MODIFICATION OF THE INTERFACE BETWEEN TiO2 AND ELECTROLYTE TOWARD HIGHER EFFICIENCY DYE SENSITIZED SOLAR CELLS

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Abstract

The objective of this thesis is to improve the photovoltaic performance of Dye-Sensitized Solar Cells (DSSCs) by modifying the interface between TiO₂ 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 TiO₂ surface through surface treatment and molecular passivation and an indirect modification to alter the TiO₂ 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 TiO₂ photoanode through surface treatment using a novel, simple, safe and effective TiF₄ hydrolysis treatment instead of the conventional TiCl₄ 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 (C₁₈H₃₇SiX₃, X is H, OCH₃ or Cl) on sensitized TiO₂ 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 TiO₂ 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. Unlike previous generations, over the past twenty years, the efficiency increased to over 11% with 1 cm$^2$ in area, because of the advancing nanotechnology.

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 TiO$_2$-electrolyte interface in liquid electrolyte cells for a better understanding of DSSCs. The study of TiO$_2$-electrolyte interfacial phenomena are scrutinized either by direct modifying TiO$_2$ via surface treatment and molecular passivation or indirect altering the TiO$_2$ 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 TiO$_2$ surface using TiF$_4$ 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. 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.

2.1.1 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

\[ \eta = \frac{P_{out}}{P_{in}} \times 100 = \frac{P_{max}}{E_{tot} A_{tot}} \times 100 = \frac{I_{sc} V_{oc} FF}{E_{tot}} \times 100 = \frac{I_{sc} V_{oc} FF}{E_{tot}} \times 100 \]  

(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
\[ \eta = J_{sc} \times V_{oc} \times FF \]  \hspace{1cm} (2)

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

The fill factor is defined in equation (3).

\[ FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}} = \frac{A_1}{A_2} \]  \hspace{1cm} (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.
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 follows:\(^3\):

\[
\begin{align*}
S^0 + h\nu & \rightarrow S^+ \quad \text{Photo-excitation} \quad (4) \\
S^+ & \rightarrow S^+ + e^- (TiO_2) \quad \text{Electron Injection} \quad (5) \\
2S^+ + 3I^- & \rightarrow 2S^0 + I_3^- \quad \text{Regeneration} \quad (6) \\
I_3^- + 2e^- & \rightarrow 3I^- \quad \text{Redox Reaction} \quad (7)
\end{align*}
\]
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 photosensitive 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.\textsuperscript{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.\textsuperscript{5} The regeneration of oxidized dye is at a time scale of nanoseconds.\textsuperscript{6, 7} The redox reaction is carried out at the counter electrode at a time scale of microseconds.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{11} Not inferior to it, arylamine organic dyes have also demonstrated high efficiency of over 10.3\%.\textsuperscript{9,12}

![Energy diagram for a DSSC](image)

**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.\textsuperscript{1,13} Simply from the semiconductor point of view, TiO\textsubscript{2} is not the ideal material for electron transport. Based on the arising concerns, many other metal oxide materials have been examined e.g. SnO\textsubscript{2}, ZnO\textsubscript{2}, and Nb\textsubscript{2}O\textsubscript{5} or even mixed metal oxides like ZnO/SnO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}/SnO\textsubscript{2}, SnO\textsubscript{2}/CeO\textsubscript{2}, and MgO/SnO\textsubscript{2}.\textsuperscript{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.\textsuperscript{14} The injection efficiency for metal oxides was reported as TiO$_2$ > Nb$_2$O$_5$ > SnO$_2$ ~ZnO.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 SCN$^-$/SCN$_3^-$ and SeCN$^-$/Se(CN)$_3^-$ were reported to be very promising options to replace iodide/triiodide against corrosion.\textsuperscript{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,N2-diphenylbenzidine) were applied and showed good performance.\textsuperscript{4, 20} Recently transition metal complexes such as cobalt complexes and nickel complexes were also investigated.\textsuperscript{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.\textsuperscript{25, 26} According to previous studies, higher donor number resulted in higher Voc but lower $J_{sc}$.\textsuperscript{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).\textsuperscript{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).\textsuperscript{25, 33}

\begin{equation}
\text{Solvent} + I_3^- \leftrightarrow \text{Solvent} \ldots I_2 + I^- \tag{8}
\end{equation}

\begin{equation}
V_{OC} = \frac{kT}{e} \ln \frac{I_{inj}}{n_{cb} k_{et} [I_3^-]} \tag{9}
\end{equation}

\begin{equation}
V_{OC} = |V_{fb} - V_{red}| \tag{10}
\end{equation}

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.\textsuperscript{34} They are nonvolatile therefore results less toxicity compared with organic electrolyte and have good solubility for most of organic or inorganic ingredients.\textsuperscript{35} In the system using $I^-/I_3^-$ as redox couple,\textsuperscript{1} 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,\textsuperscript{36} Therefore it is commonly selected as the key component in
most of the ionic electrolyte mixture. 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. Later The eutectic mixtures of imidazolium iodide salts and tetracyanoborate salts have been proven to be a successful solvent. 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. 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). However, the major disadvantage of ionic liquid electrolyte compared with organic electrolytes is their high viscosity which leads poorer diffusion of redox couple.

