Modulating optical and electrical properties of TiO₂ photoanode in dye-sensitized solar cells

Pham, Thi Thu Trang

2013

Pham, T. T. T. (2013). Modulating optical and electrical properties of TiO₂ photoanode in dye-sensitized solar cells. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54898>

<https://doi.org/10.32657/10356/54898>

NANYANG TECHNOLOGICAL UNIVERSITY

School of Materials Science and Engineering

MODULATING OPTICAL AND ELECTRICAL
PROPERTIES OF TiO_2 PHOTOANODE
IN DYE-SENSITIZED SOLAR CELLS

---

by

Author:

PHAM Thi Thu Trang

Supervisors:

Assoc. Prof. LAM Yeng Ming

Prof. Subodh MHAISALKAR

A thesis submitted to the Nanyang Technological University in partial fulfillment of the
requirement for the degree of Doctor of Philosophy

Abstract

Dye-sensitized solar cells (DSCs) are promising photovoltaics because of their low cost and facile fabrication process. The difference between DSC and other conventional solar cells is that it separates the photoelectron generation and charge transporting functions. The dye absorbs light, is excited and injects an electron into the semiconducting oxide which transports it away. The important reactions in DSC occur at the interfaces of these materials, hence the interactions between them are critical to the device performance. Light harvesting in DSCs can be improved by developing sensitizers with broad absorption spectra and high extinction coefficient ϵ or by designing semiconductor nanostructures that can enhance optical properties through phenomena such as plasmonics, photonic confinement or light scattering. This thesis focuses on a new TiO_2 nanostructure for the DSC photoanode that can enhance light harvesting while increasing film porosity. The photoanode was modified by incorporating macropores within mesoporous TiO_2 nanoparticles film to create a mixture of bimodal pore sizes. The macropores are filled with electrolyte and have different refractive index from the surrounding TiO_2 nanoparticles, thus can scatter incident light, according to Mie theory. PS and ZnO were chosen as templating agents for the formation of macropores. The former created ellipsoidal pores while the latter, after removal, left behind more spherical pores. All films containing macropores had lower surface area compared to standard films. Film thickness and macropore concentration were investigated to optimize the photovoltaic performance with suitable dye/electrolyte combination.

Optical properties of the mesoporous-macroporous films were investigated by measuring diffuse transmission and reflection in an integrating sphere, showing strong light scattering with increasing pore sizes and concentration. Finite-difference time-domain FDTD simulation was conducted to understand the influence of changing shape and dimensions of scatterers. The simulation revealed that ellipsoidal scatterers are as effective as spherical scatterers, if their concentration was sufficient. Better light harvesting from these photoanodes could be observed by investigating the IPCE (incident photon to current efficiency) of the corresponding devices. To study changes in charge recombination and electrolyte diffusion, several methods such as electrochemical impedance spectroscopy, intensity modulated voltage/photocurrent spectroscopy as well as photovoltage, photocurrent transient were employed to calculate the electron lifetime, recombination and diffusion resistance. Through these studies, it was revealed that the presence of macropores reduced the recombination between electrons in TiO_2 and electrolyte as well as enhanced the diffusion of I_3^- or Co^{3+} ions in electrolyte to improve mass transport. These enhancements became more significant when the right combination of dye and electrolyte were used to fabricate DSCs from the mesoporous-macroporous films. By using high ϵ organic dye and ionic liquid or cobalt electrolyte, the films containing macropores exhibited improved power conversion efficiency, mostly attributed to higher V_{oc} , increasing FF and J_{sc} at high light intensity. The application of these novel photoanode structures can be extended to solid-state DSCs and other architectures which requires thinner photoabsorbers.

Acknowledgement

The PhD journey has been a long and tough road but at the same time full of wonderful experiences. These experiences cannot be fulfilled with the help of many people, whom I am so glad to know in my life and have the opportunity to work under their guidance.

First of all, I would like to thank my supervisors Assoc. Prof. Lam Yeng Ming and Prof. Subodh Mhaisalkar for their continuous guidance and supervision, and for giving me the opportunity to work with the most updated and interesting ideas in the research society, as well as providing modern equipped laboratories and overseas collaborations.

I would like to thank Prof. Michael Grätzel for his wonderful invention and the invaluable opportunity to work in his lab and collaborate with him through the project. His restless guidance and intellect has facilitated in overcoming difficulties and putting us on track with the field's blooming progress.

My gratitude goes to Dr. Nripan Mathews for all his supports and cooperative discussion from the beginning of my study. I am grateful to him for correcting my mistakes, both scientifically and grammatically. I would like to extend my gratitude to Dr. Takeru Bessho, for teaching me everything from cleaning a substrate to calculating electron lifetime.

My heartfelt gratitude goes to all the respected scientists with who I have had the chance to meet and discuss my work, and obtain their encouraging input on my research. Thanks to Dr. K. Nonomura for spending his valuable time in explaining theories, techniques and finding references to help me understand different aspects of dye-sensitized solar cell and its working mechanism, and to Dr. P. Boix for teaching me EIS and its complicated analysis method. I would also like to thank Dr. Lydia Wong and Dr. M. Srinivasan for sharing their knowledge in materials synthesis and fabrication, especially at the very beginning of my project. To Dr. S. Zakeeruddin for the warm hospitality and guidance during my stay in EPFL. I am grateful for the opportunity to meet Prof. Anders Hagfeldt and Prof. Juan Bisquert and learn their opinions about my work.

Thank you to all my colleagues, fellow students and friends, with whom I have spent countless hours working in the lab and shared the learning curves, both technically and

in life lessons. Without you all, the PhD journey will be very lonely and difficult, but your great companionship has made it more relaxing and exciting every single day. So thanks to my friends both in ERI@N-Nanocluster, MSE and LPI-EPFL: Liling, Teddy, Jun Yan, Julianto, Sun Cheng, Than Zaw, Natalia, Victor, Wang Xiu, Dharani and Hemant, Yan Ling, Vera, Daymond, Jeannette, Shweta, Ee Ling and Magda, Michelle, Nuttapol, Rebecca, Ines, Nok, Aswani, Julian, Aravind and Amalie. Thanks also to all the technical staff Heryani, Gao Ying, Karis, Xiao Ting and Yanlin, who continuously helped me with every little inquiry even during weekends and holidays.

I would like to thank Bosch Asia Pacific, Singapore Economic Development Board (EDB), Nanofrontiers and their staff for their financial support. Thanks to MSE and ERI@N administrative staff for their help with all the paper work I have to complete.

Last but not least, I would like to thank my family, especially my parents, whose achievement and working spirit never fails to inspire me to follow my dreams. Thanks also to my brother and my sister-in-law, who not only support me but together share with me in this experience. I wish them all the best for their own theses.

And to many others who have touched my life, even though your names may not appear in this acknowledgment, you will always stay in my heart and I am grateful to have known and spent time with you.

Contents

Abstract	i
Acknowledgement	iii
1 Introduction	1
1.1 Background	1
1.2 Thesis objectives and scopes	5
1.3 Thesis organization	6
1.4 Thesis contribution	7
2 Literature reviews	9
2.1 Dye-sensitized solar cell	10
2.1.1 Electron generation, transport and recombination	12
2.1.2 Critical parameters	13
2.2 Optical properties of the photoanode	15
2.2.1 Mie light scattering theory in dye-sensitized solar cells	18
2.2.2 Other nanostructures to enhance light harvesting	25
2.3 Porosity of photoanode	28
2.3.1 Other components in DSCs	30
3 Methodology	33
3.1 Mesoporous-macroporous TiO ₂ films as photoanode	33
3.1.1 Synthesis	34
3.1.2 Characterization methods	39
3.1.3 Characterization results	40
3.2 Device structure	48
3.2.1 Materials	48
3.2.2 Device fabrication	51
3.2.3 Photovoltaic performance measurement	52

3.3	Summary	53
4	Understanding parameters affecting device performance	55
4.1	Background and introduction	55
4.2	Dye	56
4.3	TiO ₂ film thickness and macropore concentration	59
4.4	Electrolyte	65
4.4.1	Ionic liquid, gel electrolyte with I ⁻ /I ₃ ⁻ redox couple	65
4.4.2	Cobalt electrolytes	68
4.5	Counter electrode	70
4.6	Summary and conclusion	71
5	Light scattering	75
5.1	Background and introduction	75
5.2	Methodology	76
5.2.1	FDTD simulation set-up	76
5.2.2	Optical properties measurement and IPCE	78
5.3	Results and discussion	81
5.3.1	Simulated scattering behavior using FDTD method	81
5.3.2	Measured light scattering behavior	84
5.4	Summary	95
6	Electron recombination in DSCs with sub-micrometer cavities	99
6.1	Background and introduction	99
6.2	Characterization methods	102
6.2.1	Photoelectrochemical methods	102
6.2.2	Electrochemical impedance spectroscopy	104
6.3	Results and discussion	106
6.3.1	Effect of macropores on recombination resistance in high viscosity I ⁻ /I ₃ ⁻ electrolyte	107
6.3.2	Recombination in cobalt-based electrolyte devices	112
6.3.3	Recombination with varying macropore sizes and pore concentration	114
6.4	Summary	119
7	Mass transport limitation	121
7.1	Background and introduction	121

7.2	Characterization methods	123
7.2.1	Light intensity dependence	124
7.2.2	Electrochemical Impedance Spectroscopy	124
7.3	Results and discussion	125
7.3.1	Devices with Cobalt electrolytes	126
7.3.2	Diffusion in viscous I^-/I_3^- ionic liquid and gel electrolyte	132
7.4	Summary	136
8	Conclusions and Future outlooks	139
8.1	Summary and conclusions	139
8.2	Limitation	141
8.3	Future outlook	142
8.3.1	Further investigation of mesoporous-macroporous films	142
8.3.2	Other recommended applications	143
	Bibliography	160
A	List of abbreviations	161
B	Sensitizers presented in the thesis	163
B.1	Molecular structure	163
B.2	Absorption spectra	163
C	Optimization data	165
D	List of publications	171
D.1	Journal papers	171
D.2	Conference and poster presentations	171

List of Figures

1.1	Contribution of energy sources to the world's consumption and growth showing an increasing development of renewable energy. [8]	2
1.2	Illustrations of (a) a standard mesoporous structure and (b) a mesoporous-macroporous structure on glass-FTO substrates.	4
2.1	Schematic diagram of a Dye-sensitized solar cell	11
2.2	Energy levels in DSC showing kinetic processes occurring in the device and their time scales.	13
2.3	Current-voltage (I-V) characteristics of a typical solar cell in the dark (black curve) and under illumination (red curve). Here the open circuit voltage V_{oc} , short circuit current I_{sc} , the voltage and current at maximum power point V_{max} and I_{max} are indicated on the I-V curve.	14
2.4	Scanning electron microscope image of a typical TiO_2 mesoporous film used as photoanode in DSC [2].	16
2.5	Absorption of ruthenium(II)trisbipyridine dichloride and N3 dye in comparison with the solar spectrum [48]. The chemical structures of these dyes can be found in the appendix	17
2.6	Reflection, refracting and scattering of light. (Redrawing according to Zhang <i>et al.</i> [54]).	18
2.7	Scattering efficiency of TiO_2 particles as dependent on particle size and incident wavelength [54]	20
2.8	Calculated absorbance of 10 μm thick films binary mixture of TiO_2 particles (10 nm in radius) with varying weight fraction of large particles radius a_2 (a) and radius of 135 nm (b) according to Ferber <i>et al.</i> [55].	20
2.9	Four-flux model diagram showing the forward and backward fluxes. . . .	21
2.10	(a) TiO_2 photoelectrode with diffusion and scattering layer of variation of particle sizes; (b) IPCE of monolayer, doublelayer and multilayer diffusive and scattering DSCs [51]	23
2.11	(a) Schematic redrawn from Zhang <i>et al.</i> [59] and (b) SEM image of aggregates of nanoparticles employed by Kim <i>et al.</i> to enhance light scattering [54, 60]	24

2.12	(a) Illustration of a doublelayer photonic crystals DSC [62]; (b) SEM image of photonic crystals used in DSC [62]. (c) Measured IPCE of control sample made of nanoparticles (square symbol) and photonic crystals (round symbol) showing the increase of photocurrent at longer wavelength. The stop band position is at 610 nm. [63].	25
2.13	Schematic illustration of (a) Au nanoparticles used for plasmonics effect in TiO ₂ photoanode (from top to bottom: embedded, Au on top of TiO ₂ before and after dye-loading) [67]; and (b) plasmonic SSDSC fabrication process with silver nanoimprint back reflector as counter electrode [68]; (c) IPCE of SSDSC with Z907 (left) and C220 (right) dyes with nanoimprint back reflector compared to standard devices [68].	27
2.14	Energy levels of several Cobalt complexes as compared to I ⁻ /I ₃ ⁻ and Fc/Fc ⁺ . Redrawing figure following several references [83, 86, 87]	32
3.1	Schematic structure of TiO ₂ photoanodes employing (a) PS and (b) ZnO particles as templates for formation of macroporous cavities. It is suggested that the evaporation of binders and solvent while removing PS during sintering process causes the collapsing of pores. ZnO is removed by the acidic environment of TiCl ₄ solution during post-treatment and hence can reserve the shape of macropores.	34
3.2	Flowchart describing the synthesis process of PS/ZnO mixed with TiO ₂ pastes from commercially available Dyesol D18NR-T paste.	37
3.3	Top view FESEM images of ZnO 170 nm, 380 nm and 500 nm particles.	41
3.4	FESEM images of PS 500 nm particles.	41
3.5	Films with increasing concentration of macropores. These films became more translucent and opaque with increasing pores content.	42
3.6	Top view SEM images of D18NR-T film and films made of PS-assisted pastes (TiO ₂ :PS = 10:1 and 2:1).	42
3.7	FESEM images of ZnO-assisted films with ZnO of 170 nm, 380 nm and 500 nm.	43
3.8	Cross section SEM and FESEM images of films with PS and ZnO as templates. The shape of macropores clearly appears to be more spherical in the case of ZnO than when PS is used. The morphology of macroporous films is reproducible.	44
3.9	(a) FESEM images of ZnO particles and pores left be them before and after TiCl ₄ treatment. (b,c,d) EDX spectra and element counts of ZnO-assisted TiO ₂ films before and after TiCl ₄ treatment with 40 mM solution. Extra elements like Sn comes from FTO substrate, Si comes from glass, Pt from conducting coating layer and Cu from copper tape/sample holder.	45
3.10	Molecular formulae of a few dyes used in the project. C106 is a ruthenium-based dye, the others are organic donar- π -acceptor dyes [81, 83, 103, 104].	49

3.11	Molecular structures of (a) cobalt(II/III) tris(4,4'-di- <i>tert</i> -butyl-2,2'-bipyridine); (b) cobalt(II/III) tris(2,2'-bipyridine) used in DE1 and DE2 electrolytes, respectively.	51
3.12	(a) Schematic side view, (b) photograph of a complete cell and (c) fabrication process of a DSC	52
4.1	IV curves of devices made from C218-Z1026, D205-Z1130 and C106-Z960 dye-electrolyte systems. When pore concentration is increased to high volume ($\text{TiO}_2\text{:PS} = 2\text{:1}$ - blue curves), current is reduced with C106, while with C218 and D205, it is still enhanced. This is due to C106 having five times lower molar extinction coefficient, hence the gain of light scattering can not compensate on the loss of dye-loading.	58
4.2	IPCE of C218 and C106 devices showing the improvement of current per incident photons in the red region with presence of macro-cavities.	59
4.3	V_{oc} of devices with C218 dye, Z1026 electrolyte with varying thickness and concentration of pores	60
4.4	FF with varying thickness and concentration of pores, comparing volatile electrolyte Z1130 and ionic liquid Z952	62
4.5	J_{sc} with varying thickness and concentration of pores. DSCs are fabricated with D205 dye and Z1130 and Z952 electrolyte (I^-/I_3^- in acetonitrile solvent and ionic liquid, respectively)	63
4.6	PCE with varying thickness and concentration of pores. Full data of the thickness and concentration dependent studies with C218/D205 dyes, Z1026/Z1130/Z952 electrolytes can be found in the appendix.	65
4.7	Current dynamics of devices made from D205 dye with Z1130 and Z952 electrolytes	67
4.8	IV curves of devices made of Z952 ionic liquid and gel (Z952 with 7 wt% SiO_2 7 nm particles	68
4.9	IV curves of devices made from 4 μm films of D18NR-T and PS assisted pastes, with DE1 electrolyte at 0.1 sun, 0.5 sun and 1 sun conditions. Although all devices have comparable current at 0.1 sun, its evolution at 1 sun improves greatly by the choice of photoanode.	69
4.10	EIS spectra of DSCs made of PS-template photoanodes ($\text{TiO}_2\text{:PS} = 20\text{:1}$), D35 and cobalt electrolyte with Pt and PEDOT counter electrodes. The first arc at high frequency represent charge transfer resistance at counter electrode R_{CE} is shown dramatically reduced when PEDOT is used. Measurement performed at 0.65 V voltage bias.	72
5.1	FDTD simulation setup showing: scattering center as a core-shell object with refractive indices of the core and shell were the indices of acetonitrile and TiO_2 ; the FDTD simulation region, monitors, light source and mesh.	77

5.2	Setting up of scattering centers in FDTD simulation. (a) Varying of radius R_y (parallel to the injection direction). When R_y decreased, the shape of a sphere transformed to an ellipsoid. (b) Multiple scatterers: R_y decreased to transform the spherical scatterers to ellipsoids. Because volume of each scatterer decreased as R_y decreased, the total volume displaced by pores was reduced. (c) To increase the volume of pores, the number of ellipsoidal scatterers was increased.	79
5.3	Diagram of an integrating sphere and how sample was placed to obtain diffuse and total transmission and reflection.	80
5.4	FDTD simulated scattering cross-section of a single scatterer, with varying radius R_y . As R_y decreased, the scatterer transformed from a sphere ($R_y = 250$ nm) to an ellipsoid ($R_y < 250$ nm) and the scattering cross section decreased. The simulation is based on structure illustrated in Figure 5.2a.	82
5.5	Scattering cross-section of multiple scatterers reduced when R_y reduced from 250 nm (sphere) to $R_y < 250$ nm (ellipsoid). The simulation is based on structure illustrated in Figure 5.2b.	82
5.6	Scattering cross-section of multiple scatterers with increasing porous volumes by increasing number of scattering centers while keeping the dimension of the scatterers constant ($R_x = R_z = 250$ nm, $R_y = 132$ nm). Scattering cross section σ_{scat} increased with increasing porous volume. The red curve is the simulated result with perfect sphere ($R_x = R_y = R_z = 250$ nm) and equivalent porosity with darkest green curve. With similar porous volume, the ellipsoidal pores scattered light as strongly as the spherical pores. The simulation is based on structure illustrated in Figure 5.2c.	84
5.7	Transmission (a) and reflection (b) of TiO_2 films with varying pores concentration using PS as template. Closed symbols are total transmission(reflection). Open symbols are diffuse transmission (or reflection).	85
5.8	Calculated extinction of TiO_2 films sensitized with D205 dye with varying pores concentration using PS as template.	86
5.9	IPCE of devices fabricated with of TiO_2 films with varying pores concentration using PS as template and D205 dye in combination with Z952 and Z1130 electrolytes, showing the improvement from 640 nm onward.	87
5.10	IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with C101 dye and Z952 ionic liquid electrolyte.	88
5.11	IPCE of DSCs made with increasing thickness made with standard film D18NR-T and $\text{TiO}_2\text{:PS} = 20\text{:}1$ templates. Devices are fabricated with C106 dye and acetonitrile-based electrolyte.	89
5.12	IPCE values at 400, 500 and 600 nm versus TiO_2 thickness showing that enhancement of IPCE at 600 nm was greater than at 400 nm. The improvement by light scattering voids at 600 nm was also better than at 400 nm.	90

5.13	Transmission (a) and reflection (b) of TiO_2 films with varying macropores size using ZnO as template. Closed symbols are total transmission (reflection). Open symbols are diffuse transmission (or reflection).	91
5.14	(a) Calculated extinction of films sensitized with D35 dye. (b) IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with D35 dye and Z952 ionic liquid electrolyte	92
5.15	(a) Extinction; (b) measured and normalized IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with D205 dye, Z952 electrolyte.	93
5.16	IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with C106 dye and acetonitrile-based Z960 electrolyte. Films thickness is $3\ \mu\text{m}$	94
5.17	IPCE of DSCs made with varying pore size using ZnO templates. Devices were fabricated with SQ2 dye and acetonitrile-based electrolyte.	95
5.18	Optical depth of films created by (a) PS and (b) ZnO as templating agents.	96
5.19	Schematic diagram suggesting that with long wavelength photons (red lines), scattering by spherical macropores is too strong that losses on the side of films become dominating, while ellipsoidal pores have anisotropic light scattering, weaker in the direction perpendicular to injection plane, hence lower loss.	97
6.1	Schematic diagram illustrating electron-charge transfer processes in DSC. The recombination and trapping processes are highlighted in blue color. .	100
6.2	Schematic diagram of a DSC represented by equivalent electrical elements corresponding to each physical component forming an electrical circuit used for fitting with measured data	106
6.3	Recombination resistance of DSCs with PS as template for macropores. Comparison was done between ionic liquid and gel electrolyte	107
6.4	Chemical capacitance of devices made with ionic liquid Z952 and gel electrolyte Gel1. C_μ is measured by EIS at varying light intensity.	109
6.5	Schematic structure and FESEM cross-section images of films with standard and graded structure with scattering layer.	110
6.6	Electron lifetime and electron transport time of devices made from D35 dye and Z952 electrolyte	111
6.7	Recombination resistance of DSCs after correcting voltage according to chemical capacitance.	113
6.8	(a) EIS spectra of DSCs with varying macropores size using ZnO as template. Measurements were done at the open circuit condition of around 0.776 V. The connecting line is the fitted results using an equivalent circuit. (b) Recombination resistance of DSCs before and (c) after correcting voltage according to difference in chemical capacitance.	115

6.9	Electron lifetime of devices made from varying ZnO sizes, with same weight percentage. The size difference leads to varying of pores distribution . . .	117
6.10	Electron lifetime and electron transport time of devices made from D205 dye with Z952 electrolyte	118
6.11	Density of traps states at in relation with energy levels	119
7.1	Electrical circuit with elements representing charge transport and transfer processes in different components and interfaces of a DSC showing the diffusion of ions in electrolyte is corresponding to impedance Z_d . The right hand side is a typical set of impedance spectra measured at different bias voltage by Fabregat-Santiago [131], revealing three arcs corresponding to charge transfer at counter electrode, recombination at TiO_2 -electrolyte interface and diffusion in electrolyte.	125
7.2	J_{sc} and PCE at different light intensity of DSCs based on (a) DE2 ACN-Co(Bpy) and (b) DE1 MPN-Co(dtb) electrolytes. The linearity of photocurrent shows that the mass transport limitation is not the dominating limiting factor of photocurrent with DE2 but more severe with DE1 electrolyte.	129
7.3	(a&b) EIS spectra of devices measured at 0.55 V and 0.75 V under illumination and fitted curves from equivalent circuit. (c) Diffusion resistance of DSCs made of $8\mu\text{m}$ films from D18NR-T and $\text{TiO}_2\text{:PS} = 20\text{:}1$ pastes, using DE1 MPN-Co(dtb) electrolyte.	130
7.4	Current dynamic and photocurrent decay normalized at 1 sun (below) of devices made from D205 and Z1130 and Z952 electrolytes	132
7.5	Current dynamic and photocurrent decay normalized at 1 sun (below) of devices made from Gel electrolyte and D205 and Y196 dyes	134
7.6	Diffusion resistance of DSCs made of films from D18NR-T and $\text{TiO}_2\text{:PS} = 20\text{:}1$ pastes, ionic liquid Z952 and gel electrolytes.	136
8.1	IPCE of SSDSCs showing the improving of current density at longer wavelength range when macropores are present	144
8.2	Illustration of how mesoporous-macroporous structure can be employed in SSDSC or ETA solar cells	144
B.1	Molecular structure of Y196, C101 and SQ2 dyes	163
B.2	Absorption spectra from references.	164
C.1	V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with C218 dye and Z1026 electrolyte	165
C.2	Average V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with C218 dye and Z1026 electrolyte. The graphs show error bars due to variations in experiment data.	166

C.3	V_{oc} , as with varying thickness of D18NR-T with C218 dye and Z1026 electrolyte. The plots support the argument discussed in figure 4.3 that V_{oc} decreases with increasing film thickness, and assure that the observation is reproducible.	167
C.4	V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with D205 dye and Z1130 electrolyte	168
C.5	V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with D205 dye and Z952 electrolyte	169

List of Tables

3.1	Amount of D205 dye loaded on films that used PS as template.	47
3.2	Amount of D35 dye loaded on films that used ZnO as template.	47
3.3	Porosity and surface area of PS-assisted films.	48
3.4	Compositions of electrolytes used. Full name of chemicals can be found in the abbreviation list in Appendix A.	50
4.1	Component materials, their characteristics and effects on DSC performance	56
4.2	Photovoltaic performance of devices with C218, D205 and C106 dyes with Z1026, Z1130 and Z960 electrolytes, respectively. The photoanodes used are standard mesoporous films denoted D18NR-T (made from Dyesol 18NR-T paste) and the macroporous-mesoporous films with ratio of $\text{TiO}_2\text{:PS} = 10\text{:}1$ and $2\text{:}1$	57
4.3	Photovoltaic performance of devices with D205 dye with Z1130 and Z952 electrolytes, respectively. D18NR-T are standard cells with Dyesol paste, compared to photoanodes made from PS-templated macroporous-mesoporous films with $\text{TiO}_2\text{:PS} = 10\text{:}1$ and $2\text{:}1$	66
4.4	IV data of cells made from $4\text{ }\mu\text{m}$ films with and without macro-cavities, using DE1 electrolyte in MPN solvent at different light intensity.	70
4.5	IV data of cells made from $4\text{ }\mu\text{m}$ films with and without macropores, using DE1 cobalt electrolyte, comparing Pt and PEDOT as counter electrode catalysts.	71
5.1	Photovoltaic performance of devices with C101 dye with Z952 electrolyte. Film thickness $6\text{-}7\text{ }\mu\text{m}$	88
5.2	Molar extinction coefficient of dyes used in the experiments	96
6.1	Photovoltaic performance of devices with D35 dyes with Z952 and Gel1 electrolytes	108
6.2	IV data of DSCs made from $6\text{ }\mu\text{m}$ films, comparing standard and graded structure, with and without scattering layer, using D35 dye and Z952 ionic liquid.	111

6.3	IV data of cells made from 4 μm and 8 μm films with and without macro-cavities, using $[\text{Co}(\text{bpy})]^{3+/2+}$ in acetonitrile electrolyte (DE2), D35 dye. .	112
6.4	IV data of cells made from 4 μm films with varying macro-cavities sizes, using Z952 and D35 dye.	116
6.5	Photovoltaic performance of devices with D205 dye with Z952 electrolytes and 10 μm films	118
7.1	IV data of cells made from 4 μm films with and without macro-cavities, using ACN and MPN-based electrolytes at 0.1 and 1 sun.	127
7.2	IV data of cells made from 4 and 8 μm films with and without macro-cavities, using MPN-based electrolytes DE1.	128
8.1	Preliminary photovoltaic performance of SSDSCs made with D35 dye, doped spiro with standard D18NR-T and mesoporous-macroporous film with PS as template.	143

Chapter 1

Introduction

1.1 Background

The fossil fuel resources are on the verge of depletion leading to the dramatic increase in oil price since 1999. According to the BP Statistical Review of World Energy published in 2013, the proved reserve to production ratios have shown the remaining of oil and natural gas would last approximately 50 years, and coal about 100 years [1]. The increasing world consumption and continuous emission of carbon dioxide from fossil fuel resources has alarming effects on global climate, an impetus to find “green” and renewable alternative energy sources is increasingly important. In recent decades, renewable energy has become one of the fastest growing developments in most countries. The disaster in Japan in 2011 forced world leaders and scientists to confront the safety of nuclear energy. This was followed by many countries withdrawing from nuclear programs. Since then, renewable energy such as wind, solar and biofuel sources have become ever more popular as alternative energy sources.

The Sun has sustained life on Earth for millions of years and is still providing 120,000 terawatts of energy each day, which is approximately 6,000 times the energy consumption of the world [2]. Solar energy naturally becomes a promising candidate for the development of future “green” energy source. The first practical solar cell was developed in 1954 at Bell Laboratories and was made using silicon technology [3, 4]. Si solar cells have since become the leading photovoltaics and have dominated the industry with the number of installed modules increasing. Newer generations of solar cells are catching up

integrating of increasing efficiency, light weight features, environmentally friendly fabrication methods and low cost opportunity [5,6]. Dye-sensitized solar cell (DSC) belongs to the third generation of photovoltaics and was invented over 20 years ago. Since then, the development of DSC is being taken over 12% power conversion efficiency (PCE) and now it is ready for large scale manufacturing. The working principle of DSCs was inspired by the process of photosynthesis and hence it is usually referred to as an artificial photosynthesis device. The advantages of DSC over the previous generations of solar cells are related to its semi-transparency, flexibility to use variety of colors, designs and integration of various functional materials. It is also a promising device for low light intensity application and has demonstrated long term stability, while having lower cost in terms of manufacturing, distribution and installation [7].

Figure 1.1: Contribution of energy sources to the world's consumption and growth showing an increasing development of renewable energy. [8]

Unlike traditional silicon solar cells, DSCs separate the two functions of photoelectrons generation and transporting them. The sensitizer known as the “dye” is a photosensitive material, which has the capability of absorbing photon and excites an electron to its LUMO (lowest unoccupied molecular orbital) level, while the metal oxide semiconductor (usually TiO_2) transports the electron in its conduction band. The electrolyte then transports the ions to the dye for regeneration of the dye molecule and bring it back to its “ground” state. Because the dimension of dye molecules are nanometer in size and

a monolayer of dye occupies an area larger than its optical cross-section, it is essential to have a fairly large area of dye molecules to capture a reasonable amount of incoming light [2, 9]. The major breakthrough in the history of dye-sensitized solar cells was the use of mesoporous TiO_2 film that was reported in 1991 [10]. The internal surface area of the TiO_2 film increased by a factor of 1000 times compared to the projected area to support the monolayer of dye sensitizer. This photoanode structure that O'Regan and Grätzel introduced, consists of 20-40 nm nanoparticles connected to each other, forming a mesoporous three-dimensional network. This allows the electrolyte to percolate into the pores and at the same time, the semiconductor oxide has an enormous surface area to accommodate the dye-loading. The thicker the film, the more dye molecules can be attached to the TiO_2 surface for more light harvesting, resulting in higher photocurrent [11].

Since then, two decades have passed and although TiO_2 still gives the best reported efficiency, many other metal oxides, such as ZnO [12, 13], SnO_2 [14, 15], Nb_2O_5 , etc. [16] or more complicated ternary oxides, like SrTiO_3 [17] or Zn_2SnO_4 [18] have also been investigated. These oxides have inherently high electron mobilities, which is promising for faster electron transport and collection. One-dimensional nanomaterials, such as nanofibers [19–21], nanowires [22–24] or nanorods [25, 26], was also very promising since electrons can move in a direct path length through the crystals of nanowires/nanorods instead of hopping between nanoparticles. Core-shell structures with the possibility of better electron mobility as well as better charge separation have also been investigated [27–29]. Nevertheless, recent studies reported that, in the case of I^-/I_3^- redox couple as the electrolyte, the charge transport in TiO_2 is sufficiently good or in other words, the diffusion length for electrons in TiO_2 is much longer than the thickness of the mesoporous film. Hence, electrons are collected effectively in the interconnected nanoparticles network and higher mobility or direct electron transport path will not help to improve the charge collection [30, 31]. Following this finding, continuing studies on alternative oxides and nanostructures and morphology of semiconductor materials have still persisted, but the novelty has slowly shifted from improving electron mobility and transport to light harvesting, better interfaces with dye and electrolyte to enhance charge injection, reduce recombination and improve diffusion of ions in the network. Other than the intrinsic

property of the semiconductor, two characteristics of photoanode TiO_2 films that attract much research interest are optical property and porosity as these can contribute to the optical and electronic property of the device.

In this thesis, a new nanocrystalline structure is introduced to modulate the optical and porosity properties of DSCs for enhancing the photovoltaic performance. Sub-micrometer cavities are incorporated in the mesoporous TiO_2 , creating a mesoporous-macroporous structure (see Figure 1.2). It is hypothesized that these cavities - known as “macropores” or voids - are filled with electrolyte and have different refractive index with the surrounding TiO_2 nanoparticles, hence they can function as light scattering centers to enhance the light harvesting capability of the device. According to Mie theory, the dimension of scatterers should be comparable to the scattered wavelength, hence the dimension of macropores synthesized ranges from 150 to 500 nm. Furthermore, since the porosity of the mesoporous-macroporous structure is increased because nanoparticles are replaced by voids, the percolation and physical diffusion of the electrolyte can be improved. The interface between TiO_2 /dye/electrolyte is where critical reactions occur: injection of electrons, charge recombination and regeneration of dye molecules, was changed. These reactions can be influenced by a combination of mesopores and macropores (bimodal pore size distribution) structure and should be further investigated.

Figure 1.2: Illustrations of (a) a standard mesoporous structure and (b) a mesoporous-macroporous structure on glass-FTO substrates.

1.2 Thesis objectives and scopes

The research presented in this thesis focuses on the understanding of the impact of a mesoporous-macroporous structure as the photoanode for DSCs, its applications and influences on the device performance. The objectives and scopes of the research include:

1. **To investigate a new photoanode structure and device architecture that combines light scattering effect and addresses the mass transport limitation.** The novel mesoporous-macroporous structure is introduced for this purpose. Template materials would be synthesized and mixed with TiO_2 paste for the fabrication of photoanode films and DSCs, followed by characterization of the morphology, composition, surface area and the amount of dye-loading on films fabricated from PS and ZnO templates. The performance of this structure with varying film thickness and concentrations of macropores in combination with other components of DSC such as dye and electrolyte and their influences on power conversion efficiency will be investigated. The photovoltaic results are evaluated to determine which dye/electrolyte will benefit the most from the presence of macropores. The most suitable materials should be chosen for the further study of the effect of macropores.
2. **To obtain better understanding of the optical property and the light scattering enhancement achieved by using macropores in photoanodes.** The influence of the shape and dimension of macropores would be studied by simulation with finite-difference time-domain method (FDTD) and compared with the experimental measurement. Extinction (a combined effect of absorption and scattering) measured in an integrating sphere would be compared to corresponding incident photon to current efficiency (IPCE) result to better understand the relationship between optical properties and photocurrent.
3. **To investigate the impact of this structure on charge transport, charge recombination and ionic diffusion in the device.** We would study devices made from mesoporous-macroporous films in combination with dyes/electrolytes to show photovoltaic improvement with the presence of macropores. Recombination of electrons in the conduction band of TiO_2 and electrolyte redox couple would be

studied by measuring electron lifetime and recombination resistance. Diffusion of electrolyte would be investigated by evaluating the current response versus input illumination power and diffusion resistance measured by electrochemical impedance spectroscopy (EIS).

1.3 Thesis organization

The thesis consists of 8 chapters. Chapter 1 presents the background and the need for “green” energy and the motivation behind the research and a brief overview of the history of dye-sensitized solar cells. The motivation for creating a mixture of mesoporous and macroporous film is then introduced, followed by the objectives and contributions of the thesis.

Chapter 2 comprises of the literature review on the photoanode of DSCs. Research of the photoanode to improve optical property is discussed, highlighting the importance and interest of the different approaches.

Chapter 3 introduces choices of materials to create macropores incorporating with mesopores to form bimodal pore size TiO_2 film. Detailed synthesis of polystyrene (PS) and ZnO used as template materials are presented with the fabrication and deposition method to form TiO_2 mesoporous-macroporous films. Morphologies of screen-printed films captured by scanning electron microscope showing the differences in size and shape distribution when using the two templates.

Chapter 4 provides a better understanding of the interaction and combination between different components of DSCs with the presence of macropores. The importance of choosing a suitable dye - electrolyte combination with film thickness, film porosity, macropore size and concentration is discussed with corresponding photovoltaic performances. Influences of film thickness, macropores concentration and size are presented, together with the effect of using organic dye and viscous electrolyte and the benefit of combining it with macropores. The photovoltaic performance recommends combination of DSC components and material choice for further in-depth studies of its working mechanism.

