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**NANYANG
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**NANOSTRUCTURED COMPOSITE PHOTOANODE FOR
DYE-SENSITIZED SOLAR CELL**

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NANOSTRUCTURED COMPOSITE PHOTOANODE FOR DYE-SENSITIZED SOLAR CELL

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other university or institution.

Date

Lim Chiew Keat

Summary

Dye-sensitized solar cell (DSSC) is a new generation of solar cell technology that has the potential for highly photovoltaic conversion efficiency and relatively simple fabrication process at low production cost. DSSC is made up of the sealed sandwich structure of the transparent conducting photoanode and the conducting counter electrode filled with the redox electrolyte. The photoanode is a thick (about 10 μm) mesoporous layer made from the interconnected matrix of wide band gap oxide semiconductor (typically TiO_2) nanoparticles. The mesoporous photoanode provides a large surface area for anchoring the sensitizer dye molecules and plays a vital role in transporting the photogenerated electron from the dye sensitizer towards the electrode. An efficient transport of electron from the dye sensitizer through the mesoporous oxide layer is desirable for high charge collection efficiency at the electrode.

In this project, two novel approaches were developed in DSSC fabrication to improve the charge transport property in mesoporous photoanode and the charge collection efficiency at the electrode. The improvement in the charge transport property was achieved by incorporating N-doped TiO_2 in the mesoporous TiO_2 layer of the photoanode. The enhancement in the charge collection efficiency was achieved by utilizing the SnO_2 nanorods on Fluorine-doped Tin Oxide (FTO) glass substrate as 3D electrode.

The initial focus was on the establishment of repeatable standard DSSC device fabrication procedure to serve as the baseline for further investigation. A total of three types of TiO_2 nanomaterials were evaluated as the mesoporous TiO_2 photoanode, the Degussa P25 TiO_2 ,

the Anatase TiO_2 (Alfa-Aesar) and the freshly synthesized hydrothermal TiO_2 nanoparticles. Efforts were put in the paste formulation, the coating of the paste onto the FTO glass substrate, the thermal annealing of the paste to form the mesoporous layer and the cell assembly procedure. It was found that DSSC device with photoanode made from hydrothermal TiO_2 nanoparticles delivered the best photovoltaic performance with conversion efficiency of 4.87 %. This superiority was attributed to the smaller grain size and non-agglomerated nature of the hydrothermal TiO_2 nanoparticles that resulted in highest dye-loading and yielded the highest current density. The next optimization was on the dense TiO_2 barrier layer deposited by the atmospheric pressure chemical vapor deposition (APCVD) method onto the TCO layer. It was found that the dark current was effectively suppressed by employing a 30 nm dense TiO_2 barrier layer in between the mesoporous TiO_2 film and FTO glass substrate, the type of FTO glass substrate more stable for the formation of mesoporous TiO_2 layer. This improved the photovoltaic conversion efficiency to 5.04 %. This DSSC device structure with 10 μm thick mesoporous TiO_2 photoanode derived from hydrothermal TiO_2 nanoparticles, on 30 nm TiO_2 barrier/FTO glass substrate was established as the baseline structure and process for further improvement.

In recent years, there are great interests in doping the TiO_2 nanoparticles with metal or non-metal elements to further improve the photovoltaic performance. In this project, the nitrogen-doped TiO_2 (TiN_xO_y) nanoparticles were synthesized through the single thermal oxidation step of the paste formulated with the TiN nanoparticles. The DSSC fabricated with TiN_xO_y photoanode oxidized at 450 $^\circ\text{C}$ showed optimum conversion efficiency. However, the large agglomerated particle size in the mesoporous TiN_xO_y layer resulted in

lower specific area for dye-loading, the DSSC photovoltaic performance was less efficient as compared with the standard DSSC using TiO_2 photoanode.

The mesoporous composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanode was introduced the first time in this project to improve the performance while exploring the benefits of using TiN_xO_y nanoparticles in photoanode. The DSSC sample with about 6.4 wt% of TiN_xO_y nanoparticles in mesoporous TiO_2 layer showed the highest conversion efficiency, $\eta = 6.38\%$. The 25.6% improvement in the conversion efficiency over the standard DSSC using TiO_2 photoanode was due to the combined effects of the improved spectral response and the electron transport property of the TiN_xO_y nanoparticles embedded in the composite mesoporous $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanode.

The charge collection efficiency of DSSC was further improved using the SnO_2 nanorods as 3D electrode. The SnO_2 nanorods were deposited on the FTO glass substrate pre-coated with random SnO_2 seedings using inductively coupled plasma enhanced chemical vapor deposition (ICP-CVD) method. The DSSC with SnO_2 nanorods 3D electrode improved the conversion efficiency from $\eta = 5.04\%$ for the standard DSSC with 2D FTO electrode to $\eta = 5.70\%$ with the SnO_2 3D electrode, $\sim 13.0\%$ improvement in the conversion efficiency. This was attributed to enhanced adhesion between the mesoporous TiO_2 layer with the FTO electrode and the reduction of the electron transit time.

Finally, a DSSC with composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanode on SnO_2 nanorods 3D electrode was successfully fabricated. The combined effects of these two novel approaches simultaneously enhanced the charge transport property and the charge collection efficiency of the photoanode with an impressive 28 % improvement in the conversion efficiency over the standard DSSC was achieved.

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Table of Contents

Summary	i
Acknowledgements	iv
List of Figures	x
List of Tables	xv
List of Symbols	xvii
CHAPTER 1 INTRODUCTION.....	1
1.1 Motivations.....	1
1.2 Objective	8
1.3 Major Contributions	11
1.4 Organization of Report.....	13
CHAPTER 2 OVERVIEW OF DYE-SENSITIZED SOLAR CELL	15
2.1 History of Dye Sensitized Solar Cell (DSSC).....	15
2.2 Operating Principle of DSSC	17
2.3 Device Structure of DSSC.....	19
2.3.1 Transparent Conducting Oxide Glass Substrate	20
2.3.2 Mesoporous Nanocrystalline Oxide Semiconductor Film.....	21
2.3.3 Dye Sensitizer	29
2.3.4 Redox Electrolyte.....	30
2.4 Light Harvesting by Sensitizer	31
2.5 Charge Transfer Kinetics in DSSC	33
2.5.1 Electron Injection Processes	33
2.5.2 Electron Transport in TiO ₂ Film	34
2.5.3 Charge Recombination.....	35
2.5.4 Regeneration of Oxidized Dye Sensitizer.....	36
2.5.5 Recombination between Injected Electrons and Tri-iodide Ions (Dark Current).....	36
2.6 Equivalent Circuit Modeling and Transport Property of the DSSC.....	38
2.6.1 Electrochemical Impedance Spectroscopy (EIS).....	38
2.6.2 Intensity Modulated Photocurrent Spectroscopy (IMPS)	43
CHAPTER 3 OPTIMIZATION OF DYE-SENSITIZED SOLAR CELL DEVICE FABRICATION.....	45
3.1 Mesoporous TiO ₂ Layer as Photoanode for DSSC	47

3.1.1	Synthesis of TiO ₂ Nanoparticles by Hydrothermal Method	48
3.1.2	Paste Formulation and Deposition of Photoanode.....	49
3.1.3	Assembly of Standard DSSC Device.....	49
3.2	Characterization of TiO ₂ Nanomaterials as Photoanode.....	51
3.2.1	Crystalline Phase Structure of TiO ₂ Nanomaterials.....	51
3.2.2	Surface Morphology of TiO ₂ Nanomaterials.....	53
3.2.3	Composition Analysis of Hydrothermal TiO ₂ Nanoparticles	56
3.3	Dye Loading in Mesoporous TiO ₂ film.....	60
3.4	Photovoltaic <i>I-V</i> Characteristic of DSSC Devices	61
3.5	Incident Photon-Current Conversion Efficiency (IPCE) of DSSC Devices	64
3.6	Dense TiO ₂ Barrier Layer on FTO Electrode to Suppress Charge Recombination	65
3.6.1	Deposition of Dense TiO ₂ Barrier Layer	66
3.7	Characterization of Dense TiO ₂ Barrier Layer.....	67
3.7.1	Surface Morphology of Dense TiO ₂ Barrier Layer.....	67
3.7.2	Crystalline Phase Structure of Dense TiO ₂ Barrier Layer	69
3.7.3	Optical Transmittance of Dense TiO ₂ Barrier Layer on FTO Glass.....	70
3.8	Photovoltaic Performance of DSSC with Dense TiO ₂ Barrier Layer	71
3.9	Dark Current Measurement.....	76
3.10	Summary	77
CHAPTER 4 NITROGEN-DOPED TITANIUM DIOXIDE AS PHOTOANODE FOR DYE-SENSITIZED SOLAR CELL		79
4.1	Formation and Characterization of N-doped TiO ₂ mesoporous Photoanode.....	80
4.1.1	Thermal oxidation of TiN Nanoparticles.....	81
4.1.2	Formation of TiN _x O _y Mesoporous Film without Organic Binder	82
4.1.3	Crystalline Phase Structure of TiN _x O _y Mesoporous Film	84
4.1.4	Surface Morphology of TiN _x O _y Mesoporous Films	85
4.1.5	Composition Analysis of TiN _x O _y Mesoporous Films.....	87
4.1.6	Optical Property of TiN _x O _y Mesoporous Film	91
4.2	Photovoltaic Performance of DSSC device with TiN _x O _y as Photoanode	92
4.2.1	TiN _x O _y Photoanodes Formed from Modified TiN Paste Formulation Without Organic Binder.....	92
4.2.2	Photovoltaic Performance of DSSC Device with TiN _x O _y Photoanodes Derived from the Standard TiN Paste Formulation with Organic Binder	96
4.3	Composite TiN _x O _y -TiO ₂ as Photoanode for DSSC Device	100

4.3.1	Surface Morphology of Composite TiN_xO_y - TiO_2 Photoanodes	102
4.3.2	Optical Property of Composite TiN_xO_y - TiO_2 Photoanodes	104
4.4	Photovoltaic Performance of DSSC Devices with Composite TiN_xO_y - TiO_2 Photoanodes	105
4.4.1	Dye Loading in Mesoporous Composite TiN_xO_y - TiO_2 Photoanodes	105
4.4.2	Photovoltaic Performance of DSSC with Composite TiN_xO_y - TiO_2 Photoanodes	106
4.4.3	IPCE of DSSC with Composite TiN_xO_y - TiO_2 Photoanodes.....	109
4.5	Transport Property of the DSSC with Composite Photoanodes	110
4.5.1	Electrochemical Impedance Spectroscopy (EIS) Measurement	110
4.5.2	Intensity Modulated Photocurrent Spectroscopy (IMPS) Measurement ...	115
4.6	Summary	117
CHAPTER 5 3D ELECTRODE FOR DYE-SENSITIZED SOLAR CELL.....		120
5.1	Growth of SnO_2 Nanorods on ITO Glass Substrate	123
5.1.1	Study of Surface Morphology of SnO_2 Nanorods Deposited on ITO Glass Substrate.....	124
5.1.2	Crystalline Phase Study of SnO_2 Nanorods on ITO Glass Substrate.....	125
5.2	Growth of SnO_2 Nanorods for 3D Electrode	126
5.2.1	Direct Growth on FTO Glass Substrate	126
5.2.2	Growth from SnO_2 Seeding Layer on FTO Glass Substrate.....	128
5.2.3	Deposition of TiO_2 Barrier Layer on SnO_2 Nanorods/ SnO_2 /FTO Glass Substrate.....	130
5.3	Optical Property of SnO_2 Nanorods 3D Electrode on FTO Glass Substrate	131
5.4	Photovoltaic Performance of DSSC Device with 3D Electrode	133
5.5	IPCE of DSSC Device with SnO_2 Nanorods 3D Electrode	138
5.6	Transport Property of DSSC Device with SnO_2 Nanorods 3D Electrode.....	139
5.6.1	EIS Measurement.....	140
5.6.2	IMPS Measurement	142
5.7	Summary	145
CHAPTER 6 DYE-SENSITIZED SOLAR CELL WITH COMPOSITE PHOTOANODE ON 3D ELECTRODE		147
6.1	DSSC with Combined Novel Nanostructured Composite Photoanode --- Composite TiN_xO_y - TiO_2 Mesoporous Photoanode and SnO_2 Nanorod 3D Electrode	149
6.1.1	Fabrication of DSSC with Combined Novel Nanostructured Composite Photoanode.....	149

6.1.2	Photovoltaic Performance of DSSC with Combined Novel Nanostructured Composite Photoanode	150
6.1.3	IPCE of DSSC with Combined Novel Nanostructured Composite Photoanode.....	152
6.2	Transport Property of Combined Novel Nanostructured Composite Photoanode	153
6.2.1	EIS Measurement.....	153
6.2.2	IMPS Measurement	157
6.3	Summary	158
CHAPTER 7 CONCLUSION AND RECOMMENDATIONS.....		160
7.1	Conclusions	160
7.2	Recommendations	165
7.2.1	Reducing TiN_xO_y Nanoparticles Size	165
7.2.2	Growth of Longer SnO_2 nanorods on FTO Glass Substrate	166
7.2.3	TiO_2 nanorods/nanotubes on SnO_2 nanorods 3D electrode	168
Author's Publications.....		174
Journal Papers		174
Patent		174
International Conferences		174
References.....		176

List of Figures

Figure 1.1 (a) 2009 World Energy Consumption [1]; (b) World Energy Consumption (1990 – 2035) [2]; (c) World energy-related carbon dioxide emissions by fuel type (1990-2035) [2].	2
Figure 1.2 Three generation of solar cell technologies. (Gen-I : Silicon wafer based solar cells; Gen-II: thin film solar cells; Gen-III: novel solar cells) [6].	3
Figure 1.3 (a) Schematic representation of the operation principle of the DSSC [7]; (b) Illustration of DSSC device structure based on Grätzel's work [18].	6
Figure 2.1 Schematic of energy diagram and operating principle of DSSC [85].	17
Figure 2.2 Schematic representation of a typical DSSC structure [89].	20
Figure 2.3 Scanning electron micrograph of mesoporous TiO ₂ film on the FTO glass. The average particle size is about 20 nm [7].	21
Figure 2.4 (a) Schematic diagram of the nanowire dye-sensitized cell, based on a ZnO nanowires array; (b) The cross-sectional FESEM image of a cleaved ZnO nanowires array on FTO glass [107].	26
Figure 2.5 (a) Schematic diagram of a typical nanotube dye sensitized solar cells using back-side illumination [105]; (b) FE-SEM image of titanium nanotube arrays fabricated from anodization of titanium foil[111].	27
Figure 2.6 Spectral response of DSSCs using N3 and black dye, the incident photon to current conversion efficiency is plotted as a function of wavelength. The chemical structure of the dyes are given as well [13].	30
Figure 2.7 The evolution of conversion efficiency for DSSCs based on ruthenium complexes and organic dyes [120].	30
Figure 2.8 Schematic diagram of electron transfer kinetics in DSSCs [14].	33
Figure 2.9 Impedance spectra of DSSC measured at open circuit potential both in dark and under 1 sun. (a) Bode phase plot; (b) Nyquist plot; [138]; (c) Schematic of the equivalent circuit for the DSSC structure.	39
Figure 2.10 Impedance Nyquist spectra of DSSC at different applied bias to review the high frequency and low frequency response of the DSSC [135].	41
Figure 2.11 (a) Equivalent circuit model for DSSC; (b) Circuit model for DSSC with insulating TiO ₂ at lower applied bias; (c) Circuit model for DSSC with TiO ₂ in conductive state at applied bias closed to open circuit potential [135].	42
Figure 2.12 Illustration of a IMPS experimental setup with a DSSC device illuminated by the light emitting diode (LED) that is driven by frequency response analyzer (FRA). The amplifier A is a photocurrent amplifier [131].	43
Figure 2.13 Illustration of a typical IMPS response of a DSSC device [133].	44
Figure 3.1 General research flow for the fabrication and optimization of DSSC device in this project.	46

Figure 3.2 Assembly of standard DSSC for photovoltaic characterization.	50
Figure 3.3 XRD crystalline phase of different types of TiO ₂ nanoparticles:-Degussa P25 TiO ₂ (P25), Anatase TiO ₂ from Alfa-Aesar (ANT) and the hydrothermally TiO ₂ nanoparticles (HTT).	52
Figure 3.4 Surface morphology for different mesoporous TiO ₂ film deposited on FTO glass (a) from hydrothermal TiO ₂ (HTT); (b) from Degussa P25 TiO ₂ (P25) and (c) from commercially available anatase TiO ₂ (ANT).	54
Figure 3.5 XPS survey spectrum of mesoporous film from hydrothermal TiO ₂ nanoparticles.	57
Figure 3.6 The core level XPS spectra for (a) C 1s, (b) O 1s and (c) Ti 2p as detected in the survey scan spectrum in Figure 3.5	58
Figure 3.7 Photovoltaic <i>I-V</i> characteristic of DSSC devices with different types of TiO ₂ nanoparticles as photoanodes measured under simulated solar radiation of 100mW/cm ²	62
Figure 3.8 IPCE spectra of DSSCs fabricated using different types of TiO ₂ as photoanode.	65
Figure 3.9 APCVD system for the deposition of dense TiO ₂ barrier layer onto the heated FTO glass substrate.	66
Figure 3.10 FESEM images of dense TiO ₂ barrier layers of different thickness deposited on FTO glass substrate using APCVD method. (a) Bare FTO glass. (b) 30 nm; (c) 50 nm and (d) 100 nm.	68
Figure 3.11 XRD profile for TiO ₂ barrier layer deposited on glass substrate using APCVD system.	69
Figure 3.12 Transmittance spectra of the dense TiO ₂ barrier layer on FTO glass for different thicknesses.	71
Figure 3.13 Photovoltaic <i>I-V</i> characteristics of DSSCs with/without TiO ₂ barrier layers, measured under 100 mW/cm ² (AM 1.5) simulated solar light.	72
Figure 3.14 Schematic illustration of DSSC device (a) without TiO ₂ barrier layer resulting in the back electron transport from FTO electrode to the electrolyte; (b) with TiO ₂ barrier layer to prevent charge recombination at the FTO glass/electrolyte interface with oxidized species (I ₃ ⁻) in the electrolyte; (c) Effect of dense TiO ₂ barrier layer on the suppression of dark current in DSSC.	75
Figure 3.15 <i>I-V</i> characteristics of DSSCs with or without TiO ₂ blocking layer measured in dark condition.	76
Figure 4.1 Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of TiN nanoparticles.	82
Figure 4.2 Appearance of the mesoporous TiN _x O _y films after the oxidation of TiN films at different temperature ranging from 350 °C to 550 °C.	83
Figure 4.3 XRD patterns of TiN and TiN _x O _y mesoporous films annealed at different temperatures of 350 °C, 400 °C, 425 °C, 450 °C, 500 °C and 550 °C respectively.	85

Figure 4.4 FESEM images of mesoporous TiN_xO_y films derived from TiN paste without organic binder (oxidation temperature at 450 °C).	86
Figure 4.5 FESEM images of mesoporous TiN_xO_y films derived from TiN paste with organic binder (oxidation temperature at 450 °C).	87
Figure 4.6 XPS survey spectra for TiN and TiN_xO_y mesoporous films formed at temperature ranging from 350 °C to 550 °C.	88
Figure 4.7 XPS spectra of C 1s, O 1s, Ti 2p and N 1s for TiN and the mesoporous TiN_xO_y films annealed at different temperature from 350 °C to 550 °C.	90
Figure 4.8 Optical absorbance of TiN_xO_y mesoporous films formed at different annealing temperature ranging from 350 °C to 550 °C with TiO_2 as reference.	91
Figure 4.9 Photovoltaic performances of DSSCs with TiN_xO_y photoanodes formed at different temperature from 350 to 550 °C. The modified TiN paste was formulated without organic binder.	94
Figure 4.10 Variation of the photovoltaic conversion efficiency of DSSCs with TiN_xO_y photoanodes formed at different temperature from modified TiN paste without organic binder.	96
Figure 4.11 Photovoltaic performance of DSSCs with TiN_xO_y photoanodes formed by the oxidation of standard TiN paste at different temperature from 450 to 550 °C. The standard TiN paste was formulated with the ethyl cellulose as organic binder.	97
Figure 4.12 Comparison of photovoltaic performance of DSSC devices fabricated with TiN_xO_y photoanodes derived from different type of pastes and formed at different oxidation temperature. (■ Modified TiN paste without organic binder. ♦ Standard TiN paste with organic binder. ▲ Standard DSSC device was fabricated using standard paste formulation from hydrothermal TiO_2 nanoparticles and annealed at 450°C.).....	99
Figure 4.13 FESEM images of mesoporous films derived from (a) hydrothermal TiO_2 , (b) composite sample TN5, (c) composite sample TN10 and (d) pure TiN_xO_y (sample TN100) (deposited on FTO glass substrate with 30 nm dense TiO_2 barrier layer as photoanodes for DSSCs).	103
Figure 4.14 Optical absorbance of TiO_2 , composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ (TN1, TN5 and TN10) and TiN_xO_y (TN100) photoanodes.	104
Figure 4.15 Appearance of TiO_2 , Composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ and TiN_xO_y photoanodes after dipped in 0.25 mM N719 dye solution.	105
Figure 4.16 Photovoltaic $I\text{-}V$ characteristic of the DSSC devices with different composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanodes.	106
Figure 4.17 Conversion efficiency and dye loading of DSSCs with composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanode.	109
Figure 4.18 IPCE spectra of DSSCs samples fabricated using different photoanodes....	110
Figure 4.19 (a) Nyquist plot from EIS measurement of the DSSCs fabricated using TiO_2 and $\text{TiN}_x\text{O}_y\text{-TiO}_2$ composite photoanodes, measured under light illumination 100 mW/cm ² ; (b) Equivalent circuit model for a DSSC device.	112

Figure 4.20 Variation of transport resistance in TiO_2 and TiN_xO_y - TiO_2 composite photoanodes.	114
Figure 4.21 Bode phase plots for DSSCs fabricated with TiN_xO_y - TiO_2 composite photoanodes	115
Figure 4.22 IMPS plots for TiN_xO_y - TiO_2 composite photoanodes.....	116
Figure 4.23 Illustration of TiN_xO_y particles embedded inside the mesoporous network of hydrothermally grown TiO_2 nanoparticles.....	117
Figure 5.1 Schematic illustration of conceptual 3D electrode with SnO_2 nanorods with conventional 2D electrode for DSSC device fabrication.	122
Figure 5.2 FESEM images of the SnO_2 deposition and the preferential growth of nanorods on ITO glass substrate for the deposition time of 30 to 120 mins.	125
Figure 5.3 XRD patterns of the SnO_2 nanorod arrays deposited on ITO glass at $D_{sn} = 10$ cm for 120 min.	126
Figure 5.4 FESEM images of (a) bare FTO glass, SnO_2 deposited on FTO glass by ICP-CVD method for (b) 30 mins, (c) 60 mins, (d) 100 mins and (e) 120 mins.	127
Figure 5.5 FESEM images of SnO_2 nanorods deposited on SnO_2 /FTO glass for 120 mins inside ICP-CVD system. The SnO_2 seeding layer was deposited using SnCl_2 precursor with concentration (a) 0.05 M (b) 0.10 M (c) 0.20 M.	129
Figure 5.6 FESEM side-view images of SnO_2 nanorods on SnO_2 /FTO glass. The SnO_2 seeding layer on FTO substrate was deposited from 0.05 M SnCl_2 precursor.	129
Figure 5.7 (a) SnO_2 nanorods / SnO_2 /FTO electrode; (b) TiO_2 barrier layer on SnO_2 nanorods / SnO_2 /FTO electrode.	130
Figure 5.8 TEM images of (a) SnO_2 nanorods on FTO glass substrate; (b) Well defined crystalline structure of SnO_2 nanorods; (c) TiO_2 barrier layer coated SnO_2 nanorod arrays using APCVD system.	131
Figure 5.9 The optical transmittance curves of the SnO_2 nanorod 3D electrodes with different deposited thin film layer.....	132
Figure 5.10 Surface morphology of different transparent electrodes (a) standard FTO glass substrate (STD), (b) SnO_2 thin film on FTO glass substrate (SN0), (c) short and clustered SnO_2 nanorods (SN1) and (d) SnO_2 nanorods (SNR).....	134
Figure 5.11 Photovoltaic I - V curves of DSSCs incorporated with SnO_2 nanorods (SNR) on FTO glass substrate as 3D electrode.	135
Figure 5.12 Relative energy level of the conduction bands for SnO_2 and TiO_2 that inhibits the back electron transfer of electrons that causes the electron combination with the dyes and electrolyte [60].	136
Figure 5.13 IPCE spectra of DSSCs samples fabricated with SnO_2 nanorods 3D electrode.	139
Figure 5.14 (a) Nyquist impedance spectra from the EIS measurement for DSSCs with SnO_2 nanorods 3D electrode, with the standard DSSC (STD) as reference. The modelling	

is used to extract the equivalent resistances in DSSCs (b) Equivalent circuit model for DSSC device.	141
Figure 5.15 IMPS plots for DSSCs with SnO ₂ seeding buffer or nanorods on FTO electrode, with standard DSSC as reference.	143
Figure 5.16 Schematic illustration of charge collection pathways with SnO ₂ nanorods 3D electrode.	144
Figure 6.1 Photovoltaic <i>I-V</i> characteristic of DSSC device with composite TiN _x O _y -TiO ₂ mesoporous photoanode on the SnO ₂ nanorods 3D electrode.	151
Figure 6.2 IPCE curves for DSSC fabricated using TiN _x O _y -TiO ₂ composite photoanode on the SnO ₂ nanorods 3D electrode.	153
Figure 6.3 (a) Nyquist plot of DSSC with TiN _x O _y -TiO ₂ composite photoanode deposited on the SnO ₂ -nanorods 3D-based electrode with respect to standard DSSC under 100 mW/cm ² simulated solar light illumination at open circuit potential. The symbol corresponded to the measurement results. The lines show theoretical fits using equivalent circuit shown in the inset. (b) Equivalent circuit model for DSSC with composite TiN _x O _y -TiO ₂ photoanode on SnO ₂ nanorods 3D electrode.	154
Figure 6.4 Bode phase plots from the impedance spectra.	155
Figure 6.5 Reduction of transport resistance in the mesoporous oxide layer obtained from the impedance measurement at different applied bias.	157
Figure 6.6 IMPS plots for DSSC with TiN _x O _y -TiO ₂ composite photoanode deposited on the SnO ₂ nanorods 3D electrode, standard DSSC served as a reference for comparison.	158
Figure 7.1 Schematic illustration of problem for infiltration of TiO ₂ nanoparticles into the gaps between closely packed SnO ₂ nanorods with random growth orientation. (b) TiO ₂ nanoparticles can be easily filled into the spaces between cluster of SnO ₂ nanorods grown at regular patterned locations.	166
Figure 7.2 FESEM images of SnO ₂ nanorod arrays grown after two deposition cycles on ITO glass substrate (2 hrs + 2 hrs).....	168
Figure 7.3 The ultra-long nanorod bushes observed on the samples grown by multiple depositions.	168
Figure 7.4 Schematic illustration of TiO ₂ nanorods on SnO ₂ nanorods 3D electrode.	170
Figure 7.5 FESEM images of the TiO ₂ nanorod arrays grown on FTO glass substrate at 150 °C for 5-41 h.....	171
Figure 7.6 XRD patterns of the TiO ₂ nanorods grown on FTO glass substrate by hydrothermal at 150 °C for 14 hrs.....	172
Figure 7.7 FESEM images of TiO ₂ nanorod arrays grown on various substrates with different surface modifications at 150 °C for 14 h, (a) FTO, (b) SnO ₂ film/FTO and (c) SnO ₂ nanorods/FTO.....	173

List of Tables

Table 2.1 Reported works on metal doped-TiO ₂ as photoanode for DSSCs.	23
Table 3.1 Calculated grain size from XRD results and estimated agglomerated particle size from FESEM images for different mesoporous TiO ₂ films.....	55
Table 3.2 Summary of surface atomic concentration for each element in the hydrothermal TiO ₂ nanoparticles.	59
Table 3.3 Estimated surface composition of hydrothermally synthesized TiO ₂	59
Table 3.4 Thickness of mesoporous films and amount of dye extracted from the films deposited from different types of TiO ₂ nanoparticles.....	61
Table 3.5 Photovoltaic parameters from the <i>I-V</i> curves for DSSCs with different type of TiO ₂ nanoparticles as photoanode.	62
Table 3.6 Extracted Photovoltaic parameters of DSSCs with/without TiO ₂ barrier layers.	72
Table 4.1 Technical specification of TiN nanoparticles purchased from Hefei Kaier.	81
Table 4.2 The calculated grain size for the TiN and TiN _x O _y nanoparticles formed at different temperatures from 350 °C to 550 °C.....	85
Table 4.3 Measured Thickness of the TiN _x O _y photoanodes on DSSC devices.	93
Table 4.4 Photovoltaic parameters of DSSCs with mesoporous TiN _x O _y photoanodes	94
Table 4.5 Measured thickness of mesoporous TiN _x O _y photoanodes formed from standard TiN paste with organic binder.....	97
Table 4.6 Photovoltaic parameters of DSSCs with TiN _x O _y photoanodes deposited from standard paste formulation and annealed at different temperatures from 450 – 550 °C....	98
Table 4.7 Comparison of film thickness, particle size range and amount of N719 dye loaded into the mesoporous TiO ₂ photoanodes and TiN _x O _y photoanode.....	100
Table 4.8 Sample composition for the study of composite TiN _x O _y -TiO ₂ mesoporous photoanodes	101
Table 4.9 Film thickness and the amount of dye adsorbed on the mesoporous HT-TiO ₂ , composite TiN _x O _y -TiO ₂ and TiN _x O _y films on the FTO glass substrate.	106
Table 4.10 Photovoltaic performance of the DSSC devices based on different TiN _x O _y -TiO ₂ composite photoanodes.	107
Table 4.11 Transport Properties of the DSSCs with TiN _x O _y -TiO ₂ composite photoanodes determined using EIS and IMPS measurements.....	113
Table 5.1 Typical deposition parameters of SnO ₂ nanorod arrays on ITO glass by ICP-CVD system.	124
Table 5.2 Photovoltaic parameters of DSSCs fabricated on different types of transparent electrodes.	135
Table 5.3 Transport parameters derived from the EIS and IMPS curves	141

Table 6.1 Measured mesoporous layer thickness and amount of dye adsorbed onto the mesoporous layer of DSSC devices.	150
Table 6.2 Photovoltaic parameters for DSSC with TiN_xO_y - TiO_2 composite photoanode deposited on the SnO_2 nanorods 3D electrode.	151
Table 6.3 Transport parameters determined from the EIS and IMPS measurement.	155

List of Symbols

$h\nu$	photon energy
S°	ground state of dye sensitizer
S^*	excited state of dye sensitizer
S^+	oxidized state of dye sensitizer
α	absorption coefficient
σ	optical absorption cross section of the sensitizer
c	concentration of dye molecules
ε	molar extinction coefficient
d	thickness of the mesoporous semiconductor oxide film
λ	wavelength
φ_{inj}	quantum yield for electron injected from the excited dye molecule to the conduction band of the semiconductor oxide
η_c	electron collection efficiency
k_{inj}	rate constant for the injection of electron
V	electronic coupling between the dye sensitizer and the oxide semiconductor
$\rho(E)$	density-of-states in the conduction band of oxide semiconductor
h	Planck constant
k	Boltzman constant
q	electronic charge
T	absolute temperature
I_O	dark current
n_O	electron density on the conduction band of the oxide semiconductor in the dark
k_{et}	rate of constant for recombination
ω	angular frequency
ω_d	characteristic frequency of charge transport process in the mesoporous layer
ω_k	characteristic frequency of charge transfer and recombination processes at TiO ₂ /dye/electrolyte interface
R_t	electron transport resistance
R_{μ}	charge-transfer resistance related to recombination of electrons at the TiO ₂ /electrolyte interface.
R_S	series resistance due to the FTO glass
R_P	charge-transfer resistance at the mesoporous TiO ₂ /FTO electrode interface and counter electrode/electrolyte interface

C_p	interfacial capacitance at mesoporous FTO/TiO ₂ /electrolyte interface and counter electrode/electrolyte interface
C_μ	chemical capacitance due to the change of electron density as a function of the Fermi level
R_{TiO_2}	total resistance of the photoanode
H_{IMPS}	transfer function
ΔI	variation in the photocurrent
$\Delta \phi$	variation in photon flux
ϕ	phase angle
f_{min}	minimum frequency
t_{tr}	transit time
t_e	electron lifetime
D	average grain size
B	full width at half maximum (FWHM) of the broadened diffraction line on the 2θ scale (radians)
θ	diffraction angle
V_{OC}	open circuit voltage
J_{SC}	short circuit current density
FF	fill factor
η	conversion efficiency

CHAPTER 1 INTRODUCTION

1.1 Motivations

According to the 2011 Key Energy Statistics published by International Energy Agency (IEA), the world energy consumption in 2009 relied heavily on fossil fuels (oil, gas and coal) for about 80.9 %, 5.8 % from nuclear power, 10.2 % from biomass and waste energy, 2.3 % from hydroelectricity power and only 0.8 % from renewable energy sources like geothermal, solar, wind and thermal [1]. Renewable energies such as wind, solar, geothermal, bio-fuels are growing very rapidly in recent years. According to US Energy Information Administration (EIA), the energy required to meet the human activities was projected to increase by 52.0 % from 504.7 quadrillion BTU in 2008 to 769.8 quadrillion BTU in 2035 as shown in Figure 1.1(b) [2].

