Modeling of Nanostructured Solar Cells

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Abstract

Nowadays, people are focusing on research and development of some different kinds of solar cells as replacements for silicon based solar cells (SSCs) by using alternative technologies and low-cost materials. Polymer solar cells (PSCs) and dye-sensitized solar cells (DSCs) have been considered as promising replacements. In the last twenty years, a significant progress has been made on the improvement of the power-conversion efficiency (PCE) for both polymer and dye-sensitized solar cells, and the achieved efficiencies have evolved to around 9% for PSCs and 12% for DSCs as reported recently. However, the efficiency of polymer solar cells is still significantly lower than the traditional inorganic SSCs, which nowadays has reached nearly 26%.

In order to further optimize the performance of polymer and dye-sensitized solar cells and eventually reach the goal PCE for commercialization of nearly 15%, support and guidance from theoretical modeling will be required. Hence, in this thesis, we have achieved the ultimate efficiency of the structured polymer solar cells by using the model based on Marcus theory of electron transfer**.** By choosing different active layer materials, the upper limits of efficiency in these various polymer solar cells were calculated. Besides, we combined the light absorption coefficient into calculation, the ultimate efficiencies were largely affected, and more accurately, were significantly deduced**.** These results showed better approximation to the real experimental cases.

The dye-sensitized solar cells were fabricated by a layer of highly porous nanocrystalline TiO_2 in association with a traditional ruthenium dye as sensitizer to form the anode electrode and a layer of structured platinum/ITO as the cathode back contact. By using modeling process along with the combination of light absorption coefficient, the ultimate efficiencies for DSCs with different back contact structures were achieved. The enhanced performance compared with the traditional non-structure cells in ultimate efficiency was clearly demonstrated and can be explained by theoretical analysis.

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Chapter 1

Introduction

This chapter provides some background reviews of different types of solar cells in relevant researches. Silicon based solar cells (SSCs) have become the most used way for conversion of solar energy since the first cells were fabricated in 1950s [1][2]. However, the growth of the solar energy industry has been limited by the supply of the polysilicon material used to make SSCs. Nowadays, people are focusing on researching and developing of some different kinds of solar cells as replacements for SSCs by using alternative technologies and low-cost materials. Polymer solar cells (PSCs) have been considered as a promising replacement to the traditional silicon-based solar cells due to their impressive advantages such as flexibility, low cost of the material and fabrication, the potential for large-scale applications, and the compatibility with high-throughput commercialization, such as roll-to-roll manufacturing [1][2][3][4][5]. However, the relatively low efficiency of these polymer-based solar cells has always been a roadblock on the way to the commercialization. In the early 2012, the power conversion efficiencies of silicon based solar cells have reached to 25.47%[1]. In comparison, the reports cited efficiencies of the PSCs are no greater than 8.6% [6]. Dye-sensitized solar cells (DSCs) have been considered as another possible replacement. DSCs are attractive since the materials they are made from are abundant, non-toxic, cheap and no need for highly purified [7][8]. Besides, compared with the polymer solar cells, they are more robust and the fabrication process is repeatable. The major disadvantage is that the temperature-sensitive liquid electrolyte used in DSCs may cause not only device leakage and some serious additional problems such as potential instability [8]. Besides, the reported highest efficiency record under standard conditions [9] of 12.3% for DSCs is still a factor of 2 below that of silicon based solar cells.

1.1 Polymer Solar Cell

One of the key advantages for the flexible polymer photovoltaic technology is the low-cost and simple fabrication process, which is compatible with high-throughput manufacturing process. A traditional, yet successful technique is used for fabrication of the solution-processed bulk-heterojunction (BHJ) solar cells. This concept was first demonstrated by Professor Alan J. Heeger and his colleagues at the University of California, Santa Barbara in paper published on Science, 1995 [10]. The active layers of their polymer-based solar cells are polymers for electron-donating and fullerene materials for electron-accepting. The blended active layer can be prepared and coated on a large area by using techniques such as spin-coating, inkjet-printing, spray-coating, roller-casting etc. [10]. *Figure 1.1* shows the structure of a traditional polymer solar cell. The active layer materials are P3HT and PCBM. The energy levels of each layer for this traditional polymer solar cell are presented in *Figure 1.2*.

Figure1. 1 Schematic drawing showing the structure of traditional polymer solar cell

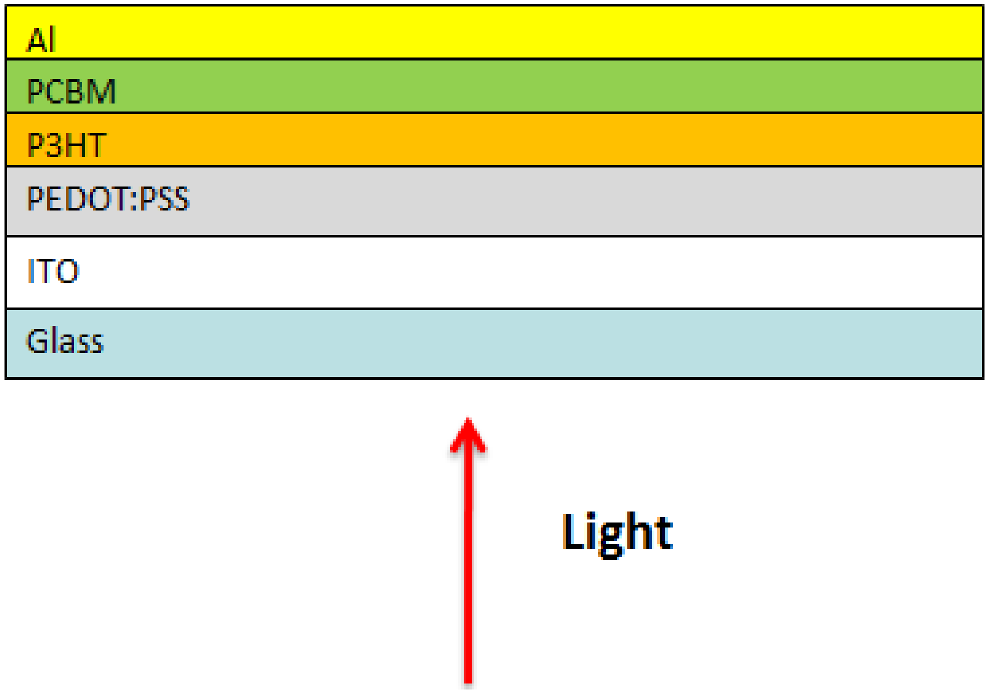
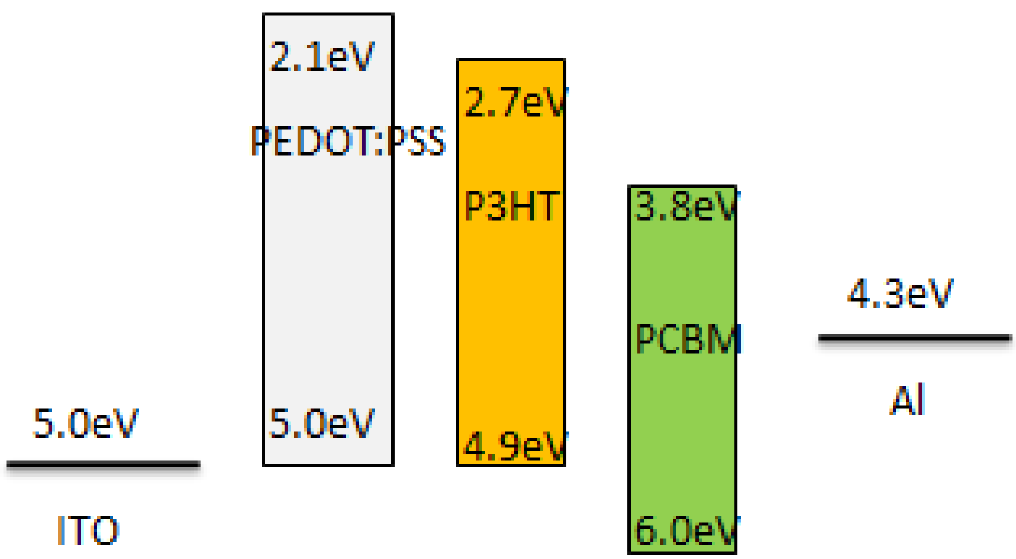