Light scattering from macropores originated from Mie scattering theory and the ex-

tended case of multiple scattering and non-spherical scatterers is discussed in Chapter 5. FDTD simulation results are shown to compare the scattering cross-section as size, shape and concentration of pores are varied. The influence of macropore size and concentration is also considered with the combination with different dyes and film thickness.

In Chapter 6, charge recombination at the interface of TiO_2 /dye/electrolyte is investigated by several methods. Photocurrent and photovoltage transient, intensity modulated photovoltage/photocurrent spectroscopy (IMVS/IMPS) and EIS techniques are employed to understand the charge recombination when charges are built up in the TiO_2 conduction band.

Chapter 7 further explains the improvement in terms of electrical properties via enhancing mass transport in porous films. The importance of combining electrolyte suffering from poor diffusion, such as cobalt electrolytes having large redox shuttles with macropores is highlighted to show a significant improvement. Current density at high light intensity input is presented to prove the improvement of mass transport with macropores.

Chapter 8 summarizes and concludes the research presented in this thesis. In the future outlook, it is discussed that macropores can be beneficial for solid-state dye-sensitized solar cell (SSDSC) in which pore filling of hole conducting material is critical. The macropores not only help to improve pore filling, but also increase light scattering in SSDSC, as this kind of device has limitation in film thickness and conventional scattering layer is not typically used.

1.4 Thesis contribution

This thesis introduces a new structure for the photoanode of DSC - a mixture of bimodal pore size known as the mesoporous-macroporous structure - that has not been studied thoroughly before. This structure opens opportunities to consider voids as efficient light scattering centers to replace sub-micrometer TiO_2 particles. The research helps to gain more insights into how this structure scatters light and improves light harvesting, how it influences the performance of DSCs and how such improvement can be analyzed. By us-

ing FDTD simulation, the Mie scattering from single and multiple light scattering centers is studied to understand the effect of size, shape and distribution of macropores in the photoanode TiO_2 film. Experimental measurement of diffuse transmission and reflection also reveals the relationship between light scattering of multiple scatterers with their size and concentration. Studying the corresponding IPCE explains the expected current improvement in individual cases and the relationship between optical property and current density. The research highlights the importance of choosing template material for the creation of macropores, the advantages and disadvantages of each material used (organic polymer (PS) and inorganic (ZnO nanoparticles)) and the possibility of impurity affecting electrical performance. Both electrochemical and photoelectrochemical characterization techniques are used to understand the charge recombination at TiO_2 /dye/electrolyte interface when macropores are present. The ion diffusion of electrolyte in these pores are shown to improve with mass transport limited cobalt electrolytes. The reduction of recombination at the interface and improvement of electrolyte physical diffusion are reasons for increasing V_{oc} and FF of the devices. The research presented in this thesis suggests a future study in pore filling improvement for solid state hole conducting material in SSDSCs.

Chapter 2

Literature reviews

The dye-sensitized solar cell (DSC) is a nanostructured photochemical device. A DSC is made up of a combination of organic and inorganic materials working closely together to function as a complete device. In a DSC, the interfaces between these materials play important roles, which are even more important than each individual component. What distinguishes it from the other categories of solar cells is that it separates the light absorption and charge transport in two different materials, known as the dye and the semiconductor, respectively. The charge separation in DSC can be ultrafast (in femto-second range), resulting in a “hot electron” that has high kinetic energy [32].

The history of DSC can be traced back to the 19th century. In 1873, Vogel discovered a way to extend the spectral sensitivity of silver halide emulsions from the blue and UV regions to the green region by using a dye. A few years later, Moser reported the first sensitized photoelectrode and its enhanced photoelectrochemical response [9]. However, not until the 1960s when Namba and Hishiki demonstrated a clear link between the two processes of photography and photoelectrochemistry by using the same dyes, it was established that the sensitization process results in charge transfer rather than energy transfer [33,34]. However at that time, not much interest was shown because the measured photocurrents were too small, since the light was only absorbed by a monolayer of dye attached on a planar surface [35]. To enhance the surface area for better absorption, Tsubomura *et al.* used porous ZnO and had obtained a conversion efficiency of 1.5% for monochromatic irradiation at 563 nm [36]. But it was not until 1991 that research in photovoltaic energy conversion by dye-sensitization became interesting and flourished after the publication of O'Regan and Grätzel reporting a device made of sensitized mesoporous

TiO₂ with a power conversion efficiency of 7.1% [10].

In the late 1980s, dye-sensitized devices did not have a very bright future because most scientists believed that it would never provide enough power, but the invention of Grätzel and O'Regan opened a new direction for researchers. Through 20 years of research and development to look for new materials, improving the efficiency as well as investigating the mechanisms behind light harvesting, charge transport and collection, the efficiency of dye-sensitized solar cell has reached 13% in laboratory scale devices [37]. Moreover, it has proven to be a highly promising technology, exceeding the scale of laboratory devices. Many big corporations have invested in R&D to produce environmentally friendly, low-cost DSCs which are capable of working in low light and indoor lighting, to name a few are Dyesol, G24i, Sony, Sharp, Toyota.... Most recently, the famous digital manufacturer Logitech has introduced the first dye-sensitized solar cell commercial product in the market: a keyboard for iPad that can work at low light intensities and can be used in total darkness for almost two years.

2.1 Dye-sensitized solar cell

A schematic structure of a dye-sensitized solar cell is presented in Figure 2.1. It consists of two transparent conducting oxide electrodes (typically fluorine-doped tin oxide (FTO) on glass) known as the photoanode and counter electrode, sandwiched with a layer of semiconductor film. The semiconductor layer is the key element of the device. Titanium dioxide, TiO₂ is commonly used to form a film of mesoporous interconnected network of nanoparticles of 20-30 nm to increase the total surface area to $\sim 50\text{-}100\text{ m}^2/\text{g}$ - a thousand folds larger as compared to a flat surface [10,38]. The dye sensitizer is the light absorbing material, attached to the large surface area of TiO₂ to form a monolayer that captures incident photons in the wavelength range limited by the characteristic absorption spectra of the dye. In between the two electrodes, an electrolyte consisting of a redox couple (most common is the iodide/tri-iodide couple I^-/I_3^- , other alternative redox couples are $\text{Co}^{2+}/\text{Co}^{3+}$, Fc/Fc^+ ...) is inserted. The counter electrode is coated with a photo-catalytic material, typically Pt nanoparticles formed by H_2PtCl_6 precursor, to efficiently reduce the oxidized redox species.

Figure 2.1: Schematic diagram of a Dye-sensitized solar cell

When the cell is illuminated, a dye sensitizer absorbs one photon and excites an electron from its highest occupied molecular orbital to its lowest unoccupied molecular orbital (i.e. from HOMO to LUMO). The excited electron is then injected into the conduction band E_c of the semiconductor TiO_2 and the dye becomes oxidized. The injection process occurs in the femto to pico seconds [11]. The injected electron diffuses through the network of interconnected TiO_2 nanoparticles following a random walk manner and reaches the FTO. The electron passes the external circuit to the counter electrode, where it combines with tri-iodide I_3^- ion in the electrolyte to form iodide I^- . The iodide ion diffuses to the site of dye molecule and gives up its electron to regenerate the oxidized dye and brings it back to the ground state. These series of events complete the cycle.

Processes in the dye-sensitized solar cells presented in Figure 2.1 are:

1. Dye absorbs photon and excites an electron to LUMO level
2. Electron is injected into the conduction band of the TiO_2
3. Electron transport in the conduction band of the TiO_2 interconnected network
4. Electron transport through external circuit
5. At the counter electrode, the electron reduces tri-iodide to iodide ions
6. Regeneration of the dye molecule

2.1.1 Electron generation, transport and recombination

The energy levels and kinetic processes involved in the dye-sensitized solar cell are illustrated in Figure 2.2. The photovoltaic conversion operation of dye-sensitized solar cells require balancing of energy level and kinetic processes to minimize the recombination steps. The forward and backward reactions happening in the device are:

Photoexcitation:	$D + h\nu \rightarrow D^*$	<i>forward</i>
Direct recombination:	$D^* + e_{LUMO}^- \rightarrow D$	<i>backward</i>
Injection:	$D^* \rightarrow D^+ + e_{(TiO_2)}^-$	<i>forward</i>
Recombination via dye:	$D^+ + e_{(TiO_2)}^- \rightarrow D$	<i>backward</i>
Regeneration of dye by iodide:	$2D^+ + 3I^- \rightarrow D + I_3^-$	<i>forward</i>
Electron transfer at counter electrode:	$I_3^- + 2e_{Pt}^- \rightarrow 3I^-$	<i>forward</i>
Back reaction:	$e_{(TiO_2)}^- + I_3^- \rightarrow I^-$	<i>backward</i>

In the dark, the Fermi level of semiconductor TiO_2 is equilibrated to the redox potential of the electrolyte ($E_{Fo}=E_{redox}$). When a photon is absorbed by the dye, an electron is excited and then injected into the conduction band of TiO_2 . The additional and accumulation of charges causes the Fermi level to rise up and define a quasi-Fermi level E_{Fn} . The photovoltage generated by the cell is defined by the difference in electrochemical potentials or energy level of electrons in TiO_2 and the redox couple in electrolyte, i.e. E_{Fn} and E_{redox} . The position of the quasi-Fermi level depends mainly on the charge generation rate, the transport rate and the recombination rate [39, 40].

For an ideal system, every photon absorbed should produce an electron that is effectively injected into the conduction band of the TiO_2 . The loss of the charge generation step is mostly due to the relaxation of dye (direct recombination or no injection), or the recombination of electron in conduction band with oxidized dye (recombination via dye). These two processes are negligible compared to the recombination of $e_{TiO_2}^-$ with I_3^- ion, especially with ruthenium complex dyes, their rate can be altered by using co-adsorbents or dye with specific moieties, which can shift the band edge of the conduction band.

Figure 2.2: Energy levels in DSC showing kinetic processes occurring in the device and their time scales.

Electron transport in TiO₂ is described to follow a diffusive process that is driven by electron concentration towards the anode, and electric field that drives drift movement is almost negligible. However, these electrons also undergo a series of trapping/detrapping events and recombination with tri-iodide in the electrolyte or oxidized dye. The diffusion (0.1-10 ms) ideally occurs on a time scale one to two orders of magnitude faster than that of recombination with the electrolyte (milliseconds to second range) to effectively drive a large fraction of electrons to the front electrode. As electrons “walk” randomly through the TiO₂ network, trapping and detrapping processes occur in a timescale of picosecond to nanosecond faster than both diffusion and recombination, and play an important role in determining the effective electron transport rate [41–43].

2.1.2 Critical parameters

To characterize a solar cell, the current-voltage (I-V) curve is measured, and the following parameters are usually determined to evaluate how good a device is, because they can be interpreted in relationship with charge transfer processes.

- **Open circuit voltage V_{oc}** is the applied external bias at which the current passing

Figure 2.3: Current-voltage (I-V) characteristics of a typical solar cell in the dark (black curve) and under illumination (red curve). Here the open circuit voltage V_{oc} , short circuit current I_{sc} , the voltage and current at maximum power point V_{max} and I_{max} are indicated on the I-V curve.

through the solar cell is zero. The open circuit voltage is the maximum voltage difference across the cell. In dye-sensitized solar cells, V_{oc} is associated to the difference between the energy level of the conduction band of the semiconductor (TiO_2) and the redox potential of the redox couple (usually I^-/I_3^-). However, in practice, the V_{oc} is influenced by shifting of the conduction band due to interaction with dye molecules, or recombination due to back reactions.

- **Short circuit current I_{sc}** is the current under illumination when zero voltage bias is applied. The short circuit current is divided by cell area to get short circuit current density J_{sc} . J_{sc} is impacted by many factors, mostly by light harvesting, injection, electron transport and collection, and diffusion of electrolyte.

$$J_{sc} = \frac{I_{sc}}{\text{cell} - \text{area}} \quad (2.1)$$

- **Fill factor FF** describes the “squareness” of the solar cell’s current-voltage characteristics curve. It is calculated by the ratio of the actual maximum power point

($P_{max} = V_{max} \times I_{max}$) to the “theoretical” maximum power point determined by V_{oc} and I_{sc} :

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} \quad (2.2)$$

- **Power conversion efficiency PCE** (η) is the ratio of the maximum electrical power output compared to the solar power input.

$$PCE = \eta = \frac{P_{out}}{P_{in}} \Rightarrow \eta_{max} = \frac{P_{max}}{P_{in}} = \frac{FF \times V_{oc} \times I_{sc}}{P_{in}} \quad (2.3)$$

- **Incident photon-to-current conversion efficiency (IPCE)** or **External Quantum Efficiency (EQE)** as a function of wavelength (λ) is calculated from the spectral response of the device. Theoretically speaking, the photocurrent density of the cell is the integration of EQE throughout the absorption spectra.

$$IPCE = EQE(\lambda) = SR(\lambda) \frac{hc}{e\lambda} \quad (2.4)$$

$$J_{sc} = \int eEQE(\lambda)\phi(\lambda) d(\lambda). \quad (2.5)$$

2.2 Optical properties of the photoanode

The 20-40 nm TiO_2 nanoparticles forming the mesoporous film and thus making up the photoanode is transparent in nature, hence sun derived photons have the possibility of passing the photoanode without being captured by any dye. To improve light harvesting, besides designing, engineering and synthesis of new dye molecules to increase the absorption spectrum, it is necessary to develop structures that are physically thin but optically thick to increase the photon path length and light harvesting [44]. By altering the structure of the semiconductor mesoporous film, several optical phenomena can be obtained based on light scattering effect, photonic confinement and plasmonics.

Absorption in DSCs remains poor in the red and near-infrared (NIR) region and

Figure 2.4: Scanning electron microscope image of a typical TiO_2 mesoporous film used as photoanode in DSC [2].

only a few NIR dyes exhibit good charge injection efficiency but the V_{oc} is still low [44]. Figure 2.5 illustrates the standard reference spectrum (AM 1.5G) and the absorption spectra of two ruthenium-based dyes (N3 and $\text{Ru}(\text{bpy})_3^{2+}$). Absorption of dyes is relatively limited in the visible range and even the best dye can cover less than a third of the solar spectrum [44]. Moreover, dyes with fairly broad absorption spectra ($\Delta\lambda \approx 350 \text{ nm}$) have rather low molar extinction coefficients ($1 - 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). New generations of lower cost organic dyes have molar extinction coefficients which are 3-4 times higher but their absorption spectra are narrower compared to ruthenium dyes [45]. Co-sensitization suggests the combination of dyes to extend the absorption spectra which is a useful strategy to enhance light harvesting [37, 46, 47].

The amount of dye attached to the TiO_2 is critically dependent on the surface area because a dense monolayer dye coverage is important to reduce charge recombination. The surface area of TiO_2 can be enhanced by decreasing the particle size down to the nanometer scale (10-20 nm in diameter). However, particle size and porosity are closely related to each other and scaling down to smaller particle size also means smaller pore size. Maintaining appropriate pore size and porosity is essential for the percolation and diffusion of electrolyte or hole transporting material [38, 49]. Moreover, further decreasing particle size is more difficult in colloid synthesis and mass production by screen-printing method. Total surface area can also be enhanced by increasing the thickness of TiO_2 film,

Figure 2.5: Absorption of ruthenium(II)trisbipyridine dichloride and N3 dye in comparison with the solar spectrum [48]. The chemical structures of these dyes can be found in the appendix

although that will eventually lead to increasing recombination sites and mass transport limitation of electrolyte that retards the photocurrent dramatically at high light intensity [50].

Beer-Lambert law expresses the absorbance of a material through the following equation:

$$A = \varepsilon cl \quad (2.6)$$

where A is the absorbance, ε is the extinction coefficient of dye, c is the concentration of dye on TiO_2 film and l is the optical thickness of the film. Hence the light harvesting efficiency (LHE) of the cell is dependent on the property of the dye (extinction coefficient and concentration) as well as the optical path length that is available within the photoanode. While improving LHE, it is essential to extend dye absorbance to a wider wavelength range, especially into the NIR region > 700 nm.

Optical path length can be increased without negative influences on electron transportation by modifying the nanostructure of the photoanode semiconductor film. Large particles can be incorporated with nanoparticles to induce light scattering within the TiO_2 film and J_{sc} improvement can be observed [51]. According to Mie-Lorenz theory, light can be scattered by spheres that have sizes similar to the desired wavelength range. Furthermore, surface plasmons can be induced by nanoparticles and photonic crystals by

periodic structures are also applied to enhance the light harvesting of DSCs [52,53].

2.2.1 Mie light scattering theory in dye-sensitized solar cells

Light scattering is a well-known optical phenomenon that involves propagation of light in the presence of non-homogeneous article(s) [52]. In general, when light encounters a non-homogeneity (the non-homogeneity article has different refractive index from the surrounding materials), the radiation may either propagate in a forward or backward direction. Forward propagation gives rise to refraction and absorption while backward components are related to reflection. Nevertheless, radiation can be spread in all directions that deviate from the incident, reflection or refraction trajectory and is known optically as light scattering. This phenomenon occurs when the dimensions of the non-homogeneous object are on the order of the wavelength of the incident light. The object that causes light scattering is known as scatterer or scattering center.

Figure 2.6: Reflection, refracting and scattering of light. (Redrawing according to Zhang *et al.* [54]).

Many theories were developed to explain the behavior of light scattering process including the most well-known theories by Rayleigh and Mie [52], typically applicable for spherical scatterers. These two theories are differentiated from each other according to the scatterer dimension's comparability to the light wavelengths. While Rayleigh scattering describes non-absorbing scatterers with small size particles, Mie scattering explains the scattering systems consisting of large particles with sizes comparable to wavelength. Mie scattering is applicable to both light absorbing and non-absorbing particles and is

not limited to particle size. The cross section of Mie scattering is expressed by [54]:

$$\sigma_{scat,Mie} = \frac{\lambda^2}{2\pi} \sum_{n=0}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \quad (2.7)$$

in which: a_n and b_n are defined by the Riccati-Bessel functions Ψ and ξ as:

$$a_n = \frac{\Psi_n(\alpha)\Psi'_n(m\alpha) - m\Psi_n(m\alpha)\Psi'_n(\alpha)}{\xi(\alpha)\Psi'_n(m\alpha) - m\Psi_n(m\alpha)\xi'_n(\alpha)} \quad (2.8)$$

$$b_n = \frac{m\Psi_n(\alpha)\Psi'_n(m\alpha) - \Psi_n(m\alpha)\Psi'_n(\alpha)}{m\xi(\alpha)\Psi'_n(m\alpha) - \Psi_n(m\alpha)\xi'_n(\alpha)} \quad (2.9)$$

The Mie scattering efficiency can be calculated by:

$$Q_{scat,Mie} = \frac{\sigma_{scat,Mie}}{\pi r^2} \quad (2.10)$$

Based on these equations, Zhang *et al.* [54] calculated the scattering efficiency of TiO_2 particles in air with refractive indices obtained from the literature [55]. Figure 2.7 shows that when the incident wavelength is at 532 nm, effective light scattering can only be observed if the diameter of the spherical scatterer is larger than 200 nm. In Figure 2.7b, it is illustrated that with an example of 200 nm spherical scatterers, light scattering occurs mainly in the wavelength range of ~ 400 nm to ~ 650 nm. It is hence predicted that to achieve effective light scattering, controlling the size of scatterer is necessary by making it comparable to the wavelength of the incident light. Moreover, Mie theory can be extended to non-spherical scatterers such as ellipsoid, polygons or random shapes. In DSCs and other photovoltaics applications, the calculation by Zhang *et al.* [54] can vary as refractive index of materials such as I^-/I_3^- electrolyte may deviate from that of air and shape of scatterers are not perfect spheres.

Simulation

Ferber *et al.* reported the influence of diameter size, concentration of light scattering centers and structure of photoanode by computer simulation [55]. The simulation models were based on the two mentioned approaches to either form binary particle mixture or

Figure 2.7: Scattering efficiency of TiO₂ particles as dependent on particle size and incident wavelength [54]

double-layer to enhance back scattering. Both assume that primary TiO₂ nanoparticles have uniform size of 20 nm and dye molecules form a monolayer covering the particles surface. In this paper, the simulation explained that absorption of the film with single size nanoparticles reached a maximum when internal surface area is largest, or when radius of nanoparticles is smallest. In a binary mixture, addition of large particles leads to decreasing internal surface area but optical absorption was ultimately increased by the light scattering (Figure 2.8). An optimal structure was proposed to be a mixture of 5 wt% large particles with radius 125-150 nm and 95 wt% nanoparticles of 20 nm diameter. Ferber also pointed out that a double-layer structure is not recommended as its optical absorbance is not as high as a mixed structure.

Figure 2.8: Calculated absorbance of 10 μm thick films binary mixture of TiO₂ particles (10 nm in radius) with varying weight fraction of large particles radius a_2 (a) and radius of 135 nm (b) according to Ferber *et al.* [55].

It is worth noting that Mie scattering is best applicable to single scattering, hence

the simulation conducted by Ferber *et al.* limited the concentration of scatterers to be 10-30% volume fraction to keep the scattering centers sufficiently apart and reduce phase effects that complicates the simulations. Nevertheless, this fraction is much smaller than in practice ($\approx 50\%$) in a conventional DSC, therefore the simulation may not reflect well the practical effect of light scattering with large particles.

Four-flux model

Another approach for theoretically calculating the Mie scattering effect in DSC is the four-flux model introduced in the 1980s to solve the radiative transfer equation in non-emitting media, which was applied in the case of Lorenz-Mie scattering centers embedded in a slab. Rothenberger *et al.* applied this method to analyze the behavior of DSCs with scattering layer in a double-layer structure [56].

Figure 2.9: Four-flux model diagram showing the forward and backward fluxes.

The four-flux model illustrates the total light flux in the film and separates it into four distinct fluxes: two collinear fluxes - one forward (I_c) and one backward direction (J_c); and two diffuse fluxes also traveling in forward (I_d) and backward direction (J_d) [53,57]. The porous medium is assumed to be isotropic and homogeneous on a micrometer scale and only absorbs and scatters light but it is not luminescent. Figure 2.9 shows the fluxes present in the film and the resulting transmission and reflection parts. The collimated unpolarized incident beam has an intensity of I_o and it is perpendicular to the boundary of the substrate. After multiple reflection and scattering at the air/glass and

glass/TiO₂ interfaces, the reflected part contributes to the collimated reflectance R_{coll} . The transmitted fraction reaches the porous TiO₂ in which forward flux I_c is attenuated due to absorption and scattering while the scattered part contributes to fluxes I_d and J_d . The collinear fraction of beam exits the film where it undergoes multiple reflections again and the specular reflection returns to the film as flux J_c and the transmitted fraction leaves the film as collinear beam T_{coll} . Diffuse fluxes I_d and J_d are partly reflected at the entrance and exit windows and partly transmitted, leading to T_d and R_d , respectively. The variation of these fluxes within the slab with thickness x can be derived by balancing energy of forward and backward scattering and absorption by the following differential equations [53, 57]:

$$\frac{dI_c}{dz} = (k + s)I_c \quad (2.11)$$

$$\frac{dJ_c}{dz} = -(k + s)J_c \quad (2.12)$$

$$\frac{dI_d}{dz} = \varepsilon k I_d + \varepsilon(1 - \zeta)s I_d - \varepsilon(1 - \zeta)s J_d - \zeta s I_c - (1 - \zeta)s J_c \quad (2.13)$$

$$\frac{dJ_d}{dz} = -\varepsilon k J_d - \varepsilon(1 - \zeta)s J_d + \varepsilon(1 - \zeta)s I_d + (1 - \zeta)s I_c + \zeta s J_c \quad (2.14)$$

Where: $k(\lambda)$ and $s(\lambda)$ are absorption and scattering coefficients, respectively and are dependent on wavelength (unit length^{-1}). ε ranges from 1 (for collimated light) to 2 (for isotropically scattered light) and is the equivalent path length for diffuse fluxes and accounts for the increase of optical length in slab dx . ζ is the forward scattering ratio coefficient and ranges from 1 (if light is scattered in the forward direction only) to 0 (backward only). The absorption of light in the film can be calculated after obtaining optimized values of parameters by applying appropriate boundary condition and fitting with experimental data. The local rate of light absorption $g(x)$ per unit volume is [56]:

$$g(x) = kA(x) + kB(x) + \varepsilon kC(x) + \varepsilon kD(x) \quad (2.15)$$

and the total absorbed flux over the film thickness is calculated from the integral:

$$G = \int_0^{x_f} g(x) dx \quad (2.16)$$

This model is important for application of determining the fraction of light scattered within the film thickness for an optimal absorption flux in the whole film.

State-of-the-art applications of scattering effect in DSCs

Figure 2.10: (a) TiO₂ photoelectrode with diffusion and scattering layer of variation of particle sizes; (b) IPCE of monolayer, doublelayer and multilayer diffusive and scattering DSCs [51]

Light scattering effect arising from large particles, following Mie theory, has been widely applied to enhance light harvesting in DSCs. The most common method is by adding large particles of 200-400 nm, forming a scattering layer in a double-layer structure or incorporating them with 20 nm particles to form a mixture structure. In fact, this method is very popular and efficient that it has become standard and routine for many reported dye-sensitized solar cell fabrication processes [50,58]. The large particles scatter light, causes multiple reflections and increases the optical path length of the photon so

Figure 2.11: (a) Schematic redrawn from Zhang *et al.* [59] and (b) SEM image of aggregates of nanoparticles employed by Kim *et al.* to enhance light scattering [54, 60]

that it is higher than the physical thickness of the film, hence increasing the possibility of photon to be absorbed by dye. Figure 2.10 shows different structures utilizing this approach [51]. Monolayer films include the standard structure that consists of 20 nm particles (N) as well as a mixture of 20 nm and 400 nm (M) particles. In a double layer configuration, the scattering layer is screen-printed on top of the transparent layer (NS), or the mixture of 20-400 nm particles are printed as the second layer (NM). Multilayer is the extended version of double layer (NMS), with the diffuse particles (of middle range size ~ 100 -200 nm) are used to enhance the light scattering effect. In this paper, Wang *et al.* has proven that the multilayer structure is better compared to the monolayer and double layer, which helps IPCE increase over the whole absorption spectra range (while double layer only increases IPCE in ranges lower than 620 nm), eventually resulting in increase of J_{sc} by 3-4 mA/cm^2 [2]. However, this effect is dependent on the characteristics of the dye sensitizer itself, especially its absorption spectra and extinction coefficient.

As Mie theory can be extended to non-spherical particles, several approaches have been explored. Nanorods, nanowires and nanofibers-based DSCs experience similar effect as the size of these materials are comparable to the desired scattering wavelength [24].

Nanocrystals of different materials are also being studied. More interestingly, spherical aggregates of oxide nanocrystallites have also been reported to have high surface area, good percolation of electrolyte and light scattering property (Figure 2.11 [54,60,61]).

2.2.2 Other nanostructures to enhance light harvesting

Beside light scattering effect, other methods to increase light harvesting in the photoanodes of DSCs by modifying the nanocrystalline film have been explored. The most promising techniques are employing photonic confinement and plasmonic effects.

Photonic crystals

Figure 2.12: (a) Illustration of a doublelayer photonic crystals DSC [62]; (b) SEM image of photonic crystals used in DSC [62]. (c) Measured IPCE of control sample made of nanoparticles (square symbol) and photonic crystals (round symbol) showing the increase of photocurrent at longer wavelength. The stop band position is at 610 nm. [63].

Well-ordered photonic crystals have been studied for their use in light scattering and light confinement in DSCs. The difference between photonic crystals compared to scattering layer is the novelty of slowing and localization of light in the high index portion [63]. One of the extraordinary properties that photonic crystals possess is the nonlinear dispersion, in which the group velocity of light becomes very small near the wavelength of a stop band - known as the photonic band gap. Hence when approaching the stop band, light becomes increasingly similar to a standing wave. By applying these properties in a dye-sensitized solar cell, several groups have observed an enhancement in efficiency [62,64]. Although increase in efficiency was a result of the enhancement of red absorbance due to slow propagation of photons in the photonic crystals, this magnitude was proven

to be the minor. The second effect, which was believed to be the major contribution, is based on disordered regions of the photonic crystals, which resulted in strong light scattering at the interfaces within the network of mesoporous TiO_2 in the photoanode of DSC [65,66].

Nevertheless, photonic crystals only enhance the light absorption at specific wavelengths, mostly at the stop band, hence it is limited compared to the light scattering effect. Moreover, it is more complicated and require additional steps of synthesis to form photonic crystals. A three-dimensional photonic crystal film for DSC is usually created by self-assembled array of polystyrene spheres, followed by infiltration of titania precursor and sintering, forming a honeycomb structure. The adhesion of this film to the substrate is known to be poor, and special treatments are necessary. Moreover, photonic crystal alone has extremely low surface area, which leads to low dye loading, and hence reduces the overall absorption and photocurrent.

Plasmonics effect

An alternative and newer approach for trapping light in the photoanodes of DSCs is plasmonics effect. Plasmons are created when the incident photon excites coherent oscillation of the free electrons in metal nanoparticles. Nanoscale metallic particles or discs are interesting materials possessing very large and easily tunable optical cross sections associated with their localized surface plasmon resonances (LSPRs), and are promising to enhance the light harvesting in photovoltaic devices [69]. Preliminary research introduced silver islands in the nanometer scale deposited by thermal evaporation on flat surfaces of TiO_2 films prior to dye-loading showing enhanced light absorption [70,71]. Following that, real devices have been demonstrated with several structures, including core-shell metal insulator nanoparticles and nanoimprint patterns formed by lithography method. Hou *et al.* investigated three different configurations of Au nanoparticles/dye/ TiO_2 as photoanode of DSCs [67]. In their study, the embedded Au particles in TiO_2 mesoporous layer showed significant enhanced photocurrent compared to conventional structure, while placing Au nanoparticles on top of TiO_2 (before or after dye-loading) did not show any positive effect (Figure 2.13a).

Because of their localized property, plasmonics does not have much effect on liquid

Figure 2.13: Schematic illustration of (a) Au nanoparticles used for plasmonics effect in TiO_2 photoanode (from top to bottom: embedded, Au on top of TiO_2 before and after dye-loading) [67]; and (b) plasmonic SSDSC fabrication process with silver nanoimprint back reflector as counter electrode [68]; (c) IPCE of SSDSC with Z907 (left) and C220 (right) dyes with nanoimprint back reflector compared to standard devices [68].

DSCs, due to the thick TiO_2 film required and the corrosive characteristic of I^-/I_3^- may etch away the metallic nanoparticles. On the other hand, solid-state DSCs may be the better choice to apply the plasmonics, and have also been explored by several research groups, either though embedded metallic nanoparticles or [68] as back reflector [72]. The thickness of the photoanode of SSDSC is limited because of the infiltration and pore-filling difficulty when using spiro-oMeTAD as the hole conducting material, hence enhancing optical property by more conventional methods like scattering layer or photonic crystals is rather challenging. Interestingly, the plasmonics effect as back reflector is shown to have potential for a range of dyes, even for organic dyes that have strong absorbing ability.

2.3 Porosity of photoanode

The porosity of the photoanode in DSCs can affect light absorption, electron diffusion and ion diffusion that can eventually influence the I-V characteristics of the device [73]. The typical porosity of DSC is about 57-60%, but it can be modified by changing particle size, binder material or the amount of binder used. The advantages of increasing porosity is improvement in ion diffusion in electrolyte and better electron diffusion while the disadvantage is lower surface area [74], hence lower dye-loading and light absorption [75]. Better pore filling of hole conducting materials in SSDSCs can also be expected if porosity and pore size increases [76].

Increasing film thickness is essential to increase the total surface area and dye-loading to maximize the light absorption. Nonetheless, some systems involving redox couples other than I^-/I_3^- , such as $\text{Co}^{2+/3+}$, viscous electrolyte or solid state hole conducting materials, face a constraint that film thickness has to be thin enough to ensure charge carriers to be collected and good ion diffusion or hole transportation. Increasing film porosity or pore size is an alternative option for better ion diffusion. In the early history of DSCs, optimizing pore size was investigated with the influence on the diffusion of electrolyte. Barbé *et al.* demonstrated two systems which have similar surface area but different pore size distributions: 4 nm and 20 nm. It was shown that when the pore size is too small, non-linearity in photocurrent is observed, indicating poor diffusion of electrolyte. More recent studies suggest that even larger pore size is necessary to reduce

mass transport limitation in ionic liquid viscous electrolytes or cobalt electrolytes [77]. Particle size of TiO_2 films strongly influences the choice of dye and electrolyte system used, especially for hole conducting materials that are sensitive to pore-filling or limited by mass transport. Nakade *et al.* [49] investigated the influence of TiO_2 nanoparticle size on the electron diffusion and recombination of DSC by studying electron lifetime using intensity modulated voltage spectroscopy (IMVS) method. Particle size affects the pore size and total surface area of the film, hence leading to variation of dye-loading and physical diffusion of electrolyte between pores. Particle size can also influence the optical property of photoanode, since large particles can scatter light.

Strategies to control porosity and pore-size

Binder

Binders are organic materials such as polymers like ethyl cellulose, poly-ethylene glycol (PEG), etc. used to make pastes for TiO_2 layer formation to assist binding the TiO_2 nanoparticles and create pores after being burnt off during sintering. When binder concentration in the paste increases, the total porosity changes, but the average pore size distribution remains centered at a size similar to the size of the nanoparticles, because the average pore size is dependent on the average cluster size [38].

Nanowires and nanorods

Although much research on vertical nanowires and nanorods for dye-sensitized solar cells have been done, most are focused on the influence of 1-dimensional nanostructure as a direct electron path length to improve charge collection [26]. Nevertheless, using nanowires and nanorods or horizontal nanofibers by electrospinning will also increase the porosity of the TiO_2 film [20].

Hollow spheres

Hollow spheres are another option to increase porosity of DSCs. In some cases, surface area is improved by surface treatment of large spheres [78, 79]. Moreover, because the average pore size is dependent on the size of the particles or average cluster, the hollow spheres or cluster of nanoparticles can have very large average pores (not uniformly

distributed), which create channels for ionic diffusion.

Relationship between coordination number and porosity

Frank *et al.* has simulated the coordination number of TiO_2 particles in relation to the porosity of the photoanode's nanoparticle films [80]. In this report, they have concluded that the critical porosity of titania film is limited to $76\% \pm 1\%$. Through the simulation and their experimental data, we learn that electron diffusion coefficient is related to porosity and the coordination number of TiO_2 nanoparticles. When increasing porosity to more than the critical value, there are more “dead ends” created, resulting in more terminating particles. Because the method of simulation is through coordination number, this limitation is independent on electrolyte or redox couple used. However, this is based on a uniformly distributed porous system. When there are two pore sizes or more distribution, the dependent on coordination number may vary.

2.3.1 Other components in DSCs

Dye

Dye is considered the crucial part in dye-sensitized solar cells. A good sensitizer should have the following essential properties [11]:

- Absorption spectrum that covers large portion of the solar spectrum, especially the visible region and near-infrared (NIR).
- Strong bond with the surface of semiconductor material (TiO_2) via the anchoring groups such as $-\text{COOH}$, $-\text{H}_2\text{PO}_3$, $-\text{SO}_3\text{H}$, etc.
- To ensure efficient injection of excited electron into conduction band of semiconductor, the LUMO level of the dye should be higher than conduction band energy level of the TiO_2 . On the other hand, the HOMO level should be lower in energy than the redox potential of the electrolyte for effective dye regeneration.
- Dye aggregation should be avoided to achieve monolayer coverage. Nevertheless, it can be improved by the aid of using co-adsorbent.

