

CHARACTERIZATION AND TREATMENT OF TITANIUM DIOXIDE, TiO₂
VIA ULTRASONIC PROCESS WITH MELASTOMA MALABATHRICUM AS
SUSTAINABLE SENSITIZER FOR PHOTOVOLTAIC SOLAR CELL

NUR MUNIRAH BINTI ABDULLAH

A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Mechanical Engineering

Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

SEPTEMBER, 2012

ABSTRACT

Dye-sensitized solar cells (DSSCs) have been fabricated with doped Titanium Dioxide, TiO_2 which are based on natural dyes from Malaysia tropical fruits, wherein contain interlocking groups; the carbonyl and hydroxyl groups of the anthocyanin molecule which enhance the photosensitization effect due to the high interaction on the surface of the film. Such a natural dye extracted from *Melastoma Malabathricum* can be subjected to molecular tailoring to give a superior dye preparation, offering a wide range of spectral absorption; covering the entire visible region (400 – 700 nm). This study is based on a series of TiO_2 preparations designated U1 and U2 (without and with additive respectively), and those treated with ultrasonic energy, namely U3 and U4 (without and with additive respectively). 10 minutes of sonication of the metal oxide led to its breakdown from agglomeration at the micro to the nano scale. Furthermore the additive (4-tert-butylpyridine) in potassium iodide, KI_3 electrolyte, effects the rate of electron injection into the oxidized dye sensitizer. Sonication of TiO_2 reduced the particle size agglomerates from 0.37 μm down to 0.15 μm ; this treatment led to a more consistency with high porosity, enabling enhance absorption and anchorage of the dye sensitizer. Sonicated sample U4, with addition of electrolyte additive gives, open circuit voltage, $V_{oc} = 0.742$ V, short circuit current, $I_{sc} = 0.36$ mA, fill factor, $FF = 57.012$ and 0.039 % of cell's efficiency. Evidently, sonication and addition of additive for KI_3 electrolyte offer enhanced capability for further application.

ABSTRAK

Sel solar pemeka warna (DSSCs) telah direka dengan Titanium Dioxida terdop, TiO_2 berasaskan pewarna semulajadi daripada buah-buahan tropika Malaysia, yang mengandungi kumpulan yang saling bertaut; kumpulan karbonil dan hidroksil molekul antosianin yang meningkatkan kesan foto-pemekaan disebabkan interaksi tinggi pada permukaan filem. Pewarna semulajadi yang diekstrak daripada *Melastoma Malabathricum* boleh berubah tertakluk kepada rekabentuk molekul untuk memberikan penyediaan pewarna yang unggul, yang menawarkan pelbagai spektrum penyerapan; meliputi seluruh julat gelombang yang boleh dilihat dengan mata kasar (400 - 700 nm). Kajian ini adalah berdasarkan satu siri penyediaan TiO_2 yang ditetapkan untuk U1 dan U2 (tanpa dan dengan penambah masing-masing), dan yang lain dirawat dengan tenaga ultrasonik, iaitu U3 dan U4 (tanpa dan dengan penambah masing-masing). 10 minit proses sonikasi menguraikan aglomerasi oksida logam daripada mikro ke skala nano. Di samping itu, bahan penambah (4-tert-butylpyridine) bagi kalium iodide elektrolit, KI_3 memberi kesan ke atas kadar suntikan elektron ke dalam pemeka pewarna teroksida. Sonikasi mengurangkan agglomerasi TiO_2 dari saiz zarah $0.37 \mu\text{m}$ kepada $0.15 \mu\text{m}$; rawatan ini menghasilkan sifat yang lebih konsisten dengan keliangan yang tinggi, membolehkan peningkatan penyerapan dan tempat berlabuh pemeka pewarna. Sampel U4 yang disonikasi, dengan bahan penambah elektrolit menghasilkan, voltan litar terbuka, $V_{\text{OC}} = 0.742 \text{ V}$, litar pintas semasa, $I_{\text{SC}} = 0.36 \text{ mA}$, faktor isi, $\text{FF} = 57.012$ dan kecekapan sel 0.039% . Proses sonikasi dan penambahan bahan penambah untuk elektrolit KI_3 menawarkan keupayaan yang boleh dipertingkatkan untuk aplikasi selanjutnya.