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. 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 TiO₂ recombine with the oxidized dye before dye regeneration (equation (12)). The triiodide ions attack the TiO₂ surface and consume the injected electrons in TiO₂ (equation (13)). Similarly, the triiodide ions attack the TCO surface and consume the injected electrons in TCO glass (equation (14)).

\[
\begin{align*}
S^* & \rightarrow S^0 + h\nu \quad (11) \\
e^- (TiO_2) + S^+ & \rightarrow S \quad (12) \\
2e^-_{TiO_2} + I_3^- & \rightarrow 3I^- \quad (13) \\
2e^-_{TCO} + I_3^- & \rightarrow 3I^- \quad (14)
\end{align*}
\]

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 TiO₂ system. 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 TiO₂ entirely. As long as there is naked TiO₂ exposed to electrolyte, the tri-iodide could recapture the injected electron, causing the current leakage.
2.3 Studies of the TiO$_2$-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, TiO$_2$ nanoparticle photoanode still holds the record for the highest power conversion efficiency.\textsuperscript{11} Instead of changing each component, because of dark reactions, modification of TiO$_2$-electrolyte interface is essential for existing design of the liquid DSSCs based on TiO$_2$. There are various ways discussed in seeking improvement in photovoltaic performance though TiO$_2$-electrolyte interface modification and these can be summarized into two major methods. One is through covering the TiO$_2$ surface directly, such as using surface treatment, a secondary thin blocking layer and co-adsorbers.\textsuperscript{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 TiO$_2$ surface.\textsuperscript{50, 51}

2.3.1 Modification through Direct Covering of TiO$_2$

Being one of the key ways of direct modification of TiO$_2$, a surface treatment step is believed to be necessary because after high temperature autoclave, normally the surface of TiO$_2$ has been damaged. Anodic electrodeposition of new TiO$_2$ on existing nanocrystalline photoanode by TiCl$_3$ was developed.\textsuperscript{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.\textsuperscript{52} There are also some other surface modification methods using TiO$_2$ precursors such as titanium isopropoxide and titanium butoxide.\textsuperscript{47, 53} So far the most common surface modification method is growing new TiO$_2$ layers through solution treatment of titanium tetrachloride.\textsuperscript{52} The major influence on device performance by TiCl$_4$ 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 TiCl₄ concerning improved electron transport, recombination, TiO₂ 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-TiO₂ 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 TiO₂ surface from interface recombination. Examples are 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 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 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 result, 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. demonstrated an effective TiO₂ 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.\textsuperscript{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.\textsuperscript{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 Voc.\textsuperscript{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 Voc. 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\%.\textsuperscript{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$_2$.\textsuperscript{67}
2.3.3 Characterization of TiO$_2$-Electrolyte Interface

To investigate the properties of TiO$_2$-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 $\omega$. 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.$^{68}$

\[
E_t = |E| \sin(\omega t)
\]

\[
l_t = |I| \sin(\omega t + \theta)
\]

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

Where $E_t$ is potential at time $t$, $|E|$ is its amplitude, $I_t$ is response at time $t$, $|I|$ is its amplitude, $\theta$ is phase, $Z_\omega$ is impedance and $|Z|$ is its amplitude.

The impedance $Z_\omega$ 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).

$$Z_\omega = Z' + jZ''$$

$$\text{Re}(Z) \equiv Z' = |Z| \cos(\theta)$$

$$\text{Im}(Z) \equiv Z'' = |Z| \sin(\theta)$$

$$\theta = \tan^{-1}(Z''/Z')$$

$$|Z| = \sqrt{(Z')^2 + (Z'')^2}$$

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. Different equivalent circuits based on transmission line approach are used to analyze different practical issues.
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.
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).\(^8\)

\[
E_F = E_c + kT \ln \left( \frac{n_e}{N_c} \right) \tag{17}
\]

where $E_F$ is the Fermi energy, $E_c$ is the conduction band energy, $kT$ is the thermal energy, $n_e$ 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.\textsuperscript{70}

\[
\frac{1}{C^2} = \frac{2}{\epsilon \varepsilon_0 A^2 e N_D} \left( E - E_{fb} - \frac{k_B T}{e} \right)
\]

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](image)

