Enhancing the conversion efficiency of dye-sensitized solar cells (DSSCS) by optimizing the photoanode and dye

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

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DYE-SENSITIZED SOLAR CELLS (DSSCs) BY
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SONG JUNLING

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**A THESIS SUBMITTED IN FULFILLMENT
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SUMMARY

With the development of economy and technology, the use of global energy is growing. People are driven to seek the renewable energy such as sunlight, wind, tides and geothermal heat due to the rapid depletion of limited and non-renewable energy resources on our planet. Dye-sensitized solar cells (DSSCs) have attracted more and more attention compared to conventional solid-state photovoltaic devices owing to their low cost, simple process of manufacture and relatively high photo-to-current conversion efficiency. In this thesis, we focus on the enhancing the conversion efficiency of dye-sensitized solar cells (DSSCs) by optimizing the photoanode and dye. This thesis is divided into nine chapters.

In chapter 1, we will give a general introduction to the photovoltaic effect and DSSCs, including operating principles and basic materials used in DSSCs.

In chapter 2, the device fabrication process and the relevant theoretical and experimental principles are briefly described. The parameters used to define the main characteristics of the cells are demonstrated and various factors influencing the photovoltaic cells are summarised.

From Chapter 3 to Chapter 7, we will systematically study the function of different photoanodes in DSSCs. A simple TiF_4 hydrolysis process followed by calcination created a uniform dispersion of F dopants into the TiO_2 nanocrystalline network, which made a favorable contribution to electron transport by retarding recombination while significantly decreasing device resistance. F-doped TiO_2 nanoparticles as a photoanode for DSSC retards charge recombination, enhances electron transport due to the decrease in grain-boundary scattering and improves charge injection between the dye and TiO_2 interface. When reduced graphene oxide (rGO) was introduced in DSSC, due to the formation of rGO- TiO_2 Schottky barrier junction, the electron

transport and the interface contact between TiO_2 and active layer was enhanced. For hollow SnO_2 and TiO_2 as scattering layer, this type of photoanode enhances the light harvesting and facilitates electrolyte diffusion. In particular, the hollow TiO_2 with F-doping could induce faster electron transfer from the photoanode to the charge collecting end, retard the electron recombination at grain-boundary and accelerate electrolyte diffusion. In these chapters, electrochemical impedance spectra are also discussed.

In chapter 8 and 9, we designed different sensitizers and performed density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation by using the Gaussian 03 program package. Appropriate candidates were then filtered according to the electron density of the ground-state of sensitizers before synthesis. The results showed that π -conjugated bridge can extend the absorption of dye molecules and strong planarity (closed-packing) can suppress the charge recombination at dye/ TiO_2 /electrolyte interface. With respect to push-pull type sensitizers with donor-bridge-acceptor (D-B-A), proper donor and acceptor functional groups and larger π -conjugating system were found to increase charge separation in the molecular structure. Furthermore, the aggregation of the sensitizer also significantly affects the cell performance.

Keywords: Aggregation, Donor-Bridge-Acceptor, Dye-Sensitized Solar Cells, Electrolyte Diffusion, Electron Transfer and Injection, F-doping Photoanode, Light Harvesting, Suppressing Recombination.

Chapter 1. Introduction

With the rapid economic development due to globalization, there has been an exponential increase in the demand for energy over the last centuries. The annual global primary energy demand came up to 4.74×10^{20} J in 2008¹ and the energy consumption will probably reach 16,800 million tons by 2030, with an average growth of 1.5% per year.²⁻³ This high energy demand is mainly met by the combustion of oil, marsh gas, coal and fossil fuels, as shown in Figure 1.1.²

Figure 1.1. Worldwide Energy Sources.²

However, limited resources on Earth prompted people to find clean, environmentally-friendly and renewable new energy in research centres. At present, we can exploit available renewable energies which include hydropower (~4%), biomass and biofuels (5%), wind power (15%) and solar power (4%), as shown in Figure 1.2. Among these renewable energies, solar power is of particular interest. The irradiate power density of the Sun to the Earth's upper atmosphere is about 1.36 kW/m^2

(5.47×10^{24} J/year and the remaining solar radiation is around 3.83×10^{24} J/per year due to 30% of the sunlight incident being reflected back) according to the equation:

$$\frac{H}{H_{constant}} = 1 + 0.0033 \cos\left(\frac{360(n-2)}{365}\right),$$

where H is the radiant power density to the Earth's upper atmosphere, $H_{constant}$ is 1.353 W/m² and n is the day of the year.^{4a} This means that the energy supply of the sun is about 10^4 times more than global energy demands. The light radiation can be utilized using the photovoltaic effect, which converts sunlight directly into electricity using semiconductor materials. In other words, solar cells with efficiency of 10% would satisfy our current energy consumption if we cover ~0.1% of the Earth's surface with solar cells.³ Therefore, researchers and organizations worldwide are turning their eyes to the Sun. As shown in Figure 1.3, sunlight is composed of about 5% UV (<380 nm), 46% Vis (380-750 nm) and 49% IR and near IR (750-1200 nm) spectra. Since the majority of the sunlight comprises of the Vis and IR region spectra, we should devote ourselves to harnessing the solar light efficiently by harvesting the sunlight in this region.

Figure 1.2. Renewable Energy Sources.³

In this chapter, the photovoltaic (PV) effect will be described. Dye-sensitized solar cells (DSSCs) as a type of PV cell will be reviewed in detail. This includes the components of the device and the function of the components, the operating principle and the challenge in this project. The work in this thesis will also be specified in this chapter.

Figure 1.3. A standard intensity spectrums on the earth's surface.^{4b}

1.1. Photovoltaic Effect

The Sun is an important energy source to humans, animals and plants on Earth. Humans can convert the incident solar radiation directly into electricity using the photovoltaic effect (PV), which is a simple and effective method to harness the Sun's energy. The PV effect was found by French physicist A. E. Becquerel in 1839.^{5a} He discovered that under illumination, current could be produced between two parallel metal electrodes containing a redox electrolyte. Subsequently, the first solar cell with ~1% conversion efficiency was invented in 1883 by Charles Fritts using an extremely thin gold film-coated semiconductor selenium to form Schottky junction.^{5b} More than 60 years later, solar cells based on modern junction semiconductor were patented by Russell Ohl in 1946.⁶⁻⁷ These practical photovoltaic cells emerged in mid-nineties in

the previous century and were boosted into the space industry in the 1960s. In the 1980s, silicon solar cells with 20% efficiency were developed. Consequently, the solar cell technology developed rapidly. At present, there are four types of high-efficiency cells: (1) multiple-junction solar cells, (2) thin-film solar cells, (3) crystalline silicon solar cell and (4) emerging solar cells including dye-sensitized solar cells, organic cells and inorganic cells as shown in Figure 1.4.⁸

Figure 1.4. Primary photovoltaic cell at present.⁸

Although photovoltaic cells show many forms, they are mainly divided into two types: *p-n* junction (silicon solar cell or inorganic thin film) and excitonic cells (DSSCs or quantum dots sensitized solar cells) based on the working principle. Figure 1.5 shows the operational model in *p-n* junction solar cells. In these photovoltaic devices, the semi-conductor materials in the device absorb the photo in the sunlight that enters the cells. An electron is excited to higher energy state by a photon than the band-gap of the semiconductor. After which, the photo-generated electrons and holes

drift to the junction *via* the electric field. However, these photo-generated electrons could be recombined due to some factors, such as the emission of photons or phonons, and thus, only the electrons in or close to the space charge region could be separated by the electric field. The electrons flow from *p*-type into *n*-type region, at the same time, the holes move to *p*-type region from *n*-type, resulting in the production of electric current across the device as shown in Figure 1.5.

Figure 1.5. The working principle of a conventional *p-n* junction solar cell under illuminations.

1.2. Dye Sensitized Solar Cells

The history of dye-sensitized solar cells (DSSCs) can be traced back to 1887 when Moser observed that the photovoltaic effect could be enhanced when erythrosin was adsorbed on silver halide electrode.⁹ After several decades of work,¹⁰⁻¹³ a dramatic breakthrough in this field was reported in 1991¹³ by Michael Grätzel and Brian O'Regan. They introduced the use of the nano-crystalline TiO₂ semiconductor in place

of a flat surface photoanode which resulted in the enhancement of the conversion efficiency of DSSCs. The concept behind DSSCs is based on wide-band gap semiconductors with a light absorbing material. The semiconductor typically used in the cell, titanium dioxide, cannot adsorb sunlight in the visible and Near IR region due to its wide band gap. Thus, use of TiO_2 itself without dye sensitizer cannot utilize sunlight to the greatest extent. The electrons are fed into the semiconductor from excited dye molecules adsorbed on its surface and are transported in the semiconductor. However, the defects of nanocrystals TiO_2 semiconductor such as trap-states on the surface and grain boundaries could block the electron transportation. Figure 1.6 shows the operating principles of dye-sensitized solar cells, which will be discussed in detail in the following part.

1.2.1. Operating Principles

Dye-sensitized solar cells (DSSCs), as a promising third generation cells, have recently become a brighter alternative owing to their low cost, relatively high conversion efficiency and environmental friendliness. The cell is mainly composed of a semiconductor material, dye molecules, an electrolyte, a counter electrode and a conducting and transparent substrate. There are several electron transfer (ET) processes in DSSCs, which coexist in the device in a parallel and competitive manner. The kinetic processes in the DSSCs are showed in Figure 1.7.^{14,16-17} Upon illumination, the dye sensitizer adsorbed on the semiconductor's surface is excited from the HOMO into the LUMO by harvesting solar energy and generating excitations in a few femtoseconds, shown in the following Eq(1):

Photo-excitation (1).

Subsequently, the electrons are injected into the semiconductor by an interfacial charge transfer very quickly, on a sub-picosecond scale (Eq (2)).

Figure 1.6. Operating Principles of Dye-Sensitized Solar Cells (white ball: TiO_2 , red ball: sensitizer).

The electrons then pass through the interconnected semiconductor network by diffusion model in a few milliseconds. At the same time, the oxidized dye (S^+) is reduced to the ground state (S) by the redox couple or hole transporting material in the electrolyte, typically I_3^-/I^- , resulting in the regeneration of dye molecular (Eq (3)).

Finally, the electrons arrived at the FTO electrode and are delivered to the external circuit. The oxidized mediators are reduced by platinum catalyst at the counter electrode (Eq (4)), completing the whole circuit.

However, there are also some associated side-processes in the device. Firstly, the photo generated electron could occur recombination. The photo-generated electrons are captured by the oxidized dye molecules (Eq (5)). Back reaction, where the electrons in TiO_2 surface react with oxidized component of the redox couple in the electrolyte, could also occur (Eq (6)).

Based on the analysis above, the enhancement of the spectral absorption of sensitizer dyes in the Vis and Near-IR region is a key factor to improve the device performance as it increases the electron injection from the excited state of dye into the conduction band (CB) of semiconductor and accelerates the charge transfer at a metal oxide/dye/electrolyte interface.¹⁵⁻¹⁹ In particular, to identify the collection of charge carriers, the electron transport in the semiconductor must be faster than the charge recombination and back reaction in the device. Since electron collection is decided by the competition between the electron transport, interfacial recombination and back reaction, we should devote ourselves to retarding the charge recombination and increasing the electron transportation in the grain and grain boundary of the photoanode in order to improve the photo-to-current conversion efficiency of the device.

Figure 1.7. Schematics of electron-transfer processes in DSSCs. k_1 , k_2 and k_3 represents the electron transfer rate constant from TiO_2 to I_3^- (back reaction), the electron recombination between the injected electron and oxidized dye (D^+) and the dye regeneration by I^- reduction, respectively.

1.3. DSSCs Basic Materials

1.3.1. Photoanodes

The semiconductor material in DSSCs is a crucial factor for the cell's performance due to its role in electron transportation. An appropriate semiconductor should be chemically stable and exhibit good coupling with dye molecules. Since the electron transportation in the photoanode is driven by a gradient of electrochemical potential owing to the absence of the electric fields in the semiconductor, the conducting band of the semiconductor should be lower than the LUMO level of the dye in order to facilitate efficient electron injection.¹⁴⁻²⁰ Titanium dioxide is a semiconductor with wide band gap that is currently widely used as a photoanode material due to its unique electrical properties. ZnO and SnO_2 semiconductors are also applied to DSSCs.^{21,22} However, there are several problems such as poor dye adsorption, weak electron

coupling with the dye and poor anti-corrosion properties. Furthermore, the dye molecules are liable to aggregation which may form multilayers on the ZnO surface,²¹ now that charge carriers are generated in a dye monolayer in the photoanode according to the results reported by B. A. Gregg et al.,^{16,26} accordingly, which will reduce the performance of the cell based on ZnO photoanode. These factors lower the solar-to-electric energy conversion efficiencies in contrast with TiO₂ photoanode. Anatase, rutile and brookite are three crystalline forms of TiO₂ and anatase TiO₂ was extensively studied and has been found to be the most appropriate for DSSCs applications.^{16,17,23,26} It is known that TiO₂ as a transition-metal oxide (d^0) and its valence band (VB) and conduction band (CB) mainly consists of O_{2p} and Ti_{3d} respectively. These electronic properties of TiO₂ could improve the electron coupling between TiO₂ and sensitizers and hence enhance the dye loading. So far, a major obstacle for the TiO₂ semiconductor in attaining higher photo-to-current conversion is the electron transport across the interconnected particle network.²³⁻²⁷ There are a large number of defects in anatase TiO₂, *e.g.* surface states, oxygen vacancies and grain boundaries, which may recombine with the electron hole pairs in the electrolyte. In addition, during the transition process, the electrons have to encounter the grain and grain boundaries which induce electron recombination between the TiO₂/dye/electrolyte interfaces before they are efficiently collected at the FTO surface. Thus, to improve the cell performance based on TiO₂ photoanode, increasing the roughness of the semiconductor for large amount of dye loading and decreasing the defects in the semiconductor should be effective ways. On the other hand, an effective strategy is accelerating the electron transportation in the semiconductor.

In a typical device, the photoanode is composed of two layers. One layer comprises 10-30 nm TiO₂ nanoparticles with a high surface area which is adapted to loading

large amount of dye molecules and the other layer consists of larger particles up to 300 – 400 nm as scattering layer in order to increase the light harvesting.¹⁴⁻²⁰

1.3.2. Dye Sensitizers

The semiconductor in DSSCs only absorb UV-light. To capture more sunlight, the dye molecules are introduced into this system to extend their spectral response to the visible region. An effective dye has to meet several prerequisites. Firstly, the lowest unoccupied molecular orbital (LUMO) of the dye should be higher than the conduction band (CB) of the semiconductor to favour electron injection. Secondly, the highest occupied molecular orbital (HOMO) of the dye should be lower than the redox couple in the electrolyte to guarantee the regeneration of the dye. Thirdly, to avoid luminescence or non-radiative decay, the dye should be able to couple with the semiconductor. Most importantly, the dye molecules should have broad absorption with high extinction coefficient in the visible region to absorb as much sunlight as possible. According to Marcus and Gerischer's theory,²⁸⁻³⁰

$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi k_b T}} \exp\left(-\frac{(\lambda + \Delta G^0)^2}{4\lambda k_b T}\right),$$
 where k_{et} is the rate of electron transfer,

$|H_{AB}|$ is the electronic coupling between the initial and final states, λ is the reorganization energy (both inner and outer-sphere), ΔG^0 is the total Gibbs free energy change for the electron transfer reaction, k_b is the Boltzmann constant and T is the absolute temperature. The injection rate of the electrons depends on the energy overlap of the LUMO of the dye sensitizer and the CB of the semiconductor. To some extent, the ability to accept electrons of semiconductor could be reflected by the density of states (DOS) of the semiconductor. Figure 1.8 shows the charge transfer from the excited state of the **N719** sensitizer to the conduction band of the TiO₂ nanoparticles.

Under visible irradiation, the electron of the **N719** sensitizer was transferred from the metal centre (Ru) to the ligand (MLCT), subsequently, the electron was injected into the conduction band of TiO₂ from the π^* orbital of the ligand.^{33,35} According to the theoretical calculation results, the dye molecule may bind to anatase (101)³²⁻³⁵ due to thermo-dynamical stability and low surface-energy (γ) (surface energies are $\gamma_{\{001\}}$ (0.90 J m⁻²) > $\gamma_{\{100\}}$ (0.53 J m⁻²) > $\gamma_{\{101\}}$ (0.44 J m⁻²)).³⁶⁻³⁸ The coordination mode of the ligand in the dye molecules can exert an influence on the injection rate according to previous investigations.³⁹⁻⁴⁰ Scheme 1.1 shows the different coordination models of a carboxyl group on the semiconductor surface.

Figure 1.8. Charge transfer from the excitation of the N719 sensitizer to the conduction band of the TiO₂ nanoparticles.³⁵

Scheme 1.1. Different coordination models of a carboxyl group on the semiconductor surface: a) monodentate with H-atom, b) monodentate without H atom, c) bridge and d) bidentate chelate. M represents the surface metal ion (e.g. Ti or Zn), R represents the other group in the dye molecules.⁴⁰

According to reported results by Meng *et al.*,¹⁹ the different protonation states and binding models can affect the rate of electron injection owing to reduced interfacial dipole moments. The dissociated adsorption of the dye (Figure 1.9c) molecules can induce faster electron injection dynamics as compared with the intact configuration (Figure 1.9(a), (b) and (d)).¹⁹

Figure 1.9. Different binding configurations of the model dye molecule bonded to the TiO_2 surface and corresponding plots of the density of states (DOS).¹⁹

At present, transition metal Ru-sensitizers are extensively studied owing to its predominant advantages such as long excited state lifetime, chemical stability, redox properties *etc.*^{16-18,34-35} For this type of sensitizers, the HOMO mainly consists of the d orbitals of Ru with partial contribution from the thiocyanate (NCS^-) coordinating ligands and the LUMO is delocalized over the π^* orbitals of bi-pyridine ligand.³⁵⁻³⁶ The structure of the common ruthenium transition metal complexes such **N3**, **N719** and **Z907** is shown in Scheme 1.2.

Scheme 1.2. Structure of **N3**, **N719** and **Z907**.

Another promising dye, termed metal free dye, also shows quite promising characteristics: (1) high molar extinction coefficient; (2) lower cost than Ru dyes and (3) easy to modify structure of the molecules by introducing different functional groups.^{11, 12} However, this type of sensitizers also possess disadvantages: (1) a sharp and narrow absorption band; (2) short emission lifetime of the π - π^* excited states; (3) insufficiency of valid charge separation as compared with the ruthenium dye and (4) dye aggregation.⁴⁰ So far, numerous metal-free organic dyes have been investigated based on the concept of donor- π -conjugation bridge-acceptor (D-B-A). Acceptor moiety in this dye molecule act as anchoring group, attaching to TiO_2 and π -substituted-conjugated group act as “bridge”, connecting the acceptor and the donor moieties. The typical structure of this type of sensitizer is shown in scheme 1.3. The

absorption of dye sensitizer would exhibit red-shift by the addition of different donor-acceptor groups which would harvest most of the visible and near IR photons in the solar spectrum. It is known that the photo-induced electron transfer occurs from donor to acceptor upon excitation and the conjugation bridge, which acts as linker, can adjust the distance between the donor and acceptor. This is an effective approach to directional charge transportation in DSSCs as it could provide an efficient intramolecule charge-transfer and accelerates the interfacial electron injection from the excited state of dye to the CB of TiO_2 while on the other hand, decelerate the interfacial electron recombination on the TiO_2 /dye/electrolyte interface.

Scheme 1.3. The structure of typical metal-free sensitizer.

The group of electron-donating moieties such as triphenylamine, aminocoumarin, (difluorenyl) phenylamine, aryl amines and indoline can fulfil this role of electron donor.⁴¹⁻⁴⁶ Oligothiophenes, thienylenevinylenes, phenylenevinylenes and dithienothiophenes act as π -conjugated bridges frequently due to their excellent charge-transport characteristics.⁴⁷⁻⁴⁸ The groups that serve as the acceptor must be rather small so as to anchor better onto TiO_2 surface. In most cases, cyanoacrylic acid group is used and rhodanine-3-acetic acid and dimeric species are also used as a

second type of acceptor. The effective metal-free dyes for the high efficiency of DSSCs must contain the functional moieties as mentioned above.⁴¹⁻⁵⁰

Porphyrins are also used as promising sensitizers for DSSCs due to their strong absorption with large absorption coefficients in the visible region and their numerous reaction sites which can be used to introduce functional groups.^{15,51-55} However, in comparison to ruthenium and metal-free sensitizers, the overall conversion efficiency of the porphyrins is still relatively low. Thus far, the highest overall efficiency $\eta = 7.1\%$ was reported by D. Officer and co-workers.⁵¹ Numerous porphyrins with various substituting groups have been synthesized and studied. The lengths of anchoring group, the junction position between the porphyrin core, the anchoring group, the donating and accepting group can affect the absorption bands, resulting in different cell performances.⁵²⁻⁵⁸

At present, the overall η of metal-free and porphyrin sensitizers are still low in contrast with ruthenium dyes. The reason may be attributed to the dye aggregation, the charge recombination resulting from the strong intermolecular π - π interaction of the dye molecules, lack of directionality in the excited state and short excitation life time.⁵¹⁻⁵⁶ However, these type of sensitizers should be studied in depth, in consideration of the cost and environmental issue.

1.3.3. Electrolyte and the Counter Electrode

The electrolyte used in DSSCs is composed of iodide/iodine redox couple in an organic solvent or ionic liquid. The most common electrolyte used in DSSCs composed of 0.1 M I₂, 0.1 M LiI, 0.5 M tertbutylpyridine and 0.6 M 1-hexyl-3-methylimidazolium iodide in methoxy-acetonitrile. To regenerate the oxidized dye faster and retard the recombination between the electron in the CB of TiO₂ and

oxidized dye, the electrolyte should have a high diffusion coefficient, high conductivity and low viscosity. The low viscosity allows the electrolyte to penetrate the semiconductor film. The chemical modification of the anionic or cationic of the ionic liquid can decrease its viscosity as the viscosity of ionic liquids depends on the interaction of coulombic and Van der Waals interactions as well as hydrogen bonding. Thus, increasing the alkyl chain length could increase the viscosity of the molten salts owing to van der Waals forces and at the same time, also decrease the conductivity.⁵⁹ The different anions in the ionic liquids also can affect the viscosity of ionic liquid.⁶⁰⁻⁶² At present, ionic liquids based on 1, 3-dialkylimidazolium iodides have been widely used as solvents for DSSCs. The common cations and anions are shown in Scheme 1.4.

Scheme 1.4. Usual molecular structures of ionic liquids (cations and anions) used in DSSCs.

