FF).^[127] To tackle this issue, we had demonstrated in previous chapter that by doping of gallium (Ga) into SnO_2 lattice, we are capable of increasing the band edge of SnO_2 and thus suppress the electron backflow process.^[223] As a result, a record high V_{oc} of ~ 0.74 V and fill factor of $\sim 73.7\%$ for SnO_2 based DSSCs were achieved and the parameters are comparable to TiO_2 based DSSC. However, the overall PCE of Ga- SnO_2 -NC is still way below than of TiO_2 based DSSC, this is because gallium doping which increases V_{oc} and FF do not significantly increase short circuit current. To increase J_{sc} , lower charge transport resistance is needed to ensure fast and efficient electron transportation across the mesoporous layer.

Molybdenum doping into different type of semiconducting materials such as TiO_2 ,^[89] ZnO ,^[224] SnO_2 ,^[225] ReSe_2 ,^[89] etc, had shown great success. Mo doped SnO_2 has been applied in high-performance lithium ion batteries, in which introduction of Mo improves charge transfer kinetics and result a better Li^+ diffusion rate.^[225] Besides, Mo-doped TiO_2 was found to exhibit better photo degradation ability in its photocatalytic property study.^[226] However, Mo doped SnO_2 has yet been investigated in DSSCs.

We demonstrate that further doping of molybdenum into Ga- SnO_2 -NC is capable of increasing the short circuit current while maintaining the high V_{oc} and FF. The molybdenum, gallium co-doped tin oxide nano-cuboid (5%Mo,Ga- SnO_2 -NC) based DSSC increases the J_{sc} remarkably without compromising the V_{oc} and FF where both maintain at a consistent value, which in turn to record a high PCE of 5.75% for

Mo,Ga-SnO₂-NC based DSSC. The doping of molybdenum was found to have decreases the series resistance of DSSC device under electrochemical impedance spectroscopy (EIS). The enhancement mechanism has been proposed and studied.

6.2 Synthesis of Mo, Ga-SnO₂-NC

The synthesis of Mo,Ga-SnO₂-NC is similar to that of Ga-SnO₂-NC (in chapter 5.2). All chemicals were purchased from Sigma-Aldrich except gallium nitrate hydrate from Alfa Aesar and absolute ethanol from Merck.

Mo,Ga-SnO₂-NCs were synthesized through hydrothermal method and tin oxide NP as seed layer for the growth of nanocuboid. 1 mmol of tin (IV) chloride pentahydrate, 0.03mmol of gallium nitrate hydrate, predetermined ammonium molybdate (0,5% molar ratio to tin chloride) and 15 mmol of sodium hydroxide were dissolved in 25ml DI water. After continuous stirring for 10 min, 60 mg of tin oxide nanoparticles was added and tip-sonicated for 50 cycles. The solution was transferred into 40 ml Teflon-lined autoclave and allow to react hydrothermally under 180°C for 24 hr. After the reaction, it was cooled down naturally under room temperature, the products were cleaned by centrifuged and rinsed thoroughly with distilled water for several cycles, and lastly dried at 70 °C.

6.3 Electrode Fabrication

Mo,Ga-SnO₂-NC powder were made into paste and fabricated into DSSC photoelectrode with the standard and exactly the procedure as Ga-SnO₂-NC in Chapter 5.3.

6.4 Characterization of physical property of Mo,Ga-SnO₂-NC

The morphology of Mo,Ga-SnO₂-NC was investigated using FESEM (JEOL JSM-6700). From the FESEM image (figure 6.1(a)), the aggregates have size range from ~100 to 300nm which is very similar to Ga-SnO₂-NC from our previous work. Besides, aggregates made up from nano-cuboids of size ranging from ~20-50 nm as shown in Figure 6.1(b). There are no significant changes in morphology with the additional doping of 5% molybdenum in to Ga-SnO₂-NC.

Figure 6.1 (a) FESEM image of Mo,Ga-SnO₂-NC photoanode semiconducting layer and (b) enlarged Mo, Ga-SnO₂-NC.

6.5 Mo,Ga-SnO₂-NC based DSSC device performance

To make a fair comparison with our previous work in Chapter 5, the results of SnO₂-NPs and Ga-SnO₂-NCs based DSSCs were used directly for comparison purpose. The dye used in this experiment was the mixture of dye D149 and N719 (same as previous chapter) where it perform the best alongside with tin oxide based DSSCs. The counter electrode used remain as a sputtered platinum on FTO electrode and the current density-voltage (J-V) curves was obtained under illumination of 100 mW cm⁻² of simulated sunlight.

