Modification of the interface between TiO₂ and electrolyte toward higher efficiency dye sensitized solar cells

Wang, Xiu

2014

Wang, X. (2014). Modification of the interface between TiO₂ and electrolyte toward higher efficiency dye sensitized solar cells. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61064>

<https://doi.org/10.32657/10356/61064>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**MODIFICATION OF THE INTERFACE BETWEEN TiO_2 AND
ELECTROLYTE TOWARD HIGHER EFFICIENCY DYE
SENSITIZED SOLAR CELLS**

**WANG XIU
SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2014**

**MODIFICATION OF THE INTERFACE BETWEEN TIO₂ AND
ELECTROLYTE TOWARD HIGHER EFFICIENCY DYE
SENSITIZED SOLAR CELLS**

WANG XIU

School of Materials Science and Engineering

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

2014

Acknowledgement

I would like to express my thanks to the School of Materials Science and Engineering, Nanyang Technological University and Ministry of Education, Singapore for giving me the opportunity to pursue my PhD study and Bosch (sea) Pte Ltd for the financial support in this project. I would like to specially thank my supervisor, Assoc Prof Chee Cheong Wong, for his encouragement, guidance and support during my study. He is always reachable and willing to discuss and share thoughts in both research and life. His attitude, passions and expertise helped me in all the time of my research and thesis writing. Without his guidance, this thesis would not have been completed.

I would also like to deeply thank Prof Subodh G. Mhaisalkar, Assoc Prof Yeng Ming Lam, Asst Prof Lydia Helena Wong and Prof Michael Grätzel for their valuable suggestions to my research work. My thanks also go to my friends and colleagues in School of Materials Science and Engineering, and Energy Research Institute @ NTU for their support and suggestions: Anantha P., Dharani Sabba, Duen Yang Ong, Eric Ng, Huu Loc Nguyen, Julianto Chua, Kazuteru Nonomura, Liling Zhang, Nripan Mathews, Qin Zhao, Sneha A. Kulkarni, Sudip K. Batabyal, Thi Thu Trang Pham, and other students and staff in the lab. I thank Xiaoyan Wang, Lidong Sun and Junling Song for the collaboration work and sharing the ideas in the field.

My thanks also go to my thesis examiners for their comments and suggestions which greatly improved this thesis. Lastly, I would like to express my sincere gratitude to my husband Xuejie and my family for their love, patience, encouragement and sacrifice that they gave me to pursue my study.

Without any of you, this would not be possible.

Table of Contents

ACKNOWLEDGEMENT.....	3
TABLE OF CONTENTS.....	4
LIST OF FIGURES.....	7
LIST OF TABLES.....	9
ABSTRACT.....	10
CHAPTER 1 INTRODUCTION.....	12
CHAPTER 2 BACKGROUND AND RELATED WORK.....	14
2.1 Dye-Sensitized Solar Cells.....	14
2.1.1 General Parameters of a DSSC.....	14
2.1.2 Design of a DSSC.....	15
2.1.3 Operation principle of a DSSC.....	16
2.1.4 Components of a DSSC.....	17
2.1.4.1 Dyes.....	17
2.1.4.2 Oxides Photoanodes.....	18
2.1.4.3 Electrolytes.....	19
2.2 Challenges in Current DSSCs.....	22
2.2.1 Dark Reactions.....	22
2.3 Studies of the TiO₂-Electrolyte Interface.....	23
2.3.1 Modification through Direct Covering of TiO ₂	23
2.3.2 Modification through Tuning Additives in Electrolyte.....	25
2.3.3 Characterization of TiO ₂ -Electrolyte Interface.....	26
2.3.3.1 Dark EIS for DSSCs.....	28
2.3.3.2 Light EIS for DSSCs.....	29
2.3.3.3 Derivation of Flat Band Potential using EIS.....	30
CHAPTER 3 MATERIALS AND CHARACTERIZATIONS.....	31
3.1 Materials.....	31
3.1.1 Photo-Sensitive Dyes.....	31
3.1.2 Electrolytes.....	31
3.1.3 Synthesis of Hydrotalcites.....	32
3.2 Fabrication of DSSCs.....	33
3.2.1 TCO Glass and Blocking Layers.....	33
3.2.2 TiO ₂ Photoanode Layer.....	34
3.2.3 Pt Counter Electrode.....	35
3.2.4 Device Assembly.....	35

3.3	Characterization	36
3.3.1	Electrochemical Analysis.....	36
CHAPTER 4 TiO₂ SURFACE TREATMENT USING TIF₄ BATH		37
4.1	Introduction	37
4.2	Experimental Details.....	38
4.3	Result and Discussion.....	39
4.4	Conclusion	48
CHAPTER 5 PASSIVATION OF TiO₂ BY SELF ASSEMBLED MONOLAYER.....		50
5.1	Introduction	50
5.2	Experimental Details.....	51
5.3	Results and Discussion	53
5.3.1	SAMs Grafting on TiO ₂	53
5.3.2	Head Group Effect of SAMs	57
5.4	Conclusion	59
CHAPTER 6 QUASI-SOLID ELECTROLYTE USING SILICA GELATOR.....		61
6.1	Introduction	62
6.2	Experimental Details.....	63
6.3	Results and Discussion	63
6.3.1	Gelation of Ionic Electrolyte by Silica Particles	63
6.3.2	Effect on Electrolyte-Counter Electrolyte Interface.....	64
6.3.3	Effect of Tuning Silica Content on Device Performance	66
6.4	Conclusion	70
CHAPTER 7 IMPROVED PERFORMANCE OF DSSCs USING HYDROTALCITE GEL ..		72
7.1	Hydrotalcite Gelation: an Investigation of Charge Transport and Shift in TiO₂ Conduction Band	72
7.1.1	Introduction	73
7.1.2	Experimental Details.....	75
7.1.2.1	Preparation of Smectite Clay	76
7.1.3	Results and Discussion	76
7.1.3.1	Optimization of Weight Percentage of Nitrate-Hydrotalcite.....	76
7.1.3.2	Optimization of the Thickness of TiO ₂ Photoanode.....	78
7.1.3.3	Nitrate-Hydrotalcite Gel in DSSCs	79
7.1.3.4	Comparison of Smectite and Nitrate-Hydrotalcite	80
7.1.3.5	Charge Transport in Gel	81
7.1.3.6	Effect of Nitrate-Hydrotalcite Gel Electrolyte on V _{OC}	86
7.2	Role of Anions in Hydrotalcite-Based Gel Electrolyte	91

7.2.1	Introduction	91
7.2.2	Experimental Details.....	93
7.2.3	Results and Discussion.....	94
7.2.3.1	Characterization of Anionic Hydrotalcite.....	94
7.2.3.2	Gelation of Different Hydrotalcite	97
7.2.3.3	Photovoltaic characteristics of varied hydrotalcite electrolyte based DSSCs	100
7.2.3.4	Effect of Anions on Voc.....	101
7.2.3.5	Effect of Anions on J_{SC}	103
7.3	Conclusions.....	104
CHAPTER 8 CONCLUSIONS		106
ENGINEERING AND SCIENTIFIC CONTRIBUTIONS		110
ABBREVIATIONS.....		112
LIST OF PUBLICATIONS.....		113
REFERENCES.....		116

List of Figures

FIGURE 1 CURRENT DENSITY-VOLTAGE (J-V) CHARACTERISTICS OF A SOLAR CELL (CURRENT DENSITY J_{MP} , VOLTAGE V_{MP} AT MAXIMUM POWER P_{MAX}).....	15
FIGURE 2 SCHEMATIC ILLUSTRATIONS OF THE TYPICAL COMPONENTS IN A DSSC.	16
FIGURE 3 ILLUSTRATION OF THE ENERGY DIAGRAM FOR A DSSC.....	18
FIGURE 4 THE IMPEDANCE PLOTTED AS VECTOR IN IMAGINARY AXES WITH THE VARIABLES EXPLAINED IN EQUATION (16).	27
FIGURE 5 NYQUIST PLOT FOR A RESISTOR AND A CAPACITOR IN PARALLEL CONNECTION.....	28
FIGURE 6 ELECTRON FLOW UNDER DARK EIS MEASUREMENT.	29
FIGURE 7 EXAMPLE OF THE PLOT OF $1/C^2$ AGAINST E FOR N TYPE MATERIALS.....	30
FIGURE 8 FLOW CHART OF SYNTHESIS PROCESS.....	33
FIGURE 9 SCHEMATICS OF FABRICATION PROCESS BY TWO HOLES FILLING OF GEL ELECTROLYTE.	36
FIGURE 10 PHOTO TO CURRENT CONVERSION EFFICIENCY OF TiF_4 TREATED DSSCS MADE OF EL-HPE AND EL-I.	39
FIGURE 11 IPCE OF TiF_4 TREATED DSSCS (ELECTROLYTE: EL-HPE; DYE: Z907).....	40
FIGURE 12 COMPARISON OF PHOTOCURRENT TO PHOTOVOLTAGE CHARACTERISTICS UNDER ILLUMINATION (SOLID SYMBOLS) AND UNDER DARK CONDITION (OPEN SYMBOLS) OF 20 MM TiF_4 (RED) TREATED AND 40 MM $TiCl_4$ (BLUE) TREATED DSSCS.	41
FIGURE 13 COMPARISON OF IPCE OF TiF_4 DEVICES AND $TiCl_4$ DEVICES.	42
FIGURE 14 TEM IMAGES OF (A) BARE TiO_2 NANOPARTICLES (B) $TiCl_4$ TREATED PARTICLES (C) TiF_4 TREATED PARTICLES.	43
FIGURE 15 (A) FLAT BAND POTENTIAL OF DIFFERENT PLANNER TiO_2 PREPARED BY ATOMIC LAYER DEPOSITION (B) MOTT-SCHOTTKY CURVES.	44
FIGURE 16 CYCLIC VOLTAMMOGRAMS OF PHOTOANODE TREATED WITH $TiCl_4$ DEVICE AND TiF_4 DEVICE. ⁷⁶	45
FIGURE 17 DARK EIS OF $TiCl_4$ DEVICE AND TiF_4 DEVICE UNDER BIAS EQUIVALENT TO THEIR VOC.....	45
FIGURE 18 TIME OF FLIGHT SECONDARY ION MASS SPECTROMETRY DATA OF ATOMIC LAYER DEPOSITED TiO_2 FILMS TREATED BY 20 MM TiF_4	46
FIGURE 19 XPS SPECTRUM OF (A) TI 2P AND (B) O 1S.....	47
FIGURE 20 ILLUSTRATION OF FLUORINE PASSIVATED TiO_2 SURFACE.	47
FIGURE 21 DEVICE PERFORMANCE WITH DIFFERENT TiO_2 PHOTOANODE FILM THICKNESSES.....	48
FIGURE 22 FTIR SPECTRA FOR PLANAR TiO_2 FILMS STAINED WITH SAM A, SAM B AND SAM C.	54
FIGURE 23 SCHEMATIC ILLUSTRATION OF OCTADECYLSILANE ASSEMBLY ON THE NAKED TiO_2 SPOTS WHICH IS NOT COVERED BY THE DYE.	55
FIGURE 24 UV-VIS ABSORPTION SPECTRA OF TiO_2 FILMS (A) WITH Z-907 DYE ALONE (B) Z-907 DYE AND SAM A (C) Z-907 DYE AND SAM B AND (D) Z-907 DYE AND SAM C.....	58
FIGURE 25 THE EQUIVALENT CIRCUIT AND NYQUIST PLOT OF SYMMETRIC CELLS WITH GELLED EL-I (15 WT % SILICA - RED SQUARE, FITTED WITH RED LINE) AND NEAT EL-I (0 WT % SILICA - BLUE SPHERE, FITTED WITH BLUE LINE). ⁸⁹	65
FIGURE 26 ILLUSTRATION OF ADSORPTION OF SILICA NANOPARTICLES ONTO COUNTER ELECTRODE. ⁸⁹	66
FIGURE 27 PCE (RED SPHERE) AND JSC (BLUE SQUARE) OBTAINED UNDER ONE SUN WITH VARIOUS SILICA CONTENTS (DATA POINTS ARE THE AVERAGE VALUES OF TWO SAMPLES; ERROR BAR REPRESENTS THE STANDARD DEVIATION). ⁸⁹	67
FIGURE 28 FORMATION OF LOCAL CONTINUOUS EXCHANGE REACTION DIFFUSION PATH WITH THE ADDITION OF SILICA NANOPARTICLES. ⁸⁹	68
FIGURE 29 DEPENDENCE OF V_{OC} (RED SPHERE) AND ELECTRON RECOMBINATION LIFETIME (BLUE SQUARE, MEASURED BY DARK EIS OF DSSCS) ON SILICA CONTENT. ⁸⁹	69
FIGURE 30 THE RELATIONSHIP OF FF (BLACK SPHERE) AND CHARGE TRANSFER RESISTANCE (BLUE SQUARE, MEASURED BY DARK EIS OF DSSCS) WITH SILICA CONTENT (DATA POINTS ARE AVERAGE VALUES OF TWO TESTS; ERROR BAR REPRESENTS THE STANDARD DEVIATION). ⁸⁹	70
FIGURE 31 VARIATION OF THE SOLAR TO ELECTRIC POWER CONVERSION EFFICIENCY AND CURRENT DENSITY FOR DIFFERENT NITRATE-HYDROTALCITE CONTENT (WT %) IN ACETONITRILE BASED LIQUID ELECTROLYTE	

UNDER ONE SUN ILLUMINATION; INSET SHOWS THE PHOTOGRAPHS OF LIQUID AND NANOCLAY GEL ELECTROLYTE.	77
FIGURE 32 SCHEMATIC REPRESENTATION OF TRANSITION FROM LIQUID ELECTROLYTE TO GEL ELECTROLYTE WITH DIFFERENT NITRATE-HYDROTALCITE CONTENT.	78
FIGURE 33 NYQUIST PLOT OF DEVICES WITH DIFFERENT PHOTOANODE THICKNESSES BASED ON 10 WT % NITRATE-HYDROTALCITE GEL ELECTROLYTE UNDER DARK CONDITION IN THE FREQUENCY RANGE OF 100KHZ-0.1HZ, AC AMPLITUDE 10 MV, AND 0.85 FORWARD BIAS.	79
FIGURE 34 PHOTOCURRENT OF G-AN AT VARIOUS ILLUMINATION CONDITIONS (0.25, 0.59, 0.86 AND 1.03 SUN). ¹¹²	82
FIGURE 35 (A) LIMITING CURRENTS FOR REACTION OF $I_3^- + 2e^- = 3I^-$ AS A FUNCTION OF CONCENTRATION ($1/3 [I^-] + [I_3^-]$) FOR PMII/ I_2 REDOX COUPLE WITH CONSTANT MOLAR RATIOS (PMII: I_2 10:1) IN ACETONITRILE. (B) CALCULATED DIFFUSION COEFFICIENT OF I_3^- FOR BOTH LIQUID AND NITRATE-HYDROTALCITE GEL. ¹¹²	84
FIGURE 36 X-RAY PHOTOELECTRON SPECTROSCOPIC SPECTRUM OF I 3D IN THE NITRATE-HYDROTALCITE POWDER EXTRACTED FROM GEL ELECTROLYTE CONTAINING 1M PMII AND 0.1 M I_2 . ¹¹²	85
FIGURE 37 X-RAY PHOTOELECTRON SPECTROSCOPIC SPECTRUM OF I 3D IN THE CARBONATE-HYDROTALCITE AS REFERENCE SAMPLE EXTRACTED FROM GEL ELECTROLYTE CONTAINING 1M PMII AND 0.1 M I_2	86
FIGURE 38 COMPARISON OF X-RAY DIFFRACTION PATTERNS OF BARE NITRATE-HYDROTALCITE POWDER (P-1) AND THE POWDER EXTRACTED FROM GEL ELECTROLYTE (P-2). ¹¹²	86
FIGURE 39 CYCLIC VOLTAMMOGRAMS OF AN BASED LIQUID (L-B) AND ITS NITRATE-HYDROTALCITE GEL ELECTROLYTE (10 WT% CONTENT LABELED AS G-B) WITH PT MICROELECTRODE (SCAN RATE 10MV/S). ¹¹²	87
FIGURE 40 CHEMICAL CAPACITANCE OF TiO_2 PHOTOANODE EXTRACTED FROM ELECTROCHEMICAL FITTING OF SEMICIRCLE OBTAINED AT INTERMEDIATE FREQUENCY REGION AT DIFFERENT OPEN CIRCUIT POTENTIALS. DIFFERENT OPEN CIRCUIT POTENTIALS ARE CONTROLLED BY APPLYING VARIOUS INTENSITY OF LED LIGHT SHINING ON DEVICES IN THE FREQUENCY RANGE OF 100 KHZ-0.1HZ AND WITH AC AMPLITUDE OF 10 MV. ¹¹²	88
FIGURE 41 TEM IMAGES AND THE HISTOGRAMS OF PARTICLE SIZES OF THE SYNTHESIZED HYDROTALCITE, IN THE ORDER OF CL-N, CL-S AND CL-C. ¹³²	95
FIGURE 42 THE SPECTRUM OF PEAK 003 OF (A) THE DRY POWDER BY XRD AND OF (B) THE HYDROTALCITE GELLED WITH ACETONITRILE BY SAXS. ¹³²	95
FIGURE 43 THE SCHEMATIC REPRESENTATION OF ANIONIC HYDROTALCITE CL-C OR CARBONATE HYDROTALCITE. ¹³²	96
FIGURE 44 THE X-RAY PHOTOELECTRON SPECTROSCOPIC SPECTRA OF N1S PEAKS OF THE SYNTHESIZED ANIONIC HYDROTALCITES (A) CL-N, (B) CL-S, (C) CL-C, AND (D) S 2P FOR CL-S. ¹³²	97
FIGURE 45 GEL FORMATIONS WITH LIQUID ELECTROLYTE THAT HAVE 10 WT % OF CL-N, CL-C AND CL-S HYDROTALCITE SAMPLES. GELATION WAS TESTED THROUGH INVERTING A SAMPLE BOTTLE AND TESTING WHETHER THE GEL STAYED ATOP. ¹³²	98
FIGURE 46 THE X-RAY PHOTOELECTRON SPECTROSCOPIC SPECTRUM OF HYDROTALCITE POWDERS EXTRACTED FROM MIMIC GEL ELECTROLYTE CONTAINING PMII AND I_2 : (A) I 3D FOR CL-N, CL-S AND CL-C, (B) N 1S FOR CL-N AND (C) S 2P FOR CL-S. ¹³²	99
FIGURE 47 X-RAY DIFFRACTION PATTERNS (PEAK 003) OF THE SYNTHESIZED NITRATE HYDROTALCITE POWDER (CL-N), THE POWDER EXTRACTED FROM MIMIC GEL ELECTROLYTE CONTAINING PMII + I_2 (CL-N-I), THE POWDER EXTRACTED FROM MIMIC GEL ELECTROLYTE CONTAINING LII (CL-N-LI) AND THE HYDROTALCITE IN ITS GEL FORM IN SOLAR CELL ELECTROLYTE (CL-N-ELG). ¹³²	99
FIGURE 48 CHEMICAL CAPACITANCE OF TiO_2 PHOTOANODE EXTRACTED FROM ELECTROCHEMICAL FITTING OF SEMICIRCLE OBTAINED AT INTERMEDIATE FREQUENCY REGION AT DIFFERENT OPEN CIRCUIT POTENTIALS. DIFFERENT OPEN CIRCUIT POTENTIALS WERE CONTROLLED BY APPLYING VARIOUS INTENSITY OF LED LIGHT SHINING ON DEVICES, FREQUENCY RANGE 100K HZ-0.1 HZ, AC AMPLITUDE 10 MV. ¹³²	103

List of Tables

TABLE 1 PHOTO-SENSITIVE DYES USED	31
TABLE 2 ELECTROLYTES USED IN THIS WORK.	32
TABLE 3 CHEMICAL ABBREVIATIONS AND NAMES.....	32
TABLE 4 PHOTOVOLTAIC PARAMETERS OF TiF_4 TREATED DSSCS WITH DIFFERENT SOLUTION CONCENTRATION AND THE REFERENCE DEVICES – 40 MM TiCl_4 TREATED DEVICES AS STANDARD CONDITION.....	40
TABLE 5 OCTADECYLSILANE SURFACE MODIFYING AGENTS STUDIED.	52
TABLE 6 OBSERVED MAJOR IR VIBRATIONS FOR THE SAMS GRAFTED ON TiO_2	55
TABLE 7 PHOTOVOLTAIC CHARACTERISTICS OF DSSCS MADE WITH TiO_2 PHOTOANODE STAINED WITH DIFFERENT TYPES OF SAMS (OCTADECYLSILANES).....	56
TABLE 8 RECOMBINATION RESISTANCE R_K AT TiO_2 -ELECTROLYTE INTERFACE DETERMINED BY EIS MEASUREMENTS.	57
TABLE 9 SERIES RESISTANCE R_S , INTERFACIAL CHARGE TRANSFER RESISTANCE OF THE ELECTROLYTE/COUNTER ELECTRODE INTERFACE R_{CT} , AND CHEMICAL CAPACITANCE C_1 AT THE ELECTROLYTE/COUNTER ELECTRODE INTERFACE EXTRACTED BY FITTING WITH THE EQUIVALENT CIRCUIT OF SYMMETRIC CELLS. ⁸⁹	65
TABLE 10 SUMMARY OF DEVICE PARAMETERS WITH DIFFERENT PHOTOANODE THICKNESSES BASED ON 10 WT % NITRATE-HYDROTALCITE GEL ELECTROLYTE.	79
TABLE 11 COMPARISON OF THE PHOTOVOLTAIC CHARACTERISTICS BASED ON LIQUID AND GEL ELECTROLYTE IN DIFFERENT SOLVENT (AN AND MPN) UNDER ONE SUN ILLUMINATION. L-MPN AND G-MPN REFER TO, RESPECTIVELY, LIQUID AND NITRATE-HYDROTALCITE GEL ELECTROLYTE PREPARED USING METHOXYPROPIONITRILE; L-AN AND G-AN REFER TO LIQUID AND NITRATE-HYDROTALCITE GEL ELECTROLYTE IN ACETONITRILE. ¹¹²	80
TABLE 12 COMPARISON OF J-V CHARACTERISTICS OF DEVICES MADE OF ELECTROLYTE GELLED BY SYNTHETIC SMECTITE CLAY (C-S), COMMERCIAL SMECTITE CLAY (C-C) AND NITRATE-HYDROTALCITE (HT-N).	81
TABLE 13 PERFORMANCE COMPARISON OF GEL AND LIQUID ELECTROLYTE WITH D35 AND N749 DYES. ¹¹²	89
TABLE 14 A COMPARISON OF THE PHOTOVOLTAIC CHARACTERISTICS OF LIQUID, GEL ELECTROLYTE AND LIQUID ELECTROLYTE WITH ADDITION OF NaOH . L- NaOH , L-NIL AND G-NIL DENOTE ELECTROLYTE CONDITIONS: LIQUID ELECTROLYTE WITH NaOH ADDED, LIQUID ELECTROLYTE AND NITRATE-HYDROTALCITE GEL WITH NO ADDITIONAL MODIFICATION. ¹¹²	90
TABLE 15 THE INTERLAYER DISTANCES OF THREE TYPES OF HYDROTALCITE IN DIFFERENT CONDITIONS: SYNTHESIZED HYDROTALCITE POWDERS, EXTRACTED HYDROTALCITE POWDER FROM THE MIMIC GEL ELECTROLYTE CONTAINING $\text{PMII} + \text{I}_2$ (DENOTED AS -I), AND EXTRACTED HYDROTALCITE POWDER FROM THE MIMIC GEL ELECTROLYTE CONTAINING LII (DENOTED AS -LI). ^{A, 132}	100
TABLE 16 COMPARISON OF THE PHOTOVOLTAIC CHARACTERISTICS OF DSSCS BASED ON LIQUID AND HYDROTALCITE (CL-N, CL-S AND CL-C) GEL ELECTROLYTE UNDER ONE SUN ILLUMINATION. ¹³²	101

Abstract

The objective of this thesis is to improve the photovoltaic performance of Dye-Sensitized Solar Cells (DSSCs) by modifying the interface between TiO_2 photoanode and electrolyte (iodide/triiodide as redox). This thesis is featured with two main approaches for improving the performance of DSSCs: a direct modification on TiO_2 surface through surface treatment and molecular passivation and an indirect modification to alter the TiO_2 surface charge through adding nanoparticles such as hydrotalcite and silica into the electrolyte. Results obtained indicate that the investigated approaches are promising in improving the photovoltaic performance of DSSCs in different aspects.