Liquid electrolytes are volatile and noxious. Hence they are difficult to encapsulate for long periods and are not environmentally friendly. To overcome this problem, several research groups have in the recent years, succeeded in using solid or quasi-solid electrolytes instead of liquid or ionic liquid as solvent, avoiding the leakage and sealing problems.^{61,63-68} These electrolytes include (1) ambient ionic liquid,⁶¹ (2) p-

type NiO semiconductor,⁶³ (3) solid state electrolyte consisting of different hole conductors,⁶⁴⁻⁶⁶ and (4) polymer electrolytes.⁶⁷⁻⁶⁸

For counter electrode, also known as photocathode, generally, platinized FTO glass surface is used for DSSCs. In the counter electrode, platinum acts as catalyst, reducing I_3^- ion back to I^- in the redox electrolyte. However, platinum is a noble metal which increases the cost of production. Therefore, novel counter electrodes have been developed for the upcoming industrialization of DSSCs. At present, poly(3,4-ethylenedioxythiophene (PEDOT),⁶⁹ V_2O_5/Al with high work-function,⁷⁰ p-type NiO were chosen as photo-cathode, which can be combined with n-type photo-anode to construct tandem solar. In addition, carbon-based materials, such as hierarchical hollow macroporous carbon,⁷¹ single-walled and multi-walled carbon nanotube were selected as substitute material for Pt counter electrode.⁷²⁻⁷³

1.4. Motivation and Objectives

This thesis is mainly focused on two strategies to improve the conversion efficiency of DSSCs: one method is improving the electron transportation and retarding the charge recombination; the other is increasing the amount of light captured using different scattering layers and different sensitizers with broad adsorption spectra. Chapter 3 and 4 address the method to increase electron transport by the addition of fluorine into the semiconductor. Chapter 5 focuses on introducing reduced graphene oxide in the photoanode to form the Schottky junction. Chapters 6 and 7 discuss how to harvest more sunlight using hollow SnO_2 and TiO_2 microparticles as the light scattering layer. Chapters 8 and 9 present recent results with new metal-free and zinc-porphyrin sensitizers based on the concept of Donor- π -bridge-Acceptor resulting in better intramolecular charge-separation, thus improving cell performance.

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Chapter 2. Experimental and Device Preparation

In this chapter, the device fabrication process and the relevant theoretical and experimental principles are briefly described. The details about each individual experiment will be illustrated in the related topics.

2.1. Device Fabrication

2.1.1. Fabrication of TiO₂ Photoanode

FTO glass was cleaned in an isopropyl alcohol and 0.1 M HCl solution using an ultrasonic bath for 30 min respectively and rinsed with water and acetone. After treatment in a UV-O₃ system (Model No. 256-220, Jelight Company, Inc) for 20 min, the conducting glass was treated by soaking in 40 mM TiCl₄ solution at 70 °C for 30 min. The treatment with TiCl₄ was carried out as reported previously in literature.¹ A layer of paste was coated on the FTO glass plates using the doctor blading technique and kept in a bottle for 3 min with ethanol (AR), relaxing to reduce the surface irregularity, subsequently, dried for 20 min at 125 °C. The doctor blading procedure was repeated until the desired thickness was achieved. The double layer electrode consists of a light scattering layer deposited on top of the transparent ~20 nm sized TiO₂ film. After deposition of the light scattering layer, the double-layered titanium dioxide film was sintered at 500 °C for ~30 min.

The whole process will be illustrated in detail below with graphical representation.

2.1.2. Fabrication of the Whole Cell

1. Put 3M Scotch tape (Scotch[®] Magic Tape) on the conducting side of FTO (F: SnO₂) glass.

2. Apply the TiO_2 paste and flatten it with a razor blade (or microscope slide) on the same side of the FTO glass.

3. Place electrode on top of a hot plate and heat at approximately 125°C for 6 min. Repeat the above process until the thickness of the film is $\sim 13\ \mu\text{m}$ ($\sim 10\ \mu\text{m}$ transparent film and $3\ \mu\text{m}$ scattering layer). Finally, the titanium dioxide layer is sintered 500°C for ~ 30 min.

4. Dip the prepared TiO_2 electrode into the dye solution (such as Z907).

5. Take out the TiO_2 /dye electrode from the dye solution and wash it with a corresponding solvent.

6. Combine the TiO_2 /dye electrode with a Pt counter electrode, which is fabricated by e-beam evaporation on the glass, and then the two electrodes were bonded together using hot-melt sealing foil (60 μm Meltoni 1170-60, Surlyn®).

7. Introduce the electrolyte between the two electrodes through a filling hole. (The filling hole produced using a sandblasting drill on the counter electrode.)

8. Then, the hole at the back of the counter electrode was sealed using the hot-melt sealing foil under a transparent glass cover by heating.

9. Finally, silver film was deposited on the FTO surface to make good contact with the external elements. This completes the fabrication process of the entire device with sandwich structure.

The SEM pictures of transparent film and scattering layer in the device is depicted in Figure 2.1.

Figure 2.1. (A) top view of transparent film; (B) top view of scattering layer and cross profiles of (C) the monolayer and (D) the bilayer in the device.

2.2. Measurement of the Photovoltaic Effect of the Cell

2.2.1. Monochromatic Incident Photon-to-Electron Conversion Efficiency (IPCE)

A data acquisition system was used to control the incident photon to-collected electron conversion efficiency measurement with Oriel QE/IPCE Kit equipment.

Under full computer control, light from a 300 W xenon lamp (Oriel, U.S.A.) was focused through a monochromator (Oriel, U.S.A) onto the photovoltaic cell under test. The equipment is depicted as Figure 2.2.

Figure 2.2. The IPCE test system for the device.²

The IPCE is decided by this equation:

$$IPCE\% = \frac{I_{sc}(A)}{P(W)} \times \frac{1240(eV \cdot nm)}{\lambda(nm)} \times 100,$$

where I_{sc} refers to the short-circuit photocurrent density generated by monochromatic light and λ (nm) and P (W) refer to the wavelength and the intensity of the monochromatic light. From the equation, the value of the IPCE reflects the number of photo-electrons in the external circuit at a corresponding monochromatic light.³⁻⁴

IPCE can also be expressed as the light harvesting efficiency ($LHE(\lambda)$) of the cell in the equation below,

$$IPCE = LHE \times \eta \times \phi,$$

ϕ is the quantum yield of charge injection, η is the charge-collecting efficiency of the FTO and $LHE = 1 - 10^{-\Gamma \sigma(\lambda)}$. Γ refers to the number of moles of dye per square centimetre of active area of the film, σ refers to the absorption cross section in units of $\text{cm}^2 \text{mol}^{-1}$ ($\sigma = \varepsilon \times 10^3 \text{ cm}^3 \text{L}^{-1}$) and ε refers to the extinction coefficient (units of $\text{M}^{-1} \text{cm}^{-1}$).⁴ Hence, the IPCE reflects the absorption properties of the dye, the amount of

adsorbed dyes on the TiO_2 surface, the quantum yield of electron injection from the excited dye to the conduct band of the TiO_2 , and the efficiency of collection of electrons in the external circuit.

2.2.2. I-V Measurement

A Sun 2000 solar simulator light source (Abet-technologies, U.S.A.) was used to give an irradiance of 100 mW cm^{-2} (the equivalent of one sun at air mass (AM) 1.5) at the surface of solar cells. The current-voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2440 digital source meter (Keithley, U.S.A.). This process was fully automated using lab tracer software. The equipment is shown in Figure 2.3.

Figure 2.3. The I-V test system for the cell.⁵

The photovoltaic performance of the cell can be evaluated by the measurement of the photocurrent-voltage curve. A typical curve is shown in Figure 2.4.

Figure 2.4. A typical I-V curve in the experiment.

The black line shows the power output at different bias. The dot in the black line indicates the maximum power point,⁶⁻⁷ the red line shows how to obtain the point, corresponding to the I_{max} and V_{max} .

The overall conversion efficiency (η) of the cell is defined as the ratio of the maximum power (P_{max}) to the incident sunlight power (P_{in}).⁸⁻¹⁵

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = \frac{I_{max} \times V_{max}}{P_{in}} = \frac{I_{sc} (mAcm^{-2}) \times V_{oc} (V) \times FF}{P_{in} (mWcm^{-2})} \times 100\% ,$$

where P_{max} is the maximum power output ($P_{max} = I_{max} \times V_{max}$), I_{sc} is the short-circuit current ($mAcm^{-2}$), V_{oc} is the open-circuit voltage (V) and FF is the fill factor.

$$(FF = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}} \times 100\%).$$

The efficiency (η) of the cell is universally decided by the following three key factors: 1) The short-circuit photocurrent density (J_{sc}), 2) open-circuit photovoltage (V_{oc}) and 3) fill factor (FF).

1) Short-Circuit Photocurrent Density (J_{sc})

The short-circuit current I_{sc} depends on the following factors: the light absorption capabilities of dyes, the high electron injection efficiencies from photo-excited dyes to the conduction band of the TiO_2 and the charge recombination between the electrolyte and the conduction band of the TiO_2 . In other words, the effective carrier diffusion length determines the short-circuit current (I_{sc}).

For a typical semiconductor diode, a current in the cell will be generated when forward bias is applied. The current is examined using its I–V characteristics. Under illumination, the current-voltage characteristic is defined using the following equation:

$I = I_{ph} - I_s(e^{qV/k_B T} - 1) = I_{ph} - I_{dark}$, where $I_{dark} = I_s(e^{qV/k_B T} - 1)$, I_s is the reverse bias saturation current (or scale current), k is the Boltzmann constant, T is the absolute temperature, q is the magnitude of charge on an electron (the elementary charge), I_{ph} is the photocurrent that depends on irradiation intensity and V is the voltage applied on the terminals of the cell.³ When the applied voltage $V = 0$, $I_{sc} = I_{ph}$.

2) Open-Circuit Voltage (V_{oc})

The V_{oc} is the voltage when the circuit is open. This means there is no current flow through the external of the device ($I = 0$ and $V = V_{oc}$). Under illumination, V_{oc} is the difference in electrical potential between the energy level of the conduction band of TiO_2 (~ -0.5 to -0.4 V vs. NHE) and the redox potential of the electrolyte (I_3^-/I^-) (~ 0.4 V vs. NHE). V_{oc} correlates logarithmically to the inverse concentration of I_3^- and increases with incident photo flux according to the following equation,

$$V_{oc} = \frac{RT}{\beta F} \ln \left(\frac{AI}{n_0 k_1 [I_3^-] + n_0 k_2 [D^+]} \right),$$

where k_1 and k_2 are the kinetic constants for the back reaction of injected electrons with tri-iodide (I_3^-) and recombination of these electrons with oxidized dye (D^+) respectively. $RT/(\beta F)$ is the thermal voltage and n_0 is the concentration of accessible electronic states in the conduction band. Nonetheless, V_{oc} is lower than the theoretical value ($\sim 0.8-0.9$ V).³ The recombination of injected electrons from dye excited state with the I_3^- ions in the electrolyte is one of the primary reasons for the reduction in V_{oc} .^{3,8-15} Another factor affecting the V_{oc} value is the shift of the TiO_2 CB level. The defects of the TiO_2 surface, the doping hetero-atom into TiO_2 and the molecules adsorbed on the TiO_2 surface could result in a shift of the CB of TiO_2 . In other words, the V_{oc} value strongly depends both on the dark current and the shift of Fermi level of TiO_2 .

3) Fill Factor

The fill factor is an important parameter for DSSC, which is decided by the ratio of the maximum power output ($J_{max} \times V_{max}$) to the product of J_{sc} and V_{oc} , which is illustrated below:

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}}$$

FF reflects the “squareness” of the solar cell, which is the area of the largest rectangle fitted in the I-V curve. FF (typically 0.6 to 0.8) is influenced by the series resistance (R_s), shunt resistance (R_{sh}) and the light intensity. The R_s is typically due to the internal resistance while R_{sh} is mainly caused by the significant power losses arising from the leakage of the current. Figure 2.5 shows the effect of R_s and R_{sh} on the device, the

increasing of R_s and the decreasing of R_{sh} could reduce the fill factor of the cell. Thus, the smaller R_s and the larger R_{sh} are good for an efficient cell.⁶

Figure 2.5. The effect of R_s and R_{sh} on the device.⁶

2.3. Characterization of Samples

The morphologies of the TiO_2 spheres and films were studied by field emission scanning electron microscopy (FESEM, JEOL JSM-6360) and transmission electron microscopy (TEM, JEOL). Powder X-ray diffraction (XRD) measurements were carried out using a Rikaku Rint-2000 instrument with $\text{Cu-K}\alpha$ radiation. Nitrogen adsorption–desorption isotherms were obtained by ASAP 2020 (Micromeritics Instrument Corp.) apparatus. All the samples were degassed at 200 °C prior to Brunauer–Emmett–Teller (BET) measurements. The fluorine doping level of the sample was determined by X-ray photoelectron spectroscopy (XPS; KRATOS, AXIS ULTRA) using a monochromatized $\text{Al-K}\alpha$ (1486.7 eV) X-ray source. The current-voltage characteristics of the cell under 100 mW cm^{-2} (AM 1.5) conditions provided by a Sun 2000 solar simulator (Abet-technologies, U.S.A.) were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2440 digital source meter (Keithley, U.S.A.). The data was recorded

using lab tracer software. The incident photon-to-current efficiency (IPCE) was obtained with Oriel QE/IPCE Kit equipment (Oriel, U.S.A.). Absorption spectra were measured on JASCO V-670 UV-Vis-Near IR spectrophotometer and photoluminescence analyses were performed on a Cary Eclipses fluorescence spectrometer. Cyclic voltammetric (CV) experiments were conducted with a computer-controlled Eco Chemie Autolab PGSTAT 100 with an ADC fast scan generator. Working electrodes were 1 mm diameter planar Pt disks, used in conjunction with a Pt auxiliary electrode and an Ag/Ag⁺ reference electrode connected to the test solution via a salt bridge containing 0.2 M tetra-butylammonium hexafluoro-phosphate (Bu₄NPF₆) in CHCl₃. Accurate potentials were obtained using ferrocene as an internal standard. Electrical impedance experiments were carried out in the dark and under illumination conditions with an autolab electrochemical workstation with a frequency range from 0.1 Hz to 1 MHz and a potential modulation of 20 mV. The forward bias is -0.69 V and open-circuit voltage in the dark and under illumination condition, respectively. The results were fitted with the Z-view software (ZView 3.1c, Scribner Associates Inc.) to appropriate equivalent circuits.

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Chapter 3. Modification of Nanocrystalline TiO₂ Electrode by Surface Treatment with Titanium (IV) Fluoride for High Efficiency of Dye Sensitized Solar Cells

3.1. Introduction

Dye sensitized solar cells (DSSCs) have attracted much attention over conventional semiconductor solar cells due to their cost advantages.¹ In a representative device, under solar illumination, charge carriers are generated by monolayers of dye molecules and subsequently injected into the semiconductor photoanode, typically a mesoporous network of nanocrystalline TiO₂. Carriers then diffuse across the interconnecting nanoparticles and finally, are collected by the F doped SnO₂ (FTO) electrode.²

Mesoporous TiO₂ is an effective photoanode because it has a large surface area for dye adsorption, a strong electronic coupling with dye molecules to enable charge injection, and a wide band gap for effective photo-carrier separation. However, a good photoanode should also provide fast charge transfer, and hence TiO₂ is lacking because its electron-mobility is only 0.1–1.0 cm² V⁻¹ S⁻¹.³ It is well known that under illumination, the photo conversion efficiency (PCE) is dominated by the kinetic competition between rate of charge transfer and recombination at the photoanode.⁴ In practice, the kinetic competition is predominantly governed by the dynamics of trapping/detrapping events in the photoanode.⁵ Due to the presence of defects and impurities, there exists a great number of unoccupied trap states, which capture mobile electrons, and have significant influence on electron transport.

Since doping is widely and successfully used in semiconductor technology to enhance electron transport, it is worthwhile to explore transport enhancement *via* tuning the photo electrochemical properties of TiO₂ by doping. Numerous attempts,

such as implantation of metal ions and doping of nonmetal ions have been explored to modify the TiO_2 for various application.^{6,7} Recently for DSSCs, Ko *et al.* showed enhancement of photocurrent and photovoltage *via* Al and W doping.⁸ Wang and Teng introduced Zn doping as a substitute for Ti^{4+} , showing improved PCE at low illumination.⁹ From a device perspective, doping with nonmetal atoms is preferable, so as not to disturb the already favourable electronic coupling between Ti^{4+} and the dye molecules, which forms the basis of superior dye adsorption and swift electron injection.¹⁰

Herein, we present the findings of enhancing electron mobility by doping F ions into the TiO_2 photoanode. Doping of F ions into TiO_2 is done *via* a hydrolysis route, which is much simpler compared to other methods based on so-gel or plasma processes. This F-doped photoanode shows retardation of recombination and improvement of photocurrent under the sun illumination. The effect of F doping on device performance is elucidated in terms of material properties and device characteristics.

3.2. Experimental Section

10 μm Nanoporous TiO_2 (Nanoxide T/SP, Solaronix) electrodes were prepared by screen-printing techniques. Briefly, FTO ($\text{SnO}_2\text{:F}$, FTO, $15\Omega/\text{square}$, Solaronix) glass was cleaned in isopropyl alcohol and 0.1 M HCl solution using an ultrasonic bath for 30 min respectively and rinsed with water and ethanol, and subsequently treated under UV- O_3 system (Model No. 256-220, Jelight Company) for 18 min. The 20 mM TiF_4 solution (adjusting the pH = 2 with 2.5 wt% ammonia solution) and 40 mM TiCl_4 treatment was performed twice (before and after depositing the mesoporous TiO_2 film at 70 $^\circ\text{C}$ for 1 h) as previously reported.¹¹ The resulting TiO_2 films (thicknesses of 10

μm , measured by the profiler, Sloan Technology, Dektak 3, including 7 μm TiO_2 nanoparticles (Solaronix T/SP) and 3 μm scattering layer (DSL 18NR-AO) were immersed in 0.3 mM *cis*-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato) (2,2'-bipyridyl-4,4'-di-nonyl)ruthenium (II) (known as **Z907**, Dyesol) in acetonitrile/tert-butyl alcohol (1:1) for 15 hrs. Then the TiO_2 photoanode and the semi-transparent counter electrode (Pt coated FTO) were bonded together using 60 μm thermal-plastic Suryln spacers. The electrode areas were around 0.28 cm^2 . After bonding, the organic electrolyte (EL-HPE, Dyesol) was filled into the sandwich cells under vacuum.

3.3. Results and Discussion

F doping in TiO_2 is confirmed by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) sputtered depth profile. Due to the difficulty of direct measurement on single nanoparticles, we used a surrogate sample of a continuous dense layer of pure anatase TiO_2 , grown by immersion of the glass substrate into Ti-precursor solution (40 mM TiCl_4) for 2 hrs. After undergoing a phase transformation upon heat treatment at $500\text{ }^\circ\text{C}$, it forms a continuous bare TiO_2 layer. This pure TiO_2 layer is then subjected to hydrolysis treatment with 20 mM TiF_4 solution followed by calcination at $500\text{ }^\circ\text{C}$. The hydrolysis of TiF_4 is accompanied by the release of F^- , which we believe is the dopant source. The hydrolysis treatment will also form a fresh thin layer of TiO_2 , around 5 nm thick.

Figure 3.1 shows that F doping is present throughout the TiO_2 layers (the pre-existing TiO_2 grown chemically in region (ii) as well as the new layer grown by TiF_4 treatment in region (i). TOF-SIMS data shows a relatively uniform doping profile which penetrates to a depth of around 35 nm, higher than the thickness of commonly

used photoanode materials (20 nm to 30 nm TiO_2 particles¹¹). The initial fluctuation of the intensity of both TiO_2 and F was due to transient ionization in the testing process. The doping concentration of F^- is around 0.01 at%, estimated by an external standard method established by Grasserbauer *et al.*¹²

Figure 3.1. TOF-SIMS sputtered depth profile of F doped TiO_2 thin film on glass substrate. Region (i) is newly grown layer by TiF_4 hydrolysis process, region (ii) is doped F in pre-existing pure TiO_2 .

Figure 3.2 shows the atomic force microscopy (AFM) images of two surface treated photoanodes. In comparison, the film with the conventional TiCl_4 treatment has a roughness of 10.5 nm, while that treated with TiF_4 has a slightly reduced roughness of 9.09 nm. In terms of available surface area for dye adsorption, these two surfaces are roughly equivalent.

Photovoltaic properties of two devices were studied in the dark and under illumination (AM 1.5 solar condition, 100 mW/cm^2). Figure 3.3(a) shows the J - V characteristics of the bare TiO_2 (device A) and TiO_2 with F doping (device B)

Figure 3.2. AFM images of TiO_2 film after TiCl_4 and TiF_4 treatment.

Figure 3.3. (a) J - V characteristics and (b) IPCE of bare TiO_2 (device A) and F-doped TiO_2 (device B) based device.

The device with F doped nanocrystalline TiO₂ photoanode shows improved cell performance through the increase of short-circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF). Table 3.1 summarizes the photovoltaic parameters of the cells measured in this study. Device **B** gives the best overall conversion efficiency (η) 6.38 % with a J_{sc} of 12.0 mA/cm², V_{oc} of 75.5 mV and FF of 71.0 %, in total a 23 % improvement of PCE compared to device **A**, with similar amount of dye adsorbed on both device **A** and device **B** as shown in Table 3.1. The J_{sc} of the cell is given by the following equation; $J_{sc} = J_{inj} - J_{loss}$, where J_{inj} is the electron injection current and J_{loss} is the total recombination current.¹³ From the measurement of J - V curves in the dark condition, it was demonstrated that the current loss in the F doped TiO₂ was strongly abated, as the dark current onset of F doped TiO₂ was shifted to a higher potential range (0.62 V) compared with that of bare TiO₂ (0.58 V), indicating that F doped photoanode can retard the electron recombination better than the un-doped TiO₂ photoanode. Fill factor can be significantly increased due to the decrease in series resistance *via* F doping. Incident photo to current conversion efficiency (IPCE) is plotted as a function of wavelength in Figure 3.3(b), showing that the IPCE enhancement in the F doped device is more substantial in the dye active range (450 - 550 nm).

The charge transport in DSSCs is analysed *via* electrochemical impedance spectroscopy (EIS), which characterizes the capacitance and resistance of a device, and the kinetic of charge transfer in the photoanodes.¹⁴ A transmission line model¹⁵ has been applied to interpret the electron transport and recombination characteristics of the TiO₂ nanocrystallites. We used this equivalent circuit to simulate the impedance spectra as shown in Figure 3.4 and Scheme 3.1 to obtain the values of the electronic elements. Typically, there are three semicircles. The first semicircle in the high-

frequency region (typically larger than 100 Hz) is attributed to the redox reaction of I^-/I_3^- at the Pt/electrolyte interface; the intermediate semicircle (in the 10 - 100 Hz range) denotes the electron transfer at the TiO_2 /dye/electrolyte interface and the third one in low frequency range (less than 10 Hz) is attributed to the diffusion of the electrolyte.¹⁶

Figure 3.4. Nyquist plots of different devices (bare TiO_2 labelled as device A and F-doped TiO_2 labelled as device B): (a) in the dark and (b) under illumination condition.

Scheme 3.1. Equivalent circuit used to fit Nyquist plots of the devices in this study.