Figure 6.2 (a) Photocurrent density vs. voltage for SnO₂-NP, Ga-SnO₂-NC, Mo,Ga-SnO₂-NC and Mo-SnO₂-NC based photoanode measured under 100 mW cm⁻² of simulated sunlight (b) Dark currents of the respective device.

Table 6.1 Comparison of photovoltaic parameters for DSSCs with SnO₂-NP, Ga-SnO₂-NC, Mo,Ga-SnO₂-NC and Mo-SnO₂-NC photoanode.

Sample	V _{oc} (V)	J _{sc} (mA/cm ²)	$FF = \frac{P_{max}}{J_{sc}V_{oc}}$ (%)	$PCE = \frac{J_{sc}V_{oc}FF}{P_{in}}$ (%)
SnO₂-NP	0.59±0.017	7.00±0.110	34.4±4.14	1.42±0.326
0%Mo, 3%Ga-SnO₂-NC	0.74±0.012	7.41±0.085	73.7±1.10	4.05±0.135
3%Mo, 3%Ga-SnO₂-NC	0.74±0.014	8.74±0.135	72.8±1.71	4.71±0.172
5%Mo, 3%Ga-SnO₂-NC	0.74±0.015	10.53±0.170	73.5±1.45	5.75±0.163
7%Mo, 3%Ga-SnO₂-NC	0.72±0.018	10.02±0.241	71.03±2.43	5.12±0.217
5%Mo-SnO₂-NC	0.61±0.021	9.74±0.150	58.1±2.31	3.45±0.247

Photo current density versus voltage plotted in Figure 6.2(a) was carried out under 100 mW cm⁻² of simulated sunlight to investigate the effect of Mo doping in DSSCs performance. From our research on the effect of gallium doping in SnO₂-NC in chapter 5, V_{oc} and FF have shown a dramatic increment while J_{sc} remain rather constant regardless of the doping percentage. However, we observed that with further doping 5% Mo into Ga-SnO₂-NC, the short circuit current increased 42.1% to 10.53 mA/cm², while V_{oc} and FF remained at ~0.74V and ~73% respectively (Table 6.1), which in turn to have increased the overall PCE by 41.9% to 5.74% efficiency. To date, the performance of Mo,Ga-SnO₂-NC is one of the best for tin oxide based DSSCs. To further prove the effect of Mo doping, 5%Mo-SnO₂-NC was synthesized without gallium doping, and it indeed shows that the J_{sc} increased to 9.74mA/cm² while V_{oc} and FF still remained similar to an un-doped tin oxide. As a result, Mo doping play a major role in increasing short circuit current and playing no part in open circuit voltage and fill factor.

Backflow of electrons from mesoporous oxide to electrolyte can be examined through the dark current of a DSSCs.^[199, 200] High onset potential of the dark current represents a lower charge recombination rate. We may observed from figure 6.2(b), the onset potential for Ga-SnO₂-NC and Mo,Ga-SnO₂-NC are very close, while the onset potential for SnO₂-NP and Mo-SnO₂-NC are almost the same. This suggest that, unlike gallium doping, molybdenum doping do not affect much on the back flow of electrons from mesoporous oxide to electrolyte. As a result, the increment in short circuit current is not due to the conserve of photoelectron from backflow towards electrolyte.

6.6 Electrochemical analysis of Ga-SnO₂-NC based DSSC

The effect of molybdenum doping in Ga-SnO₂-NC was further investigated through electrochemical impedance spectroscopy (EIS) of the DSSC through charge transport and transfer properties. Figure 6.3 below shows Nyquist plots of DSSCs equipped with Ga-SnO₂-NC, Mo,Ga-SnO₂-NC, Mo-SnO₂-NC and SnO₂-NP photoanode and measured under 100mWcm⁻² light illumination, with frequencies ranging from 0.1 to 100 kHz. The data are fitted into the equivalent circuit shown in inset of Figure 6.3, where R_s is the series resistance; R_a or R_{pt} is interfacial charge transfer resistances at the photoelectrode and counter electrode respectively; while CPE1 and CPE2 are the Helmholtz capacitance at photoelectrode and counter electrode.^[208, 209] Figure 6.3 shows Ga-SnO₂-NC and Mo,Ga-SnO₂-NC has a similar size of semicircles, which suggest that the charge transfer resistance at both counter and photoelectrode are very similar, while fitting results shows that similar R_a of 53.9Ω and 50.7 Ω for Ga-SnO₂-NC and Mo,Ga-SnO₂-NC respectively. However, the series resistance shows desirably decrease from 33.8 Ω to 29.4 Ω with 5% of molybdenum doping. The effect is much