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>
<thead>
<tr>
<th>Short Names</th>
<th>Formulas</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>N719</td>
<td>[RuL2(NCS)2]: 2 TBA (L=2,2’-bipyridyl-4,4’-dicarboxylic acid; TBA=tetra-n-butylammonium)</td>
<td>0.3 mM in acetonitrile: tert-butanol (1:1 v:v)</td>
</tr>
<tr>
<td>Z907</td>
<td>RuLL’(NCS)2 (L=2,2’-bipyridyl-4,4’-dicarboxylic acid; L’=4,4’-dinonyl-2,2’-bipyridine)</td>
<td>0.3 mM in acetonitrile: tert-butanol (1:1 v:v)</td>
</tr>
<tr>
<td>N749</td>
<td>[RuL(NCS)3]: 3 TBA (L=2,2’:6’,2”-terpyridyl-4,4’,4”-tricarboxylic acid; TBA=tetra-n-butylammonium)</td>
<td>0.3 mM in acetonitrile: tert-butanol (1:1 v:v)</td>
</tr>
<tr>
<td>D35</td>
<td>(E)-3-(5-(4-(Bis(20,40-dibutoxybiphenyl-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid</td>
<td>0.2 mM in ethanol</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Short Names</th>
<th>Composition</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL-HPE</td>
<td>N.A. It was used as purchased</td>
<td></td>
</tr>
<tr>
<td>EL-I</td>
<td>0.1 M GuNCS + 0.2 M I$_2$ + 0.5 M MBI in 65v% PMII + 35 v% EMITCB</td>
<td></td>
</tr>
<tr>
<td>EL-AN</td>
<td>1 M PMII + 0.1 M LiTFSI +0.1 M I$_2$ + 0.5 M MBI Acetonitrile</td>
<td></td>
</tr>
<tr>
<td>EL-MPN</td>
<td>1 M PMII + 0.1 M LiTFSI +0.1 M I$_2$ + 0.5 M MBI Methoxypropionitrile</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Chemical abbreviations and names

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Chemical Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMII</td>
<td>1-methyl-3-propylimidazolium iodide</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>lithium bis(trifluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>MBI</td>
<td>1-methylbenzimidazole</td>
</tr>
<tr>
<td>GuNCS</td>
<td>guanidine thiocyanate</td>
</tr>
<tr>
<td>EMITCB</td>
<td>1-ethyl-3methylimidazolium tetracyborate</td>
</tr>
</tbody>
</table>

3.1.3 Synthesis of Hydrotalcites

The hydrotalcites are synthesized as inorganic additives of electrolyte, and these hydrotalcites are important in modifying the TiO$_2$-electrolyte interface (discussed in detail in Chapter 7). The hydrotalcite compounds can be generalized in the formula of \([M^{2+} \cdot xM^{3+} (OH)_2][A^{n-} x/nzH_2O]\), 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 M$^{3+}$ over the total number of cations. A co-precipitation method was used to synthesize the nitrate/carbonate/sulfate containing Mg-Al hydrotalcite. 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.

![Flow chart of synthesis process.](image)

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 TiO₂) was normally prepared by TiX₄ (X = F or Cl) bath treatment at 70 ºC 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 TiO₂ Photoanode Layer

There were two types of paste applied to fabricate TiO₂ 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 TiO₂ 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 ºC for 6 minutes. The scattering paste was applied secondly and followed by drying again. The obtained film was finally sintered at 500 ºC for 30 minutes.

For screen print method: The nanocrystalline TiO₂ 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 ºC for 5 minutes, 375 ºC for 5 minutes, 450 ºC for 15 minutes and 500 ºC for 15 minutes.
Subsequently, the cooled films were treated again with TiX₄ (X = 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 TiO₂ 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.
3.3 Characterization

The J-V characteristics of the fabricated DSSCs were measured under an illumination with AM 1.5 (100 mW/cm²) 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 μm 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.
Surface modification of TiO₂ 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 TiO₂ is damaged. This chapter discusses the direct surface modification of TiO₂ photoanode through a simple TiF₄ hydrolysis treatment. The effect of TiF₄ concentration is studied, and 20mM TiF₄ treatment shows the best photo conversion efficiency of 6.1% with enhancement around 22% compared to standard TiCl₄ treated reference device. The IPCE spectrum shows that TiF₄ treatment helps improve efficiency gain in visible range. Besides the enhanced surface area induced larger amount the dye loading, EIS analysis shows that 20mM TiF₄ treated DSSCs show less recombination compared with standard TiCl₄ treated DSSCs. The reduced recombination of TiF₄ treated devices is believed to be due to fluorine passivation of the TiO₂ surface.

4.1 Introduction

As the performance of DSSCs strongly depends on TiO₂/dye/electrolyte interfaces, plenty of research work has attempted to modify the surface of TiO₂ to achieve higher efficiency. Anodic electrodepositing of new TiO₂ on existing nanocrystalline photoanode by TiCl₃ was developed. Later on it was displaced by TiCl₄ solution treatment as the results were similar and TiCl₄ treatment process was much easier in handling. There are also some other surface modification methods using TiO₂ precursors, such titanium isopropoxide and titanium butoxide. So far the most commonly used surface modification method is growing new TiO₂ layers through solution treatment of titanium tetrachloride.
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.\(^7\) 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.\(^7\) 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.

\[
\text{Absorption} = \epsilon \cdot [C] \cdot L
\]
Where $\varepsilon$ 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.