This study started with direct modification of TiO_2 photoanode through surface treatment using a novel, simple, safe and effective TiF_4 hydrolysis treatment instead of the conventional TiCl_4 treatment. The efficiency was enhanced by 22% compared with the reference device. To further improve the efficiency and address the dark current problem, another direct modification through the passivation of self assembled monolayer ($\text{C}_{18}\text{H}_{37}\text{SiX}_3$, X is H, OCH_3 or Cl) on sensitized TiO_2 was applied and investigated.

Besides the target on interfacial modification, to address the issues of difficult handling and leakage caused by liquid electrolyte, nanoparticles were introduced as additives to transform the liquid into a quasi-solid electrolyte and meanwhile indirectly altering the TiO_2 surface charge. Silica nanoparticles were introduced to gel the ionic electrolyte. A detailed study was carried out on how tuning silica nanoparticles affect the device performance and charge transfer at the counter electrode-electrolyte interface in binary ionic liquids based electrolyte. With synthetic nitrate-hydrotalcite as gelator, 10% improvement of efficiency was achieved. Following this, the effect of anions inside the hydrotalcite was also investigated. The results

indicated that proper selection of hydrotalcite compounds produced quasi-solid gel electrolyte, simultaneously improving the power conversion efficiency of the solar cells.

Chapter 1 Introduction

Unlike silicon solar cells, dye-sensitized solar cells (DSSCs) are based on relatively low purity materials and low cost fabrication methods. The invention of DSSCs immediately sparked the photovoltaic research. The first breakthrough of DSSCs was announced by O'Regan and Grätzel in 1991.¹ Unlike previous generations, over the past twenty years, the efficiency increased to over 11% with 1 cm² in area, because of the advancing nanotechnology.²

In DSSCs, many components together make the system work well as an efficient system. A single replacement of the component is usually not going to make the system more efficient. There are some unwanted processes such as charge recombination or dark reaction which cause power leakage under working condition. The property of the photoanode-electrolyte interface shows significant influence on the final power conversion efficiency.

The work in this thesis focuses on the modification of TiO₂-electrolyte interface in liquid electrolyte cells for a better understanding of DSSCs. The study of TiO₂-electrolyte interfacial phenomena are scrutinized either by direct modifying TiO₂ via surface treatment and molecular passivation or indirect altering the TiO₂ surface charge through adding hydrotalcite and silica nanoparticles. The effect of these methods on photovoltaic properties of DSSCs are examined and interpreted.

The organization of this thesis is as follows. Chapter 2 reviews relevant work in the area of DSSCs and gives a general background about this thesis. Chapter 3 introduces the materials used, the fabrication process of DSSCs and the characterization methods. Chapter 4 presents a direct modification method on TiO₂ surface using TiF₄ hydrolysis treatment to improve

conversion efficiency. This method is suitable and suggested for thin TiO_2 DSSCs applications, but not suitable for thicker photoanode because of the fragile mesoporous after TiF_4 treatment. This led to the work in Chapter 5 where DSSCs are improved by another direct modification on TiO_2 via molecular engineering, the passivation of self assembled monolayers (SAMs) on dyed titanium oxide by reducing the interfacial charge recombination at the TiO_2 -electrolyte interface. Chapter 6 provides a method to make a quasi-solid state solar cell using silica and a detailed study on how tuning silica nanoparticles affect the charge transfer at the counter electrode-electrolyte interface and the charge transport in the electrolyte. The first part of Chapter 7 reported improved performance of a quasi-solid-state gel electrolyte comprising of liquid electrolyte and synthetic hydrotalcite. 10% improvement in efficiency was achieved with gel electrolyte. This chapter demonstrates that adding hydrotalcite is an indirect method of modifying the TiO_2 surface though altering the surface charge of the TiO_2 . Following this, in the second part of Chapter 7 a study of anionic hydrotalcite is investigated. This work tried to understand the effect of anions on the photovoltage and photocurrent in gel electrolyte through electrochemical analysis. This study indicated that anions in the hydrotalcite structure have strong effect on changing surface charge on TiO_2 , especially the small potential determining ions such as Li^+ . With proper selection of hydrotalcite compounds, improved efficiency of solar cells can be achieved by the gel electrolyte. Chapter 8 concludes the thesis.

Chapter 2 Background and Related Work

This chapter presents general concepts of dye-sensitized solar cells and a review of the related work.

2.1 Dye-Sensitized Solar Cells

The DSSC became well known because of the breakthrough research by O'Regan and Grätzel in 1991.¹ Unlike previous technologies, DSSC is based on relatively low purity materials and low cost fabrication method. It immediately sparked a new generation of photovoltaic research. Over the last twenty years, the efficiency of a DSSC has increased to over 11% with 1 cm² in area, because of advances in nanotechnology.²

2.1.1 General Parameters of a DSSC

The efficiency of a solar cell is defined as the ratio of maximum electric output to the total incident energy input. The power conversion efficiency (PCE) is calculated using the following equation

$$\eta = \frac{P_{out}}{P_{in}} \times 100 = \frac{P_{max}}{E_{tot}A_{tot}} \times 100 = \frac{I_{sc}V_{oc}FF}{E_{tot}A_{tot}} \times 100 = \frac{I_{sc}V_{oc}FF}{E_{tot}} \times 100 \quad (1)$$

Where, P_{out} is the extractable power output, P_{in} is the power input by illumination, P_{max} is the maximum power output, E_{tot} is the total incident energy, A_{tot} is the total active area of cell, I_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, and FF is the fill factor respectively. Under the standard characterization value, AM 1.5, equation (1) can be rewritten as

$$\eta = J_{sc} \times V_{oc} \times FF \quad (2)$$

J_{sc} , V_{oc} , FF are very important parameters which can be retrieved from the J-V characteristic curve in Figure 1.

Figure 1 Current density-voltage (J-V) characteristics of a solar cell (current density J_{mp} , voltage V_{mp} at maximum power P_{max}).

The fill factor is defined in equation (3).

$$FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}} = \frac{A_1}{A_2} \quad (3)$$

2.1.2 Design of a DSSC

A general schematic presentation of the design and working principle of a DSSC is shown in Figure 2. The outer shell of a typical DSSC consists of two pieces of transparent conducting-oxide glass (TCO glass). One supports the photoanode and the other is platinized as counter electrode. They are kept at a distance by plastic sealant. The centre of the cell is made of titanium oxides in the form of mesoporous layer as photoanode. On its surface, self assembled monolayer of photo-sensitive dye molecules is attached. A redox electrolyte occupies the space between the two pieces of TCO glass.

Figure 2 Schematic illustrations of the typical components in a DSSC.

2.1.3 Operation principle of a DSSC

Since the work in this thesis is based on the iodide/triiodide liquid electrolyte, the following discussion of the working principle of a DSSC is based on this configuration. The key chemical and electrochemical reactions which occur in a DSSC can be summarized as follows³:

Generally, the operation principle can be summarized into four key steps, and each is represented using the above equation. Upon illumination, light leads the excitation of photo-sensitive dye (from its ground state to excitation state) and subsequently the generation of excitons (equation (4)). The electron is then injected from the excited dye into the photoanode (typically TiO_2) (equation (5)). The Photo-electrons diffuse through the mesoporous part and then reach the front contact (fluorine doped SnO_2 , FTO). The unbalanced hole will be carried by redox ions in the electrolyte and the dye is then regenerated (equation (6)). At the counter electrolyte part (platinized FTO), redox ions carry out the redox reaction (equation (7)). The entire process is regenerative.

The reaction time scale of each step is reported as follows: The photo-excitation process occurs in a few femtoseconds for most ruthenium dye systems.⁴ The electron injection from the excited dye to TiO_2 is ultra fast at a time scale of about 10^{-16} to 10^{-15} seconds.⁵ The regeneration of oxidized dye is at a time scale of nanoseconds.^{6, 7} The redox reaction is carried out at the counter electrode at a time scale of microseconds.⁸ Overall the fast reaction time keeps a DSSC working efficiently.

2.1.4 Components of a DSSC

2.1.4.1 Dyes

As one of the important parts of a DSSC, photo-sensitive dye molecules are used for efficiently harvesting the visible light.¹ Typically, an ideal photo-sensitive dye should have the following characteristics: 1) a high molar extinction coefficient with a broad absorption spectrum, 2) high capability to form stable monolayer on photoanode with proper steric properties to hinder current leaking from photoanode to electrolyte, 3) good energy alignment for effective charge injection (its lowest unoccupied molecular orbital should be at least 0.2

eV more negative than the conduction band of photoanode material, and its highest occupied molecular orbital should be at least 0.15 eV more positive than the redox level of electrolyte, as illustrated in Figure 3, and 4) a long lifetime with high stability against radiation and heat.^{9, 10} Thus, many photo-sensitive dyes have been designed and developed, examples being metal complex dyes, metal-free organic dyes, porphyrin dyes and phthalocyanine dyes etc. So far, metal complexes have shown a superior performance in many DSSC applications, i.e. 11.4% reported.¹¹ Not inferior to it, arylamine organic dyes have also demonstrated high efficiency of over 10.3%.^{9, 12}

Figure 3 Illustration of the energy diagram for a DSSC.

2.1.4.2 Oxides Photoanodes

Since reported by O'Regan and Grätzel, nanocrystalline titanium dioxide has been used as a key material for photoanode.^{1, 13} Simply from the semiconductor point of view, TiO₂ is not the ideal material for electron transport. Based on the arising concerns, many other metal oxide materials have been examined e.g. SnO₂, ZnO₂, and Nb₂O₅ or even mixed metal oxides like ZnO/SnO₂, Al₂O₃/SnO₂, SnO₂/CeO₂, and MgO/SnO₂.¹³ Considering the conversion efficiency as the outcome, the overall conversion efficiency by other metal oxide materials is not as high as the conventional titanium dioxides. Herein, the electronic structure of the

materials has been compared to explain the difference.¹⁴ The injection efficiency for metal oxides was reported as $\text{TiO}_2 > \text{Nb}_2\text{O}_5 > \text{SnO}_2 \sim \text{ZnO}$.¹⁴⁻¹⁶ Based on Marcus theory, under nonadiabatic condition the electron injection rate increases with the increase of the DOS (density of states) in the conduction band and titanium dioxide has a large DOS.¹⁴ Therefore, this subsequently makes titanium dioxide very efficient in DSSC application, though it is not the ideal semiconductor in other applications. To minimize the current loss during electron transport among the nanocrystalline structures (e.g. at nano-particle grain boundaries, defects and impurities), there are a lot of studies on modifying the morphology of TiO_2 photoanodes, such as nano-tube, nano-rod or nano-wire.¹⁷ Though they were found to increase electron transport, they suffer in light harvesting capability because of the lower surface area offered by 1-D structures. So far, mesoporous TiO_2 still holds the record as the best photoanode.¹¹

2.1.4.3 Electrolytes

Liquid electrolytes for DSSCs were most frequently reported as iodide/triiodine couple as the key redox mediator for hole charge transport and dye regeneration. Some of the alternative redox mediators such as $\text{SCN}^-/(\text{SCN})_3^-$ and $\text{SeCN}^-/\text{Se}(\text{CN})_3^-$ were reported to be very promising options to replace iodide/triiodide against corrosion.^{18, 19} Other than this, some organic alternatives such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and TPD (*N,N*-di-*m*-tolyl-*N,N'*-diphenylbenzidine) were applied and showed good performance.^{4, 20} Recently transition metal complexes such as cobalt complexes and nickel complexes were also investigated.²¹⁻²⁴

Besides the difference in redox couple, the electrolytes in DSSCs can be classified to three types: organic solvent based electrolyte, ionic liquid electrolyte, and quasi-solid electrolyte (gelation of the first two types).

Organic liquid electrolyte is most commonly used, and it usually provides good efficiency as it provides a good media for ion diffusion and dissolution. Among all the physical and chemical properties, the donor number of the organic solvent plays importance role which affects the extent of reaction in equation (7) towards the reverse direction.^{25, 26} According to previous studies, higher donor number resulted in higher Voc but lower Jsc.²⁵⁻²⁸ When the donor number increases, the equilibrium of the reaction in equation (8) inclines towards the right side. Therefore the concentration of I_3^- has been reduced which resulted in enhanced Voc shown in equation (9).^{25, 29-32} Higher donor number also causes elevation of the flat band potential V_{fb} of TiO_2 and results in higher Voc according to equation (10).^{25, 33}

$$V_{oc} = \left[\frac{kT}{e} \right] \ln \frac{I_{inj}}{n_{cb} k_{et} [I_3^-]} \quad (9)$$

$$V_{oc} = |V_{fb} - V_{red}| \quad (10)$$

where k , T , e , I_{inj} , n_{cb} , k_{et} , $[I_3^-]$ and V_{red} are the Boltzmann constant, absolute temperature, electronic charge, flux of injected charge, concentration of electrons in TiO_2 conduction band, rate constant for dark reaction on TiO_2 , concentration of I_3^- in electrolyte, and the reduction potential of redox couple respectively.

Ionic liquid electrolytes draw much attention in this application owing to its stable physical chemical properties.³⁴ They are nonvolatile therefore results less toxicity compared with organic electrolyte and have good solubility for most of organic or inorganic ingredients.³⁵ In the system using I^-/I_3^- as redox couple, 1-methyl-3-propylimidazolium iodide shows its superior role as it can act as solvent (with low viscosity of 880 cP) and supply the iodide for redox reaction at the same time,³⁶ Therefore it is commonly selected as the key component in

most of the ionic electrolyte mixture.³⁷ To further reduce the viscosity, tetracyanoborate is another solvent to form a binary melts with 1-methyl-3-propylimidazolium iodide. By tuning the ratio of the two chemicals, an optimal binary electrolyte was achieved as 7.6% by Kuang et al. with outstanding thermal stability at 80 °C in dark and excellent light stability under accelerated examination for 1000h.³⁸ Later The eutectic mixtures of imidazolium iodide salts and tetracyanoborate salts have been proven to be a successful solvent.³⁹ Some of the imidazolium salts with functional groups are also added in ionic liquid mixtures to raise the photovoltaic performance. For example, Chen et al. demonstrated using bis-imidazolium based poly (1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium bis(trifluoromethanesulfonyl)imide) electrolytes to formulate a thermal stable electrolyte with high conductivity owing to good charge transport through the networks formed *via* the π - π stacked rings of imidazolium.⁴⁰ The specific structure and property of the ionic liquids has also been investigated. Kawano et al. reported 1-ethyl-3-methylimidazolium dicyanamide performed better in terms of enhancing Voc compared with other structured ionic liquids (1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide, 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butylpyridinium bis(trifluoromethane sulfonyl)imide).⁴¹ However, the major disadvantage of ionic liquid electrolyte compared with organic electrolytes is their high viscosity which leads poorer diffusion of redox couple.³⁵

Recognizing the disadvantages of the liquid based electrolyte (it requires good sealing) which brings problems in fabrication and reliability, quasi-solid electrolyte was developed. Either by introducing polymer gelators or nanocomposite gelators, the gelation process increases the viscosity of the electrolyte leading to better handling properties.⁴²⁻⁴⁴ In DSSCs, we shall not focus on each component separately. All of the components together make the system works well as an efficient system. A single replacement of the component is not going to make the

system more efficient. Any replacement should be accompanied by adjusting other parts as well.

2.2 Challenges in Current DSSCs

2.2.1 Dark Reactions

In DSSCs, there are some unwanted processes, so called charge recombination or dark reaction, which cause power leakage under working condition. There are a few major dark reactions being mentioned often: The excited dye cools down to ground state without injection (equation (11)). The injected electrons in TiO_2 recombine with the oxidized dye before dye regeneration (equation (12)). The triiodide ions attack the TiO_2 surface and consume the injected electrons in TiO_2 (equation (13)). Similarly, the triiodide ions attack the TCO surface and consume the injected electrons in TCO glass (equation (14)).^{4, 30, 45, 46}

The reaction of excited dye cooling down to ground state (equation (8)) is usually negligible as the injection process mentioned is on the order of a few femtoseconds for most of reported ruthenium dye and TiO_2 system.⁴ Among the other three reactions, equation (10) is discussed more. It cannot be inhibited in liquid DSSCs because the dye can never cover the surface of TiO_2 entirely.⁴ As long as there is naked TiO_2 exposed to electrolyte, the tri-iodide could recapture the injected electron, causing the current leakage.

2.3 Studies of the TiO₂-Electrolyte Interface

Maximizing light harvesting and controlling the current loss are essential to enhance the power conversion efficiency. For this, the dye-photoanode-electrolyte interface plays a key role. Compared with other nanocomposites and structures, TiO₂ nanoparticle photoanode still holds the record for the highest power conversion efficiency.¹¹ Instead of changing each component, because of dark reactions, modification of TiO₂-electrolyte interface is essential for existing design of the liquid DSSCs based on TiO₂. There are various ways discussed in seeking improvement in photovoltaic performance through TiO₂-electrolyte interface modification and these can be summarized into two major methods. One is through covering the TiO₂ surface directly, such as using surface treatment, a secondary thin blocking layer and co-adsorbers.^{8, 47-49} The other is through indirect modification of the interface by tuning additives in electrolyte to achieve change in the surface chemistry of TiO₂ surface.^{50, 51}

2.3.1 Modification through Direct Covering of TiO₂

Being one of the key ways of direct modification of TiO₂, a surface treatment step is believed to be necessary because after high temperature autoclave, normally the surface of TiO₂ has been damaged. Anodic electrodeposition of new TiO₂ on existing nanocrystalline photoanode by TiCl₃ was developed.⁵² Later on it was displaced by TiCl₄ solution treatment as the results were similar and TiCl₄ treatment process was much easier in handling.⁵² There are also some other surface modification methods using TiO₂ precursors such as titanium isopropoxide and titanium butoxide.^{47, 53} So far the most common surface modification method is growing new TiO₂ layers through solution treatment of titanium tetrachloride.⁵² The major influence on device performance by TiCl₄ treatment is revealed by an increase of typically 10-30% in short-circuit current density and incident photon to current conversion efficiency (IPCE) compared with non-treated film. Many hypotheses have been proposed to explain the effect

of TiCl_4 concerning improved electron transport, recombination, TiO_2 purity and dye attachment. Until now, the most significant change observed in this treatment modification experimentally was the reduction in interfacial recombination rate at electrolyte- TiO_2 interface and downward shifting in the conduction band. This downward shift in conduction band and decrease in recombination rate was a combined effect observed in many studies.

Besides the surface treatment, the modification can be done by introducing insulating oxides or high band gap semiconductors as a thin layer to passivate the TiO_2 surface from interface recombination. Examples are a secondary semiconducting shell layer such as ZnO , Nb_2O_5 or a secondary layer of insulating metal oxides shell such as Al_2O_3 , CaCO_3 , BaTiO_3 , MgO and SrTiO_3 to protect the TiO_2 core.^{45, 49, 54-57} These secondary layer materials usually have more negative potential level than TiO_2 , resulting in an energy barrier which inhibits electron recombination or shifts the TiO_2 conduction band.⁴⁹ However controlling the ultrathin passivation layer is not easy or cost-effective. It can be conducted by molecular interface engineering, too.^{51, 58-61} Different from the second layer covering the entire TiO_2 surface, passivation of TiO_2 -electrolyte interface by molecules is much more targeted, as it only aims on the uncovered spots of TiO_2 where the current leaking occurs.⁶¹ As a result, passivating the TiO_2 -electrolyte interface with an insulating layer of highly selective molecules seems to be a more attractive way to inhibit the interface current loss as the molecules are able to form an ultra thin and effective insulating barrier to retard the unwanted current loss. Feldt et al. demonstrated an effective TiO_2 photoanode surface passivation technique to reduce the recombination rate by poly (methylsiloxane) in ferrocene DSSC systems.⁵⁸ Zhang et al has shown the effective co-adsorbers 4-Guanidinobutyric Acid on reducing the recombination in DSSCs.

2.3.2 Modification through Tuning Additives in Electrolyte

Interfacial chemistry plays an important role in recombination rate. Through tuning the additives in the electrolyte, the interfacial recombination can be affected significantly. Boschloo et al. has shown the investigation of the effect of tert-butylpyridine in iodide/triiodide DSSCs.⁶² 0.5 M addition of tert-butylpyridine resulted in rising of V_{OC} by 260 mV (60% of this V_{OC} enhancement is attributed to the negative conduction band shifting and 40% is attributed to the longer electron lifetime). Adding tert-butylpyridine changes the surface chemistry of TiO_2 (changing of protonation and/or small lithium ions attraction) and decreases the interfacial recombination. Besides tert-butylpyridine, other additives on changing the surface chemistry of TiO_2 have also been investigated, examples being 4-ethoxy-2-methylpyridine, benzimidazoles, primidines and guanidine thiocyanate.^{8, 63-65} Kopidakis et al. indicated that guanidine ion has the effect of reducing electrolyte recombination by a factor around 20, and moving the band edges of photoanode by 100mV positively thus resulting in enhanced V_{OC} .⁶⁵ Min et al. reported that benzimidazole derivatives altered the surface charge of TiO_2 thus shifting its band edge positively and resulted in improved V_{OC} . The photocurrent also improved by adding benzimidazole derivatives in acetonitrile electrolytes (TEMPO as mediator) with presence of lithium bis(trifluoromethanesulfonyl)imide on account of reduced recombination on TiO_2 bare surface by more than 40%.⁶⁶ The presence of small ions like lithium was investigated. A study from Furube et al. showed that lithium ion had ability to curtail the charge injection time (with lithium ion ~100 fs and without ~300fs) which was suggested to be the result of conduction band shift by TiO_2 .⁶⁷

2.3.3 Characterization of TiO₂-Electrolyte Interface

To investigate the properties of TiO₂-electrolyte interface in photovoltaic devices, electrochemical impedance spectroscopy (EIS) has to be mentioned as an excellent tool to examine the surface states or modifications of the interface. It usually measures ac current through the devices when there is a certain ac voltage is applied to it with electrical contacts at a certain angular frequency ω . Many factors can impede electron flow in an electrochemical device. These factors include electrode kinetics, chemical reactions and diffusion and so on. This causes a phase shift in the measured current.⁶⁸

$$E_t = |E| \sin(\omega t)$$

$$I_t = |I| \sin(\omega t + \theta) \quad (15)$$

$$Z_\omega = \frac{E_t}{I_t} = \frac{|E| \sin(\omega t)}{|I| \sin(\omega t + \theta)} = |Z|(\cos \theta + j \sin \theta)$$

Where E_t is potential at time t , $|E|$ is its amplitude, I_t is response at time t , $|I|$ is its amplitude, θ is phase, Z_ω is impedance and $|Z|$ is its amplitude.

The impedance Z_ω can be plotted as a vector in the imaginary plane, shown in Figure 4. It composes a real (Z') and an imaginary (Z'') part.

Figure 4 The impedance plotted as vector in imaginary axes with the variables explained in equation (16).

$$\begin{aligned}
 Z_{\omega} &= Z' + jZ'' \\
 \text{Re}(Z) &\equiv Z' = |Z| \cos(\theta) \\
 \text{Im}(Z) &\equiv Z'' = |Z| \sin(\theta) \\
 \theta &= \tan^{-1}(Z''/Z') \\
 |Z| &= \sqrt{(Z')^2 + (Z'')^2}
 \end{aligned} \tag{16}$$

Equation (15) can be expressed with Nyquist plot. Each point on the curve is its impedance at one frequency, shown in Figure 5. The measured EIS data are fitted to a model using equivalent circuits. The transmission line approach is often used to analyze porous structured DSSCs.⁶⁹ Different equivalent circuits based on transmission line approach are used to analyze different practical issues.⁶⁹

Figure 5 Nyquist plot for a resistor and a capacitor in parallel connection.

2.3.3.1 Dark EIS for DSSCs

Dark EIS measurement is useful to compare the interfacial recombination resistances of two DSSCs when they have equivalent V_{OC} . The applied potential during dark EIS measurement is at about the V_{OC} level obtained from J-V test. The applied bias elevates the potential of TCO glass contact, and the current is injected from TCO contact into TiO_2 . As the measurement is carried out under dark condition, the dye molecules have no other effect but acting as blocking coating on TiO_2 . The electrons in TiO_2 is totally supplied by outsource and then reacts with redox couple through the uncovered TiO_2 spots as illustrated in Figure 6. Therefore the comparison of recombination resistances level helps to understand the interfacial condition of the TiO_2 -electrolyte interface.