CONTENTS

TITLE	i
DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF SYMBOLS AND ABBREVIATIONS	xvii
 CHAPTER 1 INTRODUCTION	
1.1 Background	1
1.2 Problem Statement	2
1.3 Aim	3
1.4 Objectives of the research	4
1.5 Scope	4

CHAPTER 2 LITERATURE REVIEW

2.1 Solar Cells development	5
2.1.1 Three Generations of Solar Cells	6
2.2 Metal oxide semiconductors	9
2.2.1 TiO ₂ properties	11
2.2.2 Nanopowder production	12
2.2.2.1 Ultrasonic process	13
2.3 Dye sensitizer	15
2.3.1 Anthocyanin	17
2.4 Electrolyte	18
2.4 Counter Electrode	19
2.6 Dye Sensitized Solar Cell	21
2.6.1 Basic operating theory	21

CHAPTER 3 METHODOLOGY

3.1 Introduction	24
3.2 Materials and apparatus/instruments	26
3.3 Preparation of natural dye sensitizer	29
3.4 Preparation of TiO ₂ film electrode	29
3.4.1 TiO ₂ without undergo ultrasonic process	29
3.4.2 TiO ₂ with undergo ultrasonic process	30

3.5 Preparation of Carbon black plate (positive plate)	33
3.6 Assembling the photovoltaic cells	33
3.7 Characterization techniques	35
3.7.1 TiO ₂ characterization	35
3.7.1.1 X-Ray Diffractometer (XRD)	35
3.7.1.2 Field Emission Scanning Electron Microscopy	35
3.7.1.3 Surface profiler	36
3.7.1.4 Atomic Force Microscope (AFM)	36
3.7.2 Natural dye properties	36
3.7.2.1 Fourier Transform Infrared Spectroscopy (FTIR)	36
3.7.2.2 UV/VIS Spectrophotometry	37
3.7.3 Cell characterization	37
3.7.3.2 I-V measurement	37
3.7.3.2 Preliminary stability test of single solar cell upon sunlight illumination	38

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Introduction	39
4.2 Characterization TiO ₂	40
4.2.1 Microstructure of TiO ₂ coated glass	41

4.2.2 Thickness and roughness of the film	45
4.3 Characterization of natural dye sensitizer	47
4.4 Photovoltaic solar cell performance	49
4.4.1 Electrical characteristic	49
4.4.2 Outdoor stability	51
CHAPTER 5 CONCLUSION AND RECOMMENDATION	
5.1 Conclusion	54
5.2 Recommendation	55
REFERENCES	56

LIST OF TABLES

2.1	Best large-area thin film modules	7
2.2	Band positions of some common semiconductor Photocatalysts in aqueous solution at pH=1	12
3.1	High technology instrument that involved for fabrication and testing of photovoltaic solar cell.	26
3.2	Condition process for clamp-on tubular reactor	29
4.1	The electrical characterization of all prepared cells	50

LIST OF FIGURES

2.1	Evolution of the conversion efficiencies of various types of research photovoltaic cells.	6
2.2	Architecture of a dye solar cell. The semiconductor (TiO_2) and the electrolyte are located between two glass plates, coated with transparent conducting oxide (TCO). The TiO_2 is covered with a monolayer of dye and the counter electrode is coated with carbon black	8
2.3	Schematic diagram of DSSC with the highest efficiency recorded	9
2.4	Theoretical schema of DSSC where (a) photoexcitation in oxide film/dye and (b) complete circulation of electron in the circuit	10
2.5	Different naturally occurs crystalline polymorph of TiO_2 (a) anatase, (b) rutile, (c) brookite, where small red sphere: O^{2-} , big grey sphere: Ti^{4+}	13
2.6	Schematic of (a) RESS, (b) SAS, (c) PGSS and (d) DELOS.	14
2.7	Schematic representation of transient acoustic cavitation	15

2.8	Intensity distribution for agglomerates analysis results for TiO ₂ nanopowders before and after ultrasonification for commercial titanium nanopowders from three suppliers: Nanostructured & Amorphous Materials, Inc. for (a) anatase and (b) rutile, (c) anatase from Degussa, and (d) titania from TAL Materials, Inc. while (2)(a), (b), (c) and (d) represent respectively	16
2.9	Molecular structures of three most frequently applied ruthenium polypyridyl complexes for DSSCs; (a) N-3, “red dye”, (b) N-749, “black dye”, and (c) Z-907	17
2.10	Normalized absorbance vs wavelength spectra of six dyes Rose Bengal (1 X C), Eosin- Y (1 X C), Rhodamine - B (1 X C), Acridine Orange (1 X C), Fast Green (1 X C), and blended dye (1 X C: 2 X C: 3 X C: 2 X C: 1 X C) in ethanol solution and adsorbed on ZnO electrodes	18
2.11	Structural formula of anthocyanidins. Cyanin, R1 = OH, R2 = H; delphinidin, R1 = R2 = OH; peonidin, R1 = OCH ₃ , R2 = H; petunidin, R1 = OCH ₃ , R2 = OH; malvidin, R1 = R2 = OCH ₃	19
2.12	Cotton fabrics dyed with <i>Senduduk</i>	20
2.13	Structure and the viscosity of several ionic liquids	20