In Figure 3.4, the impedance spectra of the devices are measured in both (a) dark and (b) illuminated (100 mW cm^{-2}) condition under forward bias equivalent to the V_{oc} . The impedance based on Bisquert model¹⁷ can be described by the following equations.

$$Z = \left(\frac{R_w R_k}{1 + \frac{i\omega}{\omega_k}} \right)^{1/2} \coth \left[\left(\frac{\omega_k}{\omega_d} \right)^{1/2} \left(1 + \frac{i\omega}{\omega_k} \right)^{1/2} \right] \quad (1), \text{ where } \omega_k = k_{eff}, \quad \omega_d = \frac{D_{eff}}{L^2} \quad (2),$$

$$R_w = \frac{K_B T}{q^2 A n_s} \frac{L}{D_{eff}}, \quad D_{eff} = \left(\frac{R_k}{R_w} \right) L^2 k_{eff} \quad (3) \text{ Here, } Z, R_w, R_k, \omega_k, \omega_d, k_B, T, q, A, n_s, L, k_{eff}$$

D_{eff} , represent impedance, electron transport resistance, recombination resistance, rate

constant for recombination, characteristic frequency of diffusion in a finite layer, Boltzmann constant, absolute temperature, elementary charge, electrode active area, the steady state electron density, film thickness, effective rate constant for recombination and effective electron diffusion coefficient, respectively.¹⁷ As shown in Table 3.1, the D_{eff} for device **A** is smaller than that for device **B**. The electron mobility is related to the electron diffusion coefficient in the conduction band, according to Einstein relation as $D_n = \frac{k_B T}{q} \mu_n$, where μ_n is the mobility of the electron in a non-degenerate semiconductor.¹⁸ Practically, the electron mobility within the conduction band is also governed to a great extent by the dynamics of the trapping and thermal release of the electrons from energetically distributed sub-band edge states. Since D_{eff} of device **B** is larger than that for device **A**, electron mobility in F doped photoanode can be deduced to be nearly 3 times higher compared with that in bare TiO_2 . This supports the argument that by modifying the TiO_2 conduction band edge with doped F ions, fewer electrons are confined by the trapping state in the band structures. Due to the enhanced electron mobility, F doped TiO_2 significantly improves the charge transport in the photoanode, resulting in efficient current collection. Besides trapping, loss also occurs during electron transfer across the interconnected TiO_2 nanoparticles, where grain boundaries formed during calcination contribute to grain boundary scattering.¹⁹

In this work, F doping can be uniformly dispersed throughout the nanoparticles, presumably also including the grain boundary region. According to previous study, fluorine doping at grain boundaries is expected to reduce the grain boundary scattering.²⁰ Hence, it can also contribute to the faster electron transport process in photoanode. The effective carrier diffusion length ($L_{\text{eff}} = \sqrt{D_{\text{eff}} \tau}$) is the most

representative factor which can reflect the competition between charge transport and recombination process in DSSCs.²¹ F-doped TiO₂ shows a significantly increase in L_{eff} (from 21.9 μm to 28.7 μm), which indicates that F doping actually tunes the balance of competition towards transport over recombination.

Table 3.1. The photovoltaic properties parameters of bare TiO₂ (device **A**) and F-doped TiO₂ (device **B**).^a

Devices	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	D_{eff}^c (cm ² s ⁻¹) $\times 10^{-5}$	L_n (μm) ^c	Adsorbed Dye ^b (mol/cm ²) $\times 10^{-5}$
A	11.1	720	64.9	5.19	4.0	21.9	8.0
B	12.0	755	71.0	6.38	11.8	28.7	8.4

^a Performance of DSSCs was measured with an active area of 0.28 cm² under AM 1.5 (100 mW/cm²) condition. ^b The dye adsorbed on TiO₂ film was desorbed by a 0.1 M NaOH solution (water:ethanol 1:1 v/v) for 24 hrs. ^c EIS spectra were measured with 10 μm TiO₂ nanoparticle film under 50 w halogen lamp (100 mW/cm²) condition.

3.4. Conclusion

In conclusion, F-doped nanocrystalline TiO₂ used as photoanode in DSSCs shows enhancement in electron mobility at 1 sun illumination. A simple TiF₄ hydrolysis process followed by calcination can be used to create a uniform dispersion of F dopants into the TiO₂ nanocrystalline network. The F dopants in the photoanode make a favorable contribution to electron transport by retarding recombination while significantly decreasing device resistance. EIS measurements reveal the differences between F-doped TiO₂ and pure TiO₂ in electron mobility, recombination, effective carrier diffusion length and charge transfer resistance. Compared with bare TiO₂, optimized F doped TiO₂ photoanode can lead to improvement in PCE by 23%.

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Chapter 4. Effects of Fluorine Doping in TiO₂ Dye-Sensitized Solar Cells**4.1. Introduction**

DSSCs have received much research interest due to their low cost and relatively high conversion efficiency. Compared with wide-band gap semiconductors, DSSCs can convert more sunlight to electrical energy using dye molecules.¹ So far, extensive studies indicated that the performance of DSSCs are dominated by the following key factors: (i) electron injection from dye to semiconductor; (ii) the absorption spectra of dye sensitizers and (iii) electron collection within the device.² Generally, anatase TiO₂ has been widely used as the photoanode in DSSCs due to its chemical stability and favorable electronic coupling with dye molecules. However, the defects in anatase TiO₂ such as surface states and grain boundaries strongly influence the electron transfer and may increase the recombination of electron-hole pairs.

Many methods for improving electron transport in DSSCs have been attempted, for example by employing 1D TiO₂ nanowires (NW) and TiO₂ nanotube (NT) as photoanode, which could enhance electron collection efficiency with more direct transport paths compared to the random transport path in nanoparticle (NP) based photoanode.³ However, the surface area of NT or NW based photoanode is much smaller than that of NP, which leads to decreased dye loading, hence resulting in less sunlight absorption. Thus far, the record-holder photoanode for photo-to-current conversion efficiency in DSSCs is still TiO₂ NP.¹ Development of new methods for improving electron transport in TiO₂ photoanode is still a remaining challenge in DSSCs.

Generally, the random interconnection between two TiO₂ nanoparticles would reduce the electron mobility due to the scattering of free electrons in the grain-

boundary and surface-defects. Trapping sites would also strongly influence electron collection because the trapping/detrapping events dominate the electron transport process in DSSCs. Thus decreasing the defects and enhancing the electron transport in TiO₂ NP based photoanode offers the potential for higher photo-to-current conversion efficiency.

As reported previously, heteroatom-doping with metallic Zn,⁴ Nb,⁵ Nd,⁶ *etc.* and non-metallic C⁷ and N⁸ is an effective way to enhance the electron mobility, retard charge recombination and reduce the film resistance in DSSCs. Recently, N-doped TiO₂ photoanodes indicated that this kind of doping approach could successfully retard carrier-recombination.⁸ Separately, the effects of fluorine doping on the photo-catalytic activity of TiO₂ have been studied.⁹⁻¹⁰ However, few investigations on F-doped TiO₂ photoanode in DSSCs have been reported.

In this study we prepared DSSCs with F-doped TiO₂ NP as photoanode *via* a facile method and the photovoltaic and electrochemical properties of these electrodes were systemically studied. Electron transfer and charge recombination at the FTO/TiO₂/electrolyte interfaces were investigated using electrochemical impedance spectroscopy (EIS).

4.2. Results and Discussion

As shown in Figure 4.1(a), the TEM image of F-doped TiO₂ nanoparticles shows well-defined polyhedral morphologies with typical diameters of 20-30 nm. The adsorption and desorption isotherms of F-doped TiO₂ nanoparticles are shown in Figure 4.1(b) and the specific surface area of F-doped mesoporous TiO₂ spheres is 36.88 m²/g by Brunauer-Emmett-Teller (BET) measurement (Table 4.1). The roughness factor, R (μm⁻¹) of TiO₂ can be estimated by the following equation (1):

$$R = \frac{\rho(1-P)}{S} \quad (1),$$

where P is the porosity (%), S is the specific surface area (m^2/g) and ρ is the density (3.98 g/cm^3) of anatase TiO_2 .¹² The R value is approximately $79.8 \mu\text{m}^{-1}$ for the F-doped TiO_2 sample, which is a relatively large value that could adsorb enough dye to capture sunlight effectively. Figure 4.1(c) shows the X-ray diffraction (XRD) pattern of F-doped TiO_2 powder and commercial P25 calcined for 3 hrs at 500°C . Both diffraction peaks match well with the anatase TiO_2 phase (JCPDS 21-1272, space group $I4_1/amd$). According to the Scherrer equation (2),

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (2),$$

where λ , β , θ refer to X-ray wavelength (0.15418 nm), the full width half maximum and the Bragg angle, respectively. The crystal size D is calculated to be about 14.9 nm (F-doped TiO_2), which is comparable to the sizes estimated from TEM images.

X-ray Photoelectron Spectroscopy (XPS) is shown in Figure 4.1(d). The peak at 683.6 eV is assigned to F_{1s} , similar to previously reported results,¹²⁻¹⁴ which is attributed to the F^- ions formed on the TiO_2 crystal surface during the hydrolysis of the precursor, TiF_4 . The doping concentration of F is around $5.60 \text{ at\%}$, estimated by XPS results.

The peaks at 528.8 and 527.2 eV are ascribed to O_{1s} , indicating that there are two forms of O atom: O-H and Ti-O in the TiO_2 . Besides the peaks at 464.2 and 458.9 eV for $\text{Ti(IV)}_{2p3/2}$ and $\text{Ti}_{2p1/2}$, XPS spectra also reveal a new peak at 455.9 eV , which is attributed to Ti^{3+} ions, which may be converted from Ti^{4+} to preserve charge neutrality due to F doping. This reaction could also result in more O-vacancy in TiO_2 .¹²

The UV-vis absorption spectroscopy of the film with and without F doping was shown in the following figure. Compared to P25, the F-doped TiO_2 shows red-shift as shown in Figure 1.

Figure 4.1. (a) TEM images, (b) Nitrogen absorption-desorption isotherms and pore size distribution plots (inset), (c) XRD patterns and (d) XPS spectra of F-doped TiO_2 nanoparticle, (e) UV-vis absorption spectroscopy of the P25 film and F doped TiO_2 .

The incident photon-to-current efficiency (IPCE) spectra of the cell made from P25 (Device 1) and F-doped TiO₂ (Device 2), sensitized with **Z907** dye, are shown in Figure 4.2(a).

The two spectra are similar in the range of 400–700 nm due to the approximately equal amount of dye adsorption in the two cells as shown in Table 4.1. The maximum IPCE value at 530 nm of Device 2 is 57 % while that for Device 1 is 54%.

Figure 4.2. (a) Incident-photon-to-current conversion efficiency and (b) Current density–voltage curve of a DSSCs based on P25 and F-doped TiO₂ photoanodes, respectively, under AM 1.5G-one sun light intensity condition.

The *J*-*V* characteristics for both devices under 100 mW/cm² illuminations and in the dark condition are shown in Figure 4.2(b). Device 2 has a photo-to-current conversion efficiency (PCE) of 6.30% with short-circuit current density (*J*_{sc}) of 12.80 mA/cm², open-circuit voltage (*V*_{oc}) of 0.757 V and fill factor (*FF*) of 65.0%. The conversion efficiency (*η*) of device 2 is ~1.13 times higher than the control device (device 1) due to the higher *V*_{oc} and *FF* values.

*J*_{sc} strongly depends on the amount of dye adsorption on TiO₂. After normalizing for dye adsorption, the photo-current per molecule (Table 4.1, *J*'_{sc}) for Device 2

(2.51×10^{18} mA mol⁻¹) is higher than that of Device **1** (2.40×10^{18} mA mol⁻¹). The higher J_{sc} probably derives from faster electron injection rate at the dye/TiO₂ interface, which is confirmed by the higher IPCE value of Figure 4.2(a).¹ The faster injection rate can be attributed to the following factors: (i) the addition of F atom into TiO₂ could induce generation of O-vacancy and Ti³⁺, which could improve the charge injection, according to theoretical calculations.^{2,15-17} (ii) F⁻ ions doped on the TiO₂ crystal surface may lead to dye dissociation due to strong F...H-O (**Z907**) bond, which also makes electron injection faster.² Besides, on the basis of the previously reported results,¹⁵ the Ti_{6c}³⁺ (6c referring to 6-fold-coordinated Ti ions) introduced by F-doping and Ti_{6c}³⁺-OH species associated with H-doping may play an important role in injected electron-transfer and electron transport.^{2,15-17} The potential of Ti_{6c}³⁺ and Ti_{6c}³⁺-OH is 0.3 eV and 0.4 eV, respectively, below the conduction band (CB) of TiO₂. Being closest to the CB, these levels can aid trapping/detrapping events, thus enhancing the electron transport in TiO₂. Since J_{sc} is intimately dependent on electron injection and electron transport,^{2,4} these effects combine to give, as a consequence, a higher photocurrent per molecule in Device **2** in comparison with the reference device **1**.

V_{oc} is proportional to the potential difference between the Fermi energy of TiO₂ and the redox potential of electrolyte, which can be written as Equation (3):¹⁸

$$V_{oc} = \frac{k_B T}{e} \ln\left(\frac{n}{n_0}\right) \quad (3),$$

where $k_B T$ is the thermal energy, e is the elementary charge, n is the free electron concentration and n_0 is the concentration in the dark. Clearly, the recombination rate and the Fermi level of TiO₂ are the major factors affecting the open-circuit voltage obtained at any light intensity.^{1, 20-22} Presence of F dopants causes TiO₂ Fermi level to shift to a more negative position (refers to NHE),²³⁻²⁴ which leads to an increased

potential difference between TiO_2 and the electrolyte and thus a larger V_{oc} for device **2**. V_{oc} increase can also be attributed to the retardation of the dark current, as shown in Figure 4.3(b). The fill factor of device **2** is significantly increased which might arise from the decrease of the internal series resistance (R_s) and the increase of shunt resistance (R_{sh}). The addition of fluorine into the titania can suppress the electron scattering in the grain boundary²⁵ and thus increase the conductivity of the film which lowers the R_s .

Table 4.1. The performance parameters of solar cells based on different TiO_2 electrodes.

Device	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	Absorbed dye ^a (mol/cm ²)	BET surface area (m ² /g)	J'_{sc} (mA/mol)
1	12.93	0.696	62.0	5.57	5.39×10^{-8}	50 ^b	2.40×10^8
2	12.80	0.757	65.0	6.30	5.11×10^{-8}	36.88	2.51×10^8

^aThe dye adsorbed on TiO_2 film was desorbed by a 0.1 M NaOH solution (water: ethanol 1:1 v/v) for 24 hrs. ^bThe BET surface area of commercial P25 was provided by the supplier.

Table 4.2. Parameters determined by EIS measurements in this study.^a

Device	R_k (Ω)	τ (ms)	k_{eff} (S ⁻¹)	D_{eff} (cm ² s ⁻¹ x10 ⁻⁵)	L_n (μm)
Device 1	56.56	12.07	10.0	16.9	14.28
Device 2	24.68	15.92	13.2	22.3	18.84

^aEIS was measured with 13 μm thick TiO_2 nanoparticle film.

Since electrochemical impedance spectroscopy (EIS) could address issues such as the effects of electron transport in the TiO_2 network, electron recombination between the injected electron and the redox electrolyte (I_3^-) and electrolyte diffusion in the TiO_2 electrode,¹⁹⁻²² in this work we carried out EIS measurements to investigate the TiO_2 /dye/electrolyte interfacial charge transfer kinetics. As shown Figure 4.3(a) and

Table 4.2, device **1** and **2** show typical Nyquist plots at an applied bias of open circuit voltage in illumination (100 mW/cm^2) condition. Scheme 4.1 shows the equivalent circuit to fit the EIS of the devices.

Scheme 4.1. Equivalent circuit used to fit Nyquist plots of the devices in this study.

Three semi-circles exist in the region for both cells. The first semicircle in the high-frequency region ($>100 \text{ Hz}$) is attributed to the redox reaction of I^-/I_3^- at the Pt/electrolyte interface; the intermediate semicircle (in the $10\text{-}100 \text{ Hz}$ range) indicates the electron transfer at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface and the third one in low frequency range ($<10 \text{ Hz}$) is attributed to the diffusion of the electrolyte. The charge transfer resistance (R_k) at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface obtained from the intermediate semicircle is 56.56 and 24.68Ω for device **1** and **2**, respectively. The electron lifetime, τ , in the device can be estimated by Equation (4):

$$\tau = \frac{1}{2\pi f_{\max}}, \quad (4),$$

where $f_{\max}$ is the maximum frequency of the middle-frequency peak from Bode curve in Figure 4.3(b). The electron lifetime is calculated to be 12.07 and 15.92 ms for Device **1** and **2**, respectively. The longer electron lifetime for device **2** implies that electron recombination at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface is effectively reduced.²⁶ L , k_{eff} , D_{eff} and L_n represent the thickness of the film, reaction rate constant for the recombination, effective electron diffusion coefficient and effective carrier diffusion length, respectively. D_{eff} and L_n can be determined by this equation;

$$D_{eff} = \left(\frac{R_k}{R_w}\right) L^2 k_{eff} \quad L_n = \sqrt{D_{eff} \times \tau} .$$

The values for these parameters can be estimated based on Bisquert model²¹ from Nyquist and Bode plots as shown in Table 4.2 and the equivalent circuit. The L_n of device **2** is ~3.2% higher than that of device **1**, which is consistent with its higher J_{sc} . The low resistance and long electron lifetime indicate that the back reaction from TiO₂ conduction band electrons to I₃⁻ in the electrolyte is retarded and the interfacial charge transfer rate is also increased, leading to a higher FF and V_{oc} . In comparison, in N-doped cells, retardation in charge recombination, resulting from the decrease of the O-vacancy, is obtained at the cost of poor electron injection.⁸ In our case of F-doped TiO₂ electrode, enhanced electron injection, improved transport, and decreased charge recombination are obtained concurrently.

Figure 4.3. Electrochemical impedance spectra of devices based on P25 and F-doped TiO₂ as photoanode (a) Nyquist plots and (b) Bode curves under the under the illumination condition (c) Steady-state cyclic voltammograms of two devices.

To investigate the effect of the electrolyte diffusion on charge transport, we measured the steady-state current-voltage curve (Figure 4.3(c)), the results of which are analyzed using the diffusion-limited current density (j_{lim}), Equation (5):

$$j_{lim} = \frac{2n F D_{I_3^-} c_{I_3^-}}{l} \quad (5),$$

where F is Faraday's constant ($96,484 \text{ C mol}^{-1}$), $C_{I_3^-}$ is the concentration per volume unit of I_3^- , $D_{I_3^-}$ is the diffusion constant of I_3^- , n is the number of electrons transported in the each reaction (in general, $n=2$) and l is the distance between the electrodes).²⁷⁻²⁸ The analysis yields a diffusion constant of I_3^- ($D_{I_3^-}$) for device **2** ($1.34 \times 10^{-6} \text{ cm}^2/\text{s}$), similar to that of device **1** ($1.25 \times 10^{-6} \text{ cm}^2/\text{s}$), expectedly, since F doped TiO_2 should not have a measurable impact on electrolyte diffusion. These results reveal that F-doped TiO_2 as photoanode can significantly boost electron mobility due to the decrease of carrier scattering at grain-boundaries and surface-defects, while retarding charge recombination in the device.

4.3. Conclusion

In summary, we have prepared F-doped TiO_2 nanoparticle as photoanode for DSSCs and investigated the photovoltaic and electrochemical properties of the devices. The overall conversion efficiency of the F-doped photoanode is enhanced up to ~ 1.13 times compared with a control device made from commercial P25 powders, primarily due to an increased V_{oc} and FF . The amount of absorbed dye of F-doped TiO_2 is lower than that of P25; however, the photo-current per molecule for F-doped TiO_2 is higher than that of commercial P25. Therefore, the results reveal that this kind of mesoporous TiO_2 spheres used as photoanode might retard charge recombination, enhance electron transport due to the decrease in grain-boundary scattering, and improve charge injection between the dye and TiO_2 interface.

4.4. Experimental Section

Materials

Titanium (IV) fluoride was purchased from Sigma-Aldrich. Titanium(IV) *i*-propoxide (TTIP, 98 %) was purchased from Sterm Chemicals. Absolute ethanol (AR, Fisher Scientific) was used for the synthesis.

4.4.1. Preparation of F-Doped TiO₂ Spheres

Typically, Titanium (IV) *i*-propoxide (TTIP, 2.0 mmol) and (Titanium (IV) fluoride 0.16 mmol was added as F source) were dissolved in 15 mL of ethanol. The mixture was stirred for 30 min to obtain a clear solution and was hydrothermally reacted at 180 °C for 24 hrs. The light blue precipitate was cooled to room temperature, filtered and washed several times with ethanol. The filtered light blue powdery titanium oxide was then sintered at 500 °C for 2 hrs in air.

4.4.2. Synthesis of Titanium Oxide Gel

The paste was prepared according to the method as reported.²⁹ Briefly, ethylcellulose 200 cPa (0.3 g) and ethanol (5.0 mL) were stirred to form a clear gel. And titanium dioxide (0.6 g), acetic acid (0.1 mL), water (0.1 mL) and terpineol (2.0 g) were added into the mixture, and then stirred continually to form a homogenous white gel.

4.4.3. Preparation of Photoanode and Cell Assembly

Briefly, transparent conducting glass (SnO₂:F, FTO, 15 Ω/square, Solaronix) was cleaned in 0.1 M HCl solution and isopropyl alcohol using an ultrasonic bath for 30 min, respectively, and rinsed with water and ethanol. Then the FTO glass was immersed into 40 mM TiCl₄ solution at 70 °C for 30 min. Then 10.0 μm thick TiO₂ (Ti-Nanoxide T/SP, Solaronix) electrodes were prepared by doctor blading techniques

according to the method as reported.²⁴ To study the effect of F-doping on the interface in the electrode, 3 μm TiO_2 prepared (F-doped TiO_2 and commercial P25) in this study layer was coated on top of the without fluorine doped transparent TiO_2 film and then treated by 40 mM TiCl_4 solution at 70 $^\circ\text{C}$ for another 30 min and sintered at 500 $^\circ\text{C}$ for 30 min and then cooled to 80 $^\circ\text{C}$. The electrodes were immersed in 0.3 mM **Z907** in acetonitrile/*tert*-butyl alcohol (1:1) for 15 hrs, and then rinsed with acetonitrile. Platinum counter electrodes were prepared by E-beam evaporation on the FTO glass. Then dye-adsorbed TiO_2 electrode and counter electrode were stacked and sealed with 60 μm thermal-plastic Surlyn spacers at 115 $^\circ\text{C}$ for 12 s and the areas of the electrodes were around to be 0.16 cm^2 . The ionic liquid electrolyte (EL-HPE) was introduced into the sandwich cells. We name this corresponding cell as device **2** and the cell based on commercial P25 as photoanode as device **1**.

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Chapter 5. Enhancement of Photogenerated-Electron Transport in Dye-Sensitized Solar Cells with Introduction of Reduced Graphene Oxide-TiO₂ Junction

5.1. Introduction

Low-cost, highly efficient and stable energy sources, such as solar cells, are vital commodities in the energy crisis.¹ Dye-sensitized solar cell (DSSCs) is one of the most promising alternatives to the conventional inorganic semiconductor photovoltaic devices, which attracted considerable research interest during the past decade.¹⁻⁵ The best cell performance with a power conversion efficiency (PCE) of 11.2% was obtained from the *cis*-di(thiocyanato)bis(2,2'-bipyridyl-4,4''-dicarboxylate) ruthenium(II) (**N719**) sensitized solar cells.⁶⁻¹⁴ However, the **N719** dye containing the rare metal ruthenium is environmental unfriendly, of high cost, and not mass productive. These disadvantages limit its practical application.

To date, various metal-free organic dyes have been investigated, mainly based on the concept of donor-bridge-acceptor (D-B-A) system, generally, in which the dye molecules consist of coumarin or triphenylamine, conjugated systems, and cyanoacrylic acids, used as donors, bridge groups, and acceptors, respectively. However, compared with **N719**, this type of dyes yields a lower efficiency due to a lower photocurrent induced.⁶ Probably, the reason is that the electron injection of metal free dye is inferior to that of the ruthenium dye due to the short emission lifetime of the excited states and the insufficiency of valid charge separation.⁷⁻¹⁴ To improve the performance of the organic DSSCs, new materials and novel device fabrications need to be thoroughly explored.