Figure 6 Electron flow under dark EIS measurement.

2.3.3.2 Light EIS for DSSCs

Measurement of chemical capacitance shift is carried out under light condition by EIS. It is informative for the change of surface charge discussed in Chapter 6 and 7. Under different illumination condition, a DSSC generates different level of V_{OC} . The applied bias is equivalent to the generated V_{OC} . The entire device thus is under its open circuit potential. By electrochemical fitting of the EIS data, the chemical capacitance at each open circuit potential is obtained. The equilibrium Fermi energy of electrons in semiconductors can be expressed by equation (17).⁸

$$E_F = E_c + kT \ln \left(\frac{n_c}{N_c} \right) \quad (17)$$

where E_F is the Fermi energy, E_c is the conduction band energy, kT is the thermal energy, n_c is the electron concentration and N_c is the effective concentration of accessible electronic states in the conduction band. The shift in the conduction band energy can then be diagnosed from electrochemical impedance measurements of the chemical capacitance under light.

2.3.3.3 Derivation of Flat Band Potential using EIS

The Mott-schottky equation shown below can be used to derive flat band potential using EIS.⁷⁰

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_D} \left(E - E_{fb} - \frac{k_B T}{e} \right)$$

where C is the interfacial capacitance, A is the interfacial area, N_D is the donor number, E is the applied voltage, E_{fb} is the flat band potential, k_B is the Boltzmann's constant, T is the Kelvin temperature, and e is the electronic charge.

As shown in Figure 7, the plot of $1/C^2$ against E should be a straight line from which E_{fb} can be derived from the intercept on the E axis.

Figure 7 Example of the plot of $1/C^2$ against E for N type materials

Chapter 3 Materials and Characterizations

This chapter introduces the materials used, the fabrication process of DSSCs and the characterization methods applied in this thesis.

3.1 Materials

3.1.1 Photo-Sensitive Dyes

The photo-sensitive dyes are all commercially available. They are listed in Table 1 and were applied as received.

Table 1 Photo-sensitive dyes used

Short Names	Formulas	Solution
N719	[RuL ₂ (NCS) ₂]: 2 TBA (L=2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA=tetra-n-butylammonium)	0.3 mM in acetonitrile: tert-butanol (1:1 v:v)
Z907	RuLL'(NCS) ₂ (L=2,2'-bipyridyl-4,4'-dicarboxylic acid; L'=4,4'-dinonyl-2,2'-bipyridine)	0.3 mM in acetonitrile: tert-butanol (1:1 v:v)
N749	[RuL(NCS) ₃]: 3 TBA (L=2,2':6',2''-terpyridyl-4,4',4''-tricarboxylic acid; TBA=tetra-n-butylammonium)	0.3 mM in acetonitrile: tert-butanol (1:1 v:v)
D35	(E)-3-(5-(4-(Bis(20,40-dibutoxybiphenyl-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid	0.2 mM in ethanol

3.1.2 Electrolytes

The electrolytes in this work are listed in Table 2. The corresponding abbreviations of the chemical names are tabulated.

Table 2 Electrolytes used in this work.

Short Names	Composition	Solvent
EL-HPE	N.A. It was used as purchased	
EL-I	0.1 M GuNCS + 0.2 M I ₂ + 0.5 M MBI in 65v% PMII + 35 v% EMITCB	
EL-AN	1 M PMII + 0.1 M LiTFSI + 0.1 M I ₂ + 0.5 M MBI	Acetonitrile
EL-MPN	1 M PMII + 0.1 M LiTFSI + 0.1 M I ₂ + 0.5 M MBI	Methoxypropionitrile

Table 3 Chemical abbreviations and names

Abbreviations	Chemical Names
PMII	1-methyl-3-propylimidazolium iodide
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide
MBI	1-methylbenzimidazole
GuNCS	guanidine thiocyanate
EMITCB	1-ethyl-3-methylimidazolium tetracyaborate

3.1.3 Synthesis of Hydrotalcites

The hydrotalcites are synthesized as inorganic additives of electrolyte, and these hydrotalcites are important in modifying the TiO₂-electrolyte interface (discussed in detail in Chapter 7). The hydrotalcite compounds can be generalized in the formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot zH_2O]$, where M represents various metal cations with corresponding valence 2+ and/or 3+, A is the exchangeable anions of valence n and x is the molar concentration of M³⁺ over the total number of cations.⁷¹ A co-precipitation method was used to synthesize the nitrate/carbonate/sulfate containing Mg-Al hydrotalcite.⁷² In brief, 0.11 M aluminum nitrate nonahydrate (98+ %, ACS reagent, Sigma-Aldrich) and 0.33 M magnesium

nitrate hexahydrate (99%, ACS reagent, Sigma-Aldrich) were dissolved in DI water (solution 1). 3 M sodium hydroxide (97+%, Sigma-Aldrich) and 0.98 M sodium nitrate (99+%, ACS reagent, Sigma-Aldrich) and/or sodium carbonate (99.5+%, ReagentPlus, Sigma-Aldrich) and/or sodium sulfate (99.5+%, ReagentPlus, Sigma-Aldrich) were dissolved in DI water (solution 2). Solution 1 was mixed gently with solution 2 and the mixture was further stirred at 80 °C for 35-40 hours. The obtained precipitates were subsequently washed several times and then were freeze-dried for two days into powder form.

Figure 8 Flow chart of synthesis process.

The surface morphology of the hydrotalcite was analyzed using field emission scanning electron microscopy (JEOL, JSM-7600F, 5kV). The phase and crystallite size were investigated by X-ray diffraction (XRD, Bruker-AXS D8 Advance). BET surface area analysis was conducted using a NOVA 3200e (Quantachrome instrument).

3.2 Fabrication of DSSCs

3.2.1 TCO Glass and Blocking Layers

A clean TCO glass substrate is essential to prepare the blocking layer. The TCO glass was supplied by Pilkington Group Limited and WuHan Geao Instruments Science & Technology.

They were cleaned with soap, water and ethanol each for 10 minutes followed by air drying. Blocking layer is important in liquid DSSCs as it could provide good adhesion between TCO glass and mesoporous photoanode based on our observations. It is also suitable for making high efficiency DSSCs because it can retard recombination at TCO-electrolyte interface. The blocking layer (a thin layer of TiO_2) was normally prepared by TiX_4 ($\text{X} = \text{F}$ or Cl) bath treatment at $70\text{ }^\circ\text{C}$ for 30 minutes, followed by hot air sintering. The blocking layer coated TCO glass was used as substrates to prepare the photoanode.

3.2.2 TiO_2 Photoanode Layer

There were two types of paste applied to fabricate TiO_2 photoanode: a transparent paste and a scattering paste. Both of them were commercially available. The layer made by the transparent paste absorbs most of the dye and provides transport path for electrons. The layer made by the scattering paste aims to scatter the light passing through randomly for a better gain in light harvesting. The two types of paste were applied on the substrate by two methods: doctor blade technique and screen printing technique.

For doctor blade method: The TiO_2 paste was applied to the substrates as purchased. The nanocrystalline paste was firstly applied to substrates by doctor blade using plastic tap as spacer and shape definer. The film was then under drying at $110\text{ }^\circ\text{C}$ for 6 minutes. The scattering paste was applied secondly and followed by drying again. The obtained film was finally sintered at $500\text{ }^\circ\text{C}$ for 30 minutes.

For screen print method: The nanocrystalline TiO_2 paste with different thicknesses were screen-printed on the substrates followed by screen printing of a scatter layer. The prepared films were then annealed on Titanium hotplate at $325\text{ }^\circ\text{C}$ for 5 minutes, $375\text{ }^\circ\text{C}$ for 5 minutes, $450\text{ }^\circ\text{C}$ for 15 minutes and $500\text{ }^\circ\text{C}$ for 15 minutes.

Subsequently, the cooled films were treated again with TiX_4 ($X = \text{F}$ or Cl) bath solution at 70 °C for 30 minutes and sintered by hot air blowing at 500 °C for 30 minutes. After cooling, the TiO_2 films were sensitized with corresponding dye solution.

3.2.3 Pt Counter Electrode

One or two holes were drilled on the TCO glass for electrolyte-injection. The TCO glass was cleaned with 10mM diluted HCl solution and acetone alternatively for 3 cycles. The hexachloroplatinic acid (8 mM in isopropanol solution) was drop-casted on drilled conducting side of TCO glass and annealed at 400 °C for 15 minutes by hot air blowing.

3.2.4 Device Assembly

Fabrication of DSSCs was done by sandwiching dye sensitized photoanode and counter electrode with a thermal-plastic Surlyn spacer (Surlyn, Solaronix) by hot pressing at 110 °C for 15 seconds. The triiodide/iodide based liquid electrolyte was introduced into sandwiched electrodes through the pre-drilled holes (either by vacuum filling through one hole or squeeze filling through two holes shown in Figure 9). Hydrotalcite gel electrolyte was shaken to a liquid form prior to injection. As the hydrotalcite gel is thixotropic, its fluidity was increased by applying a shear force.

Figure 9 Schematics of fabrication process by two holes filling of gel electrolyte.

3.3 Characterization

The J-V characteristics of the fabricated DSSCs were measured under an illumination with AM 1.5 (100 mW/cm^2) using a solar simulator (San-EI Electric, XEC-301S) coupled with a Keithley source meter. The steady state voltammetry measurements for the electrolyte were carried out using AutoLab PGSTAT302N at a scan rate of 10 mV/s with a typical electrochemical cell (equipped with a $10 \text{ }\mu\text{m}$ radius Pt microelectrode as working electrode, and Pt foil and Pt wire as the counter electrode and quasi reference electrode respectively).

3.3.1 Electrochemical Analysis

The EIS characterization was conducted using a computer controlled AutoLab PGSTAT302N with a frequency range from 0.1 Hz to 100 KHz at potential modulation of 10 mV . The obtained experimental data were fitted with the Z-view software (ZView 3.2b, Scribner Associates Inc.) using appropriate equivalent circuits.

Chapter 4 TiO_2 Surface Treatment Using TiF_4 Bath

Surface modification of TiO_2 photoanode is often carried out to improve the performance of DSSCs. Surface treatment is one of the most commonly used modification method as it is believed that after a normal high temperature autoclave, the surface of TiO_2 is damaged. This chapter discusses the direct surface modification of TiO_2 photoanode through a simple TiF_4 hydrolysis treatment. The effect of TiF_4 concentration is studied, and 20mM TiF_4 treatment shows the best photo conversion efficiency of 6.1% with enhancement around 22% compared to standard TiCl_4 treated reference device. The IPCE spectrum shows that TiF_4 treatment helps improve efficiency gain in visible range. Besides the enhanced surface area induced larger amount the dye loading, EIS analysis shows that 20mM TiF_4 treated DSSCs show less recombination compared with standard TiCl_4 treated DSSCs. The reduced recombination of TiF_4 treated devices is believed to be due to fluorine passivation of the TiO_2 surface.

4.1 Introduction

As the performance of DSSCs strongly depends on TiO_2 /dye/electrolyte interfaces, plenty of research work has attempted to modify the surface of TiO_2 to achieve higher efficiency. Anodic electrodepositing of new TiO_2 on existing nanocrystalline photoanode by TiCl_3 was developed.⁵² Later on it was displaced by TiCl_4 solution treatment as the results were similar and TiCl_4 treatment process was much easier in handling.⁵² There are also some other surface modification methods using TiO_2 precursors, such titanium isopropoxide and titanium butoxide.^{47, 53} So far the most commonly used surface modification method is growing new TiO_2 layers through solution treatment of titanium tetrachloride.⁵²

The major influence on device performance is revealed by an increase of typically 10-30% in IPCE and J_{SC} compared with non-treated film. Many hypotheses have been proposed to explain the effect of $TiCl_4$. Most of them concern improved electron transport, recombination, TiO_2 purity and dye attachment.⁷³ O'Regan et al showed that the most significant change observed experimentally was the reduction in interfacial recombination rate at electrolyte- TiO_2 interface and downward shifting in conduction band.⁵² There is no conclusive agreement yet as it depends on the condition of the treatment process.⁷³ However, pure $TiCl_4$ is very toxic, corrosive and unstable. Hence we explore a simple and safe hydrolysis treatment by using TiF_4 solution with better gain in efficiency than standard $TiCl_4$ treatment. At the same time, fluorine treatment on the TiO_2 photoanode is also proven to be effective on improving device efficiency for quantum dot sensitized solar cells.⁷⁴

4.2 Experimental Details

The photo-electrode were treated with TiX_4 ($X = F$ or Cl) bath solution at 70 °C for 30 minutes before screen printing and after sintered by hot air blowing at 500 °C for 30 minutes. The concentration of TiF_4 solution varied during treatment in order to reach the optimum effect. However, for the concentration of $TiCl_4$ solution was fixed to 40 mM, as it was already optimized condition in our facilities with two years effort and it was used as a standard treatment process. The photoanode thickness is around 8 μm without any scatter layer. Dye Z907 was used in this chapter. The amount of dye loaded on photoanode is measured through a desorption method (dye desorbed in 0.1 M NaOH of water-ethanol solution with volume rate 1:1) according to Beer-Lambert law shown below.

$$Absorption = \epsilon * [C] * L$$

Where ϵ is the molar absorptivity or extinction coefficient stated in literature for Z907 dye, L is the pass length through sample (L equals 1cm in our experiment) and $[C]$ is the concentration of dye. The Absorption is measured by UV-vis spectroscopy.

4.3 Result and Discussion

Figure 10 shows the conversion efficiency of the DSSCs treated with different concentration of TiF_4 bath solution. The result is the average of three cells in each condition. Most ionic liquid electrolyte (EL-I) based devices have higher conversion efficiency than organic HPE electrolyte (EL-HPE) based devices. The conversion efficiencies of the cells based on EL-HPE and EL-I have similar trend: the best device performance occurred with 20mM TiF_4 treatment.

Figure 10 Photo to current conversion efficiency of TiF_4 treated DSSCs made of EL-HPE and EL-I.

Figure 11 shows the IPCE spectra of the TiF_4 treated devices with different concentrations. It was observed that larger TiF_4 concentration led to decreased IPCE in UV region. Unlike in UV region, device treated with 20 mM TiF_4 showed the best efficiency gain in visible region, mostly in the 450-600 nm range. This resulted in the highest photocurrent among all cells. The detailed photovoltaic characteristics of EL-HPE based devices are tabulated in Table 4.

Table 4 Photovoltaic parameters of TiF_4 treated DSSCs with different solution concentration and the reference devices – 40 mM TiCl_4 treated devices as standard condition.

Sample	[c] mM	η %	FF %	Voc V	Jsc mA/cm ²
F10	10	5.0 $\pm$ 0.2	64 $\pm$ 1	0.68 $\pm$ 0.01	11.61 $\pm$ 0.50
F20	20	6.1 $\pm$ 0.1	64 $\pm$ 6	0.70 $\pm$ 0.01	13.85 $\pm$ 1.62
F30	30	4.6 $\pm$ 0.2	59 $\pm$ 1	0.67 $\pm$ 0.00	11.67 $\pm$ 0.66
F40	40	4.2 $\pm$ 0.8	55 $\pm$ 3	0.67 $\pm$ 0.00	11.13 $\pm$ 1.77
Ref	40	5.0 $\pm$ 0.1	64 $\pm$ 5	0.69 $\pm$ 0.02	11.63 $\pm$ 1.14

Figure 11 IPCE of TiF_4 treated DSSCs (electrolyte: EL-HPE; dye: Z907).

The comparison and discussion later on are all based on 20 mM TiF_4 treatment and 40 mM TiCl_4 treatment as a standard. To simplify, they are called TiF_4 treatment and TiCl_4 treatment. Compared to the optimized treatment condition of TiCl_4 the surface treatment process made of optimized TiF_4 bath solution gives higher J_{sc} and better V_{oc} in DSSCs as shown in Figure 12. From the dark condition, the TiF_4 devices has higher threshold of dark voltage than TiCl_4 devices.

Figure 12 Comparison of photocurrent to photovoltage characteristics under illumination (solid symbols) and under dark condition (open symbols) of 20 mM TiF_4 (Red) treated and 40 mM TiCl_4 (Blue) treated DSSCs.

The enhanced photocurrent can be further explained by their IPCE behavior shown in Figure 13. Compared with TiCl_4 devices, TiF_4 devices have larger enhanced photocurrent collection from 400 to 650 nm. However, the peak in the UV region is reduced. IPCE is the ratio of electrons flowing through the device divided by the numbers of incident photons. There are three factors that determine the IPCE value: 1) light harvesting efficiency Φ_{LH} , which depends on absorption properties of dye, 2) injection efficiency Φ_{Inj} , which measures the yield of injection of excited electrons into TiO_2 , and 3) charge collection efficiency Φ_{CC} ,

which is mostly affected by the properties of TiO_2 photoanode.⁵² These three factors are the major components for understanding the effect the surface treatment process.

Figure 13 Comparison of IPCE of TiF_4 devices and TiCl_4 devices.

The Φ_{LH} strongly depends on the absorption coefficient of dye and the amount of dye adsorbed on the photoanode. Since all the experiments are based on single type of dye (Z907), the absorption coefficients of the dye are the same for different devices. The amount of dye adsorbed strongly depends on the morphology of the treated photoanode. Figure 14 shows the changes of morphology before and after surface treatment process. Growth of small particles was observed for both TiCl_4 and TiF_4 during surface treatment process. Compared with the TiCl_4 treated devices, the size of newly grown particles after TiF_4 treatment are much larger (3-4 nm in size) and much denser. Compared with bare TiO_2 nanoparticles, the BET surface area of TiF_4 treated devices has increased by about 10% from 50.3 to 55.5 m^2/g and the amount of dye loading has increased from 7.9 to 8.4 ($\times 10^{-8}$) mol cm^{-2} , which is about 5%. With only 5% increment in adsorbed dye, the performance of

devices has been enhanced by 20%. Thus the improvement most likely comes from the other two factors.

Figure 14 TEM images of (a) bare TiO_2 nanoparticles (b) TiCl_4 treated particles (c) TiF_4 treated particles.

The variation of Φ_{Inj} because of surface treatment by conventional TiCl_4 has been discussed in detail by Sommeling et al..⁷⁵ The Φ_{Inj} depends on the driving forces which come from the energy difference between the lowest unoccupied molecular orbital (LUMO) level of the dye and the conduction band of TiO_2 . It has been found that TiCl_4 treatment helps improve Φ_{Inj} because the conduction band of TiO_2 is lower.⁷⁵ Based on this discussion, if TiF_4 treatment could bring the conduction band of TiO_2 even lower, the TiF_4 device could have a higher Φ_{Inj} . To compare the ability of altering the TiO_2 band potential by different treatment solution, the flat band potential of TiO_2 thin films was measured using the Mott-Schottky method shown in Figure 15b. The actual ranges of measured results were illustrated as a diagram in Figure

15a. Based on this measurement, the flat band potential of TiO_2 treated by TiF_4 solution did not result in lower energy level than that treated by TiCl_4 . Therefore, referring to TiCl_4 devices, the large increment of IPCE of TiF_4 devices in the visible region could not be explained by change in Φ_{Inj} . Thus the gain of IPCE could come from the improved Φ_{CC} which means better transport or less recombination in the devices.

Figure 15 (a) Flat band potential of different planar TiO_2 prepared by atomic layer deposition (b) Mott-Schottky curves.

From the cyclic voltammetry curves in Figure 16, we observed a higher J_{lim} (saturated current density under positive bias) in the TiF_4 devices compared with that in TiCl_4 devices. Higher exchange current indicates better electrolyte diffusivity in the actual device. As both of the devices used the same electrolyte, similar spacer thickness, similar amount of dye adsorbed, and similar thickness of TiO_2 films, the most likely reason of the enhanced exchange current is the weaker blocking effect or interaction with electrolyte of TiF_4 treated films.

Figure 16 Cyclic voltammograms of photoanode treated with TiCl_4 device and TiF_4 device.⁷⁶ As shown in Figure 17, the measured recombination resistance (at dark condition by EIS) of TiF_4 device is larger than TiCl_4 devices. This large variation of recombination resistance besides surface area change could be the major reason for the observed difference in photocurrent.

Figure 17 Dark EIS of TiCl_4 device and TiF_4 device under bias equivalent to their V_{oc} .

The change in surface chemistry of TiO_2 after treatment could help us understand the change in recombination. After surface treatment of TiCl_4 and annealing, we found existence of chlorine ions on the surface of TiO_2 by X-ray photoelectron spectroscopy (XPS). This has not

been reported in other research work. However, we think that these halogen ions may play important role at the interface. Similarly, for TiF_4 treated thin films, we found considerable amount of F ions attached to the TiO_2 surfaces as shown in Figure 18.

Figure 18 Time of Flight Secondary Ion Mass Spectrometry data of atomic layer deposited TiO_2 films treated by 20 mM TiF_4 .

The F ions on the surface actually changes surface chemistry significantly. It was observed that the XPS peak at 533 eV was suppressed when the amount of F ions went up. Usually, the oxygen peaks at high energy levels are associated with organic structures. This means that with fluorine ions attached, the surface of TiO_2 is passivated from organic contaminants.

Figure 19 XPS spectrum of (a) Ti 2p and (b) O 1s.

As surface attached fluorine ions passivated the TiO_2 surface, the ionic interaction between electrolyte and the exposed TiO_2 spots could be reduced as illustrated in Figure 20. Therefore, TiF_4 treatment process is a good surface modification method and easy in handling for DSSCs application.

Figure 20 Illustration of fluorine passivated TiO_2 surface.

Figure 21 shows the results of DSSCs with TiF_4 and TiCl_4 treatment under different photoanode thickness. For thinner photoanode (less than 10 μm), devices treated with TiF_4 performed better than that treated with TiCl_4 . It suggests that TiF_4 treatment are better in thinner cell application e.g. solid DSSCs, or liquid DSSCs with high absorption coefficient dye systems. While for thicker photoanode DSSCs (up to 20 μm), the performance of both surface treatment processes are similar. One possible reason of this is that after TiF_4 treatment the thick films sacrifice some of its mechanical stability.

Figure 21 Device performance with different TiO_2 photoanode film thicknesses.

4.4 Conclusion

For the first time, a simple and effective chemical treatment via TiF_4 hydrolysis is introduced to improve the device performance in DSSCs. The efficiency is enhanced by 22% by 20 mM TiF_4 treatment compared with reference device treated by standard TiCl_4 solution. The enhancement owing to increased amount of dye loaded benefits from increased surface area

and the retardation of charge recombination. This hydrolysis treatment could be plausible for replacing the conventional TiCl_4 treatment on thinner nanostructure based DSSCs to further improve the solar cell efficiency. This method is not suitable for thicker photoanode because of the fragile mesoporous structure after TiF_4 treatment.

The contents of this chapter are adapted or reprinted from the following paper: Xiu Wang, J. L. Song, C. H. Yip, C. C. Wong, and X. W. Liu. (2011). *Influence of TiF_4 Treatment on TiO_2 Photoanode in Dye Sensitized Solar Cells*. Nanoscience and Nanotechnology Letters, 3(2), 191-194.

Chapter 5 Passivation of TiO₂ by Self Assembled Monolayer

In this chapter, dye-sensitized solar cells are improved by the passivation of different types of SAMs coating on sensitized TiO₂ photoanode by reducing interfacial charge recombination from the naked TiO₂ sites to triiodide in the liquid electrolyte. The nanocrystalline TiO₂ DSSCs were fabricated by utilizing octadecylsilane with different head groups (C₁₈H₃₇Si(OCH₃)₃, C₁₈H₃₇SiH₃, and C₁₈H₃₇SiCl₃) as coating. The effect of SAMs was evaluated on the basis of their photocurrent-voltage characteristics, Fourier transform infrared spectrometry (FTIR), UV-vis spectroscopy, and electrochemical impedance spectroscopy. The SAMs of C₁₈H₃₇Si(OCH₃)₃ and C₁₈H₃₇SiH₃ coating on dyed titanium oxide resulted in about 12% and 21% improvement respectively in device efficiency with enhanced J_{SC} and V_{OC} while C₁₈H₃₇SiCl₃ showed a decrease by 18% in efficiency. These observations are discussed based on the effect of the head group of SAMs passivated on sensitized titanium oxide.