2.14	I-V curve of counter electrode with various mixing carbon ratios	22
3.1	Flowchart of complete photovoltaic solar cell	25
3.2	Synthesis of natural dye from <i>Senduduk</i> fruit	29
3.3	Preparation of TiO ₂ film on ITO glass as electrode	30
3.4	Flowchart of treated metal oxide via ultrasonic process	32
3.5	Carbon black coated film	33
3.6	Assembled solar cell	34
3.7	Schematic diagram of measurement of halogen's lamp spectrum	38
3.8	Schematic diagram of single solar cell upon sunlight illumination	38
4.1	XRD patterns of TiO ₂ powders (a) without undergo ultrasonic process, and the rest (b) 10 minutes, (c) 20 minutes, (d) 30 minutes, (e) 40 minutes, (f) 50 minutes and (g) 60 minutes, with undergo ultrasonic process respectively	40
4.2	FESEM images of (a) untreated TiO ₂ film surface, magnification of 2000 (i), 10000 (ii), 25000 (iii), 50000 (iv), 75000 (v) and 100000 (vi)	41

4.3	FESEM images of (b) treated TiO ₂ film surface, magnification of 2000 (i), 10000 (ii), 25000 (iii), 50000 (iv), 75000 (v) and 100000 (vi)	42
4.4	Light scattering concept reproduced	43
4.5	The graph of the thickness of a film and its roughness using Surface Profiler.	44
4.6	3D surface structure of TiO ₂ film in range 25 μm ² along with histogram	45
4.7	Display clear view of grain boundaries of the film at the same area, 25 μm ² for untreated metal oxide (a), while (b) shows the data of treated TiO ₂ with Ultrasonic	46
4.8	Functional group comparison between A, commercial blackberry dye with B, local natural dye, <i>Senduduk</i> 's fruit	47
4.9	The basic molecular structure of anthocyanin and the binding with TiO ₂	48
4.10	Absorption characteristic of commercial, A and local natural dye, B	48
4.11	I-V characteristic of photovoltaic solar cell	49
4.12	I-V characteristics of a typical DSSC	50

- 4.13 Graph of the average values of Potential (V) 52
at noon (12- 1 pm) upon sunlight illumination
for ten days where respective cell;
U1(untreated TiO₂ with ultrasonic process,
without additive), U2 (untreated TiO₂
with ultrasonic process, in addition of additive),
U3 (treated TiO₂ with ultrasonic process,
without additive) and U4 (treated TiO₂ with
ultrasonic process, in addition of additive)
- 4.14 Graph of the average values of Potential (V) 52
at afternoon (3- 4 pm) upon sunlight illumination
for ten days where respective cell;
U1(untreated TiO₂ with ultrasonic process,
without additive), U2 (untreated TiO₂
with ultrasonic process, in addition of additive),
U3 (treated TiO₂ with ultrasonic process,
without additive) and U4 (treated TiO₂ with
ultrasonic process, in addition of additive)

LIST OF SYMBOLS AND ABBREVIATIONS

FF	-	Fill factor,
$\eta\%$	-	Efficiency
V_m	-	Voltage at maximum power point
I_m	-	Current at maximum power point
V_{oc}	-	Open circuit voltage
I_{sc}	-	Short circuit current
P_{in}	-	Power of the incident light
DSSC	-	Dye Sensitized Solar Cell
TiO_2	-	Titanium dioxide
TCO	-	Transparent conducting oxide
KI_3	-	Potassium Triiodide
MLCT	-	Metal to Ligand Charge Transfer
PSA	-	Particle Size Analyzer
XRD	-	Xray Diffractometer
FESEM	-	Field Emission Scanning Electron Microscopy
AFM	-	Atomic Force Microscope
FTIR	-	Fourier Transform Infrared Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background

If we look at photosynthesis organisms, the best solar cells on earth, we find that there is no waste in these natural systems; everything is biodegradable, reusable or regenerative. The earth remains as healthy after the organism dies as it was before the organism was born. If we can invest in renewable energy technologies that similarly create a complete loop between the source and the end of the technology cycle, so the condition of the environment is at least as good after we use the energy as it was before we used the energy, then we can achieve a truly sustainable energy source (Ali, S., Spring 2007).