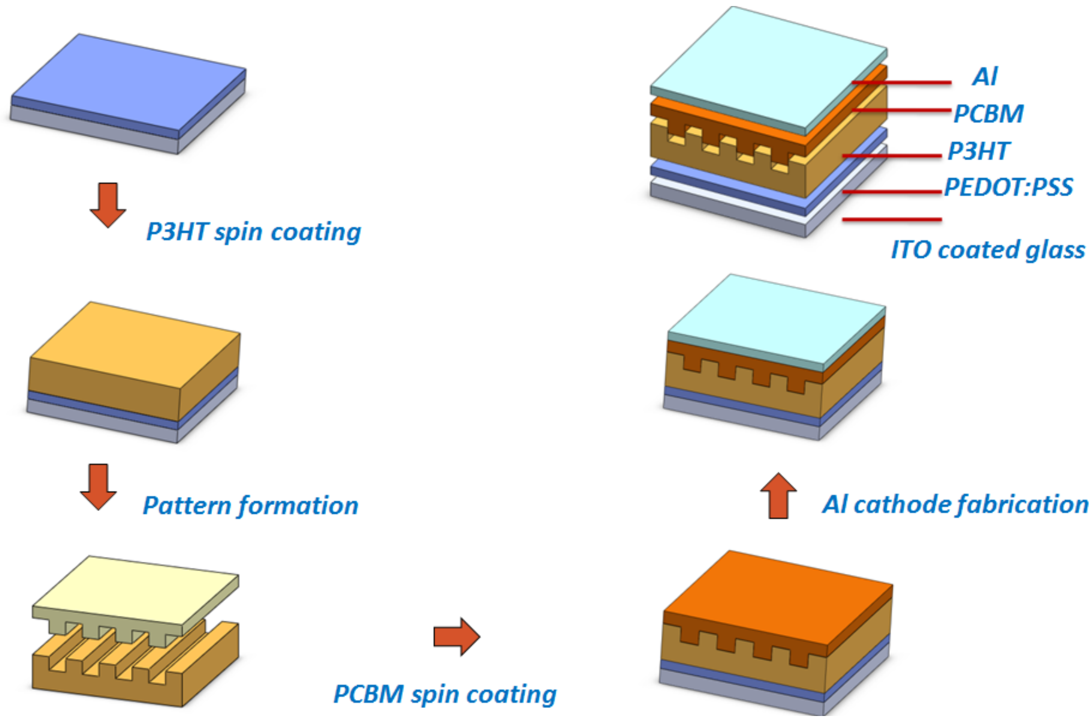
Figure1. 2 Schematic drawing showing energy levels of each layer for traditional polymer solar cell



In the last seventeen years, a significant progress has been made on the improvement of the power-conversion efficiencies of these polymer based solar cells, and the achieved efficiencies have evolved from less than 1% in the poly (phenylene vinylene) (PPV) system in 1995 [10], to 4–5% in the poly (3-hexylthiphene) (P3HT) system in 2005 [3], to around 8.6% [6] in tandem cells, as reported recently. However, the efficiency of polymer solar cells is still significantly lower than inorganic materials based solar cells, such as silicon and CIGS.

Basically, two types of polymer solar cells have been developed with different kinds of structures: (1) electron donor and acceptor (D/A) bilayer cells and (2) bulk-heterojunction cells [5]. One of the most important reasons for fabrication of structured polymer solar cells is to generate larger interfacial area in order to develop optimized device performance. Since the exciton diffusion limit in these polymer based solar cells are typically 5-10 nm, the more effective charge carrier pathways on larger interfacial areas will theoretically lead to a higher efficiency for both the bilayer and bulk-heterojunction solar cells [5]. Technologies, such as nanoimprinting and hot embossing are usually used for molds and pattern structure fabrication. *Figure 1.3* shows the typical fabrication process of a structured polymer solar cell.

Figure1. 3 Schematic drawing showing the typical fabrication process of a structured polymer solar cell



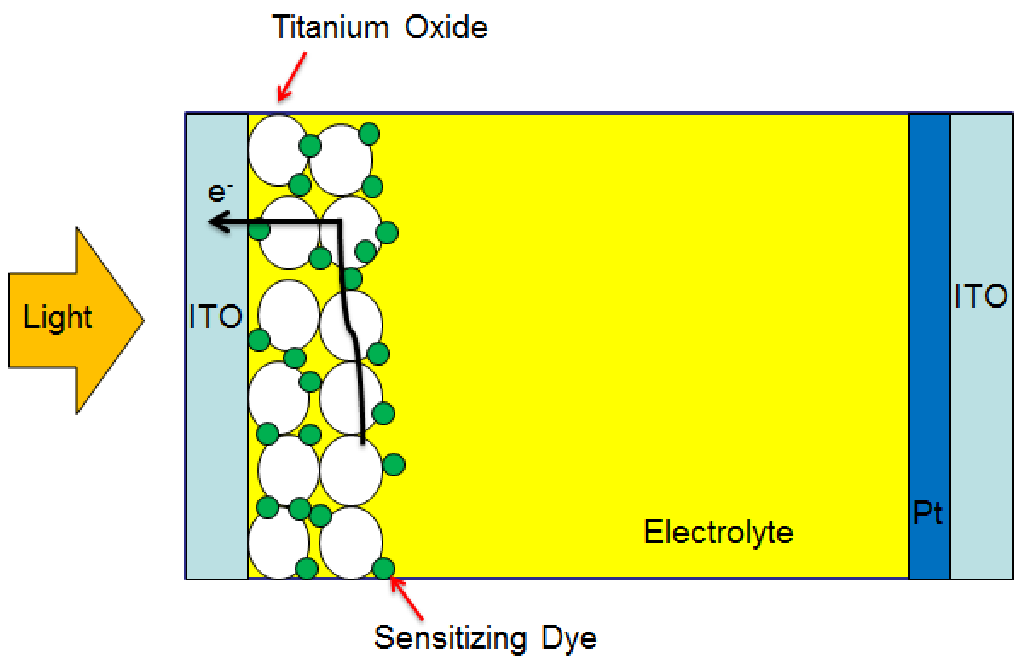
Numbers of models have been created in order to estimate and calculate the polymer solar cells efficiencies during the last 10 years. Most of these models are focused on searching the optimized position of energy levels of donor and acceptor polymer in order to achieve the maximized energy conversion efficiency, which will give guidance for the material study in polymer solar cells.

1.2 *Dye-Sensitized Solar Cell*

Since Grätzel et al. developed this new type of solar cells dye-sensitized solar cells (DSCs) in 1991 [7], DSCs have attracted considerable attention because they are made from abundant, non-toxic, cheap and no need for highly purified materials. DSCs are so unique compared with almost all other kinds of solar cells since electron transport, light absorption and hole transport are each handled by different materials [8]. The sensitizing dyes in DSCs are mostly attached and connected to a semiconductor such as TiO_2 or ZnO. The dyes are in charge of the light collection and afterwards electron transportation. The photoexcited dyes generate plenty of electrons and rapidly inject the electrons into the attached semiconductor. The electrons are then transport to the anode electrodes [11]. Redox couples then neutralize the excited dyes and reduce those back to its neutral state to fulfill the regeneration [8]. *Figure 1.4* shows the structure of a typical dye-sensitized solar cell.

Nowadays, the most popular sensitizing dyes and redox couples are ruthenium-based dyes and iodide/triiodide redox couple. However, several new records in power-conversion efficiencies are made by newly developed dyes and redox couples. Donor–pi–acceptor dyes absorb much more in almost all visible range than the traditional ruthenium-based dyes, and the new cobalt-based redox couples are considered helpful to obtain higher open-circuit voltages. Structured electrodes are also helpful for light trapping, which has been proven to be an effective strategy [12].

Figure1. 4 Schematic drawing of a typical dye-sensitized solar cell



1.3 Thesis Outline

The work contained in this thesis will focus on modeling of ultimate efficiency of nanostructured polymer solar cells and dye-sensitized solar cells. The cells are modeled with different active layer materials and nanostructured back contacts while the light absorption coefficient will be calculated and added as well into the modeling. Chapter 1 introduces some basic concepts and considerations in terms of polymer solar cell and dye-sensitized solar cells. Chapter 2 reviews the modeling process based on Marcus theory of electron transfer and discusses the modeling by using some newly and different combinations of p-type and n-type materials as the active layer in the polymer solar cell. The upper limit of the polymer solar cell efficiency could be optimized by changing the position of the acceptor LUMO for any band gap value and the difference between the acceptor LUMO and the polymer donor HOMO. Besides, the light absorption coefficient to the previous active layer materials can be mixed into the calculation of ultimate efficiency. By adding the light absorption coefficient into the expression, a more accurate and veridical result can be achieved. Chapter 3 briefly presents the fabrication and testing processes for dye-sensitized solar cell. Chapter 4 discusses the ultimate efficiency modeling of nanostructured dye-sensitized solar cell, which shows an increasing in light absorption. This kind of design leads to a light trapping and results in an advancing efficiency of the solar cells. Chapter 5 summarizes this thesis work and provides suggestions and discusses the future work.

Chapter 2

Modeling of Ultimate Efficiency of Polymer Solar Cells

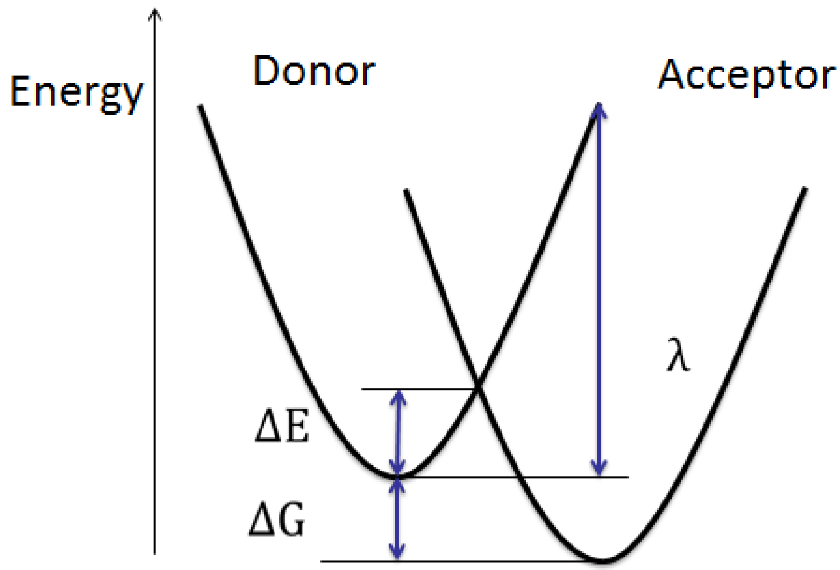
The modeling process of ultimate efficiency for polymer solar cells is presented in this chapter. The model is produced based on well-known Marcus Theory due to Rudolf Marcus, which is generally used in describing the electron transfer in electrolytes [13]. Prof. Godovsky has calculated the upper limit of the polymer solar cell efficiency in no-recombination approximation by using Marcus theory of electron transfer [16].

