



# Characterization of the Dye-Sensitized Solar Cell

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## ***Abstract***

Dye-sensitized solar cells which combine the unique properties of both the organic compound and inorganic compound have attracted the attention of scientists. This project was designed to characterize several factors which could be potentially changing the efficiency of the cells. An increase of output potential when the cell was heated over a short period of time and when thicker  $\text{TiO}_2$  was applied were observed followed by the decreasing in efficiency of over-coating and over-heating. The dark current after a long illumination was also confirmed in this project. The evidence strongly supports the electron trapping mechanism for generating the dark current.

## ***Authorship and Acknowledgement***

Regarding the *Characterization of Dye-Sensitized Solar Cell*, the goals of this project could not be achieved without the help from the people whom we are very grateful.

The primary and only person who carried out the all experiments and finished the writing is Zijian Xia. And special thanks should be given to Professor Drew Brodeur, who is the advisor of this project and whose supports and suggestions are the inspiration and motivation for Zijian to accomplish those experiments. Also, the help in the early stage from Nhi Vo and Ngoc Do, who were the previous students working in similar area, clarified the topics of this project.

## ***CHAPTER 1. INTRODUCTION***

The growing of population in the world arouses the energy concerns in all kinds of fields. According to the ExxonMobil report, the required energy in 2005 was about 210 million oil-equivalent barrels per day. This number increased to more than 300 million oil-equivalent barrels per day nowadays, with an increasing rate of 42.8% compared to the year of 2005. (ExxonMobil, 2007). It was estimated by the Energy information Administration that in 2007 primary sources of energy consisted of petroleum 36.0%, coal 27.4%, and natural gas 23.0%, amounting to an 86.4% share for fossil fuels in primary energy consumption in the world. (U.S Energy information Administration, 2008). Not only should the non-renewable properties of fossil fuel be taken into account, the amount of pollution of burning it should be considered as well. In one of the studies from U.S Environmental Protection Agency, more than 90% of greenhouse gas emissions come from the combustion of fossil fuels (U.S Environmental Protection Agency, 2009). But, due to the high cost of renewable energy and technological limits, fossil fuels are still the most popular energy resources as shown in Figure 1.

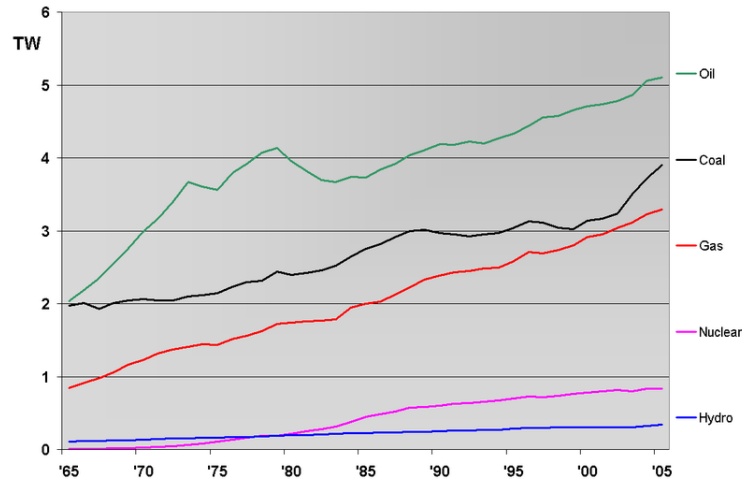


Figure 1: Rate of world energy usage in terawatts (TW), 1965–2005(Statistical Review of World Energy, 2009)

A lot of ways of substituting the fossil fuels have been developing through the past few decades. However, most of them failed to substitute fossil fuels due to lack of availability, high cost and pollution they lead to. Solar cells, one of the safest and cheaper ways to generate electricity, have been studied to a great extent since 1954. (Perlin, 2004)

A solar cell is a solid electrical device that converts solar energy directly to electricity. There are two fundamental functions of solar cells: photo-generation of charge carriers (electrons and holes) in a light-absorbing material and separation of the charge carriers to a conductive interaction to transmit electricity. Adding to the wide range of solar cells, hybrid solar cells based on inorganic and organic compounds are a promising renewable energy source.

The solar cell system we developed in this project is Dye-Sensitized Solar Cell, composed of the  $\text{TiO}_2$  layer acting as the electron carrier and the organic dye layer acting

as the electron generator, which will recover to its original state by electron donated by the electrolyte solution. The efficiency of solar cells is one of the greatest limiting factors for solar cells. In order to become an efficient solar cell, the photo sensitizer, which is the organic dye layer mentioned above must have characteristics corresponding to the spectrum of available light. Different photo sensitizers will have different absorption of available light, thus a different efficiency and cost. Based on the efficiency and cost information given, we chose the dye sensitized solar cell, which has good quantum efficiency reported. (Grätzel, 2003) Figure 2 shows the efficiency of different materials.

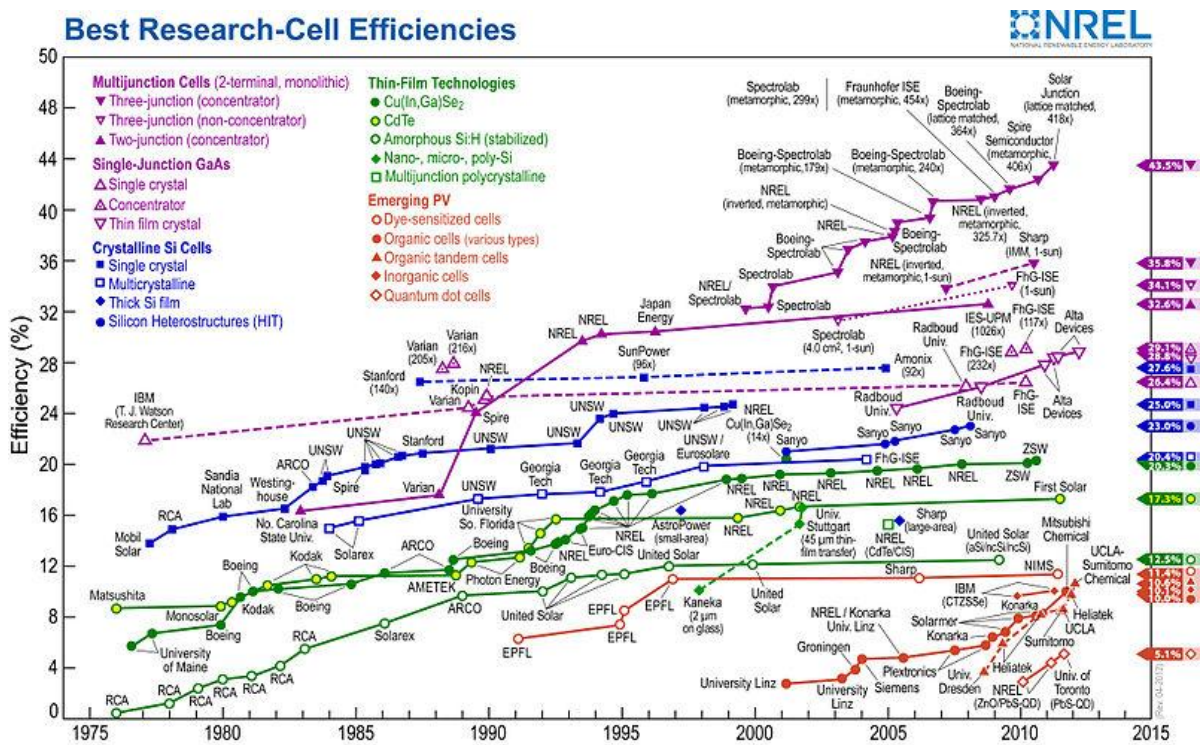


Figure 2: Solar cell energy conversion efficiencies (National Renewable Energy Laboratory , 2011)

Much research has been devoted to identification and synthesis of photo sensitized organic dyes matching the requirements. The attachment group of the dye

ensures that it spontaneously assembles as a molecular layer upon exposing the oxide film to a dye solution. This molecular dispersion ensures a high probability that, once a photon is absorbed, the excited state of the dye molecule will relax by electron injection to the semiconductor conduction band. (Grätzel, 2003)

However, not much information has been obtained for the dark current, a recently discovered phenomena which called our research group's attention greatly. Defined as the current produced without illumination, dark current is usually to be considered as the blank current. However, recently a group of researchers in this area discovered a thousand fold increase of dark current after a long period of illumination, shown in the figure 3 below. (Corey, 2002) Although this group has published the paper 10 years ago, not enough attention has been given to this phenomenon; thus, till now, there is not a common acceptable explanation. The electron trapped in the TiO<sub>2</sub> layer seems to be the best explanation but this explanation still needs to be verified. (Gregg, 2003)