The issues of sustainable energy source has aroused public awareness significantly for the past few decades especially in high demand or developing countries. As the energy usage keep on increasing, so do the climatic disruption such as Greenhouse effect which caused by the fossil fuel combustion and changed in global climate accompanied by depletion of fossil fuel reserves. These undesirable activities have enhanced the growth of renewable energy (wind turbine, biomass, water and etc.) to overcome the dearth. One of the promising renewable energy which makes used of free source of energy, the sun (3×10^{24} J per year), is solar cells. According to Gratzel, M. (2005), by covering only 0.1 % of the earth's surface with solar cells with an efficiency of 10 % would

satisfy what mankind consumes currently. This ‘converting light into electric’ technology can be classified into three groups according to present market demand: silicon bulk heterojunction cells (first-generation technology); thin film (CuInGaSe₂, [CIGS], CdTe) solar cells (second-generation) and dye sensitized solar cells (DSSC) (third-generation) (Kee, E. L. *et al.*, 2009).

Unlike silicon solar cells, DSSC comprises of 3 layers; Titanium Dioxide, TiO₂ thin film, dye sensitizer and counter electrode wherein the electrolyte acts as the electron transport. Therefore, this innovative thinking by Gratzel, M in 1991 runs the light absorption and charge carrier separately. Light is absorbed by a dye sensitizer, which is anchored to the surface of a wide band gap semiconductor (commonly TiO₂). Then, the dye is generated by electron donation from the electrolyte such as the iodide / triiodide couple (Murali, S., 2011). The operating principle of DSSC is complete once it receives back an electron from the external circuit.

In this research, a thin film using Engineering grade of TiO₂ >99 %, organic material from wild plant, Melastoma Malabathricum (*Senduduk*) fruit as dye sensitizer and Carbon black as the counter electrode is disclosed. It is known that most of the efficiency of organic dyes are typically <1 % (Zhou, H. *et al.*, 2010), but rapid research has been done recently as it promises cost reduction and environmental friendly.

1.2 Problem Statement

Running our daily life with oil or natural gas or using electricity (from power plants generated with oil and coal) enhanced Greenhouse Effect, the cause of global warming and climate disruption which are becoming more common in recent years. Besides, it also contributes to the fuel crisis whereby affect the daily expenses (foods and clothes) as it is in the same pyramid chain. Many believed that solar cell is one of the best answers of solving the problems apart from other renewable energy such as water, wind, biomass, geothermal and etc.

In the first generation of solar cell, the Silicon based has shown good performance in producing power. However, there are several constraints such as heavy weight per area panels, fragile and also very low return of investment (ROI) since. It is said that nothing in life comes without a price. The management of the hazardous production wastes and the issue of disposing of spent solar cells have yet to be resolved. Therefore, natural dye sensitized photovoltaic metal oxide is produced to overcome the dearth for energy conversion solar cell. Compared to traditional solar cells, this photovoltaic cell has the following differentiation advantages:

- Low dependence on angle of light
- Stable operating voltage in all light conditions
- Natural colors
- Optional transparency
- Aesthetically pleasing
- Manufactured as a building product
- Provides additional functionality for energy efficiency and noise reduction

1.3 Aim

The aim of this research is to replace DSSC natural dye by using low purity of treated TiO_2 (Engineering grade >99 %) via ultrasonic process and local natural dye, *Melastoma Malabathricum* (*Senduduk*) fruit, for future Green Solar Cell Technology.

1.4 Objective(s) of the research

- 1) To characterize a natural dyestuff extracted from wild plant *Melastoma Malabathricum* (*Senduduk*) fruit as sensitizer.
- 2) To determine the photovoltaic performance / efficiency (η %) of untreated and treated TiO_2 as semiconductor on ITO substrate and Carbon black as counter electrode.
- 3) Optimization of ultrasonic process with varying of time to obtain multilayer thickness of a film.

1.5 Scope

In this study, solar cells based on natural dye sensitized photovoltaic, TiO_2 semiconductor material with Engineering grade > 99 %, KI_3 liquid electrolyte and Carbon black as counter electrode were fabricated. Using the ultrasonic process for reducing agglomeration of semiconductor particles which resulting on thin film morphology, it is also emphasis on natural dye extracted from *Melastoma Malabathricum* (*Senduduk*) fruit as dye sensitizer. The physical and electrical characteristics were performed to gain maximum efficiency in order to construct a competitive solar cells's panel.