obviously proved with comparison of $\text{SnO}_2\text{-NP}$ and $\text{Mo-SnO}_2\text{-NC}$, where the R_s value decreases significantly from 60.1Ω to 35.7Ω with the doping of molybdenum. As a result, this shows that molybdenum doping has increases the conductivity of the mesoporous nano-cuboid film and significantly decreases the series resistance of the DSSC device, which in turn increases the photocurrent density and PCE.

Figure 6.3 Nyquist plots of DSSCs equipped with Ga- $\text{SnO}_2\text{-NC}$, Mo,Ga- $\text{SnO}_2\text{-NC}$, Mo- $\text{SnO}_2\text{-NC}$ and $\text{SnO}_2\text{-NP}$ based photoanode.

6.7 Conclusion

In conclusion, we have shown that Ga-SnO₂-NC based DSSCs can be further improved by further doping of molybdenum, in which it achieves higher short circuit current density while maintaining high open-circuit potential and fill-factor. As a results, Mo,Ga-SnO₂-NC exhibits one of the best power conversion efficiency of 5.75% among tin oxide based DSSCs. The improved performance is mainly due to the increase in conductivity across mesoporous Mo,Ga-SnO₂-NC layer where it significantly reduces the series resistance of the DSSC device and thus increases the short circuit current. Furthermore, this shows the potential of SnO₂ as a better alternative to TiO₂ as photoanode in DSSCs, and improved conductivity and connectivity is essential in SnO₂ based DSSCs

Chapter 7 General conclusion and suggestion for further research

7.1 General conclusions

In this dissertation, the kinetics and electrochemical processes in DSSCs are thoroughly discussed. Besides, latest research development of each component on materials and structural engineering are also reviewed. Tin oxide was the primary material used for mesoporous semiconducting photoanode in this project, and specific modification was done to enhance the charge transport and transfer process across the semiconducting layer thus improve DSSC performance.

The primary aim for this research project is to engineer and develop a novel material which has high efficient through low charge transport resistance. First accomplishment was done through synthesized a well connected sieve-like SnO₂ sheets (ASnO₂) by anodization in aqueous ammonia solution. DSSCs equipped with ASnO₂ photoanode outperform that of DSSCs equipped with same thickness of SnO₂ nanoparticle in terms of V_{oc} , J_{sc} and PCE. The enhancements mechanism were studied and found due to suppressed charge recombination and reduced charge transport resistance. Tin oxide has a weak adhesion between particles, thus this study emphasized the importance of a well-connected mesoporous structure for effective charge transfer and transport process, in which it retard charge recombination process and enhance the PCE. Hence, performance of SnO₂ based DSSCs could be improved by engineering the interconnectivity of SnO₂ structure.

Next, tin oxide has always been second to TiO₂ in pecking order for photoanode material mainly due to its lower conduction band edge which lead to lower short circuit current. However, we have demonstrated that through Ga-doping resulted

moderate up-shift of the conduction band edge and significantly improved open circuit voltage and fill factor. Ga-SnO₂-NC impedes electron recombination with the electrolyte to achieve achieves one of the highest open-circuit potential and fill-factor among tin oxide based DSSC. This study shows that manipulating the optimum level of conduction band edge is crucial in effective charge transport process, where low conduction band edge results in low open circuit voltage while too high the conduction band edge impede electron injection from dye. Furthermore, back flow of electron can be minimized through introducing a blocking layer which has higher conduction band edge.