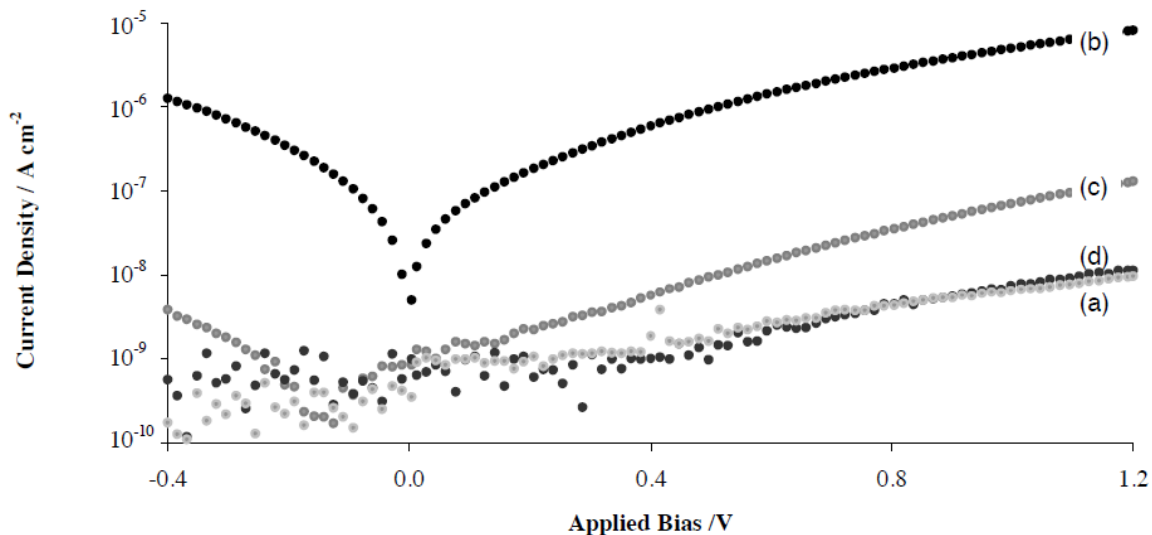


Figure 3: Dark J-V curves of an ITO/TiO<sub>2</sub> (synthesized sol-gel)/MEHPPV/Au device (a) before, (b) 1 hour after, (c) 1 day after illumination, and (d) 4 days later. (Carey, 2002)

The objective of this project is divided into two parts. The first part is to develop new dye derivatives from some simple well-known organic dyes and experimentally determine the efficiency of DSSC based on titanium dioxide. The function of DSSC should be fully understood and based on that, some of the new organic dye was designed to produce a higher efficiency. The second part of this project is to determine several factors that might influence on the performance of DSSC, such as the thickness of layers and temperature and to reproduce dark current phenomena with determining the reason why it happens.

## ***CHAPTER 2. Background and Literature Review***

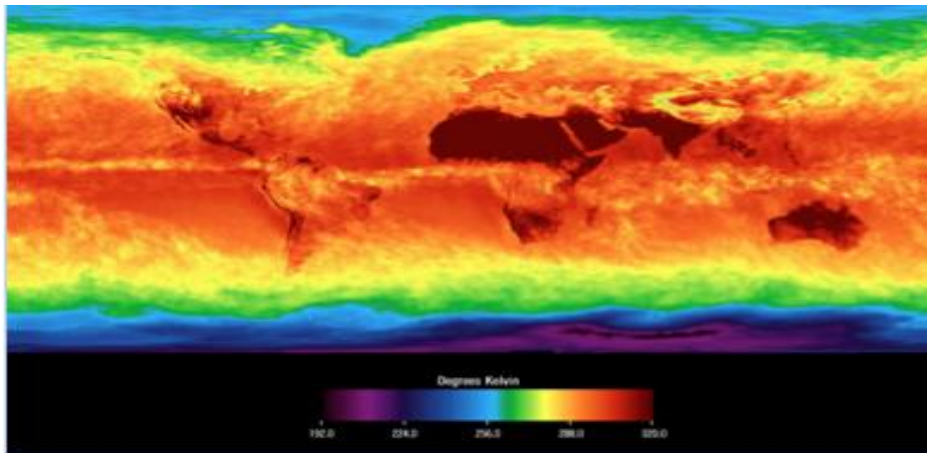
This chapter will provide the all the background information and literature review on the main topics discussed in the project, including solar energy, solar cells, dye-sensitized solar cells and photo sensitized dye. The first section is an introduction to solar energy and why we want to choose solar energy as the primary green energy resource. The second and third sections are on the development and history of solar cell and DSSC which we are interested in. The fourth section is on the function and modification of organic dye in DSSC. The fifth section is on the central part of this project which is about the dark current and the characterization of the DSSC.

### **2.1 Solar Energy**

Except fossil fuels, there are still a lot of energy resources we could utilize in the world, such as nuclear power, wind power and hydro energy. The reason why we choose solar energy instead of other energy source we could use is because solar energy possesses some advantage over the others.

Firstly, solar energy does not create greenhouse gases as it generates electricity (Pentland, 2010). A greenhouse gas can absorb radiation in the infrared range which is the fundamental cause of the greenhouse effect, the main reason leading to global warming right now.

Secondly, solar energy is easily available all around the world. Unlike wind power and hydro energy, solar energy spread out more evenly in the world, as shown in Figure 3; thus, the geographical location of a country is not likely to prevent the countries from taking advantage of solar energy. The world solar energy potential clearly indicates that most part of the world could potentially utilize the solar energy as the primary energy resources, especially for countries near the equator.



**Figure 4: NASA Map of the World Solar Energy Potential (Pentland, 2010)**

Thirdly, the solar energy is essentially inexhaustible because it is radiation from the sun and there is a large quantity of solar radiation accepted on the earth every day. The total solar energy absorbed by Earth's atmosphere, oceans and land masses is approximately 3,850,000 exajoules (EJ) per year. (Smil, 2006) From data shown in Table 1, only 0.01% of the solar energy, if used, could provide enough energy for primary energy use in 2005.

Table 1: Yearly Solar Flux and Human Energy Consumption.

<b>Solar</b>	<b>3,850,000 EJ</b>
<b>Wind</b>	2,250 EJ
<b>Biomass</b>	3,000 EJ
<b>Primary Energy Use (2005)</b>	487 EJ
<b>Electricity (2005)</b>	56.7 EJ

There are also more advantages of solar energy, such as minimum byproduct compared to other energies, no disposal method necessary, less space required and relative low cost and high efficiency. (Advantage of Solar Energy, 2011)

From the reason above, solar energy would be a prospective substitution of fossil fuels due to the reason of wide availability, relative low cost and renewable properties.

## 2.2 Solar Cells

Solar cells are one type of photovoltaic cells which generate electrical power by converting energy of light into direct current electricity by using semiconductors that exhibit the photovoltaic effect. In the photovoltaic effect, electrons are transferred between different bands (usually from the valence bands to conduction bands) within the material, resulting in the buildup of voltage between two electrodes.(Brabec & et al, 2001)  
In solar cell, the primary energy source is sunlight.

### 2.2.1 Theories

In order to understand the function of solar cells and to improve the performance of it, theories behind solar cells should be studied and well understood.

The first step in solar cell function always involves photon absorption by a semiconducting material. When the photon is absorbed, the energy of photon will be transferred to valence electrons in crystal, which excite an electron to another band, called the conduction band, in which, electrons can freely move. Figure 4 shows different band gap in conducting materials.