Renewable energies become the major alternative sources to meet the human energy demands as the fossil fuels are gradually exhausted. Moreover the rapid increase in carbon dioxide emission into atmosphere (Figure 1.1(c)), a major cause of green house effect, from the combustion of fossil fuels has also motivated the development of renewable energy. Among all the renewable energy sources such as wind, biomass, solar and etc., solar energy stands out as one of the best candidates as it is abundant, clean, safe and allows energy generation in the remote areas [3].

Figure 1.1 (a) 2009 World Energy Consumption [1]; (b) World Energy Consumption (1990 – 2035) [2]; (c) World energy-related carbon dioxide emissions by fuel type (1990-2035) [2].

Solar power is one of the fastest growing renewable energy sources worldwide. The sun provides a gigantic energy to planet Earth, at approximately 120,000 TW, which is nearly 7500 times more than the present world's energy consumption of ~16 TW [4]. The solar energy that reaches the earth can be harnessed by photovoltaic cells or so called solar cells, to generate electric power. The potential for the installation of large-scale solar power plants plays an important role in future sustainable energy system. One interesting note made by Nobel Laureate Prof. Steven Chu in 2006 was that by covering 3.86 % of

the land surface on earth with solar cells at conversion efficiency of 1.0 %, the 13 TW energy needs at that time could be met [5].

Broadly speaking, solar cells can be classified into three generations according to the progression of photovoltaic technologies [6]. They are the 1st generation (Gen-I) crystalline silicon wafer solar cells, 2nd generation (Gen-II) thin film solar cells and 3rd generation (Gen-III) advanced thin film or new concept solar cells. Figure 1.2 shows the projected solar module production cost per unit area and energy conversion efficiency for these three generations of solar cell technology [6]. There are concurrent research efforts into all these three generations of solar cell technologies to improve the conversion efficiency and reduce the cost of manufacturing.

Figure 1.2 Three generation of solar cell technologies. (Gen-I : Silicon wafer based solar cells; Gen-II: thin film solar cells; Gen-III: novel solar cells) [6].

The 1st generation solar cell (Gen-I) is represented by the large-area, high quality single junction devices built on single-crystalline or polycrystalline silicon wafers. It is the most

dominant solar cells in the commercial market with matured manufacturing know-hows. The cost of Gen-I solar modules is dominated by the material costs, mainly the cost of silicon wafer or substrate, the cost of the strengthened low-iron glass cover and the cost of encapsulation layers needed to build the module as well as the cost of module assembly. The cost reduction trend is expected to continue as the photovoltaic industry continues to grow.

The growing concerns for renewable energy at reasonable production costs have resulted in the development of so-called second generation (Gen-II) thin film solar cell technologies. These thin film solar cells utilize a very thin layer of semiconductor material with photovoltaic-active property deposited onto a substrate. The quantity of the semiconductor material deposited is normally 10 or 100 times less than the conventional Gen-I solar cells. Thus, higher throughput in the commercial manufacturing can be achieved. The Gen-II solar cells can be made of compound semiconducting materials such as cadmium telluride (CdTe), copper indium gallium selenide (CIGS), amorphous silicon and microcrystalline/amorphous silicon. These various technologies do produce solar modules with promising conversion efficiency at significantly lower production costs to compete with the cost of electricity generation from the traditional fossil fuels.

The third generation (Gen-III) solar cell technologies are developed for the enhancement of the Gen-II solar cells in energy conversion efficiency while maintaining the low production cost and the exploration of advanced new concepts. Due to extensive research and development (R&D) efforts, many advances in the new type of solar cells or photovoltaic technologies have been proposed and implemented in recent years. The Gen-III solar cell technologies include the novel devices such as dye-sensitized solar cells

(DSSCs) [7], thin film organic/polymer solar cells [8], tandem cells approach [9], multiple electron-hole pairs per photon concept [10], multi-band cells [11], thermophotovoltaic and the thermophotonic devices [12].

Over the recent years, the photovoltaic cells with three dimensional (3D) bulk junction based on mesoscopic inorganic or organic semiconductors, have been introduced and developed. The relatively simple and low cost fabrication has accelerated the commercialization process, to serve as an alternative to the existing solar cells market. [13-15]. A promising prototype of this family of device, known as the dye-sensitized solar cell (DSSC), is classified as a Gen-III solar cell technology. In DSSC device, the optical or solar light absorption relies on light-absorbing sensitizer material while the charge separation and transport processes are based on the wide band gap oxide semiconductor of nanocrystalline morphology.

The extraordinary breakthrough of the DSSC technology occurred in 1991 when O'Regan and Grätzel demonstrated an efficient fast regenerative photoelectrochemical solar cell with conversion efficiency $> 7\%$ using a mesoporous layer of titanium dioxide sensitized by a ruthenium dye and iodine redox electrolyte as depicted in Figure 1.3(a) [7]. Contrary to the expectation, this interpenetrating network of mesoscopic oxide semiconductor has shown striking high conversion efficiency, hence allowing it to compete with those conventional thin film solar cell devices.

Titanium dioxide (TiO_2) has become the favored wide band gap metal oxide semiconductor of choice following its use by Fujishima and Honda for water photolysis [16]. It is also a low cost, widely available, non-toxic and biocompatible material that is

used in domestic applications such as paint pigmentation and cosmetic additives [15]. Currently, the DSSCs have reached the conversion efficiencies of more than 12.0 % under the standard testing condition [17].

Figure 1.3 (a) Schematic representation of the operation principle of the DSSC [7]; (b) Illustration of DSSC device structure based on Grätzel's work [18].

Over the past two decades, significant research efforts have been devoted to increase the energy conversion efficiency of DSSCs. Vast amount of research efforts have been carried out concurrently on various aspects of the DSSC device structure, including the choice of wide band gap oxide semiconductor nanoparticles and the methods for the formation of the mesoporous photoanode, the selection of dye sensitizers, the selection and composition of the liquid electrolytes, the inclusion of hole conductors and the selection and construction of the front and counter electrodes, etc. Each of these development efforts aims at improving the overall photovoltaic performance of DSSCs.

The mesoporous oxide semiconductor layer, deposited on the transparent conducting oxide (TCO) glass substrate as the photoanode, is an essential constituent structure of the DSSC in separating and transferring the photo-generated electrons in the dye sensitizer towards the collection electrode. It is well known that the charge transport property of the mesoporous oxide semiconductor layer has a direct impact on the photovoltaic performance of DSSCs. Several alternative oxide semiconductor materials such as ZnO [19-22], SnO₂ [23-25], SrTiO₃ [26-28] and Nb₂O₅ [29-31] have been investigated for their potential in substituting the TiO₂ as photoanode. However, the photovoltaic performances of DSSCs using these alternative materials are still inferior compared with TiO₂. There have been great interests in recent years in doping the TiO₂ nanomaterials to further improve the photovoltaic performance of DSSCs built with such materials. For example, metal doping of TiO₂ by atoms like by Zn [32], Ta [33, 34], Zr [35] and Nb [36, 37] and non-metal doping by atoms such as N [38-46], S [47], C [48] and B [49, 50] had been reported. These efforts were shown to have promising results to various degree of success in improving the charge transport properties in DSSCs.

The charge collection efficiency is another intensely debated topic in DSSCs. Three-dimensional electrode (3D-electrode) on the transparent conducting oxide (TCO) substrate extending into the mesoporous TiO₂ matrix was proposed to enhance the current collection efficiency in DSSCs. Extending the 2D TCO electrode to 3D electrode will dramatically decrease the required distance for the photo-generated electrons to travel across the interpenetrating network of mesoporous TiO₂ oxide layer and be collected by the electrode. This is expected to reduce the electron transportation time to the charge collection electrode and higher charge collection efficiency can be achieved, leading to

improvement in DSSC photovoltaic performance [51, 52]. To-date, most of the reported works for 3D-electrode were based on indium tin oxide (ITO) glass substrate instead of fluorine-doped tin oxide (FTO) glass substrate [53-57]. Moreover, the use of doubled oxide layers such as SnO_2 and TiO_2 with different energy level have shown convincing results in promoting charge transfer and suppression of charge recombination [58-63].

1.2 Objective

The aim of this project is to improve the charge transport properties in the mesoporous photoanode and the charge collection efficiency at the electrode of the DSSC. The improvement in the charge transport in the photoanode is achieved by incorporating N-doped TiO_2 in the mesoporous TiO_2 layer of the photoanode. The charge collection efficiency is enhanced by utilizing the SnO_2 nanorods on FTO glass as 3D electrode. The ultimate aim of this project is to combine these two novel approaches simultaneously in the fabrication of DSSC in order to demonstrate the significant improvement in the solar energy conversion of DSSC.

The scope of work for this project can be categorized into the following five areas:

1. Material and device characterization for DSSC device fabrication

- The physical, chemical and optical properties of the metal oxide semiconductor nanoparticles and the resulting mesoporous photoanode were studied for better understanding of the material properties on the DSSC device performance. This

included the establishment of the necessary characterization and testing methods for the evaluation of the DSSC performance using the following tools :

- For material characterization: thermogravimetric and differential thermal analyzer (TGA-DTA), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), X-ray photoemission spectroscopy (XPS), UV-Vis spectrometer.
- For device characterization: Solar simulator for photovoltaic performance, incident photon-current conversion efficiency (IPCE), electrochemical impedance spectroscopy (EIS), intensity modulated photocurrent spectroscopy (IMPS).

2. Establishment of standard fabrication process for liquid-electrolyte DSSCs

- Standardized DSSCs fabrication procedures were established. This standard liquid-electrolyte DSSC fabrication process served as the baseline for an in-depth understanding of the DSSC device operation principles and further device improvement. The major effort was the optimization of the photoanode including the use of different types of TiO_2 nanoparticles and the effect of dense barrier layer on the TCO electrode on the suppression of electron recombination to improve the photovoltaic performance of DSSCs.

3. Nitrogen-doped TiO_2 nanomaterials as photoanode for DSSC

- Titanium nitride (TiN) nanoparticles were used as the starting materials for the formation of N-doped TiO_2 (TiN_xO_y) mesoporous photoanode by thermal

oxidation at different temperature followed by the thorough characterization of the physical, chemical and optical properties of the N-doped TiO_2 (TiN_xO_y) mesoporous photoanode.

- Investigations were carried out to study the photovoltaic performance of DSSCs and the charge transport property in the mesoporous TiN_xO_y and composite TiN_xO_y – TiO_2 photoanodes as compared to the standard DSSC device.

4. SnO_2 nanorods as 3D electrode for DSSC

- Study on the deposition of SnO_2 nanorods on TCO glass substrate using the custom-designed and built inductively coupled plasma enhanced chemical vapor deposition (ICP-CVD) system was performed to achieve the 3D electrode.
- The corresponding effects on the photovoltaic performance of DSSC device with the SnO_2 nanorods 3D electrode were studied.

5. DSSC with enhanced transport and collection efficiency

- DSSC devices with composite mesoporous TiN_xO_y – TiO_2 photoanode on SnO_2 nanorods 3D electrode were fabricated and characterized.
- The combined effects of the two novel approaches were consolidated and evaluated to explain the significant improvement in photovoltaic performance of the DSSC devices.

1.3 Major Contributions

1. TiO₂ nanoparticles were successfully synthesized using the hydrothermal process. These nanoparticles were thoroughly characterized for their physical, chemical and optical properties as compared to the commercially available TiO₂ nanoparticles. Homogenized thick pastes from different type of TiO₂ nanoparticles were formulated and deposited on TCO glass substrate as photoanode for DSSCs using the doctor blade method. Crack-free uniform mesoporous films with thickness around 10 μm were achieved after annealing at 450 °C. The fabrication procedures of DSSCs were systematically implemented for better consistency. In this project, DSSC with photoanode made of the hydrothermal TiO₂ nanoparticles was demonstrated to have better photovoltaic performance as compared with DSSCs using commercial TiO₂ nanoparticles. The improved photovoltaic performance was attributed to the smaller particle size of freshly synthesized nanoparticles and the smaller pore size in the resulting mesoporous photoanode layer. The combined effect resulted in the higher incorporation of the organic dye sensitizer molecules (dye-loading) in the mesoporous photoanode.
2. The incorporation of a thin TiO₂ barrier layer on FTO electrode glass was successfully developed using the atmospheric pressure chemical vapor deposition (APCVD) method. The dense TiO₂ barrier layer played an important role in inhibiting charge recombination due to the back flow of electrons at the FTO/electrolyte interface. The photovoltaic performance of the DSSCs with different barrier layer thickness from 30 to 100 nm were studied and evaluated. The barrier layer was found to be effective in suppressing the dark current. The TiO₂

barrier layer with thickness of 30 nm was found to give the best photovoltaic performance since it was sufficiently dense with good surface coverage for dark current suppression and thin enough for high optical transmittance.

3. The N-doped TiO_2 (TiN_xO_y) nanoparticles was formed by the thermal oxidation of commercial TiN nanoparticles. The physical, chemical, and optical properties of these TiN_xO_y nanoparticles were investigated. Photoanode using composite TiN_xO_y and hydrothermal TiO_2 nanoparticles were prepared and used in DSSC device fabrication. These DSSC devices were found to have significant improvement in the photovoltaic performance as compared with the standard DSSC. This improvement was associated to the coupling effects of improved absorption in the visible region and enhanced electron transport efficiency with the embedded TiN_xO_y nanoparticles in the mesoporous composite photoanode. The impedance measurement results and the associated equivalent circuit modeling were used to confirm these observations.
4. The SnO_2 nanorods were successfully deposited on ITO and FTO glasses using the custom-built ICP-CVD method to form the nanostructured 3D electrode for DSSCs. TEM images revealed that these SnO_2 nanorods were well-crystalline, offering an excellent advantage in transporting the collected electrons from mesoporous TiO_2 layer to the FTO glass electrode. The photovoltaic performances of DSSCs with SnO_2 nanorods/FTO as electrode were found to have noticeable improvement compared with standard DSSCs with 2D electrode. The electron transit time through the mesoporous layer was reduced drastically, signified that the charge collection efficiency was improved using the SnO_2 nanorods 3D electrode. A US patent was filed for this work on the 3D TCO electrode.

5. Finally, DSSC devices incorporating the optimized mesoporous composite TiN_xO_y - TiO_2 photoanode on SnO_2 nanorods 3D electrode were successfully fabricated. A magnificent 28% improvement in the conversion efficiency was obtained using this modified DSSC structure. The improvement was attributed to faster electron transport through the alternative routes provided by the TiN_xO_y nanoparticles embedded inside the mesoporous TiO_2 layer, and the higher charge collection efficiency due to the extension of SnO_2 nanorods 3D electrode.

1.4 Organization of Report

Chapter 1 presents the introduction, the motivation for this work, objective, major contributions and the organization of this thesis.

Chapter 2 contains the literature review of topics related to this research project. The history of the dye-sensitized solar cells is first reviewed. Then, the device operating principle and the dynamic of the electron transfer in dye-sensitized solar cells are described. Next, the development efforts performed on the DSSCs to improve the photovoltaic performance are discussed.

Chapter 3 describes the experimental design and the characterization methods used in this project. The optimization works of the mesoporous photoanode for DSSCs are also presented. The characterizations for the device fabrication and the photovoltaic performance of the DSSCs with different types of TiO_2 nanoparticles as photoanodes are reported. The effect of introducing dense TiO_2 barrier layer in DSSCs is also covered as well and the establishment of the baseline process for the fabrication of the DSSC devices.

Chapter 4 discusses the effect of introducing mesoporous TiN_xO_y as photoanode for DSSCs. The characterization of the Nitrogen-doped TiO_2 formed by the thermal oxidation of the TiN nanoparticles at different temperatures is first presented. Then, the photovoltaic properties of the DSSCs made from the mesoporous TiN_xO_y photoanodes are discussed in detail. Next, the photovoltaic performances of DSSC devices with composite TiN_xO_y - TiO_2 photoanode are presented. The electronic transport properties through the mesoporous layer are analyzed using the equivalent circuit model.

Chapter 5 details the integration of the SnO_2 nanorod arrays as 3D electrode for DSSCs. The growth of SnO_2 nanorods on different substrates are presented. Next, the effects of using these 3D electrodes on the photovoltaic properties of DSSC are discussed.

Chapter 6 presents the photovoltaic performance of the DSSC with the integration of the composite TiN_xO_y - TiO_2 photoanode on the SnO_2 nanorods 3D electrode. The combined effects of these two novel approaches to improve the photovoltaic performance of DSSC device are described.

Finally, **Chapter 7** concludes the thesis report and presents a proposal for the future direction of this research project.

CHAPTER 2 OVERVIEW OF DYE-SENSITIZED SOLAR CELL

2.1 History of Dye Sensitized Solar Cell (DSSC)

In 1837 the first batch photographic images were produced by Louis Daguerre onto a mirror-polished surface of silver coated with silver halide particles, this marked the beginning of photography. Initially, the films were insensitive to mid visible spectrum and red light. This is due to the fact that silver halides have the bandgap energies ranging from 2.7 to 3.2 eV and are insensitive to wavelengths longer than 460 nm [64]. Motivated by the photography, Edmond Becquerel discovered the photoelectric effect in 1839. Under light illumination, a current was produced between two platinum electrodes immersed in the electrolyte solution containing a metal halide salt [65]. This marked the beginning of ideas to convert light to electricity.

Later the sensitization concept was introduced by Vogel in 1873. He discovered that the photosensitivity of the silver halide emulsions could be extended to the longer wavelength by adding a dye [66]. In 1887, the concept of dye enhancement for photography and photoelectrochemical cells using the erythrosine dye on silver halide electrodes was realized by Moser [67].

The first series of detailed electrochemical and photoelectrochemical study of the semiconductor to electrolyte interface were done by Brattain and Garrett [68] and Gerischer [69] that marked the beginning of photoelectrochemical research. In 1964,

Namba and Hisiki recognized that to achieve maximum photoelectrochemical efficiency, only a closely packed monolayer of dye molecules should be adsorbed onto the semiconductor electrodes [70]. Tributsch and Gerischer (1968) [71, 72] and Hauffe (1970) [73], showed that the sensitization for both photographic and photoelectrochemical involved electron (or hole) injection from the excited state of sensitizer dye molecule rather than energy transfer. However there seemed to be little scope of practical application of the effect for solar energy conversion. This was because the photo-currents generated by sensitization of single crystal electrodes such as ZnO were very small since the dye molecules were present only as a monolayer at the surface which resulted in weak light absorption.

A worldwide quest for alternative energy sources was stimulated during the oil crisis in 1973, leading to widespread research of photoelectrochemical cells and resulted in over thousands of publication from 1925 - 1983 [74]. In 1976 Tsubomura demonstrated that larger photocurrent was obtained with around 1 % conversion efficiency by replacing the flat surface of a single crystal ZnO with a porous microcrystalline layer, thereby increasing the surface area of the semiconductor to enhance light harvesting [75].

In 1991, O'Regan and Grätzel reported that an efficient ($> 7\%$) regenerative photoelectrochemical solar cells could be fabricated using mesoporous layer of titanium dioxide as photoanode and the photoanode was sensitized by a strongly adsorbed Ruthenium dye [7]. In recent years, the discovery of the N3 sensitizer dye [76] and the panchromatic "black dye" [77] made the important contribution for the improved conversion efficiency of DSSC to more than 10% [78], and poised to compete with the more conventional thin film photovoltaic cells. The better understanding of the processes

occurring in the nanoscale as a result of R & D efforts on DSSCs also resulted in the development of new devices for solar energy conversions such as heterojunction solar cells [79], hybrid organic/inorganic solar cells [80-82], and solar hydrogen generation through tandem water splitting systems [83, 84].

2.2 Operating Principle of DSSC

Figure 2.1 gives an illustration of the primary steps involved in the conversion of photon to current in DSSC [85].

Figure 2.1 Schematic of energy diagram and operating principle of DSSC [85].

Under illumination, the photosensitizer dye molecules anchored on the mesoporous TiO_2 surface absorb the photons in the incident light flux. The dye sensitizers are excited from the ground state (S°) to the excited state (S^*), and the excited electrons from the molecule

of dye sensitizer are injected into the conduction band of the mesoporous TiO₂ photoanode. Electron injection has to be fast enough to compete against the relaxation of the dye molecules in excited state. After the injection of the excited electrons into the photoanode, the dye sensitizer is in an oxidized state (S⁺). The back transfer of electrons from the conduction band of the oxide semiconductor photoanode to the electrolyte to react with the dye cations may also happen and resulting in the charge recombination, but at a much slower rate. These processes can be described as:

Electrons in the mesoporous TiO₂ oxide semiconductor layer will be collected by the electrode, mainly by diffusion process [86-88]. The injected electrons move through the network of interconnected oxide nanoparticles by the random walk process until they reach the transparent conducting oxide (TCO) glass substrate. The electrons flow through the external load before reaching the counter electrode.

In the proper operation, the oxidized dye sensitizer (S⁺) accepts electron from the I⁻ ion, the redox mediator in the electrolyte, regenerating the dye sensitizer to ground state (S), while the I⁻ ion is oxidized to the triiodide ion, I₃⁻. The regeneration of the dye sensitizer by iodide ion intercepts the recapture of the conduction band electron by the oxidized dye. The oxidized redox mediator I₃⁻ subsequently diffuses towards the counter electrode and is reduced back to I⁻ ion. The charge transport of the injected electrons through the

nanocrystalline film to the electrode should be fast enough to minimize the electron recapture reaction (Eq. 2.7). Under illumination, the voltage generated corresponds to the difference between Fermi level of the electron in the oxide semiconductor and the redox potential of the electrolyte. This operating principle enables the DSSC to convert solar light to electric powers without suffering any permanent chemical transformation. These processes are described by:

The photon-current conversion mechanism for DSSC is different from the conventional p-n solar cells. In DSSC, light absorption and charge separation are differentiated. Upon illumination, the photogenerated electrons are injected from the dye molecules into the mesoporous TiO_2 layer while holes are not formed in the valence band of the oxide semiconductor. Thus, this leads to effective charge separation. This process is similar to photosynthesis, where the chlorophyll acts as a photosensitizer and the charge transport occurs through the membrane.

2.3 Device Structure of DSSC

The schematic structure of a typical dye-sensitized solar cell (DSSC) is shown in Figure 2.2. The structural compositions of the DSSC and their developments in recent years are described accordingly.

Figure 2.2 Schematic representation of a typical DSSC structure [89].

2.3.1 Transparent Conducting Oxide Glass Substrate

Transparent conducting oxide (TCO) glass is used as the substrate for the formation of the mesoporous TiO_2 photoanode. For high device performance, the TCO glass substrate must have high optical transparency to allow light to pass through into the photoanode and low electrical sheet resistance for the rapid collection of all the photo-generated charges and lead to the external circuitry. These properties must be stable and should not be affected by the DSSC processing temperature of up to 500°C . This is because the annealing temperature of the mesoporous TiO_2 film is normally performed at 450 to 500°C . Fluorine-doped tin oxide (FTO) film is usually the choice for TCO substrate for its better device performance and temperature stability. Indium tin-oxide (ITO) film is an alternative too but the resistance of ITO film increases significantly at temperature higher than 300°C [60].

The concept of three dimensional (3D) nanostructured electrode was first proposed by Chappel et. al. [51]. In their work, the core-shell architecture consisted of a very thin TiO_2

layer deposited on the ITO matrix allowed for very short electron transport path for collection. Since this approach was introduced, there have been similar works in creating the 3D electrode for DSSCs that aimed to reduce the recombination and improve the collection efficiency [44, 52-57, 90, 91]. Extending the current collector has generated new insights to improve the photovoltaic performances of DSSCs.

2.3.2 Mesoporous Nanocrystalline Oxide Semiconductor Film

The mesoporous nanocrystalline oxide semiconductor photoanode acts as an electron collector for electrons injected from the photo-excited dye sensitizers. The most widely used oxide semiconductor material is TiO_2 , due to its non-toxicity, being widely available, inexpensive, biocompatible and good chemical stability in solution under light irradiation.

Figure 2.3 Scanning electron micrograph of mesoporous TiO_2 film on the FTO glass. The average particle size is about 20 nm [7].

In general, the mesoporous nanocrystalline photoanode film is made from nanoparticles such as TiO_2 with particle size in the range 10 to 30 nm as shown in Figure 2.3, giving the

film the mesoporous structure. The total available surface area of the nanocrystalline particles on the mesoporous TiO_2 film is much greater than the apparent area. For example, a 1 cm^2 large mesoporous TiO_2 film with a thickness $\sim 10 \text{ }\mu\text{m}$ may have an actual particle surface area of 1000 cm^2 available for the adsorption of dye molecules, and hence increases the light harvesting efficiency of the DSSC device [3].

A. Other Semiconductor Oxides as Photoanode

In recent years, many nanosized semiconductor oxide materials such as ZnO [19-22], SnO_2 [23-25], SrTiO_3 [26-28] and Nb_2O_5 [29-31] have been investigated for their potential in substituting TiO_2 as photoanode in DSSC device [92]. However, their photovoltaic performances were still reported to be inferior as compared with TiO_2 . ZnO -based photoanode was reported to possess superior transport properties with higher electron lifetime but its low stability, especially in acidic conditions, and formation of the Zn^{2+} /dye complex on the nanoparticle surface could seriously retard the electron injection [93, 94]. SnO_2 nanomaterials suffered from fast recombination because of its inherently low conduction band edge (CBE) [95]. Nb_2O_5 could be a promising candidate for photoanode. However Nb_2O_5 has large unit cell dimension which resulted in large particle size and hence low surface area for dye anchoring [96] and therefore, the short circuit current density (J_{sc}) value and conversion efficiency were generally lower. Finally, SrTiO_3 photoanode also faced the same problem with generally large particle size that limited the dye-loading [92].

B. Doped-TiO₂ as Photoanode

In order to further improve the energy conversion efficiency of DSSCs, changing the band structure or surface states of TiO₂ using metal or non-metal material doping has gained considerable interests. Table 2.1 summarizes the recent reported works based on doped-TiO₂ as photoanode for DSSCs.

In summary, doping TiO₂ with metal or non-metal elements resulted in improved spectral response, shift of flat band potential and enhanced charge carrier transport. Among all the doping materials, N-doped TiO₂ as photoanode has proven to be a promising approach with the highest number of publications.

Table 2.1 Reported works on metal doped-TiO₂ as photoanode for DSSCs.

Dopant	Observations and Conclusions	References
Metal doping TiO₂		
Zinc (Zn)	<ul style="list-style-type: none"> ✓ Efficient electron transport. ✓ The density of empty trap states was reduced due to the elevated electron Fermi level that enhanced band bending. ✓ Prevent the decay of light-to-electric energy conversion efficiency. 	[32]
Tantalum (Ta)	<ul style="list-style-type: none"> ✓ Shifted the flat band potential positively and increased the electron density to improve the driving force of injected electrons from the LUMO of the dye to the conduction band of TiO₂, resulting in improved J_{SC}. ✓ The increased electron density accelerated the transfer rate of electrons and improved the fill factor. 	[33, 34]
Zirconium (Zr)	<ul style="list-style-type: none"> ✓ Shifted the conduction band edge toward higher energies, resulting in increased of V_{OC}. 	[35]
Niobium (Nb)	<ul style="list-style-type: none"> ✓ Increased the conductivity of the TiO₂ powder ✓ Flat-band potential (V_{fb}) has a positive shift enhanced electron injection and transfer efficiency. 	[36, 37]

Table 2.1 Reported works on non-metal doped-TiO₂ as photoanode for DSSCs.