5.1 Introduction

Due to the existence of dark reaction or current loss caused by the electron recombination at the interface between TiO₂ photoanode and iodide-triiodide electrolyte, modifying the interface to control the current loss is important for liquid DSSCs.^{4, 53, 77} There are two major methods to passivate the TiO₂-electrolyte interface. One is achieved by attempting to have a secondary semiconducting shell layer such as ZnO, Nb₂O₅ or a secondary layer of insulating metal oxides shell such as Al₂O₃, CaCO₃, BaTiO₃, MgO and SrTiO₃ to protect the TiO₂

core.^{45, 49, 54-57} These secondary layer materials usually have more negative potential level than TiO₂, resulting in an energy barrier which inhibits electron recombination or shifts the TiO₂ conduction band.⁴⁹ Another method is conducted by molecular interface engineering.^{51, 58-61} Different from the first method (the second layer covers the entire TiO₂ surface), passivation of TiO₂-electrolyte interface by molecules is much more targeted, as it only aims on the uncovered spots of TiO₂ where the current leaking occurs.⁶¹ As a comparison, passivating the TiO₂-electrolyte interface with an insulating layer of highly selective molecules seems to be a more attractive way to inhibit the interface current loss as the molecules are able to form an ultra thin and effective insulating barrier to retard the unwanted current loss. Feldt et al. has demonstrated an effective TiO₂ photoanode surface passivation technique to reduce the recombination rate by poly (methylsiloxane) in ferrocene DSSC system.⁵⁸ In this chapter, we discuss the effective interface passivation by SAM (octadecylsilanes) and the effect of their different head groups on device performance.

5.2 Experimental Details

Only SAMs with high affinity to TiO₂ surface were selected and the structures of the modifying agents are shown in Table 5, which consists of the same tail group but different head groups. To avoid the complication of monolayer thickness effect on interfacial passivation, the chain length (C₁₈H₃₇) of all the SAMs used was kept constant for maintaining similar monolayer thickness. The inorganic bath surface treatment e.g. TiCl₄ or TiF₄ was eliminated in order to eliminate the complication of uncertainties at the interface.

Table 5 Octadecylsilane surface modifying agents studied.

Surface Modifying Agents	SAMs ($C_{18}H_{37}SiX_3$)
SAM A	$C_{18}H_{37}SiH_3$
SAM B	$C_{18}H_{37}Si(OCH_3)_3$
SAM C	$C_{18}H_{37}SiCl_3$

For adsorption of SAMs on TiO_2 surface, the silanization process had been optimized to 24 hours in dry toluene. Since the SAMs chosen are all non-polar, non-polar solvent were used to dissolve the SAMs, such as toluene and hexane. In this work, toluene had been chosen as the solvent as we observed that the SAMs dissolved in hexane had poor morphology on TiO_2 film compared to that dissolved in toluene. It could be related to the faster evaporation rate of hexane, thus, there is less time for SAMs to orientate themselves leading to poor assembly morphology on TiO_2 .

The following devices are based on the same photoanode thickness (5 μm), Z907 dye and EL-I as electrolyte. Two ways of SAMs loading were performed, before and after dye loading respectively. Before dye loading: the TiO_2 photoanodes were soaked in 1M SAMs solution, rinsed with toluene and acetonitrile and then soaked into 0.3 mM Z907 dye solution. After dye loading: the sensitized TiO_2 photoanodes were rinsed with acetonitrile and toluene and then soaked into 1M SAMs solution. Prior to cell assembly, both of the two kinds of photoanodes were dried in air.

The photocurrent-voltage performance of devices was measured with an active cell area of 0.45 cm^2 . The UV-vis absorption spectra were obtained using JASCO V-670 UV-Vis-Near IR spectrophotometer. The FTIR in reflective mode was performed on the surface of the TiO_2

films. IR spectra were measured with a Perkin Elmer Spectrum GX FTIR Spectrometer. The spectra were collected from 100 scans at a resolution of 2cm^{-1} .

5.3 Results and Discussion

The solution-phase reactions of a series of octadecylsilane with TiO_2 surface have been investigated.

5.3.1 SAMs Grafting on TiO_2

Surface silanization were monitored by FTIR with the attachment of SAMs to planar TiO_2 substrate (prepared by atomic layer deposition) and the IR spectra are shown in Figure 22. Table 6 shows assignment of major peaks obtained in IR spectra of SAMs. All the samples tested were thoroughly washed prior to the measurement in order to minimize the physisorbed molecules on the TiO_2 surface. Due to the presence of SAMs on TiO_2 surface, the characteristic bonds at the 1103 cm^{-1} , 1102 cm^{-1} , and 1106 cm^{-1} are observed because of the stretching of the Si-O bond upon silanization.^{78, 79} This indicated that SAMs has been grafted onto the TiO_2 surface. Ordering of the SAMs can be accessed from the frequency of CH_2 -stretching. The frequency of CH_2 -stretching is similar to a liquid alkane (ν_a is around 2924 cm^{-1}) for randomly attached structures, while the frequency is close to a crystal alkane (ν_a is approximate from $2915\text{-}2918\text{ cm}^{-1}$) for well parked SAMs.⁷⁹ Our results indicate that SAMs (the tree types of octadecylsilanes) with well ordered structures is comparable to the reported values.

Figure 22 FTIR Spectra for planar TiO₂ films stained with SAM A, SAM B and SAM C.

The sequence of loading the SAMs and dye affects the final device performance significantly. Two processes were compared: loading SAMs before dye and after dye soaking. In the first process, the nanocomposite TiO₂ film was first soaked in SAMs solution overnight and then transferred to Z907 dye solution for overnight sensitization. Whereas in the second process, the TiO₂ film was first immersed into Z907 dye solution and then followed by being dipped into SAMs solution. There was a sharp decrease in the photovoltaic performance for the pre-modification of the SAMs on the nanocrystalline TiO₂ before dye soaking. The decrease of the color intensity of the TiO₂ film was also observed, which is assumed to be the result of the SAMs covering most of the TiO₂ surface and leaving little room for dye attachment or the strong steric effect created by SAMs layers preventing the dye to approach the TiO₂ surface. Thus loading SAMs after dye was more effective since the SAMs molecules are easy to be adsorbed onto the TiO₂ surface without hindering the sensitization of dye molecules. The SAM passivated sensitized TiO₂ photoanode is illustrated in Figure 23. According to Feldt et al., there is no new peak observed in FTIR except silanization characteristic peaks after

SAMs modification on sensitized TiO₂ film. This eliminates the possibility that SAM molecules react with dye molecules.⁵⁸

Table 6 Observed major IR vibrations for the SAMs grafted on TiO₂.

Vibration		Peak Frequency (cm ⁻¹) in the samples prepared from		
		SAM A C ₁₈ H ₃₇ SiH ₃	SAM B C ₁₈ H ₃₇ Si(OCH ₃) ₃	SAM C C ₁₈ H ₃₇ SiCl ₃
C-H	v _a (CH ₂)	2918	2919	2911
	v _s (CH ₂)	2851	2851	2845
	δ(CH ₂)	1460	1462	1463
Si-O	v(Si-O)	1103	1102	1106

Figure 23 Schematic illustration of octadecylsilane assembly on the naked TiO₂ spots which is not covered by the dye.

Photovoltaic properties of devices undertaking SAM treatment are listed in Table 7. The devices A and B show better cell performance over device R as reference, due to the increase of J_{SC} and V_{OC}. Device A exhibits the best overall conversion efficiency (η) 3.9 % with a 21 % improvement in PCE compared to device R, with Z907 dye and non-volatile ionic liquid EL-I electrolyte. However, when the treatment by SAM C was applied to TiO₂ surface, a decrease in both V_{oc} and J_{sc} was observed, which is probably induced by some dye molecules

desorbing from the TiO₂ surface, leaving less dye to harvest solar energy. Table 7 shows the photocurrent-voltage characteristics of the DSSCs employing Z907 alone (device R) or with different types of SAMs coated (device A-C).

Table 7 Photovoltaic characteristics of DSSCs made with TiO₂ photoanode stained with different types of SAMs (octadecylsilanes).

Devices	SAMs (0.3M in toluene)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	η (%)
R	Without SAMs	6.5	0.69	72	3.2
A	SAM A	7.7	0.71	71	3.9
B	SAM B	7.6	0.70	67	3.6
C	SAM C	5.4	0.67	72	2.6

Since the objective of using SAMs is to modify the TiO₂-electrolyte interface and thus reduce the recombination loss, the charge transfer characteristics of devices were analyzed by EIS. The impedance spectra of the devices were measured under forward bias of -0.69 V which is equivalent to the V_{OC} under dark condition under 50w halogen lamp (100 mW/cm²) illumination. The recombination resistances measured are listed in Table 8. The results showed that the SAM A passivation on sensitized TiO₂ film was more effective in retarding charge recombination at the TiO₂-electrolyte. The SAM passivation may not only produce the effect of surface shielding but also change the energetics of TiO₂. Without hindering the solar harvesting by dye, SAM A passivation reduces the interfacial current loss, thereby resulting in better current collection or better J_{sc} than non treated devices.

Table 8 Recombination resistance R_k at TiO_2 -electrolyte interface determined by EIS measurements.

Device	SAMs	R_k (Ω)
R	Without SAM	37.2
A	SAM A	156.9
C	SAM C	25.9

5.3.2 Head Group Effect of SAMs

In order to be a good electron barrier layer to modify the TiO_2 -electrolyte surface, the ideal SAMs should show several characteristics: 1) The size of the SAMs molecule should be appropriate so that the SAMs passivation process would not cause adverse effects on dye adsorption, 2) The SAMs molecules could be immobilized on the oxide film and provide screening effect against current loss, and 3) The molecule does not interfere with the normal photovoltaic effect of the photo-sensitive dye during the operation of the solar cell.

The UV-vis absorption spectra of the nanocrystalline TiO_2 photoanode with/without SAMs treatment are shown in Figure 24. Compared to sensitized TiO_2 film only, due to surface silanization, the absorbance (from 400-600 nm) of SAM treated films decreased to a certain extent. Among all the three SAM treated samples, SAM C showed a dramatic decrease, especially in the range of 500-600nm, which is consistent with the observation of dye desorption in the SAM solution during experimental preparation. The result is consistent with the decreased efficiency of SAM C device mentioned in the photovoltaic measurement. The lower J_{sc} was attributed to the adsorption of SAM C and the desorption of the sensitizers by the SAM C. The SAM C either blocked the access of the dye molecules to the surface or displaced some of the absorbed dye molecules which could produce considerable photocurrent under the normal operation, leading to a weaker light harvesting and a lower

observed J_{SC} and V_{OC} . The results demonstrate that the SAM C treatment onto TiO_2 film greatly interfered with the dye adsorption process and no beneficial effect was obtained.

Figure 24 UV-Vis absorption spectra of TiO_2 films (a) with Z-907 dye alone (b) Z-907 dye and SAM A (c) Z-907 dye and SAM B and (d) Z-907 dye and SAM C.

SAM A and SAM B treated devices gave an increment in J_{SC} and V_{OC} and thus increased the power conversion efficiency of the DSSCs devices. Specifically, SAM A demonstrated the strongest effect in increasing device performance. This could correlate with the head group effect of SAMs.

The grafting density (surface coverage in the SAMs) ρ of the SAMs can be calculated using the following equation⁷⁹:

$$\rho = \frac{6 \times 10^5 \times \%C}{1200 n_c - MV \times \%C} \times \frac{1}{S_{BET}} \quad (18)$$

In equation (13), %C represents the carbon weight percentage, n_c is the number of carbon atoms in SAM, MV is the molecular weight of the bonded group, S_{BET} is the BET surface area of the TiO_2 particles. Higher grafting density with higher rate constant produces a closer packed SAMs layer in a shorter period of time.

The values of grafting density on TiO₂ reported by Helmy and Fadeev are 4.84±0.1, 4.30±0.1, and 4.75±0.1 for SAM A, SAM B and SAM C respectively.⁷⁹ SAM A is the most closely packed monolayer among the three. This is owing to its smallest head group. The closely packed monolayer provided by SAM A shields the uncovered TiO₂ spots against injected electrons that recombine with redox species in electrolyte. Therefore the devices based on SAM A modification give the best Jsc and Voc. While grafting density of SAM C is higher than SAM B, the device based on SAM C performs poorer than that based on SAM B. Besides the observed severe dye desorption upon silanization, the effect of the head group on the grafting kinetics it is also important. According to the rate constants reported based on CH₂-stretching analysis, the reactivity of SAMs on TiO₂ is reported as SAM C >> SAM B > SAM A.⁷⁹ The highest reactivity of SAM C could be the reason for disturbing the dye layer attached or displacing attached dye molecules and resulting in poor light harvesting and screening effect. All these results indicate that the head group of SAMs has to be carefully chosen for a positive impact on photovoltaic performance.

5.4 Conclusion

The devices were successfully featured with the modification of SAMs as the passivation layer at the TiO₂ surface after dye loading. The passivation of SAMs with different head group (C₁₈H₃₇SiX₃, X= H, OCH₃, Cl) of the same chain length were applied and investigated. The total power conversion efficiency was improved by approximately 21 % using C₁₈H₃₇SiH₃ as the electron passivation layer and 12% using C₁₈H₃₇Si(OCH₃)₃. EIS revealed that the increase in device performance for C₁₈H₃₇SiH₃ treated devices was the effect of suppression of surface recombination from injected electrons in TiO₂ to the triiodide in the electrolyte.

The effect of different head groups of the SAMs is discussed as follows. The best passivation against interface recombination by SAM A is owing to its smallest head group, which leads to the highest packing density. Through the research in this chapter, SAM passivation on TiO_2 surface is indeed capable of improving the total power conversion efficiency with judicious selection for the side group of SAMs. To be effective in reducing recombination and in improving DSSCs performance the SAMs should possess the following properties: They should not hinder the adsorbed dye layers on TiO_2 like $\text{C}_{18}\text{H}_{37}\text{SiCl}_3$ and the SAMs having smaller head group like $\text{C}_{18}\text{H}_{37}\text{SiH}_3$ with slower rate constant (reacting with TiO_2) could provide closely packed screening layer.

Chapter 6 Quasi-Solid Electrolyte using Silica Gelator

In the previous chapters, modification of TiO_2 was conducted by fluorine passivation and SAM modification. In the following two chapters, modification of TiO_2 is conducted by modifying electrolyte. Through tuning the additives in the electrolyte, the interfacial recombination can be affected significantly. For example, adding tert-butylpyridine changes the surface chemistry of TiO_2 (changing of protonation and/or small lithium ions attraction) and decreases the interfacial recombination.⁶² Besides tert-butylpyridine, other additives on changing the surface chemistry of TiO_2 have also been investigated, examples being 4-ethoxy-2-methylpyridine, benzimidazoles, primidines and guanidium thiocyanate.^{8, 63-65} These modifications are based on liquid electrolytes which have a potential reliability or leakage issue. To improve the stability and reliability, the drive to change liquid state to quasi-solid or solid state is a much bigger concern. Thus TiO_2 -based improvement with quasi-solid or solid state electrolytes is worth investigation. The following part of this thesis attempts to modify the TiO_2 -electrolyte interface by adding nanoparticles to produce quasi-solid state solar cells.

This chapter tries to produce a quasi-solid state solar cell by adding silica gel. Gelled ionic electrolyte was synthesized with silica nanoparticles and binary ionic liquid electrolyte EL-I. Symmetric cells with various silica contents were tested using EIS to study the effect of silica nanoparticles on electrolyte-counter electrode. J-V test under various light intensities and dark EIS at various biases were conducted to study the effect of silica nanoparticles on charge transfer at the counter electrode-electrolyte interface and on charge transport in the electrolyte. It was observed that charge transfer resistance decreased and electron

recombination lifetime increased with the increase of silica content. Both photocurrent and power conversion efficiency initially decreased and then increased resulting in minimum values at around 9wt%. This observation could be attributed to the change in dominant charge transport mechanisms: with addition of silica nanoparticles, physical diffusion decreases, while exchange reaction based charge transport in electrolyte is enhanced and the enhancement of exchange reaction overcomes the exacerbation of physical diffusion at around 9wt%.

6.1 Introduction

As an alternative to the organic liquid electrolytes for DSSCs, room temperature ionic liquid has been studied intensively due to high thermal stability, negligible evaporation, non-flammability, high ionic conductivity, and wide electrochemical window.^{41, 80-82} However, the high viscosity of ionic liquids, about 100 times higher than that of acetonitrile⁴¹, limits the overall power conversion efficiency.^{38, 41} To decrease the viscosity and maintain the high ionic conductivity, a high performance binary or ternary ionic liquid mixture was utilized as major ingredients functioning as solvent.^{39, 83, 84} However as a type of liquid electrolyte, it also requires robust sealing against the leakage and handling is difficult. In further study, according to the limitations, silica nanoparticles are introduced into the ionic liquid to form silica gelled ionic electrolyte.⁴²⁻⁴⁴

It was found that DSSCs with ionic liquid electrolyte and silica-gelled electrolyte demonstrated comparable power conversion efficiencies.⁸⁵⁻⁸⁷

Considering that gelation increases the viscosity of ionic liquid electrolytes and hence adversely impacts physical ion diffusion, it has been suggested that another charge transport channel should exist in silica gelled ionic electrolyte to compensate for the decrease in

physical diffusion - the Grotthuss-type electron exchange.⁸⁸ This chapter provides a detailed study on how tuning silica nanoparticles affect the device performance, the recombination lifetime at the TiO₂-electrolyte interface and the charge transfer at the counter electrode-electrolyte interface in binary ionic liquids (PMII and EMITCB) based electrolyte (EL-I).

6.2 Experimental Details

The composition of EL-I was listed in Chapter 3. A series of weight percentages (0, 3, 6, 9, 12 and 15 wt %) of silica nanoparticles (80nm) were added into the EL-I to determine the critical volume fraction for gelation. Symmetric cells and DSSCs composed of EL-I and its silica gelled electrolyte were fabricated according to Chapter 3. The photoanode thickness is around 6 μm without scatter layer.

Symmetric cells (two platinized TCO glass with electrolyte filled inside) were measured with EIS under the bias of 0.70V and in the frequency range of 0.01Hz to 100 kHz. DSSCs were tested under various light intensities from 0.65 sun to 1 sun at room temperature. Dark EIS measurements on DSSCs were performed at different forward biases from 0.65V to 0.85V in the frequency range from 0.1 to 100000 Hz.

6.3 Results and Discussion

6.3.1 Gelation of Ionic Electrolyte by Silica Particles

Gelation occurs because of the poor colloidal stability of silica nanoparticles in the ionic liquid, which leads to a 3D interconnected outspread fractal structure.⁴⁴ The critical volume for stable gelation, in the range of 12~ 13wt%, was determined experimentally by placing gel upside down

The theoretical value of the critical volume for gelation can be calculated using equation (19).⁴⁴

$$V_c = \left[\frac{4\pi\Delta\rho g R^4}{3kT} \right]^{\frac{3-d_f}{1+d_f}} \quad (19)$$

where V_c is the critical volume fraction for gelation, $\Delta\rho$ is the density difference between the particle and the suspending fluid, R is the radius of the particle, d_f is the fractal dimension of the aggregated structure, k is the Boltzmann constant and T is the absolute temperature.

The critical volume for gelation is calculated to be 8.7 vol% and correspondingly the critical weight percentage for gelation is calculated to be 13.4 wt%. This agrees well with the experimental observations (12~13 wt% of 80 nm silica leading to gel formation).

6.3.2 Effect on Electrolyte-Counter Electrolyte Interface

The effect of gelation on charge transfer was studied by electrochemical analysis of symmetric cells (Figure 25). The values of the parameters in the equivalent circuit are summarized in Table 9.

In Figure 25, R_s represents the serial resistance of the symmetrical cell, C_1 is the electrical double layer capacity formed at the electrolyte/counter electrode interface, R_{ct} is the resistance of charge transfer from the counter electrode to the electrolyte and W_Z is warburg diffusion.⁹⁰

Figure 25 The equivalent circuit and Nyquist plot of symmetric cells with Gelled EL-I (15 wt % silica - red square, fitted with red line) and neat EL-I (0 wt % silica - blue sphere, fitted with blue line).⁸⁹

As shown in Table 9, the main difference between the symmetric cells of 0 wt% and 15 wt% electrolyte is the electrolyte-counter electrode interface. R_{ct} of 15 wt% electrolyte-counter electrode interface is only half of that of 0 wt% electrolyte, whereas C_1 of 15 wt% electrolyte-counter electrode interface is more than twice of that of 0 wt% electrolyte-counter electrode interface.

Table 9 Series resistance R_s , interfacial charge transfer resistance of the electrolyte/counter electrode interface R_{ct} , and chemical capacitance C_1 at the electrolyte/counter electrode interface extracted by fitting with the equivalent circuit of symmetric cells.⁸⁹

	R_s (Ω)	C_1 (F)	R_{ct} (Ω)
0wt%	19.49	5.801×10^{-6}	0.562
15wt%	17.06	1.2132×10^{-5}	0.2784
% difference	12.5	109.1	50.5

The decrease in charge transfer resistance and increase in double layer capacitance could be attributed to the adsorption of silica nanoparticles onto the counter electrode, which results in accumulated I^-/I_3^- ions adjacent to the counter electrode, as illustrated in Figure 26.

Figure 26 Illustration of adsorption of silica nanoparticles onto counter electrode.⁸⁹

It was proposed that for the I^-/I_3^- redox reaction happening at the counter electrode, adsorption of I^- ions to the electrode surface occurs.⁹⁰ With increased I^- concentration adjacent to the counter electrode, it is much easier for I^- to migrate to the counter electrode and adsorb onto it. Furthermore, the local concentration of I_3^- increases in the area adjacent to the counter electrode. Thus, the charge transfer resistance decreases and redox reaction rate increases.

6.3.3 Effect of Tuning Silica Content on Device Performance

The effect of silica nanoparticles on the four important parameters of DSSCs, J_{SC} , V_{OC} , FF and PCE, were studied to gain a detailed understanding of the changing of charge transport mechanism in electrolyte while gelation.

As shown in Figure 27, J_{sc} and PCE initially decrease and then increase with silica content, approaching a minimum value at about 9 wt%.

Figure 27 PCE (red sphere) and Jsc (blue square) obtained under one sun with various silica contents (data points are the average values of two samples; error bar represents the standard deviation).⁸⁹

As illustrated in Figure 28, after adding silica nanoparticles, PMI cations in the electrolyte will adsorb onto the hydrophilic and negatively charged surface of silica nanoparticles by electrostatic interaction. Due to the size effect, most silica particles congest between the top of TiO₂ films and counter electrode. This led to higher local concentration of I⁻/I₃⁻ couples,⁹¹ forming a local continuous exchange reaction diffusion path for electron hopping, expressed using equation (20). Hence exchange reaction diffusion was enhanced with the addition of silica nanoparticles. Then physical diffusion should be in conjunction with exchange reaction diffusion and the apparent diffusion coefficient is expressed by Dahms–Ruff equation as shown in equation (21).

Figure 28 Formation of local continuous exchange reaction diffusion path with the addition of silica nanoparticles.⁸⁹

$$D_{app} = D_{ex} + D_{phy} \quad (21)$$

However, physical diffusion is impeded with the increase in viscosity. A local minimum point between the enhancement of exchange reaction diffusion and the retardation of physical diffusion is reached at around 9 wt%.

Hence at first, J_{SC} will decrease when the reduction in physical diffusion rate is larger than the enhancement in exchange reaction diffusion. Then the effect of enhancement in exchange reaction diffusion overcomes the effect of increase in viscosity at about 9 wt% and J_{SC} increases with the increasing silica content afterwards until 15 wt%. Gelation occurs at 12-13 wt%. The increase of J_{SC} starts at around 9 wt%, which is just before the gelation point. This indicates that effective electrical paths form prior to structure completion.

PCE follows the same trend as J_{SC} . This means that among the three factors (J_{SC} , V_{OC} and FF), J_{SC} variation dominates the PCE change. An increase of PCE by 20.2% (pure EL-I compared to 9wt% silica content) is a result of an increase of J_{SC} by about 25.7%, a constant V_{OC} and an increase of FF by only 10.7%.

With the accumulation of PMI cations around silica nanoparticles, it is probably that there is depletion of I^-/I_3^- ions near the TiO_2 mesoporous film, which suppress the recombination at the TiO_2 -electrolyte interface.³⁰ Another possibility is that with rearrangement of ions by adding silica, TiO_2 may shift its band position. With the above possibilities, V_{OC} and recombination lifetime, obtained from the EIS measurement, increased with silica content as shown in Figure 29. This is consistent with the mechanism discussed above³⁰ that silica is able to affect the TiO_2 -electrolyte interface by reorienting the ions in the electrolyte. However, this does not produce an increase significant enough to affect the overall device performance because the V_{OC} increased by 10 mV only at most.