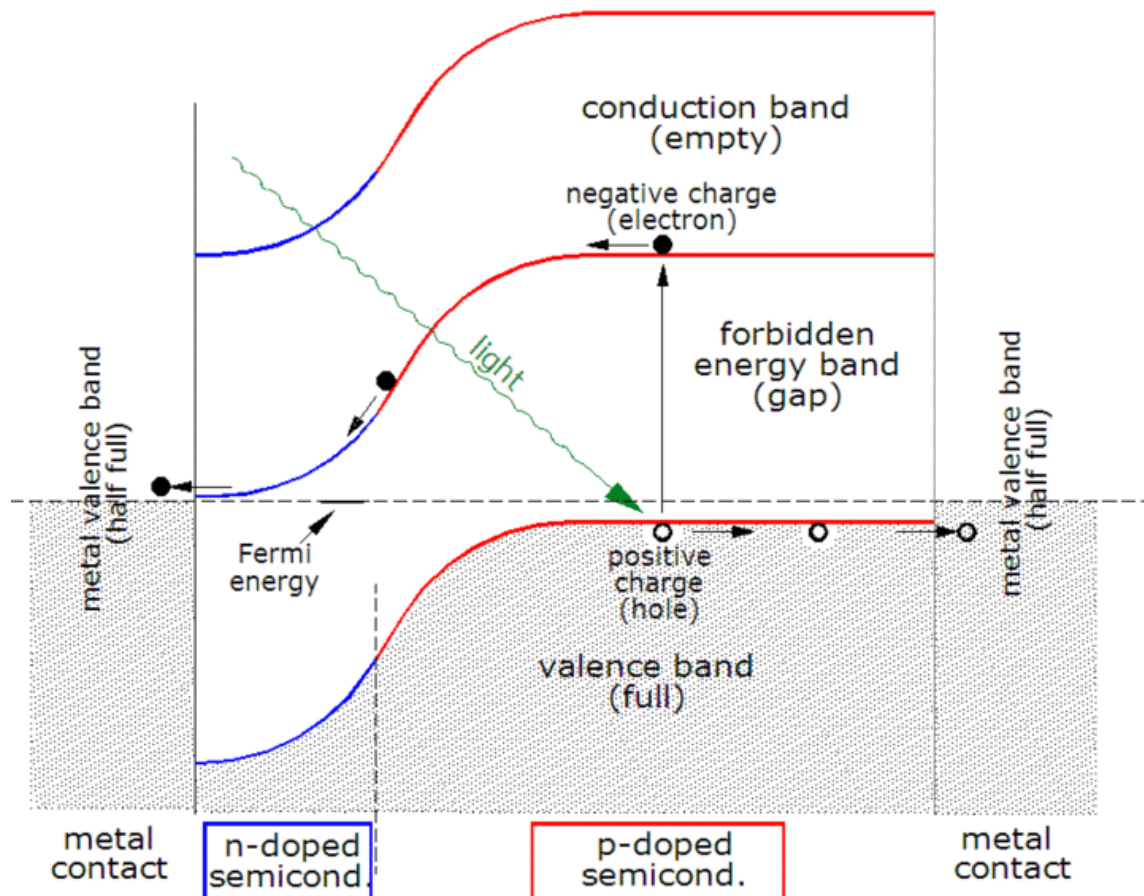


Figure 5: Band Diagram of Solar Cell (Carlson, 1985)

Then, the free electrons can move to one single direction because of the special composition of solar cells, which then generates current.

Finally, arrays of solar cell convert solar energy to electricity. (Ma & et al, 2005)

Figure 5 illustrates the theories of solar cells.

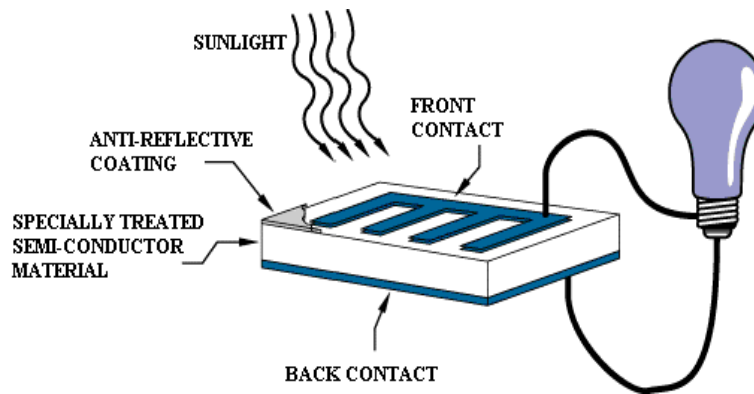


Figure 6: Mechanism of Solar Cell (NASA)

### 2.2.2 Structure

Figure 6 shows the complete structure of a common solar cell.

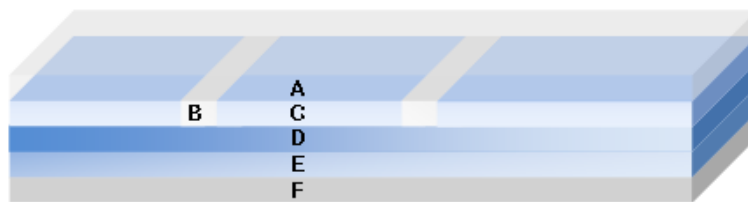


Figure 7: Structure of Photovoltaic Cell

The different parts in the solar cells are the parts listed below.

- A. Encapsulate – Encapsulate which is made of glass or other clear material such clear plastic seals the cell from the external environment.
- B. Contact Grid- The contact grid is made of a good conductor, such as a metal, and it serves as a collector of electrons.
- C. The Antireflective Coating (AR Coating) - Through a combination of a favorable refractive index, and thickness, this layer serves to guide light into the solar cell. Without this layer, much of the light would simply bounce off the surface.
- D. N-Type Silicon - N-type silicon is created by doping (contaminating) the Si with compounds that contain one more valence electrons than Si does, such as with either Phosphorus or Arsenic. Since only four electrons are required to bond with the four adjacent silicon atoms, the fifth valence electron is available for conduction.
- E. P-Type Silicon- P-type silicon is created by doping with compounds containing one less valence electrons than Si does, such as with Boron. When silicon (four valence electrons) is doped with atoms that have one less valence electrons (three valence electrons), only three electrons are available for bonding with four adjacent silicon atoms, therefore an incomplete bond (hole) exists which can attract an electron from a nearby atom. Filling one hole creates another hole in a different Si atom. This movement of holes is available for conduction.
- F. Back Contact - The back contact, made out of a metal, covers the entire back surface of the solar cell and acts as a conductor. (Specmat, 2009)

### 2.2.3 Hybrid Solar Cells

Hybrid solar cell combined both organic dye and inorganic semiconductor. This kind of solar cell takes advantage of both the organic photo sensitized dye, whose function is to absorb photon as electron donor, and the inorganic semiconductor function as the acceptor and transferring electrons. (Milliron et al, 2004)

This combination of materials in the photoactive layer can result in a greater efficiency when converting light into electricity with the rise in prices of silicon, being able to reduce the amount of it also results in a cheaper product (Günes, 2008). But the hybrid solar cell does not only possess the significant potential of lower cost, but also shows scalable solar power convention.

Although hybrid solar cell has such a great advantage, there are some challenge factors when developing it further. First, hybrid solar cells perform well on absorbing blue light, with a quantum efficiency of 70%. However, for more energy containing red light, the band gap of the semiconductor seems to be larger thus leading to a lower quantum yield. Secondly, interfaces in hybrid solar cell cause contact resistance between each layer, which should be reduced to adapt a higher efficiency. Finally, the charge transport is not ideally efficient as well. (Coakley et al, 2005)

## 2.3 Dye-Sensitized Solar Cell (DSSC)

Invented by Grätzel in 1991, a later version of dye-sensitized solar cell is a low-cost solar cell belonging to thin film solar cell. DSSC provided a technically and



economically credible alternative concept to present day p-n junction photovoltaic devices. Unlike the conventional solar cell systems in which semiconductors function as both photon absorber and charge carrier, DSSC separate these two functions to two different materials. (Grätzel, 2003) As mentioned in last section, a light sensitized organic dye functions as the photon absorber, leaving the charge carrier function to the semiconductor.

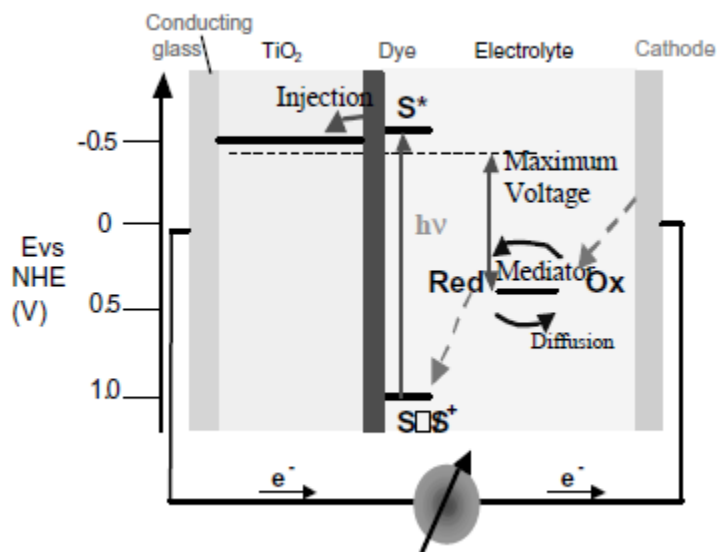


Figure 8: Principle of Operation in DSSC (Grätzel, 2003)

As shown above in Figure 7, the mechanism of DSSC is similar to that of solar cell. Photo excitation at a monolayer of organic dye results in the injection of an electron into the conduction band of oxide. Then, organic dye restores its original electron configuration by electron donation from the electrolyte, usually an organic system containing redox couples. (Grätzel, 1991)