- Photo- and thermal stable and should not desorb from the TiO_2 surface once attached.
- Solubility in solvents used in the dye loading process

Beside the mentioned characteristics, the design, engineering and synthesis of photosensitizers has evolved through the years. In the 1990s, ruthenium complexes were the most common dyes and some still remain among the best dyes up to date [81, 82]. Ru-complexes offer broad absorption spectra, however they may face serious problems with dye aggregation, have rather low extinction coefficient and are costly due to the scarcity of ruthenium metal. Newer generations of dyes include organic dyes with donor- π -acceptor architecture offer much better molar extinction coefficient although they usually have smaller absorption range. Another advantage of organic dye is that it is facile to design bulky chains in proper positions to be critically beneficial for good DSC performance. One example is functional groups like bulky alkoxy chains in the D35 dye. These screen the recombination between cobalt electrolyte and the electron in TiO_2 , making D35 dye a break through for sensitizers with very high electron lifetime [83]. Besides, interaction between dye and redox mediator is also important. Reduced contact between the acceptor side of dye with electrolyte is necessary to have good injection before recombination, but a functional group that promotes charge transfer of hole to redox mediator for better dye-regeneration is preferred [11, 84].

Electrolyte

In DSCs, the role of electrolyte is to transfer electrons from counter electrode to regenerate the oxidized dye, or in other words, to transport holes. Typically, iodide/triiodide I^-/I_3^- redox couple is employed as an efficient mediator [2], but much research has been done to discover alternatives, including cobalt complexes ($\text{Co}^{2+}/\text{Co}^{3+}$) [37, 83, 85], ferrocene (Fc/Fc^+) [44, 86]. Changing the redox potential, especially positively, increases the open circuit potential of the device, but also causes challenges for effective dye-regeneration. Moreover, due to nature of each redox couple, other charge transfer problems may surface, for example severe electron recombination between TiO_2 and oxidized dye in cobalt electrolyte [83].

Figure 2.14: Energy levels of several Cobalt complexes as compared to I^-/I_3^- and Fc/Fc^+ . Redrawing figure following several references [83, 86, 87]

Physical diffusion of electrolyte plays an important role in the performance of the device. The electron mediator has to reduce the dye cations and become oxidized, then travel to counter electrode to accept an electron to bring it back to the dye/semiconductor surface. As the transport of ions is purely diffusion, it depends strongly on the concentration of ions, viscosity and dipole moment of solvent, and pore size or “diffusion pathway” between the TiO_2 particles. For sufficient regeneration of the dye, a rather high concentration of redox mediators can be employed. Nevertheless, the concentration of mediators is limited by solubility of these compounds (especially cobalt complexes) [88] and high concentration can lead to increasing viscosity of electrolyte and formation of precipitation of polyiodide (I^-/I_3^- electrolyte) [89]. Solvent with higher donor ability can shift the conduction band negatively and increase the open circuit potential [90], but most of them are volatile and toxic and not suitable for industrialization. More non-volatile solvents, such as 3-methoxypropionitrile (MPN), offer better stability and lifetime, while having a higher viscosity, hence reduced the performance [90].

Chapter 3

Methodology

3.1 Mesoporous-macroporous TiO_2 films as photoanode

The photoanode of a dye-sensitized solar cell consists of a mesoporous film of wide band-gap metal oxide nanoparticles such as TiO_2 . The introduction of this mesoporous structure is considered a major advancement in the development of DSC [10] because the surface area of TiO_2 is increased by at least 1000 times compared to a compact film and hence the dye-loading increases tremendously. Hence, although the molar extinction coefficient of a dye molecule is lower than other light absorbing materials such as quantum dots or polymers, DSC can still function efficiently. Furthermore, the mesoporous network allows good percolation of electrolyte or hole conducting material, providing better charge collection and regeneration of the dye while minimizing recombination. Another improvement in engineering the photoanode of DSC is the introduction of a scattering layer to enhance light harvesting efficiency (LHE) [9]. Incident light can be scattered by 100-400 nm TiO_2 particles, embedded in the nanoparticle matrix or deposited on top of the transparent layer [51,91]. The double layer configuration consisting of a transparent and a scattering layer has been proven to be effective and favorable for most applications, as it is employed in most studies on DSCs including the record 12.3% PCE [37].

According to Mie scattering theory, light scattering can originate from any scattering center that has a different refractive index with the surrounding medium. Hence, the scattering from voids of similar sizes to those of scattering TiO_2 particles is proposed

[92,93]. These voids are created by incorporating templates particles in the TiO_2 mixture that will later on be removed. The templates can be polymers (such as polystyrene (PS), poly (methyl methacrylate) (PMMA)...) or rigid inorganic particles like zinc oxide ZnO or SiO_2 beads. The advantages of these macroporous cavities are that they act as both light scattering centers that enhance the LHE and as the diffusion channel for better mass transport of ions in viscous electrolytes. The usage of each material as template for creating macropores have its advantage and disadvantages that will be presented in the next sections.

3.1.1 Synthesis

Figure 3.1: Schematic structure of TiO_2 photoanodes employing (a) PS and (b) ZnO particles as templates for formation of macroporous cavities. It is suggested that the evaporation of binders and solvent while removing PS during sintering process causes the collapsing of pores. ZnO is removed by the acidic environment of TiCl_4 solution during post-treatment and hence can reserve the shape of macropores.

In this thesis, two methods of creating sub-micrometer cavities in mesoporous network of TiO_2 structure are presented: using spherical polystyrene beads and ZnO particles as templates. Both templating agents are low cost, easy to synthesize and can successfully create cavities in TiO_2 films, but each has its own advantages and disadvantages. When mixing PS with TiO_2 paste, screen-printed films were sintered at 500°C . At this temperature, solvents, binders and the PS beads were decomposed. The evaporation of these materials caused a shrinkage of the film, making the pores “collapsed” and deformed into ellipsoidal shape [94,95]. These ellipsoids had transverse diameter similar to the diameter of the PS beads while the perpendicular dimension was much smaller. ZnO particles had the advantage of maintaining the spherical shape of the pores, but high loading of ZnO in TiO_2 paste mixture resulted in a mechanically weak screen-printed film and the adhesion to FTO substrate could be poor at high thickness. The instability was related to how ZnO was removed from the TiO_2 mixture. This was usually done by treatment with TiCl_4 solution in water, in which the acidic environment causes an etching reaction to dissolve ZnO, but this also weakened the TiO_2 network surrounding the pores. Figure 3.1 shows the schematic diagram of PS or ZnO incorporated in TiO_2 film and the expected morphology of the subsequent pores.

Synthesis of Polystyrene

As a low-cost and commercially available polymer, monodispersed polystyrene spheres were synthesized following reported methods in the literature, with small adjustments to obtain desired dimensions [96].

Polymerization of PS from styrene monomer is an additional reaction. All chemicals were used as purchased unless clearly stated. Potassium persulfate (KPS 99+%) and sodium dodecyl sulfate (SDS $\geq 99\%$) were the initiator and emulsifier, respectively. To extract anti-polymerizing contaminants and purify the monomer styrene ($\geq 99\%$), it was alternately rinsed with sodium hydroxide (0.1 M solution) and deionized water three times in a separatory funnel. 50 g of SDS in 80 ml water was first added into a five-neck flask placed in a heating mantle, refluxed under N_2 atmosphere and stirred for 30 minutes until the system was stabilized at 70°C . KPS (320 g in 50 ml H_2O) was later added, followed by 190 ml deionized water and stirred slowly. Treated styrene was then added into

the system and stirred vigorously until the reaction was completed. The whole process took approximately 7-8 hours and during the polymerization, temperature was carefully monitored and adjusted to around 70°C. Collected suspension of PS in water was later separated from solvent by centrifuging at 10,000 rpm for 90 minutes, rinsed with ethanol in an ultra-sonication bath three time. Final powder of PS was dried in air overnight. This recipe resulted in PS of *ca.* 500 nm in diameter. Size of PS beads could be modified by varying the concentration of the initiator as suggested by Zhang *et al.* [96].

Synthesis of Zinc Oxide

ZnO is a widely studied material for many applications. The synthesis is relatively simple and can be done in many different ways and different nanostructures can be obtained. It was chosen as a template for macropores because it can be etched away using mild acidic solution when the screen-printed photoanode film goes through a routine TiCl_4 post-treatment usually used for better connection between the nanoparticles [97]. To synthesize ZnO particles with controlled size and monodispersity, a two-steps synthesis was adopted [13,98]. A stock solution of supernatant was prepared by adding zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2$ - Sigma Aldrich, $\geq 98\%$) with a concentration of 0.133 M in diethylene glycol (DEG - Sigma Aldrich, 99%). The solution was then stirred vigorously and heated to a critical temperature of 180°C and equilibrated for 1 hour. Precipitated ZnO could be seen when the critical temperature is reached. The suspension of ZnO in DEG after cooling down to room temperature was separated by centrifuging at 3000 rpm for 60 minutes, and the supernatant solution was collected. In the second step, a similar solution of $\text{Zn}(\text{CH}_3\text{COO})_2$ in DEG was prepared and heated to just before the critical temperature. At about 150°C, a certain amount of supernatant was added which made the temperature to drop and eventually rose again. After that, the system was equilibrated at 180°C for 1.5 hours until reaction completed. The amount of supernatant added in the second step determined the diameter of resulting ZnO particles. The more supernatant added, the smaller was the dimension. More details on ratio can be found in the literature [13,98,99].

Figure 3.2: Flowchart describing the synthesis process of PS/ZnO mixed with TiO_2 pastes from commercially available Dyesol D18NR-T paste.

Synthesis of mixture pastes

The screen-printing paste for depositing non-cracking photoanode for DSCs consists of nanoparticles (TiO_2), binder ethyl cellulose and α -terpineol as dispersant and surfactant to reduce the aggregation of the nanoparticles. Although the fabrication process of paste was widely reported, for convenience and ease of reproducibility, commercially available paste from Dyesol coded D18NR-T (with 18-20 nm TiO_2 nanoparticles) was used as the baseline material. Different templates were incorporated into this paste. D18NR-T consists of approximately 20.7 wt% TiO_2 , 69.0 wt% terpineol and ethyl cellulose of 10.3 wt% [50, 100], dissolved in absolute ethanol and stirred vigorously for 30 minutes. PS or ZnO suspension was prepared separately in absolute ethanol and later added to the paste solution, followed by sonication by a probe-sonicator (Sonic, VCX 750). This process was repeated for 6 to 7 times, alternating with 1 minute stirring to prevent overheating of the solution which can cause agglomeration of the nanoparticles. Ethanol was then removed from the solution using a rotary evaporator (40°C, 100 mbar). The process is described

in the flow chart shown in Figure 3.2.

Screen-printing of photoanode

Photoanodes were prepared on FTO (fluorine doped tin oxide) substrates (Nippon Sheet Glass - 10-14 Ω/sq). The FTO glass substrates were cleaned using detergent (Decon soap) and rinsed with de-ionized water and ethanol, then dried in air. Cleaned substrates were pre-treated with $TiCl_4$ solution (a stock solution of 2 M $TiCl_4$ solution was prepared by adding Alfa-Aesar $TiCl_4$ 99% into ice water that was frozen overnight. When used, the solution was further diluted in de-ionized H_2O to 40 mM) at 70°C for 30 minutes, then rinsed again with water and ethanol. Screen-printing was performed manually. Thickness of films were controlled by the number of screen-printing layers and viscosity of the pastes (adjusted by additional of α -terpineol if necessary, which did not affect the porosity of the film). Surface profilometer (Alpha-500) was used to measure thickness of the films. Between each layer of screen-printing, the films were rested for 1 minute, followed by heating at 125°C to dry and cool down before the deposition of the next layer. Screen-printed films were sintered at 500°C using a slow ramping process on a hotplate with air flow to prevent cracking. After cooling down to room temperature, the films would undergo a post-treatment of $TiCl_4$ solution for 30 minute at 70°C.

In the course of the project, the following sets of pastes were produced for investigation:

- Varying concentration of sub-micrometer cavities by changing the amount of PS added. The PS beads used were of 500 nm, added with the weight ratio of $TiO_2:PS = 20:1, 10:1$ and $2:1$.
- Varying size of sub-micrometer cavities by changing diameter of ZnO particles template. ZnO particles used had the diameter of *ca.* 170 nm, 380 nm and 500 nm. The weight ratio was $TiO_2:ZnO = 10:3$.

3.1.2 Characterization methods

Morphology of TiO_2 films seen from top view and cross section will be presented. The surface area of screen-printed films were measured by Brunauer-Emmett-Teller gas adsorption (BET) method. The dye desorption studies also provided information about surface area and porosity.

Imaging

Photos of TiO_2 films screen-printed on FTO substrates were taken using a digital camera. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM JSM 7600) were used to capture images of as-synthesized PS and ZnO beads and screen-printed films with top view and cross section view using secondary electron detector. An energy dispersed X-ray spectroscopy (EDX) incorporated in an FESEM was used to identify if ZnO residue was available in TiO_2 film after TiCl_4 post-treatment.

Brunauer-Emmett-Teller (BET) method

Brunauer-Emmett-Teller (BET) method uses physical adsorption of gas molecules on solid surface to measure specific surface area of materials. This method has widely been used to analyze porous medium. In order to measure the surface area of TiO_2 films when porosity changes, films were screen-printed on FTO substrates and then scraped off and the powder is studied in a BET gas adsorption/desorption instrument (NOVA 3200e). However, this method has its limitations. For films that are highly porous, their structure could be fractured and the measured surface area could differ from the real value. Furthermore, the obtained surface area is of meter square per gram (m^2/g). This is not a very meaningful unit as the TiO_2 particles used have similar dimension and density, hence the surface area should be normalized according to meter square per unit film volume (m^2/cm^3) (obtained from information of porosity).

Dye-loading

Dye-loading and desorption was a useful technique to determine the relative surface area of TiO_2 film. Films were dipped in dye solutions for several hours and then rinsed in clean acetonitrile twice. D205 dye was used with PS-templated and it could be desorbed by TBAOH solution (tetrabutylammonium hydroxide 0.1 mM in ethanol). D35 dye was used with ZnO-templated films and could be desorbed in TMAOH solution (tetramethylammonium hydroxide). The absorption of the solutions of the desorbed dye was then measured using a ultraviolet-visible (UV-Vis) spectroscopy. From that the absorption spectra, information of the amount of dye attached to the films can be deduced if proper calibration of dye concentration was carried out before.

3.1.3 Characterization results

In this section, morphology of templating agents (ZnO and PS) and screen-printed mesoporous-macroporous films are presented. The measured surface area and dye-loading studies are also included.

Morphology of ZnO and PS particles

ZnO particles were prepared using a two-step synthesis to obtain monodispersed particles (see Figure 3.3). FESEM images of supernatant (not shown here) reveals that the first step was to form ZnO seeds onto which particles would grow to achieve a more homogeneous dimension in the second step. Close up FESEM images (insets) show that the surface of ZnO particles were not smooth, they were in fact porous structure. Hence, the specific density of single ZnO particle may vary between the different synthesis, resulting in varying volume of ZnO though in terms of weight they are the same. This effect was clearly seen in different films with the same weight ratio of ZnO added to the TiO_2 paste could have varying surface area and porosity.

PS beads as prepared were separated from the solution by centrifugation and rinsed with ethanol several times. Figure 3.4 shows the 500 nm PS beads used to make PS-templated pastes.

Figure 3.3: Top view FESEM images of ZnO 170 nm, 380 nm and 500 nm particles.

Figure 3.4: FESEM images of PS 500 nm particles.

Morphology of PS-assisted and ZnO-assisted films

Figure 3.5 shows how transparent the PS-templated screen-printed films were. The photos show the templated films placed on top of a graph paper. The films became more translucent and opaque due to the macropores as compared to the transparency of stan-

Figure 3.5: Films with increasing concentration of macropores. These films became more translucent and opaque with increasing pores content.

dard D18NR-T. The level of transparency indicates that light scattering increased with increasing content of PS or number of macro-cavities formed in the film. When ZnO was used as the template, similar effect was observed.

(a) D18NR-T

(b) $\text{TiO}_2\text{:PS} = 10\text{:}1$

(c) $\text{TiO}_2\text{:PS} = 2\text{:}1$

Figure 3.6: Top view SEM images of D18NR-T film and films made of PS-assisted pastes ($\text{TiO}_2\text{:PS} = 10\text{:}1$ and $2\text{:}1$).

SEM images of D18NR-T films and PS-assisted films with two concentrations ($\text{TiO}_2\text{:PS} = 10\text{:}1$ and $2\text{:}1$) are shown in Figure 3.6. The created macropores can be seen as the dark regions in Figure 3.6b and c, while the standard film does not show any dark region because the mesopores (*ca.* 20 nm) were not able to visualize.

Higher resolution FESEM was used to study the morphology of films with ZnO particles as template (Figure 3.7). The dark regions are pores and the films have a mixture of both mesopores and macropores, relatively uniformly distributed. The size of ZnO-assisted pores were of *ca.* 170 nm, 380 nm and 500 nm corresponding to the size of the ZnO particles used.

Figure 3.7: FESEM images of ZnO-assisted films with ZnO of 170 nm, 380 nm and 500 nm.

The major difference between PS-assisted and ZnO-assisted film was only seen in the cross-sectional view. The removal of PS involved the evaporation of organic phases present in the paste and this could result in a collapsing of the pores. During the sintering process, the binders, solvents and PS are decomposed and the organic substances evaporated (upward) through the surface of the film. The evaporation caused shrinkage of the film in the direction perpendicular to the substrate. When PS beads were decomposed, at first

they left behind pores of similar shape and volume like the original PS beads. While the film was shrinking in the vertical direction, the pores would collapse in the same direction and became elliptical. ZnO on the other hand was removed by acidic environment of TiCl_4 solution which was used in post-treatment of TiO_2 film after sintering. The pores created by dissolving ZnO remained spherical in shape. (The “ellipsoidal” and “spherical” shapes are the closest approximation of standard shapes according to the SEM/FESEM images reported. The pores are not perfectly spherical or ellipsoidal because they are surrounded by nanoparticles, yet these terms can be used for more easily analyzing morphology and optical properties.)

Figure 3.8: Cross section SEM and FESEM images of films with PS and ZnO as templates. The shape of macropores clearly appears to be more spherical in the case of ZnO than when PS is used. The morphology of macroporous films is reproducible.

The biggest concern when using template particles to create macro-cavities was the residue left behind after the removal of the templating materials. PS has a decomposition temperature of $300\text{--}400^\circ\text{C}$ (melting point is around 242°C), and the sintering temperature of TiO_2 film was 500°C with air flow and holding time of 30 minutes. Therefore, PS was believed to be completely removed together with other organic compounds (binder ethyl cellulose and α -terpineol) during sintering; whereas ZnO was removed during the TiCl_4 treatment when the acidic solution etched away the ZnO particles. To ensure that ZnO was completely removed, EDX was performed for both top surface and the cross section of the films to determine the element composition.

EDX spectra before TiCl_4 treatment show that the amount of ZnO presented in the film was approximately equal to the amount of ZnO added into the paste ($\text{TiO}_2:\text{ZnO}$

(a) FESEM images

(b) Before TiCl_4 treatment (c) After TiCl_4 treatment - top surface (d) After TiCl_4 treatment - cross section

Figure 3.9: (a) FESEM images of ZnO particles and pores left be them before and after TiCl_4 treatment. (b,c,d) EDX spectra and element counts of ZnO-assisted TiO_2 films before and after TiCl_4 treatment with 40 mM solution. Extra elements like Sn comes from FTO substrate, Si comes from glass, Pt from conducting coating layer and Cu from copper tape/sample holder.

= 10:3 weight ratio). TiCl_4 solution was prepared in water, which would form $\text{Ti}(\text{OH})_4$ oligomers and HCl acid resulting in a highly acidic solution. After treatment with a 40 mM TiCl_4 solution, ZnO was etched away by HCl and almost no trace of ZnO could be found on the top surface or on the cross section film. When the film is treated with a lower concentration TiCl_4 solution (≤ 15 mM), there was a small trace amount of Zn (0.1-0.3%). This trace was not significant as the Zn-peak intensity was very low while the background of the EDX spectra was high. Due to the limitation of EDX, it was difficult to confirm the presence or absence of ZnO or any other Zn-contained compound or Zn-doped- TiO_2 in the films. On top of this, it was also suspected that during sintering, ZnO may form necks with neighboring TiO_2 particles. When the ZnO particles are removed, the surrounding TiO_2 particles that are bonded with them may be removed as well. A quantitative analysis was difficult to detect the amount of TiO_2 nanoparticles that were bonded to ZnO or removed during the etching process. In qualitative analysis, in FESEM images TiO_2 nanoparticles were seen to cover around the ZnO particles, and they were removed after the acidic TiCl_4 treatment. As a result, a small amount of TiO_2 particles were removed together with the ZnO particles during the etching process, especially the layer adjacent to FTO substrate. This suspicion arose from the fact that ZnO-assisted films were relatively poor in mechanical strength compared to PS-assisted films. This might cause the film to peel off if it was too thick. Therefore, ZnO-assisted films were limited to less than $8\mu\text{m}$ thick to ensure mechanical integrity. Nonetheless, further investigation needs to be done to understand the poorer adhesion of ZnO-templated film as compared to PS-templated films.

Surface area and dye-loading

To determine the dye loading capability of these mesoporous-macroporous films, dye loading experiments were conducted. In these experiments, films were dipped into a dye solution then rinsed with acetonitrile. After that, the dye molecules were desorb by soaking the sensitized films in an alkaline solution (TBAOH for D205 and TMAOH for D35). The TiO_2 films turned transparent/white after that, indicating the complete desorption. According to Beer-Lambert's law, the concentration of the desorption solution can be

calculated as:

$$c = \frac{A}{\varepsilon l} \quad (3.1)$$

The calculated concentration was then normalized to the thickness and the area of the films. The dye loading information on each films was given as mole per micron meter per projected cm^2 area ($\text{mol}/\mu\text{m}/\text{cm}^{-2}$). If a monolayer of dye was deposited on the film, this information was proportional to the surface area of each film. Both dyes have been well reported in the literature that can form monolayer on the TiO_2 surface [76,101,102], it is fair enough to use them to obtain dye-loading information.

Table 3.1: Amount of D205 dye loaded on films that used PS as template.

Dye	Film	Loaded dye ($\times 10^{-8} \text{mol}/\mu\text{m}/\text{cm}^{-2}$)
D205	D18NR-T	2.72
	$\text{TiO}_2\text{:PS} = 20\text{:}1$	2.59
	$\text{TiO}_2\text{:PS} = 10\text{:}1$	2.24
	$\text{TiO}_2\text{:PS} = 2\text{:}1$	1.95

Table 3.2: Amount of D35 dye loaded on films that used ZnO as template.

Dye	Film	Loaded dye ($\times 10^{-8} \text{mol}/\mu\text{m}/\text{cm}^{-2}$)
D35	D18NR-T	8.95
	ZnO = 500 nm	7.73
	ZnO = 380 nm	8.13
	ZnO = 170 nm	7.98

The porosity of the films was determined by weighing and the surface area of powder scraped from screen-printed films was measured using BET. Nevertheless, the accuracy of the porosity and surface area information obtained from these methods was limited due to the fracture of films during experiment, causing breaking of the highly porous structure. Nonetheless, the data presented in Table 3.3 for PS-assisted films suggest that the approximations by BET and weighing were agreeable to the dye-loading experiment results. In conclusion, the surface area of mesoporous-macroporous films were reduced compared to the standard film.

Table 3.3: Porosity and surface area of PS-assisted films.

Film	Porosity (%)	Surface area m^2/cm^3
D18NR-T	68.06	8.670
TiO ₂ :PS = 20:1	64.64	8.256
TiO ₂ :PS = 10:1	70.50	7.397
TiO ₂ :PS = 2:1	76.54	6.968

3.2 Device structure

Dye-sensitized solar cell consisted of two transparent conducting electrodes made of flourine-doped tin oxide (FTO) deposited on glass substrate, bonded together by a melted polymer ring (Surlyn). On the photoanode, prior to sealing, the TiO₂ film was screen-printed on FTO substrate and dipped into the dye solution. After sealing, the electrolyte was filled in through a hole drilled on the counter electrode. The counter electrode was coated with a thin layer of Pt nanoparticles or poly(3,4-ethylenedioxythiophene) (PEDOT) as catalyst. Beside semiconducting metal oxide like TiO₂ that makes up the porous network of photoanode, there was a wide range of material choices for dye, electrolyte and counter electrode catalyst. Throughout the thesis, these materials would be considered for examining the most suitable option in combination with mesoporous-macroporous films. This section introduces name, composition and codes of the materials used in the thesis and the device fabrication process.

3.2.1 Materials

Dyes

Dye is the light absorbing material in DSCs. The most common dyes are ruthenium complexes, but newer generation of dye known as organic donor- π -acceptor dye has become more popular. In this research, several dyes with varying molar extinction coefficient, different absorption profile and dye regeneration rates were employed to understand the effect when combining them with mesoporous-macroporous films. Figure 3.10 shows the molecular structures of several dyes used in the thesis. Other dyes used are presented in the appendix.

Figure 3.10: Molecular formulae of a few dyes used in the project. C106 is a ruthenium-based dye, the others are organic donor- π -acceptor dyes [81, 83, 103, 104].

Electrolytes

A variation of electrolyte compositions were used in the process of device fabrication and optimization, as well as carefully chosen for the purpose of understanding fundamental operational mechanisms. Groups of electrolytes are categorized based on their redox shuttles (I^-/I_3^- and Co^{3+}/Co^{2+} systems) and solvent choices. Although cobalt electrolytes offer promising approaches for high V_{oc} solar cells, they suffer from serious mass transport limitation due to their bulky compounds that have difficulties in diffusion. The most common solvent is acetonitrile (ACN) in mixture with valeronitrile (VaN) that gives good performance, great solubility but has high volatility and may not be suitable for further mass production and long-term stability. Robust solvents such as MPN (3-methoxypropionitrile) are preferred for the future of DSC, as they offer feasible handling in industry and decent efficiency. Ionic liquids are the most ideal liquid-like electrolyte for real life applications as they are totally non-evaporating and have long stability, however, they are too viscous to offer comparable performance to the volatile solvent based electrolytes.

Table 3.4: Compositions of electrolytes used. Full name of chemicals can be found in the abbreviation list in Appendix A.

Code	Redox couple	Solvent	Composition
Z960	I^-/I_3^-	Volatile ACN:VaN 85/15 (v/v)	1.0M DMII, 0.03M I_2 , 0.1M GNCS, 0.5M tBp, 0.05M LiI
Z1026			1.0M DMII, 0.03M I_2 , 0.02M LiI, 0.5M tBp, 0.1M GNCS
Z1130			1.0M DMII, 0.05M I_2 , 0.05M LiI, 0.05M tBp
Z952		Ionic liquid	DMII:EMII:EMT: I_2 :NBB:GuSCN of molar ratio 12:12:16:1.67:3.33:0.67
Gel1		Gel	Z952 + 7 wt% SiO_2 7 nm SiO_2
DE1	$[Co(dtb)_3]^{2+/3+}$	Robust MPN:ACN 80/20 (v/v)	0.1M $Co(dtb)_3$ .2TFSI, 0.033M $Co(dtb)_2$ .3TFSI, 0.1M LiTFSI, 0.4M tBp
DE2	$[Co(bpy)_3]^{2+/3+}$	Volatile ACN	0.2M $Co(bpy)_3$ .2TFSI, 0.066M $Co(bpy)_2$ .3TFSI, 0.1M LiTFSI, 0.4M tBp

Table 3.4 lists down the composition of electrolytes mentioned in this project. Most chosen electrolytes on one hand are previously optimized for certain dyes used in the experiments, considered giving the most suitable optimal efficiency known at the point of conducting experiments. On the other hand, some electrolytes are chosen because of their special characteristics such as low diffusion coefficient (due to bulk ankoxy groups or high viscosity) that is interesting to study and can obtain more beneficial effect from the presence of the macropores (Figure 3.11).

Counter Electrode

On the FTO-glass used for counter electrode, a hole was made by mechanical drilling or sand blasting. After that, it is cleaned with HCl (10 mM), acetone and ethanol in sonication bath for 10 minutes each. Platinum solution was prepared at 5 mM from Chloroplatinic Acid Hexahydrate $H_2PtCl_6 \cdot 6H_2O$ (Alfa Aesar) in iso-propanol. A drop of this solution was dropped on the FTO-glass then heated to 380°C for 15 minutes until

Figure 3.11: Molecular structures of (a) cobalt(II/III) tris(4,4'-di-*tert*-butyl-2,2'-bipyridine); (b) cobalt(II/III) tris(2,2'-bipyridine) used in DE1 and DE2 electrolytes, respectively.

the platinization was completed. Charge transfer resistance at the counter electrode can be reduced from $10^6 \Omega$ (bare FTO) to 10Ω after platinization [11].

In case of cobalt electrolyte, the conducting polymer Poly(3,4-ethylenedioxythiophene) PEDOT was used because charge transfer resistance between platinum and cobalt mediators is very high. Cleaned FTO electrodes are masked to the desired area by thermal tape, and PEDOT is deposited by electrodeposition at 1.2 V for 30 s from EDOT solution [105].

3.2.2 Device fabrication

Schematic side view of a DSC and the fabrication process is illustrated in Figure 3.12. Screen-printed photoanode was dipped in dye solution, then removed and sealed with prepared counter electrode by a $25\mu\text{m}$ thick Surlyn® (Dupont). The space between two electrodes was evacuated, then filled with electrolyte through the drilled hole. This hole was subsequently sealed with another sheet of Surlyn and thin cover slip glass. A metallic contact of alloy was deposited on the FTO surface of both anode and cathode for a better contact during measurement.

1. Clean FTO glass, TiCl_4 pre-treatment
2. Screen-print TiO_2 photoanode, sinter, TiCl_4 post-treatment
3. Dipped in dye-solution
4. Prepare counter electrode: drill hole, clean, platinization

5. Seal photoanode with CE by a ring of Surlyn by hot-pressing at 110°C
6. Inject electrolyte by vacuum back filling
7. Seal the hole with glass cover slip
8. Solder contact

Figure 3.12: (a) Schematic side view, (b) photograph of a complete cell and (c) fabrication process of a DSC

3.2.3 Photovoltaic performance measurement

To investigate the photovoltaic characteristics, the devices were illuminated under an AM 1.5G solar simulator equipped with a 500 W Xenon lamp. The solar simulator was

carefully calibrated using a Si photodiode (Fraunhofer) to achieve input power of 100 mW/cm² (1 sun). The current-voltage behaviour (IV curve) of DSC was measured using a Keithley source meter (2612A, dual sourcemeter, 200V). When different light intensity was needed, an absorptive neutral density filter (Newport) was inserted in the pathway between the light source and the device. External quantum efficiency (EQE) or incident-photon-to-current efficiency (IPCE) was measured to study the current response of devices at different wavelength. PVE300 module from Bentham, with dual Xenon/quartz halogen light source was used to measure IPCE (in DC mode).

Other electronic properties of DSC were studied to understand the influence of employing bimodal porous structure with mixing of macropores and mesopores as photoanode. Electron lifetime and electron transport time provided information about electron recombination and transport, measured by photocurrent and photovoltage transient or IMVS/IMPS methods. Electrochemical impedance spectroscopy (EIS) was employed to efficiently study charge transfer processes in the devices, especially interfacial charge transfer. These methods will be presented in the following chapters.

3.3 Summary

In this chapter, the bimodal porous structure of TiO₂ photoanode for DSC was introduced. This structure consists of mesoporous film mixed with macropores that are created by using template particles. The template can be PS or ZnO beads, each has its advantages and disadvantages, but both have facile and well reported synthesis procedures. PS template left some collapsed pores associated with the shrinking during sintering of organic substances and PS in the paste. According to Mie theory, the ellipsoidal pores with shrinkage lateral dimension created from PS template can result in poorer light scattering effect as compared to spherical shaped pores. With ZnO template, ZnO particles were removed by etching during acidic TiCl₄ treatment and the spherical shape of macropores is maintained much better than in the PS case. Nevertheless, complete etching of ZnO was not yet confirmed due to the lack of more precise characterization. Interconnection between ZnO and TiO₂ particles could be weakened. The mechanical strength of ZnO-assisted films was relatively poorer than PS-assisted films, suggesting

that there was probably necking between ZnO and surrounding TiO₂ particles during sintering, causing weakening of the bonding during etching process. Due to this limit, it was difficult to increase the concentration of ZnO in the paste as well as depositing thick films with ZnO template.

The dye loading experiments revealed that with the presence of macropores, the surface area of films decreased with increasing pore concentration because TiO₂ particles were replaced by voids. BET was not recommended because analysis of thin film requires Krypton gas which was not available, while powder analysis faced problems with sample preparation. To prepare samples for BET, films were screen-printed, then scraped off the substrate, during which process the highly porous films might be fractured. Nevertheless, the presented BET results with PS films show agreeable result as compared to dye-loading experiment. Overall, when high concentration of PS was added (TiO₂:PS = 2:1), highly porous film saved up to 30% of dye loading compared to standard films.

The chapter also introduced an overview of other major materials used in the device like dye, electrolyte and counter electrode catalyst. Composition of electrolytes and details in fabrication process were listed.

Chapter 4

Understanding parameters affecting device performance

4.1 Background and introduction

Dye-sensitized solar cell (DSC) is a complicated electrochemical device. Traditionally, it is believed that high purity semiconductor materials are required to create internal electric field to separate electron-hole pairs generated by photons in photovoltaic devices. In case of DSC, it makes use of large interfaces between nanoparticles and other materials for the generation of electrons from photons and can be prepared with simple chemical methods without strict purity demands. After the breakthrough seminal paper in 1991 on DSC [10], many reviews have provided a good understanding of how the device works. The DSC is an example of a molecular system in which the performance of the device is better than the sum of the individual properties of all components. The interactions between the device components, especially at the oxide/dye/electrolyte interface is complex, and not only depends on the characteristics of the materials but also on the external variables such as solar irradiation, temperature and working conditions. Therefore, performance of a DSC cannot be thoroughly predicted by theoretical calculation, but requires experiments to understand the effect of each single components and how their interaction resulting in the performance of the device.

Whilst one component can be modified in order to enhance the behavior of a certain characteristic, it may on the other hand interfere another already-well optimized property. When macropores are introduced with the desire to enhance light scattering

Table 4.1: Component materials, their characteristics and effects on DSC performance

Component	Characteristic	Effect
Dye	Molar extinction coefficient	Dye-loading $\Rightarrow J_{sc}$
	Absorption spectra	$\Rightarrow J_{sc}$
	Shift conduction band edge	Band edge bending $\Rightarrow V_{oc}$
	Ligand blocks recombination	Reduce recombination $\Rightarrow V_{oc}$
Photoanode	Particle size	Dye-loading $\Rightarrow J_{sc}$
	Pore size	Recombination sites $\Rightarrow V_{oc}$
	Porosity	Percolation of electrolyte $\Rightarrow FF$
	Film thickness	
Electrolyte	Redox potential	Relative position of energy level $\Rightarrow V_{oc}$
	Viscosity	Diffusion of ions $\Rightarrow FF, J_{sc}$ at high light intensity

and therefore light harvesting, this may result in the replacement of certain volume of TiO_2 nanoparticles, leading to a decrease in the amount of dye molecules adsorbed on the nanoparticles, which in turn decreases the light absorbed. On top of this, the interaction with electrolyte at the interface is unknown when these pores are present. In this chapter, the performance of devices containing macropores are compared to standard DSCs. Results from different dyes, electrolytes and counter electrode catalysts, and their influences on V_{oc} , J_{sc} , FF and PCE of the DSC are presented and discussed. The devices were usually made in several batches to ensure fair comparison and statistically reproducible trend of performances. For comparison between different condition plotted in each graph, the data came from a same batch (film preparation and device fabrication were made on the same day, with the same dye bath and electrolyte batch). Table 4.1 shows a summary of how characteristics of some components in DSC affect the device performance.

4.2 Dye

When macropores are introduced in the photoanode, some nanoparticles are replaced by void and the total surface area of the TiO_2 film is reduced if the thickness remains unchanged. Higher extinction coefficient dyes are preferred to compensate this loss in dye loading. Organic dyes have been identified to have high extinction coefficient, although

their absorption spectra range can be smaller than ruthenium dyes. Furthermore, as the pore size chosen is of *ca.* 500 nm, scattering occurs at longer wavelength, hence dyes with poorer absorption in the red region can benefit more from this property. C218 and D205 are two organic dyes with higher extinction coefficient [104, 106] than that of ruthenium dye C106 and are promising materials for low cost sensitizer (Table 4.2). The purpose of making DSCs from these dyes is to compare the effect of macropores present in the photoanode in each case and the resulting efficiency. The photoanode thickness for all the devices were 11 μm , which is the optimum thickness for organic solvent electrolyte (to be shown in the next section). Acetonitrile-based electrolyte was chosen for this work to compare the effect of the dye when the diffusion of the electrolyte was not limited. Each electrolyte used has previously been examined to show optimal performance with the respective dye.