2.1 Introduction

2.1.1 Marcus Theory

Marcus Theory is a theory to explain the rates of electron transfer reactions. It is originally developed by Rudolph A. Marcus in 1956, The Marcus theory clearly explained the rate for electron transport and the energy been used in the transportation from the electron donor to the electron acceptor [13]. *Fig. 2.1* shows the energy diagram for electron transfer including reorganization energy.

Figure2. 1 Energy diagram for electron transfer



The vertical axis is the free energy, and the horizontal axis represents the motion of the atomic nuclei [13].

The basic and key equation of Marcus theory is:

$$k_{et} = \frac{2\pi}{h} |H_{AB}|^2 \frac{1}{\sqrt{4\pi \lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G)^2}{4 \lambda k_b T}\right) \quad (2.1)$$

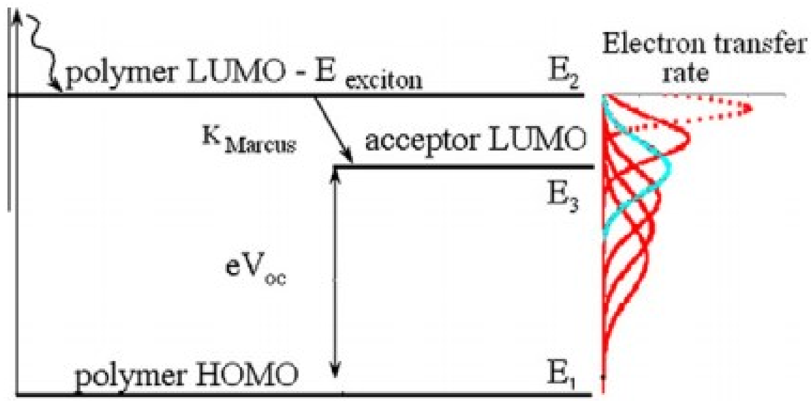
where ΔG is the free energy difference in between the electron donor and the electron acceptor, H_{AB} is describing the intersection of the wave functions and λ is the parameter describing the amount of energy required to distort the nuclear configuration of the reactants into the nuclear configuration of the products without electron transfer occurring [16].

Previous papers, such as W. Duncan et.al [14], V. Dyakonov et al [15] and Godovsky [16] have proved that it is possible to use Marcus theory of electron transfer in describing the photo-induced electron transfer process. Prof. Godovsky also provided a model for the ultimate efficiency calculation of the polymer solar cell efficiency by using Marcus theory of electron transfer.

2.1.2 Modeling of Ultimate Efficiency of Polymer Solar Cells Using Marcus Theory

Newly developed polymer solar cells, based on newly developed p-type polymer material introduced Yang Yang group have been demonstrate with a power conversion efficiencies of 8.6% and photovoltages up to 1V [6]. However, the power conversion efficiency of polymer solar cells still needs to be improved in order to be commercially available. Guidance from theoretical and simulation studies will play a key role. Modeling and simulation of the operation of polymer solar cells are required. In theoretically, polymer solar cell operation can be considered basically as electron and hole transport between donor and acceptor. Thus, Marcus theory of electron transfer can be applied to calculate the upper limit of the polymer solar cell efficiency in no-recombination approximation [16]. According to the paper *Modeling the ultimate efficiency of polymer solar cell using Marcus theory of electron transfer* [16], they determined the optimal position of the Acceptor LUMO level, as depicted at *Fig. 2.2*, giving the maximum power output.

Figure2. 2 [16] The three-level diagram for donor–acceptor polymer photovoltaic cells, right side graph - dependence of Marcus rate of electron transfer from Energy level of Acceptor for different λ. Blue curve corresponds to Acceptor LUMO level, depicted at diagram



Since they were calculating the ultimate efficiency of the cell, they assume the Fill Factor equals one. The maximum power output is then:

$P_{max} = V_{max} \cdot I_{max}$. The upper limit of V_{max} is determined by the difference $eV_{max} \sim E_1 - E_3 \sim E_g + E_2 - E_3$. ΔG, the driving force of the process, here can be replaced by $\Delta G = E_2 - E_3$. Then, the I_{max} can be achieved by replacing the main equation of the Marcus theory of electron transfer [16].

$$\frac{I_{max}}{e} = \frac{2\pi}{h} |H_{AB}|^2 \frac{1}{\sqrt{4\pi \lambda k_b T}} \exp\left(-\frac{(\lambda + E_2 - E_3)^2}{4 \lambda k_b T} \right) \quad (2.2)$$

Then P_{max} is given by combined the I_{max} and V_{max}

$$P_{max} = \frac{2\pi}{h} |H_{AB}|^2 \frac{1}{\sqrt{4\pi \lambda k_b T}} \exp\left(-\frac{(\lambda + E_2 - E_3)^2}{4 \lambda k_b T} \right) \cdot (Eg + E_2 - E_3) \quad (2.3)$$

Take derivative of the expression above and set $P_{max}{}' = 0$, then the Optimum position of Acceptor LUMO can be gained as [16]

$$E_{lumoptimal} = \frac{E_g - \lambda + \sqrt{(E_g - \lambda)^2 + 8\lambda k_b T}}{2} \tag{2.4}$$

2.2 Modeling of Ultimate Efficiency of Other Materials Based Polymer Solar Cell

Based on the position of LUMO level of acceptor, which maximizes the power output, they derived the expression for the Ultimate Efficiency of the polymer solar cells as follows.

By treating the Ultimate Efficiency of the cell with no recombination losses, thus the expression for the Ultimate efficiency of the Solar Cell will be:

$$\eta = \frac{\left[\int_{\lambda_1}^{\infty} N_{b\lambda}(T_{sun}, \lambda)\, d\lambda\right] \cdot \int_{\lambda_1}^{\infty} \alpha(T_{sun}, \lambda)\, d\lambda \cdot E_{Lumooptimal}}{\int_0^{\infty} E_{b\lambda}(T_{sun}, \lambda)\, d\lambda} \tag{2.5}$$

Where $N_{b\lambda}$ is the number of photons with corresponding energy, $\alpha(T_{sun}, \lambda)$ is the absorption coefficient and $E_{Lumooptimal}$ is the ultimate limit of energy level position [16]. We have used mentioned assumptions to calculate the Ultimate Efficiency and numerically calculated the integral, optimizing the $E_{Lumooptimal}$ for each taken Band Gap value. We modeled the Sun as black body with T = 5800 K, T_{cell} = 300 K, incident light perpendicular to the cell surface.

According to the expression for the ultimate efficiency of the solar cell, the $E_{Lumooptimal}$ can be easily gained to be 1.2576eV.

Since $1 \text{ eV} = 1.6022 \times 10^{-19}$ J , light with a photon energy of a eV has a wavelength of (in vaccum)

$$\lambda = \frac{h\,c}{h\omega} = \frac{1.240}{a}\ \mu\text{m} \tag{2.6}$$

So for an electron donor P3HT with a band gap $E_g = 2.0$ eV, the corresponding λ would be 0.62 µm

By using the numerical calculation, we can gain

$$\int_0^{0.62} N_{solar}(\lambda)\, d\lambda \approx 1.2517 \times 10^{21}\ 1/\text{s} \cdot \text{m}^2$$

Thus, by introducing the solar irradiation power on Earth

$$\int_0^{\infty} E_{b\lambda}(T_{sun}, \lambda)\, d\lambda = 1367\ \text{W/m}^2$$

We can have

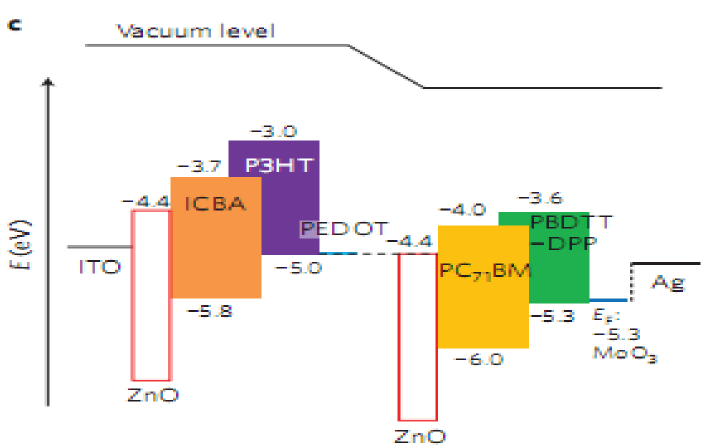
$$\eta \approx 16.2\%$$

I also tried to using these into the paper from Yang Yang's group which published on Nature Photonics [6]. In their tandem cell, they were using a different matching of the active layer for the lower band gap cell. They chose PBDTT-DPP and $PC_{71}BM$ as the P/

N type material. According to the energy level showing in the *Figure 2.3* below, I gained the $E_{lumooptimal}$ using the expression before. The number would be 1.063eV. So the optimal difference between the LUMO of the acceptor and the LUMO of the donor would be 5.3-3.6-1.063= 0.637eV. The actual difference is 0.4eV, which is just slightly higher than the minimum value (~0.3eV) for efficient charge separation, this may lead to a minimum energy loss, but the J_{sc} will be reduced. However, they mentioned the PBDTT-DPP has a higher hole mobility, which will lead to an increasing in J_{sc}.