![Conversion Efficiency Graph](image_url)

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.

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

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 TiF₄ treatment and 40 mM TiCl₄ treatment as a standard. To simplify, they are called TiF₄ treatment and TiCl₄ treatment. Compared to the optimized treatment condition of TiCl₄ the surface treatment process made of optimized TiF₄ bath solution gives higher Jsc and better Voc in DSSCs as shown in Figure 12. From the dark condition, the TiF₄ devices has higher threshold of dark voltage than TiCl₄ devices.

![Figure 12 Comparison of photocurrent to photovoltage characteristics under illumination (solid symbols) and under dark condition (open symbols) of 20 mM TiF₄ (Red) treated and 40 mM TiCl₄ (Blue) treated DSSCs.](image)

The enhanced photocurrent can be further explained by their IPCE behavior shown in Figure 13. Compared with TiCl₄ devices, TiF₄ 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 Φ₉₉, which depends on absorption properties of dye, 2) injection efficiency Φᵢᵦ, which measures the yield of injection of excited electrons into TiO₂, and 3) charge collection efficiency Φᵦ₉.
which is mostly affected by the properties of TiO₂ photoanode. These three factors are the major components for understanding the effect the surface treatment process.

The $\Phi_{\text{LH}}$ 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 TiCl₄ and TiF₄ during surface treatment process. Compared with the TiCl₄ treated devices, the size of newly grown particles after TiF₄ treatment are much larger (3-4 nm in size) and much denser. Compared with bare TiO₂ nanoparticles, the BET surface area of TiF₄ treated devices has increased by about 10% from 50.3 to 55.5 m²/g and the amount of dye loading has increased from 7.9 to 8.4 (x10⁻⁸) mol cm⁻², which is about 5%. With only 5% increment in adsorbed dye, the performance of

![Figure 13 Comparison of IPCE of TiF₄ devices and TiCl₄ devices.](image)
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 $\Phi_{\text{Inj}}$ because of surface treatment by conventional TiCl$_4$ has been discussed in detail by Sommeling et al..$^{75}$ The $\Phi_{\text{Inj}}$ 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 $\Phi_{\text{Inj}}$ 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 $\Phi_{\text{Inj}}$.

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 $\Phi_{\text{Inj}}$. Thus the gain of IPCE could come from the improved $\Phi_{\text{CC}}$ which means better transport or less recombination in the devices.

![Figure 15](image)

Figure 15 (a) Flat band potential of different planner TiO$_2$ prepared by atomic layer deposition (b) Mott-Schottky curves.

From the cyclic voltammetry curves in Figure 16, we observed a higher $J_{\text{lim}}$ (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 TiCl₄ device and TiF₄ device. As shown in Figure 17, the measured recombination resistance (at dark condition by EIS) of TiF₄ device is larger than TiCl₄ 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 TiCl₄ device and TiF₄ device under bias equivalent to their Voc. The change in surface chemistry of TiO₂ after treatment could help us understand the change in recombination. After surface treatment of TiCl₄ and annealing, we found existence of chlorine ions on the surface of TiO₂ 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$_4$.](image)

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.
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 21 shows the results of DSSCs with TiF₄ and TiCl₄ treatment under different photoanode thickness. For thinner photoanode (less than 10 um), devices treated with TiF₄ performed better than that treated with TiCl₄. It suggests that TiF₄ 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 um), the performance of both surface treatment processes are similar. One possible reason of this is that after TiF₄ treatment the thick films sacrifice some of its mechanical stability.

![Graph showing device performance with different TiO₂ photoanode film thicknesses.](image)

**Figure 21** Device performance with different TiO₂ photoanode film thicknesses.

### 4.4 Conclusion

For the first time, a simple and effective chemical treatment via TiF₄ hydrolysis is introduced to improve the device performance in DSSCs. The efficiency is enhanced by 22% by 20 mM TiF₄ treatment compared with reference device treated by standard TiCl₄ 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.

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
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. Another method is conducted by molecular interface engineering. 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. 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. 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.