CHAPTER 2

LITERATURE REVIEW

2.1 Solar cells development

As early 1839, a French physicist found that certain materials would give electric current characteristic when light hits on them. This phenomenon was described as the “photoelectric effect” until now. Later, the first solar cell was invented in 1877 with around 1% efficiency- the semiconductor selenium was coated with a thin layer of gold and became a demonstrated working principle of solar cells.

Many researches had been done and finally in 1940, the first “silicon” solar cells were produced by the American. By 1954, scientists from Bell Laboratory accidentally discovered that silicon doped with certain impurities would give rather higher efficiency up to 6 % and this resulted solar cells being used in practical application, spacecraft.

During the development of inorganic solar cells, the discovery of the sensitization of the semiconductor electrode in 1887 had aroused interest of researchers for other kind of solar cells, this followed by the discovery of the conducting polymer in 1977.

Taking nature as the best learning, a nanostructured semiconductor of dye-sensitized solar cells (DSSCs) excellently gives as high as 10 % efficiency by Gratzel and coworkers in 1991. This practical breakthrough had raised eyes browsed among researchers in order to find a low cost fabrication and convenient for mass production of solar cells. Despite of replacing the traditional energy source such as fossil fuel, oil and

gasses, it is necessary to improve the efficiency of these DSSCs for practical applications. The latest development in DSSC application is as shown in Figure 2.1.

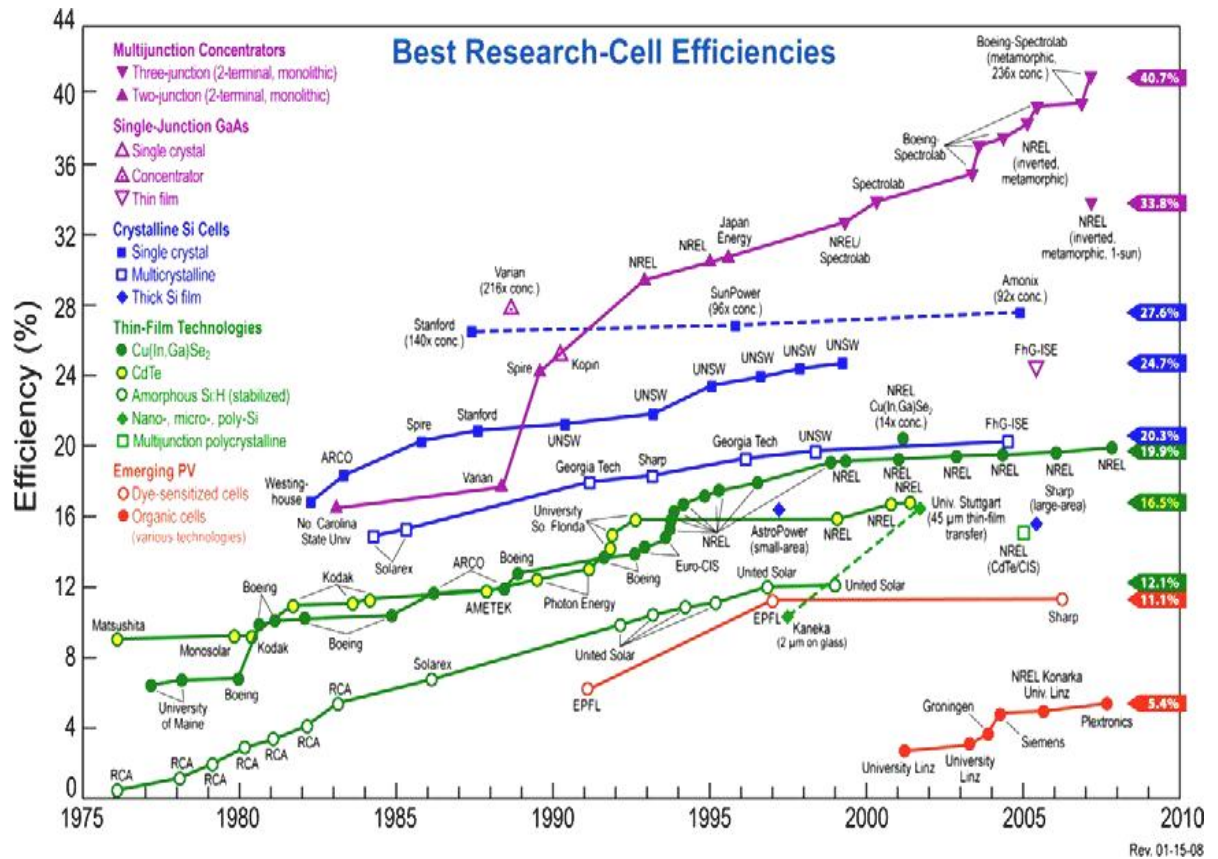


Figure 2.1: Evolution of the conversion efficiencies of various types of research photovoltaic cells (Razykov, T. M. *et al.*, 2011).