Table 4.2: Photovoltaic performance of devices with C218, D205 and C106 dyes with Z1026, Z1130 and Z960 electrolytes, respectively. The photoanodes used are standard mesoporous films denoted D18NR-T (made from Dyesol 18NR-T paste) and the macroporous-mesoporous films with ratio of $\text{TiO}_2\text{:PS} = 10\text{:}1$ and $2\text{:}1$.

TiO ₂ film	Dye Electrolyte	$\epsilon/10^4 (\lambda)$ $M^{-1} \times cm^{-1}(\text{nm})$	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	C218-Z1026	6.27 (555)	764.22	12.829	72	7.13
TiO ₂ :PS = 10:1			780.91	13.058	74	7.62
TiO ₂ :PS = 2:1			788.55	13.126	74	7.69
D18NR-T	D205-Z1130	7.47 (532)	730.38	14.638	74	7.91
TiO ₂ :PS = 10:1			746.58	15.275	73	8.32
TiO ₂ :PS = 2:1			734.40	15.487	74	8.37
D18NR-T	C106-Z960	1.87 (550)	744.37	16.501	76	9.32
TiO ₂ :PS = 20:1			743.15	17.599	77	10.12
TiO ₂ :PS = 10:1			749.94	17.101	77	9.91
TiO ₂ :PS = 2:1			764.05	15.683	77	9.32

The results of the device performance with each dye are shown in Table 4.2. The variation in the absolute value of V_{oc} between different systems depends on the position of the conduction band edge of TiO₂ - which can be easily altered by surface charge and adsorbed dipolar molecules. The presence of cations or protons can tune the conduction band E_c substantially [11]. The effect of additive such as TBP (4-*tert*-butylpyridine) changes the surface charge and results in a significant improvement in V_{oc} by raising the

Figure 4.1: IV curves of devices made from C218-Z1026, D205-Z1130 and C106-Z960 dye-electrolyte systems. When pore concentration is increased to high volume ($\text{TiO}_2:\text{PS} = 2:1$ - blue curves), current is reduced with C106, while with C218 and D205, it is still enhanced. This is due to C106 having five times lower molar extinction coefficient, hence the gain of light scattering can not compensate on the loss of dye-loading.

conduction band edge, while Li^+ or GuSCN shifts the conduction band edge positively and reduces the V_{oc} . This behavior is mainly related to the pK_a of particular dyes or surface energy caused by certain electrolytes. Since the presence of macro cavities did not influence the intrinsic properties of TiO_2 , it most likely did not affect the conduction band edge in each particular dye-electrolyte combination. With macropores, only surface area was reduced which lead to the reduction of recombination sites. V_{oc} could therefore be improved because of less recombination, and this result can be observed for all the dye-electrolyte systems discussed (Table 4.2).

J_{sc} depends greatly on the choice of dye, basically on its absorption spectra, molar extinction coefficient, position of the LUMO level for efficient injection of electron, and the amount of dye loaded on the TiO_2 film. D205 and C218 are both organic dyes with high extinction coefficient. D205 indeed has a higher extinction coefficient ($\epsilon_{D205} = 7.47 \times 10^4$ vs. $\epsilon_{C218} = 6.27 \times 10^4 \text{ M}^{-1} \times \text{cm}^{-1}$) [104,106], hence the loss due to lower surface area of D205 is not as pronounced as compared to C218. J_{sc} can be observed to improve more significantly with D205 and have higher absolute value than C218 cells, which resulted in better efficiency. When higher concentration of PS was added to $\text{TiO}_2:\text{PS} = 2:1$, although the amount of dye-loading can be reduced by 30%, but an improvement in J_{sc} with organic dyes D205 and C218 was still observed due to the strong light scattering.

On contrary, with C106 dye ($\varepsilon_{\text{C106}} = 1.87 \times 10^4 \text{ M}^{-1} \times \text{cm}^{-1}$), J_{sc} was reduced at this high concentration of macropores and significant reduction of surface area (Table 4.2). J_{sc} is balanced between the loss due to dye-loading and the gain from light scattering. Higher molar extinction coefficient dye is important to compensate the loss in photocurrent when dye-loading is remarkably reduced. Because of this finding, organic dyes are preferred for the studies of mesoporous-macroporous photoanode to highlight its benefits. The difference in absolute value of J_{sc} between different dyes is mostly dependent on their absorption spectra (appendix) and LUMO/HOMO level. The improvement of J_{sc} due to the presence of macropores because of improvement in light harvesting can be shown by investigating the IPCE of the device, which shows an increase in current generated per number for incident photons at the long wavelength (in the red region) (Figure 4.2).

Figure 4.2: IPCE of C218 and C106 devices showing the improvement of current per incident photons in the red region with presence of macro-cavities.

4.3 TiO_2 film thickness and macropore concentration

Photoanode of a DSC consists of a mesoporous film of semiconductor nanocrystals, most commonly TiO_2 . Beside the intrinsic property of the semiconducting oxide, the characteristics of photoanode include particles size, pore size and porosity and film thickness. These variations determine the total surface area on which dye can be accommodated, and the porosity influences the physical diffusion of electrolyte. In our study, particle size is fixed, while porosity increases with the introduction of macropores.

Film thickness influences the performance of a DSC dramatically [100]. With a thicker film, there are more TiO_2 nanoparticles and increasing surface area for loading dye molecules, hence more photons can be absorbed to generate higher photocurrent. On the other hand, since the TiO_2 /electrolyte interface is also the recombination site, it is essential to minimize these sites as much as possible to maintain a good V_{oc} . Furthermore, generally the first 2-3 μm in the front layer of the film (near FTO substrate) absorbs half of the incident photons [107], and the layer of film after that, despite still absorbing photons, will serve increasingly as recombination centers. To improve the dye regeneration, the electrolyte has to diffuse through the narrow porous network resulting in a longer path than in the bulk, thus causing a reduction in FF. Other than considering film thickness, pore concentration also needs to be optimized because it affects the surface area, leading to changes in the dye-uptake and the amount of recombination sites as well as diffusion path for the electrolyte. In this section, the effects of film thickness and concentration of pores created from PS template on the photovoltaic performance of DSCs are discussed.

Figure 4.3: V_{oc} of devices with C218 dye, Z1026 electrolyte with varying thickness and concentration of pores

Figure 4.3 illustrates the experimental relationship of V_{oc} versus thickness of DSCs made from varying concentration of macropores with C218 dye and Z1026 electrolyte. V_{oc} is defined as the difference between the Fermi level of semiconductor and the redox potential of redox couple. However, V_{oc} can also be impacted by the recombination

between the electron in the conduction band of TiO₂ and the oxidized species in the redox couple, or the band bending and shifting of the conduction band edge. Hence, the smaller the number of recombination sites, the higher the V_{oc} for a given dye-electrolyte combination. This is the reason why as the TiO₂ photoanode film thickness increased, V_{oc} decreased, similar to when pore concentration decreased, surface area increased and V_{oc} decreased. Although the gradient of V_{oc} vs. thickness curves may vary slightly between the different systems, they are mostly linear and shows similar trend even for different dye and electrolyte combinations. In Appendix C, error bars were included to show the deviation of device data as compared to the average value of different sets of devices.

Figure 4.4 shows the effect on FF for devices made using D205 dye with two electrolytes: Z1130 has low viscosity (with volatile organic solvent acetonitrile) and Z952 is made of highly viscous ionic liquid, which has low diffusion coefficient. The effect of thickness and pore size/concentration on FF depends strongly on the choice of electrolytes, mostly due to the limited physical diffusion with more viscous and less volatile solvents. Redox mediators usually diffuse slower through small pores environment compared to in the bulk of the electrolyte. Hence, for a thicker film, the electrolyte has to diffuse through a longer path of narrow porous film and this results in lower FF. On the other hand, if electrolyte was prepared in an organic solvent and hence the diffusion is not limited, the effect of thickness will appear to be negligible. Similar argument can be applied when larger pores are introduced. Pores in sub-micrometer size create wider pathways for the diffusion of redox shuttles, but will give more significant effect on a viscous electrolyte system compared to a volatile and low viscosity electrolyte.

From Figure 4.4, it is noticed that with Z1130 electrolyte, FF increased with increasing thickness of TiO₂ films. Although it is expected that FF should decrease as more surface area increased the recombination probability and the series resistance, the increment of the FF when the films get thicker is only seen in organic solvent based electrolyte Z1130. A possible explanation is that besides resistance from additional TiO₂ layer, series resistance is made up of 3 other components: the first two are (1) sheet resistance of FTO and (2) charge transfer resistance at the counter electrode (CE) which are fixed, and (3) resistance of the electrolyte layer R_3 . R_3 decreases with increasing TiO₂ thickness as the distance between top layer of TiO₂ and CE is shortened (Surlyn spacer thickness is

Figure 4.4: FF with varying thickness and concentration of pores, comparing volatile electrolyte Z1130 and ionic liquid Z952

fixed) [108]. Z952 ionic liquid electrolyte has very high viscosity and slow diffusion of ions, hence R_3 may not decrease as much compared to organic-solvent based. Besides, the FF in ionic liquid decreases with film thickness due to limited mass transport when electrolyte diffuses in the mesoporous films. That is why the presence and concentration of macropore does not show any influence with Z1130 as this electrolyte is not viscous, but increases the FF of Z952 devices by 2-3% because mass transport limitation is reduced [109].

Photocurrent is generated when a dye molecule absorbs a photon and excites an electron, which is then injected into the conduction band of TiO_2 . This electron travels through the network of nanoparticles and is then collected at the electrode. Therefore, current density is higher when there are more dye molecules to absorb the photons, efficient injection of electrons into conduction band of TiO_2 and sufficient transport as well as collection of these electrons. With the same dye and intrinsic property of the semiconductor, the injection usually does not change as the position of the conduction band edge and the LUMO level of dye is already defined. The amount of dye depends on the surface area of TiO_2 where it is attached to, hence the thicker the film, the more dye molecules are loaded leading to more absorption of photons and higher current density. With macropores, surface area is reduced (Chapter 3) because TiO_2 nanoparticles are

replaced by voids, and this causes a loss in photocurrent. However, since the capability of capturing a photon of the dye does not only depend on the dye characteristic, but also depends on the availability of photons, and the latter is improved by light scattering due to the macropores. In depth discussion about light scattering and harvesting of mesoporous-macroporous films will be presented in Chapter 5, but generally it is observed that the macropores scatter light and increase the optical path length of incident photon, hence increase the probability of it being captured by a dye molecule. Therefore when the macropores are introduced, although the dye-loading is decreased, the current density is not affected dramatically because of better light harvesting from scattering effect.

Figure 4.5: J_{sc} with varying thickness and concentration of pores. DSCs are fabricated with D205 dye and Z1130 and Z952 electrolyte (I^-/I_3^- in acetonitrile solvent and ionic liquid, respectively)

The dye after losing an electron becomes oxidized and needs to be regenerated by the redox couple. This is when the diffusion of electrolyte becomes important to provide sufficient supply to regenerate the dye. When films get thicker, diffusion of electrolyte becomes more difficult as the path through the porous film increases. Because diffusion of the electrolyte in the mesoporous environment is more restricted, lower probability of ions are capable of reaching the dye regeneration site. Hence, as the films get thicker, ions have to diffuse a longer path and the rate of dye regeneration is reduced. Furthermore, with thicker films, dyes in the top layer can absorb photons, but the injected electron

have to travel a long way before it reaches the electrode, during which trapping and detrapping processes occur continuously, and short electron lifetime can cause a loss of current. Therefore, the photocurrent saturates as thickness increases, and eventually will reduce because of poorer regeneration with a very thick film. This behavior has been observed in both viscous and low viscosity electrolytes. Last but not least, with macropores, it is expected that the regeneration is improved due to better diffusion of electrolyte. This is not shown clearly from the behavior of current density, but it can be one of the reason for mesoporous-macroporous devices to exhibit equal or higher current than the standard counter part, despite having lower dye-loading due to smaller surface area.

For both electrolytes (Figure 4.5), J_{sc} increased and saturated. With Z1130, the saturation point spans over a wider range of thickness compared to Z952, with which J_{sc} decreased right after it reached the saturation current. The saturation point of J_{sc} with Z952 also appeared at a thinner thickness, indicating that the limitation in electrolyte diffusion started to dominate the current loss. Higher pore concentration lead to increasing light scattering center, but back reflection would increase at the same time, together with the loss of dye-loading, resulting in a lower photocurrent with very high level of macropores ($\text{TiO}_2\text{:PS} = 2\text{:}1$). Nonetheless, considering 30% amount of dye is reduced with this level of PS content, it is a cost-over-efficiency effective approach.

Power conversion efficiency (PCE or η) is a result of a combination of changes in V_{oc} , J_{sc} and FF (Figure 4.6). With macropores, PCE increased significantly compared to standard films. PCE according to film thickness generally follows the trend of J_{sc} , that is increasing until its saturation point. The saturation point in this case also appears at a smaller thickness (8-9 μm) with electrolyte diffusion limited system (Z952) compared to less viscous electrolyte Z1130 (12 μm). These optimized values are therefore the reference for devices fabricated for further measurements and studies. The process of making devices with macropores was done exactly as making standard devices with similar yield and re-productibility.

Figure 4.6: PCE with varying thickness and concentration of pores. Full data of the thickness and concentration dependent studies with C218/D205 dyes, Z1026/Z1130/Z952 electrolytes can be found in the appendix.

4.4 Electrolyte

4.4.1 Ionic liquid, gel electrolyte with I^-/I_3^- redox couple

Ionic liquids (ILs) gained the attentions in research since the 1990s with their interesting physiochemical properties that can potentially replace organic solvents in various fields,

such as synthesis, catalysis, electrochemistry applications, etc. [110]. Ionic liquids by definition are salts with melting point around 100°C without the presence of solvent, just cations and anions. With advantages over organic solvent in terms of low vapor pressure, synthetically flexibility, large electrochemical window, non-flammability, thermal and chemical stability and relatively good ionic conductivity, ILs provide promising options for large scale production of DSCs without the concern of packaging cost and environmental friendliness. Quasi-solid state electrolytes are stable liquid or gel-like electrolyte that are promising to replace organic-solvent electrolytes because they can penetrate into the porous TiO₂ films and offer highly stable devices [111]. The main problem with these electrolytes are their high viscosity [7] that hinders the diffusion of redox mediators. Although giving lower efficiency compared to organic solvent based electrolytes due to viscosity, ILs are still important materials as electrolyte solvent because of their non-volatility is suitable for long term stability, robust and elevated temperature applications.

Table 4.3: Photovoltaic performance of devices with D205 dye with Z1130 and Z952 electrolytes, respectively. D18NR-T are standard cells with Dyesol paste, compared to photoanodes made from PS-templated macroporous-mesoporous films with TiO₂:PS = 10:1 and 2:1.

TiO ₂ film	Dye Electrolyte	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T		730.38	14.638	74	7.91
TiO ₂ :PS = 10:1	D205-Z1130	746.58	15.275	73	8.32
TiO ₂ :PS = 2:1		734.40	15.487	74	8.37
D18NR-T		728.01	11.168	75	6.17
TiO ₂ :PS = 10:1	D205-Z952	761.25	11.184	75	6.41
TiO ₂ :PS = 2:1		745.25	11.583	77	6.67

Performance of DSCs using organic solvent (Z1130) and ionic liquid (Z952) is shown in Table 4.3. In both cases, although V_{oc}, J_{sc} and FF of macroporous devices are improved, the current dynamics show that with Z952 electrolyte there is a decay of photocurrent due to limited diffusion of electrolyte at high light intensity (Figure 4.7). The current dynamic graph illustrates the J_{sc} response to a sequence of light on and off at different light intensity. When the cell is illuminated (shutter opens), current rises then it quickly reduces to its steady-state. With Z952, from 0.3 sun, a decay of current is observed as op-

posed to Z1130 electrolyte where the steady current is equal to the initial response current (flat plateau of current within the 5 seconds of illumination). The decay increases with increasing light intensity indicating that this behavior is mainly due to mass transport limitation in a viscous electrolyte system like ionic liquid Z952.

Figure 4.7: Current dynamics of devices made from D205 dye with Z1130 and Z952 electrolytes

To further investigate the macropores effect on the performance of the devices, viscous electrolyte ionic liquid (Z952) is compared to the quasi-solid I^-/I_3^- (Gel1: Z952+SiO₂ 7 nm) electrolyte, where the diffusion through the pores is poor due to their high viscosity. Figure 4.8 shows the photovoltaic performance of devices made with ionic liquid Z952 and gel electrolyte Gel1. Gel1 is formed by mixing Z952 with 7 wt% SiO₂ nanoparticles (7 nm). Z952, the eutectic melt of salts without any organic solvent is viscous in nature, when mixed with SiO₂, it can form gel which makes it much more difficult to diffuse. Therefore in both cases, with and without macropores, using Gel1 results in lower photocurrent compared to its Z952 counterpart. It is suggested that this lower current is attributed to the loss of current at high light intensity as the measurement was done at AM1.5 (air mass 1.5) or 1 sun condition, although unfortunately no data at lower light intensity was tested. When macropores were introduced, J_{sc} increased in both electrolytes by 1.4-1.7 mA/cm^2 . However, as discussed above, the presence of macropores caused the reduction in surface area and usually resulted in higher V_{oc} , which is not observed in this case.

There is a possibility that because D35 dye is known to block recombination between TiO_2 and electrolyte more efficiently than other conventional dyes thanks to its bulky anchor groups [83], the smaller surface area does not show beneficial effect compared to other dyes. Overall, with mesoporous-macroporous mixture in TiO_2 photoanode, PCE increases because of the enhancement in J_{sc} . Further discussion on diffusion of these electrolytes will be presented in Chapter 7.

Figure 4.8: IV curves of devices made of Z952 ionic liquid and gel (Z952 with 7 wt% SiO_2 7 nm particles)

4.4.2 Cobalt electrolytes

Cobalt electrolyte is the alternative to the traditional I^-/I_3^- as it offers higher voltage due to lower redox potential with reference to the Fermi level of TiO_2 . However, cobalt electrolytes suffer from seriously fast back reaction with electron in E_c of TiO_2 , hence bulky steric groups in cobalt complexes are essential to block the recombination which in turn hinders the movement of these ions. Electrolyte DE1, consisting of a bulky cobalt complex $[\text{Co}(\text{dtb})_3]^{3+/2+}$ in a robust solvent 3-methoxypropionitrile (MPN:ACN = 4:1) which has low diffusion coefficient ($5.2 \times 10^{-6} \text{ cm}^2/\text{s}$ for $[\text{Co}(\text{dtb})_3]^{3+/2+}$ in acetonitrile, measured by Feldt *et al.* [83]), is employed to study the improvement in IV performance of cobalt-based electrolyte device when macropores are present. Table 4.4 shows the photovoltaic characteristics of DSCs fabricated from DE1 with standard photoanodes

(Dyesol paste D18NR-T) and with sub-micrometer cavities with $\text{TiO}_2\text{:PS} = 20\text{:}1$ weight ratio paste, film thickness of $4\text{ }\mu\text{m}$.

Figure 4.9: IV curves of devices made from $4\text{ }\mu\text{m}$ films of D18NR-T and PS assisted pastes, with DE1 electrolyte at 0.1 sun, 0.5 sun and 1 sun conditions. Although all devices have comparable current at 0.1 sun, its evolution at 1 sun improves greatly by the choice of photoanode.

Poor FF of DSCs employing DE1 is attributed to the bulky group of di-*tert*-butyl bipyridine in $[\text{Co}(\text{dtb})_3]^{3+/2+}$ and the more viscous nature of MPN solvent causing mass transport limitation. This leads to an increase in the series resistance of the cell and fast recombination for cobalt mediators. Furthermore, J_{sc} of the D18NR-T cells is significantly lower in comparison to those using PS-assisted pastes. FF of the mesoporous-macroporous device with this electrolyte is not higher than the standard ones, and this is understandable as FF is very subjective and dependent on current, and these samples have almost 1.5 times higher J_{sc} than their standard counterparts.

Table 4.4 presents IV data at 10%, 32%, 50%, 63%, 80% and 1 sun condition. At high illumination (1 sun - AM1.5G), concentration of accumulated electrons is high and the requirement of more Co^{2+} supply for regeneration is important. However, when measuring at lower light intensity 10% sun (Figure 4.9), J_{sc} of all presented cells are comparable. It is explained previously that at higher input power, diffusion of electrolyte becomes more critically limiting the current due to high concentration of electrons. From Figure 4.9, it is seen that when sub-micrometer cavities are introduced, they accelerate the diffusion

Table 4.4: IV data of cells made from 4 μm films with and without macro-cavities, using DE1 electrolyte in MPN solvent at different light intensity.

TiO ₂ film	Light intensity	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T TiO ₂ :PS = 20:1	0.1 sun	703.8 709.8	0.835 0.850	61 62	3.56 3.23
D18NR-T TiO ₂ :PS = 20:1	0.32 sun	739.3 755.8	1.467 2.192	61 56	2.08 2.94
D18NR-T TiO ₂ :PS = 20:1	0.5 sun	756.4 774.6	1.795 2.787	60 57	1.59 2.40
D18NR-T TiO ₂ :PS = 20:1	0.63 sun	759.6 778.5	1.96 3.014	60 57	1.41 2.13
D18NR-T TiO ₂ :PS = 20:1	0.8 sun	762.0 780.4	2.197 3.279	59 57	1.24 1.83
D18NR-T TiO ₂ :PS = 20:1	1 sun	762.4 781.7	2.463 3.635	59 57	1.10 1.63

of Co^{3+/2+} species and reduce the loss of photocurrent due to charge accumulation and recombination. This behavior is observed more pronounced in system that suffers from more severe diffusion problem (i.e. MPN-Co(dtb)-DE1) than in low viscosity electrolyte that has smaller size cobalt ions (for example electrolyte containing Co(bpy)^{3+/2+} ions), proving that linearity of the relationship of photocurrent as a function of light intensity depends greatly on the limited diffusion of the electrolyte. More in depth study on mass transport limitation and the comparison between these cobalt electrolytes will be discussed in chapter 7.

4.5 Counter electrode

Counter electrode (CE) of DSCs should have high catalytic property. Graphite is the most simple and low cost material available. Platinum nanoparticles coated on transparent conducting electrode offer higher surface area and is the most commonly used up to date, but it is less competitive in electrolytes other than I⁻/I₃⁻. PEDOT (Poly(3,4-ethylenedioxythiophene)), gold and graphene are alternative materials for this application.

Table 4.5: IV data of cells made from 4 μm films with and without macropores, using DE1 cobalt electrolyte, comparing Pt and PEDOT as counter electrode catalysts.

TiO ₂ film	Counter electrode	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	Pt	822.4	1.730	40	0.576
TiO ₂ :PS = 20:1		825.1	2.626	37	0.805
D18NR-T	PEDOT	762.4	2.463	59	1.10
TiO ₂ :PS = 20:1		781.7	3.635	57	1.63

CE affects FF directly as an unsuitable CE increases sheet resistance and charge transfer resistance R_{CE} between CE and electrolyte. Table 4.5 shows the effect of changing counter electrode from platinized FTO to PEDOT when employing cobalt electrolyte. The FF is increased significantly due to the dramatic increment of charge transfer resistance R_{CE} (first semicircle in the EIS spectra - Figure 4.10). Nevertheless, there is little relation between the choice of CE and the presence of macropores and choosing a proper CE is mainly important for achieving higher PCE. Besides, in terms of analysis it provides more accurate understanding and convenience in measurement. For example, in an electrolyte system with very poor diffusion in combination with poor CE, a high R_{CE} will cause an even more extremely high series resistance, deforming the IV curve and leading to misinterpretation of data. In that case, the EIS spectra, which usually show a third arc as the diffusion resistance, but when R_{CE} is too large, the first arc (R_{CE}) and second arc (R_{rec}) occupy the whole spectra and diffusion resistance cannot be observed. PEDOT is therefore used as CE material with cobalt electrolyte to provide a better efficiency and more accurate analysis.

4.6 Summary and conclusion

In summary, this chapter has introduced us to all major components, possible materials used for each and their influences on the performance of DSC through corresponding IV characteristics. Sub-micrometer cavities used in photoanode to create mesoporous-macroporous mixture film has shown improvement on the efficiency in various systems, based on the particular properties of each material. Organic dyes having high molar extinction coefficient ϵ helps the device maintains its current when dye-loading is lowered

Figure 4.10: EIS spectra of DSCs made of PS-template photoanodes ($\text{TiO}_2\text{:PS} = 20\text{:}1$), D35 and cobalt electrolyte with Pt and PEDOT counter electrodes. The first arc at high frequency represent charge transfer resistance at counter electrode R_{CE} is shown dramatically reduced when PEDOT is used. Measurement performed at 0.65 V voltage bias.

better than ruthenium dye with low ε , and hence, will be used in further study of macrocavities photoanodes. Ionic liquid, gel and cobalt electrolyte show the benefit of having macropores that maintain current density at high light irradiation and improvement of fill factor. These behaviors are not as significant in organic solvent electrolytes. PEDOT is a better counter electrode material for cobalt electrolyte mainly for achieving better PCE. Film thickness is important and needs to be optimized for each dye-electrolyte combination. Overall the devices show optimal performance at 7-10 μm thick films for I^-/I_3^- systems. Pore concentration affects the performance significantly and is worth further investigation. Rather low content of templates ($\text{TiO}_2\text{:PS} = 20\text{:}1$) seem to show the best efficiency due to small loss of dye-loading but decent enhancement of light scattering.

Although PCE is the ultimate goal for a good performing device, it is as well important to understand the fundamental mechanism of a working device and the effect of macropores presence on each internal reaction such as electron recombination at $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface or physical diffusion of ions. Besides, many materials chosen in this thesis have novelty for high stability performance such as ionic liquid, low-cost, environmental friendly such as organic dyes and PEDOT, or are promising materials for high voltage devices such as cobalt electrolyte, despite their efficiency could be lower than some other choices. Because I-V data do not show the direct prove of what happens inside a solar cell when macropores are present, other physical measurements are nec-

essary to investigate several electron transfer processes using electrochemical impedance spectroscopy (EIS), photocurrent and photovoltage transient methods, etc. Based on the IV performance presented in this chapter, we are able to choose certain combinations of dye/electrolyte/CE material and film thickness to carry out more fundamental in depth experiments on the beneficial of macropores via the mentioned techniques on charge recombination and mass transport limitation in DSCs. These studies will be presented in the next chapters.

Chapter 5

Light scattering in mesoporous-macroporous TiO_2 photoanode in Dye-sensitized solar cell

5.1 Background and introduction

Several advances have been accomplished in terms of design of the cell and the development of understanding the structure and property relationship of DSCs leading to record power conversion efficiency. To effectively improve the photovoltaic performance, enhancing sunlight harvesting is one of the most important factors. Designing and engineering the various sensitizer families, such as donor- π -acceptor dyes having high molar extinction coefficient or broader absorption spectrum into the red and near IR region, is an effective strategy. Using co-sensitization and energy-relay dyes are promising methods to harvest a larger portion of the solar spectrum by combining different sensitizers [37,47,112]. Moreover, modifying the structure of the photoanode should also play an important role to improve the light harvesting efficiency of the solar cell. Many nanostructures that provide benefits on light scattering effect, photonic confinement, enhanced plasmonics have been investigated and there are advantages and disadvantages for each structure [54,67,74,113]. Incorporating macropores in the photoanode improves light scattering and consequently the light harvesting while eliminating the additional scattering layer of the film [92,93]. In this chapter, finite-difference time-domain (FDTD) simulation will be presented showing the effect of the size and shape of the scatterers theoretically; followed by experiments

and calculations of mesoporous-macroporous photoanode optical properties.

5.2 Methodology

Generally, Mie theory is applicable for single scatterer [52]. In DSCs, there is a large number of scattering centers available in an extended volume, hence the interaction between scattering fields needs to be taken into account. FDTD simulation was used to understand the effect of multiple scattering when sub-micrometer scattering voids are present in the photoanode. The impact of the morphology of the scatterer on scattering cross section was also studied for better understanding in our application.

Optical properties of the mesoporous-macroporous mixed TiO_2 films were studied by measuring transmission and reflection of bare films and after sensitized with several dyes of choice. Pore concentration and pore size were also investigated. Devices fabricated according to these conditions were used for IPCE (incident-photon-to-current efficiency) measurement.

5.2.1 FDTD simulation set-up

A numerical analysis was carried out to investigate the effect of size and shape of macropores on the scattering behavior of light. The experimental study shown earlier in Chapter 3 indicated that the choice of templating agents determined the size and shape of macropores dramatically, even though they had similar diameters initially. When PS was used as the template, the decomposition of PS happens together with the evaporation of other organic materials present in the paste and the resulting macropores become ellipsoidal when the pores collapsed slightly; whereas ZnO template resulted in a more spherical shape of pores. Since scattering occurs when the size of the scatterers is comparable to the wavelength of incident light, it is necessary to study the effect of size and shape on the scattering in a TiO_2 film. In practice, the shape of macropores can be slightly irregular and not perfectly spherical as they are surrounded by nanoparticles.

The finite-difference time-domain (FDTD) is a numerical method for solving the time-domain Maxwell's equation for spatio-temporal evolution of electric and magnetic (E and

Figure 5.1: FDTD simulation setup showing: scattering center as a core-shell object with refractive indices of the core and shell were the indices of acetonitrile and TiO_2 ; the FDTD simulation region, monitors, light source and mesh.

M) fields [114]. Detail explanations of FDTD simulations can be found in the literature, and many softwares are available to apply this method via a user-friendly interface that allows the creation of structures and variation in material properties to expand the theoretical analysis of device architectures [115,116]. FDTD uses electromagnetic simulation that can predict the enhanced optical responses over the considered spectral range of various materials (when materials properties such as permittivity (ϵ) and permeability (μ) values are available).

The simulation model was created in a three-dimension environment using a commercial-grade simulator based on the FDTD method to perform the calculations, known as *Lumerical* (<http://www.lumerical.com/tcad-products/fdtd/>). The macropores filled with electrolyte and the TiO_2 nanoparticles surrounding were represented as core-shell objects. The core had an ellipsoidal shape which had radii defined in three dimensions - R_x , R_y and R_z , and the refractive index used was similar to that of acetonitrile (1.3460) - which is the common solvent used in electrolyte. The shell was made of TiO_2 with constant thickness of 20 nm. The refractive index of the background was again the refractive index of acetonitrile. The light source used was a total-field scattered-field (TFSF) source, which allows the separation of the light scattering component and the incident component. The

TFSF light source sets a boundary which has the ability to “absorb” the incident wave, hence separated the computation region into two regions: one inside the boundary included the sum of the incident plane wave plus the scattered field - was called the “Total Field” region, and the other outside the border only included the scattered field (known as the “Scattered Field” region). Three-dimensional view of the simulation is shown in Figure 5.1. The light source was injected along the y-axis. Several monitors were set up to record electromagnetic fields in the environment. A set of power monitors (8) forming total transmission monitors surrounding the region of interest was set smaller than the size of light source - to record only transmitted light. A similar set of monitors was set outside the TFSF light source boundary to record only the scattered fields. Another two power monitors were set one along the y-axis and one perpendicular to it to give additional information. The mesh was used to increase accuracy of simulation region on the critical interfaces.

In order to transform the shape of a sphere to an ellipsoid (the case when template was changed from ZnO to PS in practice), the radius in the direction parallel to the injected incident light direction was varied. The variation in radius, R_y , is shown in schematic illustration in Figure 5.2a. As the interaction between the scattered fields was of interest, it is worth noting that when R_y decreased, the total volume displaced by voids was decreased and the distance between scatterers increased. Therefore, it is important to also investigate the situation where the number of scatterers was increased, to ensure similar volume displacement, i.e. porosity, in all cases. A schematic example was illustrated in Figure 5.2b.

5.2.2 Optical properties measurement and IPCE

To study the optical properties, both the transmission and the reflection of TiO_2 films on FTO-glass substrates were measured in an integrating sphere incorporated in a UV-Vis spectrophotometer. To prepare for this measurement, 3 μm thick films were screen-printed on clean- TiCl_4 treated FTO substrates and soaked in respective dye solutions before experiments. This film thickness was chosen to ensure the films are mechanically stable (because ZnO-templated films had poorer adhesion to the FTO substrate, as mentioned in Chapter 3) and avoid artifact scattering from imperfection due to experiment

Figure 5.2: Setting up of scattering centers in FDTD simulation. (a) Varying of radius R_y (parallel to the injection direction). When R_y decreased, the shape of a sphere transformed to an ellipsoid. (b) Multiple scatterers: R_y decreased to transform the spherical scatterers to ellipsoids. Because volume of each scatterer decreased as R_y decreased, the total volume displaced by pores was reduced. (c) To increase the volume of pores, the number of ellipsoidal scatterers was increased.

error when screen printing a thick film. An anti-reflecting (AR) film was applied on the front glass so that the incident light would pass through the AR film first, then the glass, the FTO, and the TiO_2 layer. The film structure and position of sample in the integrating sphere is shown in Figure 5.3.

Figure 5.3: Diagram of an integrating sphere and how sample was placed to obtain diffuse and total transmission and reflection.

Spectral current response of macropores in real devices was investigated by measuring the IPCE. When measuring IPCE, monochromatic light was used to illuminate the device and the current was measured at short-circuit condition. However, DSCs have been known to have relatively slow response because of the low electron mobility in the mesoporous

network of TiO_2 photoanode, hence IPCE should instead be evaluated considering effect of light intensity. Hishikawa *et al.* had reported that measured IPCE spectra was affected by chopping frequency as it increases when chopping frequency decreases [117]. Therefore, it was suggested that DSC should be measured in low chopping alternating current (AC) mode (1-2 Hz) or in direct current (DC) mode. Due to large number of electron traps present in TiO_2 , bias irradiation was recommended to fill the traps and improve the response of device to obtain more accurate result.

5.3 Results and discussion

FDTD simulations provided information that allowed the prediction of the scattering behavior as a function of structure where the shape of pores changed from spherical to ellipsoidal and the pore size varied. Experiment data and simulation results are presented to show the effect of pore concentration, pore size and shape, and spectral aspect of dyes and pore size combination.

5.3.1 Simulated scattering behavior using FDTD method

Scattering field surrounding a single scatterer was investigated. Light source was injected along the y-axis and the radius of scatterer parallel to that direction, R_y , was varied from 250 nm (when scatterer was a perfect sphere $R_x = R_y = R_z = 250$ nm) to 50 nm (while keeping $R_x = R_z = 250$ nm). The scattering cross section from a single scattering center was recorded by the installed monitors and this is shown in Figure 5.4. The scattering cross section decreased with reducing R_y as predicted by Mie in the case of perfect sphere [52]. More importantly, the scattering cross-section increased gradually for increasing R_y for most of the wavelengths in the studied range, with a small red-shift. The red-shift indicates that scattering became stronger at longer wavelength, especially from 500 nm onward as R_y increased.

To study multiple scattering, nine scatterers were used to imitate the distribution of macropores in the films. The scatterers were arranged in non-close packed BCC positions (body-centered cubic) with the distance between them to be at least $4 \times R$ (with $R =$

Figure 5.4: FDTD simulated scattering cross-section of a single scatterer, with varying radius R_y . As R_y decreased, the scatterer transformed from a sphere ($R_y = 250$ nm) to an ellipsoid ($R_y < 250$ nm) and the scattering cross section decreased. The simulation is based on structure illustrated in Figure 5.2a.

Figure 5.5: Scattering cross-section of multiple scatterers reduced when R_y reduced from 250 nm (sphere) to $R_y < 250$ nm (ellipsoid). The simulation is based on structure illustrated in Figure 5.2b.

$R_x = R_z = R_{y(max)}$) to ensure the scatterers were not touching each other, but closed enough for the scattered fields to interact. The trend of scattering cross section from multiple scatterers resembled that of single scattering center, nevertheless, the red-shift in the spectra when R_y increased is more significant (Figure 5.5). The scattering cross section was reduced significantly when R_y was smaller than 175 nm.