<table>
<thead>
<tr>
<th>Surface Modifying Agents</th>
<th>SAMs (C_{18}H_{37}SiX_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM A</td>
<td>C_{18}H_{37}SiH_3</td>
</tr>
<tr>
<td>SAM B</td>
<td>C_{18}H_{37}Si(OC_3)H_3</td>
</tr>
<tr>
<td>SAM C</td>
<td>C_{18}H_{37}SiCl_3</td>
</tr>
</tbody>
</table>

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 cm². 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.\textsuperscript{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$_2$-stetching is similar to a liquid alkane ($\nu_a$ is around 2924 cm$^{-1}$) for randomly attached structures, while the frequency is close to a crystal alkane ($\nu_a$ is approximate from 2915-2918 cm$^{-1}$) for well parked SAMs.\textsuperscript{79} Our results indicate that SAMs (the tree types of octadecylsilanes) with well ordered structures is comparable to the reported values.
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 TiO$_2$ film was first soaked in SAMs solution overnight and then transferred to Z907 dye solution for overnight sensitization. Whereas in the second process, the TiO$_2$ 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 TiO$_2$ before dye soaking. The decrease of the color intensity of the TiO$_2$ film was also observed, which is assumed to be the result of the SAMs covering most of the TiO$_2$ surface and leaving little room for dye attachment or the strong steric effect created by SAMs layers preventing the dye to approach the TiO$_2$ surface. Thus loading SAMs after dye was more effective since the SAMs molecules are easy to be adsorbed onto the TiO$_2$ surface without hindering the sensitization of dye molecules. The SAM passivated sensitized TiO$_2$ 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 TiO$_2$ film. This eliminates the possibility that SAM molecules react with dye molecules.$^{58}$

Table 6 Observed major IR vibrations for the SAMs grafted on TiO$_2$.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Peak Frequency (cm$^{-1}$) in the samples prepared from</th>
<th>SAM A C$<em>{18}$H$</em>{37}$SiH$_3$</th>
<th>SAM B C$<em>{18}$H$</em>{37}$Si(OCH$_3$)$_3$</th>
<th>SAM C C$<em>{18}$H$</em>{37}$SiCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H $\nu$(CH$_2$)</td>
<td>2918</td>
<td>2919</td>
<td>2911</td>
<td></td>
</tr>
<tr>
<td>C-H $\nu$(CH$_2$)</td>
<td>2851</td>
<td>2851</td>
<td>2845</td>
<td></td>
</tr>
<tr>
<td>Si-O $\nu$(Si-O)</td>
<td>1103</td>
<td>1102</td>
<td>1106</td>
<td></td>
</tr>
</tbody>
</table>

Figure 23 Schematic illustration of octadecylsilane assembly on the naked TiO$_2$ 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 ($\eta$) 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 TiO$_2$ surface, a decrease in both $V_{oc}$ and $J_{sc}$ was observed, which is probably induced by some dye molecules.
desorbing from the TiO\textsubscript{2} 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 TiO\textsubscript{2} photoanode stained with different types of SAMs (octadecylsilanes).

<table>
<thead>
<tr>
<th>Devices</th>
<th>SAMs (0.3M in toluene)</th>
<th>J\textsubscript{sc} (mA/cm\textsuperscript{2})</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Without SAMs</td>
<td>6.5</td>
<td>0.69</td>
<td>72</td>
<td>3.2</td>
</tr>
<tr>
<td>A</td>
<td>SAM A</td>
<td>7.7</td>
<td>0.71</td>
<td>71</td>
<td>3.9</td>
</tr>
<tr>
<td>B</td>
<td>SAM B</td>
<td>7.6</td>
<td>0.70</td>
<td>67</td>
<td>3.6</td>
</tr>
<tr>
<td>C</td>
<td>SAM C</td>
<td>5.4</td>
<td>0.67</td>
<td>72</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Since the objective of using SAMs is to modify the TiO\textsubscript{2}-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 Voc under dark condition under 50w halogen lamp (100 mW/cm\textsuperscript{2}) illumination. The recombination resistances measured are listed in Table 8. The results showed that the SAM A passivation on sensitized TiO\textsubscript{2} film was more effective in retarding charge recombination at the TiO\textsubscript{2}-electrolyte. The SAM passivation may not only produce the effect of surface shielding but also change the energetics of TiO\textsubscript{2}. Without hindering the solar harvesting by dye, SAM A passivation reduces the interfacial current loss, thereby resulting in better current collection or better J\textsubscript{sc} than non treated devices.
Table 8 Recombination resistance Rk at TiO2-electrolyte interface determined by EIS measurements.

<table>
<thead>
<tr>
<th>Device</th>
<th>SAMs</th>
<th>Rk (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Without SAM</td>
<td>37.2</td>
</tr>
<tr>
<td>A</td>
<td>SAM A</td>
<td>156.9</td>
</tr>
<tr>
<td>C</td>
<td>SAM C</td>
<td>25.9</td>
</tr>
</tbody>
</table>

5.3.2 Head Group Effect of SAMs

In order to be a good electron barrier layer to modify the TiO2-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 TiO2 photoanode with/without SAMs treatment are shown in Figure 24. Compared to sensitized TiO2 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 Jsc 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.](image)

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) $\rho$ of the SAMs can be calculated using the following equation\textsuperscript{79}:

$$\rho = \frac{6 \times 10^5 \times \%C}{1200 \pi n_c - MV \times \%C} \times \frac{1}{S_{BET}}$$  \hspace{1cm} (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. 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. 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 TiO₂ 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 TiO₂ like C₁₈H₃₇SiCl₃ and the SAMs having smaller head group like C₁₈H₃₇SiH₃ with slower rate constant (reacting with TiO₂) could provide closely packed screening layer.
Chapter 6  Quasi-Solid Electrolyte using Silica Gelator

In the previous chapters, modification of TiO₂ was conducted by fluorine passivation and SAM modification. In the following two chapters, modification of TiO₂ 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 TiO₂ (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 TiO₂ 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 TiO₂-based improvement with quasi-solid or solid state electrolytes is worth investigation. The following part of this thesis attempts to modify the TiO₂-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. However, the high viscosity of ionic liquids, about 100 times higher than that of acetonitrile, limits the overall power conversion efficiency. 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. 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.