2.1.1 Three Generations of Solar Cells

Solar cells are usually divided into three generations. Those generations are a point base on the order of which each became important.

The first generation is currently used in practice. It is relatively expensive to produce and very pure silicon is needed, and due to the energy-requiring process, the price is high compared to the power output (Lund, H. *et al.*, 2008). Single junction silicon devices are approaching the theoretical limiting efficiency of ~31 % as suggested thus become the main reason for the emergence of the second generation of solar cells.

The second generation contains types of solar cells that have a lower efficiency, but are much cheaper to produce, such that the cost per watt is lower than in first generation cells. Most well-known materials in this second generation are cadmium telluride (CdTe), copper indium gallium selenide (CIGS), amorphous silicon (a-Si) and micromorphous silicon (μ a-Si) (Lund, H. *et al.*, 2008).

Among major manufacturers there is certainly a trend toward second generation technologies as shown in Table 2.1, however it face difficulty on market acceptance. The product based has proven hazardous to our health and environment as Cd, As, In, Se and Te are toxic materials (Charles,C.S.,Sunao, S., & Janusz, N., 2005). Eventhough other semiconductors such as GaAs, GaAlAs, GaInAsP, InAs, InSb, and InP arise as an interesting solar cell materials because they have near-optimal band gaps, these materials are extremely expensive, and have found applications only in the space solar cells (Halme, J., 2002)

Table 2.1: Best large-area thin film modules (Razykov, T.M. *et al.*, 2011).

Company	Device	Size (cm ²)	Efficiency (%)	Power (W)	Date
Mitsubishi Heavy ^a	a-Si	15 625	6.4 (stabilized)	100	July 05
Global Solar Energy	CIGS	8709	10.2	88.9	May 05
Wurth Solar	CIGS	6500	13	84.6	June 04
United Solar	a-Si	9276	7.6 (stabilized)	70.8	Sept 97
First Solar	CdTe	6624	10.2	67.4	Feb 04
Shell Solar GMBH	CIS	4938	13.1	64.8	June 04
Sharp ^a	nano-Si	4770	11 (stabilized)	52.5	July 05
Antec Solar	CdTe	6633	7.3	52.3	June 04
Kaneka	a-Si	8100	6.3 (stabilized)	51	July 04
Shell Solar Industries	CIS	3644	12.9	46.8	May 05
Showa Shell ^a	CIGS	3459	13.4	46.45	Aug 02
EPV	a-Si	7432	5.7 (stabilized)	42.3	Oct 02

^aReported by company

The term third generation is about nanophotovoltaic solar cells technology. In 2011, Razykov, T. M. *et al.* summarized that there are a lot of ongoing researches in this area; Quantum well solar cells (QWSCs), Quantum dot solar cells (QDs) (Gimenez, S. *et al.*, 2009), Dye-sensitized solar cells (DSSCs), Organic and Polymeric solar cells (Luque, A., & Hegedus, S., 2003) and last but not least, Rectenna conversion. Each device has different potential applications and different ways of approached to overcome the production cost/efficiency trade-of. However, a greener solar cells technology should be emphasis while retaining low cost materials and manufacturing techniques with acceptable efficiency. Indeed, it is not yet widely commercialize.

As refer to Figure 2.2, the semiconductor, TiO_2 and the electrolyte are located between two glass plates, coated with transparent conducting oxide (TCO). The TiO_2 is covered with a monolayer of dye and the counter electrode is coated with Carbon black