At present, many approaches have been attempted to improve the overall efficiency of DSSCs, such as exploration of new dyes to extend the solar irradiation absorption to the infrared and near infrared regions,⁹⁻¹⁴ prevention of the dye molecules aggregation by introducing long alkyl chains,^{7,8} enhancement of sun-light harvesting by introduction of large TiO₂ nanoparticles as scattering layers on top of transparent TiO₂ films,¹⁵⁻²² and facilitation of interfacial charge-transfer by formation of a Schottky barrier between the photoanode and dye molecules through sandwiching a proper Au layer or by shifting the semiconductor's Fermi level to more negative potentials through the metal doping.^{17,18,23}

Graphene, a single atomic layer of graphite, has remarkably high electron mobility with a Fermi velocity of 10⁶ m/s, good stability and high transparency at room temperature,²⁴⁻²⁷ making it a suitable substitute to improve the overall conversion efficiency of DSSCs. Recently, the reduced graphene oxide (rGO), one type of graphene derivatives, has been used as transparent electrodes in various photovoltaic devices, such as DSSCs,²⁸ organic^{29,30} and hybrid solar cells.³¹

To the best of our knowledge, till now, no one has reported the use of rGO sheets to form the functional junction with semiconductors to improve the performance of solar cells. Herein, we report a novel and facile method to enhance the photo-current and fill factor of an organic DSSCs by introduction of a rGO layer between TiO₂ and dye to form the rGO-TiO₂ junction.

5.2. Results and Discussion

5.2.1. Preparation and Characterization of rGO/TiO₂ Films on FTO

The reduced graphene oxide (rGO) sheets were dispersed in water (concentration: 0.1 mg/mL) by reduction of the exfoliated graphene oxide (GO) sheets with hydrazine

at 80 °C for 2 hrs.³²⁻³⁴ The size of obtained rGO sheets is about several micrometers, as measured by AFM (Figure 5.1A). The Raman spectrum of rGO gives peaks at 1357, 1587, 2712 and 2944 cm^{-1} , which could be assigned to the D band, G band, 2D mode and S3 (D and G coupled) mode, respectively (Figure 5.1B). A higher peak intensity of the D band as compared with the G band is induced by more small sp^2 domains of aromaticity formed during the reduction process.³² The organic dye sensitizer, 5-(4-(bis(4-methoxyphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (**D1**) was synthesized according to the previous report.³⁵ Its structure and UV-Vis absorption spectrum in chloroform are shown in Figure 5.1C and 5.1D, respectively. In Figure 5.1D, the absorption peak at ~500 nm gives a red shift, as compared with 462 nm reported previously,³⁵ which is attributed to the solvent effect.

Figure 5.1. (A) $5 \times 5 \mu\text{m}^2$ AFM image; (B) Raman spectrum of rGO sheets on SiO_2 wafer; (C) The molecular structure and (D) UV-Vis absorption spectrum of the dye **D1**.

By using the doctor-blading technique, TiO_2 nanoparticles (casual size of ~13 nm, Solaronix, Switzerland) were first coated on the FTO substrate (Figure 5.2A) to form

10 μm thick film, referred to as TiO_2/FTO (Figure 5.2B, 5.3A). The rGO aqueous solution was sprayed onto the TiO_2/FTO substrate, which was kept at 120 $^\circ\text{C}$, to form a layer of rGO film. The coverage of rGO on TiO_2 is dependent on the amount of the sprayed rGO solution. If a small volume of the rGO solution (0.1 mL) was applied, the TiO_2 film was only partially covered by the rGO sheets and the uncovered TiO_2 particles are observed (Figure 5.3B). After increasing the coating volume of the rGO solution to 0.3 mL, the TiO_2 layer was fully covered by the rGO sheets (Figure 5.2C, 5.3C). However, if a larger amount of the rGO solution, *e. g.* 1.0 mL, was applied, a thicker but rougher rGO film was formed on top of TiO_2/FTO (Figure 5.2D, 5.3D).

Figure 5.2. $5 \times 5 \mu\text{m}^2$ AFM images of (A) TiO_2/FTO substrate and (B, C and D) rGO films coated on TiO_2/FTO substrates. The volume of rGO solution used in (B, C and D) is 0.1, 0.3 and 1.0 mL, respectively.

Raman spectrum was used to confirm the rGO films formed on TiO_2/FTO , after 0.3 mL of the rGO solution was sprayed, referred to as rGO (0.3 mL)/ TiO_2/FTO (Figure

5.4). The Raman spectra of TiO_2/FTO and $\text{rGO}/\text{TiO}_2/\text{FTO}$ showed the three similar peaks at 396 , 513 and 637 cm^{-1} , which can be assigned to the B_{1g} (ν_4), $\text{A}_{1g}+\text{B}_{1g}$ ($\nu_3+\nu_2$) and E_g mode (ν_1) from TiO_2 , respectively.³⁶⁻⁴¹ However, the Raman spectrum from $\text{rGO}/\text{TiO}_2/\text{FTO}$ shows two additional peaks at 1358 and 1589 cm^{-1} , which could be assigned to the D and G band³³ from the coated rGO layer, respectively.

Figure 5.3. SEM images of (A) FTO substrate; (B) TiO_2 film on FTO substrate; (C) and (D) fully covered rGO film on TiO_2/FTO substrate. The scale bar in (A, B, C and D) is 200, 200, 500, 200 nm, respectively.

Figure 5.4. Raman spectra of TiO_2/FTO and rGO (0.3 mL)/ TiO_2/FTO .

5.2.2. DSSCs Devices Based on rGO-TiO₂ Schottky Junctions

A detailed study of the effects of rGO films on the performance of DSSCs devices was carried out. In order to form a complete coverage and a relatively smooth rGO layer, the rGO/TiO₂/FTO photoanode was prepared by spraying 0.3 mL of the rGO solution onto TiO₂/FTO, *i.e.* rGO (0.3 mL)/TiO₂/FTO was obtained. It was noted that the thicker/rougher or partially covered rGO films coated on TiO₂/FTO result in a lower performance of DSSCs devices (see the photocurrent-voltage characteristics in Figure 5.5 and Table 5.1).

Figure 5.5. *I*-*V* curves (A) and IPCE spectra (B) of the DSSCs devices with TiO₂ photoanodes coated by rGO solution with different volumes, *i. e.* 0 mL (Device 1), 0.1 mL (Device 2), 0.3 mL (Device 3), 0.5 mL (Device 4) and 1.0 mL (Device 5).

After the TiO₂/FTO, used for the control experiment, and rGO (0.3 mL)/TiO₂/FTO photoanodes were immersed into the same **D1** dye solution for 1 h to load the dye molecules, the DSSCs devices were fabricated and tested under the same conditions (see Experimental Section for details). Figure 5.6 shows the current density-voltage (*I*-*V*) and incident photon-to-current efficiency (IPCE) curves for the TiO₂/FTO (Device 1) and rGO (0.3 mL)/TiO₂/FTO electrodes (Device 2). The obtained short-circuit

photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and overall conversion efficiency (η) are summarized in Table 5.2.

Table 5.1. Photovoltaic performances of solar cells by using different thickness of rGO-film-modified TiO_2 as electrodes.^a

Device No.	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
Device 1	16.4	0.597	52.0	5.09
Device 2	12.1	0.577	56.7	3.84
Device 3	18.2	0.576	57.9	6.06
Device 4	16.3	0.560	59.1	5.40
Device 5	14.6	0.553	59.9	4.84

^a 0 mL (Device 1), 0.1 mL (Device 2), 0.3 mL (Device 3), 0.5 mL (Device 4) and 1.0 mL (Device 5).

Figure 5.6. (A) IPCE spectra and (B) I-V curves of two DSSCs devices using TiO_2/FTO and rGO/ TiO_2/FTO as photoanode, respectively.

Table 5.2. Photovoltaic performances of solar cells device **1** and device **2**.^a

Device	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	Absorbed dye ^b (mol/cm ² × 10 ⁻⁸)
1	16.4	597	52.0	5.09	9.96
2	18.2	576	57.9	6.06	7.97

^a The active area of the photoelectrodes for DSSCs devices is kept at 0.16 cm². ^b The dye adsorbed on TiO₂ film was desorbed by a 0.1 M NaOH solution (water:ethanol 1:1 v/v) for 48 hrs.

As seen from Figure 5.6 and Table 5.2, device **2** shows a higher overall conversion efficiency (η) of 6.06%, due to high J_{sc} and FF values. Such overall conversion efficiency gives a net increase of 19.1% compared with η of 5.09% obtained in device **1**. Moreover, the IPCE peak value at 466 nm, referred to as IPCE₄₆₆ in the context, reaches as high as 97% for device **2**, an increase of 8.8% as compared with device **1**. This high photon-to-current conversion efficiency directly contributes to the high performance of the device **2**. A blue-shift of the peak in the IPCE (Figure 5.6A) compared to the absorption spectrum of dye **D1** (see Figure 5.1) is attributed to the *H*-aggregation,¹³ which mainly arises from the face-to-face π - π stacking between rGO and dye molecules.^{13,14} The enhancement of short circuit current (J_{sc}) and fill factor (FF) is probably attributed to the higher electron-transfer efficiency driven by the Schottky barrier since the amount of dye absorption for device **2** (7.97×10^{-8} mol/cm²) is lower than that of device **1** (9.96×10^{-8} mol/cm²) as shown in Table 5.2 and the improved interface contacts in dye/rGO/TiO₂ in the device, respectively.

Figure 5.7. (A) Schematic energy diagram of the DSSCs device with graphene-coated TiO₂ photoanode. Conduction band energy level, Fermi level of TiO₂, graphene and redox (I⁻/I₃⁻) are set at -4.0,⁴¹ -5.1,³⁶ -4.88,³⁹ and -4.85 eV,⁴⁰ respectively. The lowest transition energy band gap of dye is set at 2.8 eV.³⁵ (B) Schematic structure of graphene-TiO₂ junction. (C) Calculated effective potential distribution between TiO₂ and graphene.

In order to have an in-depth understanding of the experimental results, and in particular, the kinetics of the electron transport in the device, the energy potential profile of graphene-TiO₂ junction was calculated (note that graphene, instead of rGO, is used here in order to simplify the calculation, Figure 5.7), and the electrochemical impedance spectroscopy of the devices was measured (Figure 5.8).

The rGO sheets coated on TiO₂ show two characteristics: (i) high mechanic flexibility and (ii) a delocalized π - π interaction which is expected to facilitate the

perpendicular interlayer electron transfer between the closely stacked rGO sheets. The high flexibility of rGO sheets enables a tight contact between them and TiO₂ nanoparticles, thus effectively forming the rGO-TiO₂ junction, as shown in the energy diagram (Figure 5.7A).

In order to study the function of the designed rGO-TiO₂ junction in the device, based on the designed graphene-TiO₂ junction model (Figure 5.7B), the potential profile across the junction region was calculated by the first principle method based on non-equilibrium Green's function- density functional theory (NEGF-DFT) (see Experiment Section).⁴² From the calculation results (Figure 5.7C), the potential of graphene is found to be higher than that of TiO₂, indicating a potential drop to drive electrons from graphene to TiO₂ in this junction. In the case of relatively thicker rGO films, *e.g.* several layers of rGO in device **2**, their potential distribution is still well kept since the quasi-Fermi level of the thicker rGO layers will shift upward after the injection of the photo-generated electrons from the lowest unoccupied molecular orbital (LUMO) level of the dye molecules, which were absorbed onto rGO films through the π - π interactions.²³

As a result, in the dye/rGO/TiO₂ system, the electrons from the dye LUMO level will be transported easily to the conduction band of TiO₂ driven by the internal potential difference, thus enhancing the photocurrent of the device. This rGO-TiO₂ junction works as a Schottky barrier, which is also previously reported in the Au-TiO₂ based DSSCs devices.³³

Therefore, we believe that such a Schottky barrier between rGO and TiO₂ plays a key role in the enhancement of transport efficiency of the photogenerated electrons from the dye, resulting in the higher photocurrent density of 18.2 mA/cm² in device **2**.

Figure 5.8. Electrochemical impedance spectroscopy of the devices under light conditions: (A) Nyquist plots and (B) Bode plots.

The electrochemical impedance spectrum (EIS) provides understanding of electron transfer and recombination in the photoanode in DSSCs.⁴³⁻⁵¹ The Nyquist and Bode plots of the studied devices were obtained under the illumination condition measured at an open circuit bias (V_{oc} , the value is listed in Table 5.2). According to the previous report, the effective carrier diffusion length (L_n) reflects the degree of competition between charge transport and recombination in DSSCs.⁵ The value of L_n can be obtained from the equation, $L_n^2 = D_{eff} \times \tau$, where D_{eff} is the effective electron diffusion coefficient and τ is the electron lifetime. Based on the Bisquert model,⁵¹ D_{eff} is

described by the equation, $D_{eff} = (\frac{R_k}{R_w})L^2k_{eff}$ where R_w , R_k , L and k_{eff} represent the resistance of electron transport in photoanode, resistance of charge transfer related to recombination, thickness of the rGO/TiO₂ photoanode and constant of effective rate for recombination, respectively.

The values of these parameters can be estimated from the central arc of Nyquist and Bode plots, which represent the electrochemical characteristics. R_w is determined from the diameter of the middle semicircles of Nyquist plots in Figure 5.8A. k_{eff} is estimated from the maximum peak frequency (ω_{max}) in Figure 5.8B. R_k/R_w , k_{eff} , D_{eff} and the resultant L_n are shown in Table 5.3. As observed, the effective carrier diffusion length (L_n) of device **2** is ~14% higher than that of device **1**, which is consistent with the higher J_{sc} of device **2**.^{5,6} As shown in Table 5.2, the dye absorption for device **2** (7.97×10^{-8} mol/cm²) is even a bit lower than that of device **1** (9.96×10^{-8} mol/cm²), therefore, the higher photocurrent for device **2** is not attributed to higher dye loading compared with device **1**. This further confirms that device **2** can facilitate the charge transfer more efficiently driven by the rGO-TiO₂ Schottky barrier, as compared to device **1**.

Table 5.3. Parameters determined by EIS measurements in this study.^a

Device	R_k/R_w	$R_w(\Omega)$	k_{eff} (s ⁻¹)	τ (ms)	D_{eff} (cm ² s ⁻¹ ×10 ⁻⁵)	L_n (μm)
1	8.9	33.8	10.2	98.0	9.1	29.9
2	11.6	12.1	63.2	15.8	73.3	34.0

^a EIS was measured with 10 μm thick TiO₂ nanoparticle film under 50 w halogen lamp (100 mW/cm²).

It has been reported that the fill factor (FF) of DSSCs is influenced by the series resistance arising from the internal resistance of the device.⁵²⁻⁵⁴ In Table 5.2, it is shown that when the rGO was sandwiched between TiO_2 and dye, the FF increased remarkably (by $\sim 11\%$). This can be attributed to a better interface contact between the structural layers of the rGO/ TiO_2 interface. The dye **D1** used here is an organic material containing benzene and thiophene aromatic structures (Figure 5.1C). Due to the introduction of rGO between dye and TiO_2 , the flexible rGO sheets connect well with TiO_2 layer, and they can strongly absorb dye molecules through the π - π interaction. As a result, the good interface contacts in dye/rGO/ TiO_2 enable the reduction of device resistance, leading to increase of the FF value. In addition, a slight lower V_{oc} in device **2**, compared with that in device **1**, is due to the increase of charge recombination rate induced by the unreduced carboxyl groups in rGO sheets after the chemical reduction with hydrazine.⁵⁵

The power conversion efficiency (PCE), η , is defined by $\eta = J_{sc} \times V_{oc} \times FF / P_{in}$, where P_{in} is the illumination power density, which is kept constant during the measurement. In device **2**, although V_{oc} is slight fall-off, J_{sc} and FF increase remarkably. As a result, its PCE still rises to a high value of 6.06% compared with 5.09% in device **1**. This demonstrates that the DSSCs performance is greatly enhanced due to the formed Schottky barrier and the better interface contacts between active layer (dye) and semiconductor (TiO_2) after introduction of rGO film.

5.3. Conclusion

In conclusion, for the first time, rGO was introduced in DSSCs to effectively enhance the photocurrent and the fill factor, thus the overall conversion efficiency, due to the formation of rGO- TiO_2 Schottky barrier junction, the improvement of electron

transport and the interface contact between TiO_2 and active layer. The enhancement of short circuit current (J_{sc}) and fill factor (FF) of rGO/ TiO_2 based DSSCs reaches 11.0% and 11.3%, respectively, compared with DSSCs without rGO. Accordingly, the overall conversion efficiency (η) of DSSCs increases by 19.1%, from 5.09 % for the device based on the pure TiO_2 electrode (without rGO film) to 6.06 % for the device with rGO/ TiO_2 as the photoanode. Our approach for the formation of rGO-based Schottky junction allows one to design and construct functional solar cells with high sunlight-harvesting efficiency. We believe that such rGO-semiconductor junction might be widely used to other optical electronics.

5.4. Experimental Section

5.4.1. Fabrication of DSSCs

TiO_2 nanoparticle (Nanoxide T/SP, Solaronix, Switzerland) based thin film electrode was prepared on a transparent, conducting glass substrate ($\text{SnO}_2\text{:F}$, FTO, 15 Ω /square, Solaronix, Switzerland) by using the doctor-blading technique which was reported previously.⁵⁶ The resulting TiO_2 films with thicknesses of 10 μm , measured by the profiler (TENCOR P-10 Surface Profiler, California, U. S. A.). The rGO/ TiO_2 /FTO photoanodes were prepared by spraying different volumes of rGO aqueous solution onto TiO_2 /FTO substrates, which were kept at 120 $^\circ\text{C}$, to form a layer of rGO film on the top of TiO_2 /FTO. After that, the TiO_2 /FTO (used for the control experiment) and rGO/ TiO_2 /FTO photoanodes were immersed in 0.5 mM chloroform solution of **D1** for 12 hrs. After washing with chloroform, the sensitized electrode was covered with platinized conducting glass (400 $\text{\AA}$ Pt coated by e-beam evaporation on the glass) as a counter electrode. These two electrodes were bonded tightly with 60 μm thermal-plastic Suryln spacers and the areas of the electrodes were

around 0.16 cm^2 . The ionic liquid electrolyte (EL-HPE dyesol) was introduced into the sandwich cells to form the DSSCs devices.

5.4.2. Theoretical Calculation

The simulation was done by the first principle method of nonequilibrium Green's function - density functional theory (NEGF-DFT).⁵⁷⁻⁵⁹ In the calculation, a double-zeta-polarized linear combination of atomic orbitals (LCAO) defined basis set is used. This approach enables matrix calculations in the space of atomic orbitals. The junction was constructed by two layers of graphene and a small piece of anatase TiO_2 crystal. The crystal direction of TiO_2 is [001]. The bond length of both TiO_2 and graphene is assumed to be unchanged during optimizing the junction distance between the TiO_2 crystal and graphene. A self-consistent field (SCF) calculation was performed and then the potential of such structure was then determined.

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Chapter 6. Hollow SnO₂ Light-Scattering Layer Used For Dye-Sensitized Solar Cells

6.1. Introduction

Dye sensitized solar cells (DSSCs) have received considerable research interest due to its low cost, simple fabrication process and relatively high conversion efficiency.¹⁻³ It is well accepted that the performance of DSSCs can be dominated by several factors, such as the light harvesting ability of dyes, the electron transport rate at the semiconductor interface and the diffusion velocity of electrolyte. To reduce the usage of the dye without loss of the conversion efficiency of DSSCs, the light scattering layer was introduced into the DSSCs.⁴⁻⁵ In general, submicrometer/micrometer scale TiO₂ particles have been widely employed as light scattering layer to enhance the photon path length.⁴⁻⁶ ZnO as a scattering layer was also reported to enhance light harvesting.⁷⁻¹⁰

Compared to TiO₂, SnO₂ has a faster electron diffusion rate due to its higher electron-mobility (125–250 cm²V⁻¹S⁻¹; TiO₂, 10⁻⁵ cm²V⁻¹s⁻¹)^{11,12}. In addition, SnO₂ has other unique advantages that make it a suitable candidate as a DSSCs photoanode. For instance, the larger band gap of SnO₂ (3.6 eV) as compared to TiO₂ (3.2 eV) could facilitate the long-term stability of the device owing to fewer oxidative holes in the semiconductor's valence band in the photoanode.¹³⁻¹⁵ In addition, SnO₂ can act as a reflective layer, improving photocurrent density and efficiency due to the Mie scattering effect.⁵⁻⁶ However, only a few SnO₂ nanostructure based DSSCs have been reported and the efficiency is rather low.^{13,15} Qian *et al.* reported that the successful use of TiO₂ coated SnO₂ hollow microspheres as a bifunctional photoelectrode material in DSSCs in improving the overall efficiency.¹³

Herein, we report on bilayer DSSCs employing hollow SnO₂ microspheres as the top layer and TiO₂ as the bottom layer. This scattering layer is expected to enhance light-harvesting. At the same time, this hollow mesoporous structure can facilitate redox mediator diffusion, and thus the positive charges can be transported more readily than in the typical porous layer. As a result, this type of photoanode will improve the utilization of dye molecules adsorbed on scattering layer due to the electron-generation and speed up the electron transport properties. The hollow SnO₂ microspheres were synthesized by the hydrothermal method. The power conversion efficiency (PCE) of the bilayer DSSCs was found to be 4.15%.

6.2. Experimental Section

Materials

All chemicals were obtained from Sigma-Aldrich except *cis*-Bis(isothiocyanato) (2,2'-bipyridyl-4,4'-dicarboxylato) (4,4'-di-nonyl-2'-bipyridyl) ruthenium(II) (**Z907**) and electrolyte (EL-HPE), which were purchased from Dyesol Company.

6.2.1. Synthesis of Tin Oxide

SnO₂ was synthesized using similar method as reported.¹⁶ Briefly, Tin (IV) chloride (1.75 g), D-(+)-glucose (1.71 g) and deionized water (10 mL) with sulfuric acid (1 mL or 5 mL, 1 M) were mixed and the samples were synthesized under hydrothermal condition at 190 °C for 24 hrs.

As previously reported,¹⁷ owing to sulfonation process, both the thickness of hydrophilic shells and the size of microspheres increased with increasing the sulfuric acid content in the reaction system.

6.2.2. Synthesis of Tin Oxide Gel

Ethylcellulose 200 cPa (0.5 g) and ethanol (5 mL) were stirred to form a clear gel. Tin oxide (0.1 g) and terpineol (0.4 g) were then added into the mixture and then stirred continually to form a homogenous white gel.

6.2.3. Preparation of Photoanode and Cell Assembly

A 13.0 μm thick film of TiO_2 (Ti-Nanoxide T/SP, Solaronix) and 3.0 μm thick film of SnO_2 was deposited on FTO glass (SnO_2 : F, Solaronix) with screen printing method. The SnO_2 film was applied on top of the TiO_2 film as a scattering layer. The electrode was then calcinated at 500 $^{\circ}\text{C}$ for 30 min and then cooled to 80 $^{\circ}\text{C}$. The electrode was then immersed into 0.3 mM **Z907** acetonitrile/tert-butyl alcohol (1:1) solution for 15 hrs. Subsequently, the dye loaded photoanode and Pt counter electrode (400 $\text{\AA}$ Pt fabricated by e-beam evaporation) were sealed together with 60 μm thermal-plastic Suryln spacers. EL-HPE was introduced into the cell. The area of the electrode was around 0.16 cm^2 . The thickness of the film was measured by TENCOR P-10 Surface Profiler.