However, question arose that when R_y reduced, would the reducing volume displacement of the TiO_2 nanoparticles by macropores (V_{pore}/V_{total}) affect light scattering? In other words, when R_y reduced, the distance between scattering centers increased, since scattered light interacts, would this distance affect the scattering behavior of the films? To answer this question, it was essential to take into account the fact that when the scatterers changed from a sphere into an ellipsoid as one dimension, R_y , was reduced, the changes of volume displaced by macropores of these films should be reserved. We simulated the case of increasing the number of ellipsoidal scatterers per unit volume of simulation region (while ensuring the distance between two scatterers remained more than $2 \times R$ to avoid contacting between them), the porous volume created by macropores V_{pore}/V_{total} would increase from 5.8% to 11% (fixing $R_y = 132$ nm, $R_x = R_z = 250$ nm). The green curves in Figure 5.6 show that with increasing porosity (or increasing number of scatterers and reducing the distance between them), the scattering cross section increased. On the other hand, another simulation was run with $V_{pore}/V_{total} = 11\%$ with spherical pores of 250 nm radius ($R_x = R_y = R_z = 250$ nm) is illustrated as the red curve in Figure 5.6. Interestingly, although having more spherical shape, the red curve had lower scattering cross section at the 600-700 nm range compared to ellipsoidal scatterers of the same porosity (dark green curve). This simulation showed that, not only the size of scatterers is important, but the number of scatterers per unit volume that causes interaction between the scattering fields also plays a critical role in the overall scattering cross section.

This result indicated that when the macropores were templated by PS beads and collapsed into ellipsoidal shape during sintering, the resulting light scattering intensity may not be affected as long as the quantity and distance between scattering centers were sufficient. Fortunately, PS-assisted films had comparatively better mechanical strength than ZnO-assisted films, allowing higher “doping” concentration of the template particles.

Figure 5.6: Scattering cross-section of multiple scatterers with increasing porous volumes by increasing number of scattering centers while keeping the dimension of the scatterers constant ($R_x = R_z = 250$ nm, $R_y = 132$ nm). Scattering cross section σ_{scat} increased with increasing porous volume. The red curve is the simulated result with perfect sphere ($R_x = R_y = R_z = 250$ nm) and equivalent porosity with darkest green curve. With similar porous volume, the ellipsoidal pores scattered light as strongly as the spherical pores. The simulation is based on structure illustrated in Figure 5.2c.

Therefore, due to multiple scattering, PS-templated film would perform as well as ZnO-templated film although the pores of the former films were less spherical.

5.3.2 Measured light scattering behavior

When macropores were introduced in the TiO_2 film, they scattered and reflected light, giving the films a more translucent and opaque appearance compared to the transparent mesoporous film with 20 nm particles. In this section, the effect of the pore concentration and the size will be discussed, based on the optical measurement and the corresponding photovoltaic characteristics.

Effect of macropore concentration

Concentration of pores was investigated by varying weight ratio of PS template from $\text{TiO}_2\text{:PS} = 20\text{:}1$ to $10\text{:}1$ and $2\text{:}1$. When 500 nm PS particles were used, the pores collapsed

during sintering, resulting in pore size of *ca.* 500 nm in the lateral dimension and *ca.* 200 nm in the vertical direction. When pore concentration increases, total transmission was observed to reduce while the total reflection increases.

Figure 5.7: Transmission (a) and reflection (b) of TiO₂ films with varying pores concentration using PS as template. Closed symbols are total transmission(reflection). Open symbols are diffuse transmission (or reflection).

When concentration of PS increased from TiO₂:PS = 20:1 (red line) to 10:1 (green line), the transmission reduced while the reflection increased dramatically. The difference between the TiO₂:PS = 10:1 film and 2:1 film (green *and* blue line) as compared to standard sample (D18NR-T, without macropores) and 20:1 film (black *and* red line) was much smaller (Figure 5.7). Both the diffuse transmission and diffuse reflection (open symbols) increased with increasing macropores concentration. As a result, the specular transmission and reflection (difference between total and diffuse transmission/reflection) reduced significantly when the amount of PS reached 10% (TiO₂:PS = 10:1), and remained unchanged when the amount of PS increased higher (TiO₂:PS = 2:1). This suggests that the intensity of scattering saturated at around TiO₂:PS = 10:1. Beyond that, further increase in PS concentration reduced the transmission through the film while scattering was not improved. This trend was similar to the trend observed in the binary system containing two nanoparticle sizes (see Literature review in Chapter 2) reported by Ferber *et al.* [55]. Ferber mentioned that with too many scatterers, there was too much back-scattering and the internal surface area was decreased, resulting in higher reflectance but

not absorbance.

The diffused transmission and reflection of control sample (D18NR-T) and TiO_2 :PS = 20:1 sample (black and red - open symbols, Figure 5.7) peaked at 400-420 nm while the other two remained constant from 400 nm at more than 50% transmission (>30% reflection) and increased gently a longer wavelength (600 nm). This trend shows that higher concentration of macropores made the scattering become less wavelength selective as compared to the lower concentration. Besides, the scattering of higher pore concentration was better at the longer wavelength. Since TiO_2 absorbs very few photons in the visible light range, the effect of scattering on absorption only is better to be considered when dye covers the surface of TiO_2 . The scattered light increased the pathway of the photons and gave more opportunity for dye molecules to be able to capture a photon.

Figure 5.8: Calculated extinction of TiO_2 films sensitized with D205 dye with varying pores concentration using PS as template.

To study the scattering behavior in the presence of dye, the films with varying concentration of macropores were soaked in D205 dye solution (Figure 5.8) for measurement in the integrating sphere. The extinction can be calculated by using the following equation:

$$\text{Extinction} = 1 - \text{Transmittance} - \text{Reflectance} \quad (5.1)$$

From the calculated extinction value, a red shift in the absorption peak was observed at high concentration of macropores (from TiO_2 :PS = 10:1 onwards) (Figure 5.8c). The peak plateau of the absorption appeared at around 500-600 nm. With small amount

of macropores, the surface area was not reduced significantly but scattering effect was already quite significant, the red curve could be seen broader than the other three curves over the measured spectrum. With higher porosity, total surface area and hence dye-loading was reduced leading to a lower peak at 550 nm. On the other hand, absorption of film sensitized with D205 dyes was broaden at the red range (>600 nm). As the radiation of solar spectrum in this region was higher compared to 300-400 nm region, this increment in the absorption contributed more to the corresponding photocurrent.

Figure 5.9: IPCE of devices fabricated with of TiO_2 films with varying pores concentration using PS as template and D205 dye in combination with Z952 and Z1130 electrolytes, showing the improvement from 640 nm onward.

DSCs were fabricated with D205 and two electrolytes (ionic liquid Z952 and acetonitrile-based Z1130). In both cases, higher IPCE can be observed for wavelengths longer than 600 nm. As the surface area was reduced dramatically with $\text{TiO}_2:\text{PS} = 2:1$ film, the amount of dye-loading was reduced by 30% (see Chapter 3). Even with such drastic reduction in dye loading, the peak of IPCE was still comparable to that of D18NR-T paste. For Z952 electrolyte (Figure 5.9a), the blue curve had a deeper valley at 430 nm leading to the corresponding slight decrease in J_{sc} of this sample compared to control sample (11.8 vs. 12.1 mA/cm^2). This deep valley could be attributed to stronger light absorption of high concentration of I_2 in ionic liquid.

The red shift of IPCE spectra was also measured with C101 (ruthenium based) dye which has a broader absorption spectrum extending into the red region and lower molar

Figure 5.10: IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with C101 dye and Z952 ionic liquid electrolyte.

Table 5.1: Photovoltaic performance of devices with C101 dye with Z952 electrolyte. Film thickness 6-7 μm .

TiO ₂ film	Dye Electrolyte	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	C101-Z952	694.25	11.960	74	6.19
TiO ₂ :PS = 20:1		699.98	12.082	75	6.37
TiO ₂ :PS = 10:1		716.69	12.378	75	6.66
TiO ₂ :PS = 2:1		712.34	11.644	76	6.32

extinction coefficient. Due to the lower molar extinction coefficient, the effect of lower surface area was more significant because the increment due to increasing light scattering effect could not compensate with lower dye loading. Hence the blue curve with highest pore concentration was seen lower than the control sample (black curve). With lower concentration of macropores (green curve), the IPCE was broadened towards red region while the green-blue region was still maintained (400-500 nm). J_{sc} of this device was also the highest. Therefore, TiO₂:PS = 10:1 was the optimized content to create the optimal pore concentration for J_{sc} enhancement. As the macropores concentration increased, the surface area was reduced significantly while the scattering was not increased considerably, while any lower amount of PS (20:1 ratio) showed poorer scattering effect.

Effect of thickness

Figure 5.11: IPCE of DSCs made with increasing thickness made with standard film D18NR-T and TiO₂:PS = 20:1 templates. Devices are fabricated with C106 dye and acetonitrile-based electrolyte.

IPCE of devices made from PS-templated films with varying thickness was compared to the standard film D18NR-T with C106 dye - a ruthenium based dye that has a broad absorption spectrum. The IPCE increased with thickness and the presence of scattering macropores. This increase was seen in most samples, but more significant with the thicker films (10.9 μm).

The improvement in the photocurrent, J_{sc} , depends greatly on the thickness of TiO₂ layer not only electrically (as electron transport through TiO₂ network and ions diffuse in the electrolyte that was percolated in the porous media) but also optically because dyes are attached on the TiO₂ surface. As more dyes are adsorbed with increasing TiO₂ thickness, the IPCE does not increase linearly throughout the absorption spectrum. It has been discussed that photons at longer wavelengths where dye absorbs weakly can

penetrate further into the film before it is captured, hence thicker films and longer optical depth are required [91]; while photons at shorter wavelength and higher energy can be captured at the very first layer. Therefore, Kang *et al.* reported that with N719 dye, the enhancement of J_{sc} at 640 nm with increasing film thickness was larger than at the peak of the absorption spectrum which occurs at 410 and 540 nm.

Figure 5.12: IPCE values at 400, 500 and 600 nm versus TiO_2 thickness showing that enhancement of IPCE at 600 nm was greater than at 400 nm. The improvement by light scattering voids at 600 nm was also better than at 400 nm.

Similar effect was observed in our experiments with C106 dye (Figure 5.12). Because the dye absorbs poorly at the longer wavelength (600 nm and above), it requires longer optical depth to increase the absorbance, hence the influence of additional photon path length gained by light scattering was more significant. Nevertheless, if the dye absorbs poorly in the shorter wavelength, this increase in J_{sc} due to scattering effect may not be as significant. It is because photons of higher energy only needed to penetrate shortly into the TiO_2 layer before being easily absorbed by dye molecules.

Relationship between macropore size and dye using ZnO as template

To understand the effect of changing pore size of the sub-micrometer pores in TiO_2 photoanode, ZnO was used as template. The reason for choosing this material instead of PS was because after the removal of ZnO, the macropores left behind were more spherically-shaped compared to PS. Therefore, the dimension factor was more symmetric and could be interpreted to be dependent on one parameter of dimension instead of two

or three. However, because the weight ratio of $\text{TiO}_2\text{:ZnO}$ was fixed to 10:3 (and therefore assuming the total void displacement volume was fixed), unfortunately the number of scatterers also varied as the pore size changed. Furthermore, the scattering behavior of a more spherical scatterer can be better defined by Mie theory [52]. It is worth mentioning that Mie scattering is also most applicable to single scattering event, hence low concentration of scatterers make it clearer to understand the Mie theory as scattering centers are sufficiently separated away from each other.

Figure 5.13: Transmission (a) and reflection (b) of TiO_2 films with varying macropores size using ZnO as template. Closed symbols are total transmission (reflection). Open symbols are diffuse transmission (or reflection).

Figure 5.13 shows the transmission and reflection of the films with varying macropores size. With increasing pore size, the total transmittance decreased and reflectance increased despite the concentration of scatterers was reduced. The diffuse transmission of 170 nm macropores film (green line) had a relatively sharp peak at $\lambda = 385$ nm, when the macropores size increased to 380 nm, the diffuse transmission peaked at 405 nm and became a very broad spectrum that peaked at 470 nm when macropores were of 500 nm. As predicted from Mie theory, as pore size increases, the wavelength being scattered also increases.

Transmission and reflection for films with varying pore size templated by ZnO particles, sensitized with D35 dye were also measured and the extinction was calculated (Figure 5.14a). The extinction spectra show that the absorption was broaden from 550

nm onward in the presence of macropores and increased with increasing pore size. However, the corresponding IPCE of the devices made using these films (Figure 5.14b) showed that with 170 nm pores, IPCE was not higher at the longer wavelength (> 500 nm). The best IPCE was observed with 380 nm pore size, which peaked at similar efficiency as standard sample, but had a significant increment from 500 nm onward. When pore size is 500 nm, instead of getting broader, the peak red-shifted and the IPCE was lower than standard sample at the 400-500 nm range but higher from the 500-650 nm range.

Figure 5.14: (a) Calculated extinction of films sensitized with D35 dye. (b) IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with D35 dye and Z952 ionic liquid electrolyte

D205 dye was used successfully with PS-templated films as presented in the previous section. It was also used in combination with ZnO-assisted photoanodes with varying macropore sizes. The dye loading experiment was discussed in Chapter 3. ZnO - assisted sample with 500 nm macropores had the lowest dye-loading (14% lower than standard D18NR-T), followed by 170 nm, 380 nm pores, and the standard sample still had the highest dye-loading. Although the calculated extinction showed similar spectra to the PS-templated films, IPCE of the resulting devices were lower than the standard film (Figure 5.15b). The normalized IPCE of the ZnO-assisted devices were not broader than the standard sample either. This result was unexpected because D205 dye had been employed previously for even lower dye-loading films where $\text{TiO}_2\text{:PS} = 2\text{:}1$ and the IPCE was slightly lower yet broader than the standard sample, hence the observation

must be the effect of the different templates (Figure 5.9). Two possible explanations can be considered. Firstly, optically, the light in a ZnO-templated film was scattered in all angles, as the macropores are more spherical. Therefore, the scattered photons had more probability to escape the film, especially from the side, before being absorbed. In the ellipsoidal pore films templated by PS, the scattering was anisotropic, hence this effect was not as significant. Secondly, Zn compounds might not have been completely removed from the ZnO-assisted films. D205 has been known to have dye aggregation problems [104], hence the possible Zn leftover in the film may result in either more dye aggregation or dye desorption. Furthermore, Zn-compounds present in certain quantity, they decelerate the charge transport due to mismatch in the crystal structure and band energy, although this speculation may be less likely since Zn - if not removed - will be present in very small quantity.

Figure 5.15: (a) Extinction; (b) measured and normalized IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with D205 dye, Z952 electrolyte.

Further study was carried out using a dye with a broader absorption spectra but has lower molar extinction coefficient, such as C106 (ruthenium-based) absorbed on a thin film of TiO_2 (3 μm). Since C106 had lower molar extinction coefficient, when coupling with a thin TiO_2 layer, the loss of dye-loading become more noticeable. For a thin film, the IPCE at the larger wavelength was extremely poor (Figure 5.12). Nonetheless, increment with 380 nm pore size was still observed in this experiment, while 500 nm

and 170 nm pore size showed lower IPCE than the standard sample (Figure 5.16). The trend of IPCE with pore size 380 nm better than 500 nm pores and 170 nm pores was in agreement with the devices using D35 dye. Because IPCE of devices with low extinction coefficient dye is highly dependent on thickness, it is expected that the scattering effect may contribute more significantly with a thicker film.

Figure 5.16: IPCE of DSCs made with varying pore size made with ZnO templates. Devices were fabricated with C106 dye and acetonitrile-based Z960 electrolyte. Films thickness is 3 μm .

SQ2 is an unsymmetrical squaraine dye attracting research interest because of its small optical band gap, high molar absorption coefficient and the intense absorption in the far-red region. It was chosen for the investigation of the effect of macropores on the scattering behavior when the absorption spectral of the dye covers more of the red than in the blue region. The extinction spectra calculated by measuring transmittance and reflectance is shown in Figure 5.17 with the IPCE of devices made from similar films. The extinction is a combination of absorption and scattering, and because SQ2 dye only absorbs light in a rather narrow peak from 550 to less than 700 nm, the calculated extinction showing high scattering in the 400-550 nm region. The resulting IPCE shows that improvement in scattering in 400-500 nm did not lead to increasing photocurrent. On the contrary, the IPCE of ZnO-assisted devices in this region was lower than the standard sample. On the other hand, the IPCE peak at 590 nm increased, especially with 380 nm and 170 nm macropores. It is important to emphasize that the ZnO-templated films had lower dye loading than D18NR-T, yet exhibited better photocurrent response. Device with 500 nm

macropores displays unexpectedly lower current compared to the other cells. Although 500 nm ZnO-assisted film showed the lowest dye-loading in Chapter 3, this low current could also arise from the strong side and back scattering of this film.

Figure 5.17: IPCE of DSCs made with varying pore size using ZnO templates. Devices were fabricated with SQ2 dye and acetonitrile-based electrolyte.

5.4 Summary

In summary, voids created by templates such as PS or ZnO follow Mie scattering theory or its extension cases [57]. ZnO produced more spherical scattering centers, hence could provide more uniform information in terms of dimension-dependent according to Mie theory. Moreover, the interaction of scattering field and distance between scattering centers has to be taken into account. According to Beer-Lambert law, light harvesting is dependent on the molar extinction coefficient of the dye, dye concentration and optical path length. Molar extinction coefficients of dyes used in this set of experiments are presented in Table 5.2.

The FDTD simulation provided an accessible technique to predict the scattering cross section of scatterers with varying dimensions and concentrations. The simulation result revealed that despite the scattering cross section decreased dramatically when one of the dimensions reduced to transform a sphere into an ellipsoid in case of single scattering center, with multiple scatterers of sufficient distance from each other, scattering cross

Table 5.2: Molar extinction coefficient of dyes used in the experiments

Dye	$\epsilon/10^4$ $M^{-1} \times cm^{-1}$	λ nm	Ref.
C106	1.87	550	[81]
D35	2.86	463	[83]
SQ2	3.19	662	[118]
D205	7.47	554	[104]

section could be reserved. Therefore, the collapsing of macropores forming ellipsoidal scatterers in PS-templated films might not interfere the effect of light scattering.

When PS was employed to create macropores, light scattering and optical thickness improvement of mesoporous-macroporous films were proven by the increasing diffuse transmission and diffuse reflection. Corresponding IPCE was much dependent on film thickness, as IPCE of the devices were non-linear in relation to film thickness at different wavelengths. More significant improvement was shown with longer wavelength as film thickness increased. This was the reason behind using large macropores aiming to improve the long wavelength range which benefits more on the increment of optical thickness.

Figure 5.18: Optical depth of films created by (a) PS and (b) ZnO as templating agents.

ZnO-templated films had rather disappointing performance in terms of IPCE despite the optical properties comparable to PS-assisted films. As comparing optical depth, it is

Figure 5.19: Schematic diagram suggesting that with long wavelength photons (red lines), scattering by spherical macropores is too strong that losses on the side of films become dominating, while ellipsoidal pores have anisotropic light scattering, weaker in the direction perpendicular to injection plane, hence lower loss.

noted that ZnO-templated films had shorter optical depth due to its smaller concentration. On the other hand, because IPCE of ZnO-templated devices were improved with D35 and SQ2 dyes, but not with D205 dye which has higher ϵ , the lower dye-loading may not be the most influencing characteristic. Both D205 and C106 dyes, which suffer from decreasing IPCE with ZnO-templated films, have absorption spectra peaking at 550-554 nm. The strong scattering photons in these wavelengths from spherical pores templated by ZnO had escaped the film was the reason for low IPCE. Low IPCE spectra of SQ2 dye with 500 nm ZnO template further showed that large scatterers do not favor absorption despite high extinction. Due to the changes of scatterer shape, it is possible that the ellipsoids may scatter light anisotropically in the direction contained within the film while spherical voids scatterer light to the outer direction.

Overall, ZnO-templated films with 380 nm pore size was the most suitable spherical macropores to be incorporated in photoanode among the investigated sizes, as well as PS template with concentration of $\text{TiO}_2\text{:PS} = 10\text{:}1$. Both of these films have good balance of light scattering with desired wavelength range and moderate loss of dye-loading. The experiment results also agree with simulation that collapsed pores of ellipsoidal shape did not affect light scattering as long as concentration of scatterers was sufficient. Besides, the anisotropic scattering direction due to non-spherical shape might drive the scattered photons inward direction instead of escaping the film on the sides. In other words,

scattering in lateral direction (perpendicular to injection plane) of ellipsoidal scatterers are weaker, the number of photons being scattered and escaped to the side of films was reduced.

Chapter 6

Electron recombination in DSCs with sub-micrometer cavities

6.1 Background and introduction

One important characteristic that differentiates DSC from the other solar cells is that in DSC, two processes are separated: light absorption is carried out by the sensitizer and the charge carrier transport by the semiconductor oxide. When the sensitizer absorbs a photon, an electron is excited to its LUMO level and then injected in to the conduction band of semiconductor oxide (TiO_2) (Figure 6.1). The electron is transported through the TiO_2 network until it reaches the FTO electrode. To regenerate the oxidized dye, the reducing species in the redox couple needs to donate the electrons and hence become oxidized. The oxidized agent then travels to the counter electrode where charge transfer occurs. Direct recombination can happen when the excited electron in the LUMO level of the dye decays down to its HOMO level before injection occurs. The TiO_2 /dye/electrolyte interface is where the recombination between injected electrons and dye cations or with oxidized form of redox shuttle (I_3^- or Co^{3+}) occurs. Nanocrystalline materials such as TiO_2 nanoparticles in the photoanode of DSC have high surface area and the electronic disorder of metal oxide is associated with high density of sub-band gap trap states [119]. The sub-band gap trap states cause electronic loss mechanism closely associated with the trapping and detrapping process of electrons in the TiO_2 surface states. When electrons are injected, not all of them stay freely in the conduction band of TiO_2 , instead some of them go through a series of trapping and releasing from exponentially distributed sub-

band gap states. The trapped electrons in the bulk of nanoparticle cannot participate in any forward or backward reaction (that is electron diffusion or recombination). The concentration of free electrons in conduction band and therefore the electron lifetimes are modulated by the trap states.

Figure 6.1: Schematic diagram illustrating electron-charge transfer processes in DSC. The recombination and trapping processes are highlighted in blue color.

Electron recombination affects V_{oc} of the device directly. Photovoltage is defined as the difference between electron quasi-Fermi level of TiO_2 and the redox potential in electrolyte. In dark, the Fermi level equilibrates with the redox potential. Under illumination, the concentration of electrons in TiO_2 increases causing a rise in the Fermi level and the accumulated charges define the open circuit voltage. The level to which Fermi level increases depends on the balance between electron injection and electron transfer to the oxidized dye and the oxidized form of the redox couple [43]. The recombination occurs on the surface of TiO_2 , hence exposure of semiconductor surface to electrolyte should be minimized. Recombination can also influence J_{sc} of the device as it causes a loss of photo-electron. Increasing of FF can be attributed to the reduction in recombination.

To improve DSCs performance electronically, several methods have been attempted. First of all, changing the intrinsic properties of the materials, and using materials with higher electron mobility material than TiO_2 , such as ZnO , SnO_2 , have been explored.

It was believed that with better electron conductivity, the charge transport of electron in the semiconductor oxide will be faster and eventually increases the charge collection efficiency. However, recent studies show that the charge collection efficiency in I^-/I_3^- system is high enough (99%) or in other words, charge transport is fast enough and since the diffusion length in TiO_2 can be up to 70-90 μm , these changes would not make much difference [30, 31, 120]. The same conclusion can be drawn for other one-dimensional nanostructures such as nanorods, nanowires or nanofibres which were thought to improve the charge transport by reducing inter-particle hopping. The charge transport in DSC is proven to follow a “random walk” model and does not depend on any electric field [43, 75].

The second approach to minimize electronic losses in DSCs is by reducing charge recombination. Beside excited electrons that decay directly to the HOMO level of the dye, most recombination occurs between injected electron and oxidized dye or with the electrolyte. To prevent this recombination, it is important to engineer anchor groups in the dye or the redox mediator that can block this back reaction [121]. It is crucial that the coverage of dye on TiO_2 surface is completed to prevent exposure of TiO_2 to the electrolyte. On the other hand, large surface area leads to more probability of electron meeting “hole” and recombination occurs. Hence, one of the strategy to reduce loss is to reduce the available recombination sites by smaller surface area. This eventually leads to lower dye-loading, so a certain extent of optimization is necessary.

In this chapter, we will discuss the parameters to study the recombination processes in DSC employing mesoporous-macroporous photoanode, mostly on e_{TiO_2} - electrolyte reaction and the methods to measure them. The crystallinity or intrinsic property of TiO_2 particles is assumed unchanged with the introduction of macropores. Charge recombination can be altered due to the changes in surface area and concentration of redox couples around the TiO_2 surface. To explain these effects, electron lifetime, chemical capacitance and recombination resistance, etc. were investigated by measuring the photovoltage and the photocurrent transient, intensity-modulated photovoltage/photocurrent spectroscopy (IMVS/IMPS) and electrochemical impedance spectroscopy (EIS). By using these techniques, recombination resistance (R_{rec}) and electron lifetime (τ_n) reveal how difficult recombination occurs and how long electrons can stay in the conduction band of TiO_2 before recombine.

6.2 Characterization methods

In this section, photoelectrochemical and electrochemical techniques are introduced for characterization of electron recombination in DSCs.

6.2.1 Photoelectrochemical methods

Photocurrent and photovoltage transient

Photocurrent and photovoltage transient is one of the time-dependent techniques to determine the time scale of electron transport and recombination. In this method, the devices are superimposed by a white light illumination and a flashing pulse perturbation (red, green or blue) is applied. A bias voltage of magnitude exactly equal to the photovoltage generated from the white light is applied on the cell, making the Fermi level within the cell to be similar to open-circuit condition which is flat at different light intensity. When the short pulse is irradiated, extra electrons are injected and the Fermi level is shifted up. Photovoltage decay is measured at open-circuit so that all the injected electrons can only recombine in the system and there is no net current flow to the external circuit and the decay time constant is determined by a single pseudo-exponential fitting. For photocurrent, same pulse intensity is applied under short circuit condition, electrons can flow to the external circuit and we can calculate the charges generated from the short pulse [122, 123].

The chemical capacitance C_μ represents the capability to store charges [124]:

$$C_\mu = \frac{\Delta Q}{\Delta V} \quad (6.1)$$

where ΔV is the peak height of the transient voltage and ΔQ is the number of charges integrated from the transient photocurrent decay at short-circuit conditions. At certain V_{oc} , the capacitance is proportional to the density of trap states (*DOS*) at the corresponding Fermi level, therefore *DOS* distribution can be mapped out by the following

equation [125]:

$$DOS = \frac{C_\mu}{1.6 \times 10^{-19} d (1 - p)} \quad (6.2)$$

where d is thickness and p is the porosity of the film. Electron lifetime is obtained by measuring voltage decay at open-circuit condition when the device is illuminated by a white light for a certain time to a steady voltage and then switched off. The interval of the measurement is typically in a logarithmic scale, ranging from 100 μs to seconds. The measured data is then fitted by a quadruple exponential model and then differentiated against time. The apparent electron lifetime τ_n is calculated by [39]:

$$\tau_n = -\frac{k_B T}{q} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (6.3)$$

where k_B is the Boltzman's constant and T is the absolute temperature. From this information, one can expect to understand the recombination processes and electron trappings in the film and how they vary when large cavities were introduced into the conventional structures of the TiO_2 network.

Intensity-modulated voltage/photocurrent spectroscopy techniques (IMVS/IMPS)

As direct current (DC) techniques cannot provide sufficient information about the charge dynamics in DSCs, additional information should be measured with a time and frequency dependent method. DSC responds non-linearly in terms of electron recombination and transport as a function of illumination intensity. Studying the device under superimposed bias light, with a small amplitude alternating current (AC) perturbation of light intensity at varying frequency on top of that, provides more information about the device at its working condition. Rapid modulation of light intensity is obtained using light-emitting diodes (LEDs) controlled by a driver connected to a potentiostat (Autolab PGSTAT302N with FRA2 module). In IMPS, the device is illuminated under a sinusoidal modulated light and AC current response is recorded as a function of modulation frequency by a phase-sensitive detector. In IMVS, the transfer function between the modulated light and the corresponding photovoltage is measured. The characteristic response time of

photovoltage corresponds to the electron lifetime, τ_n [11].

The analysis of IMPS determines a time constant for photocurrent response τ_{pc} , which is dependent on electron transport and electron recombination.

$$\frac{1}{\tau_{pc}} = \frac{1}{\tau_{tr}} + \frac{1}{\tau_n} \quad (6.4)$$

where τ_{tr} and τ_n are the electron transport time and electron lifetime, respectively, will be retrieved by combining the two techniques [126].

6.2.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a very powerful technique to study systems with complicated interfaces like DSCs. In DSCs, TiO_2 is in contact with FTO, dye and electrolyte and most important reactions occur at the interfaces between these materials. In this method, when the cell is at open-circuit condition, a small modulated alternating voltage bias $V_{AC} = \Delta V \cdot \exp(i\omega t)$ is applied (ω is the angular frequency, t is the time), no net current was flowing before bias was applied, and after that the harmonically responding small alternating current is measured $I_{AC} = \Delta I \cdot \exp(i\omega t - \varphi)$. This current may be phase shifted by φ in respect to the applied bias and resulting in the impedance:

$$Z(\omega) = \left| \frac{\Delta V}{\Delta I} \right| \exp(i\phi) \quad (6.5)$$

For DSC, the modulation frequency can be swept in a range from MHz to 0.01 Hz resulting in a typical three arcs in the Nyquist plot response. The first arc at high frequency corresponded to the charge transfer at counter electrode, the second arc is the recombination at the interface of TiO_2 /dye and electrolyte, and the third semicircle is associated to a Nernstian diffusion process in the electrolyte [11, 127, 128].

It is important to interpret the results using suitable electrical models. Electrical circuit consisting of electrical elements such as resistors, capacitors, impedances, etc. representing different components in the device will be fitted to the measured data. Figure 6.2 shows an example of an equivalent circuit typically used to describe the components and the interfaces in a DSC. The FTO glass is assigned to a series resistor (R_s) due to its

own sheet resistance. The network of nanoparticles can be modeled by an infinite series of transport resistors (r_t) and approximated using a transmission line concept to $R_t = r_t L$ (L is the thickness of the TiO_2 film). The interface of TiO_2 /electrolyte is delineated by a R - C element consisting of a resistor and a capacitor connected in parallel. The recombination resistance represents the back transfer reaction of electron from TiO_2 to electrolyte and can be estimated as $R_{rec} = r_{rec}/L$. The macroscopic capacitance of the film C_μ is due to the total accumulation of electron density that rises the Fermi level, determined as $C_\mu = c_\mu L$ (c_μ is chemical capacitance, see Figure 6.2). At the counter electrode, the charge transfer between CE and electrolyte is represented by another R - C element. The reaction between FTO and electrolyte is neglected, providing the device has gone through a pre-treatment with TiCl_4 to create an underlayer of TiO_2 . The Nernst impedance Z_D of the diffusion of electrolyte (mainly of large ions such as I_3^- or cobalt complexes) can be expressed as [129]:

$$Z_D = \frac{W_s}{\sqrt{i\omega}} \tanh [\sqrt{i\omega\tau_d}] \quad (6.6)$$

where τ_d is the characteristic diffusion time constant and W_s is a Warburg parameter and is expressed by [130]:

$$W_s = \frac{RT}{n^2 F^2 c_{redox} A \sqrt{D_{el}}} \quad (6.7)$$

where R is the molar gas constant, T is temperature, F is the Faraday constant, c_{redox} is the concentration of redox shuttles, A is electrode area and D_{el} is diffusion constant of electrolyte.

$$\tau_d = \frac{\delta^2}{D_{el}} \quad (6.8)$$

(δ is the thickness of the Nernst diffusion layer [131]).

Figure 6.2: Schematic diagram of a DSC represented by equivalent electrical elements corresponding to each physical component forming an electrical circuit used for fitting with measured data

6.3 Results and discussion

Recombination in DSCs made of electrolytes having low diffusion coefficient like ionic liquid or gel I^-/I_3^- and $Co^{2+/3+}$ were investigated. The physical diffusion of ions in these electrolytes are slow, the probability of their oxidized component meeting an electron in TiO_2 can be high. Availability of macropores along the diffusion path can help to reduce TiO_2 surface.

A graded structure consisting of various macropore sizes gradually increases from small to large was expected to show beneficial light scattering in a larger range of wavelength would be explored. Recombination and transport in this structure was studied using IMVS/IMPS methods.

With varying pores concentration and pore size, the recombination was expected to behave differently. This experiment and result is presented in the last section of the chapter. IV characteristics can be discussed in parallel.

6.3.1 Effect of macropores on recombination resistance in high viscosity I^-/I_3^- electrolyte

As recombination depends on the probability of ions in the electrolyte meeting electrons in TiO_2 which can increase when ions diffuse slowly. Ionic liquid Z952 and gel (Z952 + SiO_2 7 nm) electrolyte were chosen to study the recombination in mesoporous-macroporous films. By using EIS, the recombination resistance R_{rec} can be determined and the variation with respect to bias is presented in Figure 6.3. Because the surface area of the experimented devices were different, it is important to evaluate the recombination when they have equivalent number of electrons in the conduction band. Therefore, the applied potential was displaced by ΔE_C so that the chemical capacitance C_μ of these devices match (C_μ is shown in Figure 6.4). The bias voltage shown in Figure 6.3 is the corrected voltage after displacement of ΔE_C .

Figure 6.3: Recombination resistance of DSCs with PS as template for macropores. Comparison was done between ionic liquid and gel electrolyte

R_{rec} for devices with standard films D18NR-T are presented as black symbol (closed symbols for IL and opened for gel electrolyte) (Figure 6.3). R_{rec} decreased when SiO_2 particles were added to IL to form gel, indicating that gel electrolyte suffered from more recombination than IL. When macropores were introduced using PS as the template with $TiO_2:PS = 20:1$ weight ratio, R_{rec} increased significantly. In this case, the presence of macropores reduced the amount of surface area available for recombination. Furthermore,

the macropores created larger space between nanoparticles for oxidized redox shuttle to diffuse further away from the surface of TiO_2 and hence reduce the chances of recombination. The effect of SiO_2 in the electrolyte should not be overlooked. When SiO_2 was added to ionic liquid, the electrolyte formed gel and became more viscous, resulting in the reduction of R_{rec} (D18NR-T films). It has been reported that nanoscale SiO_2 particles have tendency to form channels, around which I^- and I_3^- anions form continuous chains by electrostatic interactions [132]. In D18NR-T samples, the pore size was small (18-20 nm) while concentration of SiO_2 was quite high (7wt% while Shi *et al.* [132] suggested 1wt%), these chains were rigid due to the limited space between neighboring TiO_2 nanoparticles and surrounding SiO_2 , and recombination could occur like a chain reaction from one ion to another. When macropores were available, the diffusion of electrolyte was improved and recombination was minimized because ions had larger space to diffuse.

TiO_2 film	Dye Electrolyte	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	D35-Z952	698.6	6.293	76	3.334
$\text{TiO}_2\text{:PS} = 20\text{:}1$		685.3	7.695	71	3.753
D18NR-T	D35-Gel1	654.7	4.355	75	2.126
$\text{TiO}_2\text{:PS} = 20\text{:}1$		649.0	5.995	72	2.810

Table 6.1: Photovoltaic performance of devices with D35 dyes with Z952 and Gel1 electrolytes

Table 6.1 shows the performance of DSCs made from these electrolytes. Reduction of recombination usually reflects in increasing V_{oc} and FF. As discussed in Chapter 3, macropores should give rise to higher V_{oc} and FF compared to standard cells. Unfortunately in these devices those two factors are lowered when macropores are present (Table 6.1). This reduction of V_{oc} and FF was rarely observed when macropores were present as most of the systems tested show an improvement of V_{oc} (Chapter 4). Experimental variations were suspected if the film with macropores were slightly thicker than the standard sample. This error occasionally occurred because the surface roughness of macroporous film was relatively high and sometimes could not be accurately measured due to limitation of the resolution of the surface profilometer. However, in this study, this behavior of V_{oc} was mainly observed in D35 dye devices and can be attributed to the chemical structure of the D35 dye and its property. The fact that chemical capacitance C_μ of macropores

samples was higher than standard samples suggested that there was a downward shift in conduction band edge leading to lower V_{oc} despite the higher R_{rec} (Figure 6.4). D35 dye has triphenylamine (TPA) as the electron-donor linked to two substituent groups in para positions, each contains two long butoxyl chains in ortho and para positions of the phenyl rings allowing it to freely rotate. The rotation of D35 dye blocks the recombination of electron in TiO_2 and I_3^- . However, with presence of macropores, there was a possibility that other components in the electrolyte still have better access to the surface of TiO_2 due to low coordination number between nanoparticles. Hence, additives like GuSCN or Li^+ could approach between dye and TiO_2 surface and effectively shifted the conduction band downward causing lower V_{oc} [133,134]. Despite having lower V_{oc} , devices containing macropores templated by 500 nm PS still have higher power conversion efficiency thanks to the much enhanced J_{sc} . Beside the improvement in light harvesting due to light scattering effect in the presence of macropores, the diffusion of electrolytes can be enhanced with these pores to give better dye regeneration. Further discussion on mass transport limitation will be discussed in the next chapter.