After calculating the ultimate efficiency, I got an ultimate maximum efficiency of 21.7%, which is quite high number for a polymer solar cell. They have a maximum efficiency of 8.6% in real.

Figure2. 3 [6] Energy diagram of the inverted tandem devices



By using the process, I also modeled the ultimate efficiencies of some tandem cells, which has been proven as some high-efficiency polymer solar cell in the published paper. First, I checked the paper named *Graphene Intermediate Layer in Tandem Organic Photovoltaic Cells* [17], then I easily found out the Energy Levels of the active layer used in their tandem cell. They were choosing the traditional P3HT/PCBM as the materials used for bottom cell, meanwhile, the new P/N type materials combination of ZnPc/C60 for top cell. After the calculation, we can gain the results:

For bottom cell P3HT/PCBM; $\boldsymbol{E_{lumooptimal}}$ =1.2576 eV (Real number: 5.2-3.7=1.5eV)

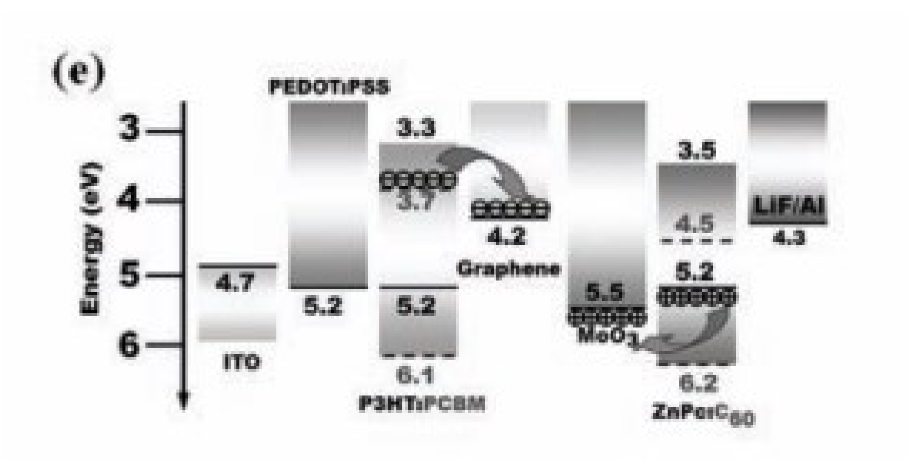
For top cell ZnPc/C60; $\boldsymbol{E_{lumooptimal}}$ =1.0626 eV (Real number: 5.2-4.5=0.7eV)

Then, for the ultimate efficiency,

For bottom cell P3HT/PCBM; the ultimate efficiency would be ~16.2%.

For top cell ZnPc/C60; the ultimate efficiency would be ~22.4%.

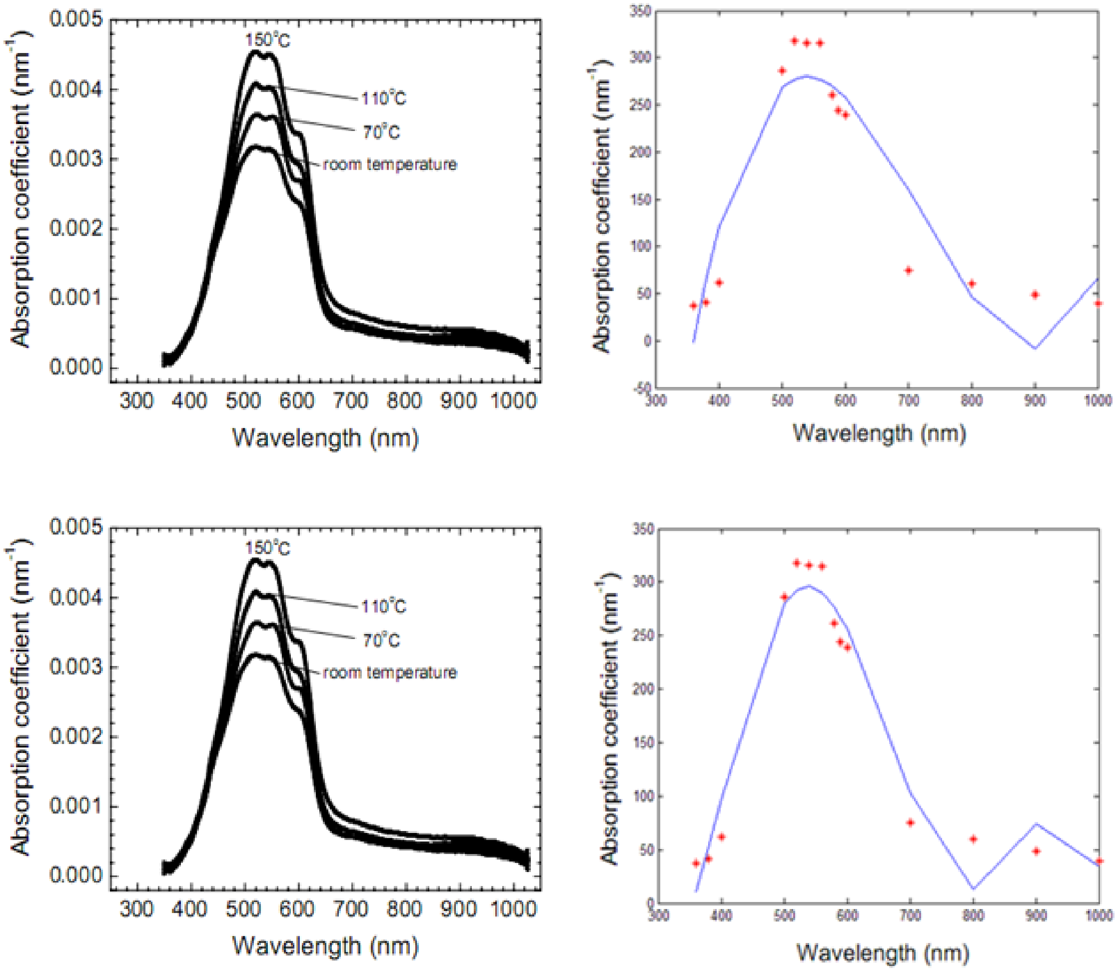
Figure2. 4 [17] Energy diagram of the tandem devices



2.3 Light Absorption Coefficient Spectrum Involved Modeling

According to the expression for the ultimate efficiency of the solar cell, we treated light absorption coefficient as equal as one when the incident light energy is large enough to excite the electrons. Obviously, that assumption is in ideal condition, while not considering the material properties. When combined the light absorption coefficient into consideration, the ultimate efficiency will be largely affected, and more accurately, should be significantly deduced. By using MATLAB POLYFIT function, we can easily do the absorption coefficient curve fitting.

Figure2. 5 Matlab fittings based on different orders for traditional materials



After the fitting, we can easily extract the function from the curve, and achieve a function in representing the relation in absorption coefficient and wavelength of the incident light. The four Figures below are showing the absorption coefficient spectrum of polymer solar cells using P3HT/PCBM as active layers. The two figures on the left showed the testing results spectrum of absorption coefficient. The measurements are gained from the paper titled *Optimizing material properties of bulk-heterojunction polymer films for* *photovoltaic applications* [18]. The first two in the first row are representing the Matlab fitting using order of three and the two in the second row are representing fitting by higher order of five. The achieved functions are showing here below;

Function with order of three:

10^5 y=$1.21*10^{-5}*x^3$ $-2.62*10^{-2}*x^2$ + 17.66*x -3532.16

Function with order of five:

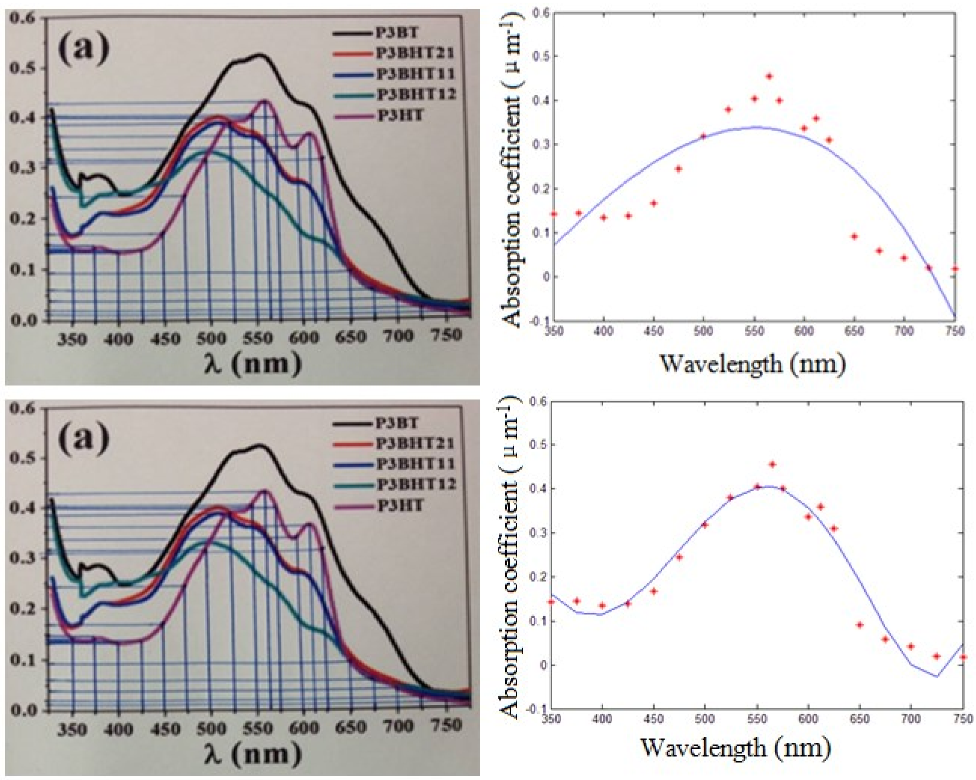
10^*y= $-1.9*10^{-14}*x^5+6.17*10^{-11}*$ x^4 $-7.68*10^{-8}*$ $x^3+4.51*10^{-5}*$ $x^2-1.24*10^{-2}*x$ +1.27

Where y axis representing the absorption coefficient, x axis representing the corresbonding wavelength.