Responding to the needs of increase short circuit current in Ga-SnO₂-NC based DSSC, molybdenum was introduced as a co-dopant to gallium through hydrothermal method. We have shown that can be further improved by further doping of molybdenum where higher short circuit current density was achieved while maintaining high open-circuit potential and fill-factor. Mesoporous Mo,Ga-SnO₂-NC has better conductivity across the layer which reflect on reduced series resistance of the DSSC device and increased short circuit current. This work provides an approach to increase conductivity of the SnO₂ layer by molybdenum doping, where free electron is created to aid for charge transportation.

7.2 Suggestions for future research on DSSC

Although high conductivity, connectivity and effective charge transportation can synergistically achieve higher PCE, they are proved in separate piece of works. As discussed in previous chapter, well-aligned nano-structure provides better conductivity and lesser surface traps where charges can direct diffusion across the

semiconducting layer to collector. While effective charge transportation through gallium and molybdenum doping allow tin oxide to have a much efficient charge transportation in which back-flow of electrons to electrolyte are impeded and transportation aided with high conductivity.^[199, 223] As a result, combination of well-connected mesoporous structure with effective charge transportation through foreign atom doping, such as Mo,Ga-SnO₂ nanotube or nanowire may further increase the conversion efficiency.

Further understanding and manipulation of conduction band edge of tin oxide, it is possible to extend others element to be doped. Since, gallium has proved to be successfully shifted the conduction band edge, while molybdenum increased the conductivity of the film, hence this opened the possibility that an element which may has the above two functions at the same time Therefore, further investigation of the doping effect of other elements is vital to explore and has the better understanding on the doping effect in tin oxide towards light harvesting in DSSC.

Interconnectivity of tin oxide particles is always an issue to be highlighted, so novel approach is to overcome this problem to make tin oxide a good alternative to titanium dioxide. 1-D CNT and 2-D graphene was proved to be a good charge transport enhancer where it effectively enhanced the charge transport to collector.^[184, 227] Incorporation of charge transport enhancer in doped tin oxide nanoparticles during the synthesis process to act as a bridge between particles would retard the issue of tin oxide having poor interconnectivity. Systematically examine the impact of charge transport enhancer in tin oxide is essential to further understand the light harvesting process in tin oxide based DSSC.

Tin oxide may not be superior in photoelectrode only; it may extend to electrolyte where it has been found positive with the incorporation of SnO₂ nanoparticles into the

polymer solid-state DSSC based on poly(ethylene oxide)/poly(ethylene glycol) dimethyl ether solid electrolyte.^[228] It improved electrolyte conductivity, rise in TiO₂ conduction band edge, suppressed electron recombination rate and decreases charge transfer resistance at counter-electrode/electrolyte interface. The enhancements are greatly associated to the strong Lewis acidic character of SnO₂ nanoparticles yielding to the formation of a I₃⁻ percolation layer for holes at the surface of SnO₂ and the reduction of the concentration of free I₃⁻ and K⁺ ions inside the pores of TiO₂.

Future research direction on new Si-CNT solar cell

High cost of manufacturing silicon based PV cell has limited the usage of public from harvesting solar energy. As a result, attention has been paid in searching for alternative of silicon based PV; DSSC, polymer solar cell, etc have been discovered.^[11, 21, 29, 31] Recently, carbon nanotube (CNT) which has unique electrical and optical properties has been used in conjunction with silicon wafer to form a CNT-Si heterojunction solar cell. This heterojunction solar cell is capable of performing up to 15% of power conversion efficiency.^[229]

Typical CNT-Si heterojunction solar cell has a similar device configuration with conventional PV Cell except that CNT film replaces the emitter layer. The operating mechanism of the device is still not clear, however it is believed in which CNT act as a p-type while silicon as n-type material.^[230] Photocurrent is hardly contributed by the excited electron in CNT film where it has a transmittance of more than 85%, thus it cannot be the dominant charge generation site. Electron-hole pairs are mainly generated from n-type silicon, subsequently the excited electron and hole created are separated into free charge carrier and diffused under the driving force of built in potential. CNT-Si solar cell was reported a 1.3% efficiency in 2007, in which Wei et

al deposited a layer of double-walled CNT on n-type silicon by chemical vapour deposition (CVD) method and emphasis on the importance of appropriate electrical contact of CNT and Si substrate.^[231] With years of intensive research, Jia et al. demonstrated a CNT-Si solar cell capable of achieving PCE of 13.8% which employed an in situ doping of CNT with 0.5M HNO₃. Without HNO₃ doping, the devices shows only 6.5% of PCE however it doubled with the treatment of HNO₃, thus it shows the importance of HNO₃ where it effectively connected all the CNT to silicon substrate and allowing rapid transport of charges between CNT and Si substrate.^[232] This shows that CNT-Si solar cell is a promising device which is capable of substituting conventional PV cell with lower cost of production.