6.3. Results and Discussion

6.3.1. Morphology and Structure Characterization of Photoanode

Figure 6.1a and b show the scanning electron microscopy (SEM) images of the bare TiO_2 film and $\text{TiO}_2/\text{SnO}_2$ film. It can be seen that the SnO_2 microspheres are uniformly dispersed on the top layer. Figure 6.1c and d show the transmission electron microscope (TEM) images of two kinds of SnO_2 microspheres. It is clear that both SnO_2 microspheres have hollow structures with inner sphere diameters of 200 and 600 nm, respectively. It has been reported that this hollow structure is beneficial in

enhancing light harvesting due to multiple light reflecting and scattering in DSSCs.³⁻⁵

Figure 6.2 shows the cross-sectional SEM images of $\text{TiO}_2/\text{SnO}_2$ in this study which confirms that the TiO_2 bottom layer and the SnO_2 top layer were deposited. Figure 6.3a shows the XRD spectra of the 200 and 600 nm SnO_2 hollow microspheres. It can be seen that all the diffraction peaks of SnO_2 hollow microspheres are in good agreement with the rutile structure of SnO_2 (JCPDS No.41-1445).¹⁶

Figure 6.1. SEM images of (a) TiO_2 film (b) TiO_2 coated with 600 nm SnO_2 film. TEM images of (c) 200 nm SnO_2 hollow microspheres (d) 600 nm SnO_2 hollow microspheres.

Figure 6.2. SEM cross profile of transparent film and scattering layer in this study.

Figure 6.3b shows the nitrogen adsorption and desorption isotherms of the 200 and 600 nm SnO₂ powders. The BET surface areas for the 200 and 600 nm SnO₂ are 25.8 cm²/g and 93.5 cm²/g, respectively. At high relative pressures (0.8~1.0), the isotherms curves exhibit a hysteresis loop (types IV, BDDT classification), indicating the presence of mesopores (type IV) in the two powders.¹⁸⁻²⁰ This can facilitate the transportation of electrolyte and the reduction of the dye in DSSCs.²¹ The dye molecules adsorbed on cells A, B and C were desorbed using a 0.1 M NaOH solution (water: ethanol 1:1 v) for 24 hrs. The amount of dye adsorbed on cells A, B and C is calculated to be 6.6, 6.9 and 7.3 ×10⁻⁶ mol/cm² respectively. Figure 6.3c shows the reflectance measurement of TiO₂, TiO₂/SnO₂ (200 nm), and TiO₂/SnO₂ (600 nm). It can be seen that the reflecting light in hollow SnO₂ is higher than TiO₂. TiO₂ nanoparticles have very weak reflectance, and the light scattering effect is usually ignored due to their size being smaller than 30 nm.²² Therefore, hollow SnO₂ can produce a greatly enhanced light harvest due to light multi-reflections and scattering.

6.3.2. Photovoltaic Performances of DSSCs

The IPCE results were shown in Figure 6.4a. It can be observed that IPCE as high as 81% was obtained at 516 nm for cell **B**. The increment in IPCE for cell **A** and **B** were primarily due to the light scattering effect of SnO₂ hollow microspheres in the DSSCs as the amount of dye absorption for the cell **A** and **B** is lower than that of cell **C**. Figure 6.4b and Table 6.1 show *I-V* characteristics of cells **A**, **B** and **C** at 100 mW/cm² (AM 1.5G). Cell **A** has conversion efficiency (η) of 4.05 % with short-circuit current density (J_{sc}) of 8.83 mA/cm², open-circuit voltage (V_{oc}) of 0.679 V and fill factor (FF) of 67.6%. Using 600 nm SnO₂ hollow microspheres coated TiO₂ as the photoanode (cell **B**), the η of cell **B** reaches 4.15% with $J_{sc} = 9.36$ mA/cm², $V_{oc} = 0.662$

V and $FF = 67.0\%$.

Table 6.1. DSSCs performance parameters of various cells.

Cell	J_{sc} (mA/ cm ²)	V_{oc} (V)	FF (%)	η (%)
A	8.83	0.679	67.6	4.05
B	9.36	0.662	67.0	4.15
C	9.23	0.706	53.6	3.49

Compared to control cell **C**, the PCE of cell **B** has improved by 19%, which is due to the increased values of J_{sc} and FF . As mentioned above, the amount of dye adsorbed on cell **A** and **B** did not increase with the SnO₂ layer, therefore, the improvement in photocurrent is possibly attributed to the multiple light reflecting and scattering in DSSCs due to the presence of the hollow structures^{1,7-10,13,22-24} rather than the amount of dye adsorbed on the photoanodes. J_{sc} values of different cells are in agreement with the IPCE values as shown in Figure 6.4a.

Figure 6.3. (a) XRD pattern of 200 and 600 nm SnO₂ hollow microspheres; (b) The nitrogen adsorption and desorption isotherms of 200 and 600 nm SnO₂ powders; (c) Reflectance spectra of TiO₂/SnO₂ (200 nm), TiO₂/SnO₂ (600 nm), and TiO₂.

Moreover, according to the previous results, these devices consisting of a mixture of tin (IV) and titania could enhance the photocurrent, which is attributed to the fact that the contribution to J_{sc} from SnO_2 is more effective in contrast with TiO_2 due to effective electron separation in SnO_2 semiconductor.²⁵ In addition, the good FF is another important factor for the high efficiency. Fill factor is enhanced by 26% as compared to that without SnO_2 scattering layer due to the decrease in series resistance (R_s).²⁵ The open circuit voltage decreases in the order of cell **C** > **A** > **B**, which can be related to the dark current.²⁶⁻²⁷

Figure 6.4b also shows the I - V characteristics of the cells in dark conditions. The open-circuit voltage onset decreases in the order of cell **C** > **A** > **B**, which means the electron recombination between photoanode and electrolyte increased as compared to cell **C** (pure TiO_2 as the photoanode) owing to the less compact and dense oxide layer which causes electron loss in the photoanode.¹⁴

Figure 6.4. (a) IPCE spectra; (b) I - V characteristics of cell **A**, **B** and **C** measured, under simulated solar illumination (AM 1.5, 100 mW/cm^2) in iodide electrolyte.

6.3.3. Diffusion Constants and EIS Measurements

To reveal the kinetics of interfacial reactions of photo-excited electrons in DSSCs, we measured EIS spectra of the as-prepared DSSCs. Figure 6.5a shows the steady-state current-voltage curves of sample **A**, **B** and **C**. The diffusion-limited current density (j_{lim}) equation (1) is shown as follows,²⁷ (1)

$$j_{lim} = \frac{2nFD_{I_3^-}c_{I_3^-}}{l} \quad (1),$$

where F is Faraday's constant (96484 C/mol), $C_{I_3^-}$ is the concentration per volume unit of I_3^- , $D_{I_3^-}$ is the diffusion constant of I_3^- , n is the number of electrons transported in each reaction (in general, $n = 2$) and l is the distance between the electrodes.

Figure 6.5. (a) steady-state current-voltage curves of cell **A**, **B** and **C**; (b) Nyquist plots of cell **A**, **B** and **C** under the illumination condition. The electric circuit is shown in the inset of Figure 6.5b.

The diffusion constants of I_3^- (D_{eff}) cell **A**, **B** and **C** are estimated to be 2.0×10^{-6} , 2.9×10^{-6} and 1.6×10^{-6} cm²/s respectively. Cell **B** has the highest diffusion constant among the three cells, which can be beneficial to the charge transfer in cell **B**.

Figure 6.5b shows Nyquist plots of cells **A**, **B** and **C** at an applied bias of V_{oc} and a frequency range from 10^{-1} Hz to 10^6 Hz, with AC amplitude of 10 mV under the

illumination of one Sun (AM 1.5 G, 100 mW/cm²). It can be seen that two semicircles were observed, one in the high-frequency region (>1k Hz) and another in the middle-frequency region (10-100 Hz). It was reported that the middle-frequency peak reflects the properties of the photoinjected electrons with the oxide semiconductor, which can be fitted to a transport resistance (R_w) and a constant phase element. The high-frequency peak can be fitted to a charge-transfer resistance (R_{ct}) and the chemical capacitance, which due to the charge transfer at the interfaces of the redox electrolyte/Pt counter electrode.²⁶⁻²⁸

According to the electric circuit shown the inset of Figure 6.5b, the R_w and R_{ct} can be obtained by Z-view software. The R_w values are 19.6, 17.7 and 21.4 Ω and the R_{ct} values are 4.03, 2.07 and 4.33 Ω for cells **A**, **B** and **C**, respectively. Therefore, cell **B** has the lowest value of R_w and R_{ct} among the three cells, indicating that more efficient charge transfer process occurs at the oxide/dye/electrolyte and electrolyte/Pt electrode interfaces.²⁶⁻²⁹ The increase of the conversion efficiency of the devices is probably ascribed to the rapid electron generation and transport in photoanode and the decrease of the series resistance. However, the use of hollow SnO₂ as a scattering layer cannot retard the charge recombination as shown in the illumination EIS spectra and J - V curves in dark conditions.

6.4. Conclusion

Z907 dye sensitized solar cell based on SnO₂ hollow microspheres was studied in this work. TiO₂/SnO₂/dye cell has a better performance than TiO₂/dye cell, which is attributed to the multiple light reflecting and scattering in the DSSCs by the presence of the hollow structure of SnO₂. This scattering layer could utilize the dye adsorbed onto the semiconductors more effectively and facilitate the photo-electron transport

across the semiconductor. From EIS and steady CV measurements, the devices with $\text{TiO}_2/\text{SnO}_2$ double layer showed a lower resistance and faster diffusion constant as compared to the device with pure TiO_2 , leading to the rapid electron generation and transportation in photoanodes with the decrease of the series resistance. As a result, a PCE of 4.15% was achieved for $\text{TiO}_2/\text{SnO}_2/\text{dye}$, which accounts for a 19% improvement as compared to the TiO_2/dye cell.

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Chapter 7. Fluorine Doped TiO₂ Hollow Spheres as Active Scattering Layer for High Efficiency Dye Sensitized Solar Cells

7.1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention as solar energy harvesting device because of their cost advantage in comparison with first generation solar cells.¹⁻⁵ In this type of solar cell, the semiconductor adsorbed by the dye transports electron to the counter electrode accompanied with the hole eliminated by the conducting materials in the electrolyte under illumination. Therefore, the semiconductor is crucial to improve the overall power conversion efficiency in DSSCs. Much effort has been devoted to increasing the surface area or the thickness of the photoanode to increase the photocurrent. In general, optimum electrode thicknesses are in the range of 10-15 μm . However, increasing continuously the thickness of the cells will augment the series resistances of the cells due to the increasing length of path-lengths between the electrons and the redox couple in the electrolyte. Thus, a scattering layer was introduced into DSSCs to enhance the photocurrent using less dyes sensitizers without sacrificing the conversion efficiency of the cell. Various types of scattering layers have been introduced such as photonic crystals and different metal oxide spheres etc.^{2,8-15} Caruso *et al.*² and Lee *et al.*⁹ reported that light harvesting can be enhanced using submicrometer sized TiO₂ due to Mie scattering. This optical scattering effect increases absorption path length of photons and improves the light confinement property in DSSCs.

For further improvement of the cell performance and in order to make full utilization of the scattering layer, the mesoporous TiO₂ should act as the light-

scattering center as well as the electricity-generation source. However, this heterogeneous double layer architecture composed of transparent and light-scattering TiO_2 could result in the additional interfacial resistance, arising from the poor contact. Furthermore, at the dye/ TiO_2 /electrolyte interface, charge recombination occurs owing to the physical contact between the electrolyte and the TiO_2 surface. Hence, it is also a necessary issue, in order to obtain excellent cell performance, to increase the electron transportation across the semiconductor interface and retard the electron recombination between the conduction band of TiO_2 and electrolyte in DSSCs.^{16,17}

Recently, studies have shown that an effective way to improve charge collection is by reducing the trap states in semiconductor *via* heteroatom-doping. This is because the reduction of trap states in the semiconductor increases the charge transfer and suppresses the electron recombination in the device.¹⁸⁻¹⁹ Hore *et al.*¹⁹ reported that hollow TiO_2 spheres facilitate the electrolyte diffusion in the DSSCs devices, which can also favour the carrier transportation due to faster regeneration of the redox shuttle at the platinized cathode.²⁰

Herein, we design a photoanode with F-doped TiO_2 hollow nanoparticles coated on the top of the transport TiO_2 nanoparticles. F-doped hollow TiO_2 were synthesized under hydrothermal conditions. A 0.97 at% F-doped hollow TiO_2 film was fabricated on the top of the TiO_2 transparent film and then sintered to form the compact multifunctional photoanode. The electron and electrolyte transfer in this photoanode were studied by electrochemical impedance spectra (EIS). The properties of optical scattering and trapping were demonstrated with finite-difference time-domain (FDTD) simulations. The results indicate that cell efficiency enhancement is mainly due to improvements in short-circuit current density, open-circuit voltage and fill factor compared with the control device (600 nm nanoparticle TiO_2 as scattering layer).

7.2. Results and Discussion

Figure 7.1 shows the morphologies of the different TiO₂ spheres in this study (nanoparticle, F-doped hollow structure TiO₂, named as NP-600, and F-HS TiO₂, respectively). NP-600, with 600 nm diameter, was composed of ~40 nm TiO₂ grains as shown in the transmission electron microscopy (TEM) image (Figure 7.1A) and the scanning electron microscopy (SEM) image illustrates that **NP-600** TiO₂ is a uniform microsphere structure with a trace amount of small microspheres. Figure 7.1B shows that **F-HS** TiO₂ is composed of *ca.* 3 μ m uniform spheres with fragmentized parts. The hollow shell contains loosely packed nanoparticles, several hundreds of nano-meters in size.

Figure 7.1. SEM images of TiO₂ microstructures (A) TiO₂ nanoparticles (**NP-600**), (B) F-doped TiO₂ hollow sphere (**F-HS**) and inset images are corresponding TEM images of TiO₂ microstructures.

X-ray diffraction patterns of NP-600 and F-HS TiO₂ are shown in Figure 7.2, which indicate that both NP-600 and F-HS TiO₂ are anatase TiO₂ phase (JCPDS 21-1272, space group $I4_1/amd$). The crystal size D is estimated according to the Scherrer equation, $D = \frac{0.89\lambda}{\beta \cos \theta}$,

where λ , β , θ , refer to X-ray wavelength (0.15418 nm), the half maximum width and the

Bragg angle respectively. D is calculated to be about 9.4 nm (NP-600) and 11.0 nm (F-HS), respectively, comparable to the sizes estimated from TEM images.

Figure 7.2. XRD patterns of **NP-600** and **F-HS** TiO_2 power.

Figure 7.3. XPS spectra of the F-doped TiO_2 hollow spheres.

The corresponding binding energy of F doped composites was investigated by X-ray Photoelectron Spectroscopy (XPS) as shown in Figure 7.3. Besides the peaks at 465.1 and 459.4 eV for Ti 2p_{3/2} and Ti 2p_{1/2}, the peaks at 530.5 eV and 685.3 eV are attributed to the O_{1s} and F_{1s} respectively, similar to previously reported results.^{18,22-23} The doping concentration of F is around 0.97 at% , estimated by XPS results. Brunauer–Emmett–Teller (BET) nitrogen gas sorption technique was employed to determine the surface areas of different morphologies of TiO₂. The typical isotherms and pore size distribution are shown in Figure 7.4. The specific surface area of NP-600 and **F-HS** TiO₂ is 50.26 m²/g and 77.83 m²/g, respectively. The pore size distribution shows the pore size of NP and FHS TiO₂ is *ca.* 40 nm and 30 nm respectively, using the Barret–Joyner–Halender (BJH) method. The porosity of **NP-600** and **F-HS** TiO₂ is 0.61% and 0.71% respectively, according to the equation (1),

$$porosity = \frac{V_p}{V_p + \frac{1}{\rho}} \times 100\% \quad (1), \text{ where } V_p \text{ is pore volume and } \rho \text{ is the density of titania}$$

(3.9 g/cm³),²³⁻²⁴ which indicate that this types of TiO₂ are capable of adsorbing large amount of dye molecules.

Figure 7.4. N₂ sorption isotherms and pore size distribution curves of different TiO₂ microstructures (inset).

To investigate the photovoltaic properties of the devices, we applied **NP-600** and **F-HS** TiO_2 as comparative scattering layers with the standard commercial transparent TiO_2 (from Solaronix) to form the mesoporous TiO_2 electrode. The incident photon-to-current efficiency (IPCE) curves for the devices are shown in Figure 7.5 (inset).

Figure 7.5. Current density–voltage and incident-photon-to-current conversion efficiency (inset) of DSSCs based on the different photoanodes under AM 1.5 G 100 mW/cm² conditions.

Compared with the control cell (device **NP-600**), device **F-HS** has higher IPCE values at 540 nm, especially over the visible light region (mainly 400 to 600 nm), which may be attributed to the Mie scattering effect and multiple reflections in the interior of the hollow structures^{2,9,12-13,16} since the amount of dye absorption for device **F-HS** is lower than that of device **NP-600**. Scattering was simulated by FDTD and shown in Figure 7.6. The 600 nm nanoparticle shows a backward scattering with wide angle, while the hollow spheres shows better light confinement in the structure which will facilitate light harvesting in the hollow structure.

Figure 7.6. The scattering images of **NP-600** (A) and **F-HS** (B) along the [100] incident light direction.

Table 7.1. The performance parameters of solar cells based on different TiO_2 scattering layer electrodes.^a

Devices	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η (%)	BET ($\text{m}^2 \text{g}^{-1}$)	Porosity (%)	Adsorbed Dye ^b (mol cm^{-2}) $\times 10^{-8}$
NP-600	10.46	0.742	68.5	5.32	50.26	61.4	4.27
F-HS	11.00	0.754	76.1	6.31	77.83	71.5	3.94

^aThe active area of the photoelectrodes was about 0.28 cm^2 . ^bThe dye adsorbed on TiO_2 film was desorbed by a 0.1 M NaOH solution (water:ethanol 1:1 v/v) for 24 hrs.

The photovoltaic properties (I-V curves) of the devices were studied under AM 1.5 (100 mW/cm^2) condition as shown in Figure 7.5. The short-circuit current densities (J_{sc}), open-circuit voltages (V_{oc}), and fill factors (FF), were summarized in Table 7.1. The overall conversion efficiency was obtained based on the equation (2),

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\% \quad (2), \text{ where } P_{in} \text{ is the incident radioactive flux. As shown in}$$

Table 7.1 and Figure 7.5, the overall conversion efficiency (η) of device **F-HS** is higher by about 19% compared with the device **NP-600**, which reaches 6.31% with a $J_{sc} = 11.00 \text{ mA/cm}^2$, $V_{oc} = 0.754 \text{ V}$ and $FF = 76.1\%$. As shown in Table 7.1, the amount of the dye-loading of devices **NP-600** is 1.1 times compared to that of device **F-HS**, hence the enhancement of η is not attributed to the amount of dye absorption. From other reports,²⁴⁻²⁷ the short circuit photo-current density mainly relies on these factors: (1) the intense light absorption capabilities of the electrode; (2) the amount of dye adsorption on TiO_2 and (3) the competition between the electron injection and the total recombination current. Thus, with the benefits from the enhanced the light harvesting for the hollow TiO_2 as scattering layer, J_{sc} of device **F-HS** is higher than that of device **NP-600**, in spite of the lesser amount of dye absorption for device **F-HS** resulting from the pore size of **F-HS** being less than that of **NP-600**. In addition, it is obvious that the dark-current of device **F-HS** was reduced (Figure 7.5) as compared with device **NP-600**, which will contribute to the increase in the charge collection. Moreover, the F dopants in the scattering layer photoanode bends the Fermi level of TiO_2 towards the energy band states near the conduction band, that is, the Fermi level of the TiO_2 has a negative shift, which scale refers to NHE. It is well known that in DSSCs, the driving force of electron mainly depends on the potential gradient.²⁴ Thus, the F-doped photoanode creates a more effective driving force which would lead to faster photo-generated carriers transfer. In addition, this void space structure facilitates the electrolyte shuttle flow in TiO_2 networks between the photoanode and the Pt counter electrode, which will be propitious to reducing the photocurrent loss owing to faster enough to regenerate the dye,²⁸ resulting in the enhancement of charge collection of the photoanode.¹⁶ Therefore, the J_{sc} of device **F-HS** is improved owing to

the synergistic effect of these factors. As commonly known, $V_{oc} = \frac{nkT}{q} \ln(\frac{I_L}{I_s} + 1)$, where kT/q is the thermal voltage, n is the weaker dependence of dark current on voltage, I_L is the photocurrent and I_s is the saturation current of the diode (typically 10^{-7} - 10^{-9} A).²⁹ The electron recombination at the TiO₂/electrolyte interface and the shift of conduction band of TiO₂ could affect the V_{oc} . Moreover, this band-edge shift is more significant than the increase in recombination rate.³⁰ From Figure 7.5(a), the dark current onset potential of device **F-HS** is larger than that of device **NP-600**, which means the dark current in device **F-HS** was suppressed compared with device **NP-600**. Therefore, these two factors, the negative shift of the TiO₂ semiconductor and the reducing of dark current, result in enhancement of the open-circuit voltage. Furthermore, F dopants in the scattering layer photoanode make a favourable contribution to electron transport by retarding recombination while significantly decreasing device resistance and provide additional charge carriers to TiO₂, enhancing conductivity.³¹⁻³³ This led to a fairly high fill factor value (76.1%) for device **F-HS**, an increase of 11.1% as compared with the device **NP-600**.

To further confirm the effects of electron transport in the TiO₂ network, electron recombination between the injected electron and the redox electrolyte (I_3^-), and electrolyte diffusion in the TiO₂ electrode, we carried out electrical impedance spectroscopy (EIS) measurements as shown in Figure 7.7 and Table 7.2. Figure 7.7 shows the EIS of the devices in this study. In the dark and forward bias (-0.69 V) condition, no electrons were injected into TiO₂ network from dye sensitizer, electrons were just transported through the interconnected TiO₂ nanoparticles, after which they then reacted with the redox electrolyte (I_3^-). Thus, the charge-transfer resistance at the TiO₂/dye/electrolyte interface (R_k) in the dark under forward bias is related to

recombination of electrons between the TiO_2 and the electrolyte. This was estimated from the middle semicircle ($1\text{-}10^2$ Hz) in the Nyquist plots.³⁴⁻⁴¹ The R_k values of device **NP-600** and **F-HS** were estimated to be $175.3\ \Omega$, and $385.4\ \Omega$, respectively. Device **F-HS** has a larger recombination resistance than device **NP-600**.

Figure 7.7. Electrochemical impedance spectra of devices based on **NP-600** and **F-HS** as photoanode under the illumination condition and in the dark condition (inset).

Table 7.2. Electrochemical Impedance Spectroscopy Measurements in this study.^a

Device	$R_w(\Omega)$	$\omega_k(\text{s}^{-1})$	$k_{eff}(\text{s}^{-1})$	$\tau(\text{ms})$
NP-600	10.4	102.7	16.7	61.1
F-HS	8.7	83.9	14.3	74.9

^a EIS spectra were measured with $16\ \mu\text{m}$ TiO_2 nanoparticle film ($13\ \mu\text{m}$ transparent TiO_2 film and $3\ \mu\text{m}$ the prepared film using the **NP-600** and **F-HS** under 50 w halogen lamp ($100\ \text{mW}/\text{cm}^2$) condition.