Figure 6.4: Chemical capacitance of devices made with ionic liquid Z952 and gel electrolyte Gel1. C_μ is measured by EIS at varying light intensity.

Electron lifetime and electron transport time can be measured using IMVS and IMPS methods as described in the previous section to provide further evidence on the reduction of recombination in the presence of macropores. A graded structure was suggested to improve light scattering effect with wider range of scattering wavelength. In this work, a multilayer photoanode with increasing macropore size, both were studied with and

without a scattering layer on top (FESEM images and its corresponding schematic structures of the films are shown in Figure 6.5). The electron lifetime and transport time of these devices employing D35 dye and ionic liquid Z952 were measured using IMVS/IMPS method.

Figure 6.5: Schematic structure and FESEM cross-section images of films with standard and graded structure with scattering layer.

Figure 6.6 shows that without scattering layer, the electron lifetime of a graded structure device increases compared to a standard device, and the electron transport time was shorter. It means that recombination is reduced and electron transport is enhanced when macropores are present. However, when a scattering layer was introduced, this effect of macropores became negligible. It is also shown that the electron lifetime in devices with scattering layer was shorter than that of non-scattering layer cells. This may be because the deposited films were thicker with the additional scattering layer, and therefore the electrolyte had to diffuse a longer distance in the film. Since this diffusion process was slow, recombination was more likely to happen in a thicker film compared to a thinner film. The result lead to higher recombination and shorter electron life time or smaller V_{oc} when scattering layer was deposited on top of the transparent layer (Table 6.2).

Although widely employed to improve the photocurrent, the scattering layer was not guaranteed to enhance the overall efficiency, since it could cause loss in photovoltage due to recombination (shorter electron lifetime) (refer to Table 6.2). The graded structure gave rise to light scattering and enhancing diffusion, hence reduced recombination (longer

Figure 6.6: Electron lifetime and electron transport time of devices made from D35 dye and Z952 electrolyte

electron lifetime) without the aid of a scattering layer. This structure gave the most optimum efficiency. Electron transport time (Figure 6.6b) of the DSC with a graded structure was the shortest, implying that the electron required the least time needed for electron to be collected at the electrode. This result proves that macropores in a graded structure replacing the scattering layer could effectively improve the performance of DSC, because the graded structure not only can enhance the light scattering but also reduce recombination while the scattering layer, inevitably caused recombination to increase.

TiO ₂ film	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	760.2	10.492	73	5.85
Graded: D18NR-T + 170 nm + 380 nm	781.2	10.334	75	6.06
D18NR-T + Scattering layer	728.8	10.851	73	5.77
Graded + Scattering layer	746.5	10.000	76	5.69

Table 6.2: IV data of DSCs made from 6 μ m films, comparing standard and graded structure, with and without scattering layer, using D35 dye and Z952 ionic liquid.

In these devices, V_{oc} is improved with macropores even though the same dye (D35) and electrolyte (Z952) combination is used as in previous experiment. The difference can be attributed to the macropore size of these devices are smaller (one layer of 170 nm and

one layer of 380 nm pores compared to 500 nm above). Secondly, as from FESEM image presented, the active layer is slightly thinner than the standard film. Nonetheless, the overall efficiency is still improved.

6.3.2 Recombination in cobalt-based electrolyte devices

The iodide/triiodide redox couple for electrolyte is limited by its high overpotential for effective dye regeneration and I_3^- has relatively high light absorption. On top of this, I^-/I_3^- electrolyte is corrosive towards metals and hence is unfavorable for industrial approaches. As a result, alternative redox mediators such as one-electron outer-sphere redox couples (eg. cobalt complexes) have gained more research attention [37, 135]. Cobalt complexes not only have lower light absorption, they also have more positive redox potential that offers better driving force for dye regeneration compared to I^-/I_3^- [136]. Unfortunately, these complexes exhibit fast recombination of electrons in TiO_2 with Co(III) species and mass transport problem leading to slow regeneration of dye. A reported strategy to improve the performance is by tuning the steric properties of both sensitizer and redox shuttles to block the recombination reaction. D35 dye having effective insulating bulky butoxyl substituents has been introduced to prevent fast recombination and improve the overall efficiency [83, 137, 138].

Table 6.3: IV data of cells made from 4 μm and 8 μm films with and without macro-cavities, using $[Co(bpy)]^{3+/2+}$ in acetonitrile electrolyte (DE2), D35 dye.

TiO ₂ film	t (μm)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	4	812.4	8.211	66	4.43
TiO ₂ :PS = 20:1		808.3	8.171	74	4.88
D18NR-T	8	665.4	7.459	47	2.34
TiO ₂ :PS = 20:1		700.4	7.187	54	2.74

When using PS-templated TiO_2 macroporous-mesoporous films for cobalt electrolytes, that may suffer from mass transport limitation due to bulky nature of cobalt mediators, the macropores are expected to show similar positive influence on recombination resistance as has been observed in ionic liquid I^-/I_3^- . Electrolyte DE2 consisting of $[Co(bpy)_3]^{3+/2+}$ in acetonitrile has been reported to have good photovoltaic performance

as compared to several other cobalt complexes with steric bulks (such as $[\text{Co}(\text{phen})_3]^{3+/2+}$, $[\text{Co}(\text{dmb})_3]^{3+/2+}$, $[\text{Co}(\text{dtb})_3]^{3+/2+}$ [83]) thanks to its relatively smaller substituent groups. As mass transport limitation in this electrolyte is smaller (more linear current response as a function of input illumination reported by Feldt *et. al.* [83] and will be discussed in the next chapter), and the effect on FF is due to the improvement of recombination (Table 6.3). The small reduction of V_{oc} has been observed in the case of ionic liquid with D35 dye. Nevertheless, when film thickness is increased to 8 μm , recombination became more dominating (as discussed in Chapter 4) in the standard films, both V_{oc} and FF increased significantly with the presence of macropores as a result of reducing recombination.

Figure 6.7: Recombination resistance of DSCs after correcting voltage according to chemical capacitance.

For further evidence, EIS measurement was conducted to show an increment in R_{rec} (Figure 6.7). R_{rec} increased as porosity increased in both electrolytes with volatile and non-volatile solvents ($[\text{Co}(\text{dtb})_3]^{3+/2+}$ in MPN solvent - coded DE1). The recombination resistance shown in Figure 6.7 was corrected according to the chemical capacitance and normalized to the surface area of each sample. There was higher R_{rec} with larger pore sizes. Under illumination, when photons excited a large number of dye molecules, Co^{2+} ions reduced the excited dye and generate high concentration of Co^{3+} ions at the surface of TiO_2 nanoparticles. As diffusion occurred, the concentration of Co^{3+} reduced gradually from TiO_2 surface towards the bulk of the electrolyte. The small pores of 20 nm in

standard mesoporous film hindered the diffusion of cobalt ions, but when macropores were available and porosity increased, the Co^{3+} ions diffused more rapidly and its concentration gradient becomes steeper near the surface of nanoparticles. The reaction of electrons in the conduction band of TiO_2 with oxidized form of the redox shuttle in the electrolyte is therefore reduced.

This effect is important for cobalt electrolyte as recombination between TiO_2 and Co^{3+} is much faster than I_3^- and even though dyes with bulky alkoxy groups like D35 have been introduced to block this interaction, other methods to reduce recombination is appreciated to obtain more opportunities in exploring other choices of sensitizers.

6.3.3 Recombination with varying macropore sizes and pore concentration

To study the effect of pore size on electron lifetime, DSCs were fabricated with D35 dye and Z952 electrolyte, the templates used for creating photoanodes macropores were ZnO particles with 170, 380 and 500 nm in diameter, with same amount $\text{TiO}_2:\text{ZnO} = 10:3$ weight ratio (with the assumption that if the density of ZnO particles remain constant, the total volume of macropores for each samples would be similar). Therefore, when the pore size changed, the distribution of macropores would vary accordingly: the larger the pore size is, the fewer and more scattered the macropores were distributed.

To study how the pore size distribution affect the device performances, EIS measurement was conducted. Generally, R_{rec} describes the difficulty for back reaction to occur between electrons in E_c of TiO_2 and electrolyte. The higher the R_{rec} , the more difficult this reaction is to occur, and hence the less recombination. In a typical Nyquist plot from EIS measurement, R_{rec} and C_μ appear in the second arc after the charge transfer resistance at the counter electrode. Figure 6.8 shows an EIS plot comparing devices with different macropore sizes using ZnO as the template. The measurements were performed at open circuit condition and light intensity was adjusted so that the shown plotted data have similar open circuit potential (OCP). In these spectra, R_{rec} increased with the presence of macropores as compared to standard sample with D18NR-T film. To study R_{rec} over a range of OCP, Figure 6.8b was obtained from several measurements at different

OCPs and fitted with an equivalent circuit. As measured, R_{rec} of ZnO-templated devices were higher compared to the standard device, which means less recombination occurred.

Figure 6.8: (a) EIS spectra of DSCs with varying macropores size using ZnO as template. Measurements were done at the open circuit condition of around 0.776 V. The connecting line is the fitted results using an equivalent circuit. (b) Recombination resistance of DSCs before and (c) after correcting voltage according to difference in chemical capacitance.

However, it was mentioned before that the position of the conduction band of TiO_2 with respect to the redox potential is influenced greatly by applied voltage, composition of electrolytes and nanostructure [139]. Because of this, the applied potential is not necessary a good reference if we need to compare the response of various devices. A fair comparison of kinetic parameters should be done under conditions that there are equivalent number of electrons in the devices in question. A more meaningful factor is

the relative position between Fermi level and the conduction band ($\Delta E = E_{Fn} - E_C$). Therefore, a displacement of ΔE_C was applied on the potential of each sample based on the chemical capacitance in a way that various samples would have similar C_μ .

After correcting the voltage so the conduction band of all samples were filled with the same amount of electrons (same chemical capacitance), Figure 6.8(c) was obtained. After correcting voltage, R_{rec} of ZnO-templated samples were lower than standard device. It can be interpreted that recombination was in fact higher in these devices. However, V_{oc} of the devices were higher than that of D18NR-T sample (Table 6.4). Another possible explanation is that trap states were lower and that fewer trapping/detrapping occurred in these devices, keeping its V_{oc} higher. Because recombination depends on the probability of an electron in conduction band to meet an ion in the electrolyte, and if the number of electrons in E_c was the same, the recombination is related to the trapping and detrapping processes. Although it remains unclear without detail evidence why R_{rec} of ZnO-templated devices were smaller than the standard samples after voltage correction, a trend can be observed that with larger macropores size, R_{rec} increased. This is expected as the larger the pores are, the lower the concentration of oxidized redox shuttle near TiO_2 will be.

Table 6.4: IV data of cells made from 4 μm films with varying macro-cavities sizes, using Z952 and D35 dye.

TiO_2 film	t (μm)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
D18NR-T	4	770.1	9.303	70	4.98
ZnO = 170 nm		772.6	8.567	75	4.96
ZnO = 380 nm		788.4	8.410	76	5.05
ZnO = 500 nm		798.5	8.510	75	5.13

Figure 6.9 shows that the electron lifetimes of these devices did not deviate significantly from each other, although a small increment was observed with larger pore size (380-500 nm). Despite the speculation that with macropores, diffusion of ions from surface of TiO_2 is faster and reduce the recombination probability, the small increment appears in this experiment indicate that amount of doping is as important as pore size. Considering the fact that the doping concentration of ZnO is quite small (10:3 ratio, which is approximately equal to $\text{TiO}_2\text{:PS} = 20\text{:}1$) leading to insignificant changes because the

total volume of macropores remain small.

Figure 6.9: Electron lifetime of devices made from varying ZnO sizes, with same weight percentage. The size difference leads to varying of pores distribution

The influence of pore concentration was then investigated using PS as template. The following figures show electron lifetime and electron transport time with increasing pore concentration, measured by photovoltage and photocurrent transient. Electron transport time increased with increasing amount of macropores (Figure 6.10b), and the electron lifetime was reduced at the same time. This observation was contrary to our expectation that electron lifetime should be longer when macropores were introduced. A possible explanation is as the porosity increased, the surface area was reduced as discussed previously leading to an increase in the number of charges per TiO_2 nanoparticle. The recombination is determined by the probability of electrons meeting I_3^- ions, the energy which electron can be excited to the state where electrochemical reaction and entropy for the reaction to happen. The latter two should be independent on nanostructures. Hence, only the probability of I_3^- meeting electron in conduction band of TiO_2 can be modulated, which in turn depends on the concentration of ions at the surface of TiO_2 and the concentration of electrons in conduction band. Although the pore size was increased, therefore I_3^- could move away from TiO_2 surface faster and reducing its concentration at the surface, the higher concentration of electrons in conduction band may still lead to higher probability of the electrons meeting I_3^- in the electrolyte.

Figure 6.10: Electron lifetime and electron transport time of devices made from D205 dye with Z952 electrolyte

TiO ₂ film	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	712	12.1	73	6.3
TiO ₂ :PS = 10:1	730	12.5	76	6.9
TiO ₂ :PS = 2:1	722	11.8	77	6.5

Table 6.5: Photovoltaic performance of devices with D205 dye with Z952 electrolytes and 10 μm films

It was explained in the literature that effective electron lifetime depends on trap occupancy and hence on the Fermi level [43]. This result indicates a possibility that the concentration of electrons in E_c of TiO₂ increased with increasing pore concentration and electrons involved in the trapping/detrapping process was reduced. If this hypothesis is correct, the quasi-Fermi level of TiO₂ would increase due to the reduction in the density of trap states and leading to an increase in the V_{oc} . Indeed, from the chemical capacitance obtained, the density of trap states (DOS) were calculated according to the thickness d and porosity p of the film (see equation 6.2). The result of DOS in relation with energy levels are presented in Figure 6.11 showing a upward bend of conduction band edge. Therefore, the V_{oc} increment as presented in the I-V characteristics (Table 6.5) was most likely attributed to conduction band bending.

Figure 6.11: Density of traps states at in relation with energy levels

6.4 Summary

The recombination between electrons in E_c of TiO_2 and I_3^- or Co^{3+} occurs at its interface with dye and electrolyte. Recombination depends on the probability of conduction band electrons meeting oxidized redox shuttle and its activation energy for the reaction to occur. The latter may not be influenced by nanostructures while by increasing pore size, it is expected that the former will be reduced, as ions diffuse better and reduce their concentration near the surface of TiO_2 . As recombination is reduced, electrons can stay longer in the conduction band and hence the electron lifetime should increase.

Ionic liquid and gel electrolyte with I^-/I_3^- redox couple were used with mesoporous-macroporous films and with graded structure (with multiple layers of increasing pore size). The recombination was improved in these cases through observation of higher R_{rec} , longer electron lifetime and shorter electron transport time. Cobalt electrolytes usually have strong recombination with electrons in TiO_2 . Our experiments with cobalt electrolytes in both volatile and non-volatile solvents have an increase of R_{rec} , resulting in an improvement in V_{oc} and FF. At the first few microns of TiO_2 film close to the FTO substrate, dyes absorb photon more strongly and injected electrons do not have to travel a long distance to the electrode, hence recombination is lower. At the top layer of TiO_2

further away from the FTO, recombination becomes more dominating. Therefore, the recombination improvement was not significant in the experiments done with varying pore size and porosity where thinner films were used. When graded films of 6 μm thickness with increasing pore size at the back layers, improvement in electron lifetime is observed to be more significant.

It is important to point out that reduction of recombination does not necessary always translate into higher V_{oc} and vice versa. In the former case, when recombination may be reduced (as evident from higher R_{rec} and/or longer electron life time τ_n), yet V_{oc} appeared lower, the reason can be: these devices were fabricated with rather thin TiO_2 films (2-4 μm) in the region where recombination was not dominating (hence the reduction of recombination does not over come other factors that affect V_{oc}); or there was a downward shift of conduction band edge. The decreasing of V_{oc} can also be attributed to increasing back reaction at the FTO/electrolyte interface, which was increased with the presence of macropores near the FTO surface. On the other hand, when V_{oc} increased but R_{rec} did not or τ_n remained the same, it can be accounted to the reduction of trapping/detrapping processes, or to the distribution of trap states and upward shift of conduction band edge.

The shifting of conduction band edge can also be associated to the approach of small ions such as Li^+ to the surface of TiO_2 . With the presence of macropores, the porosity of the TiO_2 film increases resulting in lower dye loading and overall induced charges decrease, hence the distribution of density of trap states is not deep into the forbidden band gap. It has been discussed that under illumination, injected electrons accumulate in both surface states and conduction band of semiconductor nanocrystals. The displacement between the conduction band energy and Fermi level is dependent on the concentration of charge in the conduction band Q_{cb} . When many electrons are present in TiO_2 surface, a Helmholtz layer at the TiO_2 /electrolyte interface is created to satisfy electroneutrality. The potential drop across this layer can result in shifting of the conduction band edge with respect to redox potential E_{redox} [140,141]. Therefore, although recombination is reduced with the introduction of macropores, the distribution of surface states can influence V_{oc} .

Chapter 7

Reduce mass transport limitation in quasi-solid and cobalt electrolyte DSCs with sub-micrometer cavities

7.1 Background and introduction

In liquid-state DSCs, the electrolyte serves as the “hole” conducting material. In the electrolyte, a redox couple reduces the oxidized dye and regenerate it back to its neutral state, and the positive charge is then transported to the counter electrode. The conventional redox couple iodide/triiodide I^-/I_3^- has been successful and popular thanks to its slow recombination kinetics and relatively good dye regeneration rates. I^-/I_3^- also has the major advantage of being small ions that can diffuse relatively fast within the mesopores and has good solubility. However, this system is corrosive and can dissolve many metal interconnects or sealants. On top of this, as the industrial approaches for DSCs develop, organic solvents used in electrolyte need to be replaced by robust and non-volatile solvents. Therefore, ionic liquid and gel electrolytes containing molten salts are introduced. These materials offer great opportunity for long term stability of DSCs, but they unfortunately have very high viscosity and suffer from mass transport limitation [76,142].

Several alternative redox couples have been explored by scientists that can solve the corrosive problem of I^-/I_3^- . The most outstanding one so far is Co^{2+}/Co^{3+} . Unlike I^-/I_3^- , Co^{2+}/Co^{3+} ions are surrounded by bulky ligand groups that function as an insulating layer and slow down the recombination rate between Co^{3+} and TiO_2 - which in the past used to be the biggest challenge for cobalt electrolytes. These ligands also provide

the flexibility to tune the redox potential of the cobalt complexes and giving higher V_{oc} and better opportunities to provide good dye regeneration by matching with the HOMO level of the dye. Cobalt electrolytes have less light absorption which is quite significant in the I^-/I_3^- system. However, the disadvantage of cobalt-based electrolytes is that their bulky ligand groups attached to the cobalt atom can influence the speed at which Co^{2+}/Co^{3+} diffuse significantly - up to an order of magnitude slower as compared to iodide ions [88]. This problem limits the photocurrent at high illumination intensity and reduces the performance of the device tremendously. It also makes the development of cobalt electrolyte with non-volatile and viscous solvents even more difficult compared to I^-/I_3^- .

Mass transport limitation refers to the slow physical diffusion of ions in electrolytes leading to shortage of redox mediator at the site of dye regeneration. As dye regeneration is slow, the dye stays longer at its excited state and is unable to absorb more photons, and at the same time, have higher opportunity to recombine with electrons in TiO_2 . Physical diffusion problem is affected by the size of redox mediators, their concentration in electrolyte, as well as viscosity and dipole moment of the solvent. Pore size and porosity can also affect the diffusion of electrolyte dramatically. In the early days of dye-sensitized solar cells, pore size as small as 4 nm have been studied but showed non-linearity in the current density due to mass transport limitation [38]. For organic solvent-based I^-/I_3^- electrolyte, the optimized pore size is investigated to be around 20 nm, but this needs not essentially to remain the case when solvent is changed to ionic liquid or redox mediator to cobalt or other complexes where larger ions are present [85]. Furthermore, film thickness is important as the diffusion of electrolyte in the pore is poorer than in the bulk of electrolyte (the space between top layer of TiO_2 and counter electrode). Mass transport limitation occurs in both the bulk electrolyte and in the pores between TiO_2 nanoparticles.

Mass transport limitation is responsible for poor dye regeneration causing low photocurrent at high light intensity and low fill factor due to increasing series resistance. Improving dye regeneration by reducing mass transport limitation will result in better electronic enhancement, especially with higher power input. The regeneration of dye depends on the availability of the reducing species of the redox couple. Increasing con-

centration of triiodide or Co(III) mediators can help to improve mass transfer limitation. Hence, due to high viscosity, ionic liquids (ILs) require much higher concentration of I^-/I_3^- compared to acetonitrile-based electrolytes [76]. However, the high concentration of redox couples eventually causes the viscosity to increase even higher or forming polyiodides - which are large in size and absorbs light strongly [89]. Furthermore, many redox mediators, especially cobalt complexes have poor solubility, and hence not feasible to raising concentration.

Controlling the porosity, pore-size and pore-size distribution has been proven to reduce mass transport limitation. Earlier research by Barbé *et. al.* [38] shows that small pore size such as 4 nm is insufficient for ionic diffusion, as 3 nm of the pore space has already been occupied by dye molecules. Recent study demonstrates that the typical pore size of 20 nm is suitable for the diffusion of I_3^- but not for cobalt complexes. Increasing pore size to at least 22-24 nm and porosity to 58-59% with $TiCl_4$ post-treatment is necessary for cobalt-based electrolyte devices [77, 143]. Reducing the film and spacer thickness is also a possible technique to reduce the distance which the electrolyte has to diffuse through [144]. On the other hand, increasing both porosity, pore size and reducing film thickness causes loss in surface area - and organic dye or other high extinction coefficient sensitizers should be appreciated.

In this chapter, the benefit of employing mesoporous-macroporous structured TiO_2 photoanode to reduce mass transport limitation in high viscosity iodide/triiodide electrolytes and cobalt electrolytes will be presented. Mass transport limitation is expected to be improved by the macropores that create channels for the diffusion of ions. Evaluation parameters and the methods to measure them to investigate the physical diffusion of electrolyte will be discussed.

7.2 Characterization methods

Investigation of photoresponse as a function of light intensity can be used to understand how mass transport limitation affects J_{sc} . Another method to study the mass transport problem is by using electrochemical impedance spectroscopy (EIS) to determine the diffusion resistance and this is seen at the lower frequency.

7.2.1 Light intensity dependence

In principle, as the input light intensity increases, the corresponding photocurrent should increase linearly. However, at high light intensity, more photons can reach the photoanode to excite a large number of dyes and large concentration of electrons is injected. If the diffusion of electrolyte is slow, oxidized ions cannot reach the counter electrode fast enough for charge transfer and reduced ions cannot regenerate the dye molecules efficiently. Therefore, when mass transport is limited, the dye molecules stay at their oxidized state longer instead of being regenerated to absorb more photons, leading to a loss of photocurrent. The current versus light input is hence non-linear and the efficiency is usually reduced at higher light intensity.

The relationship between photocurrent and light intensity provides information on the diffusion of electrolyte. If J_{sc} versus light intensity is linear, the mass transport limitation is not very severe. The more non-linear the relationship, the more limited the mass transport. Input light intensity was modified by inserting a neutral density filter between the light source and the device. When the device was illuminated, current decayed to an equilibrium current within a few seconds and this can be measured. This also provided information about mass transport. Therefore, the current was measured with respect to time while the solar cell was put under alternating dark and light condition and with different light intensity driven by a mechanical shutter wheel. At each light intensity, the cell was illuminated for 5 seconds, enough for the photocurrent to reach the steady state. The more J_{sc} decayed compared to its initial value, the more limited the mass transport was. This method was known as current dynamics.

7.2.2 Electrochemical Impedance Spectroscopy

EIS was introduced in the previous chapter as a powerful technique to study inter-facial and charge transfer processes in DSCs. EIS can be used to study in detail the properties of a DSC with ionic liquid in which mass transport can be the limiting factor. Fabregat-Santiago *et al.* [131] has demonstrated the usage of this method in the study of diffusion of ionic liquid at room-temperature. Ionic liquid shows a large diffusion resistance compared to organic solvent electrolyte at the low frequency region of the impedance spectra and this

has been observed. The equivalent circuit illustrating the electrical elements representing the components and interfaces in a DSC is shown in Figure 7.1.

Figure 7.1: Electrical circuit with elements representing charge transport and transfer processes in different components and interfaces of a DSC showing the diffusion of ions in electrolyte is corresponding to impedance Z_d . The right hand side is a typical set of impedance spectra measured at different bias voltage by Fabregat-Santiago [131], revealing three arcs corresponding to charge transfer at counter electrode, recombination at TiO_2 -electrolyte interface and diffusion in electrolyte.

The diffusion impedance is expressed according to the following equation:

$$Z_d = R_{dif} \frac{\tanh(i\omega/\omega_d)}{i\omega/\omega_d} \quad (7.1)$$

In which R_{dif} is the diffusion resistance, equal to the width of the third arc in figure 7.1, $i = \sqrt{-1}$, ω is the angular frequency of measurement, $\omega_d = D/L^2$ with D is the diffusion coefficient of electrolyte and L is the effective diffusion length. However, one has to keep in mind that this impedance represents the diffusion in both the bulk and the mesopores. The effective diffusion coefficient can be limited in the narrow pores as compared to in the bulk electrolyte [88].

7.3 Results and discussion

The physical diffusion of two electrolytes were studied in this work. Cobalt electrolyte containing bulky cobalt mediators (di-*tert*-butylpyridine (dtb) as ligand groups) prepared in 3-methoxypropionitrile (MPN) was compared with a more volatile and less viscous electrolyte (smaller ligand cobalt complex) in acetonitrile solvent. The former electrolyte

(DE1) was believed to suffer from mass transport limitation due to its non-volatile solvent and large size of the mediators. Performance of DSCs made from these electrolytes were compared at varying irradiation input and the diffusion resistance measured by EIS.

The second set of experiments studied the current dynamics and the diffusion resistance of I^-/I_3^- electrolytes in organic solvent, ionic liquid and gel electrolyte.

7.3.1 Devices with Cobalt electrolytes

In this approach, two different cobalt electrolytes were chosen to study the effect of macropores on the enhancement of ion diffusion. The first electrolyte, DE1, consists of bulky cobalt complexes $[\text{Co}(\text{dtb})_3]^{3+/2+}$ in non-volatile solvent 3-methoxypropionitrile (MPN:ACN = 4:1) and the second electrolyte, DE2, has smaller complexes $[\text{Co}(\text{bpy})_3]^{3+/2+}$ in acetonitrile (ACN) (volatile solvent). Although both of these electrolytes may suffer from mass transport limitation, it is expected that the performance of DE1 will be more severely affected than DE2 due to its non-volatile solvent and bulky ligands. Their diffusion coefficient as reported in the literature [83]: $5.2 \times 10^{-6} \text{cm}^2/\text{s}$ ($[\text{Co}(\text{dtb})_3]^{3+/2+}$) and $9.1 \times 10^{-6} \text{cm}^2/\text{s}$ for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ in bulk acetonitrile. $[\text{Co}(\text{bpy})_3]^{3+/2+}$ ions have been shown to have fast enough diffusion through a $6 \mu\text{m}$ film [83]. PS-assisted films with large cavities were employed to improve the diffusion for both electrolytes. The macropores were expected to have more significant influence on the DE1 electrolyte where mass transport is critical.

Table 7.1 shows the photovoltaic characteristics of DSCs fabricated using DE1 and DE2 with standard photoanodes (Dyesol paste D18NR-T) and with sub-micrometer cavities ($\text{TiO}_2:\text{PS} = 20:1$), films thickness of $4 \mu\text{m}$ were used. With volatile and less viscous electrolyte DE2, our obtained current density was agreeable to published data by Feldt *et al.* [83] for cells of $4 \mu\text{m}$ thick photoanode. At 1 sun, an increment in FF and overall PCE of DE2 device can be observed in the presence of macropores. While with DE2 (ACN-based) electrolyte, only FF was improved with the presence of macropores, when the electrolyte was switched to DE1 (large mediators in MPN), J_{sc} of macropores sample increased significantly by 1.5 times at 1 sun, leading to a higher efficiency. Although the absolute performance of DE1 was poorer than DE2, it still demonstrated that the

presence of macropores improved the J_{sc} of DE1 case and this is very promising. The lower V_{oc} obtained for DE1 because $[\text{Co}(\text{dtb})_3]^{3+/2+}$ (0.43 V *vs.* NHE) has more negative redox potential energy compared to $[\text{Co}(\text{bpy})_3]^{3+/2+}$ (0.56 V *vs.* NHE) in DE2 [138]. The difference in redox potential should result in a V_{oc} that is 130 mV for DE1, but the fact that it was only 20-40 mV lower proved that the extra alkyl ligands in $[\text{Co}(\text{dtb})]$ were capable of blocking the recombination better. Therefore, there is an advantage in using $[\text{Co}(\text{dtb})_3]^{3+/2+}$ despite its lower absolute efficiency. The significant improvement in DSCs performance with the presence of macropores in MPN-based electrolyte made it more promising for further development of robust cobalt-based devices. The performances of these two electrolytes at 0.1 sun is also included in Table 7.1 and they showed a more clear effect of mass transport limitation. The DE1 and DE2 devices had very similar J_{sc} at 0.1 sun condition (0.835-0.922 mA/cm²) indicating that they have relatively comparable ability to absorb light. Nonetheless, the J_{sc} at 1 sun was incredibly different, because the dye regeneration in DE1 electrolyte is much poorer due to mass transport limitation. Further discussion about response to light intensity will be presented in detail.

Table 7.1: IV data of cells made from 4 μm films with and without macro-cavities, using ACN and MPN-based electrolytes at 0.1 and 1 sun.

Electrolyte	TiO ₂ film	Intensity	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
DE1 - MPN-Co(dtb)	D18NR-T	0.1 sun	703.8	0.835	61	3.56
	TiO ₂ :PS = 20:1		709.8	0.850	62	3.72
	D18NR-T	1 sun	762.4	2.463	59	1.10
	TiO ₂ :PS = 20:1		781.7	3.635	57	1.63
DE2- ACN-Co(bpy)	D18NR-T	0.1 sun	770.2	0.922	82	5.80
	TiO ₂ :PS = 20:1		725.4	0.920	87	5.78
	D18NR-T	1 sun	812.4	8.211	66	4.43
	TiO ₂ :PS = 20:1		808.3	8.171	74	4.88

Using DE1, mass transport limitation was shown to be limited by thickness [38, 144]. Devices with different photoanode thickness were studied. It was confirmed that despite thicker films having more dye and better light harvesting, they also have restricted diffusion leading to poor dye-regeneration and higher recombination. These factors become more dominating resulting in reduction in both V_{oc} and J_{sc} (Table 7.2). At 8 μm , the V_{oc} of the D18NR-T sample was reduced relatively compared to the 4 μm sample, because

there is more recombination due to the slow diffusion of $[\text{Co}(\text{dtb})_3]^{3+/2+}$ species into the bulk, away from the TiO_2 surface. The higher V_{oc} of PS-assisted samples comparing to D18NR-T samples of similar thickness can also be attributed to the difference in surface area when introducing macropores, thus reducing recombination sites [93].

Table 7.2: IV data of cells made from 4 and 8 μm films with and without macro-cavities, using MPN-based electrolytes DE1.

TiO ₂ film	t (μm)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	4	762.4	2.463	59	1.10
TiO ₂ :PS = 20:1		781.7	3.635	57	1.63
D18NR-T	8	631.7	2.413	65	0.99
TiO ₂ :PS = 20:1		664.9	2.882	66	1.27

Linearity of photocurrent response

To further investigate the existence of mass transport limitation due to diffusion of electrolyte, and how macropores can improve this limitation, the steady state photocurrent density of the device at different light intensity (Figure 7.2) was measured. The more linear the relationship is, the better the device is able to reduce loss due to poor dye regeneration and maintain its J_{sc} at high irradiation. With DE2 electrolyte, when sub-micrometer cavities were introduced (red symbols), no significant change was observed compared to D18NR-T because the linearity of the photocurrent dependence on light intensity was retained rather well throughout the range of light intensity variation. On the other hand, with the mass transport limited electrolyte DE1 based on MPN solvent and bulky $[\text{Co}(\text{dtb})_3]^{2+/3+}$, the photocurrent deviation from linearity was improved significantly with increasing porosity. Although the pores collapsed during sintering, the pores created by 500 μm PS spheres still have height of *ca.* 200 μm and with of *ca.* 500 μm , and these pores act as reservoirs assisting in the diffusion of large cobalt complex ions. The reduction of excited dye under illumination subsequently generates $[\text{Co}(\text{dtb})_3]^{3+}$ ions which rapidly diffused to these macroporous “reservoirs” and away from the surface of TiO_2 , increasing the electron lifetime and reduced recombination. As the concentration of Co^{3+} in the porous film decreased because of faster diffusion to the counter electrode, this implied that higher concentration of Co^{2+} became readily available to regenerate the

dyes. Regeneration and collection efficiency at high light intensity was therefore improved with the macro-cavities, resulting in the sample with $\text{TiO}_2\text{:PS} = 20\text{:}1$ had 1.5 times higher J_{sc} at 1 sun compared to its D18NR-T (2.463 mA/cm^2) counterpart even though at 0.1 sun they have similar current response.

Figure 7.2: J_{sc} and PCE at different light intensity of DSCs based on (a) DE2 ACN- $\text{Co}(\text{Bpy})$ and (b) DE1 MPN- $\text{Co}(\text{dtb})$ electrolytes. The linearity of photocurrent shows that the mass transport limitation is not the dominating limiting factor of photocurrent with DE2 but more severe with DE1 electrolyte.

It is noticed that all cells with $8 \mu\text{m}$ films had poorer performance compared to their respective $4 \mu\text{m}$ counterpart at 1 sun. Due to mass transport limitation of the much bulkier cobalt mediators, the thickness from which mass transport became a problem was much thinner ($3\text{--}4 \mu\text{m}$) with cobalt electrolytes compared to I^-/I_3^- electrolytes (TiO_2 film can be up to $20 \mu\text{m}$ [145]). Also in Figure 7.2, only $8 \mu\text{m}$ cell with macropores and DE1 electrolyte (MPN- $\text{Co}(\text{dtb})$) showed an improvement compared to its standard D18NR-T counterpart, proving that mesoporous-macroporous film can help to improve diffusion for devices with a thicker photoanode. This is especially important when the device makes use of an electrolyte that is diffusion limited.

(a)

(b)

(c)

Figure 7.3: (a&b) EIS spectra of devices measured at 0.55 V and 0.75 V under illumination and fitted curves from equivalent circuit. (c) Diffusion resistance of DSCs made of $8\mu\text{m}$ films from D18NR-T and $\text{TiO}_2:\text{PS} = 20:1$ pastes, using DE1 MPN-Co(dtb) electrolyte.