Dopant	Observations and Conclusions	References
Lanthanide (Eu ³⁺ and Sm ³⁺ ions)	<ul style="list-style-type: none"> ✓ Down-conversion luminescence characteristics of la³⁺ ions improved UV radiation harvesting. ✓ Increased the J_{SC}. ✓ Increased open circuit potential (<i>V</i>_{OC}) through elevated the energy level of the oxide film. 	[97, 98]
Lanthanide (Er ³⁺ -Yb ³⁺)	<ul style="list-style-type: none"> ✓ Better optical scattering property. 	[99]
Aluminium (Al) / Tungsten (W)	<ul style="list-style-type: none"> ✓ The metal ion dopants induced electrical surface-state modification ✓ Changes in the surface morphology, electron transfer kinetics, and dye adsorption characteristics ✓ Enhanced <i>V</i>_{OC} and J_{SC}. 	[100]
Chromium (Cr)	<ul style="list-style-type: none"> ✓ Suppression of electron recombination leading to enhancement of J_{SC}. 	[101]
Non-Metal Doping TiO₂		
Boron (B)	<ul style="list-style-type: none"> ✓ Narrowing of band gap. ✓ Enhanced electron injection rate. ✓ Retardation of the charge recombination due to perfect matching between the LUMO of dye molecules and the conduction band of TiO₂. ✓ Enhanced electron lifetime. 	[49, 50]
Sulfur (S)	<ul style="list-style-type: none"> ✓ Improved spectral response, charge injection and electron transport efficiency. 	[47]
Carbon (C)	<ul style="list-style-type: none"> ✓ Increased surface area from the reaction between the carbon elements and oxygen from the TiO₂ lattice. 	[48]
Nitrogen (N)	<ul style="list-style-type: none"> ✓ Improved spectral response. ✓ Changed in the flat band potential resulting in the improvement of the <i>V</i>_{OC}. ✓ Enhanced electron lifetime, retarded the recombination at the TiO₂/electrolyte interface leading to enhanced J_{SC}. ✓ Increased the isoelectric point of TiO₂ nanoparticles and offered a favorable surface for the adsorption of electronegative dye molecules. ✓ Highly efficient in electron transport. ✓ Exhibited great stability. 	[38-46]

C. Nanostructured-based Photoanode

Nanoparticle films have been considered as a trademark for high porosity photoanode in DSSCs. However, it has been regarded that the nanoparticle films are not the perfect choice for efficient transport of electrons. The electron transport in the mesoporous nanoparticle film is dominated by diffusion instead of drift due to lack of a macroscopic electrostatic potential gradient in the film [102]. Charge separation without the presence of an electric field is not efficient. The slow percolation of electrons through the random network of polycrystalline nanoparticles through the trapping and de-trapping process is also a reason in limiting the further improvement in the photo-conversion efficiency achievable in nanocrystalline DSSCs. This is due to the structural disorder at the interface between two adjacent crystalline nanoparticles. The numerous grain boundaries existing in the mesoporous nanoparticle film lead to enhanced scattering of free electrons, thus reducing electron mobility [103, 104].

In order to achieve a breakthrough in the conversion efficiency of DSSCs, one-dimensional (1D) nanostructures such as nanowires and nanotubes and three-dimensional (3D) nanostructures such as branched nanowires, nanoflowers were used to facilitate a direct charge transport along the length of the nanostructures towards the electrode to minimize the effect of random charge hopping across and trapping at nanoparticles grain boundaries [18]. Hence, the charge transport and collection efficiency will be greatly improved. This enhancement in the electronic transport also allows effective light harvesting as thicker film can be used for higher dye loading with longer electron lifetime [105, 106].

The utilization of nanostructured photoanode was first demonstrated by Law et al. [107] as shown in Figure 2.4. The ZnO nanowires were grown with a high aspect ratio to provide sufficient surface area for dye anchoring. It was proven that these ZnO nanowires photoanode possessed high electron diffusion coefficients for longer charge diffusion length, superior in electron injection kinetics and higher charge collection efficiency. The internal electric field was established for efficient separation of injected electrons from the electrolyte by drifting them towards the electrode.

Figure 2.4 (a) Schematic diagram of the nanowire dye-sensitized cell, based on a ZnO nanowires array; (b) The cross-sectional FESEM image of a cleaved ZnO nanowires array on FTO glass [107].

The well-aligned and self organized TiO₂ nanotubes have also been incorporated in the dye-sensitized solar cells (DSSCs) [108-111]. These TiO₂ nanotube arrays are generally fabricated by anodization of thick titanium foil. The nanotube arrays resulting from anodization were amorphous and subsequent annealed at temperature > 450 °C to form crystalline ordered nanotubes. From the studies on the transport and recombination properties of DSSC devices using the nanotube arrays and the standard nanoparticles-based mesoporous TiO₂ film with similar thickness, it was found that the nanotube arrays

based DSSCs had greater charge collection efficiency compared to nanoparticles-based DSSCs due to the 10 times slower recombination rate [106]. This has resulted in higher short circuit current density in the nanotube based DSSCs. The conversion efficiency achieved by the best DSSCs using nanotube arrays as photoanode was over 4 % under AM 1.5 sun [105]. Figure 2.5 gives an illustration of nanotube DSSCs and the FESEM images of titanium nanotube arrays.

Figure 2.5 (a) Schematic diagram of a typical nanotube dye sensitized solar cells using back-side illumination [105]; (b) FE-SEM image of titanium nanotube arrays fabricated from anodization of titanium foil [111].

A major disadvantage of using nanotube arrays synthesized from the anodization of titanium foil ($\sim 250 \mu\text{m}$) is that the device requires backside illumination through Platinum coated counter electrode. This configuration is not optimal for the DSSCs since the platinum counter electrode can partially reflect light, and the iodine in the electrolyte can absorb photon at lower wavelength [105]. Despite these limitations, the nanotube array DSSCs are still able to exhibit respectable conversion efficiency.

In 2005, Mor et al. synthesized titanium nanotube arrays on transparent conducting glass substrate, typically Fluorine-doped Tin oxide (FTO) glass, by sputtering high quality

titanium thin film and subsequently anodized and annealed to form the transparent TiO₂ nanotube arrays [112]. However, the device showed relatively low fill factor (*FF*) value due to the poor adhesion between the barrier layer and FTO substrate that led to a higher series resistance. Moreover, the resistivity of the FTO substrate increased by ten folds after oxygen annealing step to crystalline the nanotube array [111]. Another shortcoming of using this method was the inability of forming longer nanotube (< 500 nm compared to ~ 6 μ m using titanium foil) that resulted in less photo-absorption due to lower dye loading. These are technical challenges that need to be tackled for further improvement.

In recent years, TiO₂ nanowires also attracted a lot of interests to be utilized as photoanode in DSSCs [113, 114]. Hydrothermal growth has been reported to be a novel method for the synthesis of TiO₂ nanowire array on FTO glass substrate. It was shown that nanowires possessed a low series resistance, effective in separating the photo-generated charge with low charge recombination. The photovoltaic performance of the TiO₂ nanowires with standard DSSC configuration had been demonstrated with a conversion efficiency of 5 % [113, 114].

In short, the use of nanostructured photoanodes had been demonstrated to have promising improvement in increasing electron diffusion length, suppressing back recombination and enhancing charge transport and collection efficiency. The current challenge lies on further increasing the surface area or the length of nanostructures to allow for higher dye-loading.

2.3.3 Dye Sensitizer

The dye sensitizer serves as a solar photon absorber in DSSCs. The optical properties of the sensitizer have great effect on the light harvesting efficiency and the overall photovoltaic performance. The ideal sensitizer should firmly be grafted to the mesoporous semiconductor oxide surface, have high absorption across the visible light spectrum, and inject the photo-excited electrons to the conduction band of the oxide semiconductor with near unity quantum yield. The redox potential of the dye sensitizer should be high enough for rapid regeneration through the electron donation from electrolyte. Nevertheless, it should be stable under long term solar illumination. The most commonly used dye sensitizers are the Ruthenium complex organic dye sensitizer, such as *cis*-RuL₂(NCS)₂(L₂=4,4'-dicarboxy-2,2'-bipyridyl), often referred as N3 (or N719 for the ditetrabutylammonium salt of N3) [76]. N3 dye was introduced in 1993 and the photovoltaic performance of N3 dye for DSSC remained at the top spot for 8 years till 2001, when the “black-dye” tri(cyanato)-2,2'2''-terpyridyl-4,4'4''-tricarboxylate) Ru(II) dye achieved a record of 10.4 % (AM 1.5) solar to electricity conversion efficiency [77]. This black dye can absorb light in the near-IR region up to 900 nm as shown in Figure 2.6. Besides the metal complex dyes, there has been a great interests in developing organic dyes such as coumarin [115], porphyrins [116], perylene [117] and indoline [118, 119]. In fact, the conversion efficiency of DSSC using indoline dye D205 reached 9.5 % in 2008, on par with metal complex dyes [118]. Figure 2.7 shows the evolution of the conversion efficiencies for DSSCs with ruthenium complexes and organic dyes. The main challenge lying ahead would be the long term stability of these mainly organic dyes for outdoor photovoltaic use.

Figure 2.6 Spectral response of DSSCs using N3 and black dye, the incident photon to current conversion efficiency is plotted as a function of wavelength. The chemical structure of the dyes are given as well [13].

Figure 2.7 The evolution of conversion efficiency for DSSCs based on ruthenium complexes and organic dyes [120].

2.3.4 Redox Electrolyte

The electrolyte used in the standard DSSC fabrication contains I^-/I_3^- redox ions. These redox ions serve as a charge mediator between the photoanode and the counter electrode.

Iodine (I₂) and Iodide salts such as LiI, NaI, KI, tetraalkylammonium iodide (R₄NI), and the imidazolium-derivative iodides, are dissolved in non-protonic solvents such as acetonitrile, methoxyacetonitrile to form the electrolyte. Low-viscosity solvents are preferred to improve the device performance, since high concentration iodide electrolyte might screen the absorption of dye [121]. Other redox electrolytes such as Br⁻/Br₂⁻ [122] and pseudo-halogen redox complex [123, 124] have also been used for DSSCs as well but the redox electrolyte using I⁻/I₃⁻ still gives the best photovoltaic performance.

2.4 Light Harvesting by Sensitizer

Considering a 10 μm thick mesoporous wide bandgap semiconductor oxide film consisting of 20 nm nanoparticles, the available particle surface area is estimated to be over 1000 times larger than the projected surface area. Due to the small size of the nanoparticles, this oxide film has high transparency and negligible light scattering. Hence, Lambert Beer's Law can be used to describe the light absorption of the absorbed dye sensitizer on these mesoporous semiconductor oxide film [14].

$$\alpha = \sigma c \quad (2.8)$$

where σ is the optical absorption cross section of the sensitizer and c is the concentration of dye molecules in the mesoporous film.

The value of σ is derived from the molar extinction coefficient ε of the sensitizer using the following formula:

$$\sigma = \varepsilon \times 1000 (\text{cm}^2 \text{mole}^{-1}) \quad (2.9)$$

For the widely used Ruthenium N3 or N719 dye, the optical cross section peak (absorption maximum) of this sensitizer is at 530 nm, where it has an absorption

maximum of $1.4 \times 10^7 \text{ cm}^2/\text{mole}$ and its concentration in the nanocrystalline film at full monolayer coverage is typically $2 \times 10^{-4} \text{ mole/cm}^3$. Therefore, $\alpha = 2.8 \times 10^3 \text{ cm}^{-1}$ and the absorption length $= 1/\alpha$ is $3.6 \text{ }\mu\text{m}$ for 530 nm light.

The Light Harvesting Efficiency (*LHE*) is derived from the reciprocal absorption length using:

$$LHE = 1 - T = 1 - 10^{-\alpha d} \quad (2.10)$$

where d is the thickness of the mesoporous semiconductor oxide film.

Using $d = 10 \text{ }\mu\text{m}$ and $\alpha = 2.8 \times 10^3 \text{ cm}^{-1}$, the *LHE* value can be over 90 % in the wavelength near the absorption maximum of the sensitizer. Therefore, photon with energy near to the absorption maximum of the dye would be completely absorbed even though only a monolayer of dye molecules is covering the surface of the nanoparticles.

The wavelength-dependent Incident Photon-to-Current Conversion Efficiency (IPCE), is also referred as “External Quantum Efficiency” (EQE), is determined from the measurement of the photocurrent and illumination intensity as a function of wavelength. IPCE is the ratio of the number of electrons collected at the FTO electrode to the number of photons incident on the cell at short-circuit condition. IPCE is obtained by the following equation:

$$IPCE = LHE(\lambda) \phi_{inj} \eta_c \quad (2.11)$$

LHE is the light harvesting efficiency for photons of wavelength λ , ϕ_{inj} is the quantum yield for electron injected from the excited dye molecule to the conduction band of the semiconductor oxide and η_c is the electron collection efficiency at the electrode. If both

ϕ_{inj} and η_c are close to 1, then the IPCE is determined by the *LHE* of the dye absorbed on the semiconductor oxide film.

2.5 Charge Transfer Kinetics in DSSC

The overview of the electron transfer kinetics in the DSSC is shown in the schematic diagram of Figure 2.8.

Figure 2.8 Schematic diagram of electron transfer kinetics in DSSCs [14].

2.5.1 Electron Injection Processes

Upon light illumination, the dye sensitizer will be photo-excited, leading to electron injection into the conduction band of the TiO_2 layer. Time-resolved laser spectroscopy measurements are usually used to investigate this electron injection process [125].

The injection rate of electron from the excited dye sensitizer into the conduction band of oxide semiconductor mainly depends on the structure of the adsorbed dye sensitizer molecules on the oxide semiconductor surface and the energy gap between the lowest

unoccupied molecular orbital (LUMO) level of the dye sensitizer and the conduction band level of the oxide semiconductor [14].

Based on the Fermi's golden rule expression, the rate constant for the injection of electron, k_{inj} , is given by

$$k_{inj} = \left(\frac{4\pi^2}{h} \right) |V|^2 \rho(E) \quad (2.12)$$

where V is the electronic coupling between the dye sensitizer and the oxide semiconductor, $\rho(E)$ is the density-of-states in the conduction band of oxide semiconductor, and h is the Planck constant. The value of V is associated with the overlapping of wave function of the dye sensitizer (in the excited state) and the conduction band of oxide semiconductor. It is also affected by the distance between the adsorbed dye sensitizer molecules and the oxide semiconductor surface.

In DSSC, the carboxyl group in the dye sensitizer is designed to strongly anchor onto the surface of the oxide semiconductor, resulting in large V value. Besides that, the conduction band of the oxide semiconductor has a continuous and relatively large density-of-states. Thus, the k_{inj} for the photogenerated electron injected from the dye sensitizer is very high, in the order of femtoseconds, and thus contributes to high solar energy conversion efficiency [126, 127].

2.5.2 Electron Transport in TiO₂ Film

The mechanisms involved in the electron transport through the mesoporous TiO₂ have been studied by many researchers and are still hotly debated. When the DSSC was first

presented, there had been many discussions on the highly efficient charge transport through the mesoporous TiO_2 layer. Intensity Modulated Photocurrent or Photovoltage Spectroscopy (IMPS/IMVS) [128-134], Electrochemical Impedance Spectroscopy (EIS) [135-140], transient photocurrent and photovoltage measurements [141, 142], and Open Circuit Voltage Decay (OCVD) technique [143, 144] have been used to study the transport properties of the injected electrons in the mesoporous oxide layer and the back recombination reaction with electrolyte. Several mechanisms had been proposed with respect to these measurement techniques, such as the well-known ambipolar diffusion model [86, 145], a multiple trapping/de-trapping mechanism [146-149] and an insulator-metal (Mott) transition mechanism [150].

There is no dispute that the electron conductivity in TiO_2 is very low, resulting in a relatively slow response of the photocurrent. For example, the diffusion coefficient of the electrons in the mesoporous TiO_2 film is estimated to be around $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [86]. However in DSSCs, the electron conductivity of the TiO_2 film is greatly increased due to the electron injection from the dye sensitizer under light illumination. Moreover, the conductivity and the photocurrent response of the TiO_2 film is also greatly improved by increasing the incident light intensity [151, 152]. When the injected electron fill the trap states on the surface level of the TiO_2 nanoparticles, the diffusion coefficient of the electron increase resulting in efficient transport of electron.

2.5.3 Charge Recombination

As shown in Figure 2.8, in order to accomplish effective charge separation, the charge recombination between the injected electrons in the mesoporous layer and the oxidized

dye molecules in the electrolyte must be slower than the electron injection and regeneration of sensitizer molecules with electron transfer from I^- into oxidized dyes. It was reported that the charge recombination between the injection electrons in the TiO_2 and N3 dye cations occurred at a much slower rate, in the order of microseconds to milliseconds, as compared to the ultrafast electron injection [126, 153]. This had resulted in an effective charge separation and good device performance.

2.5.4 Regeneration of Oxidized Dye Sensitizer

In order to achieve effective charge separation in DSSC, the electron transfer from I^- ion to regenerate the oxidized dye sensitizer (S^+) should occur much faster than the charge recombination process between the injected or photogenerated electron and the oxidized dye. The kinetics to regenerate the oxidized dye from the electron transferred from I^- ion had been investigated by time-resolved laser spectroscopy. It was found that the electron transfer rate from the I^- ion into the cation of the N3 dye was estimated to be 100 ns [153], around two orders faster than the recombination process.

2.5.5 Recombination between Injected Electrons and Tri-iodide Ions (Dark Current)

Recombination of injected electrons on the oxide semiconductor layer with the tri-iodide ions (I_3^-) as shown in Figure 2.8 is responsible for what is also known as dark current [154]. The electron recapture reaction is described in equation (2.7) in section 2.2.

This reaction can happen on both mesoporous TiO_2 layer and also the SnO_2 surface (FTO electrode) if the mesoporous TiO_2 layer does not fully cover the transparent conducting substrate. This recombination, similar to the injection of holes and electrons in the p-n

junction under forward bias, leads to the deterioration of photovoltaic performance. The open circuit voltage, V_{OC} of the DSSC is related to the I_{inj} and dark current in the following equation:

$$V_{OC} = \frac{kT}{q} \ln \left(\frac{I_{inj}}{I_O} + 1 \right) \quad (2.13)$$

where k is the Boltzman constant, q is the electronic charge, T is the absolute temperature, and I_O is the dark current and can be represented by the following equations:

$$I_O = qn_O k_{et} [I_3^-] \quad (2.14)$$

where n_O is the electron density on the conduction band of the oxide semiconductor in the dark, k_{et} is the rate of constant for recombination and $[I_3^-]$ is the concentration of the oxidized redox mediator in the electrolyte.

This recombination must be very slow for the DSSC to work. In fact, based on the investigation performed by Huang et al., the recombination reaction rate was estimated to be in the order of second [155]. The dark current normally occurs at the TiO_2 /electrolyte interface where the dye sensitizers are not present. A good way to suppress the dark current is to employ the pyridine derivatives such as tert-butylpyridine (TBP) in the electrolyte that would be absorbed onto the uncovered nanoparticle oxide surfaces and would lead to an improvement in the V_{OC} [155]. Another major concern is to prevent the direct contact of the electrolyte to the FTO electrode by using a dense TiO_2 barrier layer. The study on this is reported in the project.

2.6 Equivalent Circuit Modeling and Transport Property of the DSSC

2.6.1 Electrochemical Impedance Spectroscopy (EIS)

EIS has been widely employed to investigate the kinetics of electrochemical and photoelectrochemical system. It has been used to study the prominent electronic and ionic processes in DSSCs [135-140]. Under certain conditions, the electron transport in the mesoporous TiO_2 film, electron transfer at the TiO_2 /dye/electrolyte interface, electron transfer at the counter electrode, and diffusion of the redox species in electrolyte can be modeled with the equivalent circuits to explain impedance responses and phase spectra measured as a function of frequency.

The Nyquist plot (plot of imaginary impedance versus real impedance measured at varying frequency) from the EIS measurement typically consists of three semicircles. The low frequency region is attributed to the Nernst diffusion of the ions within the electrolyte. The intermediate frequency features the electron transfer at the oxide/dye/electrolyte interface. Finally, the high frequency region is attributed to the redox reaction at the platinum counter electrode and electron transfer at the mesoporous TiO_2 and FTO electrode [138]. A measured EIS spectrum is shown in Figure 2.9.

Sometimes, the low frequency peak might disappear underneath the mid-frequency peak. Based on the Bode phase diagram, the effective electron lifetime in TiO_2 film can be determined from the peak frequency of the mid-frequency area as shown in Figure 2.9 (a)/(b) [140].

Figure 2.9 Impedance spectra of DSSC measured at open circuit potential both in dark and under 1 sun. (a) Bode phase plot; (b) Nyquist plot; [138]; (c) Schematic of the equivalent circuit for the DSSC structure.

The equivalent circuit for the DSSC structure is shown in Figure 2.9(c). The circuit elements involved are defined as follow:-

- R_S is a series resistance due to the FTO glass.
- R_{P1} is charge-transfer resistance at the mesoporous TiO_2 /FTO electrode interfaces.
- C_{P1} is the interfacial capacitance at mesoporous FTO/ TiO_2 /electrolyte interfaces.
- R_t is the electron transport resistance.
- C_μ is the chemical capacitance due to the change of electron density as a function of the Fermi level.
- R_μ is a charge-transfer resistance related to recombination of electrons at the TiO_2 /electrolyte interface.
- W is the impedance of diffusion of redox species in the electrolyte.
- R_{P2} is the charge-transfer resistance at the counter electrode/electrolyte interface.
- C_{P2} is the interfacial capacitance at the counter electrode/electrolyte interface.

Using the transmission line model, the impedance function of the diffusion–reaction in the photoanode of DSSC can be represented as [137]:-

$$Z = \left(\frac{R_t R_\mu}{1 + i\omega/\omega_k} \right)^{1/2} \coth \left[\left(\frac{\omega_k}{\omega_d} \right)^{\frac{1}{2}} \left(1 + \frac{i\omega}{\omega_k} \right)^{\frac{1}{2}} \right] \quad (2.15)$$

where $\omega_d = 1/R_t C_\mu$ is the characteristic frequency of charge transport process in the mesoporous layer, $\omega_k = 1/R_\mu C_\mu$ is characteristic frequency of charge transfer and recombination processes at $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, ω is the angular frequency.

The steady state (dc) equivalent resistance in the photoanode layer in according to transmission line model is given by ($\omega \rightarrow 0$)

$$R_{TiO_2} = \sqrt{R_t R_\mu} \coth \left(\sqrt{\frac{R_t}{R_\mu}} \right) \quad (2.16)$$

Hence the equivalent resistance of the photoanode is determined by the equivalent resistance arising from the electron transport and recombination processes. These two parameters can be extracted from experimental impedance spectra. R_t could be determined from a linear part in the complex plane impedance plot, at an phase angle of 45° . The R_μ value could be reproduced from the real axis of the impedance arc in the Nyquist Plot. In the low recombination conditions, the total resistance of the photoanode can be approximated as follows [137, 156]:-

$$R_{TiO_2} = \frac{1}{3} R_t + R_\mu \quad (R_t < R_\mu) \quad (2.17)$$

The arc for the charge transfer at $\text{TiO}_2/\text{dye}/\text{electrolyte}$ is always visible in the EIS measurement of a DSSC. However, the R_t may not be visible as it can be negligibly small. Thus it may be overlapped with the counter electrode impedance arc. The other possible

occurrence to DSSC is the extremely large R_t due to the poor quality of photoanode. In this case, the general impedance equation will become Gerischer impedance:-

$$Z = \left(\frac{R_t R_\mu}{1 + i\omega/\omega_k} \right)^{1/2} \quad (2.18)$$

$$R_{TiO_2} = \sqrt{R_t R_\mu} \quad (R_t > R_\mu) \quad (2.19)$$

Both R_t or R_μ cannot be accurately determined from the impedance data. In general, Gerischer impedance is seen when the electron diffusion length is shorter than the film thickness, resulting in large recombination.

The impedance spectra at different applied biases are shown in Figure 2.10 (a)-(e). The corresponding equivalent circuits of DSSCs are depicted in Figure 2.11. At the lower applied potentials (Figure 2.10 (a)-(b)), the main feature is a simple semicircle demonstrated by the TiO_2 layer acting as an insulator. The equivalent circuit is well represented in Figure 2.11(b) that consists of parallel association of R_{TCO} and C_{TCO} in series with the equivalent resistance of the TCO layer R_S .

Figure 2.10 Impedance Nyquist spectra of DSSC at different applied bias to review the high frequency and low frequency response of the DSSC [135].

Figure 2.11 (a) Equivalent circuit model for DSSC; (b) Circuit model for DSSC with insulating TiO_2 at lower applied bias; (c) Circuit model for DSSC with TiO_2 in conductive state at applied bias closed to open circuit potential [135].

At intermediate potentials (Figure 2.10 (c)-(d)), the impedance spectra correspond to the behavior of transmission line model as described in Eq. 2.15. The diffusion characteristic could be seen in the high frequency region, with a slope close to 1. The transport resistance value can be estimated from this linear part in the complex plane impedance plot. The mid-frequency semicircle is contributed by the parallel association of the electron chemical capacitance (C_{μ}) with charge-transfer resistance (R_{μ}) along the TiO_2 /dye/electrolyte interface. As the applied potential is closed to the open circuit potential (Figure 2.10 (e)), both R_t and R_{μ} become smaller due to the increasing electron density. The equivalent circuit features a parallel connection of R_{μ} and C_{μ} in series with R_s as illustrated in Figure 2.11(c). The effects of the counter electrode and diffusion in the

electrolyte are taken into account too. Hence, with this understanding, the evolution of transport resistance in TiO_2 and other components could be determined based on the equivalent circuit at different applied biases.

2.6.2 Intensity Modulated Photocurrent Spectroscopy (IMPS)

IMPS is normally used to measure the periodic response of the photocurrent to the superposition of a small sinusoidal perturbation of the light intensity with reference to a large steady background level. This measurement has been widely used to provide the information about the dynamics of charge transport and back reaction of a DSSC [128-134]. In general, the IMPS data corresponds to the value of the transfer function between the modulated light intensity and the measured ac current of the DSSC device at short circuit condition:-

$$H_{IMPS} = \frac{\Delta I}{\Delta \phi} \exp(i \cdot \varphi) \quad (2.20)$$

where H_{IMPS} is the transfer function, ΔI is the variation in the photocurrent, $\Delta \phi$ is the variation in photon flux and φ is the phase angle. An illustration of a typical experimental setup for IMPS measurement is shown in Figure 2.12.

Figure 2.12 Illustration of a IMPS experimental setup with a DSSC device illuminated by the light emitting diode (LED) that is driven by frequency response analyzer (FRA). The amplifier A is a photocurrent amplifier [131].

Figure 2.13 illustrates a typical complex plane plot for the IMPS response at the highest light intensity used. In this plot, the photocurrent lags behind the modulated illumination, resulted in a semicircle response in the fourth quadrant (positive real, negative imaginary) of the complex plane. Under the assumptions of no electron-hole pair recombination and the electron transfer across the TCO-TiO₂ interface is much faster than the electron transfer through the mesoporous oxide layer, the phase shift of the IMPS semicircle is a result of the time delay between the generation and collection of charge carriers [132]. At high frequencies, the modulation frequency is much faster than the relaxation of the charge carrier density by transport to the contacts and or recombination by back reaction. Hence, the modulated photocurrent approaches zero. At low frequencies, the IMPS plots converge to a point on the real axis that corresponds to the steady state photocurrent of the DSSC device under measurement. The measurement frequency (f_{min}) that resulted in the lowest imaginary component in the IMPS complex plot is of special importance. At this minimal point, the modulation frequency corresponds to the rate of relaxation of charge carrier. Thus, the phase lag due to this modulated frequency (f_{min}) is equivalent to the transit time ($t_{tr} = 1/2\pi f_{min}$) or the average time required for a generated electron to be collected [134].

Figure 2.13 Illustration of a typical IMPS response of a DSSC device [133].

CHAPTER 3 OPTIMIZATION OF DYE-SENSITIZED SOLAR CELL DEVICE FABRICATION

This chapter describes the developmental efforts on the dye-sensitized solar cell (DSSC) device fabrication and characterization. Emphasis is on the optimization of fabrication process especially the photoanode for DSSC. The consistency in the device fabrication is important to ensure a good baseline process for further improvements to be reported in later chapters.

Figure 3.1 shows the general research efforts involved in this project. After the successful synthesis and characterization of the TiO_2 nanoparticles, the precursor nanoparticles were formulated into viscous pastes using suitable solvent and organic binder. The paste was then deposited onto FTO glass substrate using doctor blade method. This was then followed by annealing process to decompose the organic compounds (including the solvents and organic binder) for the formation of mesoporous TiO_2 layer on the FTO glass substrate. The mesoporous TiO_2 film was then subjected to thorough physical, chemical and optical characterizations. Further optimization works were then carried out according to the characterization results through repeated cycles. The optimized procedure for the formation of the mesoporous TiO_2 photoanode was then used as the baseline process for DSSC device fabrication. Further efforts were carried out for the developmental, characterization and optimization of the TiO_2 barrier layer on the FTO transparent

conducting electrode before the photoanode formation to improve the overall photovoltaic performance of the DSSC device.

After thorough characterization and optimization of the constituent structural components such as the photoanode and transparent conducting electrode, the assembly procedure was further optimized for the standardized DSSC device fabrication process flow. Finally, the photovoltaic performance and charge transport property of the assembled DSSCs were then characterized by the solar simulator, Incident Photon-to-current Conversion Efficiency (IPCE), Electrochemical Impedance Spectroscopy (EIS) and Intensity Modulated Photocurrent Spectroscopy (IMPS).

Figure 3.1 General research flow for the fabrication and optimization of DSSC device in this project.

3.1 Mesoporous TiO₂ Layer as Photoanode for DSSC

TiO₂ is the most widely used metal oxide semiconductor material to make the mesoporous layer in DSSC device fabrication. The mesoporous TiO₂ layer provides large surface area for anchoring the dye sensitizer dye molecules. This nanocrystalline semiconductor oxide layer on the FTO electrode (the photoanode) also serves as an electron collector for the electrons injected from the photo-excited sensitizer dye molecules under solar irradiation. The injected electrons will then be transported through the nanocrystalline TiO₂ network to the transparent conducting electrode. High quality photoanode made from TiO₂ nanoparticles were evaluated for different parameters such as the pore diameter, particle size, film thickness and the surface area for optimum photovoltaic performance.

The objective of this study was to determine the best type of TiO₂ nanoparticles as the precursor for the formation of mesoporous photoanode which would give the photovoltaic results. The DSSC with this type of photoanode will then serve as the reference for further improvement. A total of three types of TiO₂ nanoparticles, namely the Degussa P25 TiO₂ nanoparticles, the Anatase TiO₂ nanoparticles from Alfa-Aesar and the TiO₂ nanoparticles synthesized in-house using hydrothermal method, were used to prepare the photoanodes for DSSC device fabrication. The performances of DSSCs using these different types of TiO₂ photoanodes are described.

The first step in DSSC device fabrication is the conditioning of the transparent conducting oxide layer on the glass substrate, this is followed by the deposition of the viscous paste containing the precursor nanoparticles. The paste is formulated from the precursor nanoparticles. The viscous paste containing the dispersion of colloidal TiO₂ nanoparticles is casted onto the transparent conductive oxide (TCO) glass substrate using the doctor

blade deposition method or screen printing method. The mesoporous TiO_2 film is formed by thermal annealing at raised temperature of the deposited paste.