Then, based on these functions, we can do the integration of the absorption coefficient number from the wavelength range of 360 nm to 750 nm, which covers nearly the whole visble light part and the near-IR part. By adding the integration of the absorption coefficient into the ultimate efficiency calculation showed in *Equation 2.5*, we can gain a more accurate result by considering the light absorption into the calculation.

If we put our eye on the newly developed materials, for example the P3HT and $PC_{71}BM$, we can also gain a more accurate number by involved the light absorption coefficient of the blends of those two materials. The pink curves labeled P3HT in the figures below are showing the measurements of the light absorption coefficient of the blends P3HT/$PC_{71}BM$. These measurements are from published paper named *All-conjugated* *poly(3-alkylthiophene) diblock copolymer-based bulk heterojunction solar cells with controlled molecular organization and nanoscale morphology* [19].

Figure2. 6 Matlab fittings based on different orders for novel materials



The first two in the first row are representing the Matlab fitting using order of three and the two in the second row are representing fitting by higher order of five. The achieved functions are showing here below;

Function with order of three:

$$10^{*}y= -1.10*10^{-8}* x^{3}+9.42*10^{-6}* x^{2}-3.64*10^{-4}*x-0.48$$

Function with order of five:

$10^{*}y= 1.09*10^{-12}* x^{5}-2.56*10^{-9}* x^{4}+2.25*10^{-6}* x^{3}-9.20*10^{-4}* x^{2}+0.17*x-10.78$

Where y axis represents the absorption coefficient, x axis represents the corresbonding wavelength.

Then, based on these functions, we can do the integration of the absorption coefficient number in the wavelength range of 350 nm to 750 nm, which covers nearly the whole visble light part and the near-IR part.

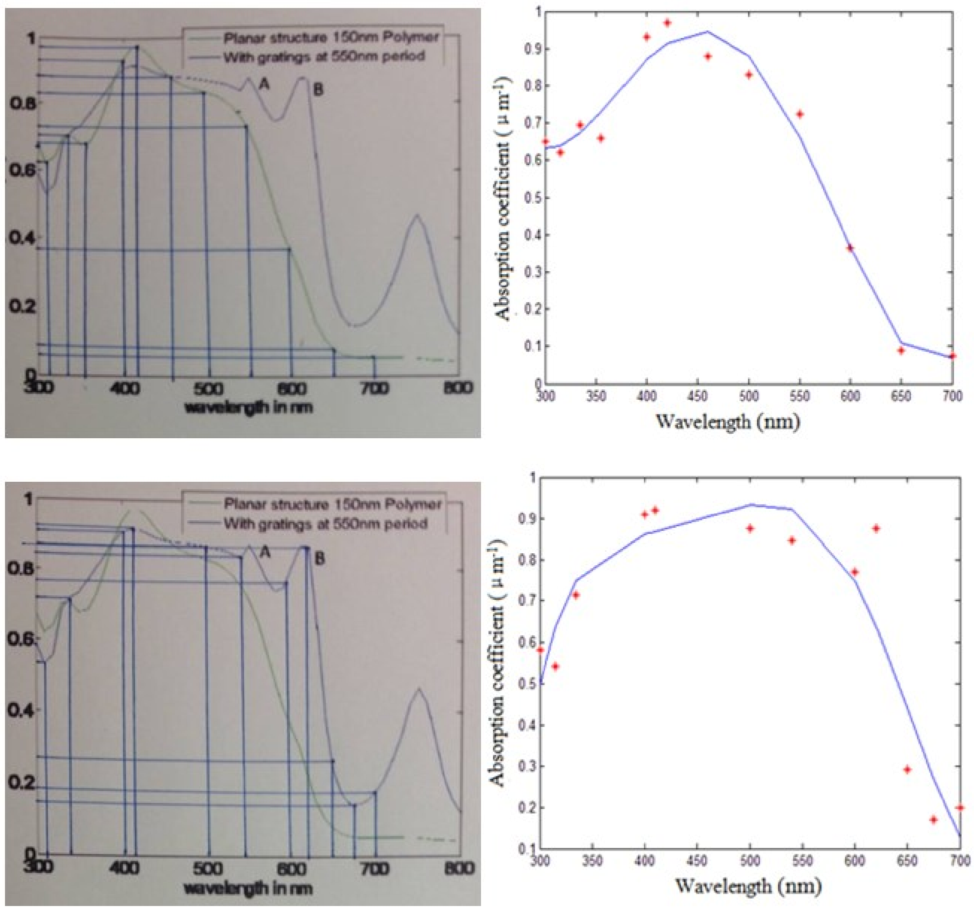
Then followed by the same steps mentioned before, we can have an accurate result.

Now with further consideration, we can also do the comparison between polymer solar cells with planar back contact and structured back contact. The green curves labeled as Planar Structure 150nm Polymer in the figures below are showing the measurements of the light absorption coefficient of the blends P3HT/PCBM with a thickness of 150nm. Besides, the back contact has a planar structure. The blue curves labeled as with gratings at 550nm period in the figures below are showing the measurements of the light absorption coefficient of the blends P3HT/PCBM with a periodic structured back contact. These measurements are from published paper named *Plasmonic nanostructures for absorption enhancement in organic solar cells* [20].

As shown in the following Figure, the light absorption coefficient spectrum showed the enhancement extending over the wavelength range from 300 nm to 800 nm (near infrared). This enhancement contributes to the increase of light scattering and/or trapping induced by the textured grating back contact. This nano-rough periodic back contact structure will efficiently improve the light scattering effect. Consequently, the multiple scattering of light will lead to an increasing of optical path length and the optical absorption, thereby increasing the absorption of the light.

Meanwhile, from the observation of those two curves, we can see from the structured one there are two additional peaks, which locate at around 550 nm and 620nm. These peaks are attributed to the plasmon resonance effect, which promoted by the structured back contact. And here the plasmon resonance effect will also lead to an enhanced light absorption , which is in consistent with the results showed in the figures. Then, if do the fittings of those two curves separately, we can also gain a more accurate number of the ultimate efficiency by involved the light absorption coefficient of those two different structures.

Figure2. 7 Matlab fittings based on different back contact structures



The first two in the first row are representing the Matlab fitting of the planar one using order of five and the two in the second row are representing fitting of the periodic structured one by order of five. The achieved functions are showing here below;

Function of solar cell with planar structure:

$$10^{*}y= -1.64*10^{-13} * x^{5} +8.42*10^{-10}* x^{4}-1.23*10^{-6} * x^{3}+ 7.54*10^{-4} x^{2}- 0.21*x+21.18$$

Function of solar cell with gratings structure:

$$10^{*}y= 2.18*10^{-12}* x^{5}-5.53*10^{-9}* x^{4}+5.50*10^{-6} * x^{3}-2.68*10^{-3} x^{2}+0.65*x-60.65$$

Where y axis represents the absorption coefficient, x axis represents the corresbonding wavelength.

2.4 Results and Discussion

By adding the integration of the absorption coefficient into the ultimate efficiency calculation as showed in *Equation 2.5*, we can gain a more accurate result by considering the light absorption into the calculation.

Finally, after the calculations, I collected all these numbers into tables.

From the Table 1, we can easily observe that by adding the light absorption into the calculation, the ultimate efficiency of polymer solar cells with active layer of P3HT/PCBM decreases dramatically from 16.2% to 9.07% by using fittings under order of 3, and to 7.90% by using fittings under higher order of 5. It can be easily explained. The original model we are using only considered the light absorption function with the Heaviside step function, and in this case, the light with the energy higher than the bandgap of the polymer were considered been all collected by the solar cell. This is actually an appropriate assumption but apparently not an accurate one. So compared with original result of 16.2%, the newly achieved results give a better approximation to the real case. According to the paper from Yang Yang's group, the efficiency of this type of polymer solar cell is about 4%.

Table2. 1 Calculation results for traditional type cells with light absorption added

Order of Fitting	Integration of Light absorption	Ultimate Efficiency (P3HT/PCBM)/ %
3	0.56	9.07
5	0.49	7.90

From the Table 2, we can easily observe that by adding the light absorption into the calculation, the Ultimate Efficiency of polymer solar cells with active layer of P3HT/PC_{71}BM decreases dramatically from 17.5% to 9.35% by using fittings under order of 3, and to 9.09% by using fittings under higher order of 5. When compared between the two different material combination, according to the chart above, there is a 3% enhancement in the light absorption, which leads to a 1.19% enhancement in ultimate efficiency.

Table2. 2 Calculation results for novel materials cells with light absorption added

Order of Fitting	Integration of Light absorption	Ultimate Efficiency (P3HT/PC_{71}BM)/ %
3	0.53	9.35
5	0.51	9.10

From the Table 3, we can easily observe that by adding the light absorption into the calculation, the Ultimate Efficiency of polymer solar cells with P3HT/PC_{71}BM decreases dramatically from 17.5% to 9.96% by using fittings under order of 5 with planar structure, and to 11.76% by using periodic structure with 550nm gratings.