It was found that DSSCs with ionic liquid electrolyte and silica-gelled electrolyte demonstrated comparable power conversion efficiencies. 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. 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. 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).\(^{44}\)

\[
V_c = \left[ \frac{4\pi \Delta \rho R^4}{3kT} \right]^{\frac{3-d_f}{1+d_f}}
\]  

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).\textsuperscript{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.\textsuperscript{89}

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ (Ω)</th>
<th>$C_1$ (F)</th>
<th>$R_{ct}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0wt%</td>
<td>19.49</td>
<td>$5.80\times 10^{-6}$</td>
<td>0.562</td>
</tr>
<tr>
<td>15wt%</td>
<td>17.06</td>
<td>$1.2132\times 10^{-5}$</td>
<td>0.2784</td>
</tr>
<tr>
<td>% difference</td>
<td>12.5</td>
<td>109.1</td>
<td>50.5</td>
</tr>
</tbody>
</table>
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 $\Gamma$/$I_3^-$ ions adjacent to the counter electrode, as illustrated in Figure 26.

![Figure 26 Illustration of adsorption of silica nanoparticles onto counter electrode.](image)

It was proposed that for the $\Gamma$/$I_3^-$ redox reaction happening at the counter electrode, adsorption of $\Gamma$ ions to the electrode surface occurs. With increased $\Gamma$ concentration adjacent to the counter electrode, it is much easier for $\Gamma$ 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%.
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, 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).
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 $\Gamma/\Gamma_3^-$ ions near the TiO$_2$ mesoporous film, which suppress the recombination at the TiO$_2$-electrolyte interface.\textsuperscript{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 above\textsuperscript{30} 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.\textsuperscript{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 Rct, 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).](image)

### 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 $\Gamma/I_3^-$ 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 [PMII]: [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 Voc. Higher Voc 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.\cite{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.\cite{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.\cite{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.\cite{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.\cite{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 %.\cite{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.\textsuperscript{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.\textsuperscript{104} Later, Park et al. deduced the unexpected benefits of clay gel electrolyte because of the light scattering capability of laponite clay.\textsuperscript{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.\textsuperscript{106} Inoue et al. showed high cell performance of 10.3% for clay gelled electrolyte, which is equivalent in performance with liquid electrolyte cells.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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, \textit{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 anions\textsuperscript{110}) 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 I\textsubscript{2} + 0.5 M MBI in acetonitrile) and EL-MPN (1 M PMII + 0.1 M LiTFSI +0.1 M I\textsubscript{2} + 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 Voc. The thickness of the photoanode is 18 µm 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 µm 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), SiO$_2$$\cdot$3.22Na$_2$O (15.45g in 25ml DI water) solution. After mixing the solution together homogeneously, 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-hydrotalcite 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.\textsuperscript{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-hydrotalcite content (wt %) in acetonitrile based liquid electrolyte under one sun illumination; inset shows the photographs of liquid and nanoclay gel electrolyte.
7.1.3.2 Optimization of the Thickness of TiO₂ Photoanode

The nitrate-hydrotalcite 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 TiO₂-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.

<table>
<thead>
<tr>
<th>Photoanode Thickness (μm)</th>
<th>PCE (%)</th>
<th>JSC (mA/cm²)</th>
<th>VOC (mV)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>7.9</td>
<td>13.4</td>
<td>861</td>
<td>0.68</td>
</tr>
<tr>
<td>16</td>
<td>8.5</td>
<td>15.9</td>
<td>850</td>
<td>0.63</td>
</tr>
<tr>
<td>18</td>
<td>9.6</td>
<td>15.2</td>
<td>846</td>
<td>0.75</td>
</tr>
<tr>
<td>20</td>
<td>8.7</td>
<td>14.9</td>
<td>816</td>
<td>0.72</td>
</tr>
</tbody>
</table>

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
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 Voc.