This means that device **F-HS** is better in retarding electron recombination between the injected electrons and the electrolyte. From the Nyquist plots under the illumination and open circuit voltage condition, the electron transport resistance (R_w), effective rate constant for recombination (k_{eff}), the frequency at the top of the media semicircle in the Nyquist plots (ω_{max}), effective electron diffusion coefficient (D_{eff}) and the mean electron life time (τ) are listed in Table 7.2, which were obtained based on Bisquert model.⁴⁰

The τ of device **F-HS** (74.9 ms) is larger than that of device **NP-600** (61.1 ms), which indicates that the electron recombination at the TiO_2 /electrolyte interface was suppressed as well as the intrinsic recombination was retarded between the grain and grain-boundaries of semiconductor for device **F-HS**.⁴¹ The low electron transport resistance and long electron life-time could result in faster electron transport and better charge-separation because the photoanode with F-doping reduces electron trapping. The semicircle in the low frequency (10^{-2} -1 Hz) region is related to the electrolyte diffusion and the impedance of electrolyte diffusion is decided by Nernst equation as

the follows,^{40b,c} $Z_n = \frac{W}{\sqrt{i\omega}} \tanh\left(\sqrt{\frac{i\omega}{K_N}}\right)$, where W is the Warburg parameter $W =$

$$\frac{kT}{n^2 e_0^2 c_{I_3^-} A \sqrt{D_{I_3^-}}} \text{ and } K_N \delta^2 = D_{I_3^-}; A \text{ is the electrode area, } e_0 \text{ is the elementary charge,}$$

k is Boltzmann constant, n is the number of electrons transported in the each reaction (in general, $n = 2$), T is the temperature, δ is the thickness of Nernst diffusion layer, which is the half of the distance between the electrodes).⁴⁰

The diffusion constant is $2.0 \times 10^{-6} \text{ cm}^2/\text{s}$ and $2.2 \times 10^{-6} \text{ cm}^2/\text{s}$ for device **NP-600** and device **F-HS**, respectively, which is comparable with the results from the diffusion-

limited current measurements and the diffusion-limited current density (j_{lim}) was obtained according to this equation:

$$j_{lim} = \frac{2n F D_{I_3^-} c_{I_3^-}}{l},$$

where F is Faraday's constant ($96,484 \text{ C mol}^{-1}$), $C_{I_3^-}$ is the concentration per volume unit of I_3^- , $D_{I_3^-}$ is the diffusion constant of I_3^- , n is the number of electrons transported in the each reaction (in general, $n = 2$) and l is the distance between the electrodes) which is $3.02 \times 10^{-6} \text{ cm}^2/\text{s}$ and $3.29 \times 10^{-6} \text{ cm}^2/\text{s}$ for device **NP-600** and device **F-HS**, respectively. This analysis indicates that the use of F doped TiO_2 as an active scattering layer can significantly improve current collection due to faster electron and electrolyte transport and reduce electron loss due to grain boundary scattering²⁰. It can also retard electron recombination between the TiO_2 and electrolyte indirectly.

Figure 7.8. Steady-state cyclic voltammograms of devices **NP-600** and **F-HS**.

7.3. Conclusion

In summary, we compared the photovoltaic properties of the two photoanodes with different compositions of TiO₂. Interestingly, the multifunctional photoanode with F-doped TiO₂ can enhance light harvesting due to optically trapping light inside the hollow shell and exhibits a fairly good scattering effect, as shown in IPCE and optical simulation. Moreover, F-doped photoanode demonstrated a considerably higher J_{sc} , V_{oc} and FF . These results were induced by the faster electron transfer from the photoanode to the charge collecting end, retardation of electron recombination at grain-boundaries and faster electrolyte diffusion. As compared with the photoanode with the 600 nm nanoparticle as the scattering layer, the overall conversion efficiency of the multifunctional photoanode was increased by 19%. This could provide a promising strategy to explore high-efficiency DSSCs.

7.4. Experimental Section

Materials

Titanium(IV) fluoride and hexadecylamine (HDA, 98%) were purchased from Sigma-Aldrich. Titanium(IV) *i*-propoxide (TTIP, 98 %) was purchased from Sterm Chemicals. Absolute ethanol (AR, Fisher Scientific), potassium chloride (AR, Fisher Scientific), ammonia solution (25 wt%, Fisher Scientific) and Milli-Q water (18.2 MΩ cm) were used for the synthesis.

7.4.1. Preparation of Sub-Micrometer Sized TiO₂ Spheres

Sub-micrometer sized TiO₂ spheres were synthesized in a similar method as reported.² Briefly, TTIP (18.00 mL) HDA (0.193 g) and 3.20 mL of KCl solution (0.1 M) were dissolved in 800 mL of ethanol under vigorous stirring at ambient temperature. The milky white precursor bead suspension was then kept static for 18 hrs and filtered after which, the beads were washed with ethanol three times and dried in air at room temperature. The precursor bead samples (0.80 g) were dispersed in a 10 mL ethanol and 5 mL Milli-Q water mixture with 1 mL ammonia. Sub-micrometer sized TiO₂ spheres were obtained by hydrothermal synthesis at 160 °C for 16 hrs. The filtered substances were then calcinated at 500 °C for 2 hrs in air.

7.4.2. Preparation of F-Doped TiO₂ Hollow Spheres

Titanium (IV) *i*-propoxide (TTIP, 2.0 mmol), Titanium (IV) fluoride (0.4 mmol was added as F source for F-doped TiO₂ hollow spheres) and urea (4.0 mmol) were dissolved in 15 mL of ethanol. *tert*-Butyl ammonium hydroxide, 1.0 M solution in methanol (TBAH, 4.0 mmol, Sigma Aldrich) was added slowly into the solution. The mixture was stirred for 30 min to obtain a clear solution. Then the mixture was processed by the hydrothermal method at 180 °C for 24 hrs. The white precipitate was cooled to room temperature, filtered and washed several times with ethanol. The filtered white powdery titanium oxide was then sintered at 500 °C for 2 h in air.

7.4.3. Synthesis of Titanium Oxide Gel

Ethylcellulose 200 cPa (0.5 g) and ethanol (5.0 mL) were stirred to form a clear gel. Titanium dioxide (0.1 g) and terpineol (0.4 g) were then added into the mixture, and stirred continually to form a homogenous white gel.

7.4.4. Preparation of Photoanode and Cell Assembly

Briefly, transparent conducting glass ($\text{SnO}_2\text{:F}$, FTO, $15 \text{ } \Omega/\text{square}$, Solaronix) was cleaned in isopropyl alcohol and 0.1 M HCl solution using an ultrasonic bath for 30 min, respectively, and rinsed with water and ethanol. After treatment in a UV- O_3 system (Model No. 256-220, Jelight Company) for 15 min, the FTO glass was immersed into 40 mM TiCl_4 solution at $70 \text{ }^\circ\text{C}$ for 30 min. Then the $13.0 \text{ } \mu\text{m}$ thick TiO_2 (Ti-Nanoxide T/SP, Solaronix) electrodes were prepared by the doctor blading technique and gradually annealed under static air flow at $325 \text{ }^\circ\text{C}$ for 5 min, $375 \text{ }^\circ\text{C}$ for 5 min, $450 \text{ }^\circ\text{C}$ for 15 min and $500 \text{ }^\circ\text{C}$ for 15 min according to the method as reported.⁴ A $3 \text{ } \mu\text{m}$ TiO_2 scattering layer was coated on top of the transparent TiO_2 film and then treated by 40 mM TiCl_4 solution at $70 \text{ }^\circ\text{C}$ for another 30 min and sintered at $500 \text{ }^\circ\text{C}$ for 30 min and then cooled to $80 \text{ }^\circ\text{C}$. The electrodes were immersed in 0.3 mM **Z907** in acetonitrile/*tert*-butyl alcohol (1:1) for 10 hrs. Rinsed with acetonitrile, the photoanodes were bonded together with platinized conducting glass ($400 \text{ } \text{\AA}$ Pt fabricated by e-beam evaporation on the glass) using $60 \text{ } \mu\text{m}$ thermal-plastic Suryln spacers. The areas of the electrodes were around to be 0.28 cm^2 . The ionic liquid electrolyte (EL-HPE) was introduced into the sandwich cells.

7.4.5. Calculation

A commercial FDTD Solutions 6.5 package was operated to simulate Mie scattering and calculate the angular scattering in a plane around the particle.²¹

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Chapter 8. Aryl/Hetero-Arylethyne Bridged Dyes: The Effect of Planar π -Bridge on the Performance of Dye-Sensitized Solar Cells

8.1. Introduction

Even though the silicon and other semiconductor based solar cells have dominated the solar-cell market for decades, dye-sensitized solar cells (DSSCs) have attracted much consideration due to their low cost and relatively high power conversion efficiency (η) in the past few years.¹⁻¹¹ In DSSCs systems, the dye sensitizers play an important role and many research groups have devoted to exploring novel ruthenium (Ru) polypyridyl complexes, such as *cis*-dithiocyanate-N,N'-bis(4-carboxylate-4-tetrabutyl-ammonium-carboxylate-2,2'-bipyridine)-Ru(II) (**N719**) that could improve the cell performance and push the efficiency above 10 % under air mass 1.5 global (AM 1.5G) irradiation.¹³⁻¹⁷ Promoted by continuous material innovation and the systematic study of device fabrication in conjugation with highly volatile electrolytes, the cells with the ruthenium polypyridyl sensitizers have reached high efficiencies of 11.1% measured under the AM 1.5 conditions.¹⁸

Due to the limited ruthenium resources and the heavy-metal toxicity, metal-free organic dyes have received vital research interest. In general, the metal-free sensitizers for DSSCs mainly comprise a large conjugated system (donor- π bridge-acceptor moieties) which can expand the absorption spectrum and thereby increase the short circuit current (J_{sc}).⁶ Furthermore, the rate of charge transfer within molecules can also be enhanced by intra-molecular donor-acceptor delivery.¹⁹ However, introducing more π -conjugated bridge moiety to conjugated dyes will lead to unfavourable π -stacked dye aggregation on TiO_2 , which may result in a decrease in DSSCs

performance.²⁰ Consequently, an appropriate bridge system is of the essence to obtain the high power conversion efficiency of organic dye sensitized solar cells. In this regard, these two factors should be adjusted to reach a compromise when designing novel dyes to improve the overall efficiency of DSSCs.

Recently, several metal-free organic dyes including coumarin,³²⁻³⁴ merocyanine,³⁵⁻³⁷ indoline,³⁸⁻⁴⁰ polyene,⁴¹⁻⁴⁴ hemicyanine,⁴⁵⁻⁴⁸ triphenylamine,³²⁻³⁴ fluorine³⁵⁻³⁷ and tetrahydroquinoline³⁸ as donating group have been developed for DSSCs. Thus far, the highest photoelectric conversion efficiency of metal-free dye sensitized solar cells was reported to be around 9 to 9.8%.³⁹⁻⁴⁰ It is well accepted that 4-methoxy-triphenylamine moiety as a donor in metal-free sensitizer can effectively suppress the dye-aggregation⁴¹⁻⁴⁸ and slowing down the recombination reactions in the cell.⁴⁵⁻⁴⁸ On the other hand, cyanoacrylic acid as an acceptor is better than other anchoring groups such as rhodanine-3-acetic acid due to its co-planarity with respect to spacer unit and good electron coupling with TiO₂.⁴⁹⁻⁵¹ In addition to the intrinsic properties of donor and acceptor, the electron transfer can also be improved when the bridge moiety can be turned on or off on demand in donor-bridge-acceptor (D-B-A) system. According to Geppert and Vivie-Riedle's results,⁵² the bridge molecule can suppress the electron transfer when the molecule is in the closed form, while in the open form, the molecule can allow the electron transfer from D *via* B to A. Moreover, experimental results indicated that linear bridge moiety with good planarity can suppress the electron recombination.⁵³

In view of the key role of bridge moiety in DSSCs systems, here, we reported the design and synthesis of three new organic dyes bearing suitable linear π -conjugated bridge moiety with good planarity as metal-free sensitizers for DSSCs:

(*E*)-3(4-(4-(Bis(4-methoxyphenyl)amino)phenyl)ethynyl)phenyl)-2-cyanoacetic acid (**D1**), (*E*)-3(4-(4-(Bis(4-methoxyphenyl)amino)phenyl)ethynyl) thiophene-2-yl)-2-cyanoacrylic acid (**D2**) and (*E*)-3-(5-(5-(2-(4-(Bis(4-methoxyphenyl)amino)phenyl)ethynyl)-thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid (**D3**) (**D1**, **D2**, and **D3** were shown in Scheme 8.1). The electrochemical and photovoltaic properties of these metal-free dyes have also been investigated.

Scheme 8.1. Molecular structures of dyes (**D1**, **D2** and **D3**).

8.2. Results and Discussion

8.2.1. Absorption Properties in Solution and on TiO₂ Film

The UV-visible absorption spectra of the three metal-free organic dyes in CHCl₃ solution and on TiO₂ films are shown in Figure 8.1a. The molar extinction coefficients decrease in the order of **D1** > **D2** > **D3** in ultraviolet region, while opposite order is

observed in the visible region and the spectra exhibit corresponding red-shift. The bands at around 350 nm are attributed to the π - π^* transition of the conjugated molecule and intra-molecular transfer between the donor and the acceptor.⁴¹⁻⁴⁴ The positions of the bands are strongly influenced by the extended conjugation and bathochrome group. The hyperchromic effect intensity of bands in UV region might be attributed to introducing planar macrocyclic structure to the bridge moiety, while the intensity of bands in visible region can be enhanced by introducing auxochrome group. The π -conjugation groups would facilitate the absorption spectra by bathochromic shift towards near IR region, which causes an improved match of the absorption bands of sensitizer to the solar radiation. It is obvious that the absorption bands of thiophene are in much longer wavelength range due to substantial resonance enhancement effect compared with benzenoid moieties.⁵⁴⁻⁵⁶

The calculated torsion angles with respect to the conjugated spacers in three D-B-A dyes are shown in Scheme 8.1. **D1** has a negligible torsion angle compared with **D2** and **D3**, and all the three dyes have small torsion angle. This indicates that triple bond can enhance the planarity compared with the other similar dyes as reported.^{41-44,55-60} Compared with the spectra in CHCl₃ solution, the absorption bands of these dyes on TiO₂ films exhibit larger red-shift and significant spectral broadening due to the interaction of the anchoring groups with the surface of TiO₂ and the *J*-aggregation of dye molecules.⁵⁷⁻⁶⁰

To investigate the degree of aggregation for these three dyes, we dipped TiO₂ film into dye solution including 0.5 mM dye and 10 mM chenodeoxycholic acid (CDCA) for 12 hrs. It was found that the CDCA coadsorbent can prevent the aggregation on TiO₂ film, which is consistent with those previously reported.⁶¹⁻⁶⁴ The aggregation of **D1**, **D2** and **D3** onto the TiO₂ surface was diminished in 10 mM CDCA in sensitizer

solution as shown in Figure 8.1b. The effect of CDCA as the co-adsorbent on cell performance needs to be investigated in details. The emission spectra of these dyes were measured in CHCl_3 (Figure 8.2). The first emission peaks of **D1** (598 nm) and **D2** (614 nm) are hypsochromically shifted by 50-60 nm relative to **D3** (661 nm), which is consistent with the results of the UV-Vis absorption spectra in CHCl_3 .

Figure 8.1. (a) UV-vis absorption spectra of the dyes in CHCl_3 solution; (b) on the TiO_2 film.

D1

D2

D3

Figure 8.2. The UV-Vis absorption and fluorescence of dye sensitizers in this study.

Table 8.1. Experimental data for the spectral and electrochemical properties of the dyes.

Dye	Abs _{max} ^a [nm]	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ^a $\times 10^4$	E _{ox} ^b [V] vs. NHE	E ₀₀ ^c [V]	E _{ox} * ^d [V] vs. NHE	ΔG_{inj} ^e /eV	ΔG_{reg} ^f /eV
D1	446	2.44	1.00	2.37	-1.37	-0.87	-0.50
D2	476	3.31	0.99	2.28	-1.29	-0.79	-0.49
D3	511	3.46	1.00	2.18	-1.18	-0.68	-0.50

^a Absorption and emission spectra of **D1**, **D2** and **D3** in chloroform solution. ^b Measured ground-state oxidation potential of the dyes. Potentials measured vs Fc⁺/Fc were converted to normal hydrogen electrode (NHE) by addition of +0.63 V. ^c 0-0 transition energy, E₍₀₋₀₎, estimated from the intercept of the normalized absorption and emission spectra in chloroform. ^d Estimated LUMO energies, E_(LUMO) vs NHE from the estimated highest occupied molecular orbital (HOMO) energies obtained from the ground-state oxidation potential by adding the 0-0 transition energy, E₍₀₋₀₎. ^e Driving forces for electron injection from the dye excited singlet state (E_{ox}*) to the conduction band of TiO₂ (-0.5 V vs NHE). ^f Driving forces for the regeneration of the dye radical (E_{ox}) by I⁻/I₃⁻ redox couple (+0.5 V vs NHE).

8.2.2. Electrochemical Properties

Cyclic voltammetry was employed to determine the oxidation potentials of the three metal-free organic dyes. The measurements were performed in CHCl₃ solution with 0.2 M *tetra*-butylammonium hexafluorophosphate (Bu₄NPF₆) using ferrocene as an internal standard at 0.63 V vs. NHE (Figure 8.3). The oxidation potential and the reduction potential correspond to the HOMO and LUMO energies, respectively. The oxidation potentials of **D1**, **D2** and **D3** are 1.00 V, 0.99 V and 1.00 V vs. NHE,

respectively, which are more positive than the that of Γ^-/I_3^- couple (0.5 V vs. NHE),⁶¹⁻⁶⁴ ensuring the regeneration of sensitizer radical cations by the electrolyte redox couple.

Figure 8.3. Cyclic voltammetry of **D1**, **D2** and **D3**.

By neglecting any entropy change during the electron-injection process,⁴⁹⁻⁵¹ the excited-state oxidation potential ($E_{(S^+/S^*)}$) of the sensitizer can be derived from the ground-state oxidation couple ($E_{(S^+/S)}$) and the 0-0 and the 0-0 excitation energy ($E_{(0-0)}$) according to Eq.(1).

$$E_{(S^+/S^*)} = E_{(S^+/S)} - E_{(0-0)} \quad (1)$$

Transition energy $E_{(0-0)}$ was estimated from the interception of the absorption and emission spectra in $CHCl_3$ solution. As shown in Table 8.1, $E_{(0-0)}$ energies for **D1**, **D2** and **D3** were extracted to be 2.37 eV, 2.28 eV and 2.18 eV, respectively. The calculated excited-state oxidation potentials for **D1**, **D2** and **D3** are -1.37 V, -1.29 V and -1.18 V vs. NHE, respectively, which are more negative than the equivalent potential for **N719** sensitizer (-0.98 V vs. NHE) and the conduction band (CB) of TiO_2 (-0.5 V vs. NHE). Therefore, there are sufficient driving forces for charge

injection to the conduction band of semiconductors.⁶⁵ From spectroscopic and electrochemical measurements, driving forces, ΔG_{inj} , for electron injection from the dye excited singlet state to the CB of TiO₂ (-0.5 V *vs.* NHE), and ΔG_{reg} , the regeneration of the dye radical cation by electrolyte redox couple ($+0.5$ V *vs.* NHE) for the dye-sensitized solar cells are extracted and shown in Table 8.1. From these data, it can be seen that both of the processes are thermodynamically feasible.

To gain insight into the electronic structures of excited states, we performed time-dependent density functional theory (TD-DFT) calculations on these three organic dyes. We calculated the contribution of singly excited state configurations to each electronic transition and the molecular orbital contributions to analyse the charge-separated states of these dyes. All the three dyes have small torsion angle as shown in Scheme 8.1. The calculated molecular orbital energy diagrams and isodensity surface plots for three dyes **D1**, **D2** and **D3** are shown in Figure 8.4.

Figure 8.4. Molecular orbital energy diagrams (TD-B3LYP/6-31G**/B3LYP/6-31G* in chloroform using C-PCM framework) and isodensity surface.

The HOMO-LUMO band gap of **D1**, **D2** and **D3** three dyes is 2.18 eV, 2.17 eV and 2.01 eV, respectively. **D3** has the smallest band-gap, causing the red-shifted absorption spectra, which is ideally preferred for DSSCs application. Compared with **D2**, **D3** with two thiophene units has lower LUMO-HOMO gap due to the increased conjugation along the dye, which is consistent with previous reports.

Meanwhile, the LUMO of **D3** is closer to the conduction band of TiO_2 than that of **D1** and **D2**. This result shows that the extended π -system could promote the intramolecular charge transfer behaviour from bridge group to acceptor group.^{13,14} Based on the calculated molecular orbital contribution (Table 8.2), we found that, among three dyes, **D3** exhibits the most obvious intra-molecular charge-separation. This means that **D3** possesses stronger photo-induced intra-molecular charge transfer properties capability than **D1** and **D2**, and the major portions of **D3** HOMO are located on the donor moiety. LUMO contains the acceptor moiety, the triple bond and the bridge, which strongly suggests that electrons move from donor moiety, passing through bridge moiety, to the acceptor and form linearly photo-excitation-induced intra-molecular charge transfer. When the π -conjugation increased, the overlapping extension can be enhanced by the bridge which might improve the electronic coupling between the dye and TiO_2 film. The excitation energies of **D1**, **D2** and **D3** were also compared by TD-DFT calculation results and shown in Table 8.3. The results clearly indicate that introduction of thiophene group in the bridge moiety increases the oscillator strength of the visible range, which could give rise to the enhancement of the solar spectrum overlap. In contrast, introducing phenyl group in the bridge moiety can obviously increase the oscillator strength in ultraviolet region though phenyl group which makes against the bathochromic effect. Both the two

dominating excited states of these three dyes originated from HOMO→LUMO and HOMO-1→LUMO contributions and the intensities are coincident with the experimental absorptions of these three dyes. Thus, the transitions give rise to an intra-molecular charge flow from the donor moiety to the acceptor moiety. Potentially, the resulting excited state is strongly coupled to the semiconductor surface, due to charge delocalization involving the cyanoacetic acid anchoring group.^{41-48,52-55}

Table 8.2. Molecular orbital contribution (MOC) of the 5 highest occupied and 5 lowest unoccupied molecular orbitals of **D1**, **D2** and **D3** calculated at the B3LYP/6-31G* level in chloroform solution.