Several types of TiO_2 nanoparticles are commonly used to prepare the colloidal TiO_2 dispersions and then the paste. TiO_2 nanoparticles can be prepared by the hydrolysis of titanium alkoxide with acid solution and then followed by peptization. After that, the colloidal is autoclaved at 150 to 250 °C for several hours to form a viscous colloidal [157-159]. The other commonly used TiO_2 nanoparticles for DSSC device fabrication is the commercial TiO_2 (Degussa P25) that is usually used as a benchmark for comparison [160, 161]. Generally, the anatase phase rather than the rutile phase of the TiO_2 is preferred to be used as photoanode. This is due to its superior light-scattering properties and higher electron mobility that are beneficial for effective light harvesting [162].

3.1.1 Synthesis of TiO_2 Nanoparticles by Hydrothermal Method

The hydrothermal TiO_2 nanoparticles was synthesized according to the procedure as reported by Barbé et al. [157]. A total of 25 ml of titanium isopropoxide (97%, Aldrich) was added slowly to 200 mL of a 0.1M nitric acid solution under vigorous stirring at room temperature. This hydrolysis process produced white precipitate. Then, the colloidal was heated to 80°C and stirred vigorously overnight for 12 hours (the so called peptization step). After the peptization, the solution was filtered and crystalline growth was performed in hydrothermal condition by autoclaving at the temperature of 200 °C for 14 hours. The freshly formed TiO_2 nanoparticles were then washed repeatedly with ethanol using centrifuge (Hermle Z366) at 10000 rpm to get rid of the water content.

3.1.2 Paste Formulation and Deposition of Photoanode

To prepare the thick paste for doctor blade deposition method, the measured amount of TiO_2 nanoparticles (either P25 TiO_2 , Anatase TiO_2 or hydrothermal TiO_2) were first dispersed in ethanol. The mixture was further dispersed using a titanium ultrasonic horn (Sonics Vibra Cell VC505, 500 W, 75×2 pulses) to form a homogenized colloidal. Next, α -terpineol (97%, Aldrich) was added into the colloidal and stirred vigorously. Finally, this homogenized colloidal was poured into the beaker containing 10 wt% ethyl cellulose (Aldrich) in ethanol solution prepared earlier. The colloidal was then heated up to 80°C under vigorous stirring for at least 15 hours to evaporate the ethanol content to give a thick homogenized paste. The thick homogenized paste was ready for deposition onto FTO glass substrate using doctor blade method. The paste was squeezed onto the FTO glass substrate through a hole on a spacer tape attached onto the FTO glass substrate. Then, the deposited paste on the FTO substrate was subjected to necessary thermal annealing process at temperature of 400 to 500°C .

3.1.3 Assembly of Standard DSSC Device

The assembly procedure of a standard DSSC device in this project is illustrated in Figure 3.2. The Fluorinated Tin Oxide (FTO) glass substrate (Hartford, TEC-7) was used after careful cleaning. The active area was defined by a hole with the size of 0.28 cm^2 cut in a 3M scotch tape. The tape was then attached to the FTO glass. The TiO_2 paste was coated on the FTO glass by doctor blade method. The paste was then annealed at 450°C in synthetic air ($\text{N}_2:\text{O}_2 = 4:1$) for 60 minutes in Lindberg tube furnace to form the mesoporous film. The thickness of the resulting mesoporous TiO_2 film was determined by

the solid content during the preparation of the colloidal and also the doctor blade distance adjustment during the paste deposition step. The film thickness was measured using surface profiler to be about 10 μm .

After that, the freshly-annealed photoanode was dipped into the 0.25 mM N719 dye solution (Solaronix) overnight for complete penetration and attachment of the dye molecules into the mesoporous layer.

Figure 3.2 Assembly of standard DSSC for photovoltaic characterization.

The platinum coated counter electrode was then clamped onto the photoanode, with the Surlyn spacer (30 μm) in between. Next, the iodide electrolyte (Solaronix, Iodolyte AN50) was filled through capillary action in vacuum condition to allow the complete

infiltration of electrolyte into the TiO₂ mesoporous film and the gap formed by the Surlyn spacer. The DSSC device was then sealed using thermoplastic. The assembled DSSC device was ready for photovoltaic testing.

In this study, a total of three types of TiO₂ photoanode for DSSC devices were prepared, namely the photoanode prepared from Degussa P25 TiO₂ nanoparticles (P25), anatase TiO₂ nanoparticles from Alfa-Aesar (ANT) and the hydrothermal TiO₂ nanoparticles (HTT).

3.2 Characterization of TiO₂ Nanomaterials as Photoanode

3.2.1 Crystalline Phase Structure of TiO₂ Nanomaterials

The crystalline phase structure of the different types of TiO₂ mesoporous film on glass substrate was investigated using the Siemens D5005 X-ray diffractometer (XRD). The X-ray source was Cu K α X-ray radiation at 1.54056 Å generated at 40 kV and 40 mA. The mesoporous film was tilted 0.5° towards the x-ray beam and fixed throughout the 2θ detector scan from 20 – 80°. The tilt angle was kept small to minimize the penetration of x-ray beam into the substrate.

Scherrer's equation was employed to estimate the average grain size (D) along the normal surface direction:

$$D = 0.9\lambda / B \cos \theta \quad (3.1)$$

where B is the full width at half maximum (FWHM) of the broadened diffraction line on the 2θ scale (radians) and θ is the diffraction angle. The grain sizes were averaged using

the values as determined from the three most prominent peaks using Scherrer's equation.

Figure 3.3 shows the XRD profiles of three different types of TiO₂ nanoparticles.

Figure 3.3 XRD crystalline phase of different types of TiO₂ nanoparticles:-Degussa P25 TiO₂ (P25), Anatase TiO₂ from Alfa-Aesar (ANT) and the hydrothermally TiO₂ nanoparticles (HTT).

From the XRD profiles as shown in Figure 3.3, the main crystalline phase for the TiO₂ sample ANT was anatase. The grain size for sample ANT was estimated to be 17.2 nm. The existence of rutile phase could be attributed to the transformation of the anatase phase to rutile phase under the annealing temperature of 450 °C. The co-existence of anatase and rutile phases was observed for TiO₂ sample P25. The grain size calculated using Scherrer equation was about 13.9 nm.

The hydrothermal TiO₂ nanoparticles (sample HTT) consisted of both anatase and brookite phase. This result was similar to the work reported by Barbé et al. [157]. The

grain size was estimated to be about 7.8 nm, which was relatively small compared with the other two samples.

3.2.2 Surface Morphology of TiO₂ Nanomaterials

The surface morphology of the mesoporous TiO₂ layers was studied by field emission scanning electron microscopy (FESEM, LEO Gemini 1550) inspection. The FESEM is capable of producing a plan view of the mesoporous film to review the surface morphology and microstructure of the mesoporous film, including the particle size, shape, uniformity and coverage, presence of hillocks or whiskers, evidence of film voids and micro-cracking, etc.

The surface morphology of the TiO₂ photoanode plays a vital role in the photovoltaic performance of the DSSC device [163]. Based on the FESEM images in Figure 3.4, the three TiO₂ films prepared from the different types of TiO₂ nanoparticles consisted of mesoporous structure with high film porosity. The mesoporous TiO₂ film consists of a three-dimensional network of interconnected nanoparticles which offers the excellent sites for anchoring the small photosensitizer dye molecules.

Under low magnification of 5000X, sample HTT and P25 were found to give crack-free mesoporous TiO₂ films, with sample HTT showing the best uniformity among all. However, micro-cracks across the film could be seen for sample ANT. Under higher magnification of 50kX, the agglomerated particle size on the mesoporous films could be estimated. The particle size of dense and compact TiO₂ film deposited from freshly synthesized hydrothermal TiO₂ nanoparticles was relatively small with uniform distribution, in the range of 15 – 30 nm.

Magnification: 5kX

50kX

Figure 3.4 Surface morphology for different mesoporous TiO_2 film deposited on FTO glass (a) from hydrothermal TiO_2 (HTT); (b) from Degussa P25 TiO_2 (P25) and (c) from commercially available anatase TiO_2 (ANT).

It is well known that Degussa P25 TiO_2 nanoparticles consists of a mixed phase of 70% anatase and 30% of rutile phase, with particle size at about 30 nm [163]. The FESEM image revealed that the agglomeration of nanoparticles was obvious in the mesoporous

TiO₂ film of sample P25, resulted in quite a large variation in the particle size, ranging from 25 – 80 nm. The surface morphology of P25 TiO₂ film was quite different from the sample HTT, few large pores up to several hundreds of nanometer in between the cluster of nanoparticles could be found. Thus, the sample P25 possessed less compact structure as compared with sample HTT.

Non-uniformity in the size and shape of the agglomerated nanoparticles could be seen for sample ANT with size ranging from around 40 nm to few hundred nanometers. There were also large agglomeration of nanoparticles with flake-like structure stacking on top of each other (image not shown). Nevertheless, the TiO₂ film still possessed a porous structure that was suitable to be used in DSSC device fabrication.

The BET characterization was carried out to determine the specific surface area of these three TiO₂ nanopowder. Based on the measurement results, the HTT possessed the largest specific surface area at 112 m²/g. The specific surface area for commercial Degussa P25 TiO₂ nanopowder is 54.9 m²/g. and the ANT nanopowder having the smallest surface area at 38.5 m²/g. Table 3.1 summarizes the calculated grain size from XRD results and estimated particle size from FESEM images for different TiO₂ nanomaterials.

Table 3.1 Calculated grain size from XRD results and estimated agglomerated particle size from FESEM images for different mesoporous TiO₂ films

Sample	Grain Size (nm)	Agglomerated particle Size (nm)	Specific surface area (m²/g)
HTT	7.8	15 - 30	112.0
P25	13.9	25 -80	54.9
ANT	17.2	40 - 120	38.5

3.2.3 Composition Analysis of Hydrothermal TiO₂ Nanoparticles

X-ray Photoemission Spectroscopy (XPS) characterization was performed to determine the stoichiometry of the hydrothermal synthesized TiO₂ nanoparticles. The X-ray photoemission spectroscopy (XPS) has been developed into the key surface characterization method over the past few decades which combines surface sensitivity with the ability to quantitatively obtain both elemental and chemical state information. XPS was carried out on the sample in the Kratos AXIS Spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation at a power of 150 W. The scanning was carried out in ultra-high vacuum with a vacuum level lower than 1x10⁻⁸ mbar. Charge neutralizer was turned on throughout the scanning. The wide survey scan spectrum in the range of 0-1200 eV was recorded in 1 eV step, with pass energy at 160 eV. It was then followed by narrow scan spectra over different elemental peaks in 0.1 eV steps at the pass energy of 40 eV.

Curve fitting was performed after Shirley background subtraction by the Lorentzian-Gaussian method (LG (30)), from which atomic concentration was calculated according to the following equation [164]:-

$$\%n_i = 100 \left[\frac{\frac{I_{ij}}{\sigma_{ij} E^{0.7}}}{\sum \frac{I_{ij}}{\sigma_{ij} E^{0.7}}} \right] \quad (3.2)$$

$$\text{where, } I_{ij} = K \cdot T(E) \cdot L_{ij}(\gamma) \cdot \sigma_{ij} \cdot n_i \cdot \lambda(E) \cdot \cos(\theta) \quad (3.3)$$

and:

- n_i : atomic quantity of element i ;
- I_{ij} : area peak j from element i ;

- K : instrumental constant;
- $T(E)$: transmission function of analyzer;
- $L_{ij}(\lambda)$: angular asymmetric factor of orbital j of element i ;
- σ_{ij} : photoionization cross-section of peak j from element i ;
- E : kinetic energy of the emitted electron;
- $\lambda(E)$: inelastic mean free path;
- θ : take-off angle of the photoelectrons measured with respect to surface normal.

Figure 3.5 shows the survey spectrum of the hydrothermal TiO_2 nanoparticles. The XPS spectrum reveals a good purity of the TiO_2 nanoparticles where only the C 1s peak was detected other than the Ti and O related species.

Figure 3.5 XPS survey spectrum of mesoporous film from hydrothermal TiO_2 nanoparticles.

Figure 3.6 displays the corresponding XPS spectra of the C 1s, O 1s and Ti 2p core level peaks. In the C 1s spectra, three peaks were observed. The low binding energy peak at 285 eV with strong intensity indicated the presence of adventitious carbon (C-H) due to

atmospheric contamination present on the solid surface [165]. All the binding energy scales were then calibrated with reference to this peak. The peak at higher binding energy at 286.3 eV was possibly due to the C-O like species [166]. The third peak at 288.9 eV was related to carbonates species [167].

Figure 3.6 The core level XPS spectra for (a) C 1s, (b) O 1s and (c) Ti 2p as detected in the survey scan spectrum in Figure 3.5

The O 1s spectra displayed asymmetrical shape and exhibited a shoulder at the high binding energy side of the spectrum. Deconvolution was performed to obtain the constituting components. The main component located at the binding energy of 529.7 eV corresponded to the lattice oxygen in O-Ti bonding [165, 168]. The other component at

binding energy of 531.3 eV was attributed to the negatively charged chemisorbed oxygen species such as O_2^- , O^- and O^{2-} [169].

The Ti 2p XPS spectra consisted of a doublet with pair peaks at 458.6 eV and 464.3 eV that were attributed to Ti 2p_{3/2} and Ti 2p_{1/2} respectively [168, 170]. Table 3.2 summarizes the surface atomic concentration of the elements present in the hydrothermal TiO₂ nanoparticles.

Table 3.2 Summary of surface atomic concentration for each element in the hydrothermal TiO₂ nanoparticles.

Element	Binding Energy (eV)	Assignment	Atomic concentration (%)
C 1s	285.0	C-H	23.54
	286.3	C-O	5.79
	288.9	Carbonate species	2.41
Ti 2p	458.6	Ti ⁴⁺	13.50
	464.3	orbital splitting	6.48
O 1s	529.7	O ²⁻	39.86
	531.3	Absorbed O species	8.64

Table 3.3 Estimated surface composition of hydrothermally synthesized TiO₂

	Atomic ratio	
	Ti	O
Hydrothermal TiO ₂	1	1.99

The estimated atomic concentration for hydrothermal TiO₂ calculated from XPS results is shown in Table 3.3. The atomic ratio of Ti⁴⁺: O²⁻ = 1: 1.99 is very near to the stoichiometry for TiO₂. Thus, it can be concluded that the TiO₂ nanoparticles were successfully grown using hydrothermal method.

3.3 Dye Loading in Mesoporous TiO₂ film

For a fair comparison in the photovoltaic performance of DSSCs fabricated from the three types of TiO₂ nanoparticles, the mesoporous photoanodes had to be fixed with same active area and comparable TiO₂ film thickness. The thickness of the different types of TiO₂ mesoporous films were measured using DEKTAK3 surface profiler.

To determine the amount of dye uptake in the mesoporous film, the sensitized mesoporous TiO₂ photoanode was immersed in the basic solution containing 5 ml of 0.1 M NaOH in water/ethanol (volume ratio 1:1) for 12 hours to allow full desorption of dye molecules into the solution. The absorbance profile of the desorbed dye solution in quartz cuvette was measured using UV-Vis spectrometer. The amount of dye uptake in the mesoporous TiO₂ film was calculated according to Beer Lambert's law:

$$A = \epsilon lc \quad (3.4)$$

where A is absorbance, ϵ is the molar extinction coefficient of N719 dye solution at 515 nm, l is the path length of the sample and c is the concentration of the dye solution. The 0.25 mM N719 dye solution was used as reference for calibration. Table 3.4 indicates the thickness of the mesoporous TiO₂ photoanode on FTO and amount of dye adsorbed onto the surface of the TiO₂ nanoparticles in the mesoporous film. All these films had similar thickness but the amount of extracted dye molecules varied significantly due to the difference in the agglomerated particle sizes, pore sizes and the existence of crack in the mesoporous films. Sample ANT had the lowest dye uptake as expected due to its poor surface morphology as identified in Section 3.2.2.

Table 3.4 Thickness of mesoporous films and amount of dye extracted from the films deposited from different types of TiO₂ nanoparticles.

Sample	Mesoporous photoanode made from	Mesoporous Film thickness (μm)	Amount of dye (mol cm ⁻² x 10 ⁻⁷)
HTT	Hydrothermal TiO ₂ nanoparticles	10.5	1.01
P25	Commercial Degussa P25 TiO ₂ nanoparticles	10.8	0.86
ANT	Commercial anatase TiO ₂ nanoparticles	11.0	0.40

3.4 Photovoltaic *I-V* Characteristic of DSSC Devices

DSSC devices with different types of TiO₂ nanoparticles as photoanodes were successfully fabricated. The DSSC device with the mesoporous TiO₂ photoanode formed from the hydrothermal TiO₂ nanoparticles film as photoanode was denoted as sample HTT. The DSSCs fabricated from commercially available Degussa P25 TiO₂ and anatase TiO₂ as photoanodes were designated as sample P25 and ANT respectively.

The assembled solar cells were tested for their *I-V* characteristics using the model XES-301S solar simulator from SAN-EI Electric fitted with a AM 1.5 light filter. The current-voltage (*I-V*) characteristic for the photovoltaic device was measured using Keithley 2400 sourcemeter, controlled by a Labview program. The simulated solar light intensity used was 100 mW/cm² (AM1.5 SUN) and was calibrated using a standard silicon solar cell (VLSI Standards Incorporated (SN 10510-0178)). During the *I-V* measurement, voltage was applied in the range of - 0.3 V to + 0.8 V. The output current (*I*) with respect to the applied bias (*V*) were recorded and the *I-V* curve was plotted for analysis. Four important photovoltaic parameters would be determined from the *I-V* curve, namely the open circuit voltage *V*_{OC}, the short-circuit current *J*_{SC}, the Fill Factor (*FF*) and the energy conversion efficiency (*η*).

The photovoltaic I - V characteristics of these DSSC devices measured are shown in Figure 3.7. The corresponding photovoltaic parameters are tabulated in Table 3.5.

Figure 3.7 Photovoltaic I - V characteristic of DSSC devices with different types of TiO_2 nanoparticles as photoanodes measured under simulated solar radiation of $100\text{mW}/\text{cm}^2$.

Table 3.5 Photovoltaic parameters from the I - V curves for DSSCs with different type of TiO_2 nanoparticles as photoanode.

Sample	Mesoporous photoanode made from	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
HTT	Hydrothermal TiO_2 nanoparticles	0.699	10.31	67.5	4.87
P25	Commercial Degussa P25 TiO_2 nanoparticles	0.707	9.85	65.9	4.59
ANT	Commercial anatase TiO_2 nanoparticles	0.690	6.15	66.3	2.84

The three types of devices had similar V_{OC} at around 0.70 V and respectable FF values. Sample HTT with the freshly synthesized hydrothermal TiO_2 nanoparticles as

photoanode, produced the highest J_{SC} at 10.31 mA/cm². This was followed by sample P25 at 9.85 mA/cm² and lastly sample ANT at 6.15 mA/cm². The discrepancy in the J_{SC} values could be attributed to the effect of crystalline phase structure of the TiO₂ nanoparticles on photovoltaic performance. According to the study carried out by Park et al. [162], the mesoporous TiO₂ film made from rutile TiO₂ nanoparticles tended to have smaller surface area to volume ratio than film with anatase TiO₂ nanoparticles. Thus rutile film would have lesser adsorbed dyes than the anatase film, contributed to lower current density. The effective electron diffusion coefficient for the rutile TiO₂ film was about one order of magnitude lower than that of the anatase film, implying that electron transport was slower in the rutile phase nanoparticles than in the anatase phase. Hence, sample P25 with the mesoporous TiO₂ film deposited from Degussa P25 TiO₂ nanoparticles containing about 30 % rutile phase, would have poorer performance as observed.

The high current density for sample HTT was also attributed to the smallest grain size and particle size of the hydrothermal TiO₂ nanoparticles and hence provided highest surface area in the mesoporous TiO₂ film for anchoring the photosensitizer dye molecules. This was evident from the measurement of the amount of dye loading in the photoanode as shown in Table 3.4. The results showed that the measurement on the amount of dye-loading was highest for sample HTT, followed by sample P25 and finally sample ANT. The amount of dye molecules adsorbed on the surface of the mesoporous TiO₂ photoanode directly affected the current density of the DSSCs. The dye loading in the sample ANT, with the largest particle size and flake-like structure, was 60 % lower than in the sample HTT. This explained the very low J_{SC} obtained in the photovoltaic I - V measurement of sample ANT. Degussa P25, a common and favourite TiO₂ nanoparticles

used as photoanode in DSSC device fabrication was observed to have agglomeration of nanoparticles as observed from the FESEM image in Figure 3.4(b) and hence resulted in lower specific area for dye loading as given in Table 3.4.

3.5 Incident Photon-Current Conversion Efficiency (IPCE) of DSSC Devices

The IPCE of a DSSC device was measured using the Bentham PVE 300 Photovoltaic Spectral Response System at room temperature with the incident light ranging from 400 – 750 nm and the sampling rate of 5 nm per second.

Figure 3.8 shows the IPCE for DSSC samples HTT, P25 and ANT. The results were in good agreement with the photovoltaic $I-V$ measurement under AM 1.5 simulated solar light illumination as shown in Figure 3.7. Sample HTT had the best IPCE among the 3 samples. The maximum IPCE value of 55 % was obtained at wavelength 520 nm, corresponded to the maximum absorption peak for N719 dye. The IPCE values for sample P25 were slightly lower than sample HTT over the visible spectrum. Finally, the sample ANT had very low IPCE values due to the very low dye-loading as given in Table 3.1.

In summary, sample HTT outperformed samples P25 and ANT. Sample HTT with mesoporous photoanode formed from hydrothermal TiO_2 nanoparticles gave the highest energy conversion efficiency of 4.87 %, which was slightly higher than sample P25 due to higher dye-loading. The photovoltaic performance for sample ANT was relatively poor with merely 2.84 % conversion efficiency. This was attributed to the large variation of the particle size and excessive agglomeration with flake-like structures in the TiO_2 mesoporous film after annealing as depicted in the FESEM image in Figure 3.4(c).

Figure 3.8 IPCE spectra of DSSCs fabricated using different types of TiO_2 as photoanode.

3.6 Dense TiO_2 Barrier Layer on FTO Electrode to Suppress Charge Recombination

A study on the role of the FTO/electrolyte interface in the back reaction of electrons with the oxidized species in the electrolyte (tri-iodide ions) was reported by Cameron et al.[171, 172]. In their study, the importance of charge recombination at the TCO glass substrate was reported to be relatively underestimated over the years and the electron recombination at FTO/electrolyte interface should not be neglected. In this project, the electron recombination at the FTO/electrolyte interface was suppressed by the incorporation of a dense TiO_2 barrier layer on the surface of FTO glass substrate.

3.6.1 Deposition of Dense TiO₂ Barrier Layer

The dense TiO₂ barrier layer was deposited using atmospheric pressure chemical vapor deposition (APCVD) method. The custom-built in-house APCVD system is capable of depositing dense TiO₂ layer over a large area with good uniformity using the Ti organometallic precursor, a volatile chemical stored in the bubbler. The inert N₂ carrier gas was allowed to flow through the bubbler and carried the Ti precursor into the deposition nozzles over the heated reaction zone. The substrate was placed on a heated reactor plate and carried by the conveyor belt to move underneath the deposition nozzles.

Figure 3.9 APCVD system for the deposition of dense TiO₂ barrier layer onto the heated FTO glass substrate.

For TiO₂ barrier layer deposition, the Ti precursor was titanium tetraisopropoxide (TTIP). Nitrogen gas carrying this vapor precursor to the deposition nozzles and mixed with the oxygen gas flew to deposition head. The deposition head/nozzle showered the precursor gas and the oxygen gas onto the substrate on the hot reactor plate heated to 450 °C. The reactor plate was allowed to move underneath the deposition head during the deposition. As the reactor plate moved underneath the deposition head, a thin and dense TiO₂ film

would be deposited on the heated substrate because of the reaction of the Ti precursor with oxygen gas. Multiple passes of the reaction plate moving underneath the deposition head were used to deposit the dense TiO₂ barrier layer onto the heated FTO glass substrate to the desired thickness. In this study, the dense TiO₂ barrier layers were deposited to the thickness of 30 nm, 50 nm and 100 nm on FTO glass substrates respectively to study the effect on the suppression of dark current in DSSC devices.

3.7 Characterization of Dense TiO₂ Barrier Layer

3.7.1 Surface Morphology of Dense TiO₂ Barrier Layer

The surface morphology of the dense TiO₂ barrier layers deposited onto the FTO glass substrates from the APCVD system was observed using FESEM as shown in Figure 3.10.

Based on the FESEM images, the 30 nm and 50 nm dense TiO₂ films have a uniform coverage over the surface of the FTO glass substrate. However, excessive preferential island growth could be observed for the 100 nm thick dense TiO₂ barrier film.

From Figure 3.10 (a), it can be seen that there are a lot of sharp edges/corners on the surface of the nanocrystalline FTO glass substrate. The deposition of the dense TiO₂ barrier layer helped to partially smooth out the sharp corners in the surface of the FTO glass substrate as shown in Figure 3.10 (b) and (c) for 30 nm and 50 nm TiO₂ barrier layers respectively.

Magnification: 20kX

50kX

Figure 3.10 FESEM images of dense TiO_2 barrier layers of different thickness deposited on FTO glass substrate using APCVD method. (a) Bare FTO glass. (b) 30 nm; (c) 50 nm and (d) 100 nm.

However, prolong deposition for 100 nm TiO₂ barrier layer promoted the re-appearance of sharp corners due to the enhanced preferential island growth of the TiO₂ nanocrystals as shown in Figure 3.10 (d). This sharp corner may create field enhancement effect and lead to the electron emission into the electrolyte for charge recombination.

3.7.2 Crystalline Phase Structure of Dense TiO₂ Barrier Layer

The crystalline phase of the dense TiO₂ barrier layer was investigated using the XRD. Figure 3.11 shows the XRD profiles for the TiO₂ barrier layers. The characteristic peaks of the XRD profiles suggested that the dense TiO₂ layer was made up of only anatase crystalline phase.

Figure 3.11 XRD profile for TiO₂ barrier layer deposited on glass substrate using APCVD system.

3.7.3 Optical Transmittance of Dense TiO₂ Barrier Layer on FTO Glass

The FTO glass substrate with a layer of 30 nm of TiO₂ barrier film remained to be transparent. Increasing the thickness of the TiO₂ barrier layer to 50 nm and 100 nm caused the TiO₂ films to become translucent and also appeared to be slightly hazy. A high optical transmittance of the FTO glass substrate with TiO₂ barrier layer is desirable for maximum light to pass through and to be absorbed by the dye-sensitizer in the mesoporous TiO₂ photoanode. This feature is an important parameter that will directly affect the overall photovoltaic conversion efficiency of the DSSCs.

Figure 3.12 shows the UV-Vis transmittance spectra of the TiO₂ barrier layers with different thicknesses on FTO glass substrate. The bare FTO substrate is used as a reference. The optical transmittance reduced by only 5 – 10% over the visible range from 450 – 750 nm for the FTO substrate with 30 nm TiO₂ barrier layer (sample BL30). On the other hand, the FTO substrates with thicker dense TiO₂ barrier layers (50 nm for sample BL50 and 100 nm for sample BL100) resulted in lower transmittance as more light was absorbed and reflected in the thicker films. Sample BL50 and BL100 have similar transmittance profile for wavelength from 420 nm to 680 nm. This could be explained by the coupling effects of light trapping and scattering of thicker film. The optical absorption edge for samples with dense TiO₂ barrier layers were red-shifted from around 350 nm to 400 nm and this effect was attributed to the absorption of TiO₂ film.

Figure 3.12 Transmittance spectra of the dense TiO_2 barrier layer on FTO glass for different thicknesses.

3.8 Photovoltaic Performance of DSSC with Dense TiO_2 Barrier Layer

DSSC devices were fabricated to study the effect of TiO_2 barrier layers on the photovoltaic performance of the DSSCs with the aim to find the optimum TiO_2 barrier layer thickness that could minimize the charge recombination effect as well as to improve the collection efficiency of the injected photo-generated electrons in the FTO electrode. The TiO_2 barrier layer was coated on the FTO glass substrate using APCVD method. After the formation of the mesoporous layers from hydrothermal TiO_2 nanoparticles, the photoanodes were dipped into the N719 dye sensitizer solution overnight for dye loading. The DSSC devices were assembled following standard cell assembly procedure as described in section 3.1. The photovoltaic I - V curves of the DSSCs with TiO_2 barrier

layers varying from 30 nm, 50 nm and 100 nm are shown in Figure 3.13 together with the DSSC without barrier layer (Sample DSC0) as reference. The extracted photovoltaic parameters of these DSSCs are summarized in Table 3.6.

Figure 3.13 Photovoltaic I - V characteristics of DSSCs with/without TiO_2 barrier layers, measured under 100 mW/cm^2 (AM 1.5) simulated solar light.

Table 3.6 Extracted Photovoltaic parameters of DSSCs with/without TiO_2 barrier layers.

Sample	Description	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
DSC0	DSSC without barrier layer	0.695	10.25	66.5	4.72 ± 0.10
BL30	DSSC with 30 nm TiO_2 barrier layer	0.706	10.56	67.6	5.04 ± 0.10
BL50	DSSC with 50 nm TiO_2 barrier layer	0.705	10.51	66.5	4.93 ± 0.15
BL100	DSSC with 100 nm TiO_2 barrier layer	0.708	10.39	63.4	4.71 ± 0.15

Compared to standard DSSC without the TiO_2 barrier layer, DSSCs with the TiO_2 barrier layers had noticeable improvement in solar energy conversion efficiency and short-circuit

current density. Sample BL30 yielded the best performance with $\eta = 5.04\%$ followed by sample BL50 ($\eta = 4.93\%$). Both the sample DSC0 and BL100 demonstrated similar conversion efficiency at around 4.72% . The enhancement was mainly contributed by the improvement in the short-circuit current density, J_{sc} .

The short-circuit current of DSSC is mainly influenced by the charge generation/collection efficiency and the charge recombination at the photoanode [173]. The charge (electrons) generation/collection efficiency is determined by the amount of adsorbed sensitizer dye molecules, and the charge transport in the mesoporous TiO_2 photoanode. In this study, the same type of hydrothermal TiO_2 nanoparticles were used in making the mesoporous TiO_2 oxide layer with similar thickness ($\sim 10\ \mu\text{m}$) while the dye loading was carried out at the same time and should be the same. Hence, the charge generation/collection efficiency should be similar for these DSSCs and not responsible for the variation in the photovoltaic conversion efficiency. The remaining cause for the enhancement in the J_{sc} of the DSSCs with dense TiO_2 barrier layer should be due to the reduction in the charge recombination at electrode/electrolyte interface. The barrier layer on the FTO glass substrate helped to reduce the direct contact of the electrolyte with the FTO substrate and hence reduce the recombination sites (at the bare FTO surface) so that the charge recombination in the DSSC was effectively reduced. This reduction in charge loss mechanism would enable the injected electron from excited dye molecules to be more effectively collected by the FTO electrode, via the mesoporous and dense TiO_2 barrier film [154]. The overall J_{sc} values for sample DSSCs with barrier layer (BL30: $10.56\ \text{mA}/\text{cm}^2$, BL50: $10.51\ \text{mA}/\text{cm}^2$ and BL100: $10.39\ \text{mA}/\text{cm}^2$) were higher than DSSC without the barrier layer (DSC0: $10.25\ \text{mA}/\text{cm}^2$).