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.\(^{112}\)

<table>
<thead>
<tr>
<th>Solar Cells(^a)</th>
<th>PCE (%)</th>
<th>$J_{SC}$ (mA/cm(^2))</th>
<th>$V_{OC}$ (mV)</th>
<th>FF</th>
<th>$\Delta$PCE(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-MPN</td>
<td>7.0</td>
<td>15.2</td>
<td>741</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>G-MPN</td>
<td>7.9</td>
<td>15.4</td>
<td>843</td>
<td>0.61</td>
<td>13%</td>
</tr>
<tr>
<td>L-AN</td>
<td>8.8</td>
<td>15.3</td>
<td>786</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>G-AN</td>
<td>9.6</td>
<td>15.1</td>
<td>846</td>
<td>0.75</td>
<td>9%</td>
</tr>
</tbody>
</table>

\(^a\)Data are obtained with photoanode 5+2 layers;  
\(^b\)Calculated 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).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>PCE (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-N</td>
<td>7.9</td>
<td>13.4</td>
<td>861</td>
<td>0.68</td>
</tr>
<tr>
<td>C-S</td>
<td>6.9</td>
<td>11.7</td>
<td>794</td>
<td>0.74</td>
</tr>
<tr>
<td>C-C</td>
<td>6.5</td>
<td>10.7</td>
<td>810</td>
<td>0.72</td>
</tr>
<tr>
<td>Liquid</td>
<td>7.2</td>
<td>13.0</td>
<td>820</td>
<td>0.67</td>
</tr>
</tbody>
</table>

aData 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 Grotthus type or exchange-reaction process $\Gamma + I_3^- \rightarrow I_3^- + \Gamma$ may also assist the current flow.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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).\textsuperscript{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 ($I_{\text{lim}}$) in cyclic voltammograms, corresponding to the reaction $I_3^- + 2e^- = 3I^-$, is given by\textsuperscript{114}
where \( D \) is diffusion coefficient of redox species, \( r \) is the microdisk electrode radius, and \( c \) is the total concentration of the redox species (\( 1/3 \left[ \Gamma \right] + \left[ \text{I}_3^- \right] \)). If physical diffusion and Grotthus mechanism are conjugated, then

\[
D = D_{\text{phys}} + D_{\text{ex}}
\]

\[
= D_{\text{phys}} + \frac{1}{6} k_{\text{ex}} \delta^2 c
\]

(23)

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

\[
I_{\text{lim}} = 8Fr \left( D_{\text{phys}} c + \frac{1}{6} k_{\text{ex}} \delta^2 c^2 \right)
\]

(24)

Consequently, according to equation (24), 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 \([\text{PMII}]: [\text{I}_2] = 10:1\), 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 \([\text{PMII}]: [\text{I}_2] = 10:1\). Furthermore, the calculated physical diffusion coefficient of \( \text{I}_3^- \) 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 \( D_{\text{I}_3^-} \) in
nanoclay gel is slightly smaller than that in liquid, it does not result in major deficiency in photocurrent collection.

![Graph showing limiting currents and diffusion coefficients](image)

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.\textsuperscript{112}

The clay powder extracted from the nitrate-hydrotalcite gel was checked using XPS. The two peaks found (Figure 36) correspond to iodide ions.\textsuperscript{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-hydrotalcite particles (Figure 36). In addition, the presence of iodide was not found in a reference carbonate-hydrotalcite 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 affinity$^{71}$ 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$_2$.]({figure36.png})

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$_2$.}$^{112}$
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 TiO$_2$ 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).](image)

$3I^- - 2e^- \rightarrow I_3^-$

$I_3^- + 2e^- \rightarrow 3I^-$

$3I^- - 2e^- \rightarrow I_3^-$

$G-B$

$L-B$

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-hydrotalcite. 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.\textsuperscript{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.\textsuperscript{62, 123, 124} However, in DSSCs, the nanoparticles used are too small to support a significant band bending.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 -0.77 eV$^{127}$ vs. NHE respectively. The Fermi level of TiO$_2$ is at -0.4eV $\sim$ -0.5eV$^{128,129}$. 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 ~0.3eV required for effective injection.$^{130}$

Table 13 Performance comparison of gel and liquid electrolyte with D35 and N749 dyes.$^{112}$

<table>
<thead>
<tr>
<th>Solar Cells$^d$</th>
<th>PCE (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF</th>
<th>$\Delta$PCE$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-D35</td>
<td>5.9</td>
<td>11.9</td>
<td>712</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>G-D35</td>
<td>6.5</td>
<td>11.7</td>
<td>769</td>
<td>0.72</td>
<td>10%</td>
</tr>
<tr>
<td>L-N749</td>
<td>7.0</td>
<td>11.4</td>
<td>697</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>G-N749</td>
<td>5.6</td>
<td>10.1</td>
<td>768</td>
<td>0.73</td>
<td>-20%</td>
</tr>
</tbody>
</table>

$^d$Data 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-hydrotalcite acts like base which can shift up the conduction band of TiO₂, 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 (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-hydrotalcite 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 TiO₂ 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-hydrotalcite gel with no additional modification.\textsuperscript{112}