	Energy/eV	Donor	Triple-bond	Bridge	Acceptor
D1					
HOMO-4	-6.983	99.9	0.0	0.0	0.0
HOMO-3	-6.850	67.3	3.1	15.2	14.5
HOMO-2	-6.291	99.8	0.1	0.0	0.0
HOMO-1	-6.041	53.3	17.4	19.1	10.2
HOMO	-4.904	88.9	5.1	3.7	2.2
LUMO	-2.737	7.9	6.3	29.7	56.1
LUMO+1	-1.002	52.3	13.2	15.2	19.3
LUMO+2	-0.524	99.9	0.0	0.1	0.0
LUMO+3	-0.308	0.3	0.0	99.1	0.6
LUMO+4	-0.136	98.9	0.7	0.2	0.2
D2					
HOMO-4	-7.010	96.1	0.5	1.5	1.9
HOMO-3	-6.762	66.3	2.6	15.0	16.0

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HOMO-2	-6.310	99.8	0.2	0.0	0.0
HOMO-1	-5.926	42.4	14.2	26.8	16.7
HOMO	-4.926	85.4	5.3	5.7	3.5
LUMO	-2.749	9.3	7.3	37.9	45.5
LUMO+1	-1.099	43.1	11.4	24.6	20.9
LUMO+2	-0.552	99.9	0.0	0.1	0.0
LUMO+3	-0.159	97.4	0.8	1.2	0.5
LUMO+4	-0.067	66.7	1.8	20.6	10.9
D3					
HOMO-4	-6.936	81.1	3.5	9.6	5.8
HOMO-3	-6.430	54.9	6.5	24.9	13.7
HOMO-2	-6.297	99.8	0.1	0.0	0.0
HOMO-1	-5.618	33.3	9.1	46.6	11.1
HOMO	-4.824	80.4	6.2	11.4	2.0
LUMO	-2.819	3.9	3.1	53.2	39.8
LUMO+1	-1.587	20.1	9.7	52.0	18.2
LUMO+2	-0.550	46.8	5.3	38.2	9.7
LUMO+3	-0.499	100.0	0.0	0.0	0.0
LUMO+4	-0.119	99.1	0.8	0.1	0.0

Table 8.3. Computed excited energies (eV), oscillator strengths (*f*) for **D1**, **D2**, and **D3** in chloroform calculated using TD-B3LYP/6-31G*//B3LYP/6-31G* using C-PCM framework.

	nm	cm ⁻¹ (×1000)	eV	<i>f</i>	Assignment H = HOMO, L = LUMO, L+1 = LUMO+1, <i>etc.</i>
D1					
	638.5	15.7	1.94	0.9358	H-0->L+0(+92%)
	410.6	24.4	3.02	0.9669	H-1->L+0(+87%)
	375.4	26.6	3.30	0.0107	H-2->L+0(+99%)
	353.6	28.3	3.51	0.3327	H-0->L+1(+83%), H-3->L+0(+6%)
D2					
	637.9	15.7	1.94	1.0566	H-0->L+0(+90%)
	424.9	23.5	2.92	0.8808	H-1->L+0(+84%)
	376.5	26.6	3.29	0.0125	H-2->L+0(+99%)
	359.3	27.8	3.45	0.2470	H-0->L+1(+82%), H-3->L+0(+9%)
D3					
	697.0	14.3	1.78	0.9931	H-0->L+0(+92%)
	487.3	20.5	2.54	1.0352	H-1->L+0(+83%)
	423.0	23.6	2.93	0.3406	H-0->L+1(+85%)
	379.3	26.4	3.27	0.0050	H-2->L+0(+99%)
	369.3	27.1	3.36	0.0830	H-3->L+0(+84%)

The incident monochromatic photon-to-current conversion efficiency (IPCE) values for the three organic dyes are shown in Figure 8.5. The IPCEs are represented by Eq. (2):

$$IPCE(\%) = \frac{1240(eVnm)J_{ph}[mAcm^{-2}]}{\lambda[nm]\phi[mWcm^{-2}]} \times 100(2)$$

Where J_{ph} is the short-circuit photocurrent density for monochromatic irradiation, λ and ϕ are the wavelength and the intensity of the monochromatic light, respectively. The highest IPCE values for **D1**, **D2** and **D3** are found to be around 80%, 80% and 90%, respectively.

Figure 8.5. IPCE values for DSSCs based on the three organic dyes.

There are some red-shift in the IPCE compared to the absorption spectra in Figure 8.1, which can be attributed to the aggregation of the dyes on TiO_2 ⁵¹⁻⁶⁵ and the interaction of the anchoring groups with the TiO_2 surface.^{45-46,54-56} These results also show that the absorption intensity in 350-400 nm region can be increased by the rigid

functional group because of the high molar extinction coefficient as well as p- π -conjugated bridge which would extend the absorption of dye molecule as mentioned above.

The photocurrent-voltage curves of the sensitizers are shown in Figure 8.6. In this work, we selected **Z907** dye as control in comparison with our three organic dyes and all devices were fabricated under similar conditions. The short-circuit current densities, J_{sc} , open-circuit voltages, V_{oc} , fill factor; FF and power conversion efficiencies of the cells, η are summarized in Table 8.4.

Figure 8.6. Photocurrent density–photovoltage curve of three dyes sensitized cells under AM 1.5 G radiation (100 mW cm^{-2}).

The **D3**-sensitized cell device gives the best performance and offers J_{sc} of 11.39 mA/cm^2 , V_{oc} of 0.637 V and FF of 69.2% , respectively. The overall conversion efficiency η can be calculated according to Eq. (3),

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (3),$$

where P_{in} represents the intensity of the incident light (mW/cm^2). Among the three organic dyes, **D3** shows the highest efficiency of 4.98% which reaches around 82% of the value for **Z907** under similar conditions. **D2** shows an efficiency of 3.86%, while **D1** gives the lowest overall efficiency of 3.21%. The poor efficiency of **D1**-sensitized cell is attributed to the lower light harvesting ability in the visible range, evidenced by the UV-vis absorption spectra (Figure 8.1). While **D3** shows the highest J_{sc} , which is consistent with its broad absorption spectra. The open circuit voltage (V_{oc}) increases in the order of **D1** < **D3** < **D2**.

Under illumination condition, V_{oc} of the cell is potential difference between the quasi-Fermi level of the electrons (E_{Fn}^*) in the nanocrystalline TiO_2 film and E_{redox} of the electrolyte, also V_{oc} depends logarithmically on the inverse concentration of I_3^- and increases with incident photo flux according to the equation below,⁶⁶

$$V_{oc} = \frac{RT}{\beta F} \ln \left(\frac{AI}{n_0 k_1 [\text{I}_3^-] + n_0 k_2 [\text{D}^+]} \right),$$

where k_1 , k_2 is the kinetic constant for the back reaction of injected electrons with triiodide (I_3^-) and recombination of these electrons with oxidized dye (D^+), respectively, $RT/(\beta F)$ is the thermal voltage and n_0 is the concentration of accessible electronic states in the conduction band. Since the recombination of dye can be omitted, the electron recombination between the injected electron from the conduct band of TiO_2 and the triiodide could reduce the V_{oc} .⁵⁶

According to the similar results, which were reported previously, the aggregation of the dye and the orientation of the dye on TiO₂ surface can aggravate charge recombination. The rigid conjugate molecules are easy to aggregate due to strong dipole-dipole interaction.⁶⁷⁻⁶⁹ What's more, when the dye molecules are adsorbed on TiO₂ surface, which can affect the fermi level of conduction band of TiO₂, resulting in a negative shift and this shift is increased with the increasing dipole at the dye/TiO₂ interface.⁷⁰ This band-edge shift is more significant than the increase in recombination rate. Thus, the V_{oc} of **D2** gave the highest value and the **D1** gave the lowest value and due to the different level of π -stacked aggregation and band-edge shift.⁶⁶⁻⁷⁴

Table 8.4. DSSCs performance parameters of various dyes.^a

Dye	$J_{sc}(\text{mA}/\text{cm}^2)$	V_{oc} (V)	$FF(\%)$	η (%)
D1	6.95	0.623	74.2	3.21
D2	8.04	0.684	70.1	3.86
D3	11.29	0.637	69.2	4.98
Z907	15.11	0.686	58.9	6.11

^a Performance of DSSCs was measured with a working area of 0.16 cm².

To further investigate the internal resistance, the kinetics of charge transfer and recombination in the devices, we carried out the electrochemical impedance spectroscopy (EIS) measurement in the dark and under illumination conditions. Figure 8.7 shows the Nyquist plots for the devices in the dark and under illumination conditions. The equivalent circuit is shown in Scheme 8.2. The R_s represents the series resistance consisting of all ohmic components in the device, R_1 and R_2 are charge transfer resistance components forming a parallel circuit with constant phase elements

(*CPE1* and *CPE2*) and *W1* is the Finite-Length Warburg element for Nernst diffusion impedance. Three semicircles were observed at various frequency ranges.

Scheme 8.2. Equivalent circuit of used to fit Nyquist plots.

Figure 8.7. Nyquist plots of three devices in the dark (inset) and illumination condition.

The first semicircle in the high-frequency region is attributed to the redox reaction of I/I_3^- at the Pt/electrolyte interface, the central semicircle denotes the electron transfer at the oxide/dye/electrolyte interface and the low frequency one is caused by

ion diffusion within the electrolyte.⁶⁶⁻⁷⁴ the dark condition, the impedance spectra were obtained under forward bias (-0.65 V), the charge-transfer resistance related to the recombination of electron, R_k , was estimated from the diameter of the central circle. The R_k value increases in the order of **D3** (69.6 Ω) < **D2** (129.3 Ω) < **D1** (175.5 Ω). In the dark condition, under reverse bias, TiO₂ is an insulator and the dye molecules with different dielectric constant, which are also insulating in the ground state and hence the injected electrons through TiO₂/dye were coupled to that of I⁻/I₃⁻ ions in electrolyte. Then the dye coating as tightly packed insulating monolayer leads to a barrier blocking the dark current,⁷⁰⁻⁷⁴ and as mentioned above, the bridge molecule can suppress the electron transfer when the molecule is in the closed form.⁴⁶ Accordingly, the recombination resistance at the TiO₂/dye/electrolyte interface decreased in this order of **D3**<**D2**<**D1** may be resulted from those factors.

Under illumination (50 mW cm⁻², open-circuit voltage (OCV)) conditions, which gives rise to new processes at the TiO₂/dye/electrolyte interface including the electron injection from excited dye to TiO₂, recombination with the oxide dye, and regeneration of the sensitizer.⁶⁶ The results are also in good agreement with the trend of dark-current in photocurrent-voltage curves. These data suggest that the charge recombination was retarded with the increase of the planarity of dye molecules. And also, under illumination conditions, the diameter of the intermediate-frequency semicircle in the Nyquist plot increases in the order of **D3** < **D2** < **D1**, which indicates that the electrons generation and transport are enhanced in the order of **D3** > **D2** > **D1**. From these data, it can be seen that planar conjugation bridge retards the charge recombination and intramolecular charge transfer increases the charge-injection rate. The cell performance can be improved by harmonizing these factors.

8.3. Conclusion

In summary, we have designed three new linear dye molecules with good planarity and investigated the effect of the bridge moiety on the properties of dye-sensitized solar cells. The results based on UV-Vis absorptions, TD-DFT calculations, photovoltaic experiment and EIS show that π -conjugated bridge can extend the absorption of dye molecule and strong planarity (closed-packing) can suppress the charge recombination at TiO_2 /electrolyte interface. Improving the cell performance has been demonstrated for the dye molecules with large-conjugated planarity and p- π conjugation as bridge due to the retarded recombination and enhanced light harvesting, which provides a skillful strategy to explore metal-free sensitizers with high photo-to-current conversion efficiency. To further improve the cell performance of DSSCs based on metal-free dyes, we will focus on the development of novel organic sensitizers with large planar donor- π bridge-acceptors in the future. Currently, the study of the coadsorbent effect on these conjugated molecules and the rate of charge transfer between the sensitizers and TiO_2 surface is in progress.

8.4. Experimental Details

8.4.1. Materials and Instrumentation

All reactions were carried out under Ar atmosphere. Solvents were dried by standard procedures.

8.4.2. Calculation Method

We performed time-dependent density functional theory TD-DFT calculation by using the Gaussian 03 program package.⁷⁵⁻⁷⁷ The geometries of the three metal-free

organic dyes in vacuo were optimized using density functional theory (DFT) with the B3LYP density functional and the 6-31G* basis set.⁷⁵⁻⁷⁷ All optimized geometries were subjected to vibrational frequency analysis, and characterized as a minimum (no imaginary frequencies). The time-dependent DFT (TD-DFT) at the level of B3LYP/6-31G* was carried out to study the excited state of selected molecules. The absorption spectra were simulated by the 20 lowest spin-allowed singlet transitions and the C-PCM frameworks were used to describe the electrostatic solute–solvent interactions.⁷⁵⁻⁷⁶ The contribution of single excited state configurations to each electronic transition of the three metal-free organic dye analogues were calculated using the Swizard program, version 4.2.⁷⁶⁻⁸¹ Graphical molecular orbital were generated with the Gauss View software program (version 3.09)⁷⁶⁻⁸¹ and the molecular orbital contributions from the groups of atoms were obtained from the VMOdes A 7.1.⁸²

8.4.3. Solar Cell Fabrication

The transparent conducting glass (SnO₂:F, FTO, 15Ω/square, Solaronix) electrodes into a 0.04 M TiCl₄ aqueous solution for 1 hr at 70 °C until the TiCl₄ was hydrolyzed, then washing the electrodes with distilled water to remove residual TiCl₄, and TiO₂ (Ti-Nanoxide T/SP, Solaronix) paste were deposited on the treated transparent conducting glass with screen printing method and sintered at 500 °C in air for 30 min and then cooled to room temperature. 400 nm TiO₂ scatter layer (DSL 18NR-AO) were deposited on the TiO₂ film and sintered at 500 °C in air for another 30 min. Then the TiO₂ (7+5 μm) film electrode were soaked in a chloroform solution containing 0.5 mM organic dye for 12 hrs at room temperature and then washed with ethanol and dried in dry air. A sandwich cell was prepared using the dye-sensitized electrode as the working electrode and a platinum-coated conducting glass electrode as the counter

electrode. The counter electrode used was a 400 Å Pt fabricated by e-beam evaporation on a commercial indium tin oxide glass. The two electrodes separated by 60 μm thermal-plastic Suryln spacers were bonding together, and the electrolyte (EL-HPE) was introduced between the electrodes by capillary action.

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Chapter 9. Design, Synthesis and Photovoltaic Properties of Push-Pull Type of Zinc-Porphyrin Chromophores Sensitizers

9.1. Introduction

Dye-Sensitized Solar Cells (DSSCs) have attracted considerable attention as conventional solid-state photovoltaic devices for the conversion of solar energy to electric power¹. Organic and inorganic dyes suitable for DSSCs have been under intensive investigation.¹⁻³ The major ongoing research has focused on ruthenium (Ru) polypyridyl complexes, where the maximum solar-to-electric conversion efficiency of 11% has been claimed.³ However, traditional ruthenium dyes are expensive and have a comparatively lower molar extinction coefficient. Thus it is necessary to find cheaper and safer alternatives for the dyes in DSSCs. Recently, some new types of organic dyes have been investigated as the sensitizers in solar cell. For example, Hara^{4,5} and Yanagida⁶ and co-workers reported an organic dye containing a donor group (dialkylaminophenyl group) and an acceptor group (cyanoacrylic acid).

Metal-porphyrin complexes which have strong absorption intensity at Soret and moderate Q bands are optimum candidates for DSSCs. To date, diverse porphyrins with chromophores have been designed, synthesized and employed in DSSCs and the conversion efficiencies achieved are around 5–7%.⁷⁻¹² Under standard global AM 1.5 solar conditions, the highest overall conversion efficiency was found to be 7.1% by using a metalloporphyrin-based DSSCs with zinc-5,10,15,20-tetratolylporphyrin-2-(but-2-enylidene)malonic acid as the sensitizer.¹³ In comparison with Ru-based DSSCs, porphyrin-based DSSCs still show relatively low conversion efficiency. To address

this issue, the rational designing of porphyrin derivatives by introducing various electron-withdrawing groups and electron-donating groups to the metalloporphyrin analogue would be a strategic advantage in tuning photochemical property of metalloporphyrins, which offer the opportunity for the improvement of the conversion efficiency of cells.

In principle, the appropriate dye should satisfy several criteria. Firstly, the ground state of the dye is regenerated by the electrolyte which means the redox couple of the electrolyte should be higher than the highest occupied molecular orbital (HOMO) of dye. Secondly, the electron from the photo-excited dye should be injected into the conducting band (CB) of semiconductors quickly which implies that the CB should be appropriately below the lowest unoccupied molecular orbital (LUMO) of dye.¹⁰ The dye should also have an appropriate structure that allows efficient charge separation, the push-pull type of dye suit this point perfectly. Moreover, a strong conjugation across the donor, bridge and anchor which allows good electronic coupling between the LUMO of the dye and the TiO₂ conduction band should exist to ensure high charge transfer rates.

Following these principles, we designed a push-pull type of metalloporphyrin derivatives as DSSCs dyes in this work. This push-pull type of dye is an unsymmetrical donor-bridge-acceptor (D-B-A) analogue linked to an electron-withdrawing group and an electron-donating group in opposite directions as shown in Figure 9.1. We expect that the suitable selection of these functional groups would tune the energy gap between the HOMO and LUMO thereby matching the redox couple of the electrolyte and the conduction band edge level of semiconductor. In addition, D-B-A metalloporphyrin analogues would enhance photo-induced intra-molecular charged transfer properties which may accelerate the rate of electron injection from the dye

molecule into the conduction band of the semiconductor. We performed the density functional theory (DFT) calculations to virtually screen candidate analogues in terms of molecular energy levels and found two compounds, Zn(II)-5,15-bisphenyl-10-(4-diphenylamino)phenyl-20-(4-carboxymethylphenyl)-porphyrin (**ZnNDBAD**) and Zn(II)-5,15-bisphenyl-10-(4-diphenylamino) phenyl-20-(2-nitro-4-carboxy-methyl-phenyl)-porphyrin (**ZnNDNAD**), that are suitable as sensitizers in DSSCs as they had the proper HOMO and LUMO locations.

Figure 9.1. Molecular orbital energy levels (eV) of compound **1-8** calculated using B3LYP/6-31G* in vacuum for the various dyes originated from compared to results for a model of a TiO₂ nanoparticle.

We then synthesized these two metalloporphyrin analogues. The metalloporphyrin without a donating group, Zn(II)-5,10,15-trisphenyl-20-(4-carboxymethylphenyl)-porphyrin (**ZnTPPAD**), was employed as a reference to evaluate the effects of unsymmetrical DBA metalloporphyrin analogues on the photovoltaic properties. Finally, **ZnNDBAD**, **ZnNDNAD** and **ZnTPPAD** are adsorbed onto TiO₂ electrodes to test cell performances in DSSCs.

9.2. Experimental Section

9.2.1. Calculation Method

We performed density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation by using the Gaussian 03¹⁴ program package. The geometries of the three metalloporphyrin compounds in vacuum were optimized using density functional theory (DFT) with the B3LYP density functional¹⁴ and the 6-31G* basis set. All optimized geometries were subjected to vibrational frequency analysis, and characterized as a minimum (no imaginary frequencies). The time-dependent DFT (TD-DFT) at the level of B3LYP/6-31G* was carried out to study the excited state of selected molecules. The absorption spectrums were simulated by the 20 lowest spin-allowed singlet transitions and the C-PCM¹⁵ frameworks were used to describe the electrostatic solute–solvent interactions. The contribution of the singly excited state configurations to each electronic transition of the three metalloporphyrin analogues were calculated using the Swizard program, version 4.2.¹⁶ Graphical molecular orbital were generated with the Gauss View software program (version 3.09)¹⁴ and the molecular orbital contributions from the groups of atoms were obtained from Aomix program.¹⁶

9.2.2. Material and Instrumentation

All chemicals were obtained from commercial sources and used without further purification. Unless otherwise noted, all reactions were carried out in oven dried glassware under an atmosphere of nitrogen and distilled solvents were transferred by syringe. Solvents and reagents were purified according to the standard procedure prior to use. Evaporation of organic solutions was achieved by rotary evaporation with water bath temperature below 40 °C.

9.2.3. Preparation of Metalloporphyrin Modified TiO₂ Electrode

The $5.0 \pm 0.2 \mu\text{m}$ thick films of nanocrystalline TiO₂ (Ti-Nanoxide T/SP, Solaronix) were deposited on transparent conducting glass (SnO₂:F, FTO, 15 Ω/square, Solaronix) with the doctor blade squeegee method. After heating to 450 °C for 2 hrs, TiO₂ substrates were cooled down and were prepared for dye loading. Then the TiO₂ plates (electrodes) were dipped into 0.4 mM dye solution in THF and left for 2 hrs, and taken out and rinsed with methanol. A sandwich cell was prepared using the dye-sensitized electrode as the working electrode and a platinum-coated conducting glass electrode as the counter electrode. The counter electrode used was a 400 Å Pt fabricated by e-beam evaporation on a commercial indium tin oxide glass. The two electrodes separated by 50 μm thermal-plastic Surlyn spacers were bonded together and the electrolyte, composed of 0.1 M I₂, 0.1 M LiI, 0.5 M *tert*-butylpyridine, and 0.6 M 1-hexyl-3-methylimidazolium iodide in methoxy-acetonitrile, was introduced in between the electrodes by capillary action.

9.3. Results and Discussion

9.3.1. DFT Calculations

We designed different electron donating and withdrawing groups, and filtered the appropriate candidates according to the electron density of the ground-state of metalloporphyrin derivatives before synthesis. Figure 9.1 shows the relative molecular orbitals of metalloporphyrin analogues, the potential of these compounds are referred to vacuum. A good candidate for dye molecules should have more positive HOMO level than the reduction potential of Γ/I_3^- , at the same time; its LUMO level should be more negative than the conduction band of TiO_2 . It should also have an intense absorption in the visible region due to small HOMO-LUMO gap and possess photo-induced intra-molecular charge transfer properties. From Figure 9.1, The ground state of compound **ZnNDBAD** has its LUMO at -2.18 eV, right above the conduction band (CB) of TiO_2 , which will facilitate the electron injection from LUMO of sensitizer to the CB of TiO_2 and has its HOMO at -5.02 eV, right below the Γ/I_3^- reduction potential, which indicates that the redox couple could reduce the oxidized dye sensitizer. While the ground state of compound **ZnNDNAD**'s LUMO is -2.73 eV and its HOMO is located at -5.00 eV. What's more, compounds **ZnNDBAD** and **ZnNDNAD** have small HOMO-LUMO band gap, which will best satisfy the requirements of dye sensitizers. Thus we selected compounds **ZnNDBAD** and **ZnNDNAD** for further studies in the following experiments. Compound **ZnTPPAD** has been chosen as reference to investigate the electron donating and withdrawing effects.

Scheme 9.1. Chemical structures of metalloporphyrin derivatives used in this study.

To gain insight into the electronic structure of excited states, TD-B3LYP calculations were performed in tetrahydrofuran (THF) solution (C-PCM model) with geometries obtained in vacuum. Since the contribution of the molecular orbitals (MO) plays crucial role in the determination of the charge-separated states of complexes,¹⁰ we examine the molecular orbital contributions for **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**. The chemical structures of these three dyes are shown in Scheme 9.1.

The excited state molecular orbitals of the three compounds are plotted in Figure 9.2. There are similar electronic structures for the cores of **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**. The changes in the withdrawing and donating moieties are the cause of the differences in electron densities on the anchor group (carboxyl group) in the LUMOs. The HOMO is populated on the donor fragment and the LUMO on the acceptor fragment, which suggests the formation of a charge-separated state between the donor and acceptor during photo-induced electron transfer. Table 9.1 show the major portions of the molecular orbitals. The HOMO-LUMO gaps are calculated at 2.80 eV, 2.64 eV and 2.37 eV for the excited states of **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**, respectively. The HOMO of **ZnTPPAD** is mainly localized on the porphyrin ring with little contribution from the benzoic acid moieties, and from Table 9.1 and Table 9.2, the HOMO and HOMO-1 of **ZnTPPAD** are almost degenerate couple. The LUMO is mainly distributed on the porphyrin ring with little contribution from the benzoic acid moieties. The LUMO of **ZnNDBAD** is similar to that of **ZnTPPAD** except that its HOMO contains the porphyrin ring and substituted diphenylamino moieties. It is obvious there is spatial charge separation between HOMO and LUMO of **ZnNDBAD**.