The heart of this solar cell is composed of nano-particles of meso-porous (with the pore width of 2-50 nm) oxide layer, which allows electronic conduction taking place. Since inorganic nano-particles have several advantages such as size tenability and high absorption coefficients, it is always the first choice when considering the cost and performance, etc. The material choice is mainly  $\text{TiO}_2$ (Anatase), crystal structure of which is shown in Figure 8, but alternatives such as  $\text{ZnO}$  and  $\text{Nb}_2\text{O}_5$  have been investigated as well. (Tennakone et al, 1999) Titanium dioxide was recognized as semiconductor of choice due to its great properties in photochemistry and photo-electrochemistry; it is a low-cost, widely available, non-toxic and biocompatible semiconductor material. Besides, experimental results showed meso-porous  $\text{TiO}_2$  layer has a highly efficient charge transport. (Nelson, 1999)

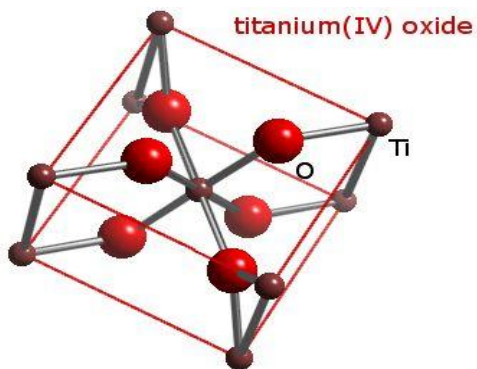


Figure 9: Titanium (IV) Oxide Lattice Structure (WebElements)

The organic dye layer is another important part in DSSC, functioning as the photon absorber. The organic dye can be composed of a metal center, usually Platinum and Ruthenium, and a conjugated organic system, such as polypyridine, phthalocyanines and porphyrins. If the use of noble metal is limited, and DSSC itself does not require

elaborate apparatus to manufacture, DSSC is an attractive system we could use. Recently, organic dye without the metal center is also reported but at a lower electron transfer efficiency. (Hara et al, 2003)

Like mentioned above, DSSC does not require elaborate apparatus to manufacture. Materials inside the DSSC are either low cost or could be synthesized easily from natural products. Although its conversion efficiency is less than the best thin-film cells, in theory its price/performance ratio (kWh/(m<sup>2</sup> annum dollar)) should be high enough to allow them to compete with fossil fuel electrical generation by achieving grid parity. (Tributsch, 2004) So, in this project, we choose DSSC as our interested topic to study.

## **2.4 Organic Dye in DSSC**

### **2.4.1 Porphyrins and Phthalocyanines**

Organic dye, functioning as an electron donor via photon excitation, is the essential part of dye-sensitized solar cells. Generally, sensitizers have the structure of  $ML_2X_2$ , where L stands for 2,2'-bipyridyl-4,4'-dicarboxylic acid, M is osmium or ruthenium, and X is halide, cyanide or thiocyanide. Figure 10 shows a commonly used ruthenium complex in DSSC, called N3 complex, standard dye in DSSC at once. (Grätzel, 1991)

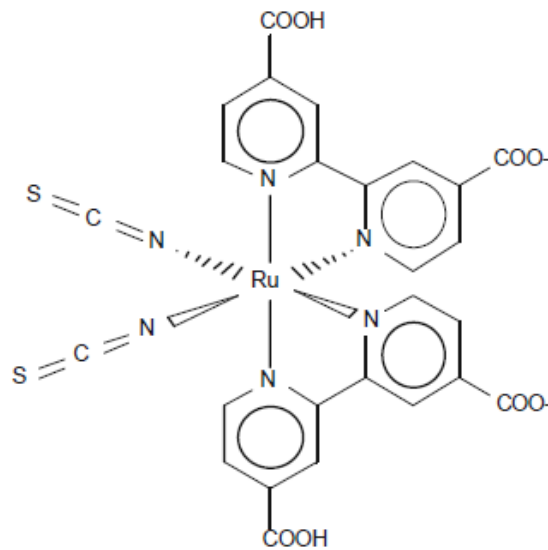


Figure 10: The structure of N3 Ruthenium Complex used as charge transfer sensitizer in DSSC (Grätzel, 1991)

Considering the price and feasibility in our lab, porphyrins and phthalocyanines attract particular attention. Porphyrins are the active center of chlorophyll, coordinated with  $Mg^{2+}$ , with the function of absorbing the photons in photosynthesis. (Petit et al, 1992) Comparing DSSC with biological photosynthesis, it is interesting how porphyrins will work in the DSSC. Approximately, 25% of the artificial organic pigment and dye are derivatives of phthalocyanines. (Löbbert, 2002) Phthalocyanines also show great activity in photochemistry. (McKeown, 1998) However, both porphyrins and phthalocyanines cannot compete with N3 dye because porphyrins lack red light and near IR absorption. Phthalocyanines do show this absorption, but the problem of unsuitable LUMO energy level, which is too low for electron transfer to  $TiO_2$  conduction band, seems to be intractable so far. (Grätzel, 2003)

One strategy to solve this problem is to develop some new dyes for the DSSC.

Recently, a remarkable improvement on dye performance was made by Hara, using the coumarine and polyene organic dye, with the high efficiency reaching up to 7.7% in full sunlight. (Hara et al, 2003) Another strategy to broaden the absorption spectrum is combining different kinds of organic dyes. Such a dye mixture has been applied to mesoporous TiO<sub>2</sub> films in the form of mixtures of porphyrins and phthalocyanines. The result was similar to the addition of optical effects of the two sensitizers. (Fang et al, 1997)

The other strategy for this problem is to seek some natural products with the ability to absorb the photons, such as the chlorophylls mentioned above. The commonly used natural product is anthocyanins, which is rich in the tissue of plants. The particular high content of the anthocyanins in raspberry and the accessibility of the fruit offer a great source of the anthocyanins, which has the absorbance range complimentary to that of chlorophyll. (Cherepy, et al, 1997) In literature, the anthocyanins were also used in dye-sensitized solar cells. (Grätzel, 2003)

For this project in our group, due to the limit of financial support and amount of time and technique we have, besides the porphyrins and phthalocyanines, the other options we have is the anthocyanins in raspberry juice instead of expensive and high-technique associated ruthenium complexes. The combination of different dyes also opens a new method to increase efficiency of photon absorption without synthesizing new dyes.

### 2.4.2 Quantum Dot Dye and Its Problems

Semiconductor quantum dots are another option for panchromatic sensitizers. These are semiconductor particles whose size is small enough to produce quantum confinement effects. The absorption spectrum for such quantum dots can be adjusted by changing the particle size. Thus, the band gap for designed material, such as InAs and PbS, could be adapted to match the value of 1.35eV, ideal for single junction solar quantum converter. (Grätzel, 2003)

One problem associated with this method is the photo-corrosion of the quantum dots could almost certainly happen if the junction contact is a liquid redox electrolyte. On the other hand, these semiconductor materials show strong resistance to solid photo-corrosion.(Plass et al, 2002)

The advantage of using this kind of sensitizers is their high extinction coefficient which allows the use of thinner film of mesoporous oxide, thus increasing the overall efficiency of DSSC. (Grätzel, 2003)

### 2.4.3 New Organic Dyes

Recently, more and more research is conducted to decrease the price-efficiency ratio in the new organic dye synthesis and application in DSSC. A research group led by Hara in Japan recently achieved the highest efficiency using pure organic dye, structured as below, as 6% of the photon conversion, with NKX-2311.(Hara, 2001) In addition, the group also developed other efficient polyene dye photo-sensitizer for nano TiO<sub>2</sub> DSSC

with  $\eta=6.8\%$  under AM 1.5 radiation. (Hara, 2003)

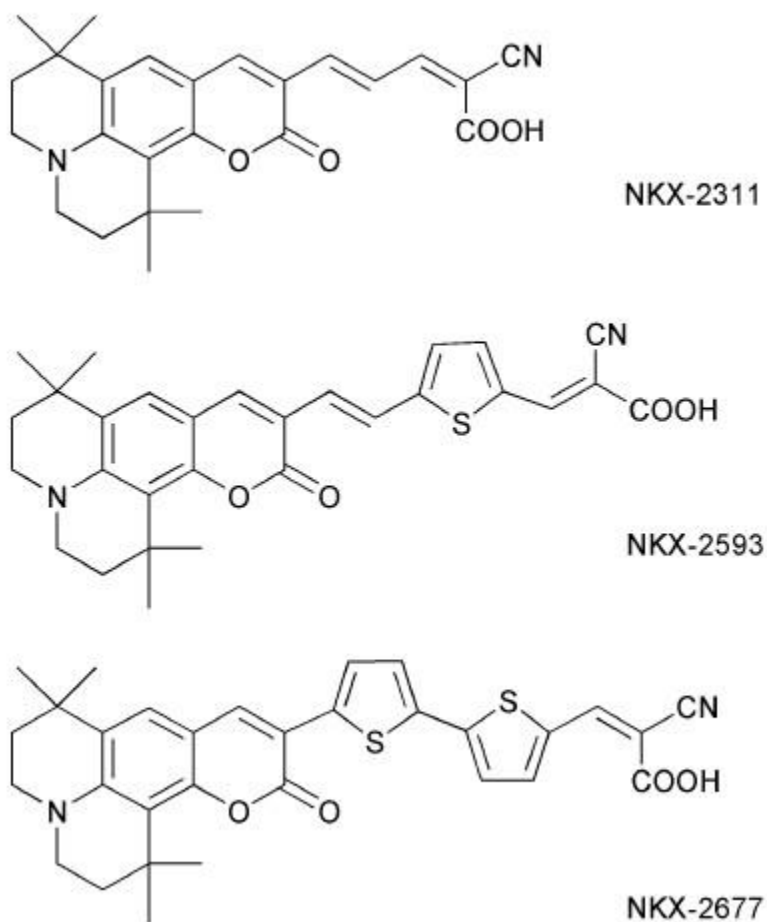


Figure 11: The organic dye developed by Prof. Hara(Hara, 2003)