Table2. 3 Calculation results for novel materials with light absorption added

Type	Integration of Light absorption	Ultimate Efficiency ($P3HT/PC_{71}BM$)/ %
Planar	0.62	9.96
Structure	0.73	11.76

Then, in order to give a clear summary, I draw the following curves to show the difference in light absorption between the $P3HT/PC_{71}BM$ and P3HT/PCBM at the visible and near-IR light wavelength range.

Figure2. 8 Differences in light absorption between the P3HT/PC71BM and P3HT/PCBM

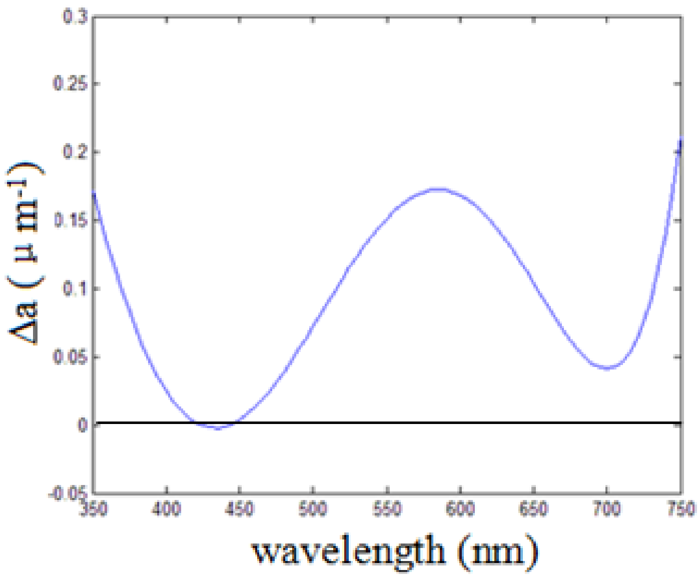


Table2. 4 Ultimate efficiency comparison between novel materials cells and traditional cells

Type	*Integration of Light absorption*	*Ultimate Efficiency / %*
$P3HT/PC_{71}BM$	*0.51*	*9.10*
P3HT/PCBM	*0.49*	*7.90*

When compared between the two different material combination, according to the chart above, there is a ~5% enhancement in the light absorption, which leads to a ~12% in ultimate efficiency. The *Figure 2.8* above shows the Δa (the difference in light absorption between the P3HT/$PC_{71}BM$ and P3HT/PCBM). The curve shows an enhanced light absorption in all range, which the Δa is above zero.

Figure2. 9 Differences in light absorption between the planar and structured samples

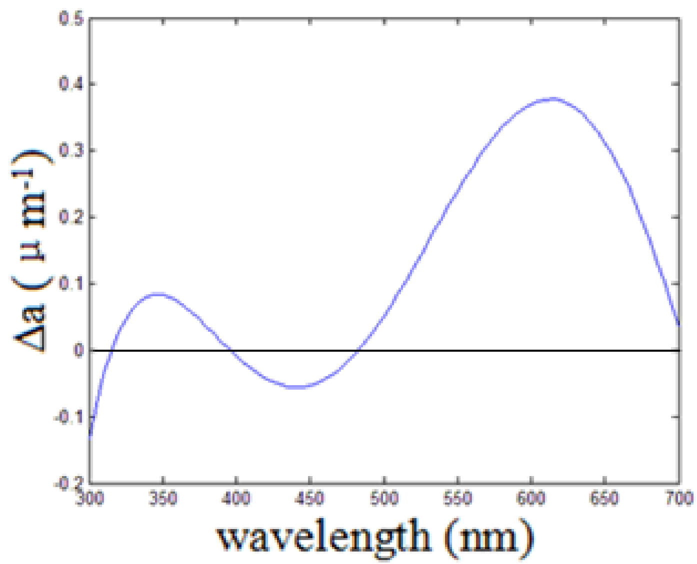


Table2. 5 Ultimate efficiency comparison between structured and unstructured cells

Type	Integration of Light absorption	Ultimate Efficiency (P3HT/$PC_{71}BM$)/ %
Planar	0.62	9.96
Structure	0.73	11.76

When compared between the two different active layer structure, according to the chart above, there is a ~15% enhancement in the light absorption. The *Figure 2.9* above shows the Δa (the difference in light absorption between the planar one and structured one). Except for a short range near the wavelength of 300 nm, the curve shows an enhanced light absorption, which the Δa is always above zero.

Chapter 3

Fabrication and Testing of Dye-sensitized Solar Cells

3.1 Introduction

Dye-sensitized solar cells show great promise since the fabrication process of dye-sensitized solar cells is simple and repeatable. The dye-sensitized solar cells are also more robust than polymer solar cells. The basic components are usually the oxide semiconductor, the sensitizing dye, the electrolyte and the electrodes. For the optimization of the DSC, light trapping can be used for improving photon absorption. Nanoparticles implantation and structured front/ back contact electrodes are ways to accomplish the light trapping [21].

3.2 Fabrication and Testing of Dye-sensitized Solar Cell

3.2.1 Fabrication Details

The key technique is Doctor Blade Technique. ITO (Indium doped Tin Oxide) glass (1 by 2 cm, 1slide for 1 cell), ruthenium dye (N719) and the TiO_2 paste are prepared before the sample assembling. A rectangular spacer is cut as a reservoir for holding the electrolyte. Cut a plastic film (Scotch tape) with having dimensions of 1 cm by 1.5 cm. Make a rectangular hole in the center of the film.

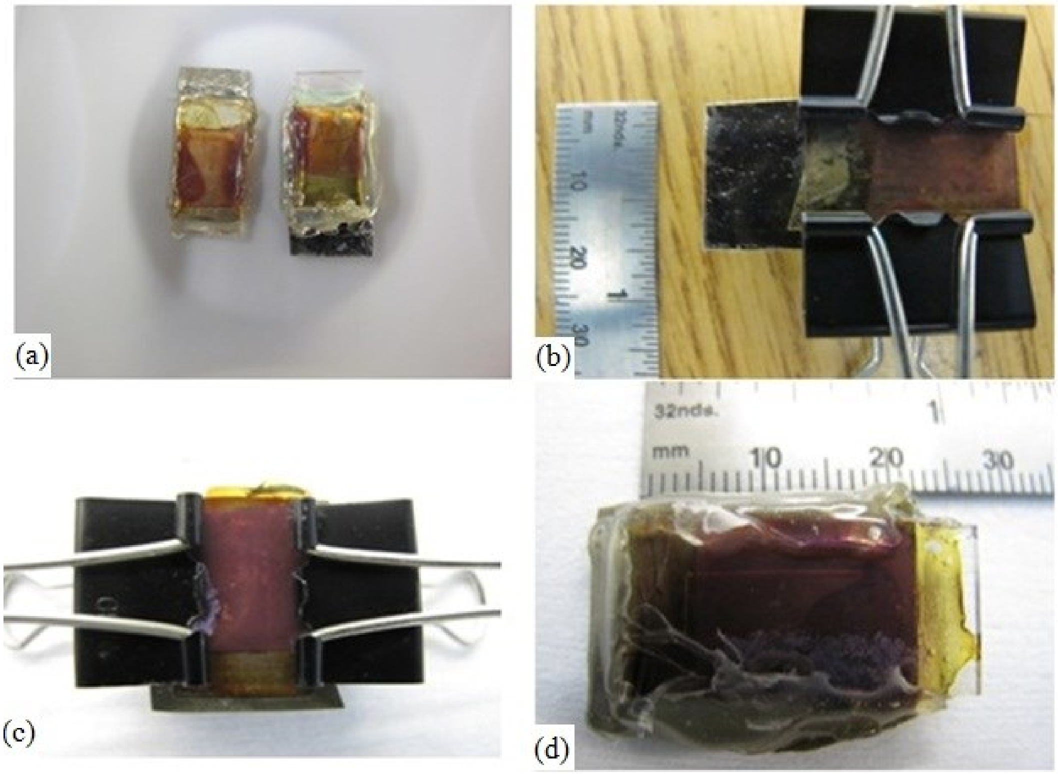
Then attach the Scotch tape on the conducting side of ITO glass (anode electrode). Inject the TiO_2 and use the doctor blade method to flat the surface. Put the sample under UV light exposure for overnight. Put the sample into the dye for at least 30 min in order to attach enough dye onto the TiO_2.

Attach the spacer on the electrode and quickly inject some drops of the electrolyte solution into the reservoir in order to avoid the evaporation of the electrolyte.

Put Platinum plate or Platinum deposited ITO electrode on the conducting surface of another ITO glass as a counter electrode. For samples with structured back contact, put the Platinum/ ITO/ PS film into the sealed oven at 150 degree C for at least 30 min until the films turn into flat type. Then put the structured plate on the conducting surface as a counter electrode. Finally, fix the two electrodes with binder clips.

Figure 3.1 shows the samples with or without structured counter electrode. The sample showed in the bottom right figure is then sealed with epoxy.

Figure3. 1 The pictures of the samples with (c) (d) / without (a) (b) structured Pt/ITO counter electrodes



3.2.2 Testing Details

I-V Measurements

I-V measurements of the DSCs were under AM 1.5 solar simulator (100 mW cm^{-2}). The photovoltaic characteristics of DSC were obtained by using electrochemical Analyzer (CHI630C). The voltage step and delay time of the photocurrent were 10 mV and 50 ms, respectively. *Figure 3.2* shows the curves of I-V measurements for samples with or without structured Platinum/ITO counter electrodes. The table below shows the calculated PCEs for the two types of cells.