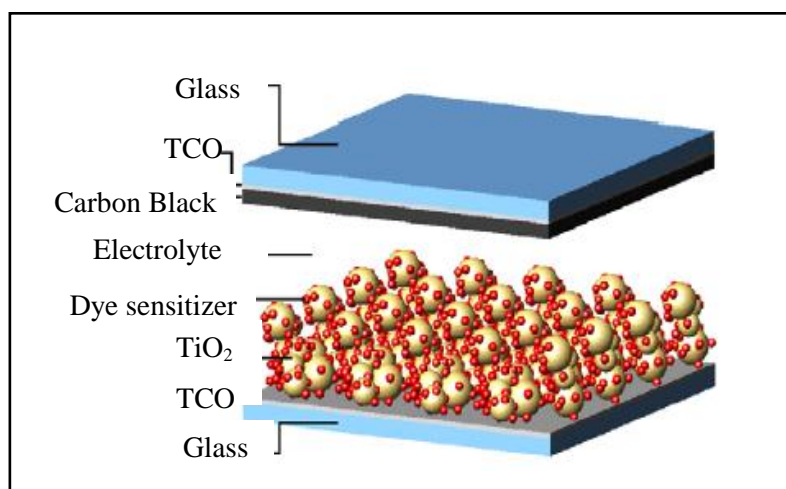


Figure 2.2: Architecture of a dye solar cell (Sastrawan, R., 2006).

2.2 Metal oxide semiconductors

Semiconductor or an insulator is a concept where the valence band is completely filled with electrons in bonding states so that the electrons conductivity cannot occur. There are no vacant levels of similar energy on neighbouring atoms. Its anti-bonding states (the conduction band) are completely empty at absolute; insulators. However, as in semiconductor materials, as the temperature increases, electrons in the valence band with sufficient energy will be excited to the energy gap into the conduction band. When this phenomenon occurs, these excited electrons can move and the material can be said in electrically conductive state. This concept similarly goes to conductive materials in much easier manner since the band gap are very small. The bands in different types of materials are presented in Figure 2.3.

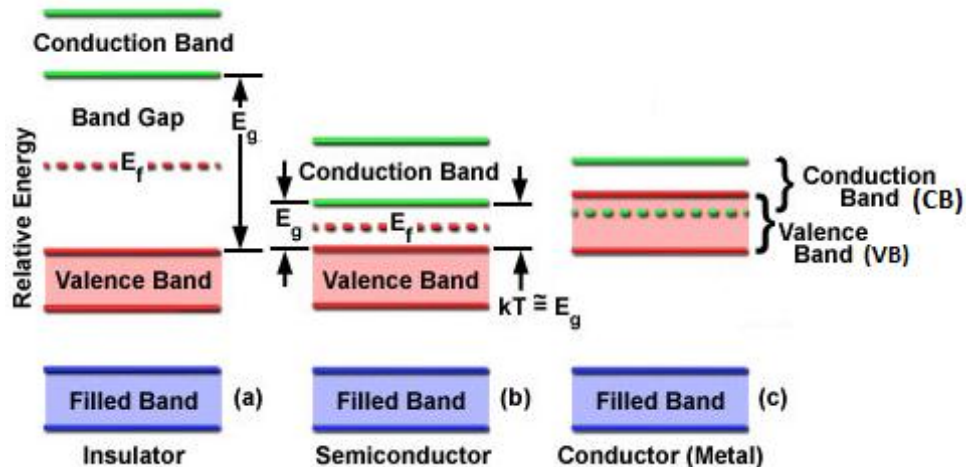


Figure 2.3: Band gap energy concept which represented by the variable $E(g)$, while kT is the thermal excitation energy and $E(f)$ is the Fermi energy (Davidson, M. W, 2006)

Thus, photocatalysis is a technique where light is used to irradiate the surface of a semiconductor material to achieve the transformation of a molecule in contact with the surface, either in solution or in the gas phase. The primary criteria for good oxide and sulfide semiconductor photocatalysts for organic compound degradation are that the redox potential of the $H_2O/\cdot OH$ ($OH^- = \cdot OH + e^-$; $E_0 = -2.8$ V) couple lies within the

band-gap domain of the material and they are stable over prolonged periods of time (Hoffmann, M. R.*et al.*, 1994; Wolf, E. L., 2009). Furthermore, the radiation must be equal or lower wavelength than that calculated by the Planck's equation and listed as in Table 2.1.

$$\lambda = hc/ E_b \quad (2.1)$$

Where, λ = Wavelength

h = Planck's constant (6.626×10^{-34} J.s)

c = Speed of light (3×10^8 m/s)

E_b = Energy of a photon

Table 2.1: Band positions of some common semiconductor photocatalysts in aqueous solution at pH=1 (Sumandeep, K., 2007).