In the very paper, this group also suggested the feasible method of increasing efficiency is to increase the  $\pi$ -conjugation by extending the  $-\text{CH}=\text{CH}-$  unit of NKX-2311. (Hara, 2003) The other paper about derivative of hemicyanine dye with efficiency about 5.4% was also reported without metal center. (Yao, 2003)

These new organic dyes instead of the meta-centered organic complexes improve the efficiency of DSSC. However, for this project with limit amount of budget, time and

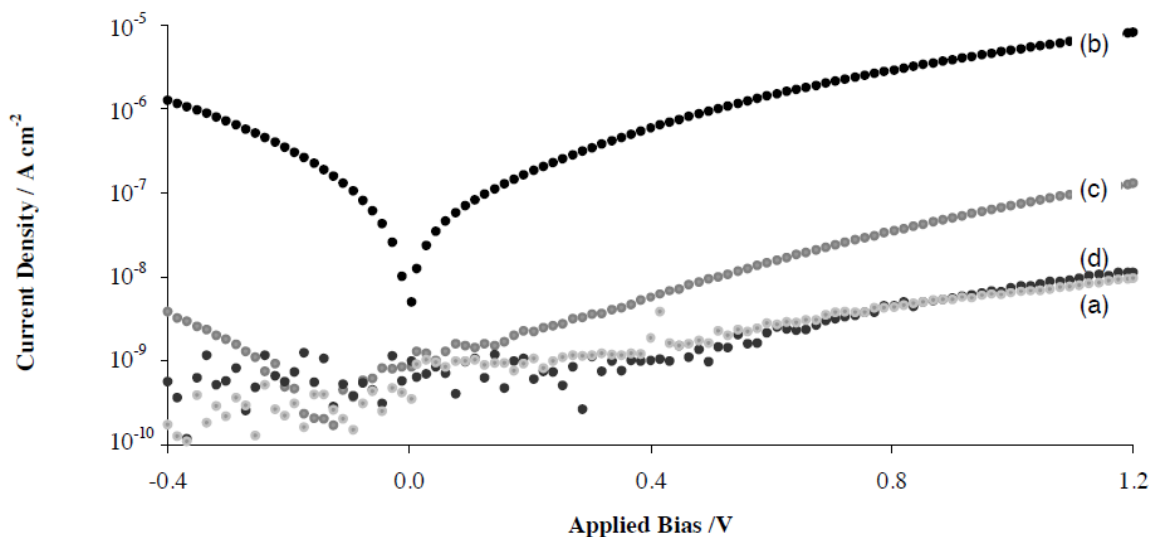
technique to synthesize these dyes, we will only discuss in this chapter and if we do have time, we probably will test this.

## 2.5 Dark Current

Dark current, defined in physics as the relatively small electric current flowing out of a system in the absence of the photon, called the team's attention after a group of high school students practiced assembly of the solar cell. Physically, the dark current is proposed to result from the random generated electrons and holes at the depletion region. So, when calculating the photon-generated current, the researchers always need to be concerned about the dark current and during the calculation, the current due to dark current should be eliminated to produce accurate result.

However, recently, Carey's research group at Oxford University found out the dark current increases after illumination, under the bias of ITO/TiO<sub>2</sub>/MEHPPV/Au devices. Besides, the dark current increases several orders (~1000 times) greater than that before the illumination. The paper also pointed out that under sufficient illumination and vacuum (10<sup>-2</sup> bar), the dark current turns to the original value in the scale of days. (Carey, 2004)





**Figure 12: Dark J-V curves of an ITO/TiO<sub>2</sub> (synthesized sol-gel)/MEHPPV/Au device (a) before, (b) 1 hour after, (c) 1 day after illumination, and (d) 4 days later. (Carey, 2002)**

The author provided us several probable explanations and the group ruled out most of them, including increasing of temperature under illumination and photo oxidation of MEHPPV molecule. The paper reported the only possibility they left over was the electron trapping in the TiO<sub>2</sub>, which is proposed by another group studied the same device using TiO<sub>2</sub>, but they did not report any dark current results. (Gregg, 2003) Hence, although it was suggested, there is still a lack of enough experimental data to determine the reason why dark current increase by unusual amount.

Interestingly though, a group of high school students did the same experiment with the similar device this summer with our group and surprisingly enough, they got the similar results with that group who study the dark current in TiO<sub>2</sub> for a while, which is after several days, even under the 1 atm pressure, the cell made by students still shows readings – although almost nothing, in the absence of the light. The random error was ruled out by switching several different cells and different multi-meters. This interesting

result was reported and got noticed by the group. Unfortunately, the cells of the students made were disposed after the result had been recorded. Thus, the report can not be verified by the group.

Several other possible explanations which were listed below were proposed by the group. And the group will test these possibilities and try to come out a reasonable explanation for these phenomena. If time is allowed, the group should also try to generalize for other solar cell devices.

- The lag time before the photoelectric system reach its maximum photon-generated voltage suggested that the electron might not get enough energy at first. Hence it is possible after the illumination the energy residue can still excite the electron to make the dark current increase.
- The MEHPPV is a large conjugated molecule. Although from the group's suggestion, the photon-oxidation was ruled out. However, the longer MEHPPV, the easier to excite an electron with lower energy and harder for the free-moving electrons to get to the end of the chain. Hence, this assumption can be proved or ruled out by using different molecular weight of MEHPPV or other dye molecules.

## **CHAPTER 3. METHODOLOGY**

Based on the scientific references found in earlier literature chapter, the prototype of “hybrid dye sensitized solar cell based on TiO<sub>2</sub>/graphite” was constructed. In this chapter, details of procedures to conduct the experiments will be presented. The preparation of dyes will also be provided in this section. The different techniques will be demonstrated and discussed in this section as well.

### **3.1 Assembling the Dye-Sensitized Solar Cell**

1. Determine the conductive side of glass in the model kit by touching both of protruding leads of the multi-meter with one side of the glass. The conductive side could be identified with average resistance from 20-38 ohms.
2. Fix three sides of the plate using tape with the conductive sides facing up shown by Fig.13.



**Figure 13: Fix the conductive side by tape.**

3. Prepare the titanium dioxide paste by adding a few drops of very dilute acetic acid (0.035M) to 1 gram (about 2 table spoons) TiO<sub>2</sub>. The resulting mixture was grinded in a mortar and pestle until a colloidal suspension with a smooth

consistency (like cake icing) was observed. (Grazel, 2005).

4. Add 2-3 drops of the  $\text{TiO}_2$  suspension onto the conductive side and spread out the  $\text{TiO}_2$  evenly on the surface of the plate with glass rod. Carefully remove the tape without perturbing the  $\text{TiO}_2$  layer.
5. Dry the glass with  $\text{TiO}_2$  under room temperature over 4 hours and then heat to  $420^\circ\text{C}$  for another 20 min, until the dried  $\text{TiO}_2$  turns brown and then white again.
6. While heating, light the candle and coat the conductive side of the other piece of glass with graphite over 45 sec.
7. Cool both plates to room temperature.
8. Submerge the plate with  $\text{TiO}_2$  face-down in the dye solution and take out quickly but carefully without cracking the  $\text{TiO}_2$ .
9. Wash the dye layer with ethanol carefully.
10. Clamp both the plates together and apply 2 drops of  $\text{KI/I}_2$  electrolyte solution onto the interface between the two plates.
11. Allow the electrolyte to cover the surface of  $\text{TiO}_2$  by capillary action.
12. Measure the photo-voltage under the UV and fluorescent light after forming a circuit using a multimeter.

## 3.2 Preparing the Dye Solution

### 3.2.1 Synthesis of Copper Phthalocyanines

Copper Phthalocyanines was the first dye molecule we chose to synthesize because the easy accessibility of starting material and the simple experiment procedure.