Diffusion resistance

Diffusion resistance, R_{dif} , indicates the difficulty in the physical diffusion of mediators in electrolyte for both in bulk (the space between top layer of TiO_2 and counter electrode) and through the porous photoanode. R_{dif} usually appears as the third semicircle in EIS spectrum at low frequency [131]. As the measurement was carried out under illumination and by applying a bias voltage on the cell from -0.05 V to above its V_{oc} (over 0.8 V in this case), the diffusion resistance R_{dif} , if significant enough, only appear at the region along the IV curve where photocurrent is not saturated, meaning from about 0.1 V before the V_{oc} onward. However, if the R_{dif} is very large, because its time constant is close to that of recombination resistance, sometimes these 2 semicircles in the impedance spectroscopy are overlapping (Figure 7.3a), causing difficulty in fitting suitable value in the equivalent circuit. Therefore, we only present diffusion resistance value from 0.6 V, although we usually observe the evolution of the third semicircle from around 0.5-0.55 V.

Figure 7.3b illustrates the full spectra measured at 0.75 V for devices made from D18NR-T and $\text{TiO}_2\text{:PS} = 20\text{:}1$ pastes, showing more clearly the three semicircles representing resistance of charge transfer at counter electrode, R_{CE} , recombination at $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, R_{rec} , and diffusion resistance, R_{dif} , according to the sequence of appearance. As seen in Figure 7.3c, diffusion resistance of D18NR-T sample was more than 1.5 times higher than that of $\text{TiO}_2\text{:PS} = 20\text{:}1$, indicating that the ions moved slower in the network of mesopores compared to films with macropores. This restriction arises from the high local concentration of $[\text{Co}(\text{dtb})_3]^{3+}$ and the small size of pores between TiO_2 particles. Even when macropores were introduced, they acted as “concentrated” porosity rather than uniformly distributed porosity, and the hindrance of ions diffusions were still present at areas where only mesopores were available. The resulting resistance could be the average between high diffusion resistance in 20 nm pores and smaller resistance in 200-500 nm pores because mass transport limitation became less severe with wider path for the movement of cobalt complexes [143]. However, increasing porosity has its limitation as it reduces the dye-loading and coordinating number of neighbouring particles [146].

7.3.2 Diffusion in viscous I^-/I_3^- ionic liquid and gel electrolyte

Concentration of redox shuttles in I^-/I_3^- electrolytes is much higher than in cobalt electrolytes mainly due to better solubility. Nevertheless, the diffusion of these electrolytes is still difficult if the solvent is highly viscous. Both I^-/I_3^- ionic liquid and gel electrolytes were used to improve the stability of the devices but unfortunately, because of their high viscosity, they can give rise to diffusion problem. The diffusion problems offered by these solvents can be reduced with the use of macropores.

Current dynamics

Figure 7.4: Current dynamic and photocurrent decay normalized at 1 sun (below) of devices made from D205 and Z1130 and Z952 electrolytes

The dependence of photocurrent with varying input power can provide us with in-

formation about the kinetics processes in the devices. Figure 7.4 showed the current dynamics of devices with D205 dye, with two electrolytes - Z1130 (in volatile solvent acetonitrile) and viscous ionic liquid Z952. The current dynamic shows photocurrent transient when the cells underwent large modulation (on/off) of incident light at different intensity. When the shutter was opened, maximum photocurrent was generated followed by a decay and the current would reach its equilibrium state in a few seconds. When dyes absorb incident photons, they generate and inject electrons into the conduction band of TiO_2 , after all recombination and trapping/detrapping processes, the electrons were collected at the electrode, reflecting the maximum current. However, the photocurrent later on would be dependent on the regeneration of dyes, and if dyes are not effectively regenerated, absorption would be reduced. This happens when diffusion of electrolyte is limited and more often observed at high light intensity. Figure 7.4a proves that mass transport limitation is negligible in volatile electrolyte while it becomes more of an issue with ionic liquid at higher light intensity from 0.3 sun and above (Figure 7.4b).

Looking at the 1 sun current transient (Figure 7.4c and d), we can further confirm that mass transport was not limited in Z1130 - the organic solvent-based electrolyte - as its current did not decay from its initial response even at 1 sun. With ionic liquid Z952, the current transient at 1 sun was normalized to show that with increasing porosity and macropores, the magnitude of current decay was reduced and the steady state current could be improved compared to standard mesoporous system. However, considering that the presence of large cavities should promote the diffusion of electrolyte much better, this improvement was quite small.

To further study the system for better understanding and find materials that would benefit more from macropores in terms of reducing mass transport, more viscous electrolyte was used by mixing SiO_2 7 nm nanoparticles with ionic liquid Z952 (Gel1). This is a quasi-solid state gel, and it can offer a more facile application for industrial approach, as it does not require drilling a hole on counter electrode for electrolyte injection because the gel does not flow. We expected that if the viscosity of electrolyte increases even higher, improvement from macropores may appear more significant.

Figure 7.5 shows the current dynamics and current transient normalized at 1 sun of gel electrolyte devices made with D205 and Y196 dyes. Surprisingly, although viscosity

Figure 7.5: Current dynamic and photocurrent decay normalized at 1 sun (below) of devices made from Gel electrolyte and D205 and Y196 dyes

increased with introducing SiO₂ nanoparticles in the electrolyte, the current decay still did not show very significant improvement with macropores when D205 was used. On the other hand, with Y196 dye, the current response was improved significantly with the presence of macropores, and the current decay decreased with increasing concentration of these macropores. More than 2 mA/cm² was lost in the case of standard film D18NR-T due to mass transport, while with high concentration of PS used in the paste, this lost was reduced significantly to 0.5 mA/cm² only. The initial current response of D18NR-T is actually higher, probably because it had higher surface area, but it could not maintain the current due to poor dye regeneration and large current decay caused a huge loss, leading to lower steady state current as compared to TiO₂:PS = 2:1 sample.

The difference between D205 and Y196 dyes in terms of current decay was probably

due to the dye regeneration kinetic of the two dyes. Daeneke *et al.* has proven that when driving force for dye regeneration is higher than $\Delta E = 0.2 - 0.25$ eV, the regeneration reaction becomes more controlled by diffusion, or in other word by mass transport [147]. The HOMO level of Y196 is at -5.26 eV (not published data), hence the driving force for dye regeneration is about $\Delta E \approx 0.41$ eV while D205 has $\Delta E \approx 0.21$ eV [101]. This interesting information indicates that dye regeneration rate plays an important role in current loss and can benefit greatly from the creation of macropores. This result also shows that Y196 could possibly have better dye regeneration in $\text{Co}^{2+/3+}$ electrolyte which has even lower redox potential compared to I^-/I_3^- .

Diffusion resistance

EIS measurement can be used to determine the diffusion resistance and investigate the processes that occur in DSCs better. D35 dye was used together with ionic liquid Z952 and gel electrolyte (Gel1 - Z952+ SiO_2) because its molecular structure and LUMO/HOMO resembles that of Y196 dye, hence the effect in mass transport will be more predominating.

The result showed no significant deviation of R_{dif} between ionic liquid and gel electrolytes. It is agreeable with current transient of D205 dye devices shown previously that the diffusion is not influenced significantly when changing from ionic liquid to gel electrolyte despite the viscosity increases as gel electrolyte behaves like quasi-solid. The reason could be because the original ionic liquid is indeed already too viscous that the diffusion depends mainly on concentration of redox shuttle I^-/I_3^- , which is relatively high in both electrolytes. On the other hand, the introduction of macropores still causes R_{dif} to decrease, stating that porosity is extremely important to the diffusion of electrolyte even when viscosity does not show significant influence.

Due to the excess concentration of I^- and its smaller size, the limitation of current density in DSCs due to diffusion is proportional to the diffusion rate of I_3^- ions. According to Papageorgiou *et al.* [148], effective diffusivity is attributed to (i) the availability of void (pores) in the area normal to the direction of ions flow, (ii) how tortuous the diffusion paths are and (iii) the varying cross-sectional areas of pores. Nevertheless, the same author has discussed that tortuousity is a minor factor, yet the availability of void is important, explaining that increasing the porosity encourages ions diffusion. In the

Figure 7.6: Diffusion resistance of DSCs made of films from D18NR-T and TiO₂:PS = 20:1 pastes, ionic liquid Z952 and gel electrolytes.

literature, it has been proven that the effective diffusion coefficient of electrolyte is reduced by up to one third in the nanopores [88, 148] as compared to in the bulk. The diffusion coefficient is shown to increase with increasing pore-size in a bimodal pores structure [149]. The improvement of R_{dif} presented here further confirms that diffusion of I_3^- is less hindered when sub-micrometer pores are available in the diffusion path. R_{dif} is subjected to both diffusion resistance of electrolyte percolated in the pores and that in the bulk, but the difference shown suggests that the diffusion of ions in the macropores is improved as these devices have the same bulk electrolyte thickness.

7.4 Summary

Diffusion of ions in electrolyte percolated in the porous network of TiO₂ film and in the bulk is limited by the concentration and the size of ions and electrolyte's viscosity, resulting in poor FF and a non-linearity in photocurrent vs. light intensity. This behavior is referred to as mass transport limitation. Increasing pore size can improve the mass transport of ions (especially I_3^- and Co^{3+}). Improvement in diffusion of electrolyte is proven by smaller diffusion resistance R_{dif} when macropores are presented. Better mass transport is also observed in more linearity of photocurrent with increasing light intensity and less decay of current response from maximum current to steady-state under large

modulation (on/off) in current dynamics and current transient. Lower R_{dif} leads to increasing FF. This observation appears more significant for electrolytes that suffer from serious mass transport limitation as it is either viscous due to non-volatile solvent like ionic liquid or gel, low concentration of redox shuttles because of low solubility or large radii with bulky anchoring groups and dye with slower regeneration rate.

It is believed that higher porosity will have more positive effect on reducing mass transport problem and a follow up study is necessary to optimize the system and to obtain a better understanding. Moreover, it has been suggested that increasing porosity is as important as increasing cross-sectional area of pores [148–150]. The movements on ions through pores resembles the flow of a liquid through “funnel” and large pores with higher cross-sectional area will have more benefit. Yang *et al.* has proven that a bimodal pore size is better for ion diffusion compared to a unimodal system [149].

Because diffusion properties are dependent on the choice of dyes and electrolytes, the effect of macropores should be incorporated with appropriate combination of dye and electrolyte for best benefits in photovoltaic performance. Film thickness and porosity concentration should also be taken in consideration for investigation. Although depending on the choice of dye and electrolyte, in general, better ion diffusion will allow higher current density, especially at high power input. FF is increased more significantly if the electrolyte has high viscosity as R_{dif} is reduced, although if current is improved, this increment may not be observed. An additional advantage with better diffusion can lead to improvement of recombination, because if I_3^- (or Co^{3+}) can diffuse faster away from the TiO_2 surface, the probability of it to recombine with electron is reduced. Overall, optimum point of PCE can be obtained that shows improvement compared to standard transparent D18NR-T photoanodes. Enhancing diffusion is increasingly important for real life application as DSCs are often limited by the volatility of their electrolytes and the requirement for high quality sealant, which can be replaced by non-volatile solvent or ionic liquid/gel that typically suffer from mass transport limitation.

Chapter 8

Conclusions and Future outlooks

8.1 Summary and conclusions

Since the introduction of mesoporous TiO_2 nanoparticles film as the photoanode for dye-sensitized solar cell in O'Regan and Grätzel's 1991 Nature paper, research on the field of dye-sensitized solar cell has been continuously developing. In this thesis, sub-micrometer cavities were created by employing templating agents such as PS and ZnO to form a more porous TiO_2 photoanode for DSCs. Cross section SEM images revealed that macropores in PS-templated films were collapsed while ZnO left behind pores of more spherical shape. This mesoporous-macroporous structure had bimodal pore size and exhibited certain advantages over standard mesoporous films in terms of light scattering and improving ionic diffusion in the electrolyte. The dye-loading experiments showed that in both cases, the surface area of mesoporous-macroporous films were reduced because nanoparticles were replaced by voids, and hence the amount of dye loading could be decreased by up to 30%. The lower dye-loading offers advantage of in terms of material saving - since dye is one of the most expensive materials in the device - while having comparable performance.

Photovoltaic performance of DSC was improved with the presence of sub-micrometer cavities in several dye-electrolyte combinations. Organic dyes showed advantages for maintaining current density despite the lower dye-loading because of their high molar extinction coefficient ε and were found to be suitable to combine with macropores. Electrolytes that have diffusion problems such as ionic liquid, gel and cobalt complexes could benefit more from macropores than volatile solvent based electrolytes. With these elec-

trolites, current density at high light intensity input could be enhanced, current versus light intensity became more linear and FF showed much improvement. The influence of film thickness and pore concentration on the performance and optimization of these two parameters was illustrated. Overall, efficiency could increase by 0.3-0.8% PCE higher than the standard samples.

By using FDTD simulation, we investigated the scattering cross section σ_{scat} of multiple scattering centers of various sizes and shapes. The simulation result revealed that when the shape of scattering centers changed from spherical to ellipsoidal by reducing the radius parallel to light incident direction, σ_{scat} was not reduced if the total volume displacement of pores were reserved. This finding assured that with sufficient concentration of macropores, the collapsed ellipsoidal shape of pores created by PS template did not affect the expected light scattering effect of the film. All films containing macropores showed strong light scattering effect although ZnO-templated samples did not have satisfying IPCE results as compared to PS-templated devices. Overall, the best performing films among the experimented were ZnO of 380 nm and PS 500 nm of concentration $\text{TiO}_2\text{:PS} = 10\text{:}1$. These films had the optimum compensation between the loss of amount of dye-loading and the gain in light scattering in the red region.

Recombination of electrolyte with electron in conduction band of TiO_2 happens at the interface of these materials and was expected to be reduced when pore size increased. In the presence of macropores, I_3^- and Co^{3+} ions diffused away from the surface of TiO_2 faster and reduced their probability of meeting e_{TiO_2} . Reduction of recombination when macropores were present could be observed via the increase of recombination resistance R_{rec} measured by EIS, or the longer electron lifetime τ_n , resulting in an improvement of V_{oc} and occasionally FF. However, in certain cases, a higher R_{rec} did not result in higher V_{oc} or vice versa. The reason was explained by the shifting of conduction band edge that caused V_{oc} to change despite the reduction of recombination.

Mass transport of ionic diffusion of electrolyte percolated in the mesoporous TiO_2 film limits the dye regeneration rate and current density. Introduction of macropores resulted in improving diffusion as shown by reduction in diffusion resistance R_{dif} measured using EIS method. As a result, the current density - especially at high light intensity - was much improved. When the device was illuminated, it exhibited an initial current that would

decay to a more steady state within a few seconds due to mass transport limitation. The presence of macropores reduced this decay as compared to standard devices, keeping the initial current of the device better. The effect was observed more significantly with dyes for which the regeneration rate are more dependent on electrolyte diffusion. Mesoporous-macroporous films were used for devices DE1 electrolyte (with $[\text{Co}(\text{dtb})_3]^{2+/3+}$ ions in MPN solvent) - which has low diffusion coefficient and was limited by diffusion of ions. The photocurrents of these devices at high light intensity (1 sun) were increased by two times compared to the mesoporous films D18NR-T. The higher current with this less volatile solvent opened up more opportunities to employ robust cobalt electrolytes for better stability applications.

8.2 Limitation

Although a thorough research project was conducted, the investigation of incorporating macropores in mesoporous TiO_2 film as photoanode of DSC presented in this thesis still has several limitations. First of all, the purity of ZnO-templated film was not confirmed because EDX may not be sensitive enough to examine if any Zn-compounds were left over after surface treatment with TiCl_4 solution, and further investigation is necessary. The relatively poorer performance of ZnO-templated devices in terms of IPCE as compared to PS-templated counterparts, despite the similar optical properties can possibly be associated with the impurity of these films. Secondly, although suggested by FDTD simulation that ellipsoidal shape scatterers could perform as good as spherical ones if there was sufficient concentration of scattering centers; it was not clear whether ellipsoidal scatterers could perform even better than spherical scattering centers because the scattering angle of the former could propagate in more preferred directions. The FDTD simulation is also limited due to the assumption of “standard” shapes, assuming that the pores are in perfect ellipsoidal or spherical shapes, while in practice there are variations due to experiments. A distribution of multiple pore sizes and pore agglomeration was not taken into account, and requires further investigation. Thirdly, electron recombination was quite inconsistent with the trend of V_{oc} . Speculation could be made related to bending of conduction band edge of TiO_2 but this hypothesis was not yet confirmed. The

recombination could also be related to the impurity of ZnO-templated films. Last but not least, due to limitation of time and resources, only several dimensions of scatterers and concentrations have been studied. Finer tuning of these parameters was necessary in combination with suitable dye and electrolyte to optimize the effect of macropores.

8.3 Future outlook

8.3.1 Further investigation of mesoporous-macroporous films

The limitations of this thesis suggest that further investigation can be done for better understanding and optimization of the structure. First of all, the FDTD simulation conducted was a preliminary study with only the refractive index of TiO_2 and acetonitrile representing the electrolyte. In reality, I_3^- absorbs light quite strongly and the absorption spectrum of dye should be taken into consideration. A model incorporating the information of dye and electrolyte will provide more quantitative information about the light harvesting efficiency. In future study, the irregular shapes and merging of pores should also be into consideration. Secondly, the improvement in ion diffusion in electrolyte has been proven by the decrease of R_{dif} . The improvement in mass transport limitation has resulted in faster dye regeneration. The rate of dye regeneration can be quantitatively studied by photoinduced absorption spectroscopy (PIA). This is important when the mesoporous-macroporous structure is incorporated with dyes having low dye regeneration rate. Thirdly, exploring other templating agents to create more variety of sizes and shapes of macropores can be interesting. As suggested before, the anisotropic scattering of ellipsoidal scattering centers can be more beneficial than the spherical scatterers. Nanorods or nanodiscs are synthesized easily and can be able to be used as template to create elongated shapes of pores that can scatter light and have higher surface area.

Table 8.1: Preliminary photovoltaic performance of SSDSCs made with D35 dye, doped spiro with standard D18NR-T and mesoporous-macroporous film with PS as template.

TiO ₂ film	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18NR-T	834.9	5.947	45	2.237
TiO ₂ :PS = 20:1	805.8	6.651	49	2.650

8.3.2 Other recommended applications

Solid-state dye-sensitized solar cells

All-solid-state solar cell is the future of dye-sensitized solar cell, as it can be very stable and suitable for mass production, although for now it remains costly due to rather limited choices of hole transporting materials (HTMs) [151, 152]. The most commonly used HTMs are organic semiconductor small molecules or polymers, such as spiro-OMeTAD (spiro) [151] or poly(3-hexylthiophene) P3HT [153]. These materials are usually deposited by spin-coating, which has the drawback of pore filling and infiltration ability. In-situ synthesis of organic [154] or inorganic [155] HTMs can solve the problem of pore-filling and even produce high efficiency, but the synthesis remains complicated. Because of the wettability and pore-filling difficulty of organic HTMs, large pore size can be explored to improve the performance.

Since SSDSC requires very thin film to ensure good pore filling and HTM penetration, the conventional double layer film structure (the second layer is the scattering layer) cannot be applied. Hence, light scattering in normal SSDSC is rather limited. The scattering effect from voids in mesoporous-macroporous film can improve light harvesting without the use of a second layer. On top of that, because of the presence of macropores, pore filling is expected to be enhanced and thicker film can therefore be possible. Some preliminary data of SSDSCs made with D35 dye and spiro as HTM (doped with FK102 [152]) show that the current density and FF of macropores samples can be improved from the standard sample (Table 8.1). The result is promising as the photocurrent is improved significantly. Nonetheless, further studies need to be completed with investigation of other dyes. Fabrication process should be taken into consideration for optimization as the organic HTM is sensitive to moisture and requires more restrict environment.

Figure 8.1: IPCE of SSDSCs showing the improving of current density at longer wavelength range when macropores are present

The IPCE of these devices are measured to show improvement especially from 450 nm onward. The normalized IPCE (not shown) indicates that the improvement is more significant on the longer wavelength (550 nm). Further optimization can be performed to improve the power conversion efficiency. More in-depth investigation and fundamental studies are definitely interesting for future work.

Extremely thin absorber solar cells

Figure 8.2: Illustration of how mesoporous-macroporous structure can be employed in SSDSC or ETA solar cells

A new architecture based on DSC known as extremely thin absorber solar cells (ETA) has been introduced recently. This device architecture utilizes inorganic semiconductors, such as PbS, CdS, CdSe, Sb₂S₃, etc. as light absorbing materials [156–158]. The high light

harvesting and ability for tuning band gap of these materials have made them increasingly attractive. The deposition of these inorganic semiconductors is usually done by chemical bath deposition. Solid state hole transporting material is usually used in these devices because of better band energy compatibility and faster hole transport. The coverage of these sensitizers on the surface of TiO_2 and pore filling of the HTM is very critical to reduce the fast charge recombination in these devices. By incorporating macropores in the TiO_2 films, it is possible to obtain a better coverage of inorganic semiconductors and thin blocking layer to provide better electronic properties of the ETA solar cells.

Bibliography

- [1] British Petroleum. BP Statistical Review of World Energy. Technical Report June, 2013.
- [2] Michael Grätzel. Recent Advances in Sensitized Mesoscopic Solar Cells. *Accounts of Chemical Research*, 42(11):1788–98, November 2009.
- [3] D. M. Chapin, C. S. Fuller, and G. L. Pearson. A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power. *Journal of Applied Physics*, 25(5):676, 1954.
- [4] John Perlin. The Silicon Solar Cell Turns 50. *National Renewable Energy Laboratory*, 2004.
- [5] Robert F. Service. Can the Upstarts Top Silicon? *Science*, 319(5864):718–720, 2007.
- [6] Adolf Goetzberger, Joachim Luther, and Gerhard Willeke. Solar cells: past, present, future. *Solar Energy Materials & Solar Cells*, 74:1–11, 2002.
- [7] Yu Bai, Yiming Cao, Jing Zhang, Mingkui Wang, Renzhi Li, Peng Wang, Shaik M. Zakeeruddin, and Michael Grätzel. High-performance dye-sensitized Solar Cells Based on Solvent-free Electrolytes Produced from Eutectic Melts. *Nature Materials*, 7(8):626–630, 2008.
- [8] British Petroleum. BP Energy Outlook 2030. Technical report, 2012.
- [9] Michael Grätzel. Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 4(2):145–153, October 2003.
- [10] Brian C. O'Regan and Michael Grätzel. A Low-cost, High-efficiency Solar Cell Based on Dye-sensitized Colloidal TiO₂ Films. *Nature*, 353(6346):737–740, 1991.
- [11] Anders Hagfeldt, Gerrit Boschloo, Licheng Sun, Lars Kloo, and Henrik Pettersson. Dye-sensitized Solar Cells. *Chemical Reviews*, 110(11):6595–6663, 2010.
- [12] Karin Keis, Eva Magnusson, Henrik Lindström, Sten-Eric Lindquist, and Anders Hagfeldt. A 5% Efficient Photoelectrochemical Solar Cell Based on Nanostructured ZnO Electrodes. *Solar Energy Materials and Solar Cells*, 73(1):51–58, May 2002.

- [13] Qifeng Zhang, Tammy P. Chou, Bryan Russo, Samson A. Jenekhe, and Guozhong Cao. Polydisperse Aggregates of ZnO Nanocrystallites: A Method for Energy-Conversion-Efficiency Enhancement in Dye-Sensitized Solar Cells. *Advanced Functional Materials*, 18(11):1654–1660, June 2008.
- [14] Yosuke Fukai, Yusuke Kondo, Shogo Mori, and Eiji Suzuki. Highly Efficient Dye-sensitized SnO₂ Solar Cells Having Sufficient Electron Diffusion Length. *Electrochemistry Communications*, 9(7):1439–1443, 2007.
- [15] Akihiro Furube, Miki Murai, Sadayuki Watanabe, Kohjiro Hara, Ryuzi Katoh, and M. Tachiya. Near-IR Transient Absorption Study on Ultrafast Electron-injection Dynamics from a Ru-Complex Dye into Nanocrystalline In₂O₃ Thin Films: Comparison with SnO₂, ZnO, and TiO₂ Films. *Journal of Photochemistry and Photobiology A: Chemistry*, 182(3):273–279, 2006.
- [16] Kazuhiro Sayama, Hideki Sugihara, and Hironori Arakawa. Photoelectrochemical Properties of a Porous Nb₂O₅ Electrode Sensitized by a Ruthenium Dye. *Chemistry of Materials*, 10(12):3825–3832, December 1998.
- [17] Shelly Burnside, Jacques-E. Moser, Keith Brooks, Michael Grätzel, and David Cahen. Nanocrystalline Mesoporous Strontium Titanate as Photoelectrode Material for Photosensitized Solar Devices: Increasing Photovoltage through Flatband Potential Engineering. *The Journal of Physical Chemistry B*, 103(43):9328–9332, October 1999.
- [18] Xiaoxu Ji, Xintang Huang, Jinping Liu, Jian Jiang, Xin Li, Ruimin Ding, Yingying Hu, Fei Wu, and Qiang Li. Hydrothermal Synthesis of Novel Zn₂SnO₄ Octahedron Microstructures Assembled with Hexagon Nanoplates. *Journal of Alloys and Compounds*, 503(2):L21–L25, August 2010.
- [19] Mi Yeon Song, Do Kyun Kim, Seong Mu Jo, and Dong Young Kim. Enhancement of the Photocurrent Generation in Dye-sensitized Solar Cell based on Electrospun TiO₂ Electrode by Surface Treatment. *Synthetic Metals*, 155(3):635–638, December 2005.
- [20] S. Uchida, A. Kumar, R Jose, and Seeram Ramakrishna. Spray Deposition of Electrospun TiO₂ Nanorods for Dye-sensitized Solar Cell. *Nanotechnology*, (18):365709, 2007.
- [21] R. Jose, A. Kumar, V. Thavasi, and Seeram Ramakrishna. Conversion Efficiency Versus Sensitizer for Electrospun TiO₂ Nanorod Electrodes in Dye-sensitized Solar Cells. *Nanotechnology*, 19:424004, 2008.
- [22] Matt Law, Lori E. Greene, Justin C. Johnson, Richard Saykally, and Peidong Yang. Nanowire Dye-sensitized Solar Cells. *Nature Materials*, 4(6):455–459, June 2005.
- [23] Xinjian Feng, Karthik Shankar, Oommen K Varghese, Maggie Paulose, Thomas J Latempa, and Craig a. Grimes. Vertically Aligned Single Crystal TiO₂ Nanowire Arrays Grown Directly on Transparent Conducting Oxide Coated Glass: Synthesis Details and Applications. *Nano Letters*, 8(11):3781–3786, 2008.

- [24] Emil Enache-Pommer, Bin Liu, and Eray S. Aydil. Electron Transport and Recombination in Dye-sensitized Solar Cells Made from Single-crystal Rutile TiO₂ Nanowires. *Physical Chemistry Chemical Physics*, 11(42):9648–52, November 2009.
- [25] Soon-Hyung Kang, Sang-hyun Choi, Moon-Sung Kang, Jae-yup Kim, Hyun-sik Kim, Taeghwan Hyeon, Yung-Eun Sung, By Soon, and Hyung Kang. Nanorod-Based Dye-Sensitized Solar Cells with Improved Charge Collection Efficiency. *Advanced Materials*, 20(1):54–58, January 2008.
- [26] Bin Liu and Eray S. Aydil. Growth of Oriented Single-crystalline Rutile TiO₂ Nanorods on Transparent Conducting Substrates for Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 131(11):3985–90, March 2009.
- [27] Shlomit Chappel, Si-guang Chen, and Arie Zaban. TiO₂ - Coated Nanoporous SnO₂ Electrodes for Dye-Sensitized Solar Cells. *Solar Cells*, 18(24):3336–3342, 2002.
- [28] Yishay Diamant, Shlomit Chappel, S.G. Chen, Ophira Melamed, and Arie Zaban. Core-shell Nanoporous Electrode for Dye Sensitized Solar Cells: the Effect of Shell Characteristics on the Electronic Properties of the Electrode. *Coordination Chemistry Reviews*, 248(13-14):1271–1276, July 2004.
- [29] Matt Law, Lori E. Greene, Aleksandra Radenovic, Tevye Kuykendall, Jan Liphardt, and Peidong Yang. ZnO-Al₂O₃ and ZnO-TiO₂ Core-Shell Nanowire Dye-Sensitized Solar Cells. *Journal of Physical Chemistry B*, 110(45):22652–22663, November 2006.
- [30] J.R. Jennings, Feng Li, and Qing Wang. Reliable Determination of Electron Diffusion Length and Charge Separation Efficiency in Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C*, 114(1):14665–14674, 2010.
- [31] Kai Zhu, Song-Rim Jang, and Arthur J. Frank. Impact of High Charge-Collection Efficiencies and Dark Energy-Loss Processes on Transport, Recombination, and Photovoltaic Properties of Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry Letters*, 2(9):1070–1076, May 2011.
- [32] Michael Grätzel, Microbe Species, and Island Biology. Solar Cells to Dye for. *Nature*, 421(February):586–587, 2003.
- [33] Susumu Namba and Yasushi Hishiki. Color Sensitization of Zinc Oxide with Cyanine Dyes. *The Journal of Physical Chemistry*, 770(2):774–779, 1965.
- [34] H. Gerischer. Electrochemical Techniques For The Study Of Photosensitization. *Photochemistry and Photobiology*, 16:243–260, 1972.
- [35] MP Dare-Edwards. Sensitisation of Semiconducting Electrodes with Ruthenium-based Dyes. *Faraday Discussions of the Chemical Society*, 69:285–298, 1980.
- [36] H. Tsubomura, M. Matsumura, Y. Nomura, and T. Amamiya. Dye Sensitized Zinc Oxide: Aqueous Electrolyte: Platinum Photocell. *Nature*, 261(June 3), 1976.

- [37] Aswani Yella, Hsuan-Wei Lee, Hoi Nok Tsao, Chenyi Yi, Aravind Kumar Chandiran, Mohammad Khaja Nazeeruddin, Eric Wei-Guang Diao, Chen-Yu Yeh, Shaik M. Zakeeruddin, and Michael Grätzel. Porphyrin-sensitized Solar Cells with Cobalt (II/III)-based Redox Electrolyte Exceed 12 percent Efficiency. *Science (New York, N. Y.)*, 334(6056):629–34, November 2011.
- [38] C.J. Barbé, Francine Arendse, Pascal Comte, Marie Jirousek, Frank Lenzmann, Valery Shklover, and Michael Grätzel. Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications. *Journal of the American Ceramic Society*, 80(12):3157–3171, 1997.
- [39] Laurence M. Peter. Characterization and Modeling of Dye-Sensitized Solar Cells. *Journal of Physical Chemistry C*, 111(18):23N–25N, 2007.
- [40] Jörg Ferber and Joachim Luther. Modeling of Photovoltage and Photocurrent in Dye-Sensitized Titanium Dioxide Solar Cells. *The Journal of Physical Chemistry B*, 105(21):4895–4903, May 2001.
- [41] Jenny Nelson. Continuous-time Random-walk Model of Electron Transport in Nanocrystalline TiO₂ Electrodes. *Physical Review B*, 59(23):374–380, 1999.
- [42] N. Kopidakis, E. A. Schiff, N.-G. Park, J. van De Lagemaat, and A. J. Frank. Ambipolar Diffusion of Photocarriers in Electrolyte-Filled , Nanoporous TiO₂. *Journal of Physical Chemistry B*, 104:3930–3936, 2000.
- [43] Laurence M. Peter. "Sticky Electrons" Transport and Interfacial Transfer of Electrons in the Dye-sensitized Solar Cell. *Accounts of Chemical Research*, 42(11):1839–47, November 2009.
- [44] Brian E. Hardin, Henry J. Snaith, and Michael D. McGehee. The Renaissance of Dye-sensitized Solar Cells. *Nature Photonics*, 6(3):162–169, February 2012.
- [45] Yousuke Ooyama and Yutaka Harima. Molecular Designs and Syntheses of Organic Dyes for Dye-Sensitized Solar Cells. *European Journal of Organic Chemistry*, 2009(18):2903–2934, June 2009.
- [46] Hiroshi Imahori, Tomokazu Umeyama, and Seigo Ito. Large pi-aromatic Molecules as Potential Sensitizers for Highly Efficient Dye-sensitized Solar Cells. *Accounts of chemical research*, 42(11):1809–18, November 2009.
- [47] Brian E. Hardin, Eric T. Hoke, Paul B. Armstrong, Jun-Ho Yum, Pascal Comte, Tomas Torres, Jean M. J. Frechet, Mohammad Khaja Nazeeruddin, Michael Grätzel, and Michael D. Mcgehee. Increased Light Harvesting in Dye-sensitized solar Cells with Energy Relay Dyes. *Nature Photonics*, 3(June):406–411, 2009.
- [48] Rubipy Scientific Inc. Rubipy, 2012.
- [49] S. Nakade, Y. Saito, W. Kubo, T. Kitamura, Y. Wada, and S. Yanagida. Influence of TiO₂ Nanoparticle Size on Electron Diffusion and Recombination in Dye-Sensitized TiO₂ Solar Cells. *The Journal of Physical Chemistry B*, 107(33):8607–8611, August 2003.

- [50] Seigo Ito, Takurou N. Murakami, Pascal Comte, Paul Liska, Carole Grätzel, Mohammad Khaja Nazeeruddin, and Michael Grätzel. Fabrication of Thin Film Dye Sensitized Solar Cells with Solar to Electric Power Conversion Efficiency over 10%. *Thin Solid Films*, 516(14):4613–4619, 2008.
- [51] Zhong-Sheng Wang, Hiroshi Kawauchi, Takeo Kashima, and Hironori Arakawa. Significant Influence of TiO₂ Photoelectrode Morphology on the Energy Conversion Efficiency of N719 Dye-sensitized Solar Cell. *Coordination Chemistry Reviews*, 248(13-14):1381–1389, July 2004.
- [52] Akira Ishimaru. *Wave Propagation and Scattering in Random Media*. IEE Press and Oxford University Press, reissued edition, 1997.
- [53] Bruno Maheu and G. Gouesbet. Four-flux Models to Solve the Scattering Transfer Equation: Special Cases. *Applied optics*, 25(7):1122–1128, 1986.
- [54] Qifeng Zhang, Daniel Myers, Jolin Lan, Samson A. Jenekhe, and Guozhong Cao. Applications of Light Scattering in Dye-sensitized Solar Cells. *Physical chemistry chemical physics : PCCP*, 14(43):14982–98, November 2012.
- [55] Jörg Ferber. Computer Simulations of Light Scattering and Absorption in Dye-sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, 54(1-4):265–275, July 1998.
- [56] Guido Rothenberger, Pascal Comte, and Michael Grätzel. A contribution to the Optical Design of Dye-sensitized Nanocrystalline Solar Cells. *Solar Energy Materials & Solar Cells*, 58(3):321–336, November 1999.
- [57] Bruno Maheu, J. N. Letoulouzan, and G. Gouesbet. Four-flux Models to Solve the Scattering Transfer Equation in Terms of Lorenz-Mie Parameters. *Applied optics*, 23(19):3353, October 1984.
- [58] Sarmimala Hore, C. Vetter, R. Kern, H. Smit, and Andreas Hinsch. Influence of Scattering Layers on Efficiency of Dye-sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, 90(9):1176–1188, May 2006.
- [59] Qifeng Zhang. Light Scattering with Oxide Nanocrystallite Aggregates for Dye-sensitized Solar Cell Application. *Journal of Nanophotonics*, 4(1):041540, May 2010.
- [60] Yong Joo Kim, Mi Hyeon Lee, Hark Jin Kim, Gooil Lim, Young Sik Choi, Nam-Gyu Park, Kyungkon Kim, and Wan In Lee. Formation of Highly Efficient Dye-Sensitized Solar Cells by Hierarchical Pore Generation with Nanoporous TiO₂ Spheres. *Advanced Materials*, 21(36):3668–3673, September 2009.
- [61] Jiangfeng Qian, Ping Liu, Yang Xiao, Yan Jiang, Yuliang Cao, Xinping Ai, and Hanxi Yang. TiO₂ - Coated Multilayered SnO₂ Hollow Microspheres for Dye-Sensitized Solar Cells. *Advanced Materials*, 21(36):3663–3667, September 2009.