Figure 29 Dependence of V_{OC} (red sphere) and electron recombination lifetime (blue square, measured by dark EIS of DSSCs) on silica content.⁸⁹

One of the factors affecting FF is the total series resistance of the cell resulting from the material resistance to current flow. FF increases when total series resistance decreases. The charge transfer resistance at electrolyte-counter electrode interface R_{ct} , obtained from the EIS

measurement and is a component of the total series resistance, decreases when silica content increases. This decrease in R_{ct} , which could be explained by the adsorption of the silica nanoparticles to the counter electrode as explained earlier, could be one of the reasons leading to the increase of FF with increasing silica content, as presented in Figure 30.

Figure 30 The relationship of FF (black sphere) and charge transfer resistance (blue square, measured by dark EIS of DSSCs) with silica content (data points are average values of two tests; error bar represents the standard deviation).⁸⁹

6.4 Conclusion

Silica gelled ionic electrolyte was formed with silica nanoparticles of 80nm as gelators at the content between 12 and 13 wt%, which agrees with the theoretical calculation. The charge transfer resistance decreased with increasing silica content, which could be due to the adsorption of silica nanoparticles onto counter electrode surface. Both short-circuit current density and power conversion efficiency decreased initially and then increased with silica content. The minimum value is at about 9 wt%. This was probably due to the enhancement of

exchange reaction diffusion with the addition of silica nanoparticles. A local minimum point between the enhancement of exchange reaction diffusion and the retardation of physical diffusion is reached at about 9wt%. It is proposed that adsorption of PMI cations onto the silica nanoparticle surfaces results in a local accumulation of I^-/I_3^- redox couples, forming the continuous path for exchange reaction diffusion. Electron recombination lifetime increases with the addition of silica nanoparticles, which can be explained by the depletion of I_3^- ions adjacent to the TiO_2 mesoporous film or band shift of TiO_2 due to reorientation of ions by adding silica. However the role of silica on changing the TiO_2 -electrolyte interface is not significant enough to achieve higher conversion efficiency.

The contents of this chapter are adapted or reprinted from the following paper: Shengnan Huang, Xiu Wang, and Chee Cheong Wong. (2013). *Silica Nanoparticle Gelled Ionic Electrolyte for Dye Sensitized Solar Cells*. Nanoscience and Nanotechnology Letters, 5, 1-4.

Chapter 7 Improved Performance of DSSCs using Hydrotalcite Gel

In the previous chapter, silica is used to form a quasi-solid state solar cell. However, silica does not affect much of the TiO_2 -electrolyte interface. Different from what we expected, silica affects mainly the charge transport in electrolyte, not the interfacial recombination. In this chapter, another type of nanoparticles, hydrotalcite, was used to modify the TiO_2 -electrolyte interface in quasi-solid state DSSCs.

7.1 Hydrotalcite Gelation: an Investigation of Charge Transport and Shift in TiO_2 Conduction Band

Clay or clay-like minerals play a promising role as gelating additives in quasi-solid-state electrolyte in DSSCs because of high chemical stability, unique swelling capability, ion exchange capability and good rheological properties. Here we report the improved performance of DSSCs by a quasi-solid-state gel electrolyte made from liquid electrolyte and synthetic nitrate-hydrotalcite. The charge transport mechanisms in the gel electrolyte and the hydrotalcite interactions with TiO_2 -electrolyte interface are discussed in detail. The electrochemical analysis reveals that the charge transport is solely based on physical diffusion at the ratio of $[\text{PMII}]: [\text{I}_2] = 10:1$. The calculated physical diffusion coefficient shows that the diffusion of redox ions is not affected much by the viscosity of the gel. Adding nitrate-hydrotalcite to the electrolyte has the effect of buffering the protonation process at TiO_2 -electrolyte interface, resulting in a conduction band up-shift and a boost in V_{oc} . Higher V_{oc} with undiminished photocurrent was achieved with nitrate-hydrotalcite gel electrolyte for

both organic and inorganic dye (D35 and N719) systems. The power conversion efficiency was increased by 10%, compared to that of the liquid electrolyte. The power conversion efficiency can reach 10.1% under 0.25 sun and 9.6% under one sun. Other factors such as weight percentage of nanoclay in electrolyte, photoanode thickness, illumination intensity, the solvent type of the electrolyte and the comparison of nitrate-hydrotalcite and smectite clay have also been investigated. This study demonstrates that nitrate-hydrotalcite in the electrolyte not only solidifies the liquid electrolyte to prevent solvent leakage, but also facilitates the improvement in power conversion efficiency.

7.1.1 Introduction

For liquid DSSCs, several critical technical problems limit the long-term performance and practical applications, in particular the leakage or evaporation of volatile solvent.⁹²⁻⁹⁶ Consequently much attention has been focused on improving the liquid electrolytes or substituting liquid electrolytes with solid-state or quasi-solid-state electrolytes.^{97, 98} Some efforts have been made to fabricate solid-state DSSCs, which did not require hermetic sealing. However, lower solar to electric PCE was observed compared with that of liquid DSSCs, which may be due to low hole conductivity, poor pore-filling ability and/or poor electrode contact.^{48, 94, 99} Recently, quasi-solid state electrolytes have emerged to be very good candidates for DSSCs because of their twin attributes: the cohesive property of a solid and the diffusive capacity of a liquid.²⁵ One particular approach is to form the quasi-solid-state electrolyte using inorganic nanoparticles as additives in various ionic liquids in order to increase the viscosity as well as the electrode-electrolyte interfacial contact.^{100, 101} For example, a composite ionic liquid electrolyte formed by adding silica nanoparticles to 1-methyl-3-propylimidazolium iodide showed a high conversion efficiency of 7.0 %.⁴²

Compared to liquid devices, the advancement of quasi-solid state DSSCs is still a gradual process.

Recently, clay or clay-like minerals have attracted attention as an additive in electrolyte because of their high chemical stability, unique swelling ability, ion exchange capability, abundance in nature, and good rheological properties.^{102, 103} Tu et al. demonstrated that polymer-gelled DSSCs incorporated with montmorillonite clay showed enhancement in efficiency due to a decrease in electrolyte-contact resistance.¹⁰⁴ Later, Park et al. deduced the unexpected benefits of clay gel electrolyte because of the light scattering capability of laponite clay.¹⁰⁵ Further, Tsui and co-workers attempted to use modified montmorillonite with long alkyl chain to form clay type nanocomposite and proposed that the space between the clay could offer wider transfer path for iodide/triiodide.¹⁰⁶ Inoue et al. showed high cell performance of 10.3 % for clay gelled electrolyte, which is equivalent in performance with liquid electrolyte cells.¹⁰⁷

Even though nanoclay has proven to be one of the promising additives to gel the liquid electrolyte, efficiency enhancement of the top performing cells is still in progress.^{105, 107} As discussed above, besides solidifying the electrolyte, the role played by clay or clay-like additives on the photo-electrochemical performance of the device has not yet been elucidated in detail. According to earlier studies in photochemistry and photo-catalysis, smectite clay hinders the diffusion of anions, while cations incorporated in the clay films can induce electro-catalytic effects.^{108, 109} Apparently, a lot of study needs to be carried out to reveal the effect of clay or clay like additives in photovoltaic devices, *viz* the particle interaction with the electrolyte of DSSCs, especially in its gel form, and the correlation of interaction with charge transport mechanism in the device. The clay or clay-like additives used in previous studies were mainly of smectite/montmorillonite type, which belong to the family of cationic

clays (hydroxides layers with negative charge). Since the active redox species (triiodide/iodide) present in the current DSSC systems are anions, anionic hydrotalcite (the net positive charge of octahedral layers is balanced by an equal negative charge from the interlayer anions¹¹⁰) additives in the gel electrolyte may be expected to have better ability in terms of interaction/intercalation with the electrolyte.

In this chapter, we report the synthesis of a quasi-solid-state gel electrolyte which consists of liquid electrolyte and synthetic nitrate-hydrotalcite that solidifies the liquid electrolyte and improves the PCE. Cyclic voltammetry provides the information on the charge transport in gel electrolyte whereas electrochemical impedance spectroscopy gives a broad view of resistance and capacitance of each component. The obtained results are combined in a coherent picture in order to identify the effect of nitrate-hydrotalcite in gel electrolyte system. A comparison of the performance of smectite clay and hydrotalcite was conducted to support our expectation for hydrotalcite to perform better.

7.1.2 Experimental Details

The liquid electrolyte was EL-AN (1 M PMII + 0.1 M LiTFSI + 0.1 M I₂ + 0.5 M MBI in acetonitrile) and EL-MPN (1 M PMII + 0.1 M LiTFSI + 0.1 M I₂ + 0.5 M MBI in methoxypropionitrile). The hydrotalcite or smectite gel electrolytes were prepared by dispersing different weight percentage of hydrotalcite or smectite powder into the liquid electrolyte. The mixture was sonicated for 5-10 minutes at room temperature and subsequently homogenized using ultrasonic homogenizer. Liquid electrolyte solidification i.e. gel formation occurred after adding more than 10 wt% of the nitrate-hydrotalcite. The content of smectite in its gel is also 10 wt%. The prepared gel electrolyte was subsequently used for device testing.

Nitrate-hydrotalcite based gel electrolyte was shaken to form a liquid prior to be injected into the cell through the holes of the counter electrode. As the gel electrolyte is thixotropic, its fluidity is increased by applying mechanical shear force.

The cells had an active area of 0.28 cm^2 . The dye used in this chapter was N719, unless otherwise specified as D35 or N749 for comparison study in the discussion of the nitrate-hydrotalcite effect on V_{oc} . The thickness of the photoanode is $18 \text{ }\mu\text{m}$ unless otherwise specified in the section of the optimization of the thickness of TiO_2 photoanode. The steady state voltammetry measurements were carried out using AutoLab PGSTAT302N at scan rate of 10 mV/s . A typical electrochemical cell was equipped with a $10 \text{ }\mu\text{m}$ radius Pt microelectrode as working electrode, Pt foil as the counter electrode and Pt wire as the quasi reference electrode.

7.1.2.1 Preparation of Smectite Clay

For synthesized smectite clay, the precursors started with MgCl_2 (2.38g in 25ml DI water) solution and NaOH (1g in 15ml DI water), $\text{SiO}_2 \cdot 3.22\text{Na}_2\text{O}$ (15.45g in 25ml DI water) solution. After mixing the solution together homogenously, the mixture was transfer into the thermal bomb. The reaction time was kept at 250°C for 2 hours. The powder obtained was washed throughout and kept in freeze-drying for 2 days.

7.1.3 Results and Discussion

7.1.3.1 Optimization of Weight Percentage of Nitrate-Hydrotalcite

Figure 31 shows the variation of PCE and J_{sc} with different nitrate-hydrotalcite content (wt %) in the acetonitrile (AN) based liquid electrolyte under one sun illumination. When less than 5 wt % of nanoclay was added into electrolyte the efficiency dropped from 8.8 % to 8.4 %. However, further addition of the nanoclay up to 10 wt % resulted in enhancement of

efficiency. As illustrated in Figure 32, initial addition of nanoclay (e.g. 2 wt %) makes random dispersion of the particles inside the liquid electrolyte, which can provide an obstacle for the transport of the redox ion. Further addition of nanoclay up to 10 wt % enhances the PCE, which could be due to the gradual organization of nanoclay particles forming continuous network. The maximum PCE of 9.6 % was achieved by the device with 10 wt % nanoclay, which coincided with the gelation point of the liquid electrolyte. This could be due to the well arranged layered structures of nitrate-hydroxalcite formed in liquid electrolyte, which could provide good diffusion or ionic conduction path for redox species (Figure 32 (iv)). However, further addition of nanoclay could lead to particle aggregation that disturbs ion transport, resulting in a decrease of the PCE. This decrement in efficiency of adding more clay beyond 10 wt% is in good agreement with the previous studies of similar systems.⁶² The explanation presented in the schematics (Figure 32) correlates with the observed trend of J_{SC} . Hereafter, 10 wt % nanoclay gel electrolyte is selected for subsequent characterizations.

Figure 31 Variation of the solar to electric power conversion efficiency and current density for different nitrate-hydroxalcite content (wt %) in acetonitrile based liquid electrolyte under one sun illumination; inset shows the photographs of liquid and nanoclay gel electrolyte.

Figure 32 Schematic representation of transition from liquid electrolyte to gel electrolyte with different nitrate-hydroxalcalite content.

7.1.3.2 Optimization of the Thickness of TiO_2 Photoanode

The nitrate-hydroxalcalite gel device parameters (J_{SC} , V_{OC} , FF and PCE) with different photoanode thicknesses are listed in Table 10. Device efficiencies were found to increase with the increase of the photoanode thickness up to 18 μm , and the best PCE of 9.6 % was achieved. However, further increase of the photoanode thickness produced lower J_{SC} , V_{OC} and hence lower PCE. It is well known that the amount of dye adsorption increases with photoanode thickness, which enhances J_{SC} . However, recombination resistance at TiO_2 -electrolyte interface decreases with photoanode thickness as shown in Figure 33. This implies more current loss due to recombination for thicker photoanode. In addition, V_{OC} is also affected by the recombination process, and hence it is lower for thicker film. The combined effect of J_{SC} , V_{OC} and FF results in decrease of PCE when the thickness is larger than 18 μm . Furthermore, it is also noticed that films thicker than 20 μm ‘peel off’ very easily, resulting in poor current density.

Table 10 Summary of device parameters with different photoanode thicknesses based on 10 wt % nitrate-hydrotalcite gel electrolyte.

Photoanode Thickness (μm)	PCE (%)	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF
12	7.9	13.4	861	0.68
16	8.5	15.9	850	0.63
18	9.6	15.2	846	0.75
20	8.7	14.9	816	0.72

Figure 33 Nyquist Plot of devices with different photoanode thicknesses based on 10 wt % nitrate-hydrotalcite gel electrolyte under dark condition in the frequency range of 100KHz-0.1Hz, ac amplitude 10 mV, and 0.85 forward bias.

7.1.3.3 Nitrate-Hydrotalcite Gel in DSSCs

The J-V characteristics of the DSSCs with 10 wt % nitrate-hydrotalcite gel electrolyte under one sun illumination are listed in Table 11. Better device performance was observed using AN rather than MPN as solvent to prepare the electrolyte. In fact, the higher device efficiencies for AN based electrolyte are mainly owing to the better fill factor which reflects the resistance level in the device. It could be due to the higher ionic conductivity of AN over

MPN.¹¹¹ Even so, irrespective of the solvent, higher PCE was achieved for nitrate-hydrotalcite gel devices: comparable J_{sc} and FF with liquid ones, along with significant enhancement in V_{oc} .

Table 11 Comparison of the photovoltaic characteristics based on liquid and gel electrolyte in different solvent (AN and MPN) under one sun illumination. L-MPN and G-MPN refer to, respectively, liquid and nitrate-hydrotalcite gel electrolyte prepared using methoxypropionitrile; L-AN and G-AN refer to liquid and nitrate-hydrotalcite gel electrolyte in acetonitrile.¹¹²

Solar Cells ^a	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	ΔPCE^b
L-MPN	7.0	15.2	741	0.62	
G-MPN	7.9	15.4	843	0.61	13%
L-AN	8.8	15.3	786	0.73	
G-AN	9.6	15.1	846	0.75	9%

^aData are obtained with photoanode 5+2 layers;
^bCalculated using $\Delta PCE = (PCE_G - PCE_L)/PCE_L$

7.1.3.4 Comparison of Smectite and Nitrate-Hydrotalcite

In the literature, most clay gelled DSSCs were based on cationic clay such as smectite clay. Since this work is a pioneering attempt in using anionic hydrotalcite, a comparison of J-V performance of devices based on smectite gel and nitrate-hydrotalcite gel electrolyte was conducted and the results are listed in Table 12. Two types of smectite clay were used (synthetic smectite and commercial smectite clay) and they were added at the same weight percentage of 10 wt %. Based on the results, different effects of adding smectite and nitrate-hydrotalcite were observed. Both smectite gelled devices C-S and C-C had enhanced FF compared with liquid device, while their J_{sc} and V_{oc} dropped significantly. However, nitrate-hydrotalcite gelled device HT-N maintained similar J_{sc} and FF with liquid device but

obtained a great enhancement in V_{OC} . Overall the device based on anionic nitrate-hydrotalcite performed much better than cationic smectite clay in terms of power conversion efficiency. This is what we expected since the charge orientations of cationic clay and anionic hydrotalcite are different. Although both hydrotalcite and smectite are layered structure, the chemical composition plays importance role. In cationic clay, the cations located between plates are exchangeable with liquid media. On the contrary, in hydrotalcite, anions are located between plates and are exchangeable with anions in liquid media. In DSSCs, especially when triiodide is the redox mediator, the hydrotalcite structure has better ability in terms of interaction/intercalation with the electrolyte.

Table 12 Comparison of J-V characteristics of devices made of electrolyte gelled by synthetic smectite clay (C-S), commercial smectite clay (C-C) and nitrate-hydrotalcite (HT-N).

Electrolyte	PCE (%)	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF
HT-N	7.9	13.4	861	0.68
C-S	6.9	11.7	794	0.74
C-C	6.5	10.7	810	0.72
Liquid	7.2	13.0	820	0.67
^a Data are obtained with photoanode 3+2 layers				

7.1.3.5 Charge Transport in Gel

The observed J_{SC} for both liquid and gel electrolyte devices are comparable; moreover, the linear increase of J_{SC} with light intensity clearly indicates that the reaction rate of redox ions to dye is fast enough for regeneration (Figure 34). It suggests that viscosity of the gel does not affect much of charge transport in the electrolyte. Unlike in some other types of polymer/gel system, DSSCs often perform better under low intensity illumination because J_{SC} is limited by diffusion under high intensity illumination.^{80, 113} It was proposed that in nanocomposite gelled electrolyte (typically ionic liquids), besides the physical diffusion (in

most liquid systems), another type of charge transport mechanism named Grotthuss type or exchange-reaction process $\Gamma + \text{I}_3^- \rightarrow \text{I}_3^- + \Gamma$ may also assist the current flow.¹¹⁴⁻¹¹⁶ In such cases, rapid charge transfer is enabled even in a viscous medium since physical species movement is not necessary for charge transport. It may be due to the adsorption of redox ions on particle surface forming a dense and oriented redox region by electrostatic interaction which may act as rapid charge transport path with an exchange-reaction.^{100, 117, 118} It has also been shown that the clay or clay-like mineral significantly affects the diffusion of the ions if applied on electrodes.^{108, 119, 120} Taking into account these arguments for nitrate-hydrotalcite gel system, it can be seen that fundamental studies, such as the charge transport mechanism and equilibrium potentials of redox couple in the gel system, have not been carried out yet, although the understanding of such characteristics is crucial for DSSC applications.

Figure 34 Photocurrent of G-AN at various illumination conditions (0.25, 0.59, 0.86 and 1.03 sun).¹¹²

Steady state cyclic voltammetric analysis was carried out in order to understand the charge transport mechanism in nitrate-hydrotalcite gel electrolyte system. The limited current (I_{lim}) in cyclic voltammograms, corresponding to the reaction $\text{I}_3^- + 2\text{e}^- = 3\text{I}^-$, is given by¹¹⁴

$$I_{lim} = 8FDrc \quad (22)$$

where D is diffusion coefficient of redox species, r is the microdisk electrode radius, and c is the total concentration of the redox species ($1/3 [I^-] + [I_3^-]$). If physical diffusion and Grotthus mechanism are conjugated, then

$$\begin{aligned} D &= D_{phys} + D_{ex} \\ &= D_{phys} + \frac{1}{6}k_{ex}\delta^2c \end{aligned} \quad (23)$$

where, D_{phys} and D_{ex} are the respective coefficients based on simple physical diffusion and Grotthus/exchange reaction, k_{ex} is the exchange reaction rate constant, and δ is the centre to centre intersite distance at the exchange reaction. Substituting equation (19) to equation (17), we have

$$I_{lim} = 8Fr(D_{phys}c + \frac{1}{6}k_{ex}\delta^2c^2) \quad (24)$$

Consequently, according to equation (24)¹¹⁴, pure physical diffusion predicts linear relationship of limiting current as a function of total concentration of redox species, while pure exchange predicts quadratic behavior. As shown in Figure 35, at fixed ratio of [PMII]: [I₂] = 10:1, limiting current with concentration of redox species exhibits linear relation with correlation coefficients $R^2 > 0.985$. It clearly indicates that the charge transportation in nitrate hydrotalcite gel electrolyte is conducted solely by physical diffusion at the ratio of [PMII]: [I₂] = 10:1. Furthermore, the calculated physical diffusion coefficient of I₃⁻ shows independence with concentration variation, which also supports a typical physical diffusion behavior. Although the gel electrolyte is viscous in nature, redox ions can still diffuse smoothly, owing to the unique properties of nanoclay forming 3-D networks and providing channels for diffusion which is different from silica gel system. Although calculated $D_{I_3^-}$ in

nanoclay gel is slightly smaller than that in liquid, it does not result in major deficiency in photocurrent collection.

Figure 35 (a) Limiting currents for reaction of $I_3^- + 2e^- = 3I^-$ as a function of concentration ($1/3 [I^-] + [I_3^-]$) for PMII/ I_2 redox couple with constant molar ratios (PMII: I_2 10:1) in acetonitrile. (b) Calculated diffusion coefficient of I_3^- for both liquid and nitrate-hydroxalcite gel.¹¹²

The clay powder extracted from the nitrate-hydroxalcite gel was checked using XPS. The two peaks found (Figure 36) correspond to iodide ions.^{121, 122} The presence of iodide ions in the clay powder clearly reveals that besides diffusing through the network structure, the iodide ions are also accommodated by the nitrate-hydroxalcite particles (Figure 36). In addition, the presence of iodide was not found in a reference carbonate-hydroxalcite sample (Figure 37) which was extracted from electrolyte under the same procedure (both of the reference sample

and nitrate-hydrotalcite clay used are homogenized with electrolyte first. Then they are subsequently centrifuged and washed in acetonitrile for more than 8 cycles). Thus the probability of existence of iodide contaminants in the nitrate-hydrotalcite powder is eliminated. The presence of iodide ions in the nitrate-hydrotalcite clay could be due to their exchange with the original nitrate ions. However due to the similarity in size and ion affinity⁷¹ of I_3^- and NO_3^- ions, no significant peak shift in the XRD spectrum is observed (Figure 38). The presence of iodide indicates that the nitrate hydrotalcite is able to interact with electrolyte. Considering the charge balance, when redox diffuses through the nanoclay networks, accommodated iodide may come from the exchange between redox and nitrate ions. Different from the spherical structure of silica, the layered structure of hydrotalcite facilitates the exchange of ions.

Figure 36 X-ray photoelectron spectroscopic spectrum of I 3d in the nitrate-hydrotalcite powder extracted from gel electrolyte containing 1M PMII and 0.1 M I_2 .¹¹²

Figure 37 X-ray photoelectron spectroscopic spectrum of I 3d in the carbonate-hydrotalcite as reference sample extracted from gel electrolyte containing 1M PMII and 0.1 M I₂.

Figure 38 Comparison of X-ray diffraction patterns of bare nitrate-hydrotalcite powder (P-1) and the powder extracted from gel electrolyte (P-2).¹¹²

7.1.3.6 Effect of Nitrate-Hydrotalcite Gel Electrolyte on V_{OC}

Shown clearly in Table 11, the nitrate-hydrotalcite nanoclay addition in liquid electrolyte enhances the V_{OC} . The theoretical V_{OC} in DSSCs is determined by the potential difference between the Fermi energy of TiO₂ electrode and the redox potential of triiodide/iodide in

electrolyte. The equilibrium potential of triiodide/iodide redox couples can be determined from the potential where the current become zero by ultra-microelectrode. According to steady-state voltammetric study (Figure 39), the redox potential remains unchanged after adding nitrate-hydrotalcite to the electrolyte. Consequently, the improvement of V_{OC} can only be attributed to the change in Fermi energy of TiO_2 . The equilibrium Fermi energy of electrons in semiconductors can be expressed by equation (17).

The shift in the conduction band energy can be diagnosed from electrochemical impedance measurements of the chemical capacitance under light. Figure 40 shows the chemical capacitance versus open circuit potential of TiO_2 based on different weight percentages of nitrate-hydrotalcite in electrolyte. At fixed capacitance, a continuous right shift of open circuit potential is observed with nitrate-hydrotalcite content. Therefore, according to the equation described, the observed V_{OC} enhancement is attributed to the conduction band shifting to higher energy level after adding nitrate-hydrotalcite.