There are two commonly used protocols for synthesizing copper phthalocyanines, microwave irradiation and direct heating. Although the most commonly used one is the microwave irradiation with high yield and easier isolation and workup method (Shaabani, 1998), our group decided to use the direct heating method because of the difficulty of instrumental handling.

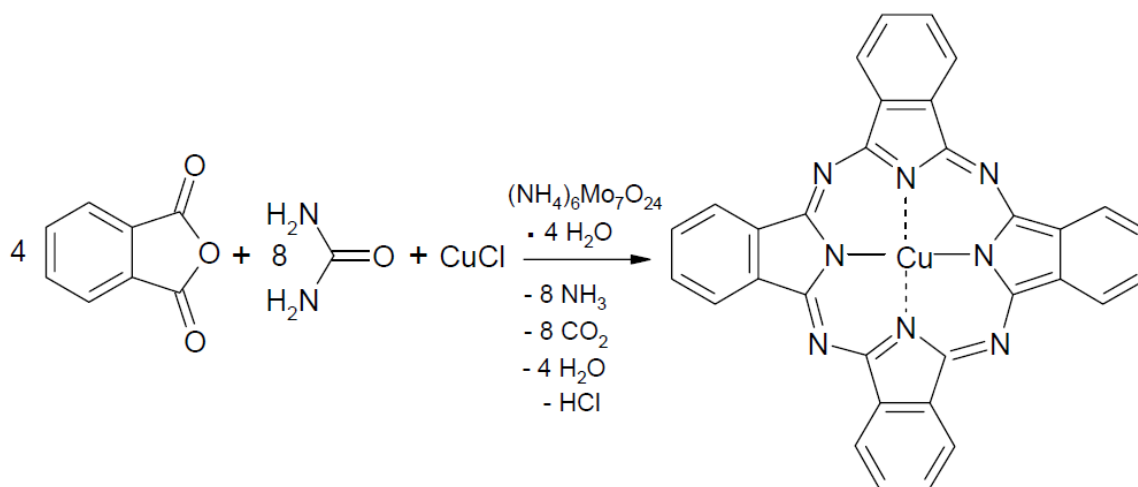


Figure 14: synthesis scheme of copper phthalocyanines (Moser and Thomas, 1963)

Reaction apparatus was a test tube (18\*125mm) set up in the 320 degree of centigrade oil bath. The temperature was carefully controlled.

In the test tube, 1.84 g (30.7 mmol) of urea, 0.89 g (6.0 mmol) of phthalic anhydride and 167 mg (1.67 mmol) of copper (I) chloride was charged. The mixture was well swirled with a glass rod over 5 min to obtain a thoroughly mixture. Next, 25 mg (0.02 mmol) of ammonium heptamolybdate was charged to the test tube followed by another mixing over 3 min. Then, the test tube was heated by the oil bath over 5 min. The melting of the entire solid was first observed. When the color turned to greenish blue, the

heating apparatus was removed and the mixture was allowed to cool to room temperature.

The work up procedure was composed of two steps. At the first stage, 2.5 mL of conc. HCl was added to the crude product with 20 mL of water. The mixture was swirled over 10 min to get rid of the un-reacted starting material. After filtration, the filtrate was discarded. Then, the solid on the filter was washed with 20 mL of ethanol. Solid was then removed from the filter paper and allowed to dry under air. (Yield: 0.381 g, 44.1%)

### **3.2.2 Preparation of the Raspberry Dye Solution**

Raspberry juice, rich in anthocyanine, is a great source of dye in our dye-sensitized solar cell. (Wu, 2004) Smestad developed the nano-TiO<sub>2</sub>/raspberry DSSC in 1998. (Smestad, 1998) This kind of DSSC provides very stable photo-voltage. Due to the easy accessibility and stable outcome, the raspberry was among the best choices of the dyes.

Preparation of the raspberry solution requires some skill of filtration. 4-5 pieces of frozen raspberry were grinded in a mortar until a crude mixture was observed, usually about 4-5 min. The crude mixture was then transferred slowly to a pre-assembled filtration apparatus. If the resulting mixture is very thick, i.e., no filtrate, several drops of water or acetone was used to wash the mixture and add the total liquid amount. A spatula or a glass rod can be used to swirl the mixture to give off more solution.

The resulting solution, although might not be chemically pure, is rich of anthocyanine; thus, it could be used in DSSC.

### 3.3 Control Experiment I: Graphite Layer Thickness Dependence

Provided in protocol and other literatures (Grazel, 2005, etc), coating graphite onto the conductive side is one of crucial steps for making the DSSC. However, few literatures went into details in the potential influence of graphite layer on the efficiency of the solar cell. So, our group decided to test the dependence of the thickness of graphite layer with the performance of the cell.

The experiment was conducted using control experiment. First solar cell was designed to be a blank experiment, i.e, no graphite layer on the conductive side. Although it might not provide any useful information now, since it has been already known that the graphite layer is necessary for cell functioning properly, it is important to have a complete comparison with this blank control group.

Then, the graphite layer was controlled by manipulating the time over the candle flame. In order to ensure the minimum random error, the candle used was the same with minimum perturbation. Difference in thickness of graphite can be tracked by the color of coating. The results from heating over 45 sec and 90 sec were compared over 4 days' time scale.

### 3.4 Control Experiment II: TiO<sub>2</sub> Layer Thickness Dependence

TiO<sub>2</sub> layer is the carrier of electron after it is excited by the organic dye. As the thickness of graphite was recognized, it is necessary to recognize the semiconductor layer thickness dependency.

This experiment is relatively easier to control than others, because the thickness of TiO<sub>2</sub> in this project was controlled by the tape thickness. Thus, by layering several pieces of tape on one side and then following the same rolling procedure as used for a normal cell, we can control the thickness of TiO<sub>2</sub> in this simple way. However, it was only possible to measure several distinctive data point, i.e the integer times of thickness of the tape, because it is impossible to tape any decimal layer of tapes on the glass. Besides, the result was not that accurate, but the error was carefully controlled. All of the measurements were taken at the same temperature, amount of illumination and pressure.

### **3.5 Control Experiment III: Temperature Dependence**

Temperature dependence of the performance of DSSC was proposed in the paper by the group which tested the dark current. (Carey, 2002) This group disproved this factor because the increase in temperature was found to have tiny influence on the system compared to the relative huge increase in dark current they got experimentally. Without doubt, our group trusts their published result but reproduction was considered necessary to verify this result.

This control experiment was conducted by the way shown below. For each dye we



used in the cell, we tested at 40-50, 60-70, 80-90 degree of centigrade over 6 min. The data were recorded every 45 sec. In order to prevent the cell from overheating, the cells were put onto the heating plate before temperature was increased.

The plot was drawn with the  $t=0$  when the hot plate was turned on. The trend for different dyes was collected and analyzed.

### **3.6 Dark Current Measurement**

In order to get stable and reliable result, the tested cells were only those cells which were able to produce stable and large enough voltage.

The test was conducted under 298 K, 1 atm pressure. The tested cells were first illuminated by the fluorescent light over 12 hours. The reading of multi-meter was recorded as  $t=0$ . Then, the tested cells were kept in a dark cabinet with the protruding leads of multi-meter attached. The reading was recorded over 4 days, simulating the same data recording over four days in Carey's group.

## CHAPTER 4. RESULTS AND DISCUSSION

In this section, results from each experiment mentioned in the methodology chapter are presented and analyzed. Explanations are proposed for each result. If not mentioned specifically, all of the results were measured under 298K, 1 atm pressure with the illumination of fluorescent light. Unless specified, all of the measurements in tables have units of Volts.

### 4.1 Regular Photo-voltage Production

Results of first several testing cells were shown in the result table below. Two different dye solutions were applied to the solar cells.

**Table 2: Results of regular photo-voltage production (organic dye: phthalocyanines)**

Cell No.	Electrolyte	Dye	V1(20 min)	V2(12h)	V3(48h)	V4(4d)
1	KI/I <sub>2</sub>	Phthalocyanines	0.209	0.269	0.459	0.121
2	KI/I <sub>2</sub>	Phthalocyanines	0.090	0.120	0.101	0.062
3	KI/I <sub>2</sub>	Phthalocyanines	0.216	0.146	0.133	0.086
4	KI/I <sub>2</sub>	Phthalocyanines	0.080	0.061	0.002	0.002

Note: The cell 1 and 2 were coated with graphite by burning on the Bunsen burner. The cell 3 and 4 were coated with graphite by burning on the candle. After measurement, the cells were stored without illumination.