When the nitro group is introduced into the anchoring group, the HOMO and LUMO of the **ZnNDNAD** are more separated than of **ZnNDBAD**. The LUMO is

close to the acceptor moieties, although nitro-withdrawing group has a few contributions, it can further stabilize the whole porphyrin molecule by the strong electron-withdrawing group. The HOMO is mainly localized on the porphyrin ring and the substituted diphenylamino moieties, similar to **ZnNDBAD**. Obviously, the structure with a strong electron-donating group on one side and a strong electron-withdrawing group on the other side will facilitate spatial charge separation. Especially, the HOMOs of **ZnNDBAD** and **ZnNDNAD** were also partially distributed on the porphyrin ring, suggesting considerable interactions between the donor and acceptor entities. The locations of the HOMO and LUMO of **ZnNDBAD** and **ZnNDNAD** also suggest the formation of a diphenyl-benzenamine-benzoic-acid/nitro-benzoic-acid (donor^{•+}-acceptor^{•-}) charge-separated state during the photo-induced charge transfer. The excitation energies of **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD** are shown in Table 9.2. Introducing Ph₂N group in the donor (D) moiety and nitro-group in the acceptor (A) moiety can obviously increase the oscillator strength of the Q-band and also give rise to the red-shift of absorption peaks, which will overlap the solar spectrum especially at the visible range.

9.3.2. UV-Vis Absorption in Solution and on TiO₂ Film & Fluorescence Emission Spectra

The UV-Vis spectra of metalloporphyrins in THF solvent are shown in Figure 9.3(a). All these compounds exhibit two distinct regions in their UV-Vis absorption spectra. The most intense absorption band, commonly referred to the Soret band, exists in the 400-430 nm regions. The Soret band is clearly the most intense peak observed in Figure 9.3 for all the metalloporphyrin sensitizers investigated in this study. The three compounds possess two Q bands in the 500- 650 nm region. The series of bands

between 400 and 650 nm attribute to π - π^* absorptions of the conjugated macrocycle.^{17,18} According to our calculation results of the excited state of the metalloporphyrins based on time-dependent density functional theory (TD-DFT), the vibrational mode Q(0,0) of the $S_0 \rightarrow S_1$ transition. This is consistent with previous reports.¹⁸⁻²⁵ The molar extinction coefficients in the Soret-band region increase in the

Figure 9.2. Molecular orbital diagrams of **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**.

order of **ZnTPPAD** < **ZnNDBAD** < **ZnNDNAD** and the spectra have a slight red-shift in the same order. It is worth comparing our calculated electronic structure to the available spectroscopic data obtained in the context of the present investigation. The spectroscopic data are found to be consistent with the trends in the HOMOs and Soret bands are mainly corresponding to the $S_0 \rightarrow S_2$ transition while the Q-bands are corresponding to the higher vibrational mode Q (1, 0) and the lowest energy LUMOs energies calculated for the excited state of **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**.

Figure 9.3. UV-visible absorption spectra of the three metalloporphyrins dyes in THF solution (a) and adsorbed on TiO_2 (b).

As shown in Figure 9.3(b), the absorption band (*ca.* 400-460 nm) of dyes attached to TiO₂ film are broader and slightly red-shifted for all three compounds compared to those observed in THF solution, implying that the aggregation of dye occurred on the TiO₂ surface which in turn led to a red-shift (so-called *J*-aggregates¹⁸). Similar observations have been reported on the binding of carboxyphenyl zinc porphyrin on nanotube TiO₂ surfaces.^{22,25} The *J*-aggregates of dye molecules were believed to be in a head-to-tail arrangement (end-to-end stacking), forming a *J*-dimer.

The emission spectra of porphyrins **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**, shown in Figure 9.4, were obtained at room temperature in THF solution. The emission maxima are independent of the excitation wavelength between 400 and 600 nm, and the spectra show characteristic double-shoulder peaks around 615 and 655 nm for metalloporphyrins **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD**, similar to that reported in other zinc porphyrins.^{18,22,25} The emission maxima for **ZnNDNAD** are slightly red-shifted as compared to those for **ZnNDBAD** and **ZnTPPAD** which is consistent with the results on the UV-visible absorption spectra.

Figure 9.4. Emission spectra of metalloporphyrins in THF solution.

9.3.3. Photo Electrochemical Measurements in DSSCs

IPCE measurements were performed to compare the efficiency of each sensitizer over the sunlight spectral region. The overall IPCE results for these compounds are shown in Figure 9.5. The system IPCE values were as high as 23% in the range 400 to 450 nm. It is evident that upon comparison to the UV-Vis spectrum of the dye, electron injection in this region originated in the excitation of the Soret band. Q-band photo-excitation also contributed to the overall photocurrent at lower photon energies, with IPCE values about 4%.

Figure 9.5. *J-V* characteristics measured under the illumination of AM 1.5G full sunlight (100 mW/ cm⁻²) for metalloporphyrins and **Z907** and photocurrent action spectra obtained with **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD** anchored on nanocrystalline TiO₂ films (inset).

The respective extinction coefficients of the three compounds foredoom the significant difference in the IPCE values between Soret and Q-band regions. The spectra of the three complexes adsorbed onto 5- μ m-thick TiO₂ electrodes are similar to

those of the corresponding solution spectra but exhibit a small red shift due to the interaction of the anchoring groups with the surface (Figure 9.5 (inset)).¹⁸ The diphenyl-benzenamine-substituted metalloporphyrin dye sensitizer, **ZnNDBAD**, revealed far larger IPCE values than **ZnTPPAD** systems. Maximum efficiencies were 23% and 16%, respectively, both of which occurred in the Soret band region. However, the photocurrent associated with Q-band absorption was small for **ZnNDBAD** and **ZnTPPAD** systems. The **ZnNDNAD** system has the smallest IPCE values. As stated in the former section, dyes in this study aggregate on the TiO₂ surface and the absorption of **ZnNDNAD** on TiO₂ was broadened more than the other two zinc dyes. From Figure 9.5, there is an absence of an aggregate absorption band in the photocurrent action spectrum of the zinc porphyrin compounds which suggests that aggregates do not contribute to any current generation. Consequently, we could draw the conclusion that the reason why photons excited from the monomers is the most effective way of producing charge-separated states is probably due to the less aggregation between the stacks and the semiconductor as reported.^{26,27}

9.3.4. Photovoltaic Measurements

The dye solution was prepared in THF solution (0.4 mM). The hot TiO₂ electrodes (80 °C) were immersed into the dye solution for 2 hrs. The results obtained for current voltage (*I*-*V*) curves for all systems when illuminated are shown in Figure 9.5. The short-circuit current densities, J_{sc} , open-circuit voltages, V_{oc} , fill factors, *FF* and power conversion efficiency of the cell are summarized in Table 9.3 under standard global AM 1.5 solar conditions. Comparison of the metalloporphyrin-sensitized DSSCs results reveals that DSSCs based on **ZnNDBAD** shows the best performance (J_{sc} of 2.83 mA/cm², V_{oc} of 0.62 V and *FF* of 45.59%), which reaches 19% with respect to an

Z907-based device fabricated under the similar conditions. Although the dye **ZnNDNAD** molecule shows the biggest intra-molecular charge separation according to calculation results of the excited state of the metalloporphyrin, it had the poorest performance. Besides intra-molecular charge separation, there are several other critical factors influencing the power conversation efficiency, such as band gap of porphyrin-sensitizers and aggregation degree of metalloporphyrin on TiO_2 . In the case of **ZnNDNAD**, introduction of the nitro-group may facilitate self-aggregation of metalloporphyrin by π -packing¹³ and aggregation on the TiO_2 surface^{12, 27, 28} resulting in a decrease of the conversion efficiency. Some research groups have also demonstrated that the moderate performance of the porphyrin sensitized solar cell can be ascribed to the porphyrin molecules aggregating onto TiO_2 nanoparticle surface.²⁸ Hence, we should minimize the aggregation of the porphyrin sensitizer when we design and synthesize the dyes molecules.

9.4. Conclusion

In summary, dye photosensitizers consisting of unsymmetrical push-pull type zinc-porphyrins was applied in DSSCs and demonstrated their ability to facilitate intramolecular charge separation. A set of metalloporphyrin derivatives have also been synthesized to investigate the effect of substituted acceptor and donor groups on the optical and photovoltaic properties of metalloporphyrin. Together with DFT and TD-DFT calculations, we demonstrated that the TiO_2 solar cell with unsymmetrical donor-bridge-acceptor structures **ZnNDBAD** sensitizer showed an improved cell performance compared to the **ZnTPPAD** sensitized reference cell. Not only can intra-molecular charge separation facilitate the improvement of the power conversion efficiency of solar cell, but the aggregation of metalloporphyrin on TiO_2 surface also

affect the cell performance. Due to the interplay of various factors, the best performance achieved by the DSSCs was the **ZnNDBAD** sensitized TiO₂ solar cell which yielded the maximum IPCE value of 23% and power conversion efficiency η of 0.80 % under standard AM 1.5 conditions. Our results suggest that push-pull type zinc-porphyrins sensitizers with donor-bridge-acceptor (DBA) larger π -conjugating system could increase the photo-to-current efficiency and the position of withdrawing group is important for designing and synthesizing the effective metalloporphyrin-sensitized solar cell. We should also minimize the aggregation of the porphyrin sensitizer at the same time when we design and synthesize the dye molecules.

Table 9.1. Molecular orbital contribution (MOC) of the 5 highest occupied and 5 lowest unoccupied molecular orbitals of **ZnTPPAD**, **ZnNDBAD** and **ZnNDNAD** calculated at the B3LYP/6-31G* level in THF solution.

	MO	Energy/eV	Fragment (MOC, %)					
ZnTPPAD			Zn	Porphyrin- core	Ph-1	Ph-2	D	A
	LUMO+4	-0.25	0.1	1.8	0.7	0.9	0.1	96.2
	LUMO+3	-0.69	0.0	88.5	3.1	2.6	2.8	2.8
	LUMO+2	-1.36	0.1	8.1	0.1	0.2	0.2	91.4
	LUMO+1	-2.28	0.2	94.4	2.0	2.0	0.5	0.6
	LUMO	-2.32	0.2	92.0	0.5	0.5	1.9	4.6
	HOMO	-5.14	2.2	86.1	2.9	2.9	2.9	2.6
	HOMO-1	-5.33	0.0	97.9	0.5	0.5	0.5	0.4
	HOMO-2	-6.34	20.4	78.4	0.0	0.0	0.0	0.0

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	HOMO-3	-6.58	0.6	66.4	13.1	15.6	3.7	0.4
	HOMO-4	-6.59	0.1	78.7	5.3	8.0	6.9	1.0
ZnNDBAD								
	LUMO+4	-0.37	0.0	0.6	0.1	0.1	98.8	0.1
	LUMO+3	-0.70	0.0	84.0	2.8	2.5	7.6	2.9
	LUMO+2	-1.36	0.1	8.2	0.1	0.2	0.3	91.2
	LUMO+1	-2.28	0.2	94.5	1.9	2.0	0.5	0.6
	LUMO	-2.31	0.2	91.4	0.5	0.5	2.5	4.7
	HOMO	-4.94	0.7	26.8	0.8	0.7	70.0	0.7
	HOMO-1	-5.21	1.5	61.3	2.0	2.2	30.4	2.0
	HOMO-2	-5.32	0.0	97.9	0.5	0.5	0.5	0.4
	HOMO-3	-6.34	20.4	78.4	0.0	0.0	0.0	0.0
	HOMO-4	-6.57	0.6	72.5	11.4	11.4	3.7	0.2
ZnNDNAD								
	LUMO+4	-0.76	0.0	83.8	2.5	2.3	6.3	5.0
	LUMO+3	-1.70	0.1	6.6	0.0	0.1	0.2	93.0
	LUMO+2	-2.30	0.2	92.8	1.9	2.0	0.5	2.4
	LUMO+1	-2.36	0.2	90.6	0.5	0.5	2.3	5.6
	LUMO	-2.58	0.1	2.6	0.0	0.1	0.0	97.1
	HOMO	-4.95	0.6	22.6	0.6	0.6	74.7	0.5
	HOMO-1	-5.24	1.7	65.7	2.3	2.5	25.7	1.7
	HOMO-2	-5.36	0.0	98.0	0.5	0.5	0.5	0.4
	HOMO-3	-6.37	20.4	78.4	0.0	0.0	0.0	0.0
	HOMO-4	-6.59	0.6	70.3	12.4	12.5	4.0	0.1

Table 9.2. Computed excited energies (eV), oscillator strengths (f) and two highest electronic transition configurations for the optical transitions below 3.2 eV for ZnTPPAD, ZnNDBAD, and ZnNDNAD in THF calculated using TD-B3LYP/6-31G**/B3LYP/6-31G* using C-PCM framework.

	nm	eV	f	Composition
ZnTPPAD				
1	539.4	2.30	0.0405	H-0->L+0(+62%) H-1->L+1(41%)
2	537.4	2.31	0.0193	H-0->L+1(+59%) H-1->L+0(+44%)
3	403.3	3.07	1.6804	H-1->L+1(+41%) H-0->L+0(+22%)
4	400.7	3.09	1.6164	H-1->L+0(+42%) H-0->L+1(25%)
5	369.5	3.36	0.0877	H-0->L+2(+89%)
ZnNDBAD				
1	559.3	2.22	0.1733	H-0->L+0(+76%) H-2->L+1(+20%)
2	552.4	2.24	0.0284	H-0->L+1(+67%) H-2->L+0(28%)
3	511.8	2.42	0.0388	H-1->L+0(+63%) H-2->L+1(23%)
5	403.6	3.07	1.7806	H-2->L+1(+39%) H-1->L+0(+21%)
6	399.7	3.10	1.5769	H-2->L+0(+40%) H-1->L+1(24%)
7	379.0	3.27	0.1643	H-0->L+2(+76%) H-1->L+2(12%)
ZnNDNAD				
1	564.6	2.20	0.1520	H-0->L+1(+76%) H-2->L+2(+14%)
2	553.5	2.24	0.0238	H-0->L+2(+64%) H-2->L+1(23%)
3	545.4	2.27	0.0331	H-2->L+0(+89%)
4	515.8	2.40	0.0175	H-1->L+1(+62%) H-2->L+2(27%)
5	425.7	2.91	0.1883	H-0->L+3(+65%) H-1->L+3(22%)
6	403.6	3.07	1.2464	H-2->L+1(+34%) H-1->L+2(21%)
7	399.6	3.10	1.3859	H-2->L+2(+30%) H-0->L+3(23%)
8	383.3	3.23	0.3031	H-1->L+3(+67%) H-0->L+3(+10%)
9	381.7	3.25	0.4087	H-2->L+3(+77%)

Excited energies with oscillator strengths having <0.01 eV are ignored.

Table 9.3. Detailed photovoltaic parameters of metalloporphyrins as sensitizer.

Electrode	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
ZnNDBAD	0.617	2.83	45.9%	0.80%
ZnTPPAD	0.531	1.69	39.1%	0.35%
ZnNDNAD	0.511	1.02	40.9%	0.21%
Z907	0.660	14.54	44.7%	4.28%

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Chapter 10. Conclusions and Outlooks

The objective of this work is to focus on the enhancement of the conversion of dye sensitized solar cells (DSSCs). In this thesis, my strategy to improve the efficiency of DSSCs is mainly concentrated on increasing light harvesting and electron collection. Light harvesting could be enhanced by expanding the absorption spectra to Vis and Near IR region and improving the sun-light harvesting *via* introducing the scattering layer, while electron collection could be increased by improving the electron transport through the photoanode and reducing the charge recombination in the device. In other words, the thesis covers the efficiency improvement of DSSCs from two main aspects: photoanode and dye optimization.

For the optimization of photoanode, F-doping into TiO_2 semiconductor to enhance electron transport, reduced graphene oxide to form Schottky barrier junction and hollow SnO_2 and TiO_2 as scattering layer to increase the light harvesting was employed. For dye optimization, main work was done on π -conjugated bridge to extend the absorption spectrum and to suppress the charge recombination, as well as push-pull type sensitizers with donor-bridge-accepts to increase charge separation.

The thesis contains valuable findings and contributions to the improvement of the conversion efficiency of DSSCs.

10.1. Conclusions

The summary of my contributions to improve the conversion efficiency of DSSCs is as follows: Improving the adsorption spectra using different sensitizers based on the concept of donor- π -bridge-acceptor

I. Suppressing the charge recombination using linear bridge group

- II. Systematically investigating the effect of donor, linear bridge and acceptor
- III. Increasing the sun-light harvesting using hollow structure scattering layers
- IV. Improving the electron transportation and electron injection by the addition of fluorine into the semiconductor

According to the above analysis in the chapter 3 to chapter 9, I could draw these conclusions as the following:

(1) The TiO₂ mesoporous layer with uniform F doping was prepared by using a less toxic and more environmentally friendly method by using TiF₄ replacing the commonly used HF and successfully applied in DSSCs *via* doctor-blading technique. The improved cell performance is attributed to an enhanced interfacial charge transfer rate between the interconnected TiO₂ and a higher injection rate from dye to TiO₂, which are attributed to the formation of Ti³⁺ and F⁻ ions in the semiconductor and a reduction in interfacial recombination between TiO₂ and electrolyte. This photoanode could also significantly boost electron mobility and electron transport. The mechanisms of the electron transfer and charge recombination at the FTO/TiO₂/electrolyte interfaces were investigated using electrochemical impedance spectroscopy (EIS).

(2) The reduced graphene oxide (rGO) was introduced into the photoanode and formed the rGO-TiO₂ junction. The rGO layer served as an efficient electron transport channel from dye molecules to TiO₂ photoanode, due to the formation of rGO-TiO₂ Schottky barrier junction. This functional junction improved the interface contact between the dye and TiO₂, and enhanced the photogenerated-electron transport/injection efficiency in the photoanode. The experimental data is supported by theoretical studies of the

potential drop from the graphene to TiO_2 and the electron transport kinetics in the rGO- TiO_2 junction investigated by electrochemical impedance spectra (EIS).

(3) The hollow SnO_2 microspheres were synthesized by a facile hydrothermal method. This hollow SnO_2 microsphere as scattering layer was applied to DSSCs on the top layer of transparent TiO_2 . The light multi-reflections and scattering was studied by reflectance spectra. In addition, the kinetics of interfacial reactions of photo-excited electrons in DSSCs was investigated by EIS spectra. Due to the reduced transfer resistances, faster diffusion constants and enhanced light harvesting, the performance of the bilayer DSSCs with SnO_2 top layer is better than that without SnO_2 top layer.

(4) Fluorine doped TiO_2 hollow spheres as a scattering layer was applied to dye-sensitized solar cell (DSSCs) system, the overall efficiency of photoanode was increased by 19% in comparison with the control device with 600 nm TiO_2 nanoparticles. The synthesized TiO_2 hollow spheres show a better light confinement in the device which will facilitate light harvesting by increasing the light path length infinitely. Moreover, the conversion efficiency of the solar device could be achieved by using less amount of dye without compensating the solar light harvesting, contributing to the cost efficiency of the device. Furthermore, the F-doped photoanode is propitious to the charge collection due to the improvement of electron transport and retardation of recombination. FDTD simulation of optical scattering confirms the increase of light path due to Mie scattering within and outside the hollow spheres. The electron transport kinetics in the device was also investigated by electrochemical impedance spectra (EIS).

(5) In this thesis the effect of the donor, bridge and acceptor group was studied. Before synthesis, TD-DFT calculation was carried out to screen the appropriate sensitizers. The results show that the sensitizers with push-pull framework could facilitate the

intramolecular charge separation, the absorption spectra of the dye molecules can be extended through introducing strong electron donating groups and electron withdrawing groups and more π -conjugated bridge groups.

The molecules with linear bridge moiety show better planarity, which could suppress the electron recombination. Similar with the function of molecular switches by light controllable when the molecule is in the closed form, the electron transfer could be suppressed, while in the open form, the molecule can allow the electron transfer from donor (D) *via* bridge (B) to acceptor (A). In addition, the unidirectional current was formed.

10.2 Outlooks

In the future work with regards to improvement of the cell performance, the following studies are proposed.

- (1) Panchromatic absorber with high molar extinction coefficient needs to be found to enhance the cell performance. Since the short electron lifetime is the bottleneck for organic sensitizers, the aim to solve this problem is to reduce the charge recombination by introducing more appropriate bridge moiety in this system, at the same time; introducing better donor and acceptor to facilitate the intramolecular charge-separation, and acceptor with strong withdrawing groups will be made for the electron injection due to the strong electron coupling with TiO_2 semiconductor.
- (2) Design and synthesize molecules with strong withdrawing groups, such as sulfonic acid or phosphonic acid group, as the coadsorbent, which could prevent the organic sensitizer from aggregating on the TiO_2 , as well as the appearance of coadsorbent is

expected to aid the increase in the open circuit voltage of the solar cells due to the enhanced electron lifetime in the TiO₂ nanoparticles accompanied by the conduction band of TiO₂ up-shift.

(3) Design and synthesize uniform hollow F-doped TiO₂ with high surface area as the photoanode, this photoanode could not only serve as the photoactive layer but also ensure adequate light trapping in the devices, which means this monolayer could utilize the incident light more efficiently due to the light-scattering centre and the electricity-generation source. What is more, this monolayer structure could significantly boost electron mobility and electron transport due to the decrease of carrier scattering at grain-boundaries and surface-defects, while retarding charge recombination in the device.

(4) The DSSCs's sealing remained an urgent issue to be solved. Therefore the ionic-liquid or quasi-solid state electrolytes need to be synthesized. The viscosity and the electric conductivity need to be considered.

(5) Pt as counter electrode is expensive. Thus, cheap materials with high catalytic activities need to be exploited. For example, using graphene as a suitable substitute could improve the overall conversion efficiency of DSSCs due to high electron mobility and good stability.

(6) The dynamic of the charge transport and charge recombination need to be studied in details using transient absorption spectra or other time-resolved spectroscopy.

PUBLICATIONS

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by Introducing Reduced Graphene Oxide-TiO₂ Junction
Jun-Ling Song, Zong-You Yin, Xue-Wei Liu THE 8TH INTERNATIONAL
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ELECTROCHEMICAL SYSTEMS SCIENTIFIC PROGRAM July 11-15, 2010,
(Oral Presentation, Session 1: 13)

2. Hollow SnO₂ Light-Scattering Layer Used for Dye-Sensitized Solar Cells

Junling Song, Beeluan Lim, Jiehua Liu, Weiqiao Deng, Xuwei Liu*

6th Asian-European Synposium on Metal Mediated Efficient Reaction, 7th-9th
June, 2010, (poster presentation).

INDEX OF ABBREVIATIONS

AM 1.5 G	Incident air mass 1.5 global spectrum
BET	Brunauer-Emmett-Teller
EIS	Electrochemical impedance spectroscopy
CB	Conduction band
CV	Cyclic voltammetry
DFT	Density functional theory
DOS	Density of states
DSSC	Dye Sensitized Solar Cell
FF	Fill factor
FTO	Fluorine doped tin oxide
HOMO	Highest occupied molecular orbital
I-V	Current-voltage
IPCE	Incident photon to current efficiency
I_{sc}	Short circuit photocurrent (mA)
J_{sc}	Short circuit photocurrent density (mA/cm ²)
LHE	Light harvesting efficiency
LUMO	Lowest unoccupied molecular orbital
MLCT	Metal-to-ligand charge transfer transitions
N3	<i>cis</i> -dithiocyanatobis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II)
N719	<i>cis</i> -bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium
NHE	Normal hydrogen electrode
NIR	Near infrared

Publication and Index of Abbreviations

MWCNT	Multi-walled carbon nanotubes
PCE	Photo to current conversion efficiency
PV	Photovoltaic
SEM	Field emission scanning electron microscopy
SWCNT	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
TCO	Transparent conducting oxide
TDDFT	Time dependent density functional theory
UV	Ultraviolet
VB	Valence band,
Vis	Visible light
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Z907	<i>cis</i> -bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(2,2'-bipyridyl-4,4'-di-nonyl)ruthenium (II)