- [62] Stefan Guldin, Sven Huttner, Matthias Kolle, Mark E. Welland, Peter Muller-Buschbaum, Richard H. Friend, Ullrich Steiner, and Nicolas Tetreault. Dye-Sensitized Solar Cell Based on a Three-Dimensional Photonic Crystal. *Nano Letters*, 10(7):2303–2309, May 2010.
- [63] Suzushi Nishimura, Neal Abrams, Bradley A. Lewis, Lara I. Halaoui, Thomas E. Mallouk, Kurt D. Benkstein, Jao van de Lagemaat, and Arthur J. Frank. Standing Wave Enhancement of Red Absorbance and Photocurrent in Dye-sensitized Titanium Dioxide Photoelectrodes Coupled to Photonic Crystals. *Journal of the American Chemical Society*, 125(20):6306–10, May 2003.
- [64] Chan Hoe Yip, Yet-Ming Chiang, and Chee Cheong Wong. Optical Absorption in a Finite Three-dimensional Photonic Crystal Thin Film Solar Cell. *Journal of the Optical Society of America B*, 27(5):920, April 2010.
- [65] A. Mihi and H. Míguez. Origin of Light-harvesting Enhancement in Colloidal-Photonic-crystal-based Dye-sensitized Solar Cells. *The journal of physical chemistry. B*, 109(33):15968–76, August 2005.
- [66] Lara I. Halaoui, Neal M Abrams, and Thomas E. Mallouk. Increasing the Conversion Efficiency of Dye-sensitized TiO₂ Photoelectrochemical Cells by Coupling to Photonic Crystals. *The journal of physical chemistry. B*, 109(13):6334–42, April 2005.
- [67] Wenbo Hou, Prathamesh Pavaskar, Zuwei Liu, Jesse Theiss, Mehmet Aykol, and Stephen B. Cronin. Plasmon Resonant Enhancement of Dye Sensitized Solar Cells. *Energy & Environmental Science*, 4(11):4650, 2011.
- [68] I-Kang Ding, Jia Zhu, Wenshan Cai, Soo-Jin Moon, Ning Cai, Peng Wang, Shaik M. Zakeeruddin, Michael Grätzel, Mark L. Brongersma, Yi Cui, and Michael D. McGehee. Plasmonic Dye-Sensitized Solar Cells. *Advanced Energy Materials*, 1(1):52–57, January 2011.
- [69] Carl Hagglund, Michael Zach, and Bengt Kasemo. Enhanced Charge Carrier Generation in Dye Sensitized Solar Cells by Nanoparticle Plasmons. *Applied Physics Letters*, 92(1):013113, 2008.
- [70] Manabu Ihara, Kanako Tanaka, and Keiji Sakaki. Enhancement of the Absorption Coefficient of cis-(NCS) 2 Bis (2, 2'-bipyridyl-4, 4'-dicarboxylate) ruthenium (II) Dye in Dye-Sensitized Solar Cells by a Silver Island. *Journal of Physical Chemistry B*, 101:5153–5157, 1997.
- [71] Stacey D Standridge, George C Schatz, and Joseph T. Hupp. Distance Dependence of Plasmon-enhanced Photocurrent in Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 131(24):8407–9, June 2009.
- [72] Michael D. Brown, Teeraporn Suteewong, R. Sai Santosh Kumar, Valerio D’Innocenzo, Annamaria Petrozza, Michael M. Lee, Ulrich Wiesner, and Henry J. Snaith. Plasmonic Dye-sensitized Solar Cells Using Coreshell Metalinsulator Nanoparticles. *Nano letters*, 11:438–445, 2011.

- [73] M. Ni, M. Leung, D. Leung, and K. Sumathy. An Analytical Study of the Porosity Effect on Dye-sensitized Solar Cell Performance. *Solar Energy Materials and Solar Cells*, 90(9):1331–1344, May 2006.
- [74] Yasuhiro Tachibana, Kohjiro Hara, Kazuhiro Sayama, and Hironori Arakawa. Quantitative Analysis of Light-Harvesting Efficiency and Electron-Transfer Yield in Ruthenium-Dye-Sensitized Nanocrystalline TiO₂ Solar Cells. *Chemistry of Materials*, 14(6):2527–2535, June 2002.
- [75] Jenny Nelson and Rosemary E. Chandler. Random Walk Models of Charge Transfer and Transport in Dye Sensitized Systems. *Coordination Chemistry Reviews*, 248(13-14):1181–1194, July 2004.
- [76] Shaik M. Zakeeruddin and Michael Grätzel. Solvent-Free Ionic Liquid Electrolytes for Mesoscopic Dye-Sensitized Solar Cells. *Advanced Functional Materials*, 19(14):2187–2202, July 2009.
- [77] Hoi Nok Tsao, Pascal Comte, Chenyi Yi, and Michael Grätzel. Avoiding Diffusion Limitations in Cobalt(III/II)-Tris(2,2'-Bipyridine)-Based Dye-Sensitized Solar Cells by Tuning the Mesoporous TiO₂ Film Properties. *Chemphyschem : a European journal of chemical physics and physical chemistry*, pages 1–7, July 2012.
- [78] Jong Hyuk Park, Sun Young Jung, Raehyun Kim, Nam-Gyu Park, Junkyung Kim, and Sang-Soo Lee. Nanostructured Photoelectrode Consisting of TiO₂ Hollow Spheres for Non-volatile Electrolyte-based Dye-sensitized Solar Cells. *Journal of Power Sources*, 194(1):574–579, 2009.
- [79] Dehong Chen, Fuzhi Huang, Yi-Bing Cheng, and Rachel A. Caruso. Mesoporous Anatase TiO₂ Beads with High Surface Areas and Controllable Pore Sizes: A Superior Candidate for High-Performance Dye-Sensitized Solar Cells. *Advanced Materials*, 21(21):2206–2210, June 2009.
- [80] Jao van de Lagemaat, Kurt D. Benkstein, and Arthur J. Frank. Relation between Particle Coordination Number and Porosity in Nanoparticle Films: Implications to Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry B*, 105(50):12433–12436, December 2001.
- [81] Yiming Cao, Yu Bai, Qingjiang Yu, Yueming Cheng, Shi Liu, Dong Shi, Feifei Gao, and Peng Wang. Dye-Sensitized Solar Cells with a High Absorptivity Ruthenium Sensitizer Featuring a 2-(Hexylthio)thiophene Conjugated Bipyridine. *The Journal of Physical Chemistry C*, 113(15):6290–6297, April 2009.
- [82] Chia-Yuan Chen, Mingkui Wang, Jheng-Ying Li, Nuttapol Pootrakulchote, Leila Alibabaei, Ngoc-le Cevey-Ha, Jean-David Decoppet, Jia-Hung Tsai, Carole Grätzel, Chun-Guey Wu, Shaik M. Zakeeruddin, and Michael Grätzel. Highly Efficient Light-harvesting Ruthenium Sensitizer for Thin-film Dye-sensitized Solar Cells. *ACS nano*, 3(10):3103–9, October 2009.
- [83] Sandra M. Feldt, Elizabeth A. Gibson, Erik Gabrielsson, Licheng Sun, Gerrit Boschloo, and Anders Hagfeldt. Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-efficiency Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 132(46):16714–24, November 2010.

- [84] William H. Nguyen, Colin D. Bailie, Julian Burschka, Thomas Moehl, Michael Grätzel, Michael D. McGehee, and Alan Sellinger. Molecular Engineering of Organic Dyes for Improved Recombination Lifetime in Solid-State Dye-Sensitized Solar Cells. *Chemistry of Materials*, 25:1519–1525, 2013.
- [85] Hoi Nok Tsao, Chenyi Yi, Thomas Moehl, Jun-Ho Yum, Shaik M. Zakeeruddin, Mohammad Khaja Nazeeruddin, and Michael Grätzel. Cyclopentadithiophene Bridged Donor-Acceptor Dyes Achieve High Power Conversion Efficiencies in Dye-Sensitized Solar Cells Based on the tris-Cobalt Bipyridine Redox Couple. *ChemSusChem*, 4(5):591–4, May 2011.
- [86] Torben Daeneke, Tae-Hyuk Kwon, Andrew B. Holmes, Noel W. Duffy, Udo Bach, and Leone Spiccia. High-efficiency Dye-sensitized Solar Cells with Ferrocene-based Electrolytes. *Nature chemistry*, 3(3):213–7, March 2011.
- [87] Mingkui Wang, Carole Grätzel, Shaik M. Zakeeruddin, and Michael Grätzel. Recent Developments in Redox Electrolytes for Dye-sensitized Solar Cells. *Energy & Environmental Science*, 5(11):9394, 2012.
- [88] Jeremy J. Nelson, Tyson J. Amick, and C. Michael Elliott. Mass Transport of Polypyridyl Cobalt Complexes in Dye-Sensitized Solar Cells with Mesoporous TiO₂ Photoanodes. *Journal of Physical Chemistry C*, 112:18255–18263, 2008.
- [89] Gerrit Boschloo and Anders Hagfeldt. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. *Accounts of Chemical Research*, 42(11):1819–1826, November 2009.
- [90] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, and Hironori Arakawa. Influence of Electrolytes on the Photovoltaic Performance of Organic Dye-sensitized Nanocrystalline TiO₂ Solar Cells. *Solar Energy Materials & Solar Cells*, 70:151–161, 2001.
- [91] Hironori Arakawa, Takeshi Yamaguchi, Akihito Takeuchi, Shinya Agatsuma, Multi-layered Tio, and The Tio. Efficiency Improvement of Dye-Sensitized Solar Cell by Light Confined Effect. *2006 IEEE 4th World Conference on Photovoltaic Energy Conference*, pages 36–39, May 2006.
- [92] Sarmimala Hore, Peter Nitz, Carmen Vetter, Christof Prahl, Michael Niggemann, and Rainer Kern. Scattering Spherical Voids in Nanocrystalline TiO₂- Enhancement of Efficiency in Dye-sensitized Solar Cells. *Chemical communications*, (15):2011–3, April 2005.
- [93] Thi Thu Trang Pham, Takeru Bessho, Nripan Mathews, Shaik M. Zakeeruddin, Yeng Ming Lam, Subodh Mhaisalkar, and Michael Grätzel. Light Scattering Enhancement from Sub-micrometer Cavities in the Photoanode for Dye-Sensitized Solar Cells. *Journal of Materials Chemistry*, 22:16201–16204, 2012.
- [94] Siavouche Namet-Nasser and Muneo Hori. Void Collapse and Void Growth in Crystalline Solids. *Journal of Applied Physics*, 62(7):2746, 1987.
- [95] Darren Crowdy and Laurent Duchemin. The Effect of Solid Boundaries on Pore Shrinkage in Stokes Flow. *Journal of Fluid Mechanics*, 531:359–379, May 2005.

- [96] Jianhui Zhang, Zuo Chen, Zhenlin Wang, Weiyi Zhang, and Naiben Ming. Preparation of Monodisperse Polystyrene Spheres in Aqueous Alcohol System. *Materials Letters*, 57(28):4466–4470, October 2003.
- [97] P.M. Sommeling, Brian C. O'Regan, R. R. Haswell, H. J. P. Smit, N. J. Bakker, J. J. T. Smits, Jan M. Kroon, and J. a. M. van Roosmalen. Influence of a TiCl_4 Post-treatment on Nanocrystalline TiO_2 Films in Dye-sensitized Solar Cells. *The journal of physical chemistry. B*, 110(39):19191–7, October 2006.
- [98] H. Wang, K.P. Yan, J. Xie, and M. Duan. Fabrication of ZnO Colloidal Photonic Crystal by Spin-coating Method. *Materials Science in Semiconductor Processing*, 11(2):44–47, April 2008.
- [99] E Seelig. Self-assembled 3D Photonic Crystals from ZnO Colloidal Spheres. *Materials Chemistry and Physics*, 80(1):257–263, April 2003.
- [100] Seigo Ito, Peter Chen, Pascal Comte, Mohammad Khaja Nazeeruddin, Paul Liska, and Michael Grätzel. Fabrication of Screen-printing Pastes from TiO_2 Powders for Dye-sensitized Solar Cells. *Progress in photovoltaics: Research and applications*, 15(May):603–612, 2007.
- [101] Daibin Kuang, Satoshi Uchida, Robin Humphry-Baker, Shaik M. Zakeeruddin, and Michael Grätzel. Organic Dye-sensitized Ionic Liquid Based Solar Cells: Remarkable Enhancement in Performance through Molecular Design of Indoline Sensitizers. *Angewandte Chemie (International ed. in English)*, 47(10):1923–7, January 2008.
- [102] Xiao Jiang, Karl Martin Karlsson, Erik Gabrielsson, Erik M. J. Johansson, Maria Quintana, Martin Karlsson, Licheng Sun, Gerrit Boschloo, and Anders Hagfeldt. Highly Efficient Solid-State Dye-Sensitized Solar Cells Based on Triphenylamine Dyes. *Advanced Functional Materials*, 21(15):2944–2952, August 2011.
- [103] Renzhi Li, Jingyuan Liu, Ning Cai, Min Zhang, and Peng Wang. Synchronously Reduced Surface States, Charge Recombination, and Light Absorption Length for High-Performance Organic Dye-Sensitized Solar Cells. *Journal of Physical Chemistry B*, 114(13):4461–4464, 2010.
- [104] Seigo Ito, Hidetoshi Miura, Satoshi Uchida, Masakazu Takata, Koichi Sumioka, Paul Liska, Pascal Comte, Péter Péchy, and Michael Grätzel. High-conversion-efficiency Organic Dye-sensitized Solar Cells with a Novel Indoline Dye. *Chemical communications*, (41):5194–6, November 2008.
- [105] Haining Tian, Ze Yu, Anders Hagfeldt, Lars Kloo, and Licheng Sun. Organic Redox Couples and Organic Counter Electrode for Efficient Organic Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 133(24):9413–22, June 2011.
- [106] Renzhi Li, Jingyuan Liu, Ning Cai, Min Zhang, and Peng Wang. Synchronously Reduced Surface States, Charge Recombination, and Light Absorption Length for High-Performance Organic Dye-Sensitized Solar Cells. *Journal of Physical Chemistry B*, 114(13):4461–4464, 2010.

- [107] Seigo Ito, Shaik M. Zakeeruddin, Pascal Comte, Paul Liska, Daibin Kuang, and Michael Grätzel. Bifacial Dye-sensitized Solar Cells Based on an Ionic Liquid Electrolyte. *Nature Photonics*, 2(11):693–698, October 2008.
- [108] Liyuan Han and Ashraful Islam. Highly Efficient Dye-sensitized Solar cells. *Proceedings of SPIE*, 7416:74160X–74160X–8, August 2009.
- [109] Seigo Ito, Shaik M. Zakeeruddin, Robin Humphry-Baker, Paul Liska, R. Charvet, Pascal Comte, Mohammad Khaja Nazeeruddin, Péter Péchy, M. Takata, H. Miura, S. Uchida, and Michael Grätzel. High-Efficiency Organic-Dye-Sensitized Solar Cells Controlled by Nanocrystalline-TiO₂ Electrode Thickness. *Advanced Materials*, 18(9):1202–1205, 2006.
- [110] Peng Wang, Shaik M. Zakeeruddin, Jacques-E. Moser, Robin Humphry-Baker, and Michael Grätzel. A Solvent-Free SeCN-/(SeCN)₃ Based Ionic Liquid Electrolyte for High-efficiency Dye-sensitized Nanocrystalline Solar Cells. *Journal of the American Chemical Society*, 126:7164–7165, 2004.
- [111] Peng Wang, Shaik M. Zakeeruddin, Pascal Comte, Ivan Exnar, and Michael Grätzel. Gelation of Ionic Liquid-based Electrolytes with Silica Nanoparticles for Quasi-solid-state Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 125(5):1166–7, February 2003.
- [112] Brian E. Hardin, Alan Sellinger, Thomas Moehl, Robin Humphry-Baker, Jacques-E. Moser, Peng Wang, Shaik M. Zakeeruddin, Michael Grätzel, and Michael D. McGehee. Energy and Hole Transfer Between Dyes Attached to Titania in Cosensitized Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 133(27):10662–7, July 2011.
- [113] Seung-Hyun Anna Lee, Neal M. Abrams, Paul G. Hoertz, Greg D. Barber, Lara I. Halaoui, and Thomas E. Mallouk. Coupling of Titania Inverse Opals to Nanocrystalline Titania Layers in Dye-sensitized Solar Cells. *The journal of physical chemistry. B*, 112(46):14415–21, November 2008.
- [114] Allen Taflove. Application of Finite-Difference Time-Domain Method to Sinusoidal Steady-state Electromagnetic Penetration Problems. *IEEE Transactions on electromagnetic Competibility*, EMC-22(3):191–202, 1980.
- [115] Keat G. Ong, Oomman K. Varghese, Gopal K. Mor, Karthik Shankar, and Craig a. Grimes. Application of Finite-Difference Time Domain to Dye-sensitized Solar Cells: The Effect of Nanotube-array Negative Electrode Dimensions on Light Absorption. *Solar Energy Materials and Solar Cells*, 91(4):250–257, February 2007.
- [116] Jinyao Tang, Ziyang Huo, Sarah Brittman, Hanwei Gao, and Peidong Yang. Solution-processed Core-shell Nanowires for Efficient Photovoltaic Cells. *Nature nanotechnology*, 6(9):568–72, September 2011.
- [117] Yoshihiro Hishikawa, Masatoshi Yanagida, and Naoki Koide. Performance Characterization of the Dye-sensitized Solar Cells. In *Proceedings of 31st IEEE Photovoltaic Specialists Conference, Florida*, pages 67–70, 2005.

- [118] Thomas Geiger, Simon Kuster, Jun-Ho Yum, Soo-Jin Moon, Mohammad Khaja Nazeeruddin, Michael Grätzel, and Frank Nüesch. Molecular Design of Unsymmetrical Squaraine Dyes for High Efficiency Conversion of Low Energy Photons into Electrons Using TiO₂ Nanocrystalline Films. *Advanced Functional Materials*, 19(17):2720–2727, September 2009.
- [119] Punniamoorthy Ravirajan, Ana M. Peiró, Mohammad Khaja Nazeeruddin, Michael Grätzel, Donal D. C. Bradley, James R. Durrant, and Jenny Nelson. Hybrid Polymer/Zinc Oxide Photovoltaic Devices with Vertically Oriented ZnO Nanorods and an Amphiphilic Molecular Interface Layer. *The journal of physical chemistry. B*, 110(15):7635–9, April 2006.
- [120] Halina K. Dunn and Laurence M. Peter. How Efficient Is Electron Collection in Dye-Sensitized Solar Cells? Comparison of Different Dynamic Methods for the Determination of the Electron Diffusion Length. *The Journal of Physical Chemistry C*, 113(11):4726–4731, March 2009.
- [121] John N. Clifford, Gökhan Yahioğlu, Lionel R. Milgrom, and James R. Durrant. Molecular Control of Recombination Dynamics in Dye sensitised Nanocrystalline TiO₂ Films. *Chemical communications (Cambridge, England)*, (12):1260–1, June 2002.
- [122] N.W Duffy, L.M Peter, and K.G.U Wijayantha. Characterisation of Electron Transport and Back Reaction in Dye-sensitised Nanocrystalline Solar Cells by Small Amplitude Laser Pulse Excitation. *Electrochemistry Communications*, 2(4):262–266, April 2000.
- [123] N.W Duffy, L.M Peter, R.M.G Rajapakse, and K.G.U Wijayantha. A Novel Charge Extraction Method for the Study of Electron Transport and Interfacial Transfer in Dye Sensitised Nanocrystalline Solar Cells. *Electrochemistry Communications*, 2(9):658–662, September 2000.
- [124] Brian C. O'Regan and Frank Lenzmann. Charge Transport and Recombination in a Nanoscale Interpenetrating Network of n-Type and p-Type Semiconductors: Transient Photocurrent and Photovoltage Studies of TiO₂/Dye/CuSCN Photovoltaic Cells. *The Journal of Physical Chemistry B*, 108(14):4342–4350, April 2004.
- [125] Brian O'Regan, Frank Lenzmann, Ruud Muis, and Jeannette Wienke. A Solid-State Dye-Sensitized Solar Cell Fabricated with Pressure-Treated P25-TiO₂ and CuSCN: Analysis of Pore Filling and IV Characteristics. *Chemical Materials*, 14:5023–5029, 2002.
- [126] G. Schlichthörl, N. G. Park, and Arthur J. Frank. Evaluation of the Charge-Collection Efficiency of Dye-Sensitized Nanocrystalline TiO₂ Solar Cells. *Journal of Physical Chemistry B*, 103:782–791, 1999.
- [127] Juan Bisquert, Francisco Fabregat-Santiago, Ivan Mora-Sero, Germà Garcia-Belmonte, and Sixto Gimenez. Electron Lifetime in Dye-Sensitized Solar Cells: Theory and Interpretation of Measurements. *The Journal of Physical Chemistry C*, 113(40):17278–17290, 2009.

- [128] Janne Halme, Paula Vahermaa, Kati Miettunen, and Peter Lund. Device physics of Dye Solar cells. *Advanced materials (Deerfield Beach, Fla.)*, 22(35):E210–34, September 2010.
- [129] Francisco Fabregat-Santiago, Juan Bisquert, Germà Garcia-Belmonte, Gerrit Boschloo, Anders Hagfeldt, and Francisco Fabregat-santiago. Influence of Electrolyte in Transport and Recombination in Dye-sensitized Solar Cells Studied by Impedance Spectroscopy. *Solar Energy Materials and Solar Cells*, 87(1-4):117–131, May 2005.
- [130] Qing Wang, Jacques-E. Moser, and Michael Grätzel. Electrochemical Impedance Spectroscopic Analysis of Dye-sensitized Solar cells. *The journal of physical chemistry. B*, 109(31):14945–53, 2005.
- [131] Francisco Fabregat-santiago, Juan Bisquert, Emilio Palomares, Luis Otero, Daibin Kuang, Shaik M. Zakeeruddin, and Michael Grätzel. Correlation between Photovoltaic Performance and Impedance Spectroscopy of Dye-Sensitized Solar Cells Based on Ionic Liquids. *Journal of Physical Chemistry C*, 111(17):6550–6560, 2007.
- [132] Jifu Shi, Ling Wang, Yanliang Liang, Shengjie Peng, Fangyi Cheng, and Jun Chen. All-Solid-State Dye-Sensitized Solar Cells with Alkylloxy-Imidazolium Iodide Ionic Polymer / SiO₂ Nanocomposite Electrolyte and Triphenylamine-Based Organic Dyes. *Journal of Physical Chemistry C*, 114:6814–6821, 2010.
- [133] Changneng Zhang, Yang Huang, Zhipeng Huo, Shuanghong Chen, and Songyuan Dai. Photoelectrochemical Effects of Guanidinium Thiocyanate on Dye-Sensitized Solar Cell Performance and Stability. *The Journal of Physical Chemistry C*, 113(52):21779–21783, December 2009.
- [134] Yu Bai, Jing Zhang, Yinghui Wang, Min Zhang, and Peng Wang. Lithium-modulated Conduction Band Edge Shifts and Charge-Transfer Dynamics in Dye-sensitized Solar Cells Based on a Dicyanamide Ionic Liquid. *Langmuir : the ACS journal of surfaces and colloids*, 27(8):4749–55, April 2011.
- [135] Shawn A. Sapp, C. Michael Elliott, Cristiano Contado, Stefano Caramori, and Carlo Alberto Bignozzi. Substituted Polypyridine Complexes of Cobalt(II/III) as Efficient Electron-transfer Mediators in Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 124(37):11215–22, September 2002.
- [136] Benjamin M. Klahr and Thomas W. Hamann. Performance Enhancement and Limitations of Cobalt Bipyridyl Redox Shuttles in Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C*, 113(31):14040–14045, August 2009.
- [137] Xiao Jiang, Tannia Marinado, Erik Gabrielsson, Daniel P. Hagberg, Licheng Sun, and Anders Hagfeldt. Structural Modification of Organic Dyes for Efficient Coadsorbent-Free Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C*, 114(6):2799–2805, February 2010.
- [138] Sandra M. Feldt, Gang Wang, Gerrit Boschloo, and Anders Hagfeldt. Effects of Driving Forces for Recombination and Regeneration on the Photovoltaic Performance of Dye-Sensitized Solar Cells using Cobalt Polypyridine Redox Couples. *The Journal of Physical Chemistry C*, 115(43):21500–21507, November 2011.

- [139] Francisco Fabregat-Santiago, Germà Garcia-Belmonte, Ivan Mora-Sero, and Juan Bisquert. Characterization of Nanostructured Hybrid and Organic Solar Cells by Impedance Spectroscopy. *Physical chemistry chemical physics*, 13(20):9083–118, May 2011.
- [140] G. Schlichthörl, S. Y. Huang, J. Sprague, and Arthur J. Frank. Band Edge Movement and Recombination Kinetics in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells: A Study by Intensity Modulated Photovoltage Spectroscopy. *The Journal of Physical Chemistry B*, 101(41):8141–8155, October 1997.
- [141] Juan Bisquert, David Cahen, and Gary Hodes. Physical Chemical Principles of Photovoltaic Conversion with Nanoparticulate, Mesoporous Dye-sensitized Solar Cells. *The Journal of Physical Chemistry B*, 108:8106–8118, 2004.
- [142] Yiming Cao, Jing Zhang, Yu Bai, Renzhi Li, Shaik M. Zakeeruddin, Michael Grätzel, and Peng Wang. Dye-Sensitized Solar Cells with Solvent-Free Ionic Liquid Electrolytes. *Journal of Physical Chemistry C*, 112:13775–13781, 2008.
- [143] Hui-Seon Kim, Soo-Byung Ko, In-Hyuk Jang, and Nam-Gyu Park. Improvement of Mass Transport of the [Co(bpy)₃](II/III) Redox Couple by Controlling Nanostructure of TiO₂ Films in Dye-sensitized Solar Cells. *Chemical communications (Cambridge, England)*, 47(47):12637–9, December 2011.
- [144] M. Liberatore, A. Petrocco, F. Caprioli, C. La Mesa, F. Decker, and Carlo Alberto Bignozzi. Mass Transport and Charge Transfer Rates for Co(III)/Co(II) Redox Couple in a Thin-layer Cell. *Electrochimica Acta*, 55(12):4025–4029, April 2010.
- [145] Mohammad Khaja Nazeeruddin, Etienne Baranoff, and Michael Grätzel. Dye-sensitized Solar Cells: A Brief Overview. *Solar Energy*, 85(6):1172–1178, June 2011.
- [146] Kurt D. Benkstein, Nikos Kopidakis, J. van de Lagemaat, and Arthur J. Frank. Influence of the Percolation Network Geometry on Electron Transport in Dye-Sensitized Titanium Dioxide Solar Cells. *The Journal of Physical Chemistry B*, 107(31):7759–7767, August 2003.
- [147] Torben Daeneke, Attila J. Mozer, Yu Uemura, Satoshi Makuta, Monika Fekete, Yasuhiro Tachibana, Nagatoshi Koumura, Udo Bach, and Leone Spiccia. Dye Regeneration Kinetics in Dye-sensitized Solar Cells. *Journal of the American Chemical Society*, 134(41):16925–8, October 2012.
- [148] N. Papageorgiou, C. Barbe, and Michael Grätzel. Morphology and Adsorbate Dependence of Ionic Transport in Dye Sensitized Mesoporous TiO₂ Films. *The Journal of Physical Chemistry B*, 102:4156–4164, 1998.
- [149] Guan-Jun Yang, Chang-Jiu Li, Sheng-Qiang Fan, and Jin-Cheng Gao. Influence of Pore Structure on Ion Diffusion Property in Porous TiO₂ Coating and Photovoltaic Performance of Dye-sensitized Solar Cells. *Surface and Coatings Technology*, 205(10):3205–3210, February 2011.

- [150] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, and Michael Grätzel. The Performance and Stability of Ambient Temperature Molten Salts for Solar Cell Applications. *Journal of Electrochemical Society*, 143(10):3099–3108, 1996.
- [151] Udo Bach, D. Lupo, Pascal Comte, Jacques-E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and Michael Grätzel. Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. *Nature*, 395(6702):583–585, 1998.
- [152] Julian Burschka, Amalie Dualah, Florian Kessler, Etienne Baranoff, Ngoc-Lê Cevey-Ha, Chenyi Yi, Mohammad Khaja Nazeeruddin, and Michael Grätzel. Tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) as p-Type Dopant for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells. *Journal of the American Chemical Society*, 133(45):18042–5, November 2011.
- [153] Lei Yang, Ute B. Cappel, Eva L. Unger, Martin Karlsson, Karl Martin Karlsson, Erik Gabriellsson, Licheng Sun, Gerrit Boschloo, Anders Hagfeldt, and Erik M. J. Johansson. Comparing spiro-OMeTAD and P3HT hole conductors in efficient solid state dye-sensitized solar cells. *Physical chemistry chemical physics*, 12:779–789, 2012.
- [154] Kazuhiro Manseki, Wirat Jarernboon, You Youhai, Ke-Jian Jiang, Kazuharu Suzuki, Naruhiko Masaki, Yukyeong Kim, Jiangbin Xia, and Shozo Yanagida. Solid-state Dye-sensitized Solar Cells Fabricated by Coupling Photoelectrochemically Deposited poly(3,4-ethylenedioxythiophene) (PEDOT) With Silver-paint on Cathode. *Chemical communications (Cambridge, England)*, 47(11):3120–2, March 2011.
- [155] In Chung, Byunghong Lee, Jiaqing He, Robert P. H. Chang, and Mercouri G. Kanatzidis. All-solid-state Dye-sensitized Solar Cells with High Efficiency. *Nature*, 485(7399):486–489, May 2012.
- [156] Soo-Jin Moon, Yafit Itzhaik, Jun-Ho Yum, Shaik M. Zakeeruddin, Gary Hodes, and Michael Grätzel. Sb₂S₃-Based Mesoscopic Solar Cell using an Organic Hole Conductor. *The Journal of Physical Chemistry Letters*, 1(10):1524–1527, May 2010.
- [157] Jeong Ah Chang, Jae Hui Rhee, Sang Hyuk Im, Yong Hui Lee, Hi-jung Kim, Sang Il Seok, Mohammad Khaja Nazeeruddin, and Michael Grätzel. High-performance Nanostructured Inorganic-Organic Heterojunction Solar Cells. *Nano letters*, 10(7):2609–12, July 2010.
- [158] Hui-Seon Kim, Chang-Ryul Lee, Jeong-Hyeok Im, Ki-Beom Lee, Thomas Moehl, Arianna Marchioro, Soo-Jin Moon, Robin Humphry-Baker, Jun-Ho Yum, Jacques-E. Moser, Michael Grätzel, and Nam-Gyu Park. Lead Iodide Perovskite Sensitized All-solid-state Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Scientific reports*, 2:591, January 2012.

Appendix A

List of abbreviations

AC	Alternating current
ACN	Acetonitrile
AM	Air mass
AR	Anti-reflecting
Co(dtb)	Cobalt di- <i>tert</i> -butyl bipyridine
Co(bpy)	Cobalt bipyridine
CE	Counter electrode
D18NR-T	Dyesol paste coded 18NR-T (particle size 18 nm)
DC	Direct current
DMII	1,3-dimethylimidazoliumiodide
DSC(s)	Dye-sensitized solar cell(s)
EDX	Energy dispersed X-ray spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EMII	1-ethyl-3-methylimidazoliumiodide
EMT	1-ethyl-3-methylimidazolium tetracyanoborate
FDTD	Finite-Difference Time-Domain
FESEM	Field-emission scanning electron microscope/microscopy
FTO	Flourine-doped tin oxide
GuSCN	guanidinium thiocyanate
HTM	Hole transporting material
IPCE	Incident photon to current efficiency
I-V	Current-voltage

IL	Ionic liquid
IMPS	Intensity Modulated Photocurrent Spectroscopy
IMVS	Intensity Modulated Photovoltage Spectroscopy
J-V	Current density-voltage
KPS	Potassium persulfate
LED	Light-emitting diode
LHE	Light harvesting efficiency
MPN	3-methoxypropionitrile
NBB	N-butylbenzimidazole
PCE	Power conversion efficiency
PEDOT	Poly(3,4-ethylenedioxythiophene)
PS	Polystyrene
R_{coll}	Collimated reflection
R_{diff}	Diffuse reflection
R_{CE}	Charge transfer resistance at counter electrode
R_{dif}	Diffusion resistance
R_{rec}	Recombination resistance
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope/microscopy
T_{coll}	Collimated transmission
T_{diff}	Diffuse transmission
TiO ₂	Titanium dioxide
TBAOH	Tetrabutylammonium hydroxide
TMAOH	Tetramethylammonium hydroxide
XRD	X-ray diffraction
ZnO	Zinc oxide

Appendix B

Sensitizers presented in the thesis

B.1 Molecular structure

Figure B.1: Molecular structure of Y196, C101 and SQ2 dyes

B.2 Absorption spectra

(a) D205 dye [104]

(b) C218 dye [103]

(c) C101 and C106 dye [81]

(d) D35 dye [83]

(e) SQ02 dye [118]

Figure B.2: Absorption spectra from references.

Appendix C

Optimization data

Figure C.1: V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with C218 dye and Z1026 electrolyte

Figure C.2: Average V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with C218 dye and Z1026 electrolyte. The graphs show error bars due to variations in experiment data.

Figure C.3: V_{oc} as with varying thickness of D18NR-T with C218 dye and Z1026 electrolyte. The plots support the argument discussed in figure 4.3 that V_{oc} decreases with increasing film thickness, and assure that the observation is reproducible.

Figure C.4: V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with D205 dye and Z1130 electrolyte

Figure C.5: V_{oc} , J_{sc} , FF and PCE as with varying thickness and concentration of pores with D205 dye and Z952 electrolyte

Appendix D

List of publications

D.1 Journal papers

1. Thi Thu Trang Pham, Takeru Bessho, Nripan Mathews, Shaik M. Zakeeruddin, Yeng Ming Lam, Subodh Mhaisalkar, and Michael Grätzel. Light Scattering Enhancement from Sub-micrometer Cavities in the Photoanode for Dye-sensitized Solar Cells. *Journal of Materials Chemistry*, 22, 16201-16204, 2012.
2. Thi Thu Trang Pham, Teck Ming Koh, Kazuteru Nonomura, Nripan Mathews, Yeng Ming Lam, and Subodh Mhaisalkar. Reducing Mass Transport Limitation in Cobalt Electrolyte Based Dye-sensitized Solar Cell by Photoanode Modification. *RSC Advances* (in review)
3. Natalia Yantara, Thi Thu Trang Pham, Nripan Mathews, and Subodh Mhaisalkar. Photon Management in All Metal Oxide Solar Cell. *Applied Physics Letters* (submitting).
4. Julianto Chua, Thi Thu Trang Pham, Dharani Sabba, Nripan Mathews, and Subodh G. Mhaisalkar. Analysis of electron collection behavior in solid state mesoscopic solar cells via variation of electron transport distance (under preparation).
5. Dharani Sabba, Hemant Kumar, Natalia Yantara, Thi Thu Trang Pham, Nam-Gyu Park, Michael Grtzel and Subodh Mhaisalkar. High efficiency electrospun TiO₂ nanofiber based hybrid organic-inorganic perovskite solar cell. *Nanoscale* (in review)

D.2 Conference and poster presentations

1. Thi Thu Trang Pham, Takeru Bessho, Nripan Mathews, Shaik M. Zakeeruddin, Yeng Ming Lam, Subodh Mhaisalkar, and Michael Grätzel. Sub-micrometer cavities in photoanode for dye-sensitized solar cells: Enhancing light harvesting and reducing cost of dye-sensitizer - *Photovoltaics Asia Pacific Conference (PVAP)* - Singapore 2012.
2. Thi Thu Trang Pham, Takeru Bessho, Nripan Mathews, Shaik M. Zakeeruddin, Yeng Ming Lam, Subodh Mhaisalkar, and Michael Grätzel. Polystyrene templated-TiO₂ film for dye-sensitized solar cell - *International Conference on Materials for Advanced Technologies (ICMAT)* - Singapore 2011.

3. Thi Thu Trang Pham, Yeng Ming Lam, Subodh Mhaisalkar. Photonic crystals for dye-sensitized solar cell *Center for Functional Nanostructures (CFN) summer school on Nanophotonics* Germany 2010.
4. Thi Thu Trang Pham, Yeng Ming Lam, Subodh Mhaisalkar. Titanium dioxide nanostructures for photovoltaics *First annual workshop on Energy Research* Singapore 2009.