**Table 3: Results of regular photo-voltage production (organic dye: raspberry juice)**

Cell No.	Electrolyte	Dye	V1(20 min)	V2(12h)	V3(4d)
1	KI/I <sub>2</sub>	Raspberry	0.158	0.143	0.243
2	KI/I <sub>2</sub>	Raspberry	0.121	0.138	0.078
3	KI/I <sub>2</sub>	Raspberry	0.143	0.167	0.000

Note: The KI/I<sub>2</sub> solution was reapplied to the 3rd cell but still no current was produced.

The possibility of regeneration of photo-voltage with reapplication of electrolyte solution was confirmed by the data shown below.

Table 4: Result of reapplication of electrolyte

Cell No.	Electrolyte	Dye	V1(20 min)	V2(12h)	V3(48h)	V4(4d)	V5(2 weeks)
1	KI/I <sub>2</sub>	Phthalocyanines	0.209	0.229	0.459	0.121	0.227
2	KI/I <sub>2</sub>	Phthalocyanines	0.090	0.120	0.101	0.062	0.118

Note: These two cells were the same with the cell 1 and 2 in table 2. The reapplication of electrolyte occurred 20 min before the measurement had been taken.

Both of the cells were able to regenerate almost 100% of its capability (compare to V2, measured after 12h) to produce the photo-voltage after the reapplication of electrolyte. This fact infers the recycling of DSSC was possible and reproduction of the current was very feasible.

## 4.2 Results of Graphite Layer Thickness Dependence

Cell 1, with no graphite coating, served as the control group. Cell 2 and 3, with different graphite thickness, served as the experimental group.

Table 5: Results of graphite thickness dependence

Cell No.	Electrolyte	Dye	V <sub>1</sub> (20 min)	V <sub>2</sub> (12h)	V <sub>3</sub> (48h)	V <sub>4</sub> (4d)
1	KI/I <sub>2</sub>	Raspberry	0.003	0.000	0.002	0.001
2	KI/I <sub>2</sub>	Raspberry	0.108	0.273	0.266	0.285
3	KI/I <sub>2</sub>	Raspberry	0.111	0.245	0.213	0.260

Note: Cell 2 was heated by the candle over 45 sec. Cell 3 was heated by the same candle over 2 min. The TiO<sub>2</sub> layer was carefully controlled to be approximately the same thickness throughout the cell itself and among the 3 cells. The reapplication of electrolyte solution occurred before the V<sub>4</sub> had been measured.

Although the graphite dependence could not be fully determined by this experiment itself, two conclusions can be made from this table. The graphite layer was definitely necessary for dye-sensitized solar cell; otherwise it won't produce any photo-voltage, inferred by the cell 1. However, if the graphite thickness is enough, over-coating resulting from heating over a longer period of time will not produce conspicuous

increasing voltage for the cell.

If the graphite thickness could be controlled more carefully, a plot of graphite thickness versus the voltage production can be made. However, the data showed that it is unlikely that any further increase in graphite thickness will improve the efficiency. More conclusive result can be made, i.e. what is the minimum amount of graphite necessary for the solar cell function.

### 4.3 Results of TiO<sub>2</sub> Layer Thickness Dependence

All of the experiments were conducted under 1 atm and 25 °C. The graphite coating time was about 35-40 sec. Dye solution applied to the cells was saturated phthalocyanines solution in acetone. Electrolyte solution used was 2% KI/I<sub>2</sub> aqueous solution. The results were listed in the table below.

**Table 6: results of TiO<sub>2</sub> layer thickness dependency**

Thickness(in mm)	V <sub>1</sub> (20 min)	V <sub>2</sub> (12 h)	V <sub>3</sub> (48 h)
0.03	0.194	0.267	0.262
0.09	0.262	0.306	0.296
0.15	0.308	0.332	0.340
0.18	0.321	0.357	0.356
0.21	0.317	0.352	0.343
0.24	0.319	0.327	0.330
0.27	0.303	0.307	0.311

The data showed the optimum thickness of  $\text{TiO}_2$  was about 5-6 layer of the tape, which was about 0.15 - 0.18 mm of  $\text{TiO}_2$ . The increasing trend when the  $\text{TiO}_2$  layer was thin could be explained in two ways. First,  $\text{TiO}_2$  serves as the electron carrier in the dye-sensitized solar cells. It is possible that carriers in our solar cell were not enough when thickness was too low. Once more  $\text{TiO}_2$  was applied to the cell; the increasing carrier increased the efficiency to carry the electrons resulting in the increase of output. The second rationale was explained by the mini-pores in the  $\text{TiO}_2$  which served as an important component for the electron carrying. The possible increase of the number of mini-pores as increasing the thickness of  $\text{TiO}_2$  at relatively low thickness improved the electron carrying ability of this semiconductor.

Explanation of decreasing in output and stable result from relatively large thickness could also proposed by our group. Because the semiconductor and graphite were on the different electrode, and the dye solution was in between both of the electrodes, the photon, in order to excite the electron from the dye molecule, must pass through the  $\text{TiO}_2$  layer which received the photons first. Too much  $\text{TiO}_2$  will obviously absorb or block the photon to make the way to dye molecules. Based on this data, the prediction could be made that if the thickness of the  $\text{TiO}_2$  layer becomes infinity, if it is achievable, the output of the solar cell will approach 0 because the thickness of  $\text{TiO}_2$  prevents photon from reaching the dye molecules.

Experiment stopped after 0.27 mm as a result from difficulty of achieving thickness more than that. Based on the data we obtained and the explanation we proposed,

no further experiment is necessary because it is still not probable that the further increase of thickness will improve the efficiency of solar cell and it is also obvious that the output of the infinite thickness of  $\text{TiO}_2$  will be 0 which also supports the previous prediction.

Since not enough data was obtained from different dye molecules, no general conclusion could be made on this section. However, because different dye molecules absorb at different wavelengths, it is possible that different dye molecules will have specific different optimum thicknesses of the  $\text{TiO}_2$  layer. However, the same trend for the thickness of  $\text{TiO}_2$  is expected because the reason of decreasing for all kinds of cells should be similar. The overall trend of semiconductor layer dependence was shown below in Figure 15.

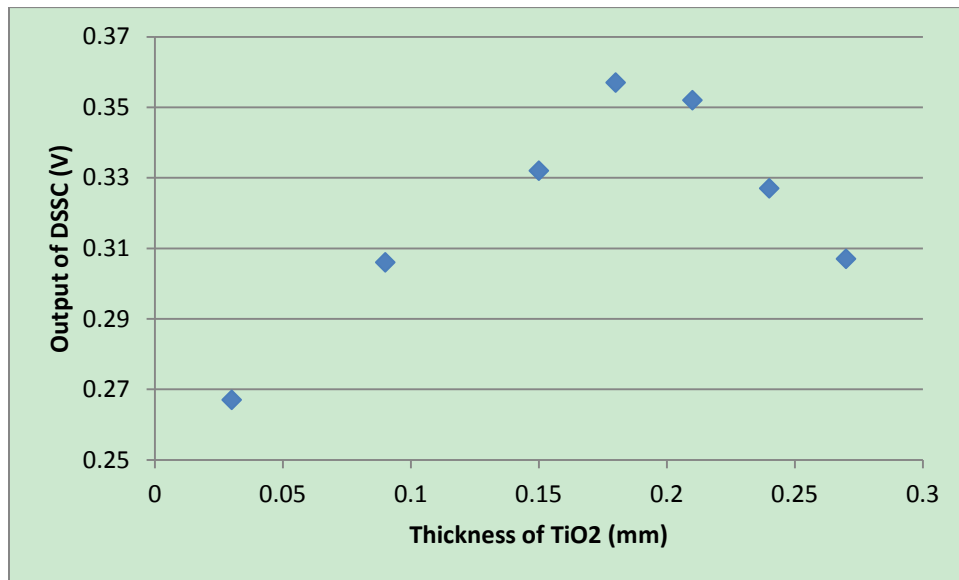


Figure 15: Trends of DSSC Output at 12hr vs. Thickness of  $\text{TiO}_2$  Layer

## 4.4 Results of Temperature Dependence

**Table 7: Results of Temperature Dependence**

Time(s)	V(mV) 40-50 °C		V(mV) 60-70 °C		V(mV) 80-90 °C	
	Phthalocyanines	Raspberry	Phthalocyanines	Raspberry	Phthalocyanines	Raspberry
<b>0</b>	312	458	297	367	216	142
<b>45</b>	314	462	301	372	218	147
<b>90</b>	315	465	303	374	223	160
<b>135</b>	314	466	304	373	209	171
<b>180</b>	310	465	300	369	192	153
<b>225</b>	307	465	297	361	167	131
<b>270</b>	301	460	292	353	154	117
<b>315</b>	298	451	286	344	150	105
<b>360</b>	293	443	279	330	149	101

In the table 7 listed above, when the temperature of the systems varied from 40 °C to 90 °C, the output of the system changed dramatically, however with a trend of increasing in a short amount of time and then decreasing at an almost constant rate.