Figure3. 2 The I-V curve measurements of the samples with (b)/ without (a) structured Platinum/ITO counter electrodes

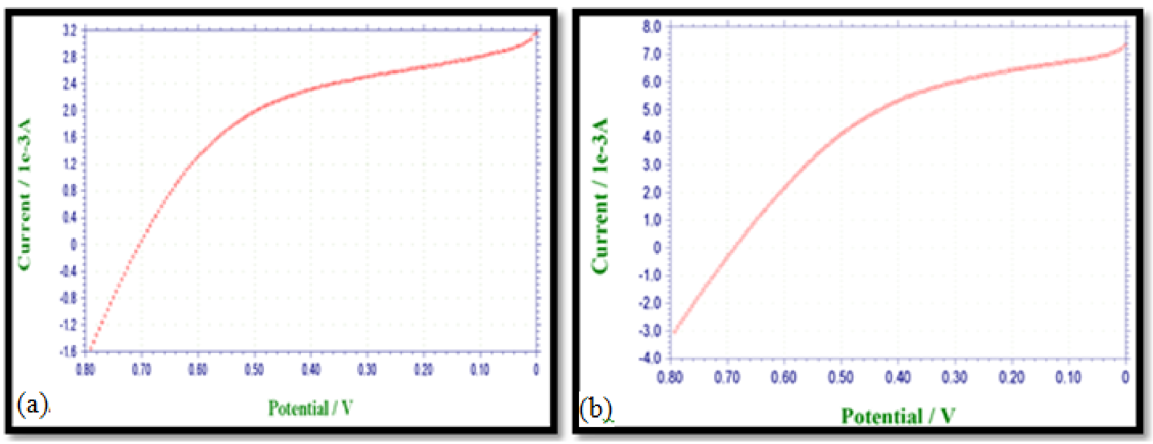


Table3. 1 PCE of the samples with (a)/ without (b) structured Platinum/ITO counter electrodes

Type	Effective Area / mm^2	I_{max} / mA	V_{max} / V	PCE / %
Planar	82.7	2.4	0.40	1.10
Structure	100.5	5.2	0.38	2.07

Reflection Measurements

It is quite hard to directly achieve the absorption coefficient spectrum, since we have structured back contact, which is not at the titanium oxide side, for one type of our samples. In order to achieve the absorption coefficient spectrum, we came up with an idea that if we can get the reflection spectrum, then we can easily get the absorption since the back contact of these samples are thick enough to be considered as opaque. The spectra for the visible and near IR can be recorded with nonpolarized light in a spectrometer with integrating sphere according to Haug et al . (Lambda 900, Perkin Elmer) [22]. However, when the incident light came into the structured sample, the reflection can be both scattering and diffusion. Then it will become a big challenge to collect all these reflected light, a specific integrating sphere would be needed. Since there is no time for the fabrication of this kind of specific sphere, we will use the results from other papers.

Chapter 4

Modeling of Ultimate Efficiency of Dye-sensitized Solar Cells

4.1 Introduction

Even though the dye-sensitized solar cells showed a higher power conversion efficiency record (12.3%) compared with the polymer based solar cells (8.6%), the efficiency is still not reaching the goal for commercialization (15%). Simplified and up-to-date models and simulations are required to contribute to the optimization of the performance of dye-sensitized solar cells.

An electrical model of the dye-sensitized solar cell was presented by J. Ferber et al. in 1998 [23]. However, the model is not up-to-date. The materials and parameters are based on old numbers and old materials. Besides, since they took the recombination into consideration, the modeling process is quite complex. The model created by them cannot easily be used in simulations of the newly developed materials and structures.

4.2 *Modeling the Ultimate Efficiency of Dye-sensitized Solar Cell with a Planar Back Contact*

Due to the well-known Rudolf Marcus's Theory is a model to describe the electron transfer in electrolytes, which was then generalized [13]. We can use this theory to model the Ultimate Efficiency of the dye-sensitized solar cells.

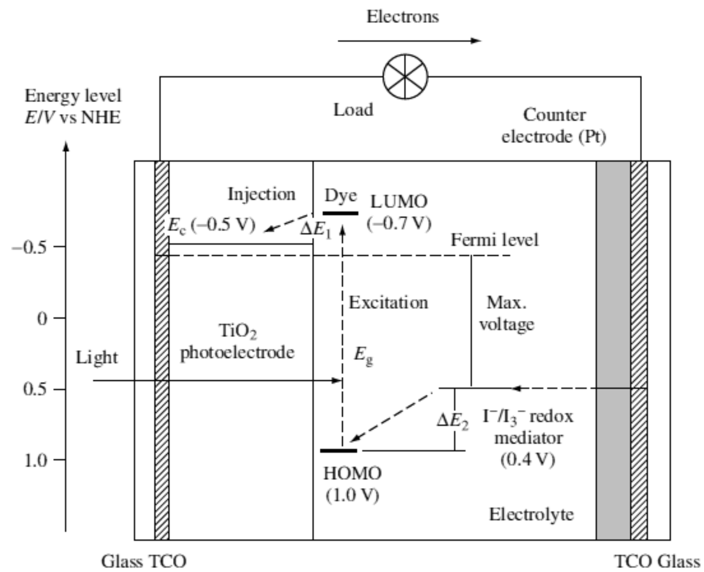
The equation we have figured out still can be applied here.

$$\eta = \frac{\left[\int_{\lambda_1}^{\infty} N_{b\lambda}(T_{sun}, \lambda)\, d\lambda\right] \cdot \int_{\lambda_1}^{\infty} \alpha(T_{sun}, \lambda)\, d\lambda \cdot E_{Lumooptimal}}{\int_0^{\infty} E_{b\lambda}(T_{sun}, \lambda)\, d\lambda}$$

One important thing still need to be mentioned here is that the previous equation we obtained is based on a no-recombination approximation. However, there is mainly three electron loss reactions happened in dye-sensitized solar cells; Without considering those three recombination situations, the ultimate efficiency might be higher than the real number.

In order to complete the modeling process, firstly, the optimized energy levels still need to be found. According to the *Figure 4.1*, the band gap of the ruthenium dye can be easily extracted. The band gap would be 1.7 eV.

Figure4. 1 [24] Schematic diagram showing energy levels of the photoelectrode, dye and redox



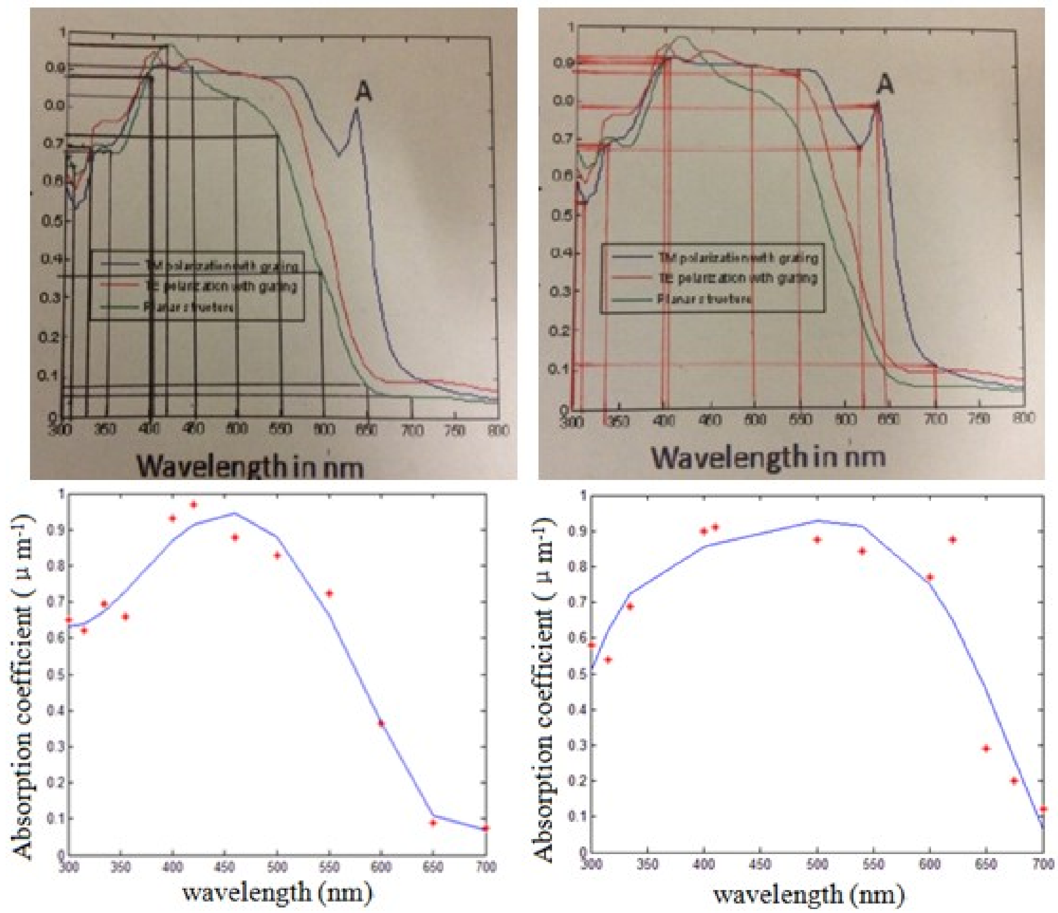
According to the expression for the ultimate efficiency of the solar cell, the $E_{Lumooptimal}$ can be easily gained to be 1.0626 eV. Then using the expression mentioned before, we can get an Ultimate Efficiency of ~22.4%. This number is higher than the traditional P3HT/PCBM polymer solar cell, and nearly even with the numbers from some short band gap polymer solar cells. This number is higher than the ultimate efficiencies by using other models [12], which are nearly 14%, however, we do not consider the three recombination processes which will influence the efficiency of the dye-sensitized solar cell.