Many other reports had also demonstrated that the presence of a barrier layer at the transparent conducting electrode was essential for good functioning DSSC devices [154, 173-180]. In their work, the electrochemical impedance spectroscopy (EIS) was normally used to study the interface between the FTO glass and the mesoporous TiO_2 layer. It has been shown that the reduction in the interfacial charge transfer resistance could be observed with the dense TiO_2 blocking layer. This implied that the presence of a thin dense TiO_2 barrier layer on the FTO glass substrate would provide good adhesion between FTO glass substrate and the active mesoporous TiO_2 layer and accommodate electron transport from the mesoporous TiO_2 nanoparticles to FTO electrode [181-184]. At the same time, the TiO_2 barrier layer also suppressed the electron back transport from the FTO electrode to the electrolyte by inhibiting direct contact. This effect of preventing charge recombination by the dense TiO_2 barrier layer in DSSC device is schematically shown in Figure 3.14.

The closely packed dense TiO_2 barrier also provided effective blocking to the oxidized ions species in the electrolyte from migrating to the conducting photoanode to initiate charge recombination with the electrons in FTO electrode and hence prevented the reduction in photocurrent. However, thicker TiO_2 barrier layer did not give good result in the photocurrent density of the DSSC. This could be explained by the poorer optical transmittance of the thicker TiO_2 barrier film that partially blocked the incoming light to be absorbed by the dye sensitizer. Moreover, thicker barrier layer also introduced an additional series resistance in the DSSC device, resulting in lower fill factor and overall solar cell efficiency. As a consequence, considerable reduction in the fill factor (FF) value and lower conversion efficiency could be seen for sample BL100 (63.44%).

Figure 3.14 Schematic illustration of DSSC device (a) without TiO_2 barrier layer resulting in the back electron transport from FTO electrode to the electrolyte; (b) with TiO_2 barrier layer to prevent charge recombination at the FTO glass/electrolyte interface with oxidized species (I_3^-) in the electrolyte; (c) Effect of dense TiO_2 barrier layer on the suppression of dark current in DSSC.

3.9 Dark Current Measurement

The recombination of excited/injected electrons at the FTO/electrolyte and the TiO_2 /electrolyte interfaces are the two major factors that contributed to dark current [185]. Since the same hydrothermal TiO_2 nanoparticles were used for the mesoporous oxide layer, the contribution in dark current due to the recombination at the TiO_2 /electrolyte interface in this study could be neglected. Therefore, only the interface at the FTO electrode and electrolyte is responsible for variation in the dark current in this work. Figure 3.15 compares the dark current characteristics of DSSCs with and without the blocking layer.

Figure 3.15 I - V characteristics of DSSCs with or without TiO_2 blocking layer measured in dark condition.

The I - V curves demonstrated that the dense TiO_2 barrier layers effectively suppressed the charge recombination and the dark current. The inclusion of the dense TiO_2 barrier layer

on the surface of the FTO electrode also helps to increase the V_{OC} of the DSSC devices as shown in Figure 3.14 and Table 3.4. The reduction in dark current in these DSSCs did not show too much variation as long as a thin TiO_2 barrier layer was present. Thicker TiO_2 barrier layer did not bring any further improvement. Hence, a 30 nm TiO_2 barrier layer would be adequate to suppress the charge recombination at the FTO/electrolyte interface and is chosen as the standard step in all subsequent study.

In summary, the optimum thickness for the TiO_2 barrier layer was found to be 30 nm. Inclusion of the 30 nm TiO_2 barrier layer in DSSC device structure had minimum effect on the optical transmittance of the photoanode but the dark current would be sufficiently reduced, leading to better photovoltaic performance.

3.10 Summary

In this chapter, the fabrication, characterization and optimization works were described in details especially on the mesoporous TiO_2 photoanode, for the fabrication of standard DSSC devices that would serve as a baseline for all subsequent improvement.

A total of three types of TiO_2 nanoparticles were evaluated as mesoporous TiO_2 photoanode, specifically the Degussa P25 TiO_2 , Anatase TiO_2 (Alfa-Aesar) and the hydrothermal TiO_2 nanoparticles. The physical and chemical properties of these three different TiO_2 nanomaterials were thoroughly characterized. The DSSC devices with the mesoporous TiO_2 film fabricated from all these different type of TiO_2 nanoparticles were evaluated for their photovoltaic responses. The DSSC devices with hydrothermal TiO_2 nanoparticles as photoanode were demonstrated to give the best photovoltaic performance with conversion efficiency at 4.87 %. The superiority in the PV performance was

attributed to the smaller grain/particle size for these freshly synthesized TiO_2 nanoparticles. This resulted in highest dye-loading which yielded highest current density.

The effect of the dense TiO_2 barrier layer deposited using the APCVD method on FTO glass for the suppressing of electron back transport from the FTO electrode to the electrolyte was also investigated. The photovoltaic I - V characteristics of the DSSC devices with barrier layers exhibited improved performance over the standard DSSC device with bare FTO electrode. To maintain high optical transmittance, employing 30 nm TiO_2 barrier layer in between the mesoporous TiO_2 film and FTO glass would be sufficiently effective in suppressing the back transport of electron in the FTO electrode into the electrolyte.

In conclusion, the optimized standard DSSC device structure and fabrication procedure was established. This standard DSSC would have the 30 nm dense TiO_2 barrier layer deposited onto the FTO electrode and the mesoporous TiO_2 photoanode made from the hydrothermal TiO_2 nanoparticles. The hydrothermal TiO_2 nanoparticles were formulated into thick paste with organic binder (EC) and α -terpineol and deposited on the glass substrate using doctor blade method. The annealing of this photoanode was carried out at 450 °C in tube furnace for 60 minutes in synthetic air. All subsequent fabrication procedure of DSSC device would be carried out according to this standard assembly process as described. The N719 dye sensitizer would be used as light absorbing material and the iodide/tri-iodide species as electrolyte in all the DSSC devices. This optimized standard DSSC device structure would serve as reference for all further improvement.

CHAPTER 4 NITROGEN-DOPED TITANIUM DIOXIDE AS PHOTOANODE FOR DYE-SENSITIZED SOLAR CELL

The mesoporous titanium dioxide (TiO_2) film is the essential structural component that has significant impact on the solar energy conversion efficiency of the dye-sensitized solar cell (DSSC) devices.

In recent years, there are great interests in doping the TiO_2 nanomaterials for the purpose to improve the photovoltaic performance of DSSC devices. For example, research results were performed on DSSCs with mesoporous TiO_2 photoanode using metal element doping such as Zn [32], Ta [33, 34] and Nb [35] and non-metal element doping such as N [38, 41-45], S [47] and B [49, 50].

Among all these doping materials, N-doped TiO_2 nanomaterials were reported to give promising improvement in the photovoltaic response of DSSC devices. In general, the N-doped TiO_2 was synthesized through high temperature annealing in N-element contained environment (such as N_2 , NH_3 , urea) [41, 45], wet-chemical process (sol-gel and solvothermal) [39, 43] and by reactive sputtering in nitrogen based plasma or nitrogen ion implantation [186].

It has also been shown that the N-doped TiO_2 nanomaterials could be formed by thermal oxidation of precursor TiN nanomaterials to give TiN_xO_y nanomaterials and were reported to have improved photoelectrochemical and photocatalytic properties [187-190].

However, there was no report on using such TiN_xO_y nanomaterials for DSSC device. This project is the first to evaluate the use of such N-doped TiO_2 (TiN_xO_y) nanomaterials as mesoporous photoanode in DSSC device. The N-doped TiO_2 mesoporous photoanode was formed by using the single step thermal oxidation of Titanium Nitride (TiN) nanomaterials coated on the FTO glass substrate.

In this chapter, DSSC devices with mesoporous photoanode layers made of N-doped TiO_2 (hereafter denoted as TiN_xO_y) nanoparticles or composite TiN_xO_y - TiO_2 nanoparticles consisting of both TiN_xO_y and hydrothermal TiO_2 nanoparticles in different ratio (weight ratio) were fabricated and their photovoltaic characteristics were evaluated. The TiN_xO_y nanoparticles were formed by thermal oxidation of TiN nanoparticles and their physical, chemical and optical properties will be studied. The crystalline phase structure of the TiN_xO_y nanoparticles was observed by the X-ray diffractometer (XRD) while the surface morphology of the mesoporous films was inspected using field emission scanning electron microscope (FESEM). The chemical composition of the TiN_xO_y layer was studied using X-ray Photoemission Spectroscopy (XPS). The optical properties of the TiN_xO_y nanoparticles were evaluated by UV-Vis spectrometer. Finally, the photovoltaic properties of the fabricated DSSC devices were investigated and the effect of utilizing TiN_xO_y nanoparticles in mesoporous photoanodes discussed in detail.

4.1 Formation and Characterization of N-doped TiO_2 Mesoporous Photoanode

The starting TiN nanoparticles used in this project were purchased from Hefei Kaier and the technical specification is given in Table 4.1.

Table 4.1 Technical specification of TiN nanoparticles purchased from Hefei Kaier.

Technical specification	color	purity	nominal particle size	specific surface area
	black	>99.2 %	20 nm	48 m ² /g

4.1.1 Thermal oxidation of TiN Nanoparticles

The thermal oxidation of the 20 nm TiN nanoparticles was monitored using the Perkin Elmer thermogravimetric analyzer (TGA-7) and the differential thermal analyzer (DTA-7). Fixed amount of TiN nanoparticles were loaded into the TGA/DTA system and oxidized in Zero-Air. The temperature scan was from room temperature to 700 °C and the heating rate was set at 10 °C/min, close to the heating rate used for oxidation of TiN precursor for the formation of TiN_xO_y photoanode in the tube furnace. The thermal analysis results of precursor TiN nanoparticles are showed in Figure 4.1. From the TGA curve, the initial gradual weight loss at around 100 °C to 300 °C was due to the evaporation of mainly moisture and other chemicals absorbed on the surface of the nanoparticles.

As observed from the DTA curve in Figure 4.1, the exothermic process started gradually at 400 °C and peaked at 487 °C due to the oxidation of TiN to TiN_xO_y. The conversion (oxidation) of the 20 nm TiN to TiN_xO_y (or finally TiO₂) was completed at around 550 °C.

From the TGA curve, the experimental weight-gain corresponding to the oxidation process of TiN precursor to TiN_xO_y, was estimated to be approximately 22 %, slightly lower than the theoretical value of 29 % for a complete oxidation of TiN to TiO₂. This result suggested that certain amount of nitrogen content was still retained in the oxidized

TiN_xO_y nanoparticles giving the N-doped TiO₂ the favourable photoelectrochemical and photocatalytic properties.

Figure 4.1 Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of TiN nanoparticles.

4.1.2 Formation of TiN_xO_y Mesoporous Film without Organic Binder

Based on the above thermal decomposition analysis result, the oxidation temperature for the conversion of 20 nm TiN nanoparticles to mesoporous TiN_xO_y layer for DSSC device fabrication was selected to be from 350 °C to 550 °C. Since the oxidation temperature lower than 450 °C was used in this study, organic binder such as ethyl cellulose (EC) could not be used to formulate the paste for deposition on FTO glass substrate for DSSC device fabrication. The EC requires a temperature above 450 °C for complete decomposition. Instead, the TiN nanoparticles were dispersed in the α -terpineol solvent to form the paste. To prepare the paste, 0.75 g of TiN nanoparticles were first dispersed in 10 ml ethanol using ultrasonication. Then, 2 ml of α -terpineol was added slowly into the well

dispersed TiN colloidal under vigorous stirring condition. After that, the TiN colloidal was heated up to 80 °C on hotplate under vigorous stirring condition for at least 15 hrs to evaporate the ethanol content. Finally, the resulting homogenized thick paste was ready for deposition on FTO glass using doctor blade method.

After depositing the TiN paste onto the FTO glass substrate, the formation of mesoporous TiN_xO_y layer was carried out by the oxidation of TiN film in tube furnace at the temperature from 350 – 550 °C for 1 hour in synthetic air ($\text{N}_2:\text{O}_2 = 4:1$) at the flow rate of 1 standard litre per minute (1 slm). The physical appearance of the TiN_xO_y mesoporous films on the FTO glass substrates are shown in Figure 4.2. The thickness of the mesoporous films measured using surface profiler was around 6 – 7 μm . The TiN_xO_y mesoporous film formed at 350 °C had similar colour as the original TiN nanoparticles as shown in Figure 4.2. With increasing oxidation or annealing temperature from 350 to 425 °C, the mesoporous TiN_xO_y layers were found to have a gradual change of color from dark blue to grey. With further increase in the annealing temperature to 450 °C, a pale yellow film was obtained. At the oxidation temperature of 500 °C or above, the TiN_xO_y mesoporous films appeared to be whitish, similar to the colour of mesoporous TiO_2 film.

Figure 4.2 Appearance of the mesoporous TiN_xO_y films after the oxidation of TiN films at different temperature ranging from 350 °C to 550 °C.

4.1.3 Crystalline Phase Structure of TiN_xO_y Mesoporous Film

The XRD analysis profiles showing the crystalline phase structures of the TiN_xO_y mesoporous films formed at different temperature are shown in Figure 4.3, and the pure TiN sample was used as reference. The TiN sample oxidized/annealed at 350 °C and the pure TiN sample have similar XRD profiles, with only the cubic sodium chloride-type TiN crystalline structure. Upon annealing at 400 °C, the main phase as determined from the XRD profile changed to the TiO_2 anatase phase with a small trace of TiO_2 rutile phase. The initial cubic phase of TiN was still detected. This indicated that the oxidation of the TiN precursor to form TiN_xO_y started at this temperature, in good agreement with the results from DTA-TGA measurements. Only anatase and rutile phases of TiO_2 present when the oxidation temperature was ≥ 425 °C. The rutile phase of TiO_2 became more prominent as the temperature increased to 500 °C or higher. The calculated grain size for the TiN and TiN_xO_y nanoparticles formed at different temperatures from 350 °C to 550 °C are shown in Table 4.2. The calculated grain size for TiN_xO_y oxidized at 350 °C was based on the cubic sodium chloride-type of TiN crystalline structure as only TiN crystalline phase can be observed. When the oxidation was carried out at 400 °C, the calculated grain size was based on the anatase TiO_2 crystalline structure. Hence, there is a big discrepancy in the calculated grain size for TiN and TiN_xO_y nanoparticles formed at temperatures from 350 °C and 400 °C.

Figure 4.3 XRD patterns of TiN and TiN_xO_y mesoporous films annealed at different temperatures of 350 °C, 400 °C, 425 °C, 450 °C, 500 °C and 550 °C respectively.

Table 4.2 The calculated grain size for the TiN and TiN_xO_y nanoparticles formed at different temperatures from 350 °C to 550 °C

Sample	Oxidation Temperature (°C)	Calculated grain size (nm)
TiN	Pure TiN precursor	14.5
TiN_xO_y	350	17.1
	400	7.4
	425	8.5
	450	8.6
	500	10.2
	550	12.1

4.1.4 Surface Morphology of TiN_xO_y Mesoporous Films

The TiN paste formulated without the organic binder ethyl cellulose was deposited on the FTO glass substrate using doctor blade method. After the oxidation process, the TiN_xO_y mesoporous films were obtained. The mesoporous films appeared to be homogeneous under visual inspection with minor inhomogeneity at the edges of the film. The TiN_xO_y

mesoporous films formed at different temperatures have similar surface morphology as shown in Figure 4.4.

The TiN_xO_y film had a porous structure with the TiN_xO_y nanoparticles being held together throughout the oxidation process. The FESEM images also revealed that the mesoporous film was composed of a three-dimensional network of interconnected nanoparticles. Large variation in the agglomerated particle size ranging from 30 to 100 nm could be observed. Some large voids/pores as large as several hundreds of nanometer could be found. This indicated that the TiN_xO_y mesoporous film deposited from the TiN paste formulated without the organic binder had a less compact structure and had significant lower specific surface area for dye-anchoring.

Magnification: 30 kX

50kX

Figure 4.4 FESEM images of mesoporous TiN_xO_y films derived from TiN paste without organic binder (oxidation temperature at 450 °C).

As noted in Figure 4.4, large pores/voids existed in the mesoporous TiN_xO_y film with the modified TiN paste. It was thus worthwhile to evaluate the TiN paste prepared by standard formulation with organic binder ethyl cellulose so as to reduce the void/pores and achieve a more compact, uniform and thicker mesoporous TiN_xO_y film after

annealing. The TiN paste was prepared with standard formulation using ethyl cellulose as organic binder. Figure 4.5 shows the FESEM images for mesoporous TiN_xO_y film derived from standard TiN paste with organic binder and formed at 450 °C in N_2/O_2 gases for 1 hour. The TiN_xO_y nanoparticles were well-distinguished from each other with less voids/pores in the mesoporous film. However, a large variation in the agglomerated particle size was still observed. Nevertheless, the mesoporous TiN_xO_y film deposited and formed from TiN paste with organic binder was more compact and homogeneous.

Figure 4.5 FESEM images of mesoporous TiN_xO_y films derived from TiN paste with organic binder (oxidation temperature at 450 °C).

4.1.5 Composition Analysis of TiN_xO_y Mesoporous Films

XPS characterization was performed to determine the presence of O-Ti-N bonding in the mesoporous TiN_xO_y films as the confirmation of the N-doping in the TiO_2 film. Figure 4.6 displays the survey spectra of the TiN and the TiN_xO_y layers annealed at different temperature in N_2/O_2 gases for 1 hr. The XPS analysis exhibited a good purity in these films with only Ti, O and N species present as well as the C 1s peak. Figure 4.7 shows the corresponding zoom-in XPS spectra of the C 1s, O 1s, Ti 2p and N 1s peaks and their

de-convolutions for the mesoporous TiN_xO_y films annealed at different temperature from 350 °C to 550 °C, with the TiN sample as reference.

Based on the C 1s spectra, three peaks were identified for all the samples. The low binding energy peak at 285 eV with strong intensity was the result of the presence of adventitious carbon (C-H) due to atmospheric contamination present on the solid surface [165]. All the binding energy scales was calibrated with reference to this peak. The higher binding energy peak at 286.3 eV was due to the C-O like species [166]. The third peak at 288.9 eV was related to carbonate species [167].

Figure 4.6 XPS survey spectra for TiN and TiN_xO_y mesoporous films formed at temperature ranging from 350 °C to 550 °C.

The spin-orbit doublet of Ti 2p peaks in the annealed TiN_xO_y mesoporous films formed at temperature ≥ 400 °C were well de-convoluted into two peaks at 458.6 eV and 464.3 eV, with a split of 5.7 eV between the doublets. This doublet was associated to the Ti^{4+}

species [167, 189, 191, 192]. For TiN_xO_y sample annealed at 350 °C, extra peak at 456.2 eV and 461.9 eV could be found. This doublet was characterized as Ti 2p_{3/2} and 2p_{1/2} levels for TiN [191].

For TiN_xO_y mesoporous films oxidized at temperature ≥ 400 °C, the O 1s spectra displayed asymmetrical shape and exhibited a shoulder at the high binding energy side of the spectrum. By curve fitting, the main component located at binding energy 529.7 eV corresponded to the lattice oxygen of TiO_2 [165, 167, 168, 191]. The other component at binding energy 531.3 eV was assigned to mixed contributions from surface hydroxides and the negatively charged oxygen chemisorbed species such as O_2^- , O^- and O^{2-} [167, 169, 191]. The de-convolution of O 1s spectra for TiN_xO_y mesoporous film oxidized at 350 °C resulted in an extra peak centered at 533.4 eV which can be attributed to -NO, -NO₂ species [191, 193].

The existence of the N in the TiN_xO_y after the thermal oxidation was confirmed in the N 1s spectra. N-doped TiO_2 was prepared by substituting the oxygen sites in the O-Ti-O bonding structure with nitrogen atom to form the N-Ti-O bonding structure. The 396 eV peak was usually designated as chemically bound N- species within the crystalline TiO_2 lattice but this peak did not always appear [166, 167, 189, 191, 192, 194, 195]. The peak at around 398 – 400 eV was originated from the anionic N incorporated into the TiO_2 crystalline structure to form the O-Ti-N linkage [166-168, 191, 192, 196]. Lastly, the peak at around 404 eV was due to the molecular absorbed nitrogen species [189, 197]. However for our case, the approach was slightly different. The N-doped TiO_2 was obtained through the thermal oxidation of TiN, in which oxygen species were introduced into the Ti-N structure. Based on the N 1s spectra for samples oxidized at temperature $\geq$

400 °C, a total of two peaks were detected at binding energy 399.5 eV and 403.3 eV for the mesoporous TiN_xO_y films formed by the oxidation of TiN nanoparticles. The peak at 399.5 eV can be assigned as O-Ti-N bonding structure, indicating the incorporation of oxygen species into the Ti-N linkage after the thermal oxidation of TiN nanoparticles. The peak at binding energy 403.3 eV is due to the molecular absorbed nitrogen species on the surface of the mesoporous TiN_xO_y films. For TiN_xO_y mesoporous film oxidized at 350 °C, the peak at 396.2 eV was assigned as $\beta\text{-N}$, corresponded to Ti-N bonds [167, 189, 191, 195, 197]. This chemical composition analysis had indicated the presence of the N-doping (as O-Ti-N bonding) in the mainly TiO_2 composition (O-Ti-O bonding).

Figure 4.7 XPS spectra of C 1s, O 1s, Ti 2p and N 1s for TiN and the mesoporous TiN_xO_y films annealed at different temperature from 350 °C to 550 °C.

4.1.6 Optical Property of TiN_xO_y Mesoporous Film

The optical absorption profiles for the mesoporous TiN_xO_y films and the mesoporous TiO_2 film from hydrothermal TiO_2 nanoparticles are shown in Figure 4.8. Based on the optical absorption measurement results, it was observed that there was a transition of absorption profile for TiN_xO_y , from a near constant absorbance for the mainly TiN nanoparticles to the absorption profile towards that of TiO_2 . The sample annealed at 350 °C was a total black film and had nearly constant absorbance over the measurement wavelength range. A similar case occurred for the TiN_xO_y mesoporous film annealed at 400 °C, whereby the absorption edge was not obvious. Upon oxidation at temperature 425 °C, the absorption edge at around 400 – 500 nm began to appear. The three samples annealed at 450 °C, 500 °C and 550 °C had well-defined absorption edge, at around 400 nm which was higher than that of the TiO_2 film at 300 nm.

Figure 4.8 Optical absorbance of TiN_xO_y mesoporous films formed at different annealing temperature ranging from 350 °C to 550 °C with TiO_2 as reference.

A clear distinction between the optical absorption curves of TiO_2 and TiN_xO_y mesoporous films would be the extra absorption shoulder/tail from 400 to 500 nm and the red-shift of absorption edge as compared to TiO_2 film. The absorption shoulder diminished with increasing TiN_xO_y formation temperature. In other words, the amount of N-doping (O-Ti-N bonds) in the TiN_xO_y nanoparticles would decrease with the increase of oxidation temperature. At higher formation temperature such as 550 °C, the optical profile for TiN_xO_y film was similar to the TiO_2 nanomaterials as the amount of N-doping became lesser.

4.2 Photovoltaic Performance of DSSC device with TiN_xO_y as Photoanode

4.2.1 TiN_xO_y Photoanodes Formed from Modified TiN Paste Formulation Without Organic Binder.

After the complete characterization of TiN_xO_y mesoporous films formed at different temperatures, the next step was the fabrication and characterization of DSSC devices using these TiN_xO_y mesoporous films as the photoanodes. The DSSC devices fabrication followed the same procedure for standard DSSC as described in Chapter 3. The TiN_xO_y mesoporous films were formed on FTO glass substrate with a 30 nm dense TiO_2 barrier layer deposited by APCVD method. The only variation was the method to prepare the thick paste containing the TiN nanoparticles.

As mentioned previously in Section 4.1, the oxidation temperature for the formation of the mesoporous TiN_xO_y layer involved in this study was from 350 to 550 °C, organic binder such as ethyl cellulose (EC), could not be used in the paste formulation, since temperature higher than 450°C would be required to decompose the organic binder. The TiN

nanoparticles paste was only formulated with α -terpineol as solvent. The modified precursor TiN paste was coated onto the FTO glass substrate with the dense TiO_2 barrier layer using the doctor blade method. After deposition of the paste, the mesoporous TiN_xO_y photoanode was formed by oxidation at different temperatures in tube furnace under synthetic air flow of 1 slm. The DSSC devices fabricated using this modified TiN paste would be denoted as “temperature-L”. For example, the DSSC sample fabricated with TiN_xO_y mesoporous layer as photoanode formed from this modified paste and annealed at 450 °C was named “450-L”. The thickness of the mesoporous TiN_xO_y films was measured using surface profiler and was adjusted to around 6 -7 μm for better consistency in the study and the thickness measurements are given in Table 4.3. Increasing the mesoporous film thickness to around 10 μm using this modified TiN paste

Table 4.3 Measured Thickness of the TiN_xO_y photoanodes on DSSC devices.

Sample	TiN_xO_y Photoanode	
	Forming Temperature (°C)	Thickness (μm)
350-L	350	6.2
400-L	400	7.0
425-L	425	6.5
450-L	450	6.7
500-L	500	6.8
550-L	550	6.4

The photovoltaic performance of the DSSCs using mesoporous TiN_xO_y photoanodes formed at different temperatures are shown in Figure 4.9. The corresponding photovoltaic parameters are tabulated in Table 4.4. As expected, the sample 350-L and 400-L had very poor photovoltaic performance due to the incomplete oxidation of the 20 nm TiN nanoparticles at such low temperature. The photoanode for sample 350-L contained mainly the TiN nanoparticles, onto which the N719 dye molecules would be difficult to

anchor. For sample 400-L, the TiN nanoparticles were only partially oxidized to give a TiN/TiN_xO_y core-shell structure. Only the surface of the nanoparticles where the oxidation was completed could serve as the platform for dye-anchoring. Increasing the oxidation temperature to ≥ 425 °C, the DSSC photovoltaic performance started to improve.

Figure 4.9 Photovoltaic performances of DSSCs with TiN_xO_y photoanodes formed at different temperature from 350 to 550 °C. The modified TiN paste was formulated without organic binder.

Table 4.4 Photovoltaic parameters of DSSCs with mesoporous TiN_xO_y photoanodes

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	η (%)
350-L	0.480	0.09	48.8	0.02
400-L	0.623	1.33	64.2	0.53
425-L	0.697	3.50	70.0	1.72
450-L	0.709	5.77	69.5	2.87
500-L	0.711	5.65	70.6	2.86
550-L	0.707	4.89	69.8	2.39

The conversion efficiency of DSSCs with TiN_xO_y photoanodes formed at different temperature from modified TiN paste without organic binder is summarized in Figure 4.10. DSSCs with TiN_xO_y photoanodes formed at higher temperature from 450 to 550 °C would result in better photovoltaic performance, especially for sample 450-L and 500-L. Apart from the dye-loading effect, higher formation/annealing temperature of the mesoporous TiN_xO_y layer also promoted grain growth and resulted in better interconnectivity between the nanoparticles. It also enhanced adhesion between the mesoporous films and the FTO electrode. In summary, this improved the charge transport through the mesoporous layer towards the electrode. Nitrogen doping of the TiO_2 and the existence of the O-Ti-N bonds in sample 450-L and 500-L increased the absorption edge to 400 nm as compared to 300 nm for anatase TiO_2 film and the extra absorption shoulder/tail also promoted the self-sensitizing effect of the mesoporous TiN_xO_y layer.

However, the degradation of photovoltaic performance above 500 °C can be observed too. This can be explained by the diminishing of N-content in the TiN_xO_y based on the XPS profile. The improved absorption shoulder was also reduced to TiO_2 -like profile. Besides that, higher annealing temperature also promoted grain growth as shown in table 4.2, leading to the reduction in the overall specific surface area for dye-loading. The rutile phase of TiO_2 also becomes more prominent as the oxidizing temperature increases. As discussed in Chapter 3, the anatase of TiO_2 is preferred for achieving higher photovoltaic responses in DSSC. Hence, the photovoltaic performance degrades when the annealing above 500 °C was performed.

Figure 4.10 Variation of the photovoltaic conversion efficiency of DSSCs with TiN_xO_y photoanodes formed at different temperature from modified TiN paste without organic binder.

4.2.2 Photovoltaic Performance of DSSC Device with TiN_xO_y Photoanodes Derived from the Standard TiN Paste Formulation with Organic Binder

From previous section, DSSC devices with TiN_xO_y photoanodes derived from modified TiN paste formulated without organic binder and formed/annealed at 450 °C or higher were found to have better photovoltaic performance. Hence, DSSC devices with mesoporous TiN_xO_y photoanodes formed on the FTO glass substrate (with 30 nm dense TiO₂ barrier layer) by depositing the standard TiN paste with organic binder, ethyl cellulose, using doctor blade method were fabricated. Different annealing temperatures of these photoanode from 450 to 550 °C were carried out. These mesoporous TiN_xO_y layers were adjusted to about 10 μm as measured using surface profiler and the results are tabulated in Table 4.5.

Table 4.5 Measured thickness of mesoporous TiN_xO_y photoanodes formed from standard TiN paste with organic binder.

Sample	TiN_xO_y Photoanode	
	Forming Temperature ($^{\circ}\text{C}$)	Thickness (μm)
450S	450	10.5
500S	500	10.8
550S	550	10.3

DSSC devices were fabricated and the photovoltaic I - V curves were measured. Figure 4.11 shows the photovoltaic performance of the DSSCs measured under simulated solar light illumination (AM 1.5 SUN). Table 4.6 summarizes the photovoltaic parameters extracted from the I - V curves.

Figure 4.11 Photovoltaic performance of DSSCs with TiN_xO_y photoanodes formed by the oxidation of standard TiN paste at different temperature from 450 to 550 $^{\circ}\text{C}$. The standard TiN paste was formulated with the ethyl cellulose as organic binder.

Table 4.6 Photovoltaic parameters of DSSCs with TiN_xO_y photoanodes deposited from standard paste formulation and annealed at different temperatures from 450 – 550 °C.

Sample	V_{OC} (V)	J_{SC} (mA/cm^2)	$FF(\%)$	η (%)
450S	0.734	7.00	67.7	3.47
500S	0.740	6.06	69.5	3.12
550S	0.750	5.70	67.1	2.85

Photovoltaic performance of these DSSC devices followed the same trend as those using modified TiN paste without organic binder as reported in previous section. Once again, mesoporous TiN_xO_y photoanode formed at 450 °C (sample 450S) exhibited the best photovoltaic performance with the highest conversion efficiency of 3.47 % as compared with the other two samples formed at higher temperature of 500 °C and 550 °C (Sample 500S and 550S). In summary, mesoporous TiN_xO_y formed by oxidation of standard TiN paste at 450 °C for 1 hour would contribute to the optimum photovoltaic performance.