Despite CNT-Si solar cell has a lower cost of production than that of PV cell, it still need some complicated and demanding steps for fabrication such as patterning for electrode, CVD grow of CNT etc.. Herein we demonstrate a much cost effective and easily fabricated CNT-Si solar cell with a PCE of 1.01% which is capable of generate photo-current in both directions (front and back). The device has a configuration of ITO-CNT-Si-ITO, where ITO (indium doped tin oxide substrate) act as a transparent electrodes while filtered multi-walled CNT (MWCNT) film and 200 μ m n-type Si substrate form the core of the cell. This device has the advantage of ease of fabrication where MWCNT deposited do not need complicated deposition method and patterning of electrode can be avoided by having ITO which has high transmittance under visible light. Furthermore, the effective area is much bigger compare with typical CNT-Si cell, due to employ of ITO as electrode where sacrifice of area for contact with opaque electrodes are not needed.

Preparation of MWCNT film

All chemicals were purchased from Sigma-Aldrich unless specifically stated. MWCNT film is prepared by simple filtering method, where 3ml of 1% Chitosan in mixture of water and acetic acid, 17ml of DI water and 10mg of MWCNT were mixed under room temperature and pressure. Subsequently, the mixture was tip sonicated for 2 hours (2s sonication and 2s pause for each cycle) to effectively disperse the MWCNT in water. Next, the mixture solution was filtered using vacuum pump with nitrocellulose filter paper, and the area of the filtered firm was controlled at 12.5 cm². The MWCNT film on filter paper was then dried at 70°C. Finally, the MWCNT film was carefully peeled off from filter paper.

Device fabrication

To fabricate the new type of CNT-Si solar cell with the configuration ITO-CNT-Si-ITO as shown in Figure 7.1 below, n-type silicon wafer with resistivity of 10 $\Omega\cdot\text{cm}$ and thickness 200 μm (purchased from latech) and area of 1cm² was clean with Hf with full care. After wafer was cleaned and dried, it was then deposit a thin layer of MWCNT with the same solution of that used to prepare MWCNT film by spray method. The sprayed MWCNT was introduced to promote better adhesion towards silicon wafer surface. Subsequently, filtered MWCNT was transferred on top of the sprayed MWCNT forming the core of the device. Finally, the device was completed with two ITO sandwiched the core component.

Figure 7.1 Schematic diagram of new type of CNT-Si solar cell

The morphology of the MWCNT film was investigated using FESEM. Figure 7.2 (a) below shows the morphology of filtered MWCNT film, while Figure 7.2 (b) shows the enlarged MWCNT film where MWCNT is in the form of bundles after filtration. The thickness of the film was also investigated to be around $10\mu\text{m}$.

Figure 7.2 (a) Standard and (b) enlarged SEM image of MWCNT film

The current-voltage tests of MWCNT-Si solar cells were performed similar to that of DSSC which is under one sun condition using a solar light simulator (Abet Technologies S2000 with 550W xenon lamp and an AM 1.5 filter, 100 mW/cm^2).

This new CNT-Si solar cell hold the same working principle with that of conventional CNT-Si solar cell where electron-hole pairs are mainly generated from n-type silicon, subsequently the excited electron and hole created are separated into free charge carrier and diffused under the driving force of built in potential and band bending in the contact region as shown in Figure 7.3 below.^[233] The present of a thin layer of native SiO_x is expected after the silicon is exposed to air for few hours.