4.3 Modeling the Ultimate Efficiency of Dye-sensitized Solar Cell with a Structured Back Contact

Now with further consideration, we can also do the comparison between dye-sensitized solar cells with planar back contact and structured back contact. The green curves labeled as Planar Structure in the figures below are showing the measurements of the light absorption coefficient spectrum. Besides, the back contact has a planar structure. The blue curves labeled as with gratings at 400nm period in the figures below are showing the measurements of the light absorption coefficient spectrum with a periodic structured back contact.

Then, if do the fittings of those two curves separately, we can also gain a more accurate number of the ultimate efficiency by involved the light absorption coefficient of those two different structures.

Figure4. 2 Matlab fittings based on different back contact structures



The first two in the first row are representing the Matlab fitting of the planar one using order of five and the two in the second row are representing fitting of the periodic structured one by order of five. The achieved functions are showing here below;

Function of solar cell with planar structure:

$10^{*}y= -1.53 *10^{-13} * x^{5} +9.59*10^{-10}* x^{4}-2.23*10^{-6} * x^{3}+ 3.43*10^{-4} x^{2}- 0.14*x+33.34$

Function of solar cell with gratings structure:

$10^{*}y= 3.43*10^{-12}* x^{5}-3.51*10^{-9}* x^{4}+6.57*10^{-6} * x^{3}-8.28*10^{-3} x^{2}+1.54*x-40.23$

Where y axis represents the absorption coefficient, x axis represents the corresbonding wavelength.

By adding the integration of the absorption coefficient into the ultimate efficiency calculation as showed in before, we can gain a result which is more realistic and accurate. Thus, the ultimate efficiency for the planar type would deduct to ~10.13% and ~12.02% for the structured type.

4.4 Results and Discussion

Even though we did not get the measurement results of the absorption coefficient for our samples, however, we do get the testing results of the current- voltage (I-V) curve of our samples. As shown in Fig. 3.2, the (I-V curve) spectrum showed the enhancement extending both from voltage and current density when comparing between the structured sample and the planar sample. These enhancement leads to a better performance which proves that the structured back contact do helpful for increasing the efficiency of the dye-sensitized solar cell. We contribute this enhancement to the increase of light scattering and/or trapping induced by the textured platinum/ITO back contact. The multiple scattering of light will lead to an increasing of optical path length and the optical absorption, thereby increasing the IPCE.

Besides, we also fabricated samples with different thickness of ITO layer on the back contact. For the sample with 16 nm ITO layer, the IPCE spectrum showed a reduction compared with sample with 30 nm ITO layer. This decrease is probably due to the transmission effect occurred on the thin Pt/ITO back contact. The total thickness (66 nm) of back contact might not be large enough to ensure a complete reflection.

Chapter 5

Summarization

5.1 Conclusion and Future Work

The modeling of ultimate efficiency of the polymer solar cells with different novel active layer materials was accomplished**.** The upper limits of efficiency combined with the light absorption coefficient in these cells were calculated and analyzed. More realistic results were gained compared with previous modeling.

Dye-sensitized solar cells with structured cathode back contact were fabricated and tested. Better performance compared with the traditional planar cells in ultimate efficiency was demonstrated and then measurements proved.

The reflection measurements can be done in the future work. The reflection testing can be used as a way to indirectly obtain the absorption coefficient spectrum. An integrated sphere is still needed for the scattered and diffused light collection.

5.2 Project Conclusions

Since the growth of the solar energy industry has been limited by the demand of polysilicon materials, alternative technologies and low-cost materials are required to fill the needs. Polymer solar cells and dye-sensitized solar cells have been considered as promising replacements. However, the relatively low efficiency of these types of solar cells has been becoming a roadblock on the way to the commercialization.

Many researchers are then focusing on developing some models to give theoretical guidance on improving the power conversion efficiency of the solar cells. However, most of the models up to now are neither thoughtful nor up-to-date. Mostly are based on traditional materials such as P3HT, PCBM and have no light absorption spectrum involved.

The modeling of ultimate efficiency with different novel active layer materials combined with the light absorption coefficient was accomplished dealing with the polymer solar cells**.** Structured cathode back contact can be added to the dye-sensitized solar cells for the enhancement of light scattering inside the cell, which will lead to a better performance in solar cell efficiency.

Besides, for dye-sensitized solar cells, structured TiO_2 anode contact and nanoparticles can also be fabricated into the cells to improve the light absorption. The ultimate efficiency can still be modeled by using the same process.

References

[1]. Jacob Lund, Rasmus Røge, Ren´e Petersen, Tom Larsen (2006). *Polymer Solar Cells*. Retrieved from Aalborg University, Faculty of Physics and Nanotechnology, Program on How Can Polymer Solar Cells Be Produced and Characterized Web site: http://repetit.dk/files/projects/p4.pdf

[2]. Mikkel Jørgensen, Kion Norrman, Suren A. Gevorgyan, Thomas Tromholt, Birgitta Andreasen, and Frederik C. Krebs, *Stability of Polymer Solar Cells,* Adv. Mater. 2012, 24, 580

[3]. Gang Li, Vishal Shrotriya, Jinsong Huang, Yan Yao, Tom Moriarty, Keith Emery and Yang Yang, *High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends*, Nature Materials. 2005, 4, 864

[4]. Liqiang Yang, Tim Zhang, Huaxing Zhou, Samuel C. Price, Benjamin J. Wiley and Wei You, *Solution-Processed Flexible Polymer Solar Cells with Silver Nanowire Electrodes*, ACS Appl. Mater. Interfaces 2011, 3, 4075

[5]. Ximin He, Feng Gao, Guoli Tu, David Hasko, Sven Huttner, Ullrich Steiner, Neil C. Greenham, Richard H. Friend and Wilhelm T. S. Huck, *Formation of Nanopatterned Polymer Blends in Photovoltaic Devices*, Nano Lett. 2010, 10, 1302

[6]. Letian Dou, Jingbi You, Jun Yang, Chun-Chao Chen, Youjun He, Seiichiro Murase, Tom Moriarty, Keith Emery, Gang Li and Yang Yang, *Tandem polymer solar cells featuring a spectrally matched low-bandgap polymer*, Nature Photonics 2012, 6, 180

[7]. B. O'Regan, M. Grätzel, *A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films*, Nature 1991, 353, 737

[8]. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, *Dye-sensitized solar cells*, Chem. Rev. 2010, 110, 6595

[9]. A. Yella, *Porphyrin-sensitized solar cells with cobalt(II/III)-based redox electrolyte exceed 12 percent efficiency*, Science 2011, 334, 629

[10]. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions*, Science 1995, 270, 1789

[11]. W.R. Duncan, O. Prezhdo, *Theoretical studies of photoinduced electron transfer in dye-sensitized TiO2*, Annu. Rev. Phys. Chem. 2007, 58, 143

[12]. Brian E. Hardin, Henry J. Snaith and Michael D. McGehee, *The renaissance of dye-sensitized solar cells*, nature photonics 2012, 6, 162

[13]. R.A Marcus, *On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I*, J. Chem. Phys., 1956, 24, 996

[14]. W.R. Duncan, O. Prezhdo, *Theoretical studies of photoinduced electron transfer in dye-sensitized TiO2*, Annu. Rev. Phys. Chem., 2007, 58, 143

[15]. C. Deibel, T. Strobel, V. Dyakonov, *Role of Charge Transfer States in Organic Donor-Acceptor Solar Cells*, Adv. Mat., 2010, XX, 1

[16]. D. Godovsky, *Modeling the ultimate efficiency of polymer solar cell using Marcus theory of electron transfer*, Organic Electronics 2011, 12, 190

[17]. Shi Wun Tong, Yu Wang, Yi Zheng, Man-Fai Ng and Kian Ping Loh, *Graphene Intermediate Layer in Tandem Organic Photovoltaic Cells*, Adv. Funct. Mater. 2011, 21, 4430

[18]. Y. Ding, P. Lu, and Q. Chen, *Optimizing material properties of bulk-heterojunction polymer films for photovoltaic applications*, Proc. of SPIE, 2008, 7099, 19

[19]. Ming He, Wei Han, Jing Ge, Yuliang Yang, Feng Qiu and Zhiqun Lin, *All-conjugated poly(3-alkylthiophene) diblock copolymer-based bulk heterojunction solar cells with controlled molecular organization and nanoscale morphology*, Energy Environ. Sci., 2011, 4, 2894

[20]. Aimi Abass. (2009). *Plasmonic nanostructures for absorption enhancement in organic solar cells.* Unpublished master dissertation, Ghent University, Belgium

[21]. Wenbo Hou, *Plasmon resonant enhancement of dye sensitized solar cells*, Energy Environ. Sci., 2011, 4, 4650

[22]. F.-J. Haug, T. Söderström, O. Cubero, V. Terrazzoni-Daudrix, and C. Ballif, *Plasmonic absorption in textured silver back reflectors of thin film solar cells,* J. Appl. Phys., 2008, 104, 064509

[23]. J. Ferber, R. Stangl, J. Luther, *An electrical model of the dye-sensitized solar cell*, Sol. En. Mat., 1998, 53, 29

[24]. M.S. Roy, P. Balraju, M. Kumar, G.D. Sharma, *Dye-sensitized solar cell based on Rose Bengal dye and nanocrystalline TiO_2*, Sol. Energ. Mat. Sol., 2008, 92, 909