Figure 4.12 compares the photovoltaic performance of DSSCs with TiN_xO_y photoanodes formed from the two different TiN paste formulations (with or without organic binder) as compared with the standard DSSC device using hydrothermal TiO_2 (HT- TiO_2) as photoanode. DSSC device fabricated with hydrothermal TiO_2 as photoanode showed better photovoltaic conversion efficiency at ~ 5.0 %, while the maximum conversion efficiency for TiN_xO_y -based DSSCs was about 3.5 %. This poorer result could be explained by the relatively large size of the agglomerated TiN_xO_y nanoparticles (30 – 100 nm), formed by the oxidation of the commercially available precursor TiN nanoparticles as compared to the hydrothermal TiO_2 nanoparticles (15 to 30 nm). This difference would translate to the reduction of overall specific surface area in the mesoporous photoanode for dye-anchoring.

To determine the amount of dye uptake in the photoanode, the sensitized HT-TiO₂ and TiN_xO_y photoanodes were separately immersed in the basic solution containing 5 ml of 0.1 M NaOH in water/ethanol (volume ratio 1:1) for 12 hrs to allow full desorption of dye. The amount of dye uptake for HT-TiO₂ photoanode was calculated to be 1.05×10^{-7} mol/cm², which was about 53 % higher than that in the TiN_xO_y photoanode (0.49×10^{-7} mol/cm²) as shown in Table 4.7.

Thus, a fair comparison between the DSSCs with TiO₂ and TiN_xO_y photoanodes could not be made. In order to explore the advantage of incorporating TiN_xO_y nanoparticles as photoanode while having comparable dye loading amount, DSSCs with composite photoanodes derived from pastes containing small amount of TiN_xO_y nanoparticles in the mainly hydrothermal TiO₂ nanoparticles were studied.

Figure 4.12 Comparison of photovoltaic performance of DSSC devices fabricated with TiN_xO_y photoanodes derived from different type of pastes and formed at different oxidation temperature. (■ Modified TiN paste without organic binder. ● Standard TiN paste with organic binder. ▲ Standard DSSC device was fabricated using standard paste formulation from hydrothermal TiO₂ nanoparticles and annealed at 450°C.)

Table 4.7 Comparison of film thickness, particle size range and amount of N719 dye loaded into the mesoporous TiO₂ photoanodes and TiN_xO_y photoanode.

Photoanode	Description	Thickness (μm)	Particle Size Range (nm)	Dye Loading (mol/cm ² x 10 ⁻⁷)
HT-TiO ₂	Hydrothermally grown TiO ₂ nanoparticle as photoanode formed at 450°C from standard paste formulation.	10.7	10 - 30	1.05
TiN _x O _y	TiN _x O _y photoanode formed at 450°C from standard TiN paste formulation.	10.5	30 - 100	0.49

4.3 Composite TiN_xO_y-TiO₂ as Photoanode for DSSC Device

The advantages of using TiN_xO_y nanoparticles in DSSC fabrication were demonstrated in the previous sections. However, due to the larger particle size and the non-homogenized agglomerated particle size distribution, the surface area of the mesoporous TiN_xO_y film available for dye-loading was significantly lower than the mesoporous TiO₂ film derived from hydrothermal TiO₂ nanoparticles. Thus, to level the amount of dye loading in the mesoporous film, composite photoanodes consisting of a small percentage of TiN_xO_y nanoparticles in mesoporous TiO₂ layer were proposed in this project for DSSCs. In this study, a small amount of TiN nanoparticles was mixed with the hydrothermal TiO₂ nanoparticles to form the paste formulation with organic binder ethyl cellulose and solvent α -terpineol. First, 0.75 g of mixed TiN and hydrothermal TiO₂ nanoparticles in different weight ratio were added into 10 ml of ethanol and dispersed using ultrasonication. The dispersed colloidal was then added with α -terpineol and stirred vigorously. This homogenized colloidal was poured into the beaker containing 0.275 g ethyl cellulose in 2.75 ml ethanol solution prepared earlier. The colloidal was then heated

up to 80 °C under vigorous stirring for at least 15 hours to evaporate the ethanol content. The samples with different weight ratio of TiN to TiO₂ nanoparticles used in the paste formulation are summarized in Table 4.8. The mixed homogenized pastes were ready for deposition on FTO glass (with 30 nm dense TiO₂ barrier layer by APCVD method) using the Doctor Blade method. The deposited paste was then subjected to oxidation/annealing at 450 °C in tube furnace for 1 hour under N₂/O₂ glass flow (1 slm) to convert the paste into the composite mesoporous TiN_xO_y-TiO₂ photoanode. The samples were then dipped into the 0.25 mM N719 dye solution overnight for anchoring the dye molecules to the mesoporous photoanodes. The photoanodes were then assembled into DSSC devices for photovoltaic characterization. A total of five different types of photoanodes were used to fabricate the DSSC devices, including the pure hydrothermal TiO₂ nanoparticles, TiN_xO_y (TN100) and composites TiN_xO_y -TiO₂ with different weight percentage of TiN_xO_y nanoparticles to the hydrothermal TiO₂ nanoparticles (TN1 for 1 wt% , TN5 for 5 wt% and TN10 for 10 wt% TiN in the precursor mix of nanoparticles).

Table 4.8 Sample composition for the study of composite TiN_xO_y-TiO₂ mesoporous photoanodes

Sample	Composition of precursor nanoparticles to form mesoporous composite layer		Estimated weight ratio of different nanoparticles in composite mesoporous film	
	TiN	TiO ₂	TiN _x O _y (from TiN)*	Hydrothermal TiO ₂
HT-TiO ₂	0	100	0	100
TN1	1	99	1.2	98.8
TN5	5	95	6.4	93.6
TN10	10	90	12.5	87.5
TN100	100	0	100	0

* : assume complete oxidation of TiN to TiO₂

4.3.1 Surface Morphology of Composite TiN_xO_y - TiO_2 Photoanodes

The morphology of the pure TiO_2 (HT- TiO_2), composite TiN_xO_y - TiO_2 and TiN_xO_y photoanodes are shown in Figure 4.13. All the mesoporous films possessed the porous structure. The hydrothermal TiO_2 nanoparticles has relatively small particle size at around 15 - 30 nm, leading to densely packed structure. Comparably, the agglomerated particle size of the mesoporous TiN_xO_y photoanode was around 30 -100 nm, considerably bigger than the TiO_2 nanoparticles. The pores between the TiN_xO_y nanoparticles in the pure mesoporous TiN_xO_y film (TN100) were relatively larger. Large void spaces between the clusters of the particles were observed as shown in Figure 4.13(d). As discussed previously, this highly porous and less compact structure of mesoporous TiN_xO_y film as compared to mesoporous TiO_2 film resulted in a significant reduction in the specific particle surface area for anchoring of the dye molecules. For the composite films (TN5 and TN10), a very compact film comparable to mesoporous TiO_2 film was observed. The difference in the sizes between the two types of nanoparticles (hydrothermal TiO_2 nanoparticles and TiN_xO_y from oxidation of TiN precursor nanoparticles) was relatively significant. The TiN_xO_y nanoparticles can be spotted to be randomly distributed in the compact hydrothermal TiO_2 nanoparticles matrix. The larger TiN_xO_y nanoparticles were surrounded by the smaller size TiO_2 nanoparticles creating an interpenetrating network. If the amount of TiN_xO_y nanoparticles was relatively small (~1 to 10 wt %) in the composite TiN_xO_y - TiO_2 mesoporous films, the relative compact mesoporous film structure (as the TiO_2 film) would still allow high enough dye loading. For these composite mesoporous TiN_xO_y - TiO_2 films, the contribution of TiN_xO_y nanoparticles to the DSSC photovoltaic performance can be explored without significant variation to the dye loading effect.

Magnification: 5kX

50kX

Figure 4.13 FESEM images of mesoporous films derived from (a) hydrothermal TiO_2 , (b) composite sample TN5, (c) composite sample TN10 and (d) pure TiN_xO_y (sample TN100) (deposited on FTO glass substrate with 30 nm dense TiO_2 barrier layer as photoanodes for DSSCs)

4.3.2 Optical Property of Composite TiN_xO_y - TiO_2 Photoanodes

The UV-Vis spectra of the TiO_2 , composite TiN_xO_y - TiO_2 and TiN_xO_y samples are represented in Figure 4.14. The TN100 sample exhibited a significant absorption tail in the visible region between 350 - 500 nm, which is the typical absorption phenomenon for N-doped TiO_2 . For the composite films TN5 and TN10, the absorption was improved for this region at around 350 -500 nm, compared to pure TiO_2 sample. This was due to the presence of the small amount of TiN_xO_y particles embedded inside the photoanode. The sample for TiO_2 and TN1, on the other hand had similar absorption profile. In short, the extra absorption shoulder in the region 350 – 500 nm due to the incorporation of TiN_xO_y nanoparticles in the composite TiN_xO_y - TiO_2 mesoporous films could be beneficial for light harvesting in the DSSCs.

Figure 4.14 Optical absorbance of TiO_2 , composite TiN_xO_y - TiO_2 (TN1, TN5 and TN10) and TiN_xO_y (TN100) photoanodes.

4.4 Photovoltaic Performance of DSSC Devices with Composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ Photoanodes

4.4.1 Dye Loading in Mesoporous Composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ Photoanodes

The appearance of the photoanodes after N719 dye-loading step is shown in Figure 4.15. Significant difference in the dye loading of these photoanodes (HT-TiO_2 , composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ and TiN_xO_y) can be observed due to the variation in particle size. The thickness of the mesoporous films was measured using DEKTAK3 surface profiler. The procedure to determine the amount of dye uptake in the photoanode was described in Section 3.3. Table 4.9 summarizes thickness of these mesoporous films on FTO glass substrate and the amount of dye adsorbed onto the mesoporous photoanodes. All these mesoporous films had a film thickness of about 10 μm and the amount of dye loading was comparable for sample TiO_2 , TN1 and TN5 composite films with relatively low TiN_xO_y composition. With increasing amount of TiN_xO_y nanoparticles in the film, the dye loading started to drop and reduced to less than 50 % for the pure TiN_xO_y (TN100) sample.

Figure 4.15 Appearance of TiO_2 , Composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ and TiN_xO_y photoanodes after dipped in 0.25 mM N719 dye solution.

Table 4.9 Film thickness and the amount of dye adsorbed on the mesoporous HT-TiO₂, composite TiN_xO_y-TiO₂ and TiN_xO_y films on the FTO glass substrate.

Photoanode	Thickness of mesoporous film (μm)	Amount of dye (mol cm ⁻² x 10 ⁻⁷)
TiO ₂	10.6	1.08
TN1	10.3	1.04
TN5	10.8	1.01
TN10	10.9	0.93
TN100	10.5	0.49

4.4.2 Photovoltaic Performance of DSSC with Composite TiN_xO_y-TiO₂ Photoanodes

The photovoltaic current-voltage (I - V) characteristic of the assembled DSSCs with composite mesoporous TiN_xO_y-TiO₂ photoanodes were measured under the simulated solar light intensity of 100 mW/cm², as shown in Figure 4.16. The extracted photovoltaic parameters, including the open circuit current (V_{OC}), short circuit current density (J_{SC}), Fill Factor (FF) and the conversion efficiency are summarized in Table 4.10.

Figure 4.16 Photovoltaic I - V characteristic of the DSSC devices with different composite TiN_xO_y-TiO₂ photoanodes.

Table 4.10 Photovoltaic performance of the DSSC devices based on different TiN_xO_y - TiO_2 composite photoanodes.

Photoanode	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
TiO ₂	0.705	11.09	65.1	5.08
TN1	0.706	11.66	69.2	5.69
TN5	0.715	13.00	68.6	6.38
TN10	0.719	12.01	68.6	5.89
TN100	0.726	7.08	67.8	3.49

From the photovoltaic I - V characteristics, DSSCs with composite TiN_xO_y - TiO_2 photoanodes had significant improved performance as compared to the standard DSSC using pure hydrothermal TiO_2 nanoparticles as mesoporous photoanode. The best photovoltaic performance was obtained from sample TN5, with the conversion efficiency of 6.38 %. This value was 25.6 % higher compared to the standard DSSC sample with mesoporous TiO_2 photoanode with the efficiency of 5.08 %. The enhancement in the conversion efficiency mainly came from the highest J_{SC} obtained for sample TN5 (13.0 mA/cm^2). It is known that the two notable parameters that influence the current density are the amount of dye uptake and charge transport in the mesoporous layer. In our case, the dye absorbed was inversely proportional to the amount of TiN_xO_y nanoparticles added into the TiO_2 matrix due to its larger particle size. For the composite samples, TN1, TN5 and TN10, the amount of dye adsorbed were slightly lower than the standard TiO_2 samples, but the inclusion of the small amount of the N-doped TiO_2 (TiN_xO_y) nanoparticles must have significant contribution to enhance the electron transport in the composite mesoporous TiN_xO_y - TiO_2 layers which resulted in the marked improvement in photovoltaic performance and higher J_{SC} . This was attributed to the TiN_xO_y nanoparticles that were embedded inside the mesoporous TiO_2 layer, assisting the charge transport of the injected electrons from photo-excited dye molecules under illumination. However, for

sample TN10, the conversion efficiency was lower than the sample TN5. This was because the improvement in the charge transport was offset by the lowering in dye loading. Thus, the efficiency was lower as compared to TN5. The enhanced absorption tail in the 400 – 500 nm region (Figure 4.14) for the TiN_xO_y nanoparticles might also have contributed to the improved photovoltaic performance.

On the other hand, the sample TN100 had the lowest conversion efficiency among all the DSSCs due to the much lower amount of dye loading as given in Table 4.9. Comparing the TiO_2 and TN100 samples, there was about 60 % reduction in the amount of dye absorption (Table 4.9). Despite having larger particle size as compared to the TiO_2 nanoparticles, the mesoporous TiN_xO_y film also possessed large pore size that reduced the available surface area (as observed from the FESEM image in Figure 4.16). Thus, when the TiN_xO_y nanoparticles were introduced to be used as the photoanode, the surface area for dye anchoring was greatly reduced, resulting in a very low J_{SC} value. Meanwhile, a small improvement in the V_{OC} for TN samples could be observed too. Tian et al. explained this phenomenon as the change in the flat-band potential of N-doped TiO_2 with respect to the redox potential of the electrolyte [42]. Figure 4.17 summarizes the conversion efficiency and dye loading of DSSC with different weight % of TiN_xO_y in TiO_2 photoanode.

Figure 4.17 Conversion efficiency and dye loading of DSSCs with composite TiN_xO_y - TiO_2 photoanode.

4.4.3 IPCE of DSSC with Composite TiN_xO_y - TiO_2 Photoanodes

The IPCE measurements of the composite samples are shown in Figure 4.18. The results obtained were consistent with the photovoltaic performance of the DSSCs. The higher IPCE values at around 520 nm for composite samples (TN1, TN5, TN10) could be attributed to the improvement in the charge transport and collection as compared to sample TiO_2 . For the composite TN samples, the IPCE values were improved remarkably for the region at around 400 – 550 nm, as compared to TiO_2 sample. This characteristic can be attributed to the improved absorption of TiN_xO_y in that region. As discussed earlier in section 4.1.6 and 4.3.2, the photoresponse of TiN_xO_y in these wavelengths was attributed to the TiN_xO_y nanoparticles behaving like the self-sensitizer that absorb light to generate more electron-hole pairs that would improve the overall light harvesting efficiency (LHE), leading to improved IPCE performance

Figure 4.18 IPCE spectra of DSSCs samples fabricated using different photoanodes.

4.5 Transport Property of the DSSC with Composite Photoanodes

4.5.1 Electrochemical Impedance Spectroscopy (EIS) Measurement

EIS is a powerful steady-state technique for study of electrochemical system. In general, it is performed to investigate the electronic and ionic processes in DSSC devices. A theoretical model based on the spectra can be elaborated to interpret the frequency responses of different interfaces in DSSC devices. The electron transport rate and lifetime could be derived under different operating conditions. In this project, the electrochemical impedance measurements were carried out at room temperature using the Metrohm Autolab System in the frequency range of 1 mHz to 1000 kHz a, both in dark condition and simulated solar light illumination with intensity 100 mW/cm². The EIS measurement was performed at different bias conditions, including the open-circuit, of the DSSC with the applied ac amplitude of 10 mV. The equivalent circuit model based on the general

transmission line model of DSSC was proposed to study the electrical and transport properties of DSSCs.

Nyquist plots from the EIS measurements of the DSSCs fabricated using TiO_2 and composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanodes are shown in Figure 4.19. In general, three semi-loops in the order of increasing frequency can be observed from the Nyquist plot. The low frequency region (at high Z' value) was attributed to the Nernst diffusion within the electrolyte, while the intermediate frequency (main loop) featured the electron transport in the mesoporous layer of TiO_2 and $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface (R_μ). Lastly, the high frequency peak (at low Z' values) corresponded to the charge transfer at the Pt-counter electrode/electrolyte and mesoporous TiO_2/FTO electrode interfaces [137, 138]. The EIS measurements were fitted to the equivalent circuit based on the general transmission line model for DSSCs as shown in Figure 4.19(b) [138]. The fitted parameters as determined from the equivalent circuit model are provided in Table 4.11.

It should be noted that the series resistances (R_s) for the electrical contacts to the TCO electrode were similar at about 10.6 – 11.8 Ω for all the samples due to the same experimental setup in device fabrication. This indicated good consistency in the device fabrication and measurement carried out. The value of R_p was affected by the charge transfer at the Pt-counter electrode/electrolyte and FTO/ TiO_2 interfaces. Since the same Pt-back electrode was used, the slight reduction in the R_p values for TN samples could be attributed to the better conductivity and connectivity between the mesoporous oxide layer/FTO electrode interface.

The second semicircle at the middle frequency range showed much lower charge transfer resistances at the mesoporous oxide/dye/electrolyte interface (R_{μ}) for TN samples over the TiO_2 counterpart under illumination. This reduction showed that the integration of TiN_xO_y particles improved the conductivity of the films, allowing efficient transfer of electrons from the photo-excited dye molecules to the mesoporous oxide layer. However, there was an increased in the values of R_{μ} from sample TN5 and TN10. As discussed previously, the amount of TiN_xO_y nanoparticles embedded into the TiO_2 matrix came at a cost of lower dye-loading due to its larger particle size. Thus, the electron density for TN10 was reduced as compared with TN5 and resulting in higher R_{μ} value [137, 140].

Figure 4.19 (a) Nyquist plot from EIS measurement of the DSSCs fabricated using TiO_2 and $\text{TiN}_x\text{O}_y\text{-TiO}_2$ composite photoanodes, measured under light illumination 100 mW/cm^2 ; (b) Equivalent circuit model for a DSSC device.

Table 4.11 Transport Properties of the DSSCs with TiN_xO_y - TiO_2 composite photoanodes determined using EIS and IMPS measurements.

Sample	R_s (Ω)	R_t (Ω)	R_μ (Ω)	R_p (Ω)	R_{TiO_2} (Ω)	Electron lifetime, t_e (ms)	Electron transit time, t_{tr} (ms)
TiO_2	11.8	1.47	18.1	1.58	18.59	7.6	5.03
TN1	11.3	0.90	17.3	1.40	17.60	7.6	5.03
TN5	10.6	0.51	13.6	1.36	13.77	9.3	4.00
TN10	11.6	0.33	14.5	1.45	14.61	10.4	4.00

Note: $R_{\text{TiO}_2} = \frac{1}{3} R_t + R_\mu$

The transport resistances through the interpenetrating network of mesoporous oxide layer was plotted and shown in Figure 4.20. Under different forward bias, it was observed that the transport resistance decreased with the added amount of TiN_xO_y nanoparticles. This decrease in the R_t was attributed to the higher conductivity of the TiN_xO_y particles embedded inside the mesoporous TiO_2 layer. The fact that R_μ (transport at mesoporous oxide/dye/electrolyte interface) values were much larger than R_t (transport through nanoparticles network) for all the samples was an indication of low recombination loss and a proof of good quality photoanode [156].

The total photoanode resistance can be estimated based on the equation $R_{\text{TiO}_2} = \frac{1}{3} R_t + R_\mu$ (eq. 2.17) under low recombination condition [137, 156]. The reduction in the values of R_{TiO_2} with the incorporation of TiN_xO_y nanoparticles in the composite photoanode suggested that the overall conductivity of the mesoporous films were improved to provide a faster electron transport through the TiO_2 network, and enhanced the charge collection efficiency at the electrode. Overall, this would improve the J_{SC} of the DSSCs, resulting in higher conversion efficiency.

Figure 4.20 Variation of transport resistance in TiO₂ and TiN_xO_y-TiO₂ composite photoanodes.

The bode phase plots from the EIS measurement, as shown in Figure 4.21, could be used to determine the electron lifetime (t_e), which is considered as the average time for an electron in TiO₂ to recombine with species in electrolyte or TiO₂ layer [136]. As observed from the data obtained, the incorporation of TiN_xO_y nanoparticles improved the electron lifetime by about 22.0 % from sample TiO₂ to sample TN5 (see Table 4.11). This could be attributed to the larger TiN_xO_y nanoparticles in the composite photoanode and hence resulting in lesser grain boundaries and successfully suppressed of charge recombination [42, 198].

Figure 4.21 Bode phase plots for DSSCs fabricated with $\text{TiN}_x\text{O}_y\text{-TiO}_2$ composite photoanodes

4.5.2 Intensity Modulated Photocurrent Spectroscopy (IMPS) Measurement

IMPS is an optical modulation technique that has proved to be a powerful characterization tool for elucidating the dynamic response of photoelectrochemical modules. IMPS measurement is used to provide the information regarding the electron collection time or the equivalently mass transport of charge carriers in the mesoporous wide band gap semiconductor film. In this study, the transport of the electrons was characterized by IMPS under short circuit condition (Metrohm Autolab system). A red light emitting diode (LED, 632 nm) was used as the modulated light source to ensure a homogenous distribution in the TiO_2 film. The IMPS plot displays a semicircle in the complex plane. The IMPS measurements were carried out to determine the average time constant required for the electron to transport from the oxidized dye, through the mesoporous oxide

semiconductor layer and collected at the FTO electrode. This time constant is considered as the transit time (t_{tr}), and can be estimated from $t_{tr} = (2\pi f_{min})^{-1}$, where f_{min} is the frequency giving the lowest imaginary component in IMPS plot as shown in Figure 4.22.

Figure 4.22 IMPS plots for TiN_xO_y - TiO_2 composite photoanodes.

In our case, the electron transit time was shorter than the electron lifetime, indicated that the electron transport was efficient for achieving high charge collection efficiency. The transit times were shorter for sample TN5 and TN10, compared with sample TiO_2 and TN1 (see Table 4.11). Thus, this implied that the integration of TiN_xO_y nanoparticles could improve the electron transport property by introducing extra pathways for the electrons to transport through the oxide layer [199].

This phenomenon is schematically explained and depicted in Figure 4.23, where small amount of TiN_xO_y nanoparticles were embedded within the network of the smaller size hydrothermal TiO_2 nanoparticles, creating an interpenetrating oxide network. While

maintaining high surface area for dye adsorption, the TiN_xO_y particle embedded inside the film played a key role in providing an alternative conduction path for the injected electrons to transport through the mesoporous film efficiently. Owing to this reason, the charge carrier lifetime and transit time can be reduced significantly. This subsequently enhanced the charge collection efficiency at the electrode, contributing to higher current density and the overall conversion efficiency.

Figure 4.23 Illustration of TiN_xO_y particles embedded inside the mesoporous network of hydrothermally grown TiO_2 nanoparticles.

4.6 Summary

The mesoporous TiN_xO_y (N-doped TiO_2) layer can be synthesized through the single thermal oxidation step of the paste formulated with the TiN nanoparticles at different temperatures from 350 – 550 °C. The oxidation process converts the TiN nanoparticles into TiN_xO_y nanoparticles, starting at ~ 400 °C to give both anatase and rutile phases of

TiO₂ as observed using XRD. The presence of O-Ti-N linkage in the TiN_xO_y was confirmed using XPS. In addition, the optical absorption profile of the mesoporous TiN_xO_y film has also revealed an extra absorption shoulder at the 400 – 500 nm region. The size of the agglomerated particle size of the mesoporous TiN_xO_y film observed by FESEM was not uniform, in the range of 30 – 100 nm. The DSSCs fabricated using these TiN_xO_y photoanodes showed optimum conversion efficiency for samples annealed at 450 °C. However, the energy conversion efficiencies obtained are low compared with the standard DSSCs using TiO₂ photoanodes due to the low specific area for dye-loading.

In order to improve the overall performance while exploring the benefits of using TiN_xO_y nanoparticles in photoanode, the TiN_xO_y nanoparticles were successfully integrated into the mesoporous TiO₂ layer derived from hydrothermal TiO₂ nanoparticles to form the composite photoanode. The DSSCs with composite photoanodes improved the photovoltaic performances. Among these samples, the sample TN5 with about 6.4 wt% of TiN_xO_y nanoparticles in the mesoporous TiO₂ layer showed the highest conversion efficiency with $V_{oc} = 0.715$ V, $J_{SC} = 13.0$ mA/cm², Fill Factor = 68.6 % and the energy conversion efficiency, $\eta = 6.38$ %. The 25.6% improvement in the conversion efficiency over the standard DSSC using mesoporous TiO₂ photoanode was due to the combined effects of the extra absorption region and the lowering of charge transport resistance. Higher IPCE values obtained for the DSSCs with composite photoanodes, especially in the wavelength range of 400 – 500 nm, indicated that the TiN_xO_y nanoparticles embedded inside the composite photoanode act as additional centers for the co-sensitization effect. Furthermore, these composite photoanodes also offered lower charge transport resistance by providing alternative conduction path through the mesoporous film. As a result, faster

electron transport through the interpenetrated oxide layer was achieved. This in turns improved the charge collection efficiency at the electrode. All these results supported the integration of TiN_xO_y in TiO_2 photoanode and was beneficial for achieving higher current density in DSSCs, which subsequently improved the overall photovoltaic performance.

CHAPTER 5 3D ELECTRODE FOR DYE-SENSITIZED SOLAR CELL

For DSSC to achieve higher solar energy conversion efficiency, the electron transport efficiency in the mesoporous photoanode and the charge collection efficiency at the FTO electrode must be improved while the charge loss due to electron recombination at the electrode/electrolyte interfaces has to be suppressed. To achieve these goals, extensive studies have been done to evaluate the use of nanostructured electrodes for DSSC devices.

The conventional two dimensional (2D)-based electrode has been reconfigured to three dimensional (3D)-based electrode to enhance the charge collection efficiency. By extending the electron collection electrode to 3D, the average transport distance that an injected electron from the photo-excited dye molecule must travel to the collection electrode would be shortened and the problem of electron recombination could also be reduced.

The concept to extend the 2D transparent conducting oxide (TCO) electrode for DSSCs 3D-electrode was firstly introduced by Chappel et al. to reduce the electron transport path [51]. Since then, there have been numerous studies of similar concepts to create 3D electrode. In general, most of these works on the realization of 3D electrode for DSSCs were based on ITO glass substrate. However, the use of ITO as electrode for DSSCs has limited success. The low resistivity of ITO is due to the large free carrier densities. These free carriers are generated from both Sn dopants and ionized oxygen vacancy donors.

Each Sn dopant offers one electron and one oxygen vacancy contributes two electrons. The resistances of ITO increases significantly at annealing temperatures higher than 300 °C is due to the oxygen in the synthetic air bonded to a portion of the oxygen-vacant structure within the ITO, leading to the loss of oxygen vacancies and subsequently decrease its conductivity [200, 201]. Hence, ITO glass is not suitable to be used for DSSCs as the sintering temperature for mesoporous TiO_2 layer formation are generally above 450 °C[60]. Thus, Fluorine-doped tin oxide (FTO) film is usually the choice for TCO substrate for better device performance.

Besides that, it has been reported that the enhanced electron transport properties for DSSCs could be observed by utilizing 1-D nanostructures like nanotubes, nanorods and nanowires of metal oxide in conjunction with nanoparticle films to form the hierarchical structure for photoanode [202-205]. This composite nanostructure has been designed to take advantage of the improved electron transport along the nanorods and surface area provided by the nanoparticles, yielding good charge collection and light harvesting.

In this work, the SnO_2 nanorods were grown on both ITO and FTO glass substrate. As presorted in the literature, SnO_2 is an excellent metal oxide semiconductor with higher electron mobility and larger band gap (3.6 eV) than TiO_2 . Hence, SnO_2 allows for faster transport of photogenerated electrons and exhibits excellent long-term stability compared to TiO_2 for DSSCs applications. However, the conduction-band edge of SnO_2 is positively shifted 300 mV with respect to the TiO_2 has resulted in lower trapping density for electron and promoted faster interfacial electron recombination. Besides that, photoanode with SnO_2 also possessed less adsorption of the dye with acidic carboxyl groups due to a lower isoelectric point. Both reasons have contributed to the limited success of SnO_2 -based

DSSCs [62]. Hence, the double-layered and composite photoanode consisting of two different metal oxides such as SnO_2/ZnO [206] and $\text{SnO}_2/\text{TiO}_2$ [58-63] were introduced to achieve fast electron transport, slow interfacial electron recombination and large specific surface area for photoanode in DSSC. This has proven to be a promising strategy to obtain high efficiency DSSCs. Furthermore, SnO_2 is the choice of material for realizing the 3D electrode as it is the same oxide material for the conductive layer in FTO glass.

Combining all these advantages, the efforts to grow SnO_2 nanorods on both ITO and FTO glass substrate were carried out in this study. The schematic illustration of the conceptual 3D electrode on FTO glass substrate using SnO_2 nanorods in comparison with the conventional 2D electrode for DSSCs is shown in Figure 5.1.

Figure 5.1 Schematic illustration of conceptual 3D electrode with SnO_2 nanorods with conventional 2D electrode for DSSC device fabrication.

This chapter summarizes the study on the development of 3D electrode for DSSCs. Section 5.1 describes the effort on the developing 3D electrode by depositing SnO₂ nanorods on ITO glass while Section 5.2 describes the effort on depositing SnO₂ nanorods on FTO glass substrate. This is followed by the physical and optical characterizations of SnO₂ nanorods in Section 5.3. After that, the photovoltaic performance and electron transport property in the mesoporous layer and the 3D electrode of DSSCs with SnO₂ nanorods 3D electrode will be described in Section 5.4 and 5.5.