<table>
<thead>
<tr>
<th>Solar Cells\textsuperscript{a}</th>
<th>PCE (%)</th>
<th>J Sc (mA/cm²)</th>
<th>V Oc (mV)</th>
<th>FF</th>
<th>Dye\textsuperscript{b}(x10⁻⁸ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-NaOH</td>
<td>6.4</td>
<td>12.5</td>
<td>767</td>
<td>0.67</td>
<td>4.0</td>
</tr>
<tr>
<td>L-Nil</td>
<td>7.8</td>
<td>14.6</td>
<td>733</td>
<td>0.73</td>
<td>3.9</td>
</tr>
<tr>
<td>G-Nil</td>
<td>8.4</td>
<td>14.3</td>
<td>830</td>
<td>0.71</td>
<td>4.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Data are obtained with photoanode 4+1 layers; \textsuperscript{b}Measured in 0.1 M NaOH in water+ethanol (1:1 v:v)

A further investigation on mechanism of hydrotalcite shifting the conduction band of TiO₂ 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. 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.\textsuperscript{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.\textsuperscript{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\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-} and SO\textsubscript{4}\textsuperscript{2-} respectively as examples) on the capability of gel formation, the chemical interaction with electrolyte and the characteristics of devices. The anions (NO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-} and SO\textsubscript{4}\textsuperscript{2-}) were selected based on their well-known difference in ion exchange capacity (NO\textsubscript{3}\textsuperscript{-}<SO\textsubscript{4}\textsubscript{2-}<CO\textsubscript{3}\textsuperscript{2-}).\textsuperscript{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\textsubscript{2} and the other contains LiI. For convenience hydrotalcite with exchangeable anions NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsubscript{2-} and CO\textsubscript{3}\textsuperscript{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 0.28cm². 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 - 105 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 Ka (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 10μm 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 CO$_3^{2-}$ [71]. In addition, as shown in Figure 43, strong electrostatic attraction between CO$_3^{2-}$ 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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 I2 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 3d5/2, 619 eV 3d3/2) 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 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.\textsuperscript{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 + 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).\textsuperscript{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>
<thead>
<tr>
<th>Nitrate HT</th>
<th>d (Å)</th>
<th>Sulfate HT</th>
<th>d (Å)</th>
<th>Carbonate HT</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL-N</td>
<td>23.7</td>
<td>CL-S</td>
<td>23.6</td>
<td>CL-C</td>
<td>23.4</td>
</tr>
<tr>
<td>CL-N-I</td>
<td>23.7</td>
<td>CL-S-I</td>
<td>23.6</td>
<td>CL-C-I</td>
<td>23.4</td>
</tr>
<tr>
<td>CL-N-Li</td>
<td>25.3</td>
<td>CL-S-Li</td>
<td>25.2</td>
<td>CL-C-Li</td>
<td>25.1</td>
</tr>
</tbody>
</table>

*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 Voc over the liquid cells (denoted as Liq). Specifically, the observed trend in Voc is in the order of G-C > G-S > G-N > Liq, while the observed trend in Jsc 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 $J_{sc}$ among the gel devices (the $J_{sc}$ is comparable to that with Liq). The enhancement by 8% in PCE compared to the liquid cell benefited mainly from the enchantment 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 $J_{sc}$.

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

<table>
<thead>
<tr>
<th>Solar cells$^a$</th>
<th>PCE (%)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>$D_{13}$ $(10^{-6} \text{cm}^2/\text{s})^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-N</td>
<td>8.4</td>
<td>14.3</td>
<td>830</td>
<td>0.71</td>
<td>4.0</td>
</tr>
<tr>
<td>G-S</td>
<td>7.4</td>
<td>11.9</td>
<td>835</td>
<td>0.74</td>
<td>3.1</td>
</tr>
<tr>
<td>G-C</td>
<td>6.6</td>
<td>10.2</td>
<td>846</td>
<td>0.77</td>
<td>3.2</td>
</tr>
<tr>
<td>Liq</td>
<td>7.8</td>
<td>14.6</td>
<td>753</td>
<td>0.71</td>
<td>4.4</td>
</tr>
</tbody>
</table>

$^a$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 TiO$_2$ 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 TiO$_2$, 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 TiO$_2$ 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 nitrate 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.
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.\textsuperscript{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.\textsuperscript{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 Jsc 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 ~0.3eV between the conduction band of TiO₂ 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 Jsc 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 NO₃⁻, CO₃^{2-}
and SO₄^{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 TiO₂. When ion affinity increases, Jsc 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:


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 (C$_{18}$H$_{37}$SiX$_3$, X= H, OCH$_3$, 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 Voc. Higher Voc 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 TiO₂. 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/\text{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 TiO₂ mesoporous film.

For possible future work, DSSC is a device whose performance is highly determined by interfacial property. Besides TiO₂-electrolyte interface, electrolyte-counter electrode interface also plays a very important role. Since the TiO₂-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:


Conference Papers:


References