Figure 7.3 Working principle base on band diagram of new CNT-Si

The fabricated CNT-Si solar cell were then evaluated under the illumination of one sun condition (100 mW cm^{-2}) on both silicon and CNT surface. Figure 7.4 (a) depicts the current density-voltage (J-V) curves of CNT-Si solar cell illuminated under two different surfaces. As shown in Table 7.1, a power conversion efficiency (PCE) of 1.01%, high short circuit current density (J_{sc}) of 10.5 was observed with illumination on Si surface. However, low fill factor and open circuit voltage (V_{oc}) have drag down the overall performance of the cell. From the basic understanding of CNT-Si solar cell, Si is the major component which responsible for electron-hole pair creation. However, CNT has been found capable of generating electron-hole pair as photocurrent of 3.27

mA/cm² was generated under illumination of 100mW/cm². Despite the PCE of only 0.25% when MWCNT under illumination, it shows the device is capable of working in both directions. MWCNT which do not have bandgap has arguably causes significant charge relaxation from its conduction band to valence band. Furthermore, n type silicon has been replaced with n+ and p+ silicon (0.1 $\Omega\cdot\text{cm}$) to investigate the band matching with MWCNT. However, Figure 7.4(b) shows that n+ and p+ silicon fail to generate photocurrent under illumination of light. This is likely to be due to n+ which has too high the conduction band edge as well as the valence band edge has causes exited electron to recombine with valence band of the silicon rather than transfer to MWCNT. While p+ semiconductor has too low the conduction band edge, thus excited electron experience a high barrier of electron transfer, as a result p+ semiconductor also fail to effectively act as active component of MWCNT-Si solar cell.

Figure 7.4 Current density-voltage (J-V) curves of (a) CNT- n type Si solar cell illuminated under two different surfaces and (b) CNT- n+ or p+ type Si solar cell

Table 7.1 Summary of CNT-Si solar cell performance from both Si and CNT sides of 1 sun illumination

	Si side	CNT side
J_{sc} (mA/cm²)	10.5	3.27
V_{oc} (V)	0.32	0.23
FF (%)	30.0	33.6
PCE(%)	1.01	0.25

Effect of the thickness of SiO_x towards the performance

By introducing a thin layer of silicon oxide in between CNT and silicon wafer and forming a metal-insulator-semiconductor structure can dramatically improve the solar cell device performance. The oxide layer has change the transport mechanism of the charge transport from thermionic to tunneling and neglect the electron from recombine with the hole in MWCNT.

The effect of growing SiO_x layer has been investigated in our device where by silicon wafer was exposed to HNO₃ vapor and the thickness was controlled by the duration of exposure to HNO₃. It was found that silicon wafer without exposed to HNO₃ exhibit the best performance in terms of PCE. While expose to HNO₃ gradually decreases the performance with increasing expose of HNO₃ duration. It shows that the native oxide of SiO_x layer is enough to act as the blocking layer in MWCNT-Si solar cell, while too thick of SiO_x has causes electron fail to tunnel through the oxide layer. Table 7.2 below shows the MWCNT-Si solar cell performance under HNO₃ vapor treatment for duration of 0, 1, 10, 20 second(s).

Table 7.2 Performance parameters of MWCNT-Si with treatment of HNO₃ for a period of 1, 10, 20 second(s).

	0 sec	1 sec	10 sec	20 sec
Jsc	10.5	4.47	1.37	1.11
Voc (V)	0.32	0.29	0.25	0.14
FF (%)	30.0	36.7	39.9	29.9
PCE (%)	1.01	0.47	0.14	0.05

In conclusion, we have showed MWCNT-Si solar cell is promising device where it has an extreme low cost and ease of fabrication. MWCNT film can easily been obtained through simple filtration method, while Si wafer with common clean method and two ITO glass as two electrode to form a solar cell with a PCE of 1.01%. Besides, further investigation on the effects of oxide or blocking layer on MWCNT-Si solar cell were also investigated by HNO₃ treatment. However it shows that MWCNT-Si with a very thin layer of native oxide perform the best while treatment of HNO₃ degraded the overall PCE, mainly due to blockage of electron tunnelling.

Last but not least, the newly developed MWCNT-Si solar cell is in the early stage of development, so there are a few area of improvement can be done on this solar cell system. Oxide layer in between MWCNT and silicon proved to be vital in electron-hole pair separation, and native oxide with thickness of few nanometers proved to have best performance. However, native oxide is understood to have poor quality and have a lots of defects or traps which may hinder electron tunneling across the layer. As a result, well grown silicon dioxide on the silicon wafer will definitely enhance the charge separation process, which in turn to boost both photocurrent and fill factor. Moreover, filtered MWCNT used in this device is in random orientation where the MWCNT may not have the best contact with silicon wafer. Thus, well aligned

MWCNT or SWCNT can increase the effective contact area with silicon and more junction to be formed for effective light harvesting.

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