5.1 Growth of SnO₂ Nanorods on ITO Glass Substrate

The SnO₂ nanorod arrays were grown on the ITO glass substrate in the custom built inductively coupled plasma enhanced chemical vapour deposition (ICP-CVD) system. The growth conditions were the same as those used to grow SnO₂ on Si wafers previously reported by our group [207, 208]. Inductively coupled plasma (ICP) generation method was used to generate the plasma and it was generated by a 13.56 MHz 1.2 kW radio-frequency generator coupled to the copper coil circled outside the cylindrical quartz deposition chamber. Dibutyltin diacetate ((C₄H₉)₂Sn(OOCCH₃)₂) was used as the Sn precursor. The precursor chemical was stored inside a metal bubbler at the temperature of 90 °C. The TCO glass substrate were attached to a 4 inch silicon wafer (acting as the holder) and placed in the downstream of the plasma inside the ICP-CVD system at the distance D_{sn} of 10 cm from the gas nozzles. Inert Argon gas was used as the carrier gas at a flow rate of 50 sccm to carry the Sn precursor chemical vapour into nozzles inside the quartz reaction chamber and mixed with the oxygen gas stream at the flow rate of 50 sccm. The reaction of the Sn precursor chemical and oxygen under the plasma excitation

would initiate the deposition of SnO₂ film or SnO₂ nanorods onto the TCO glass substrates (ITO or FTO glass substrate). The typical growth parameters are listed in Table 5.1.

Table 5.1 Typical deposition parameters of SnO₂ nanorod arrays on ITO glass by ICP-CVD system.

RF power	1.2	kW
Tune	33	
Reflected power	0.03	kW
Precursor temperature	90	°C
Gas line temperature	100	°C
O ₂	50	sccm
Ar carrier gas	50	sccm
Pressure	90	mTorr
Deposition time	30 – 140 min	min
Substrate	TCO film (ITO, FTO) on glass substrate	
Substrate to nozzle distance (D_{sn}) (funnel-type nozzle)	10	cm

5.1.1 Study of Surface Morphology of SnO₂ Nanorods Deposited on ITO Glass Substrate

The growth of SnO₂ nanorods on the TCO glass substrate were carried out in the ICP-CVD system for different deposition time of 30 - 120 mins. Figure 5.2 shows the surface morphology of the resultant SnO₂ deposition on the ITO glass substrate for different deposition time. Based on these results, deposition time of 30 min was not long enough and no SnO₂ nanorod was grown on the surface of the ITO glass (Figure 6.2a). After deposition time was increased to 60 min, only few short SnO₂ nanorods were sparsely grown on surface of the ITO glass (Figure 6.2b). More SnO₂ nanorods were observed after deposition time was increased to 100 min (Figure 6.2c) and longer deposition time of

120 mins helped to promote the preferential growth of longer and denser SnO₂ nanorods on the surface of the ITO glass (Figure 6.2d).

Figure 5.2 FESEM images of the SnO₂ deposition and the preferential growth of nanorods on ITO glass substrate for the deposition time of 30 to 120 mins.

5.1.2 Crystalline Phase Study of SnO₂ Nanorods on ITO Glass Substrate

Figure 5.3 shows the XRD patterns of the SnO₂ nanorod arrays deposited on ITO glass at $D_{sn} = 10$ cm for 120 min. Besides the diffraction peaks that originated from the ITO substrate, all the new main peaks could be indexed by the SnO₂ crystalline phases. This result confirmed the growth of crystalline SnO₂ nanorods on the surface of the ITO glass.

Figure 5.3 XRD patterns of the SnO_2 nanorod arrays deposited on ITO glass at $D_{sn} = 10$ cm for 120 min.

5.2 Growth of SnO_2 Nanorods for 3D Electrode

5.2.1 Direct Growth on FTO Glass Substrate

SnO_2 nanorods have been successfully deposited on various substrates including SiO_2/Si wafer and ITO glass. However, Fluorine-doped tin oxide (FTO) glass is usually the choice for TCO substrate for DSSCs due to the high thermal stability. The initial attempts to grow the SnO_2 nanorods on the FTO glass were not successful (Figure 5.4). No nanorod could be observed on the FTO substrate for prolonged growth time from 30 to 100 mins. For the growth time of 120 mins, only few very short SnO_2 nanorods were sparsely grown on the FTO glass substrate. The self-etching effect caused by the fluorine atoms/radicals released from the FTO layer due to sputtering effect by the fluorine radicals/ions inside the plasma was the dominant reason in suppressing the preferential growth of the SnO_2

nanorods on FTO glass. In order to solve this problem, a thin SnO_2 buffer/seeding layer was first deposited by the sol-gel spin coating method to passivate the FTO surface and prevent the direct contact of the plasma with the FTO, hence suppressed the release of fluorine radicals from the FTO layer and to promote the preferential growth of the SnO_2 nanorods on FTO glass substrates.

Figure 5.4 FESEM images of (a) bare FTO glass, SnO_2 deposited on FTO glass by ICP-CVD method for (b) 30 mins, (c) 60 mins, (d) 100 mins and (e) 120 mins.

5.2.2 Growth from SnO₂ Seeding Layer on FTO Glass Substrate

Different concentration of SnCl₂·2H₂O in ethanol (0.05 M, 0.10 M and 0.20 M) was used as precursor to deposit a thin dense SnO₂ buffer/seeding layer by spin coating method. The SnCl₂·2H₂O coated on the FTO glass was annealed to form the dense SnO₂ film at 450 °C for 1 hour in synthetic air (N₂:O₂ = 4:1) at 1 slm using Lindberg tube furnace.

Dense SnO₂ nanorods were deposited in the ICP-CVD system, Figure 5.5 shows the FESEM images of the SnO₂ nanorods deposited on the SnO₂/FTO glass substrate after deposition for 120 mins. It can be seen that the SnO₂ buffer layers promoted the preferential growth of SnO₂ nanorods. Dense and long SnO₂ nanorods could be seen protruded from the substrate where the SnO₂ buffer/seeding was deposited from 0.05 M SnCl₂ solution (Figure 6.5a). These nanorods were closely packed and grown in random directions, not perpendicular to the substrate as the surface of the substrate is rough. This microstructures on FTO glass can be described as 3D electrode with hybrid 1D SnO₂ nanorods grown on a 2D SnO₂/FTO glass. A US patent application based on the novel 3D transparent conducting oxide electrode was submitted.

For the TCO glass substrates with SnO₂ buffer film deposited from 0.10 M and 0.20 M SnCl₂ solution, the SnO₂ nanorods were much shorter but a rather uniform SnO₂ films were formed. Bead-like structures could be observed and this was attributed to the presence of continuous buffer layer with higher SnCl₂ precursor concentration which did not promote the preferential growth of SnO₂ nanorods.

The side-views of the SnO₂ nanorods on SnO₂/FTO glass substrate are shown in Figure 5.6. A thin seed layer could be observed at the boundary between the nanorods and FTO

glass. The SnO_2 nanorods were needle-like shape and the diameter at the root was about 20 nm. The length of the nanorod could reach up to about 550 nm.

Figure 5.5 FESEM images of SnO_2 nanorods deposited on SnO_2/FTO glass for 120 mins inside ICP-CVD system. The SnO_2 seeding layer was deposited using SnCl_2 precursor with concentration (a) 0.05 M (b) 0.10 M (c) 0.20 M.

Figure 5.6 FESEM side-view images of SnO_2 nanorods on SnO_2/FTO glass. The SnO_2 seeding layer on FTO substrate was deposited from 0.05 M SnCl_2 precursor.

5.2.3 Deposition of TiO₂ Barrier Layer on SnO₂ Nanorods/SnO₂/FTO Glass Substrate

A thin TiO₂ barrier layer was deposited onto the SnO₂ nanorods using the APCVD system at 450 °C. Figure 5.7 shows that the SnO₂ nanorods before and after being coated with the thin TiO₂ barrier layer in the APCVD system. The TiO₂ thin film totally covered the SnO₂ nanorods over the entire substrate, creating the SnO₂/TiO₂ core sheath structures and changing the needle-like shape of the SnO₂ nanorods to nanorod-like SnO₂/TiO₂ core sheath morphology. The nanorod shape observation was supported by the TEM image as shown in Figure 5.8(c), in which the TiO₂ barrier layer covered the SnO₂ nanorods with a thickness of about 5 nm. As mentioned in Chapter 3, the TiO₂ barrier layer on the FTO electrode was important to prevent the charge recombination in the DSSCs to directly improve the device performance. The TEM images also revealed that the SnO₂ nanorods grown had very well-defined crystalline structure. Hence, these SnO₂ nanorods and promote the transport of the collected electrons in the mesoporous layer, to travel along the axis of the nanorods towards the FTO collecting electrode on the glass substrate.

Figure 5.7 (a) SnO₂ nanorods /SnO₂/FTO electrode; (b) TiO₂ barrier layer on SnO₂ nanorods /SnO₂/FTO electrode.

Figure 5.8 TEM images of (a) SnO₂ nanorods on FTO glass substrate; (b) Well defined crystalline structure of SnO₂ nanorods; (c) TiO₂ barrier layer coated SnO₂ nanorod arrays using APCVD system.

5.3 Optical Property of SnO₂ Nanorods 3D Electrode on FTO Glass Substrate

Optical UV-Vis spectrometer was used to investigate the optical transmission of the SnO₂ nanorods 3D electrode on FTO glass substrate after the deposition of various seeding layer from 0.05 M SnCl₂ precursor; SnO₂ nanorods and the final TiO₂ barrier layer. A high transparency of the 3D electrode was desirable for optimum light absorption by the light sensitizer in the mesoporous TiO₂ layer. Figure 5.9 shows the measured optical transmission results. The deposition of the SnO₂ seeding layer on the FTO glass substrate

caused only a slight reduction in the optical transmission of the glass electrode. The presence of the SnO_2 nanorods restored the excellent transmission of the glass electrode. This phenomenon was attributed to the light scattering or guarding effects of the SnO_2 nanorods that were grown randomly and non-perpendicularly to the FTO glass substrate. The further deposition of TiO_2 barrier layer on the SnO_2 nanorods/ SnO_2 seeding layer/FTO glass substrate caused some reduction in the transmission for the UV light from wavelength 300 nm to 400 nm.

Figure 5.9 The optical transmittance curves of the SnO_2 nanorod 3D electrodes with different deposited thin film layer.

This results showed that the additional layer of SnO_2 nanorods on SnO_2 /FTO substrate did not alter the transmittance values and remained at around 80% for the visible light wavelength from 400 to 800 nm. The TiO_2 barrier layer deposited using APCVD method

caused the optical absorption edge for the 3D electrode to red-shift from 300 nm to about 400 nm due to the absorption on the TiO_2 barrier layer.

With the successful formation of 3D electrode structure with the SnO_2 nanorods on SnO_2/FTO glass, DSSCs were fabricated with this 3D electrode structure to evaluate the effects on the photovoltaic performance.

5.4 Photovoltaic Performance of DSSC Device with 3D Electrode

DSSC devices were fabricated to investigate the effects of 3D electrode on the photovoltaic performance in comparison with the standard DSSC (Sample STD) with flat 2D FTO electrode. For sample SN0, thin SnO_2 layer was deposited on FTO glass substrate using ICP-CVD system without the SnO_2 seeding layer. For sample SN1, the SnO_2 buffer layer was first deposited in 0.2 M SnCl_2 precursor solution and then the thin SnO_2 layer was deposited in the ICP-CVD system to give clustered short nanorods. For sample SNR, SnO_2 random SnO_2 seedings were first deposited using 0.05 M SnCl_2 precursor solution, it was then followed by the preferential deposition of SnO_2 nanorods in the ICP-CVD system to give the dense SnO_2 nanorods 3D electrode. The surface morphology on the transparent electrodes of these samples are shown in Figure 5.10.

Figure 5.10 Surface morphology of different transparent electrodes (a) standard FTO glass substrate (STD), (b) SnO_2 thin film on FTO glass substrate (SN0), (c) short and clustered SnO_2 nanorods (SN1) and (d) SnO_2 nanorods (SNR).

The DSSCs were successfully fabricated on these electrodes using the standard DSSC fabrication process. A thin 30 nm TiO_2 barrier layer was deposited on these electrodes before the formation of the 10 μm thick mesoporous TiO_2 photoanode using the hydrothermal TiO_2 nanoparticles as described in Chapter 3. The photovoltaic performances of these samples were characterized and the I - V curves are shown in Figure 5.11, with standard DSSC (STD) as reference for comparison. The photovoltaic parameters extracted from the I - V curves are tabulated in Table 5.2.

Figure 5.11 Photovoltaic I - V curves of DSSCs incorporated with SnO_2 nanorods (SNR) on FTO glass substrate as 3D electrode.

Table 5.2 Photovoltaic parameters of DSSCs fabricated on different types of transparent electrodes.

Sample	Transparent Electrode	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
STD	standard DSSC on FTO	0.702	10.57	67.9	5.04
SN0	with only SnO_2 buffer film on FTO	0.708	11.49	63.6	5.17
SN1	short/clustered SnO_2 nanorods on SnO_2/FTO	0.705	11.36	66.5	5.33
SNR	3D-based SnO_2 nanorods on SnO_2/FTO	0.705	12.44	65.0	5.70

From the I - V characteristic curves as shown in Figure 5.11 and summary in Table 5.2, the open-circuit voltage, V_{OC} for the four DSSC samples remained almost constant at ~ 0.705 V. There was a gradual increase in the short-circuit current density, J_{SC} with the inclusion of various type of SnO_2 buffer layer underneath the mesoporous TiO_2 layer on FTO glass substrate for sample SN0, SN1 and SNR. This improvement can be explained by the

relative conduction band location of the SnO_2 buffer layer with respect to the mesoporous TiO_2 layer (photoanode) as previously reported. Referring to the bandgap positions of the SnO_2 and TiO_2 oxide semiconductors as shown in Figure 5.12, incorporation of $\text{SnO}_2/\text{TiO}_2$ coupled photoelectrode suppressed the back electron transfer (charge recombination between the electrons injected into the conduction band of the TiO_2 oxide semiconductor and the oxidized sensitizer dye molecules) due to the difference in energy levels. Electrons that were injected from the excited state of dye sensitizer into the conduction band of mesoporous TiO_2 oxide semiconductor layer would quickly migrate to the lower conduction band of the SnO_2 layer. This implied a better charge separation in the coupled system enhanced by fast electron transfer process between the two oxide semiconductors with different conduction band energy levels [58-61]. Thus, the J_{SC} values for DSSC samples with extra SnO_2 layer would be higher as compared to the standard DSSC sample (STD) in general.

Figure 5.12 Relative energy level of the conduction bands for SnO_2 and TiO_2 that inhibits the back electron transfer of electrons that causes the electron combination with the dyes and electrolyte [60].

Incorporating a thin SnO₂ layer in sample SN0 resulted in a slight enhancement in J_{SC} (11.49 mA/cm²) as compared to normal standard DSSC sample STD with normal FTO glass substrate as electrode only (10.57 mA/cm²). However, this improvement in J_{SC} was offset by the reduction in the Fill Factor (SN0: 63.62% vs. STD: 67.86%) due to higher resistivity with the introduction of SnO₂ layer on FTO glass substrate. The 2D SnO₂/FTO electrode did not improve the specific surface area to create more interfaces between the mesoporous TiO₂ oxide layer and the charge collection at FTO electrode. Hence, the overall improvement in the conversion efficiency was not significant.

For sample SN1, the SnO₂ layer deposition gave short SnO₂ clusters without well-defined SnO₂ nanorods, only slight improvement in the energy conversion efficiency (SN1: 5.33 %) was obtained as compared to the sample SN0 (5.17 %) with flat SnO₂ layer. A closer observation at photovoltaic parameters as shown in Table 5.2 revealed that the J_{SC} value obtained was actually very similar to SnO₂ thin film without the nanorods. In fact, the improvement in the fill factor was observed which can be attributed to the reduced recombination and lower interfacial charge transfer resistance at the FTO/TiO₂ interface. The 3D effect was not prominent when short SnO₂ nanorods were used as electrode.

On the other hand, when the longer, well-crystallized SnO₂ nanorods were introduced to the FTO electrode, the improvement in energy conversion efficiency became obvious. Sample SNR with SnO₂ nanorods 3D electrode showed marked enhancement in energy conversion efficiency (η : 5.70 %) especially in the J_{SC} value. This showed that the SnO₂ nanorods 3D electrode played the role in assisting the charge transport along the length of the nanorod towards the FTO electrode, lowering the chance of random charge hopping

and trapping across the grain boundaries of the nanoparticles in the mesoporous TiO₂ photoanode.

The *FF* values for sample SN1 (66.52 %) and SNR (65.04 %) were higher than the sample SN0 (63.62 %) with flat SnO₂ film deposited on FTO electrode. Due to the increase in the surface-to-volume ratio of the electrode that created extremely large interfaces between the mesoporous TiO₂ oxide layer with the FTO electrode could boost the charge transfer and collection efficiency at the electrode. This advantage has clearly compensated the increase of resistivity of the electrode due to the SnO₂ layer. The energy conversion efficiency of DSSC with SnO₂ nanorods 3D electrode (sample SNR) was 13 % higher than the standard DSSC (sample STD) with 2D electrode, as a result of enhanced conduction of electrons to the FTO via the SnO₂ nanorods array.

5.5 IPCE of DSSC Device with SnO₂ Nanorods 3D Electrode

The IPCE curves for these samples are shown in Figure 5.13, with the standard DSSC (STD) as reference. These results were consistent with the photovoltaic *I-V* performance of the DSSCs. According to the equation (2.11), $IPCE = LHE(\lambda) \phi_{inj} \eta_c$, the light harvesting efficiency (*LHE*) and the quantum yield for electron injection from the excited sensitizer to the conduction band of the semiconductor oxide (ϕ_{inj}) should be constant in this case since the same type of mesoporous TiO₂ layer and N719 dye were used to fabricate the DSSCs. Thus, the consistent improvement in higher IPCE values over the visible light spectrum for SN samples (SN0, SN1 and SNR) implied that the charge collection efficiency (η_c) has improved. With SnO₂ nanorods 3D electrode, sample SNR outperformed the other samples. The highest IPCE value for sample SNR was 64 % at the

wavelength of 520 nm (corresponds to the maximum absorption peak of N719 dye). This was 7 % higher than the standard DSSC (57 %). Once again, the advantage of enhanced charge collection with the incorporation of SnO₂ nanorods 3D electrode with the nanorods protruding into the mesoporous TiO₂ photoanode has been proven.

Figure 5.13 IPCE spectra of DSSCs samples fabricated with SnO₂ nanorods 3D electrode.

5.6 Transport Property of DSSC Device with SnO₂ Nanorods 3D Electrode

To investigate the electron transport properties of DSSCs with SnO₂ nanorods 3D electrode as compared with standard DSSC, the EIS and IMPS measurements were used to study the effect.

5.6.1 EIS Measurement

The EIS measurements were carried out at room temperature using the Metrohm Autolab System for the frequency range from 1 mHz to 1000 kHz, under simulated solar light illumination at the intensity 100 mW/cm². The applied bias was set to be the open circuit potential (V_{OC}) of the DSSC and the ac amplitude was set at 10 mV.

The Nyquist impedance plots from the EIS measurements of the DSSCs with SnO₂ 3D electrodes are shown in Figure 5.14. In general, three semicircles in the order of increasing frequency can be observed from the Nyquist plot. The low frequency loop (at the higher real part resistance of the Nyquist plot) was attributed to the Nernst diffusion within the electrolyte, while the intermediate frequency loop was contributed by the electron transport in the mesoporous layer of TiO₂ and TiO₂/dye/electrolyte interface. Lastly, the high frequency loop (at the lower real part resistance of the Nyquist plot) corresponded to the charge transfer at the Pt-counter electrode/electrolyte and FTO/TiO₂ interfaces [138]. The equivalent circuit diagram was fitted based on the general transmission line model for DSS as shown in the inset of Figure 5.14. The resistance model parameters as extracted from the equivalent circuit model are summarized in Table 5.3.

Figure 5.14 (a) Nyquist impedance spectra from the EIS measurement for DSSCs with SnO₂ nanorods 3D electrode, with the standard DSSC (STD) as reference. The modelling is used to extract the equivalent resistances in DSSCs (b) Equivalent circuit model for DSSC device.

Table 5.3 Transport parameters derived from the EIS and IMPS curves

Sample	Electrode	R_s (Ω)	R_p (Ω)	R_μ (Ω)	Transit time, t_{tr} (ms)
STD	standard transparent FTO	10.9	1.72	16.6	5.03
SN0	with only SnO ₂ film on FTO	13.3	1.29	16.5	3.17
SN1	clustered/short SnO ₂ nanorods on SnO ₂ /FTO	12.8	1.15	15.9	3.17
SNR	SnO ₂ nanorods on SnO ₂ /FTO (3D electrode)	12.5	1.13	16.0	2.52

Based on these results, the equivalent model series resistance (R_s) for the FTO electrode increased with the incorporation of SnO₂ layer by about 1.6 to 2.4 Ω for SN samples ($\sim$ 13.0 Ω) as compared with standard DSSCs (10.9 Ω). This was in a good agreement with the reduction of fill factor (FF) values for the photovoltaic I - V curve given in Table 5.2.

The higher series resistance was due to the additional SnO₂ layer on the FTO electrode, especially for sample SN0 without the SnO₂ nanorods.

The value of R_P was affected by the charge transfer at the Pt-counter electrode/electrolyte and FTO/TiO₂ interfaces. Since the same Pt-back electrode was used, the variation in R_P would be attributed to the variation introduced into FTO/TiO₂ interface. The results suggested that with the presence of the SnO₂ layer beneath the mesoporous TiO₂ layer, the charge transfer resistance would be reduced. A respectable 35 % decrease in the value of R_P was observed for sample SNR (1.13 Ω) with SnO₂ nanorods 3D electrode as compared with the standard DSSC ($\sim$ 1.70 Ω). This indicated that the SnO₂ nanorods grown by the ICP-CVD system significantly improved the contact/adhesion between the FTO electrode and mesoporous TiO₂ layer. Moreover, as shown in Figure 5.12, the conduction band of SnO₂ was also lower than that of TiO₂. Thus, the SnO₂ nanorods also served as a mediator layer which promoted the electron transfer between the mesoporous TiO₂ layer and FTO electrode. On the other hand, the R_{μ} values for all the samples did not vary significantly since the same type mesoporous layer from the same type of hydrothermal TiO₂ nanoparticles were used in this study.

5.6.2 IMPS Measurement

Further investigation on the average time required for the photo-generated electron to travel before being collected by the FTO electrode was carried out using IMPS measurement under short-circuit condition. A red-light laser diode (632 nm) was used as the modulated light source for homogeneous distribution of the illumination onto the

DSSC. The transit time (t_{tr}) was determined from the f_{min} ($t_{tr} = 1/2\pi f_{min}$) extracted from the IMPS plots as shown in Figure 5.15.

The transit times estimated from these IMPS curves for different DSSCs are tabulated in Table 5.3. Incorporating the SnO₂ layer on the FTO helped to reduce the electron transit time from 5.03 ms for standard DSSC sample (STD) to 3.17 ms. A respectable 37 % reduction in the t_{tr} was observed for sample SN0 and SN1. When the SnO₂ nanorods were introduced to form the 3D-electrode, a tremendous 50 % reduction in the t_{tr} was achieved. This implied that the protrusion of these well-crystalline SnO₂ nanorods into the mesoporous TiO₂ layer as shown in Figure 5.10 would significantly shorten the time required by the electrons to travel before being collected at the FTO electrode due to the conduction in the SnO₂ nanorods.

Figure 5.15 IMPS plots for DSSCs with SnO₂ seeding buffer or nanorods on FTO electrode, with standard DSSC as reference.

This phenomenon is schematically illustrated in Figure 5.16. In general case, the N719 dye molecules were adsorbed onto the mesoporous TiO_2 nanoparticles. Under illumination, the photogenerated electron would be separated and injected into the conduction band of mesoporous TiO_2 layer. Due to the interpenetrating nature of the TiO_2 nanoparticles in the mesoporous film, random charge hopping, scattering and trappings/de-trappings of these injected electrons on the grain boundaries across the TiO_2 nanoparticles might occur before successfully collected at the FTO electrode. However, with the incorporation of SnO_2 nanorod arrays on the FTO electrode embedded between the FTO electrode and the mesoporous TiO_2 layer, the electron charge transit time would be minimized.

Figure 5.16 Schematic illustration of charge collection pathways with SnO_2 nanorods 3D electrode.

5.7 Summary

The SnO₂ nanorods were grown in the ICP-CVD system starting from the SnO₂ seedings randomly distributed on the FTO glass substrate. These random SnO₂ nanorods coated on FTO surface changed the surface morphology from the 2D planar electrode to 3D electrode. This SnO₂ nanorods 3D electrode significantly improved the surface aspect ratio of the anode, created an immense interface between the mesoporous TiO₂ layer and the FTO electrode. In other words, these SnO₂ nanorods provided a very large platform to collect the photogenerated electrons. Moreover, SnO₂ is also a good candidate as its conduction band is in the favoured location with respect to TiO₂, promoting the transfer of electrons while constraining the recombination process. The contact/adhesion between the mesoporous TiO₂ layer with the FTO electrode was improved for efficient transfer of electron. The protruding effects of the SnO₂ nanorods also significantly reduced the distance that the electrons needed to travel before being collected. Upon collected, these well-crystalline nanorods performed the role to assist the charge transport along the length of the nanorods towards the FTO electrode. Thus, the electron transit time was reduced by about 50 %. The overall result contributed to higher charge collection efficiency, leading to an overall improvement in the photovoltaic performance.

However, there are few drawbacks of the current system using the SnO₂ nanorods as 3D electrode. One major concern regarding this these closely packed SnO₂ nanorods was the infiltration of TiO₂ nanoparticles into the small gaps in between the SnO₂ nanorods, especially if the larger size TiN_xO_y nanoparticles were to be used as mesoporous oxide layer for photoanode formation. Hence, growth of SnO₂ nanorods with higher aspect ratio at regular patterned locations is expected to alleviate this concern. This recommendation

has been included in future works. Besides that, the optimum effect of integrating these 3D electrodes for DSSC has not been achieved yet due to the limitation in the length of the SnO₂ nanorods grown by the ICP-CVD system. It is believed that if longer SnO₂ nanorods extending to few micrometers can be grown on the TCO substrate, the transit time of the photo-generated electrons can be further reduced leading to significant increase in the photovoltaic performance. Hence, growing longer SnO₂ nanorods on the FTO glass has been proposed as future works as well.

CHAPTER 6 DYE-SENSITIZED SOLAR CELL WITH COMPOSITE PHOTOANODE ON 3D ELECTRODE

In this project we have developed two novel approaches to enhance the photovoltaic performance of Dye-Sensitized Solar Cell (DSSC). In Chapter 4 we described our first novel pioneer approach for the in-situ formation of N-doped TiO_2 (TiN_xO_y) mesoporous layer as the photoanode for DSSC device fabrication. The mesoporous TiN_xO_y layer was formed in-situ by the oxidation at 450°C in synthetic air of the paste formulated from the TiN nanoparticles. We have also successfully demonstrated for the first time the advantage of using mesoporous composite TiN_xO_y - TiO_2 photoanode for DSSC by the in-situ oxidation at 450°C in synthetic air of the composite paste coated onto FTO glass substrate. The composite paste was formulated with the mixture of TiN nanoparticles and hydrothermal TiO_2 nanoparticles according to various weight ratio using suitable organic binder and solvent. DSSC sample (TN5) with mesoporous composite TiN_xO_y - TiO_2 photoanode, formed from paste blended from 5 wt% of TiN nanoparticles in hydrothermal TiO_2 matrix, achieved a remarkable photovoltaic conversion efficiency of 6.38 % as compared with the standard DSSC made from the hydrothermal TiO_2 nanoparticles with conversion efficiency of 5.08 %. This corresponded to an increment of 1.3 % (or an improvement of 25.6 % relative to the conversion efficiency of the standard DSSC).

The higher photovoltaic conversion efficiency in DSSC with composite TiN_xO_y - TiO_2 mesoporous photoanode could be due to combined effects of the self-sensitizing effect arising from the extra absorption tail of the embedded N-doped TiO_2 (TiN_xO_y) nanoparticles in the visible wavelength range from 400 nm to 550 nm as well as the enhancement in electron transport property through the embedded TiN_xO_y nanoparticles in the mesoporous TiO_2 nanoparticle matrix.

The second novel approach we had developed for the improvement of the DSSC performance was the technology for the deposition of SnO_2 nanorods to form the 3D electrode for DSSC device as reported in Chapter 5. The DSSC sample SNR using this SnO_2 nanorod 3D electrode achieved a photovoltaic conversion performance of 5.7 % and outperformed the standard DSSC with standard flat 2D FTO electrode with the conversion efficiency of 5.04%. This improvement in photovoltaic performance was the result of improved electron collection efficiency by the SnO_2 nanorods embedded in the mesoporous TiO_2 matrix. The embedded SnO_2 nanorods have promoted the transfer of electrons in the mesoporous TiO_2 matrix to the charge collection electrode and significantly reduced the travelling distance and time of photo-generated electrons injected from the excited dye molecules through the mesoporous TiO_2 layer to the SnO_2 nanorods and then collected at the FTO electrode.

In this chapter we describe our effort to combine the advantages of these two novel approaches and fabricate the DSSC (sample named as TN5-SNR) with composite TiN_xO_y - TiO_2 mesoporous photoanode and SnO_2 nanorods 3D electrode and compare the photovoltaic performance with the standard DSSC (STD).

6.1 DSSC with Combined Novel Nanostructured Composite Photoanode --- Composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ Mesoporous Photoanode and SnO_2 Nanorod 3D Electrode

6.1.1 Fabrication of DSSC with Combined Novel Nanostructured Composite Photoanode

The fabrication of the DSSC with combined novel nanostructured photoanode including composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ Mesoporous Photoanode and SnO_2 Nanorod 3D Electrode started with the formation of the 3D electrode. SnO_2 nanorods deposited on the FTO glass substrate using ICP-CVD method according the detailed procedure as described in Chapter 5. After that, a 30 nm dense TiO_2 barrier layer was deposited on this 3D electrode using the APCVD method. Next the composite The composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ Mesoporous Photoanode was then formed by the oxidation of the composite paste deposited using doctor blade method. The composite paste was formulated from 5 wt% of precursor TiN nanoparticles with the balanced hydrothermal TiO_2 nanoparticles blended with suitable organic binder and solvent using the paste formation procedure as optimized and in Chapter 4. This composite paste on the SnO_2 nanorod 3D electrode was subjected to the thermal annealing/oxidation at the temperature of 450 °C in tube furnace with synthetic air (N_2/O_2) flow rate of 1 slm. The freshly formed composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ Mesoporous Photoanode was then loaded with the sensitizer dye molecules by dipping into the 0.25 mM N719 dye solution for overnight. Finally, the DSSC device (sample named as TN5 - SNR) with this combined novel nanostructured composite photoanode was assembled for photovoltaic characterization. A standard DSSC device (STD) fabricated with hydrothermal TiO_2 nanoparticles deposited on FTO glass (with 30 nm dense TiO_2 barrier layer) was used as reference for comparison. Table 6.1 summarizes the measured thickness and the amount of dye adsorbed onto mesoporous layer of the fabricated DSSC

devices. The sample TN5 and SNR from the previous experiments were included for comparison.