For cells which incorporated raspberry extractions as the organic dye solution, a sharp increase of output was usually observed in the first several data points, which was considered as the increase of temperature facilitating electron excitation by increasing the rate of photon absorption. However, the decrease of output after about 3 min was considered as breaking the electron cycle by the evaporation of the electrolyte solution so

that no aqueous medium for the redox reaction to take place; thus, electrons could not regenerate in the organic dye.

For cells which used saturated phthalocyanines solution as the dye, the increase of output was not that evident, although the temperature increased to 90 °C. This result could be interpreted as the great efficiency of photon absorbance so that the effect of temperature increase would not be obvious to observe in this system. Another reason might be the difference in the viscosity of these two solutions. The raspberry juice has a higher viscosity compared to phthalocyanine solution; thus, an increase in temperature might facilitate the permeation of the dye solution into the electron carrier, which essential will cover a greater surface area and then improve the efficiency of the cell. The reason of decrease of output would be proposed as the same with that of raspberry cells.

From Figure 16 and 17, a trend of increasing rate of output decrease with the increasing temperature was observed for both of the dye solution cells. The reason we proposed is very self-explanatory: increasing of temperature also increases the rate of vaporization; thus it took less time to evaporate the same amount of solvent with a higher temperature. Then, the rate of decreasing output was greater than those with a lower temperature. Thus, this result also confirmed the explanation given above.



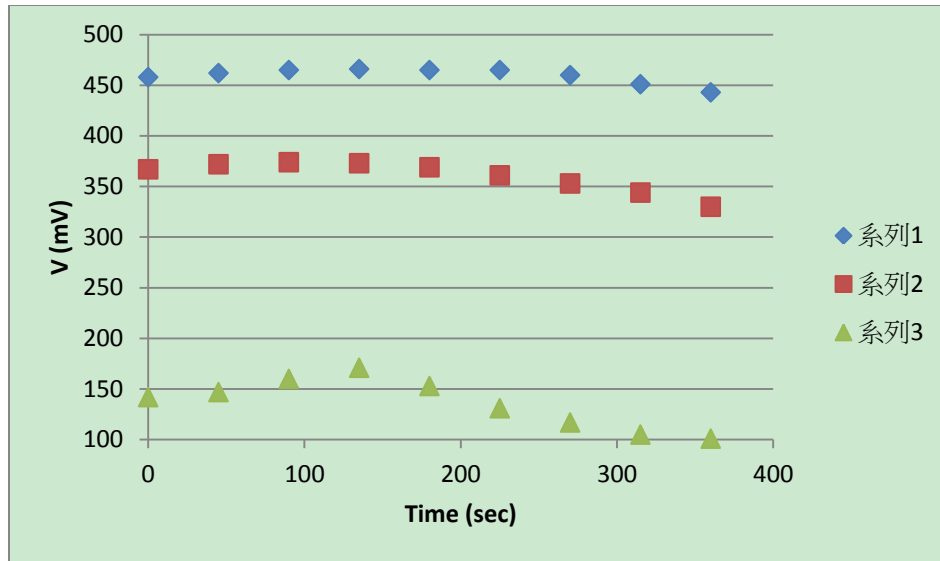


Figure 16: The result of Raspberry Cells. Series 1 is 40-50 °C, series 2 is 60-70 °C, series 3 is 80-90 °C.

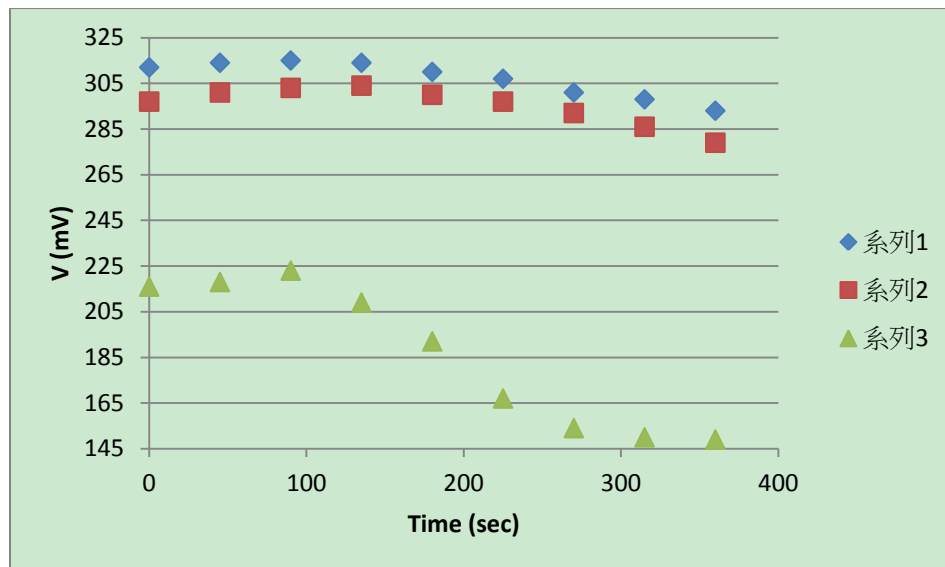


Figure 17: The result of Phthalocyanines Cells. Series 1 is 40-50 °C, series 2 is 60-70 °C, series 3 is 80-90 °C.

From Series 1 in the Figure 16, the output stabilized from 90-225 seconds suggests the optimum temperature of the raspberry cell might be 40-50 °C. Based on the trials above, in all of the cases, a short-length of heating caused an increase in the output value, which might be maintained if the cells are removed from the heat source.

## 4.5 Results of Dark Current

Listed out in the table below, the output of a dye-sensitized solar cell was not as appreciable as the results listed in the paper of Carey's group. However, for the raspberry juice solar cell, 0.018 V at 20 min and 0.006 V at 12 hrs, compared the 0.003 V produced by the control solar cell in the graphite thickness experiments, shows some photoelectrical activity happening in the solar cell. The difference in the results for cells made from different dyes strongly suggests that the dye property might have influence on both the performance and the lag time of the dark current.

**Table 8: Results of Dark Current**

Cell No.	V <sub>0</sub> (0 min)	V <sub>1</sub> (20 min)	V <sub>2</sub> (4h)	V <sub>3</sub> (12h)	V <sub>4</sub> (2d)
1	0.417	0.018	0.011	0.006	0.001
2	0.341	0.007	0.003	0.001	0.001

Note: The 1<sup>st</sup> cell was made from the raspberry extraction and 2<sup>nd</sup> cell was made from saturated phthalocyanines acetone solution. Except this difference, all other condition of those two cells was the same.

One of the possible explanations is that it takes time for dye molecules to absorb photons, so it might also take time for dye molecules to transfer those excited electrons to the carrier molecules. Other than that, the mini-pores in the carrier molecule would trap the electrons thus it might have lagged current in two days.

The proposed reason for the disagreement of the results in Carey's paper and this project was considered to be the condition where the measurement was taking place. The

vacuum was applied when Carey's group measured the dark current. However, due to limit of technology, time and budget, my group could not afford the vacuum measurement.

## ***CHAPTER 5. CONCLUSION AND RECOMMENDATION***

Desired dye-sensitized solar cell system based on TiO<sub>2</sub> and raspberry or phthalocyanines was constructed and characterized after three terms of works. By the end of the final term, I have successfully accomplished the characterization of graphite layer dependence, titanium (IV) oxide layer dependence, temperature dependence and dark current characterization.

My control experiment confirmed the necessity of the graphite layer and discovered the over-coating of the graphite would not affect the output of the experiment in an evident amount. My controlled experiment discovered the optimum thickness of TiO<sub>2</sub> layer would be 0.018-0.021 mm to this system and any layer thicker than this would potentially decrease the output of the cell by blocking the photon transfer, proposed by me.

In the temperature dependence frontier, I discovered the increase of temperature to 40 °C results in the optimum temperature of raspberry cells. And the general trend of the temperature dependence is increase of output over the first several data points and then sharply decrease after the maxima achieves. Raspberry cells tended to increase more than phthalocyanine cells.

The dark current was observed in this project with a shorter lasting time and smaller amount compared to the published result, which was considered due to the

vacuum conditions in the paper and fine technology they used in the project. However, the existence of dark current was confirmed by this project.

The project overall was considered successful resulting from the data which agreed with the published results and the trends I have concluded from controlled experiments. On the other hand, due to the limitation of several factors, the dark current could not be measured at vacuum condition and different dye solution could not be incorporated in this project.

In the future project, the dependence and dark current using different dye samples should be determined to discover any dependence between the last time or the magnitude of dark current and the identity or character of the dyes. Heating experiment should be reproduced to confirm the general trend of my results. And any further thoughts on this project should be considered and turned into control experiment to carry out.

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