Figure 39 Cyclic voltammograms of AN based liquid (L-B) and its nitrate-hydrotalcite gel electrolyte (10 wt% content labeled as G-B) with Pt microelectrode (scan rate 10mV/s).¹¹²

The change in V_{OC} with different weight percentages of nanoclay should be due to the basic nature of nitrate-hydroxalcalcite. Usually, the surface of TiO_2 can be more or less protonated depending on the pH of electrolyte or some potential determining ions like lithium ion.¹²³ Adding a base in electrolyte deprotonates the surface of TiO_2 and results in alternation of surface potential, which is the origin of band bending adjacent to the surface.^{62, 123, 124} However, in DSSCs, the nanoparticles used are too small to support a significant band bending.¹²³ As a consequence, the entire conduction band of the TiO_2 film shifts with the surface potential and hence results in enhancement in V_{OC} for devices with gel electrolyte. The phenomenon was also observed in the study of the effect of 4-tert-butylpyridine which was often reported to act as a base in DSSCs.⁶²

Figure 40 Chemical capacitance of TiO_2 photoanode extracted from electrochemical fitting of semicircle obtained at intermediate frequency region at different open circuit potentials. Different open circuit potentials are controlled by applying various intensity of LED light shining on devices in the frequency range of 100 KHz–0.1Hz and with ac amplitude of 10 mV.¹¹²

Therefore, the origin of V_{OC} enhancement in nitrate-hydrotalcite gel electrolyte can be attributed to a shift of the conduction band energy of TiO_2 to higher energy level. This can be further verified using various dye systems with different LUMO levels. The obtained device performance with different dyes as a sensitizer using the nitrate-hydrotalcite gel electrolyte is shown in Table 13. For organic dye D35, similar enhancement in the device performance is obtained mainly due to the V_{OC} enhancement and negligible change in J_{sc} . However, for ruthenium based N749 dye, although enhancement in V_{OC} was observed, overall PCE decreased because of the decrement in J_{sc} . According to the literature, LUMO levels of D35, N719 and N749 dyes are at -1.37eV^{125} , -1.15eV^{126} and -0.77eV^{127} vs. NHE respectively. The Fermi level of TiO_2 is at $-0.4\text{eV} \sim -0.5\text{eV}^{128, 129}$. The LUMO levels of D35 and N719 dyes are high enough and do not affect the electron injection although there is upward shift in the conduction band of TiO_2 after adding nitrate-hydrotalcite nanoclay to the electrolyte. However, the LUMO level of N749 is lower than that of N719. In this case, the additional effect of nitrate-hydrotalcite electrolyte on escalating the conduction band of TiO_2 could cause deficiency in electron injection as there is a minimum energy difference of $\sim 0.3\text{eV}$ required for effective injection.¹³⁰

Table 13 Performance comparison of gel and liquid electrolyte with D35 and N749 dyes.¹¹²

Solar Cells ^a	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	ΔPCE^b
L-D35	5.9	11.9	712	0.70	
G-D35	6.5	11.7	769	0.72	10%
L-N749	7.0	11.4	697	0.77	
G-N749	5.6	10.1	768	0.73	-20%

^aData are obtained with photoanode 5+2 layers for D35, and 3+2 layers for N749

^b $\Delta PCE = (PCE_G - PCE_L)/PCE_L$

Nitrate-hydroxalcalite acts like base which can shift up the conduction band of TiO_2 , and it is superior to basic salt additive as shown in Table 14. The amount of NaOH added in electrolyte is calculated by obtaining an equal pH value ($\text{pH} = 10$) in water as 10 wt% of nanoclay added. Adding NaOH also enhances the V_{OC} but not as efficiently as adding nanoclay. However, the J_{SC} drops significantly compared to the pure liquid cell. The J_{SC} drop is not due to dye desorption by alkaline source because the amount of dye loaded on photoanode is comparable after exposing to electrolyte. However, while adding NaOH in electrolyte, small amount of aggregation of electrolyte species were observed. This degradation of electrolyte with the presence of NaOH could be responsible for the decreased J_{SC} . Unlike strong alkaline salts directly dissolving in electrolyte, the nitrate-hydroxalcalite is acting more like a buffering source preventing electrolyte being too acidic due to the presence of large amount of iodide/iodine ions. Thereby, it may change the protonation of TiO_2 surface or the concentration of some potential determining ions like lithium.

Table 14 A comparison of the photovoltaic characteristics of liquid, gel electrolyte and liquid electrolyte with addition of NaOH. L-NaOH, L-Nil and G-Nil denote electrolyte conditions: liquid electrolyte with NaOH added, liquid electrolyte and nitrate-hydroxalcalite gel with no additional modification.¹¹²

Solar Cells ^a	PCE (%)	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF	Dye ^b ($\times 10^{-8}$ mol)
L-NaOH	6.4	12.5	767	0.67	4.0
L-Nil	7.8	14.6	733	0.73	3.9
G-Nil	8.4	14.3	830	0.71	4.1

^aData are obtained with photoanode 4+1 layers;

^bMeasured in 0.1 M NaOH in water+ethanol (1:1 v:v)

A further investigation on mechanism of hydroxalcalite shifting the conduction band of TiO_2 is conducted and discussed in the next section of this chapter.

7.2 Role of Anions in Hydrotalcite-Based Gel Electrolyte

Clay, as a gelator in electrolytes, can resolve the liquid leakage issue in DSSCs. As a continued study, anionic hydrotalcite is used in DSSCs as a gelator to help the formation of gel electrolyte. Hydrotalcite were synthesized with three types of exchangeable anions (NO_3^- (CL-N), CO_3^{2-} (CL-C) and SO_4^{2-} (CL-S) respectively), with similar morphology through the co-precipitation method. It was observed that gel formation of hydrotalcite depends strongly on the type of exchangeable anions in the hydrotalcite. The work in this chapter tries to understand the effect of anions on the photovoltage and photocurrent in gel electrolyte through electrochemical analysis. When the ion affinity increases, the V_{OC} increases. This is attributed to the Li^+ intercalation with hydrotalcite compound which results in the elevation of the conduction band of TiO_2 . However, when ion affinity increases, the J_{SC} decreases. This is a result of decreasing diffusion coefficient of triiodide together with increasing difficulty in the injection process. For the anions having low ion affinity in the hydrotalcite, the high viscosity of gel does not affect the diffusion of redox couple significantly. Furthermore, this study indicates that the proper selection of hydrotalcite compounds can produce a quasi-solid-state gel electrolyte while simultaneously improving power conversion efficiency of solar cells. The device performance has been improved from 7.8% with liquid electrolyte to 8.4% with hydrotalcite gel electrolyte.

7.2.1 Introduction

Previous studies have shown the promising role of nanoclay in the development of quasi-solid electrolyte. Various mechanisms were proposed to describe the role of clay in electrolytes. Such examples include enlarging channels for ion transfer, light scattering capability, reduction in electrode/electrolyte contact resistance and so on.¹⁰⁴⁻¹⁰⁶ According to these studies, the benefits of clay do not just reside in solidifying the electrolyte which leads

to more stability against leakage. The dramatically increased viscosity, as a result of clay induced gelation, does not affect the photocurrent collection actually. Based on previous studies in photochemistry and photocatalysis, the smectite clay on its modified electrodes hindered the diffusion of anions, and cations incorporated in the clay films could induce electro-catalytic effects.^{108, 109} Certainly, more effort is required in revealing the effects of clay in photovoltaic devices. More effort is also required for the study of the correlation of the interaction between clay and the charge transport dynamics in device. In Chapter 6, adding nitrate-hydrotalcite (which has similar role of clay) to the liquid electrolyte showed improved device efficiency compared to unmodified electrolyte and smectite clay modified electrolyte.¹¹², This chapter clarifies that the charge transport in clay gel electrolyte occurs only by physical diffusion through a network formed by the clay, being different from the Grotthus type charge transport in silica gel. The repulsion from the original anions in the clay should not be neglected because the transport of iodide/triiodide serves as a critical efficiency-relevant component in the current DSSCs. The original anions definitely play an important role in determining the properties of the gel electrolyte and its device performance. This chapter reports the effect of different types of exchangeable anions in the anionic hydrotalcite (using NO_3^- , CO_3^{2-} and SO_4^{2-} respectively as examples) on the capability of gel formation, the chemical interaction with electrolyte and the characteristics of devices. The anions (NO_3^- , CO_3^{2-} and SO_4^{2-}) were selected based on their well-known difference in ion exchange capacity ($\text{NO}_3^- < \text{SO}_4^{2-} < \text{CO}_3^{2-}$).¹³¹ To study the interaction between hydrotalcite nanoparticles and the electrolyte, two types of mimic electrolytes were used. One of them contains PMII and I_2 and the other contains LiI. For convenience hydrotalcite with exchangeable anions NO_3^- , SO_4^{2-} and CO_3^{2-} are designated as CL-N, CL-S and CL-C respectively.

7.2.2 Experimental Details

The obtained nanoclay powder was then homogenized into gel with the liquid electrolyte. The liquid electrolyte was EL-AN. The mixture containing the liquid electrolyte and 10 wt% of nanoclay was sonicated for 5-10 minutes with bath sonicator and subsequently homogenized into gel form using probe ultrasonic homogenizer.

The photocurrent-voltage characteristics were measured with a cell area of 0.28cm^2 . The morphology of the hydrotalcite was characterized with a transmission electron microscopy (TEM, JEOL 2100F operating at 200kV). The phase composition was analyzed by X-ray diffraction (XRD, Bruker-AXS D8 Advance) and small angle X-ray scattering (SAXS). BET surface area was measured by surface area analyzer (NOVA 3200e, Quantachrome instrument). EIS was conducted using electrochemical station (Autolab, PGSTAT302N) under open circuit potential under LED illumination with testing frequency varying from 10^{-1} - 10^5 Hz and AC amplitude of 10 mA. The chemical capacitance was obtained by electrochemical fitting software (Scribner Associate Inc., Zview 3.2b). Elemental composition for nanoclay sample before and after mixing with electrolyte was investigated by XPS (Kratos-Axis spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer). C 1s was calibrated to 284.5 eV for all samples. The ion diffusion was measured by steady state cyclic voltammetry in scan rate of 10mV/s using Pt microelectrode with radius of 10 μm as working electrode, Pt foil as counter electrode and Pt wire as reference.

7.2.3 Results and Discussion

7.2.3.1 Characterization of Anionic Hydrotalcite

The TEM images of synthesized hydrotalcite samples are shown in Figure 41. Three types of samples were synthesized, namely CL-N, CL-S and CL-C, respectively. These powders have a size of 50-80 nm and a thickness of a few nanometers. The BET surface area measured for CL-N, CL-S and CL-C are 113 m²/g, 105 m²/g and 128 m²/g respectively. Calculated from XRD, the interlayer distances of dry powders are 23.7, 23.6 and 23.4 Å respectively. Calculated from SAXS, the interlayer distances for hydrotalcite gelled with acetonitrile are 23.9, 23.9 and 23.5 Å respectively for CL-N, CL-S and CL-C (Figure 42). The difference in interlayer distances reflected the difference in the ionic strength of the anions, i.e. CL-C has the shortest interlayer distance because of its largest ion affinity of CO₃²⁻.⁷¹ In addition, as shown in Figure 43, strong electrostatic attraction between CO₃²⁻ anions and hydroxide plate restricted the lattice expansion of CL-C in gel. On the contrary, the CL-N and CL-S with anions having less ionic strength showed larger lattice expansion.

Figure 41 TEM images and the histograms of particle sizes of the synthesized hydrotalcite, in the order of CL-N, CL-S and CL-C.¹³²

Figure 42 The spectrum of peak 003 of (a) the dry powder by XRD and of (b) the hydrotalcite gelled with acetonitrile by SAXS.¹³²

Figure 43 The schematic representation of anionic hydrotalcite CL-C or carbonate hydrotalcite.¹³²

It is necessary to ensure that each hydrotalcite sample contains only one type of exchangeable anion for fair comparison of the effect of anions. The hydrotalcites are two-dimensional materials, with interlayer distance of 2-3 nanometers which is within the scanning capability of XPS. Thus, XPS is selected for verifying the chemical composition through elemental analysis of hydrotalcite powder. Here, one thing that we would like to mention is that nitrate ions were present in the form of magnesium nitrate and aluminum nitrate in the precursor during synthesis of hydrotalcite samples. CL-N has no alternative and has to preserve the nitrate ions in the structure because of the unbalanced charge in layers and the presence of the only source of anion in the precursor. The absence of N 1s peak (shown in Figure 44) in CL-C and CL-S clearly indicated that nitrate anions were completely removed after synthesis. The S 2p peak confirms that SO_4^{2-} has entirely replaced NO_3^- in CL-S hydrotalcite. Similarly, CO_3^{2-} should replace the NO_3^- in CL-C since the selectivity of CO_3^{2-} is even higher than SO_4^{2-} . C 1s was not used as the indicator for the presence of CO_3^{2-} since C 1s is the reference for XPS.

The results above indicate that before being assembled into DSSCs, the three synthesized hydrotalcite exhibited no distinct deviations of morphology. The elemental confirmation by XPS also ensures that the observed effects discussed later on are solely based on the exchangeable anion present in the respective hydrotalcite samples.

Figure 44 The X-ray photoelectron spectroscopic spectra of N1s peaks of the synthesized anionic hydrotalcites (a) CL-N, (b) CL-S, (c) CL-C, and (d) S 2p for CL-S.¹³²

7.2.3.2 Gelation of Different Hydrotalcite

Figure 45 shows the gelation capability of the three types of hydrotalcite samples. In terms of gel formation ability, with the same weight percentage of hydrotalcite to electrolyte ratio (10 wt %), CL-N and CL-S formed stable gels with the electrolyte, but CL-C was not a good gelator with even more than 10 wt %. As observed in SAXS analysis, it is not surprising that strong ionic strength of CO_3^{2-} restricts the expansion of CL-C in acetonitrile.

Figure 45 Gel formations with liquid electrolyte that have 10 wt % of CL-N, CL-C and CL-S hydrotalcite samples. Gelation was tested through inverting a sample bottle and testing whether the gel stayed atop.¹³²

The mimic redox electrolyte which contains PMII and I_2 in acetonitrile was used to investigate the interaction between redox ions and hydrotalcite after gel formation. The tested samples were extracted from the mimic gel electrolyte and analyzed by XPS subsequently. In Figure 46 (a) the presence of I 3d peaks (631 eV $3d_{5/2}$, 619 eV $3d_{3/2}$) indicates that CL-N and CL-S accommodated parts of iodide ions. However, the absence of Iodide was observed in the CL-C. As shown in Figure 46 (b) and (c), the original anions were still found to be present, which indicates that the accommodated iodide did not replace the original anions fully. This is also further illustrated in the XRD results in Figure 47 (the calculated interlayer distances are in Table 15). No shift of peak position or change of interlayer distance was observed after accommodation with iodide (comparison between CL-N-I and CL-N). This could be the result of the difference in ion exchange capability. In this case, the total exchange of anions is not favorable in energy as the ion affinity of iodide is weaker than that of the other three types of anions, especially for carbonate which has the highest ion affinity.⁷¹

Figure 46 The X-ray photoelectron spectroscopic spectrum of hydrotalcite powders extracted from mimic gel electrolyte containing PMII and I₂: (a) I 3d for CL-N, CL-S and CL-C, (b) N 1s for CL-N and (c) S 2p for CL-S.¹³²

Figure 47 X-ray diffraction patterns (peak 003) of the synthesized nitrate hydrotalcite powder (CL-N), the powder extracted from mimic gel electrolyte containing PMII + I₂ (CL-N-I), the powder extracted from mimic gel electrolyte containing LiI (CL-N-Li) and the hydrotalcite in its gel form in solar cell electrolyte (CL-N-ELG).¹³²

Apart from investigating the accommodation of redox anions, the interaction between hydrotalcite and the small cation Li^+ which is present in the electrolyte used in solar cells was also studied using another mimic electrolyte containing LiI . One observation is that the interlayer distances for all hydrotalcite samples were larger, shown in Table 15. Based on the XRD analysis of CL-N and CL-N-I shown in Figure 47, iodide accommodation did not cause the interlayer distance of the hydrotalcite to change. Thus, the expansion of interlayer could be attributed to the Li intercalation. Furthermore, the expanded interlayer distance of the Li -intercalated hydrotalcite is almost the same with that in the gel electrolyte of solar cells (which was measured in gel condition by SAXS).

Table 15 The interlayer distances of three types of hydrotalcite in different conditions: synthesized hydrotalcite powders, extracted hydrotalcite powder from the mimic gel electrolyte containing $\text{PMII} + \text{I}_2$ (denoted as -I), and extracted hydrotalcite powder from the mimic gel electrolyte containing LiI (denoted as -Li).^{a, 132}

Nitrate HT	d (Å)	Sulfate HT	d (Å)	Carbonate HT	d (Å)
CL-N	23.7	CL-S	23.6	CL-C	23.4
CL-N-I	23.7	CL-S-I	23.6	CL-C-I	23.4
CL-N-Li	25.3	CL-S-Li	25.2	CL-C-Li	25.1
^a Calculated from XRD spectrum.					

7.2.3.3 Photovoltaic characteristics of varied hydrotalcite electrolyte based DSSCs

The photocurrent-voltage (J-V) characteristics of the DSSCs with 10 wt% hydrotalcite gel electrolyte were summarized in Table 16. G-N, G-S and G-C refer to the gel based solar cells fabricated using CL-N, CL-S and CL-C respectively. The gel based devices (G-N, G-S and G-C) exhibited superior V_{oc} over the liquid cells (denoted as Liq). Specifically, the observed trend in V_{oc} is in the order of $G-C > G-S > G-N > \text{Liq}$, while the observed trend in J_{sc} is in

the order of G-C < G-S < G-N < Liq. Among the three types of gel electrolyte, G-N showed the highest PCE since it has the highest Jsc among the gel devices (the Jsc is comparable to that with Liq). The enhancement by 8% in PCE compared to the liquid cell benefited mainly from the enhancement in Voc. Consequently, the correlation between the anions present in the hydrotalcite samples and the gel electrolyte performance in a DSSC can be studied through two means: evaluating the effects of promoting high Voc and varying Jsc.

Table 16 Comparison of the photovoltaic characteristics of DSSCs based on liquid and hydrotalcite (CL-N, CL-S and CL-C) gel electrolyte under one sun illumination.¹³²

Solar ^a cells ^a	PCE (%)	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF	D _{I3-} (10 ⁻⁶ cm ² /s) ^b
G-N	8.4	14.3	830	0.71	4.0
G-S	7.4	11.9	835	0.74	3.1
G-C	6.6	10.2	846	0.77	3.2
Liq	7.8	14.6	753	0.71	4.4
^a Data are obtained with photoanode 4+1 layers; ^b Calculated from C-V measurement					

7.2.3.4 Effect of Anions on Voc

The origin of Voc can be traced back to the energy difference between redox potential of iodide/triiodide and the Fermi level of TiO₂ photoanode. In the observations in Chapter 6, no shift in the equilibrium potential of redox couple was observed in the hydrotalcite gel electrolyte.¹¹² Hydrotalcite which acts like buffering medium changes the surface protonation of the TiO₂, thereby alters the chemical capacitance. By electrochemical impedance analysis, the shift of the chemical capacitance to higher potential can be studied and this is shown in Figure 48. The trend of the shift in chemical capacitance correlates well with the observed trend of Voc. Larger shift of chemical capacitance of TiO₂ toward higher potential indicates

that TiO_2 has a higher conduction band position. CL-C shows the highest capability to shift the conduction band of TiO_2 towards higher energy level, followed by CL-S and CL-N.

It is interesting to study how hydrotalcite compounds alter the TiO_2 surface. It is typical that TiO_2 surface is more or less protonated depending on the surrounding electrolyte.¹³³ Similarly, in organic solvents, small cations attracted to TiO_2 surface change the protonation process, too. Thus, Li^+ , which affects the potential in the electrolyte, largely determines the energetics of the TiO_2 /electrolyte interface.¹³³ As discussed earlier in the gelation of different hydrotalcite, some of the Li^+ enters the nanostructure instead of being intercalated to TiO_2 due to electrostatic attraction of anions in hydrotalcite. Previous studies have shown that Li^+ intercalation in TiO_2 brings down the conduction band.¹³⁴ Therefore, by intercalating, hydrotalcite serves like a base that balances the excess Li^+ ions close to the TiO_2 site. Having different ion affinity, the ability of the three hydrotalcites to attract Li^+ is also different; as a result, variations in the conduction band shift were observed. Sulfate ions and divalent carbonate have stronger capability of attraction for Li^+ than mono-valent nitrated ion. Since carbonate ion is the strongest in ion attraction to Li^+ , the change in the chemical capacitance is thus the most significant among all.

Figure 48 Chemical capacitance of TiO_2 photoanode extracted from electrochemical fitting of semicircle obtained at intermediate frequency region at different open circuit potentials.

Different open circuit potentials were controlled by applying various intensity of LED light shining on devices, frequency range 100K Hz-0.1 Hz, ac amplitude 10 mV.¹³²

7.2.3.5 Effect of Anions on J_{SC}

Photocurrent collection depends strongly on the speed of charge transport in the electrolyte. As found in Chapter 6, charge transport in the hydrotalcite gel is based on physical diffusion.¹¹² The channels in hydrotalcite network are responsible for the diffusion process. Therefore stronger repulsion between the redox couple and the anions may encumber the charge transport more. By correlating the PCE values with diffusion coefficients of I_3^- that are listed in Table 16, the diffusion coefficient of triiodide was found to strongly depend on the type of anions. Nitrate ion has slightly higher ion affinity than iodide. Its gel electrolyte (gel with CL-N) showed similar diffusion coefficient and photocurrent with liquid electrolyte. However, for strong ion affinity ions such as sulfate and carbonate, the measured diffusion coefficients of triiodide are much lower than that in CL-N gel. This shows that the strong repulsion between the anions in the hydrotalcite and the redox ions resulted in difficult

photocurrent collection. In addition, it was observed that the diffusion coefficients of triiodide in the gel with CL-S and in the Gel with CL-C are similar. The device characteristics indicated that the observed J_{sc} of G-C was much lower than that of G-S. This may be a result from the elevated conduction band. The EIS analysis suggested that G-C has higher position of conduction band than G-N and G-S, which is shown in Figure 48. In general, minimum energy difference of $\sim 0.3\text{eV}$ between the conduction band of TiO_2 and the LUMO level of dye is required for effective injection. The elevated conduction band can reduce the driving force for injection, resulting in a lower J_{sc} for G-C compared to those of G-S and G-N.

7.3 Conclusions

In the first part of this chapter, we have achieved a 10 % improvement in PCE for nitrate hydrotalcite gel electrolyte solar cells (PCE = 9.6%) compared to their liquid electrolyte counterparts (PCE = 8.8 %) under one sun illumination. In this gel system, charge transport is through physical diffusion, where the ions can diffuse smoothly through the channels developed by the hydrotalcite networks. Thus, the calculated physical diffusion coefficient is not affected much by the viscosity of the gel electrolyte. The observed V_{oc} enhancement is due to the conduction band up-shifting. The maximum PCE of 10.1% was achieved under 0.25 sun. This study demonstrates that this gel electrolyte improves PCE while resolving critical problems of liquid electrolyte such as solvent leakage.

The work in the second part of this chapter demonstrated the effect of anions of the hydrotalcite on its photovoltaic properties. Three types of hydrotalcite clay, with NO_3^- , CO_3^{2-} and SO_4^{2-} anions, were studied in DSSC applications. The study shows clearly that proper selection of hydrotalcite not only solidifies the electrolyte against the leakage problem, but also increased the conversion efficiency of the solar cell. When ion affinity increases, V_{oc}

increases. This can be attributed to the Li^+ intercalation with the hydrotalcite compound, which resulted in the elevation of the conduction band of TiO_2 . When ion affinity increases, J_{sc} decreases. This is a result of the decreasing diffusion coefficient of triiodide and the increasing difficulty in the injection process.

Overall speaking, in this chapter, hydrotalcite gel not only achieves the purpose of improving interfacial recombination by forming a quasi-solid state solar cell but also improves the cell performance.

The contents of this chapter are adapted or reprinted from the following papers:

Xiu Wang, Sneha A. Kulkarni, Bruno Ieiri Ito, Sudip K. Batabyal, Kazuteru Nonomura, Chee Cheong Wong, Michael Grätzel, Subodh G. Mhaisalkar and Satoshi Uchida. (2013). *Nanoclay Gelation Approach toward Improved Dye-Sensitized Solar Cell Efficiencies: An Investigation of Charge Transport and Shift in the TiO_2 Conduction Band*. ACS Applied Materials & Interfaces, 5(2), 444-450.