Table 6.1 Measured mesoporous layer thickness and amount of dye adsorbed onto the mesoporous layer of DSSC devices.

Sample	Photoanode		Amount of dye (mol cm ⁻² x 10 ⁻⁷)
	Structure	Thickness (μm)	
STD	Standard DSSC with HT-TiO ₂ photoanode	10.6	1.04
SNR	DSSC with HT-TiO ₂ photoanode with SnO ₂ nanorods 3D electrode	10.7	1.04
TN5	DSSC with composite TiN _x O _y -TiO ₂ photoanode formed from 5wt% TiN in TiO ₂ paste	10.8	1.01
TN5-SNR	DSSC with composite TiN _x O _y -TiO ₂ photoanode deposited on the SnO ₂ nanorods 3D electrode	10.5	0.98

6.1.2 Photovoltaic Performance of DSSC with Combined Novel Nanostructured Composite Photoanode

The photovoltaic current-voltage (I - V) characteristic of the assembled DSSC device with composite TiN_xO_y-TiO₂ photoanode on SnO₂ nanorods 3D electrode (sample TN5-SNR), and the standard DSSC (sample STD), were measured under the simulated solar light intensity 100 mW/cm² (AM 1.5 SUN) as shown in Figure 6.1. The extracted photovoltaic parameters including the open circuit current (V_{OC}), short circuit current density (J_{SC}), Fill Factor (FF) and the photovoltaic conversion efficiency are summarized in Table 6.2. The photovoltaic I - V results for sample TN5 and SNR were taken from the previous experiments.

Under 100 mW/cm² (AM 1.5) simulated solar light illumination, sample TN5-SNR has a V_{OC} of 0.719 V, a J_{SC} of 13.31 mA/cm², a FF of 67.5 % and conversion efficiency η of

6.50 %. Comparing the results of standard DSSC (sample STD) with a conversion efficiency of 5.04%, the sample TN5-SNR achieved a much better photovoltaic performance, with increment of 22.3% in the J_{SC} and 28 % in conversion efficiency.

The sample TN5-SNR also demonstrated improved photovoltaic performance with respect to sample TN5 and sample SNR. The synergetic effects of composite TiN_xO_y - TiO_2 photoanode and the SnO_2 nanorods 3D electrode were combined and utilized to enhance the charge transport property and the charge collection efficiency of the DSSC device.

Figure 6.1 Photovoltaic I - V characteristic of DSSC device with composite TiN_xO_y - TiO_2 mesoporous photoanode on the SnO_2 nanorods 3D electrode.

Table 6.2 Photovoltaic parameters for DSSC with TiN_xO_y - TiO_2 composite photoanode deposited on the SnO_2 nanorods 3D electrode.

Sample	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
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STD	0.705	10.88	66.5	5.09
TN5	0.715	13.00	68.6	6.38
SNR	0.705	12.44	65.0	5.70
TN5-SNR	0.719	13.31	67.5	6.50

6.1.3 IPCE of DSSC with Combined Novel Nanostructured Composite Photoanode

The IPCE of sample TN5-SNR and the standard DSSCs (sample STD) are shown in Figure 6.2. It was found that by introducing the composite photoanode on 3D electrode, the photoresponse of the DSSC device was boosted. As the dye-loading on both samples were comparable as given in Table 6.1, the significant 10 % increase in the quantum efficiency for sample TN5-SNR over the visible light range from 400 – 675 nm implied that the electron transport property and collection efficiency in the composite TiN_xO_y - TiO_2 composite photoanode and the SnO_2 nanorod 3D electrode have been greatly improved. This improvement could be attributed to the synergistic effects of the TiN_xO_y - TiO_2 composite photoanode and the SnO_2 nanorods 3D electrode. Due to its higher conductivity, the TiN_xO_y nanoparticles embedded inside the mesoporous TiO_2 layer offered an alternative conduction path for the photo-generated electrons to be transported through the interpenetrating mesoporous oxide layer. At the same time, the SnO_2 nanorods have provided a very large charge collection matrix that allowed for the massive charge transfer between the TiO_2 and FTO electrode. This action was further supported and enhanced by the alignment in the conduction band locations that promoted the charge transfer/collection while suppressed the recombination process at the same time. The improvement in the photoresponse at wavelength 400 - 450 nm, also corresponded to the absorption shoulder/tail of TiN_xO_y nanoparticles, suggested that co-sensitization effect by the TiN_xO_y nanoparticles might also act as self-sensitizer as well to generate the extra

electrons to be collection by the 3D electrode that partly contributed to higher current density.

Figure 6.2 IPCE curves for DSSC fabricated using $\text{TiN}_x\text{O}_y\text{-TiO}_2$ composite photoanode on the SnO_2 nanorods 3D electrode.

6.2 Transport Property of Combined Novel Nanostructured Composite Photoanode

6.2.1 EIS Measurement

The charge transport property in the DSSC with composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanode deposited on the SnO_2 nanorods 3D electrode was further investigated using EIS and IMPS measurements. The EIS measurement was carried out to determine the impedances of the solar cells. On the other hand, the IMPS measurements were carried out under short-circuit condition and modulated by a red-light laser diode (632 nm), to determine

the electron transit time (t_{tr}) through the mesoporous oxide semiconductor layer to be collected by the electrode.

Figure 6.3 (a) Nyquist plot of DSSC with $\text{TiN}_x\text{O}_y\text{-TiO}_2$ composite photoanode deposited on the SnO_2 -nanorods 3D-based electrode with respect to standard DSSC under 100 mW/cm^2 simulated solar light illumination at open circuit potential. The symbol corresponded to the measurement results. The lines show theoretical fits using equivalent circuit shown in the inset. (b) Equivalent circuit model for DSSC with composite $\text{TiN}_x\text{O}_y\text{-TiO}_2$ photoanode on SnO_2 nanorods 3D electrode.

The Nyquist plot from the EIS measurements and the equivalent circuit diagram based on the general transmission line model are shown in Figure 6.3. The corresponding Bode phase plots from the impedance measurements are shown in Figure 6.4. The parameters extracted from the circuit model are tabulated in Table 6.3.

Figure 6.4 Bode phase plots from the impedance spectra.

Table 6.3 Transport parameters determined from the EIS and IMPS measurement.

Sample	R_s (Ω)	R_p (Ω)	R_t (Ω)	R_μ (Ω)	R_{TiO_2} (Ω)	Electron Lifetime (t_e) (ms)	Electron Transit time (t_{tr}) (ms)
STD	11.0	1.58	0.91	17.2	17.50	7.0	5.03
TN5-SNR	12.1	1.15	0.39	13.0	13.13	9.1	2.52

Based on the results obtained from the impedance spectra, there was a 27 % drop in the value of R_p for sample TN5-SNR (1.15 Ω) as compared with STD sample (1.58 Ω). The reduction was attributed to the enhanced adhesion at the FTO/TiO₂ interface, as the same Pt-back electrode was used. This result also suggested that using the SnO₂ layer beneath the TiO₂, the charge transfer resistance from TiO₂ layer to FTO was reduced. The second semicircle at the middle frequency range showed much lower charge transfer resistance at

the mesoporous oxide/dye/electrolyte interface (R_μ) for sample TN5-SNR (13.0 Ω) over the standard DSSC (17.2 Ω) under solar light illumination. The main reason for this 24 % reduction was due to the embedded TiN_xO_y nanoparticles in the mesoporous TiO_2 photoanode that improved the conductivity of the films and allowed efficient transfer of electrons from the photo-excited dye sensitizer molecules to the mesoporous oxide semiconductor layer. Nevertheless, a slight increase in the series resistance for sample TN5-SNR was observed due to the additional SnO_2 thin layer on FTO glass.

The impedance measurements were also carried out within a range of bias potentials to determine the transport resistance in the oxide layer. The extracted transport resistances from the impedance spectra are shown in Figure 6.5. Under different forward bias, lower transport resistance was obtained for sample TN5-SNR with respect to the standard DSSC (STD). This reduction was attributed to the higher conductivity of the TiN_xO_y particles embedded inside the mesoporous TiO_2 layer.

Based on the overall measurement data, the values for R_μ were much larger than R_t for all the data obtained indicating a low recombination loss and a finger-print of good quality photoanode [156]. Under this condition, the total photoanode resistance was estimated based on the equation $R_{\text{TiO}_2} = \frac{1}{3}R_t + R_\mu$ for low recombination. By associating all the experimental data, a remarkable 24 % reduction in the R_{TiO_2} was obtained for sample TN5-SNR (13.13 Ω) as compared with sample STD (17.50 Ω). This improvement resulted in higher efficiency in the transfer of electron through the interpenetrating oxide layer, which in turns led to higher current density and energy conversion efficiency.

Figure 6.5 Reduction of transport resistance in the mesoporous oxide layer obtained from the impedance measurement at different applied bias.

6.2.2 IMPS Measurement

The electron transit time (t_{tr}), which is the average time required for an electron to travel across the oxide semiconductor layer, could be determined from the IMPS curves based on the f_{min} ($t_{tr} = 1/2\pi f_{min}$) as shown in Figure 6.6. A significant 50 % reduction in the transit time for sample TN5-SNR (2.52 ms) was obtained as compared to standard DSSC (5.03 ms). The TiN_xO_y nanoparticles embedded inside the mesoporous TiO_2 photoanode provided an alternative path in the oxide layer for faster transport of electron. Once the electron was transferred to SnO_2 , the nanorods offered a direct pathway for the electrons to be transported to the FTO electrode. The combined advantages granted by these two novel approaches have shorten the total travelling time of the photogenerated electron before being collected at the electrode.

Figure 6.6 IMPS plots for DSSC with TiN_xO_y - TiO_2 composite photoanode deposited on the SnO_2 nanorods 3D electrode, standard DSSC served as a reference for comparison.

6.3 Summary

The SnO_2 nanorods 3D electrode was successfully deposited using ICP-CVD method. The mesoporous composite TiN_xO_y - TiO_2 photoanode was formed on this 3D electrode from the paste mixed with 5 wt% TiN in TiO_2 paste with standard formulation. By incorporating these two novel approaches, the DSSC device with composite TiN_xO_y - TiO_2 photoanode on SnO_2 nanorods 3D electrode was also successfully fabricated and characterized for its photovoltaic performance. As compared to the standard DSSC device with mesoporous TiO_2 layer as photoanode on FTO glass substrate (2D electrode), an overall increment of 28 % in the conversion efficiency relative to the standard DSSC was achieved. The EIS measurement showed that the adhesion between the mesoporous TiO_2 /electrode was enhanced through the SnO_2 nanorods layer. The decrease in charge

transfer resistance at the mesoporous oxide/dye/electrolyte interface allowed efficient electron transfer from the photo-excited dye sensitizer molecules to the oxide semiconductor layer. Lower charge transport resistance through the mesoporous TiN_xO_y - TiO_2 film was observed due to the higher conductivity of TiN_xO_y nanoparticles in the mesoporous film. This resulted in 24 % reduction in the resistance of the composite TiN_xO_y - TiO_2 photoanode. Besides that, the IMPS results also showed that the transit time of a photogenerated electron through the mesoporous layer and collected at the FTO electrode was significantly reduced by 50 %, resulted in higher charge collection efficiency at the electrode. In short, by incorporating the composite TiN_xO_y - TiO_2 photoanode on SnO_2 nanorods 3D electrode, the DSSC device has demonstrated improved charge transport in the photoanode and the charge collection efficiency by the electrode. Combining these two novel approaches has resulted in significant improvement in the solar energy conversion efficiency of DSSC devices.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

This chapter provides a summary of the work accomplished in this project and the evaluation of results on the systematical characterization of various dye-sensitized solar cells (DSSCs) fabricated. The fabrication, characterization and optimization works were described in details especially on the mesoporous TiO_2 photoanode, for the fabrication of standard DSSC device that served as a baseline for all subsequent improvement. This was followed by the study of N-doped TiO_2 (TiN_xO_y) as photoanode for DSSC. DSSC with composite photoanode formed from the incorporation of small amount of TiN_xO_y nanoparticles embedded within the network of the smaller size hydrothermal TiO_2 nanoparticles. After that, the utilization of SnO_2 nanorods as 3D electrode for DSSC was evaluated for its efficiency in charge collection. Finally, a DSSC consisted of mesoporous composite TiN_xO_y - TiO_2 layer formed on SnO_2 nanorods 3D electrode was fabricated and investigated to meet the objective of this thesis.

A total of three types of TiO_2 nanoparticles were evaluated in this project as the mesoporous TiO_2 photoanode for dye-sensitized solar cell fabrication, specifically the Degussa P25 TiO_2 , Anatase TiO_2 (Alfa-Aesar) and the hydrothermal TiO_2 nanoparticles. The physical and chemical properties of these three different TiO_2 nanomaterials were thoroughly characterized. The photovoltaic responses of DSSC devices with mesoporous TiO_2 photoanodes fabricated from all these three types of TiO_2 nanoparticles were

evaluated. It was found that the DSSC device with hydrothermal TiO_2 nanoparticles as photoanode demonstrated best photovoltaic performance with conversion efficiency at 4.87 %. The superiority in the photovoltaic performance was attributed to the smaller grain size and non-agglomerated nature for these freshly synthesized TiO_2 nanoparticles. This resulted in highest dye-loading which in turns yielded highest photovoltaic current density.

The optimization of photoanode was further carried out with dense TiO_2 barrier layer on FTO glass substrate. The dense TiO_2 barrier layer deposited using the APCVD method on FTO glass was found to suppress the electron back transport from the FTO electrode to the electrolyte. The DSSC devices with barrier layers exhibited improved performance over the DSSC device with bare FTO electrode. The highest photovoltaic conversion efficiency of 5.04 % was achieved for the DSSC employing a thin 30 nm dense TiO_2 barrier layer in between the mesoporous TiO_2 film and FTO glass. This thin 30 nm TiO_2 barrier layer would be sufficiently effective in suppressing the back transport of electron in the FTO electrode into the electrolyte and still maintained high optical transmittance to give the best photovoltaic I - V characteristics. Based on these optimization results, standard DSSC device structure and fabrication procedure were established. The standard DSSC was made from photoanode with TiO_2 mesoporous film deposited using the hydrothermal TiO_2 nanoparticles, with a 30 nm dense TiO_2 barrier layer on top of the FTO electrode.

The mesoporous TiN_xO_y (N-doped TiO_2) layer was synthesized through the single thermal oxidation step of the paste formulated with the TiN nanoparticles at different temperatures from 350 – 550 °C. As observed using XRD, the oxidation process converted the TiN

nanoparticles into TiN_xO_y nanoparticles, starting at $\sim 400^\circ\text{C}$ to give both anatase and rutile phases of TiO_2 . The presence of O-Ti-N linkage in the TiN_xO_y was confirmed using XPS. In addition, extra absorption shoulder/tail in the visible light wavelength range from 400 to 500 nm for the mesoporous TiN_xO_y film was observed. The size of the TiN_xO_y nanoparticles in the mesoporous TiN_xO_y film observed through FESEM was not uniform, with the agglomerated particles size in the range of 30 to 100 nm. The DSSCs fabricated using these TiN_xO_y photoanodes showed optimum conversion efficiency for samples annealed at 450°C . The low specific area for dye-loading due to the large agglomerated particle size in the mesoporous TiN_xO_y film affected the photovoltaic conversion efficiency of these DSSC using the TiN_xO_y photoanodes as compared with the standard DSSC using mesoporous TiO_2 photoanode.

The mesoporous composite TiN_xO_y - TiO_2 photoanode was first introduced in this project to improve the overall performance while exploring the benefits of using TiN_xO_y nanoparticles in the photoanode for the DSSC. The TiN_xO_y nanoparticles were successfully integrated into the mesoporous layer of TiO_2 to form the composite photoanode and the DSSCs with composite photoanodes were found to have improved photovoltaic performances. Among these samples, the sample TN5 with about 6.4 wt% of TiN_xO_y nanoparticles in mesoporous TiO_2 film showed the highest conversion efficiency, $\eta = 6.38\%$. The increase of 1.34 % (or 25.6 % improvement) in the conversion efficiency over the standard DSSC using TiO_2 photoanode ($\eta = 5.04\%$) was due to the combined effects of the extra optical absorption tail in the N-doped TiO_2 (TiN_xO_y) nanoparticles and the lowering of charge transport resistance through the embedded TiN_xO_y nanoparticles. The TiN_xO_y nanoparticles embedded inside the composite photoanode act as additional

centers for the co-sensitization effect. Furthermore, these composite photoanodes also offered lower charge transport resistance by providing alternative conduction path through the TiN_xO_y in the mesoporous film for the rapid electron transport through the interpenetrated oxide layer. This in turns improved the charge collection efficiency at the electrode.

SnO_2 nanorods were successfully grown by the ICP-CVD system on the FTO glass substrate chemically coated with random SnO_2 seeding layer. The SnO_2 nanorods protruded randomly from the FTO layer, changing the surface morphology from the 2D planar electrode to 3D electrode. This SnO_2 nanorods 3D electrode significantly improved the surface aspect ratio of the anode, created an immense interface between the mesoporous TiO_2 layer and the FTO electrode to collect the photo-generated electrons. SnO_2 was chosen as the choice of material to create the 3D electrode as its conduction band is in the favoured location with respect to TiO_2 in promoting the transfer of electrons while constraining the recombination process. The DSSC with SnO_2 nanorods 3D electrode demonstrated improved conversion efficiency from $\eta = 5.04\%$ for the standard DSSC with 2D FTO glass substrate as electrode to $\eta = 5.70\%$ with the SnO_2 3D electrode, $\sim 13.0\%$ improvement in the conversion efficiency. The contact/adhesion between the mesoporous TiO_2 layer with the FTO electrode was found to improve for efficient transfer of electron. The electron transit time was also reduced by about 50 %. The overall process contributed to higher efficiency in charge collection, leading to an overall improvement in the photovoltaic performance.

Finally, the DSSC with TiN_xO_y - TiO_2 composite photoanode deposited on the SnO_2 -nanorods 3D electrode was also successfully fabricated. The SnO_2 nanorods 3D electrode

was successfully deposited using ICP-CVD method. The mesoporous composite TiN_xO_y - TiO_2 layer was formed on this 3D electrode from the paste formulated with 5 wt% of TiN nanoparticles with the balance hydrothermal TiO_2 nanoparticles. As compared to the standard DSSC device with mesoporous TiO_2 layer as photoanode on FTO glass substrate (2D electrode), an impressive 28 % improvement in the conversion efficiency was achieved. The EIS measurement showed that the adhesion between the mesoporous TiO_2 /FTO electrode was enhanced through the SnO_2 nanorods layer. The decrease in charge transfer resistance due to the TiN_xO_y nanoparticles embedded in TiO_2 matrix at the mesoporous oxide/dye/electrolyte interface allowed efficient electron transfer from the photo-excited sensitizer dye molecules to the oxide semiconductor layer. Lower charge transport resistance through the mesoporous TiN_xO_y - TiO_2 film was observed too. There was a 24 % reduction in the charge transport resistance of the composite TiN_xO_y - TiO_2 photoanode and 50 % reduction in the transit time of a photogenerated electron through the mesoporous layer and collected at the FTO electrode. This novel approach to fabricate a DSSC with the incorporation of the composite TiN_xO_y - TiO_2 photoanode on SnO_2 nanorods 3D electrode, has demonstrated improved charge transport in the photoanode and the charge collection efficiency by the electrode that subsequently lead to a significant improvement in the solar energy conversion efficiency. The simple single step formation of the composite TiN_xO_y - TiO_2 photoanode also has the potential for low cost high volume manufacturing for the DSSC in the future.

7.2 Recommendations

7.2.1 Reducing TiN_xO_y Nanoparticles Size

The commercially available precursor TiN nanoparticles used in this study to form the N-doped TiO_2 (TiN_xO_y) have the nominal particle size of 20 nm and specific surface area of $48 \text{ m}^2/\text{g}$. However large agglomerated TiN_xO_y nanoparticle sizes existed in the mesoporous TiN_xO_y layer with large variation ranging from 30 to 100 nm as observed from the FESEM images (see Figure 4.4 for pure mesoporous TiN_xO_y photoanodes without organic binder, 4.5 and 4.13d for the mesoporous TiN_xO_y photoanodes with organic binder in the formulation of the pastes respectively in Chapter 4). There were also large void spaces in the mesoporous TiN_xO_y layer between the agglomerated nanoparticles. Pore size of several hundreds of nanometer between the agglomerated nanoparticles could be found too. To fully explore the advantage of TiN_xO_y nanoparticles as photoanode, the nanoparticle size should be reduced so as to increase the specific surface area for dye-loading.

High energy ball milling process has been proven to be very effective route to prepare the nanosized powder/nanoparticles [209, 210]. Thus, it is expected the size of the precursor TiN nanoparticles can be reduced by using high energy ball milling process. Several high energy ball milling processing parameters should be considered for further investigation, include the milling speed and time, type of high density containers/balls, milling condition (dry/ wet milling) and the weight ratio of powder to balls in the container during the milling process. Higher specific surface area for dye loading would be expected in the mesoporous TiN_xO_y film if the size of the commercially TiN nanoparticles can be reduced and thus improves the overall photovoltaic performance.

7.2.2 Growth of Longer SnO₂ nanorods on FTO Glass Substrate

SnO₂ nanorods were successfully grown on the FTO glass substrate using ICP-CVD method in the project. These SnO₂ nanorods were closely packed but generally grown in random directions and not perpendicular to the substrate. One major concern regarding this nanorod structure was the infiltration of TiO₂ nanoparticles into the small gaps in between the SnO₂ nanorods, especially if the larger size TiN_xO_y nanoparticles were to be used as mesoporous oxide layer for photoanode formation. SnO₂ nanorods with large aspect ratio grown at regular patterned locations is expected to alleviate this concern. Figure 7.1 illustrate schematically the challenge of infiltrating TiO₂ nanoparticles into the small gaps between the cluster of patterned SnO₂ nanorods on FTO glass substrate.

Figure 7.1 Schematic illustration of problem for infiltration of TiO₂ nanoparticles into the gaps between closely packed SnO₂ nanorods with random growth orientation. (b) TiO₂ nanoparticles can be easily filled into the spaces between cluster of SnO₂ nanorods grown at regular patterned locations.

The typical thickness of the mesoporous TiO_2 film photoanode was about 10 μm . However, the length of the SnO_2 nanorods grown by the ICP-CVD system was around 550 nm after single growth cycle of 2 hrs. Multiple deposition cycles were previously tried on ITO glass in order to increase the length of the nanorods. ITO glass substrate was used to eliminate the parameter introduced by SnO_2 seeding layer. Figure 7.2 shows the surface morphology and cross sectional view of then SnO_2 nanorods grown after two deposition cycles (2 hrs + 2 hrs). No obvious changes could be observed on the surface morphology (Figure 7.2a). The length of the nanorods was estimated to be around 700 nm (Figure 7.2b), slightly longer than previous case. However some interesting growth results were observed, some randomly distributed ultra-long (several micros) nanorod bushes could be observed on the ITO surface were found as depicted in Figure 7.3.

It is believed that if longer SnO_2 nanorods extending to around 1 μm can be grown on the TCO substrate, the transit time of the photo-generated electrons can be further reduced. Thus, the effects of different deposition parameters, including the RF power, nozzle-to-substrate distance etc should be investigated to study their influences on the surface morphology of the SnO_2 nanorods and to deposit longer nanorods.

Figure 7.2 FESEM images of SnO₂ nanorod arrays grown after two deposition cycles on ITO glass substrate (2 hrs + 2 hrs)

Figure 7.3 The ultra-long nanorod bushes observed on the samples grown by multiple depositions.

7.2.3 TiO₂ nanorods/nanotubes on SnO₂ nanorods 3D electrode

In recent years, hydrothermally growth of TiO₂ nanotubes on FTO glass substrate had been reported [114]. It was reported that DSSC device made with the TiO₂ nanotube arrays had better electron charge collection efficiency as compared to standard DSSC device made with TiO₂ nanoparticles of similar thickness on FTO glass substrate due to the 10 times slower recombination rate [106]. Thus, the use of TiO₂ nanotube arrays permitted a direct charge transport along the length of the nanotube towards the electrode,

avoiding random charge hopping across and trapping at nanoparticles grain boundaries [18].

Based on the SnO₂ nanorods 3D-electrode demonstrated in this project, we propose to use the core-sheath nanostructure approach as the photoanode for DSSC device with the TiO₂ nanorods(or nanotubes) grown on the SnO₂ nanorods as shown schematically in Figure 7.4 .

The first advantage of using this core-sheath nanostructure would be the difference in the conduction band energy level between these two types of oxide semiconductors that promotes charge transfer and retard recombination. The nano-structural disorders between two adjacent crystalline nanoparticles that caused the scattering of free electrons and reduced the electron mobility could be tackled by using this core-sheath nanostructure. The epitaxial growth of the TiO₂ nanorods/nanotubes on the SnO₂ nanorods helps to eliminate the abrupt interfaces and hence reduces the scattering of injected electrons from the photo-excited sensitizer dye molecules. SnO₂ has lower conduction band level than TiO₂ and this promotes the electron transfer from the TiO₂ sheath to the core SnO₂ nanorods. Electrons would then travel rapidly in the SnO₂ core to the FTO electrode for the enhancement of effective electron collection.

Figure 7.4 Schematic illustration of TiO₂ nanorods on SnO₂ nanorods 3D electrode.

Some preliminary experiments for the epitaxial growth of TiO₂ nanorods/nanotubes on the SnO₂ nanorods had been tried. The TiO₂ nanorod arrays were successfully grown on FTO glass substrate from titanium isopropoxide (TTIP) in hydrochloric acid solution by hydrothermal method at 150 °C for different times. Figure 7.5 shows the FESEM images of the TiO₂ nanorod arrays grown on FTO glass substrate at 150 °C for 5 - 40 hrs. During the first 5 hrs growth, only short TiO₂ nanorods were observed in Figure 7.5a and sparse nanorods were grown after 8 hrs (Figure 7.5b). Extended growth was performed for 14 hrs, the SnO₂-TiO₂ core-sheath nanostructure of the composite nanorods were found to grow longer and the shape of the nanorods/nanotubes were rectangular (Figure 7.5c). Continuously grown for 41 hrs produced larger nanorods (Figure 7.5d). The cross-sectional image in Figure 7.4e shows that the nanorods were grown in random direction, with a diameter of 20-80 nm and length of 500 nm. The XRD profile for the TiO₂

nanorods grown on FTO glass substrate is shown in Figure 7.6 and the TiO_2 nanorods consisted of rutile phase with (001) preferential orientation.

Figure 7.5 FESEM images of the TiO_2 nanorod arrays grown on FTO glass substrate at 150 °C for 5-41 h.

Figure 7.6 XRD patterns of the TiO_2 nanorods grown on FTO glass substrate by hydrothermal at 150°C for 14 hrs.

The FESEM images of TiO_2 nanorod arrays grown on different substrates at 150°C for 14 hrs are shown in Figure 7.7. Compared with the TiO_2 nanorods grown on FTO glass substrate, the diameter of the TiO_2 nanorod arrays on SnO_2 film deposited by ICP-CVD system were smaller (Figure 7.7b). Figure 7.6c shows that less dense TiO_2 nanorods were grown from the dense SnO_2 nanorods 3D electrode. This structure was different from the original concept shown in Figure 7.4. Modifications in the growth process for both SnO_2 and TiO_2 nanorods are proposed for the study of enhanced growth from the FTO substrate. Less dense SnO_2 nanorods on the FTO glass may be preferred to facilitate the growth of core sheath structure.

Figure 7.7 FESEM images of TiO₂ nanorod arrays grown on various substrates with different surface modifications at 150 °C for 14 h, (a) FTO, (b) SnO₂ film/FTO and (c) SnO₂ nanorods/FTO.

Author's Publications

Journal Papers

- [1] **Chiew Keat Lim**, Hui Huang, Chee Lap Chow, Pei Yun Tan, Xiaofeng Chen, Man Siu Tse, Ooi Kiang Tan, *Enhanced Charge Transport Properties of Dye-Sensitized Solar Cells Using TiN_xO_y Nanostructure Composite Photoanode*, J. Phys. Chem. C, **2012**, 116 (37), pp 19659–19664.
- [2] **Chiew Keat Lim**, Hui Huang, Chinsheng Chua, Man Siu Tse, Ooi Kiang Tan, *Improved Charge Collection Efficiency of Dye-Sensitized Solar Cells Using SnO_2 nanorods as 3D-Electrode*. (Manuscript in preparation)

Patent

- [1] Hui Huang, O.K. Tan, M.S. Tse and **C.K. Lim**, *Inorganic nanorods and a method of forming the same, and a photoelectrode and a photovoltaic device comprising the inorganic nanorods*, USA patent (Filed, VJP Ref: P104925).

International Conferences

- [1] **Chiew Keat Lim**, Man Siu Tse, Ooi Kiang Tan, *"Improved photovoltaic properties of dye-sensitized solar cells using TiN_xO_y - TiO_2 composite photoanode"*, 19th International Conference on Photochemical Conversion and Storage of Solar Energy, 29 July – 3rd Aug 2012 Pasadena, California.
- [2] **Chiew Keat Lim**, Man Siu Tse, Ooi Kiang Tan, *" TiN_xO_y as photoelectrode for dye-sensitized solar cells"*, The 5th MRS-S Conference on Advanced Materials, 20- 22 March 2012, Singapore
- [3] **Chiew Keat Lim**, Man Siu Tse and Ooi Kiang Tan, *"Inorganic Light Absorbing Semiconductor for Solid State Self-Sensitized Solar Cells"*, Materials Research Society 2011 Spring Meeting, April 25 - 29, 2011 San Francisco, California.

- [4] Hui Huang, **C.K. Lim**, M.S. Tse and O.K. Tan, “*3D-Transparent Conductive Oxides with SnO₂ Nanorod Arrays*”, Materials Research Society 2011 Spring Meeting, April 25 - 29, 2011 San Francisco, California.
- [5] Hui Huang, **C.K. Lim**, M.S. Tse and O.K. Tan, “*High Efficiency Dye-sensitized solar cells with 3D Nano-electrode*”, The 15th International Conference on TiO₂ Photocatalysis: Fundamentals and Applications, November 15-18, 2010, Town & Country Resort, San Diego, California, USA.
- [6] Hui Huang, **C.K. Lim**, Y.Z. Wei, C.S. Chua, M.S. Tse and O.K. Tan, “*Solid Dye-sensitized Solar Cells with Nanorod Electrodes*”, 5th Asian Conference on Electrochemical Power Sources, Sept. 17-20 2010, Singapore.
- [7] Hui Huang, **C.K. Lim**, Y.Z. Wei, C.S. Chua, M.S. Tse and O.K. Tan, “*Dye-sensitized Solar Cells with 3D Nanorod Electrodes*”, 5th Aseanian Conference on Dye-sensitized and Organic Solar Cells, August 25-28 2010, Huangshan China.

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