Xiu Wang, Ran Deng, Sneha A. Kulkarni, Xiaoyan Wang, Stevin Snellius Pramana, Chee Cheong Wong, Michael Grätzel, Satoshi Uchida and Subodh G. Mhaisalkar. (2013). *Investigation of the Role of Anions in Hydrotalcite for Quasi-Solid State Dye-Sensitized Solar Cells Application*. Journal of Materials Chemistry A, 1(13), 4345-4351.

Chapter 8 Conclusions

The objective of this thesis was to modify the interface between TiO_2 photoanode and liquid electrolyte (iodide/triiodide as redox) in order to improve the photovoltaic performance of DSSCs. It featured with two main different approaches for improving the performance of DSSCs: a direct modification on TiO_2 surface through surface treatment and molecular passivation and an indirect modification to alter the TiO_2 surface charge through adding nanoparticles such as hydrotalcite and silica. The results obtained showed that the investigated approaches are promising in improving photovoltaic performance in different ways.

Direct modification of TiO_2 photoanode was carried out through surface treatment using a simple, new, safe and effective TiF_4 hydrolysis treatment instead of the conventional TiCl_4 treatment. The effect of TiF_4 concentration is studied, and the efficiency is enhanced by 22% by 20 mM TiF_4 treatment compared with reference device treated by standard TiCl_4 solution. The enhancement owing to increased amount of dye loaded benefits from increased surface area and the retardation of charge recombination. The reduced recombination of TiF_4 treated devices is likely due to fluorine passivation of the TiO_2 surface. This hydrolysis treatment could be feasible for replacing the conventional TiCl_4 treatment on thinner nanostructure based DSSCs to further improve the solar cell efficiency. This method is not suitable for thicker photoanode because of the fragile mesoporous structure after TiF_4 treatment.

The TiO_2 -electrolyte interface was also studied by another direct modification method: the passivation of self assembled monolayer on dye sensitized TiO_2 photoanode. The passivation of SAMs with different head group ($\text{C}_{18}\text{H}_{37}\text{SiX}_3$, $\text{X} = \text{H}, \text{OCH}_3, \text{Cl}$) of the same chain length

were applied and investigated. The total power conversion efficiency was improved by approximately 21 % using $C_{18}H_{37}SiH_3$ as the electron passivation layer and 12% using $C_{18}H_{37}Si(OCH_3)_3$. EIS reveals that the increase in device performance for $C_{18}H_{37}SiH_3$ treated devices is the effect of suppression of surface recombination from injected electrons in TiO_2 to the triiodide ions in the electrolyte. The best passivation against interface recombination is $C_{18}H_{37}SiH_3$, owing to its smallest head group, which leads to the highest packing density. To be effective in reducing recombination and in improving DSSCs performance the SAMs should possess the following properties: not hinder the adsorbed dye layers on TiO_2 , have smaller head groups, have slower rate constant (reacting with TiO_2) so as to provide closely packed screening layers.

Beside the target on interfacial modification, to address the issue of difficulty in handling and leakage caused by liquid electrolyte, nanoparticles were introduced as additive to transform the liquid into a quasi-solid electrolyte and meanwhile altering the TiO_2 surface charge. We achieved improved performance of DSSCs by a quasi-solid-state gel electrolyte made from liquid electrolyte and synthetic nitrate-hydrotalcite. The calculated physical diffusion coefficient shows that the diffusion of redox ions is not affected much by the viscosity of the gel. Adding nitrate-hydrotalcite to the electrolyte has the effect of buffering the protonation process or changing the surface charge density like Li^+ at TiO_2 -electrolyte interface, resulting in a conduction band up-shift and a boost in V_{oc} . Higher V_{oc} with undiminished photocurrent was achieved with nitrate-hydrotalcite gel electrolyte for both organic and inorganic dye (D35 and N719) systems. The power conversion efficiency was increased by 10%, compared to that of the liquid electrolyte.

Following that, the effect of anions inside the hydrotalcite was investigated. When the ion affinity increases, the V_{oc} increases. This is attributed to the Li^+ intercalation with

hydrotalcite compound which results in the elevation of the conduction band of TiO_2 . However, when ion affinity increases, the J_{SC} decreases. This is a result of decreasing diffusion coefficient of triiodide together with increasing difficulty in the injection process. For the anions having low ion affinity in the hydrotalcite, the high viscosity of gel does not affect the diffusion of redox couple significantly. Furthermore, this study indicated that the proper selection of hydrotalcite compounds can produce a quasi-solid gel electrolyte, and improve the efficiency of the solar cells at the same time. The device performance has been improved from 7.8% with liquid electrolyte to 8.4% with hydrotalcite gel electrolyte. Silica nanoparticles were introduced to gel the ionic electrolyte at the content between 12 and 13 wt%, which agrees with the theoretical calculation. The charge transfer resistance decreased with increasing silica content, which could be due to the adsorption of silica nanoparticles onto counter electrode surface. Both short-circuit current density and power conversion efficiency decreased initially and then increased with silica content, with a turnaround point at about 9 wt%. This was probably caused by the enhancement of exchange reaction diffusion with the addition of silica nanoparticles. A local minimum point between the enhancement of exchange reaction diffusion and the retardation of physical diffusion is reached at about 9wt%. It is proposed that adsorption of PMI^+ cations onto the silica nanoparticles surfaces resulted in a local accumulation of I^-/I_3^- redox couples, forming the continuous path for exchange reaction diffusion. Electron recombination lifetime increased with the addition of silica nanoparticles, which can be explained by the depletion of I_3^- ions adjacent to the TiO_2 mesoporous film.

For possible future work, DSSC is a device whose performance is highly determined by interfacial property. Besides TiO_2 -electrolyte interface, electrolyte-counter electrode interface also plays a very important role. Since the TiO_2 -electrolyte interface and the electrolyte-counter electrode interface form a single complete system for electron transfer, the defect or

weak point of one component will cause short-board effect of the overall performance. To achieve better performance, modification of the electrolyte-counter electrode interface is also worth investigation. Furthermore, Pt is used commonly as the counter electrode. Pt is expensive and considering the cost of manufacturing, other materials might be used as counter electrode to make charge transfer perform better on this interface.

Engineering and Scientific Contributions

The engineering contributions of this thesis are as follows.

- This thesis provides proper applications for each type of TiO_2 -electrolyte interface modification method.
- Compared with conventional TiCl_4 treatment, TiF_4 hydrolysis treatment improves device performance effectively in DSSCs when the photoanode thickness is relatively thin.
- Different from TiF_4 , the application of SAMs is not restricted by photoanode thickness and SAMs are able to generally reduce interfacial recombination regardless of the sensitizer. Another advantage of SAMs is that they can be applied with different sensitizers such as dye, quantum dots or other semiconductor materials.
- In most types of gelator, to achieve a quasi-solid state cell, the performance is compromised compared with the liquid cell. In this thesis, hydrotalcite gel not only achieves the purpose of improving interfacial recombination by forming a quasi-solid state cell but also improves the cell performance.

The scientific contributions of this thesis are as follows.

- Through the TiF_4 modification method, it is understood that fluorine passivated TiO_2 as photoanode can reduce the interfacial recombination and improve the power conversion efficiency.
- Compared with other nano particle gelator, hydrotalcite not only produces a quasi-solid state cell but also improves the cell efficiency. This provides possibilities of better quasi-solid state solar cells in future (there are thousands of types of hydrotalcite to use). Proper sensitizer can be selected by matching the energy level of hydrotalcite-modified photoanode. Compared with silica gel, the charge transport mechanism in hydrotalcite gel is based on physical diffusion which makes hydrotalcite applicable in diffusion based

redox mediator. Hydrotalcite can be used for various modifications by adjusting the structure and chemical composition and these modifications affect the performance of solar cells. This thesis demonstrated that different anions produces different effect on V_{OC} and changes the conduction band. The mechanism of this modification is through lithium ion intercalation or change of protonation. This mechanism provides a direction for other modifications in future.

Abbreviations

DSSC: Dye-Sensitized Solar Cell

DOS: Density of States

EIS: Electrochemical Impedance Spectroscopy

FTIR: Fourier Transform Infrared Spectrometry

FTO: Fluorine Doped SnO₂

IPCE: Incident Photon to Current Conversion Efficiency

LUMO: Lowest Unoccupied Molecular Orbital

PCE: Power Conversion Efficiency

SAM: Self Assembled Monolayer

SAXS: Small Angle X-ray Scattering

TEM: Transmission Electron Microscopy

TCO: Transparent Conducting-Oxide

XPS: X-ray Photoelectron Spectroscopy

XRD: X-Ray Diffraction

List of Publications

Journal Papers:

- [1] Xiaoyan Wang, Lidong Sun, Sam Zhang and **Xiu Wang**. (2014). *Ultralong, small-diameter TiO₂ nanotubes achieved by an optimized two-step anodization for efficient dye-sensitized solar cells*, ACS Applied Materials & Interfaces, 6 (3): 1361–1365.
- [2] Xiaoyan Wang, Lidong Sun, Sam Zhang, **Xiu Wang**, Kaifu Huo, Jijiang Fu, Hairong Wang and Dongliang Zhao. (2013). *A composite electrode of TiO₂ nanotubes and nanoparticles synthesised by hydrothermal treatment for use in dye-sensitized solar cells*. RSC Advances, 3(27), 11001-11006.
- [3] Shengnan Huang, **Xiu Wang**, and Chee Cheong Wong. (2013). *Silica Nanoparticle Gelled Ionic Electrolyte for Dye Sensitized Solar Cells*. Nanoscience and Nanotechnology Letters, 5, 1-4.
- [4] **Xiu Wang**, Ran Deng, Sneha A. Kulkarni, Xiaoyan Wang, Stevin Snellius Pramana, Chee Cheong Wong, Michael Grätzel, Satoshi Uchida and Subodh G. Mhaisalkar. (2013). *Investigation of the Role of Anions in Hydrotalcite for Quasi-Solid State Dye-Sensitized Solar Cells Application*. Journal of Materials Chemistry A, 1(13), 4345-4351.
- [5] **Xiu Wang**, Sneha A. Kulkarni, Bruno Ieiri Ito, Sudip K. Batabyal, Kazuteru Nonomura, Chee Cheong Wong, Michael Grätzel, Subodh G. Mhaisalkar and Satoshi Uchida. (2013). *Nanoclay Gelation Approach toward Improved Dye-Sensitized Solar Cell Efficiencies: An Investigation of Charge Transport and Shift in the TiO₂ Conduction Band*. ACS Applied Materials & Interfaces, 5(2), 444-450.
- [6] Junling Song, Hong Bin Yang, **Xiu Wang**, Si Yun Khoo, C. C. Wong, Xue-Wei Liu and Chang Ming Li. (2012). *Improved Utilization of Photogenerated Charge Using Fluorine-Doped TiO₂ Hollow Spheres Scattering Layer in Dye-Sensitized Solar Cells*. ACS Applied Materials & Interfaces, 4(7), 3712–3717.
- [7] Jenny Gun, Sneha A. Kulkarni, **Wang Xiu**, Sudip K. Batabyal, Sergey Sladkevich, Petr V. Prihodchenko, Vitaly Gutkin, Ovadia Lev. (2012). *Graphene Oxide Organogel Electrolyte for Quasi Solid Dye Sensitized Solar Cells*. Electrochemistry Communications, 19, 108-110.

- [8] Zhihui Jiao, **Xiu Wang**, Jinmin Wang, Lin Ke, Hilmi Volkan Demir, Tien Wei Koh and Xiao Wei Sun. (2012). *Efficient Synthesis of Plate-Like Crystalline Hydrated Tungsten Trioxide Thin Films with Highly Improved Electrochromic Performance*. Chemical Communications, 48, 365-367.
- [9] Lidong Sun, Sam Zhang, **Xiu Wang**, Xiao Wei Sun, Duen Yang Ong, Xiaoyan Wang, Dongliang Zhao. (2011). *Transition from Anodic Titania Nanotubes to Nanowires: Arising from Nanotube Growth to Application in Dye-Sensitized Solar Cells*. ChemPhysChem, 12, 3634-3641.
- [10] Lidong Sun, Sam Zhang, **Xiu Wang**, Xiao Wei Sun, Duen Yang Ong and Aung Ko Ko Kyaw. (2011). *A Novel Parallel Configuration of Dye-Sensitized Solar Cells with Double-Sided Anodic Nanotube Arrays*. Energy and Environmental Science, 4, 2240-2248.
- [11] **Xiu Wang**, J. L. Song, C. H. Yip, C. C. Wong, and X. W. Liu. (2011). *Influence of TiF_4 Treatment on TiO_2 Photoanode in Dye Sensitized Solar Cells*. Nanoscience and Nanotechnology Letters, 3(2), 191-194.

Conference Papers:

- [12] Xiaoyan Wang, Sam Zhang, Lidong Sun, **Xiu Wang**, Duen Yang Ong and Dongliang Zhao. (2012, Jul). *The Growth Mechanism of Double-Layered TiO_2 Nanotubes*. Paper presented at The 6th International Conference on Technological Advances of Thin Films & Surface Coatings (ThinFilms2012), Singapore.
- [13] Xiaoyan Wang, Sam Zhang, **Xiu Wang**, Lidong Sun, Kaifu Huo, Jijiang Fu and Dongliang Zhao. (2012, Jul). *Hydrothermal Treatment of Double-Layered TiO_2 Nanotubes for Application in Dye-Sensitized Solar Cells*. Paper presented at The 6th International Conference on Technological Advances of Thin Films & Surface Coatings (ThinFilms2012), Singapore.
- [14] **Xiu Wang**, Ran Deng, C.C. Wong, Sneha A. Kulkarni. (2012, Mar). *Effect of Anionic Nanoclay for Dye-Sensitized Solar Cell Application*. Paper presented at The 6th International Conference on Technological Advances of Thin Films & Surface Coatings (ThinFilms2012), Singapore.
- [15] P Anantha, **Xiu Wang** and C. C. Wong. (2012, Jan). *One-Step Synthesis of Stable Gold Nanoparticles on Eco-Friendly Ionic Liquid*. Paper presented at Materials Research Society, Boston, USA.

- [16] **Xiu Wang**, Chan-Hoe Yip, C.C. Wong. (2010, Jul). *Nanostructured TiO_2 as blocking layer for Dye-sensitized solar cells*. Paper presented at International Conference on Technological Advances of Thin Films & Surface Coatings, Harbin, China.

References

1. O'Regan, B.; Grätzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* 1991, 353, 737-740.
2. Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D., Solar cell efficiency tables (version 39). *Progress in Photovoltaics: Research and Applications* 2012, 20, 12-20.
3. Papageorgiou, N.; Grätzel, M.; Infelta, P. P., On the relevance of mass transport in thin layer nanocrystalline photoelectrochemical solar cells. *Solar Energy Materials and Solar Cells* 1996, 44, 405-438.
4. Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L., Interfacial recombination processes in dye-sensitized solar cells and methods to passivate the interfaces. *The Journal of Physical Chemistry B* 2001, 105, 1422-1429.
5. Bräm, O.; Cannizzo, A.; Chergui, M., Ultrafast fluorescence studies of dye sensitized solar cells. *Physical Chemistry Chemical Physics* 2012, 14, 7934-7937.
6. L., W. A. V.; S., C. A. Q.; S., J. A. H., The chemistry and physics of dye-sensitized solar cells In *Solar Cells - Dye-Sensitized Devices*, Kosyachenko, L. A., Ed. InTech: Winchester, 2011.
7. Bisquert, J.; Palomares, E.; Quiñones, C., Effect of energy disorder in interfacial kinetics of dye-sensitized solar cells with organic hole transport material. *The Journal of Physical Chemistry B* 2006, 110, 19406-19411.
8. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H., Dye-sensitized solar cells. *Chemical Reviews* 2010, 110, 6595-6663.
9. Liang, M.; Chen, J., Arylamine organic dyes for dye-sensitized solar cells. *Chemical Society Reviews* 2013, 42, 3453-3488.
10. Mishra, A.; Fischer, M. K. R.; Bäuerle, P., Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules. *Angewandte Chemie International Edition* 2009, 48, 2474-2499.
11. Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D., Solar cell efficiency tables (version 40). *Progress in Photovoltaics: Research and Applications* 2012, 20, 606-614.
12. Zeng, W.; Cao, Y.; Bai, Y.; Wang, Y.; Shi, Y.; Zhang, M.; Wang, F.; Pan, C.; Wang, P., Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. *Chemistry of Materials* 2010, 22, 1915-1925.
13. Ito, S.; Makari, Y.; Kitamura, T.; Wadab, Y.; Yanagida, S., Fabrication and characterization of mesoporous SnO₂/ZnO composite electrodes for efficient dye solar cells. *Journal of Materials Chemistry* 2004, 14, 385-390.
14. Thavasi, V.; Renugopalakrishnan, V.; Jose, R.; Ramakrishna, S., Controlled electron injection and transport at materials interfaces in dye sensitized solar cells. *Materials Science and Engineering: R: Reports* 2009, 63, 81-99.

15. Ai, X.; Anderson, N. A.; Guo, J.; Lian, T., Electron injection dynamics of Ru polypyridyl complexes on SnO₂ nanocrystalline thin films. *The Journal of Physical Chemistry B* 2005, 109, 7088-7094.
16. Ai, X.; Guo, J.; Anderson, N. A.; Lian, T., Ultrafast electron transfer from Ru polypyridyl complexes to Nb₂O₅ nanoporous thin films. *The Journal of Physical Chemistry B* 2004, 108, 12795-12803.
17. Sun, L.; Zhang, S.; Wang, X.; Sun, X. W.; Ong, D. Y.; Kyaw, A. K. K., A novel parallel configuration of dye-sensitized solar cells with double-sided anodic nanotube arrays. *Energy & Environmental Science* 2011, 4, 2240-2248.
18. Oskam, G.; Bergeron, B. V.; Meyer, G. J.; Searson, P. C., Pseudohalogens for dye-sensitized TiO₂ photoelectrochemical cells. *The Journal of Physical Chemistry B* 2001, 105, 6867-6873.
19. Bergeron, B. V.; Marton, A.; Oskam, G.; Meyer, G. J., Dye-sensitized SnO₂ electrodes with iodide and pseudohalide redox mediators. *The Journal of Physical Chemistry B* 2005, 105, 937-943.
20. Zhang, Z.; Chen, P.; T. N, M.; Zakeeruddin, S. M.; Grätzel, M., The 2,2,6,6-tetramethyl-1-piperidinyloxy radical: an efficient, iodine- free redox mediator for dye-sensitized solar cells. *Advanced Functional Materials* 2008, 18, 341-346.
21. Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M., CoII(dbbip)₂²⁺ complex rivals tri-iodide/iodide redox mediator in dye-sensitized photovoltaic cells. *The Journal of Physical Chemistry B* 2001, 105, 10461-10464.
22. Nelson, J. J.; Amick, T. J.; Elliott, C. M., Mass transport of polypyridyl cobalt complexes in dye-sensitized solar cells with mesoporous TiO₂ photoanodes. *The Journal of Physical Chemistry C* 2008, 112, 18255-18263.
23. Li, T. C.; Spokoyny, A. M.; She, C.; Farha, O. K.; Mirkin, C. A.; Marks, T. J.; Hupp, J. T., Ni(III)/(IV) bis(dicarbollide) as a fast, noncorrosive redox shuttle for dye-sensitized solar cells. *Journal of the American Chemical Society* 2010, 132, 4580-4582.
24. Spokoyny, A. M.; Li, T. C.; Farha, O. K.; Machan, C. W.; She, C.; Stern, C. L.; Marks, T. J.; Hupp, J. T.; Mirkin, C. A., Electronic tuning of nickel-based bis(dicarbollide) redox shuttles in dye-sensitized solar cells. *Angewandte Chemie International Edition* 2010, 49, 5339-5343.
25. Wu, J.; Lan, Z.; Hao, S.; Li, P.; Lin, J.; Huang, M.; Fang, L.; Huang, Y., Progress on the electrolytes for dye-sensitized solar cells. *Pure and applied chemistry* 2008, 80, 2241-2258.
26. Kebede, Z.; Lindquist, S.-E., Donor-acceptor interaction between non-aqueous solvents and I₂ to generate I₃⁻, and its implication in dye sensitized solar cells. *Solar Energy Materials and Solar Cells* 1999, 57, 259-275.
27. Hara, K.; Horiguchi, T.; Kinoshita, T.; Sayama, K.; Arakawa, H., Influence of electrolytes on the photovoltaic performance of organic dye-sensitized nanocrystalline TiO₂ solar cells. *Solar Energy Materials and Solar Cells* 2001, 70, 151-161.
28. Fukui, A.; Komiya, R.; Yamanaka, R.; Islam, A.; Han, L., Effect of a redox electrolyte in mixed solvents on the photovoltaic performance of a dye-sensitized solar cell. *Solar Energy Materials and Solar Cells* 2006, 90, 649-658.

29. Cahen, D.; Hodes, G.; Grätzel, M.; Guillemoles, J. F.; Riess, I., Nature of Photovoltaic Action in Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry B* 2000, 104, 2053-2059.
30. Huang, S. Y.; Schlichthörl, G.; Nozik, A. J.; Grätzel, M.; Frank, A. J., Charge Recombination in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells. *The Journal of Physical Chemistry B* 1997, 101, 2576-2582.
31. Schlichthörl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J., 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* 1997, 101, 8141-8155.
32. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M., Conversion of light to electricity by cis-X2bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes. *Journal of the American Chemical Society* 1993, 115, 6382-6390.
33. Hong, J. S.; Joo, M.; Vittal, R.; Kim, K.-J., Improved Photocurrent-Voltage Characteristics of Ru(II)-Dye Sensitized Solar Cells with Polypyrrole-Anchored TiO₂ Films. *Journal of The Electrochemical Society* 2002, 149, E493-E496.
34. Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M., A binary ionic liquid electrolyte to achieve $\geq 7\%$ power conversion efficiencies in dye-sensitized solar cells. *Chemistry of Materials* 2004, 16, 2694-2696.
35. Wachter, P. Studies of charge transport and phase transition equilibria in blends of ionic liquids for dye-sensitized solar cells. University of Regensburg, Regensburg, 2008.
36. Lee, C.-P.; Chen, P.-Y.; Ho, K.-C., Ionic liquid based electrolytes for dye-sensitized solar cells. In *Ionic Liquids: Theory, Properties, New Approaches*, Kokorin, A., Ed. InTech: 2011.
37. Fei, Z.; Kuang, D.; Zhao, D.; Klein, C.; Ang, W. H.; Zakeeruddin, S. M.; Grätzel, M.; Dyson, P. J., A supercooled imidazolium iodide ionic liquid as a low-viscosity electrolyte for dye-sensitized solar cells. *Inorganic Chemistry* 2006, 45, 10407-10409.
38. Kuang, D.; Klein, C.; Zhang, Z.; Ito, S.; Moser, J.-E.; Zakeeruddin, S. M.; Grätzel, M., Stable, high-efficiency ionic-liquid-based mesoscopic dye-sensitized solar cells. *Small* 2007, 3, 2094-2102.
39. Bai, Y.; Cao, Y.; Zhang, J.; Wang, M.; Li, R.; Wang, P.; Zakeeruddin, S. M.; Gratzel, M., High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nature Materials* 2008, 7, 626-630.
40. Chen, X.; Zhao, J.; Zhang, J.; Qiu, L.; Xu, D.; Zhang, H.; Han, X.; Sun, B.; Fu, G.; Zhang, Y.; Yan, F., Bis-imidazolium based poly(ionic liquid) electrolytes for quasi-solid-state dye-sensitized solar cells. *Journal of Materials Chemistry* 2012, 22, 18018-18024.
41. Kawano, R.; Matsui, H.; Matsuyama, C.; Sato, A.; Susan, M. A. B. H.; Tanabe, N.; Watanabe, M., High performance dye-sensitized solar cells using ionic liquids as their electrolytes. *Journal of Photochemistry and Photobiology A: Chemistry* 2004, 164, 87-92.
42. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M., Gelation of ionic liquid-based electrolytes with silica nanoparticles for quasi-solid-state dye-sensitized solar cells. *Journal of the American Chemical Society* 2003, 125, 1166-1167.

43. Ueno, K.; Hata, K.; Katakabe, T.; Kondoh, M.; Watanabe, M., Nanocomposite ion gels based on silica nanoparticles and an ionic liquid: ionic transport, viscoelastic properties, and microstructure. *The Journal of Physical Chemistry B* 2008, 112, 9013-9019.
44. Ueno, K.; Inaba, A.; Kondoh, M.; Watanabe, M., Colloidal stability of bare and polymer-grafted silica nanoparticles in ionic liquids. *Langmuir* 2008, 24, 5253-5259.
45. Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R., Slow charge recombination in dye-sensitized solar cells (DSSC) using Al₂O₃ coated nanoporous TiO₂ films. *Chemical Communications* 2002, 1464-1465.
46. Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A., Influence of electrolyte in transport and recombination in dye-sensitized solar cells studied by impedance spectroscopy. *Solar Energy Materials and Solar Cells* 2005, 87, 117-131.
47. Menzies, D. B.; Dai, Q.; Bourgeois, L.; Caruso, R. A.; Cheng, Y.-B.; Simon, G. P.; Spiccia, L., Modification of mesoporous TiO₂ electrodes by surface treatment with titanium(IV), indium(III) and zirconium(IV) oxide precursors: preparation, characterization and photovoltaic performance in dye-sensitized nanocrystalline solar cells. *Nanotechnology* 2007, 18, 125608-125619.
48. Gui, E. L.; Kang, A. M.; Pramana, S. S.; Yantara, N.; Mathews, N.; Mhaisalkar, S. G., Effect of TiO₂ mesoporous layer and surface treatments in determining efficiencies in antimony sulfide-(Sb₂S₃) sensitized solar cells. *Journal of the Electrochemical Society* 2012, 159, B247-B250.
49. Diamant, Y.; Chappel, S.; Chen, S. G.; Melamed, O.; Zaban, A., Core-shell nanoporous electrode for dye sensitized solar cells: the effect of shell characteristics on the electronic properties of the electrode. *Coordination Chemistry Reviews* 2004, 248, 1271-1276.
50. Biancardo, M.; West, K.; Krebs, F. C., Optimizations of large area quasi-solid-state dye-sensitized solar cells. *Solar Energy Materials and Solar Cells* 2006, 90, 2575-2588.
51. Zhang, Z.; Zakeeruddin, S. M.; O'Regan, B. C.; Humphry-Baker, R.; Michael, G., Influence of 4-guanidinobutyric acid as coadsorbent in reducing recombination in dye-sensitized solar cells. *The Journal of Physical Chemistry B* 2005, 109, 21818-21824.
52. O'Regan, B. C.; Durrant, J. R.; Sommeling, P. M.; Bakker, N. J., Influence of the TiCl₄ treatment on nanocrystalline TiO₂ films in dye-sensitized solar cells. 2. charge density, band edge shifts and quantification of recombination losses at short circuit. *The Journal of Physical Chemistry C* 2007, 111, 14001-14010.
53. Menzies, D.; Cervini, R.; Cheng, Y.-B.; Simon, G. P.; Spiccia, L., Titanium isopropoxide post-treatment of titanium dioxide electrodes for use in dye-sensitized solar cells. *Journal of the Australian Ceramic Society* 2003, 39, 108-113.
54. Kim, K. E.; Jang, S.-R.; Park, J.; Vittal, R.; Kim, K.-J., Enhancement in the performance of dye-sensitized solar cells containing ZnO-covered TiO₂ electrodes prepared by thermal chemical vapor deposition. *Solar Energy Materials and Solar Cells* 2007, 91, 366-370.
55. Zaban, A.; Chen, S. G.; Chappel, S.; Gregg, B. A., Bilayer nanoporous electrodes for dye sensitized solar cells. *Chemical Communications* 2000, 2231-2232.
56. Ganapathy, V.; Karunakaran, B.; Rhee, S.-W., Improved performance of dye-sensitized solar cells with TiO₂/alumina core-shell formation using atomic layer deposition. *Journal of Power Sources* 2010, 195, 5138-5143.

57. Park, N.-G.; Kang, M. G.; Kim, K. M.; Ryu, K. S.; Chang, S. H., Morphological and photoelectrochemical characterization of core-shell nanoparticle films for dye-sensitized solar cells: Zn-O type shell on SnO₂ and TiO₂ cores. *Langmuir* 2004, 20, 4246-4253.
58. Feldt, S. M.; Cappel, U. B.; Johansson, E. M. J.; Boschloo, G.; Hagfeldt, A., Characterization of surface passivation by poly(methylsiloxane) for dye-sensitized solar cells employing the ferrocene redox couple. *The Journal of Physical Chemistry C* 2010, 114, 10551-10558.
59. Zhang, Z.; Evans, N.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M., Effects of ω -guanidinoalkyl acids as coadsorbents in dye-sensitized solar cells. *The Journal of Physical Chemistry C* 2007, 111, 398-403.
60. Hara, K.; Dan-oh, Y.; Kasada, C.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H., Effect of additives on the photovoltaic performance of coumarin-dye-sensitized nanocrystalline TiO₂ solar cells. *Langmuir* 2004, 20, 4205-4210.
61. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Charvet, R.; Humphry-Baker, R.; Gratzel, M., Enhance the performance of dye-sensitized solar cells by co-grafting amphiphilic sensitizer and hexadecylmalonic acid on TiO₂ nanocrystals. *The Journal of Physical Chemistry B* 2003, 107, 14336-14341.
62. Boschloo, G.; Hagman, L.; Hagfeldt, A., Quantification of the effect of 4-tert-butylpyridine addition to I⁻/I₃⁻ redox electrolytes in dye-sensitized nanostructured TiO₂ solar cells. *The Journal of Physical Chemistry B* 2006, 110, 13144-13150.
63. Kusama, H.; Arakawa, H., Influence of pyrimidine additives in electrolytic solution on dye-sensitized solar cell performance. *Journal of Photochemistry and Photobiology A: Chemistry* 2003, 160, 171-179.
64. Kusama, H.; Arakawa, H., Influence of benzimidazole additives in electrolytic solution on dye-sensitized solar cell performance. *Journal of Photochemistry and Photobiology A: Chemistry* 2004, 162, 441-448.
65. Kopidakis, N.; Neale, N. R.; Frank, A. J., Effect of an adsorbent on recombination and band-edge movement in dye-sensitized TiO₂ solar cells: evidence for surface passivation. *The Journal of Physical Chemistry B* 2006, 110, 12485-12489.
66. Min, J.; Won, J.; Kang, Y. S.; Nagase, S., Benzimidazole derivatives in the electrolyte of new-generation organic dye-sensitized solar cells with an iodine-free redox mediator. *Journal of Photochemistry and Photobiology A: Chemistry* 2011, 148-153.
67. Furube, A.; Katoh, R.; Hara, K.; Sato, T.; Murata, S.; Arakawa, H.; Tachiya, M., Lithium Ion Effect on Electron Injection from a Photoexcited Coumarin Derivative into a TiO₂ Nanocrystalline Film Investigated by Visible-to-IR Ultrafast Spectroscopy. *The Journal of Physical Chemistry B* 2005, 109, 16406-16414.
68. Macdonald, J. R.; Johnson, W. B., Fundamentals of impedance spectroscopy. In *Impedance spectroscopy emphasizing solid materials and systems*, Macdonald, J. R., Ed. Wiley-Interscience: 1987.
69. Bueno, P. R.; Gabrielli, C., Porous (Nanostructured) Electrode Geometry. In *Nanostructured materials for electrochemical energy production and storage*, Leite, E. R., Ed. Springer: Sao Carlos-SP, 2009; pp 127-138.

70. Gelderman, K.; Lee, L.; Donne, S. W., Flat-Band Potential of a Semiconductor: Using the Mott–Schottky Equation. *Journal of Chemical Education* 2007, 84, 685-688.
71. Miyata, S., Anion-exchange properties of hydrotalcite-like compounds. *Clays and Clay Minerals* 1983, 31, 305-311.
72. Wegrzyn, A.; Rafalska-Lasocha, A.; Majda, D.; Dziembaj, R.; Papp, H., The influence of mixed anionic composition of Mg-Al hydrotalcites on the thermal decomposition mechanism based on in situ study. *Journal of Thermal Analysis Calorimetry* 2010, 99, 443-457.
73. Lee, S.-W.; Ahn, K.-S.; Zhu, K.; Neale, N. R.; Frank, A. J., Effects of TiCl_4 treatment of nanoporous TiO_2 films on morphology, light Harvesting, and charge-carrier dynamics in dye-sensitized solar cells. *The Journal of Physical Chemistry C* 2012, 116, 21285-21290.
74. Samadpour, M.; Boix, P. P.; Giménez, S.; Irají Zad, A.; Taghavinia, N.; Mora-Seró, I. n.; Bisquert, J., Fluorine treatment of TiO_2 for enhancing quantum dot sensitized solar cell performance. *The Journal of Physical Chemistry C* 2011, 115, 14400-14407.
75. Sommeling, P. M.; O'Regan, B. C.; Haswell, R. R.; Smit, H. J. P.; Bakker, N. J.; Smits, J. J. T.; Kroon, J. M.; van Roosmalen, J. A. M., Influence of a TiCl_4 post-treatment on nanocrystalline TiO_2 films in dye-sensitized solar cells. *The Journal of Physical Chemistry B* 2006, 110, 19191-19197.
76. Wang, X.; Song, J. L.; Yip, C. H.; Wong, C. C.; Liu, X. W., Influence of TiF_4 treatment on TiO_2 photoanode in dye sensitized solar cells. *Nanoscience and Nanotechnology Letters* 2011, 3, 191-194.
77. Hara, K.; Arakawa, H., Dye-sensitized solar cells. In *Handbook of Photovoltaic Science and Engineering*, Luque, A.; Hegedus, S., Eds. John Wiley & Sons: Hoboken, 2003.
78. Tian, R.; Seitz, O.; Li, M.; Hu, W. W.; Chabal, Y. J.; Gao, J., Infrared characterization of interfacial Si-O bond formation on silanized flat SiO_2/Si surfaces. *Langmuir* 2010, 26, 4563–4566.
79. Helmy, R.; Fadeev, A. Y., Self-assembled monolayers supported on TiO_2 : comparison of $\text{C}_{18}\text{H}_{37}\text{SiX}_3$ (X) H, Cl, OCH_3), $\text{C}_{18}\text{H}_{37}\text{Si}(\text{CH}_3)_2\text{Cl}$, and $\text{C}_{18}\text{H}_{37}\text{PO}(\text{OH})_2$. *Langmuir* 2002, 18, 8924-8928.
80. Kubo, W.; Kambe, S.; Nakade, S.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S., Photocurrent-determining processes in quasi-solid-state dye-sensitized solar cells using ionic gel electrolytes. *The Journal of Physical Chemistry B* 2003, 107, 4374-4381.
81. Ong, D. Y.; Yip, C. H.; Ng, C. M.; Wong, C. C., Electrolyte-Less Dye-Sensitized Solar Cells (FTO/ TiO_2 /Dye/Metal). *Nanoscience and Nanotechnology Letters* 2011, 3, 186-190.
82. Kuang, D.; Wang, P.; Ito, S.; Zakeeruddin, S. M.; Grätzel, M., Stable mesoscopic dye-sensitized solar cells based on tetracyanoborate ionic liquid electrolyte. *Journal of the American Chemical Society* 2006, 128, 7732-7733.
83. Wang, P.; Wenger, B.; Humphry-Baker, R.; Moser, J.-E.; Teuscher, J.; Kántlehner, W.; Mezger, J.; Stoyanov, E. V.; Zakeeruddin, S. M.; Grätzel, M., Charge separation and efficient light energy conversion in sensitized mesoscopic solar cells based on binary ionic liquids. *Journal of the American Chemical Society* 2005, 127, 6850-6856.

84. Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Graetzel, M., A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells. *The Journal of Physical Chemistry B* 2003, 107, 13280-13285.
85. Kubo, W.; Murakoshi, K.; Kitamura, T.; Yoshida, S.; Haruki, M.; Hanabusa, K.; Shirai, H.; Wada, Y.; Yanagida, S., Quasi-solid-state dye-sensitized TiO₂ solar cells: effective charge transport in mesoporous space filled with gel electrolytes containing iodide and iodine. *The Journal of Physical Chemistry B* 2001, 105, 12809-12815.
86. Kubo, W.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S., Quasi-solid-state dye-sensitized solar cells using room temperature molten salts and a low molecular weight gelator. *Chemical Communications* 2002, 0, 374-375.
87. Wang, P.; Zakeeruddin, S. M.; Grätzel, M., Solidifying liquid electrolytes with fluorine polymer and silica nanoparticles for quasi-solid dye-sensitized solar cells. *Journal of Fluorine Chemistry* 2004, 125, 1241-1245.
88. Papageorgiou, N.; Athanassov, Y.; Armand, M.; Bonhote, P.; Pettersson, H.; Azam, A.; Grätzel, M., The performance and stability of ambient temperature molten salts for solar cell applications. *Journal of the Electrochemical Society* 1996, 143, 3099-3108.
89. Huang, S.; Wang, X.; Wong, C. C., Silica Nanoparticle Gelled Ionic Electrolyte for Dye Sensitized Solar Cells. *Nanoscience and Nanotechnology Letters* 2013, 5, 542-545.
90. Hauch, A.; Georg, A., Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells. *Electrochimica Acta* 2001, 46, 3457-3466.
91. Berginc, M.; Hočevár, M.; Opara Krašovec, U.; Hinsch, A.; Sastrawan, R.; Topič, M., Ionic liquid-based electrolyte solidified with SiO₂ nanoparticles for dye-sensitized solar cells. *Thin Solid Films* 2008, 516, 4645-4650.
92. Michael, G., Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry* 2004, 164, 3-14.
93. Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Gratzel, M., Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. *Nature* 1998, 395, 583-585.
94. Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Nazeeruddin, M. K.; Sekiguchi, T.; Gratzel, M., A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte. *Nature Materials* 2003, 2, 402-407.
95. Wu, J. H.; Hao, S. C.; Lan, Z.; Lin, J. M.; Huang, M. L.; Huang, Y. F.; Fang, L. Q.; Yin, S.; Sato, T., A thermoplastic gel electrolyte for stable quasi-solid-state dye-sensitized solar cells. *Advanced Functional Materials* 2007, 17, 2645-2652.
96. Mulmudi, H. K.; Batabyal, S. K.; Rao, M.; Prabhakar, R. R.; Mathews, N.; Lam, Y. M.; Mhaisalkar, S. G., Solution processed transition metal sulfides: application as counter electrodes in dye sensitized solar cells (DSCs). *Physical Chemistry Chemical Physics* 2011, 13, 19307-19309.
97. Leijtens, T.; Ding, I.-K.; Giovenzana, T.; Bloking, J. T.; McGehee, M. D.; Sellinger, A., Hole transport materials with low glass transition temperatures and high solubility for application in solid-state dye-sensitized solar cells. *ACS Nano* 2012, 6, 1455-1462.

98. Stathatos, E.; Lianos, P.; Lavrencic-Stangar, U.; Orel, B., A high-performance solid-state dye-sensitized photoelectrochemical cell employing a nanocomposite gel electrolyte made by the sol-gel route. *Advanced Materials* 2002, 14, 354-357.
99. Stergiopoulos, T.; Arabatzis, I. M.; Katsaros, G.; Falaras, P., Binary polyethylene oxide/titania solid-state redox electrolyte for highly efficient nanocrystalline TiO₂ photoelectrochemical cells. *Nano Letters* 2002, 2, 1259-1261.
100. Katakabe, T.; Kawano, R.; Watanabe, M., Acceleration of redox diffusion and charge-transfer rates in an ionic liquid with nanoparticle addition. *Electrochemical and Solid-State Letters* 2007, 10, F23-F25.
101. Usui, H.; Matsui, H.; Tanabe, N.; Yanagida, S., Improved dye-sensitized solar cells using ionic nanocomposite gel electrolytes. *Journal of Photochemistry and Photobiology A: Chemistry* 2004, 164, 97-101.
102. Jung, Y.; Son, Y.-H.; Lee, J.-K.; Phuoc, T. X.; Soong, Y.; Chyu, M. k., Rheological behavior of clay-nanoparticle hybrid-added bentonite suspensions: specific role of hybrid additives on the gelation of clay-based fluids. *Applied Materials & Interfaces* 2011, 3, 3515-3522.
103. Lotsch, B. V.; Ozin, G. A., Photonic clays: a new family of functional 1D photonic crystals. *ACS Nano* 2008, 2, 2065-2074.
104. Tu, C.-W.; Liu, K.-Y.; Chien, A.-T.; Yen, M.-H.; Weng, T. H.; Ho, K.-C.; Lin, K.-F., Enhancement of photocurrent of polymer-gelled dye-sensitized solar cell by incorporation of exfoliated montmorillonite nanoplatelets. *Journal of Polymer Science: Part A: Polymer Chemistry* 2008, 46, 47-53.
105. Park, J. H.; Kim, B.-W.; Moon, J. H., Dual functions of clay nanoparticles with high aspect ratio in dye-sensitized solar cells. *Electrochemical and Solid-State Letters* 2008, 11, B171-B173.
106. Tsui, M.-C.; Tung, Y.-L.; Tsai, S.-Y.; Lan, C.-W., A nano quasi-solid electrolyte with modified nano-clay applied to dye-sensitized solar cells. *Journal of Solar Energy Engineering* 2011, 133, 011002.
107. Inoue, T.; Uchida, S.; Kubo, T.; Segawa, H., High performance quasi-solid dye-sensitized solar cells with nano clay electrolyte. *MRS Fall Meeting* 2009.
108. Ghosh, P. K.; Bard, A. J., Clay-modified electrodes. *Journal of the American Chemical Society* 1983, 105, 5691-5693.
109. Fitch, A., Clay-modified electrodes: a review. *Clays and Clay Minerals* 1990, 39, 391-400.
110. Misra, C.; Perrotta, A. J., Composition and properties of synthetic hydrotalcites. *Clays Clay Miner.* 1992, 40, 145-150.
111. Chen, C.-L.; Teng, H.; Lee, Y.-L., In situ gelation of electrolytes for highly efficient gel-state dye-sensitized solar cells. *Advanced Materials* 2011, 23, 4199-4204.
112. Wang, X.; Kulkarni, S. A.; Ito, B. I.; Batabyal, S. K.; Nonomura, K.; Wong, C. C.; Grätzel, M.; Mhaisalkar, S. G.; Uchida, S., Nanoclay gelation approach towards improved dye-sensitized solar cell efficiencies: an investigation of charge transport and shift in TiO₂ conduction band. *ACS Applied Materials & Interfaces* 2013, 5, 444-450.

113. Nogueira, A. F.; Longo, C.; Paoli, M.-A. D., Polymers in dye sensitized solar cells: overview and perspectives. *Coord. Chem. Rev.* 2004, 248, 1455-1468.
114. Kawano, R.; Watanabe, M., Equilibrium potentials and charge transport of an I-/I₃- redox couple in an ionic liquid. *Chemical Communications* 2003, 330-331.
115. Rowley, J. G.; Farnum, B. H.; Ardo, S.; Meyer, G. J., Iodide chemistry in dye-sensitized solar cells: making and breaking I-I bonds for solar energy conversion. *J. Phys. Chem. Lett.* 2010, 1, 3132-3140.
116. Jeon, J.; Kim, H.; Goddard, W. A.; Pascal, T. A.; Ga-In Lee; Kang, J. K., The role of confined water in ionic liquid electrolytes for dye-sensitized solar cells. *J. Phys. Chem. Lett.* 2012, 3, 556-559.
117. Kang, M.-S.; Ahn, K.-S.; Lee, J.-W., Quasi-solid-state dye-sensitized solar cells employing ternary component polymer-gel electrolytes. *J. Power Sources* 2008, 180, 896-901.
118. Nazmutdinova, G.; Sensfuss, S.; Schrodner, M.; Hinsch, A.; Sastrawan, R.; Gerhard, D.; Himmler, S.; Wasserscheid, P., Quasi-solid state polymer electrolytes for dye-sensitized solar cells: effect of electrolyte components variation on the triiodide ion diffusion properties and charge-transfer resistance at platinum electrode. *Solid State Ionics* 2006, 177, 3141-3146.
119. Ghosh, P. K.; Mau, A. W.-H.; Bard, A. J., Clay-modified electrodes: Part II. Electrocatalysis at bis(2,2'-bipyridyl) (4,4'-dicarboxy-2,2'-bipyridyl)Ru(II)-dispersed ruthenium dioxide-hectorite layers. *J. Electroanal. Chem. Interfacial Electrochem.* 1984, 169, 315-317.
120. White, J. R.; Bard, A. J., Clay modified electrodes: Part IV. The electrochemistry and electron spin resonance of methyl viologen incorporated into montmorillonite films. *J. Electroanal. Chem. Interfacial Electrochem.* 1986, 197, 233-244.
121. Furlani, C.; Mattogno, G.; Polzonetti, G.; Barbieri, R.; Rivarola, E.; Silvestri, A., Relationship between XPS core binding energies and atomic charge in adducts of Sn^{IV} derivatives with pyrazine, and comparison with mossbauer isomer shift data. *Inorg. Chim. Acta* 1981, 52, 23-28.
122. Gaarenstroom, S. W.; Winograd, N., Initial and final state effects in the ESCA spectra of cadmium and silver oxides. *J. Chem. Phys.* 1977, 67, 3500-3507.
123. Grätzel, M.; Durran, J. R., Dye-sensitized mesoscopic solar cells. In *Nanostructured and photoelectrochemical systems for solar photon conversion*, Archer, M. D.; Nozik, A. J., Eds. Imperial College Press: London, 2008.
124. Mora-Sero, I.; Bisquert, J., Fermi level of surface states in TiO₂ nanoparticles. *Nano Lett.* 2003, 3, 945-949.
125. Hagberg, D. P.; Jiang, X.; Gabrielsson, E.; Linder, M.; Marinado, T.; Brinck, T.; Hagfeldt, A.; Sun, L., Symmetric and unsymmetric donor functionalization. comparing structural and spectral benefits of chromophores for dye-sensitized solar cells. *J. Mater. Chem.* 2009, 19, 7232-7238.
126. Matar, F.; Ghaddar, T. H.; Walley, K.; DosSantos, T.; Durrant, J. R.; O'Regan, B., A new ruthenium polypyridyl dye. TG6, whose performance in dye-sensitized solar cells is surprisingly close to that of N719, the 'dye to beat' for 17 years. *J. Mater. Chem.* 2008, 18, 4246-4253.
127. Yang, S.-H.; Wu, K.-L.; Chi, Y.; Cheng, Y.-M.; Chou, P.-T., Tris(thiocyanate) ruthenium(II) sensitizers with functionalized dicarboxyterpyridine for dye-sensitized solar cells. *Angew. Chem., Int. Ed.* 50, 8270-8274.

128. Sun, Y.; Onicha, A. C.; Myahkostupov, M.; Castellano, F. N., Viable alternative to N719 for dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* 2010, 2, 2039-2045.
129. Angelis, F. D.; Fantacci, S.; Mosconi, E.; Nazeeruddin, M. K.; Gratzel, M., Absorption spectra and excited state energy levels of the N719 dye on TiO₂ in dye-sensitized solar cell models. *J. Phys. Chem. C* 2011, 115, 8825-8831.
130. Marinado, T.; Hagberg, D. P.; Hedlund, M.; Edvinsson, T.; Johansson, E. M. J.; Boschloo, G.; Rensmo, H.; Brinck, T.; Sun, L.; Hagfeldt, A., Rhodanine dyes for dye-sensitized solar cells: spectroscopy, energy levels and photovoltaic performance. *Physical Chemistry Chemical Physics* 2009, 11, 133-141.
131. Fu, X.; Qutubuddin, S., Polymer-clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer* 2001, 42, 807-813.
132. Wang, X.; Deng, R.; Kulkarni, S. A.; Wang, X.; Pramana, S. S.; Wong, C. C.; Gratzel, M.; Uchida, S.; Mhaisalkar, S. G., Investigation of the role of anions in hydrotalcite for quasi-solid state dye-sensitized solar cells application. *Journal of Materials Chemistry A* 2013, 1, 4345-4351.
133. Saelim, N.-o.; Magaraphan, R.; Sreethawong, T., TiO₂/modified natural clay semiconductor as a potential electrode for natural dye-sensitized solar cell. *Ceramics International* 2011, 37, 659-663.
134. Jennings, J. R.; Wang, Q., Influence of lithium ion concentration on electron injection, transport, and recombination in dye-sensitized solar cells. *The Journal of Physical Chemistry C* 2010, 114, 1715-1724.