Semiconductor	Valence band (V vs NHE)	Conductance band (V vs NHE)	Band gap (eV)	Band gap wavelength (nm)
TiO ₂	+3.1	-0.1	3.2	387
SnO ₂	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387
ZnS	+1.4	-2.3	3.7	335
WO ₃	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	496
CdSe	+1.6	-0.1	1.7	729

According to Hoffmann, M. R.*et al.*, (1994), Diebold, U., (2002) and Sumandeep, K., (2007), TiO₂ has proven to be the most suitable for widespread environmental applications compared to other semiconductor as it is biologically and chemically inert; stable with respect to photocorrosion and chemical corrosion, inexpensive material, instead of high photosensitivity and high structure stability under solar irradiation and in solutions.

2.2.1 TiO₂ properties

The crystallite TiO₂ comprises of three structures as shown in Figure 2.4 namely anatase, rutile and brookite, of which brookite is very difficult to obtain and therefore not practical for DSSC used. As for rutile, it absorb light in the near UV-region with band-gap (3.0 eV) excitations lead to generation of holes and causes long term stability of the solar cell. However, anatase is dominant in low temperatures (<800 °C) with 3.23 eV band-gap. The Fermi level of anatase is 100 mV higher than that of rutile, which leads to higher open circuit potential (V_{oc}). Moreover, the greater surface area of anatase (rutile is estimated to be at least 25 % lower surface area than anatase) is responsible for efficient dye loading, leads the higher photocurrent, consequently, higher photovoltaic performance (Park, N. G., 2010; Attaf, B. (Ed.), 2011).

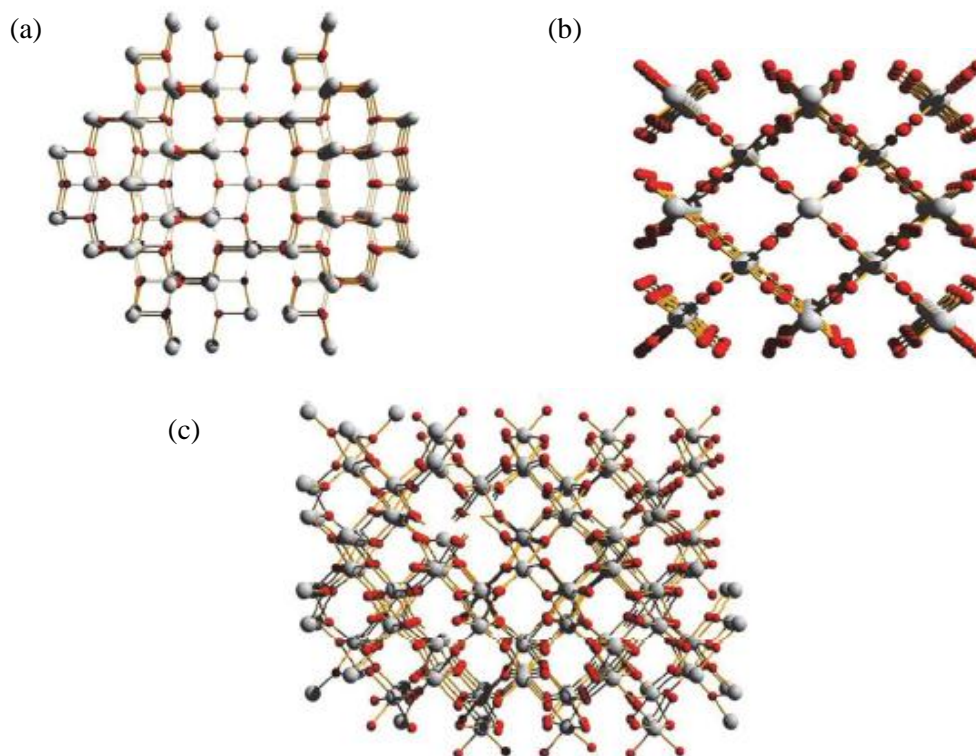


Figure 2.4: Different naturally occurs crystalline polymorph of TiO₂ (a) anatase, (b) rutile, (c) brookite, where small red sphere: O²⁻, big grey sphere: Ti⁴⁺ (Attaf, B. (Ed.), 2011).

2.2.2 Nanopowder production

One of the well-known modifications is through developed particle size from the scale range of 10^{-9} m and this is called Nanostructured materials. These technologies have opened up new possibilities and opportunity in many applications such as in electronics, energy, materials chemistry, and biology. In 2004, Gordillo, G, & Hailey, X. reported a supercritical fluids (SCF) technique in comparison with the Rapid expansion of Supercritical Solutions (RESS), the Supercritical Anti-Solvent (SAS), the Particles from Gas Saturated Solutions (PGSS), and the Depressurization of Expanded Liquid Organic Solution (DELOS) for nano-powder production as shown in Figure 2.5 below.

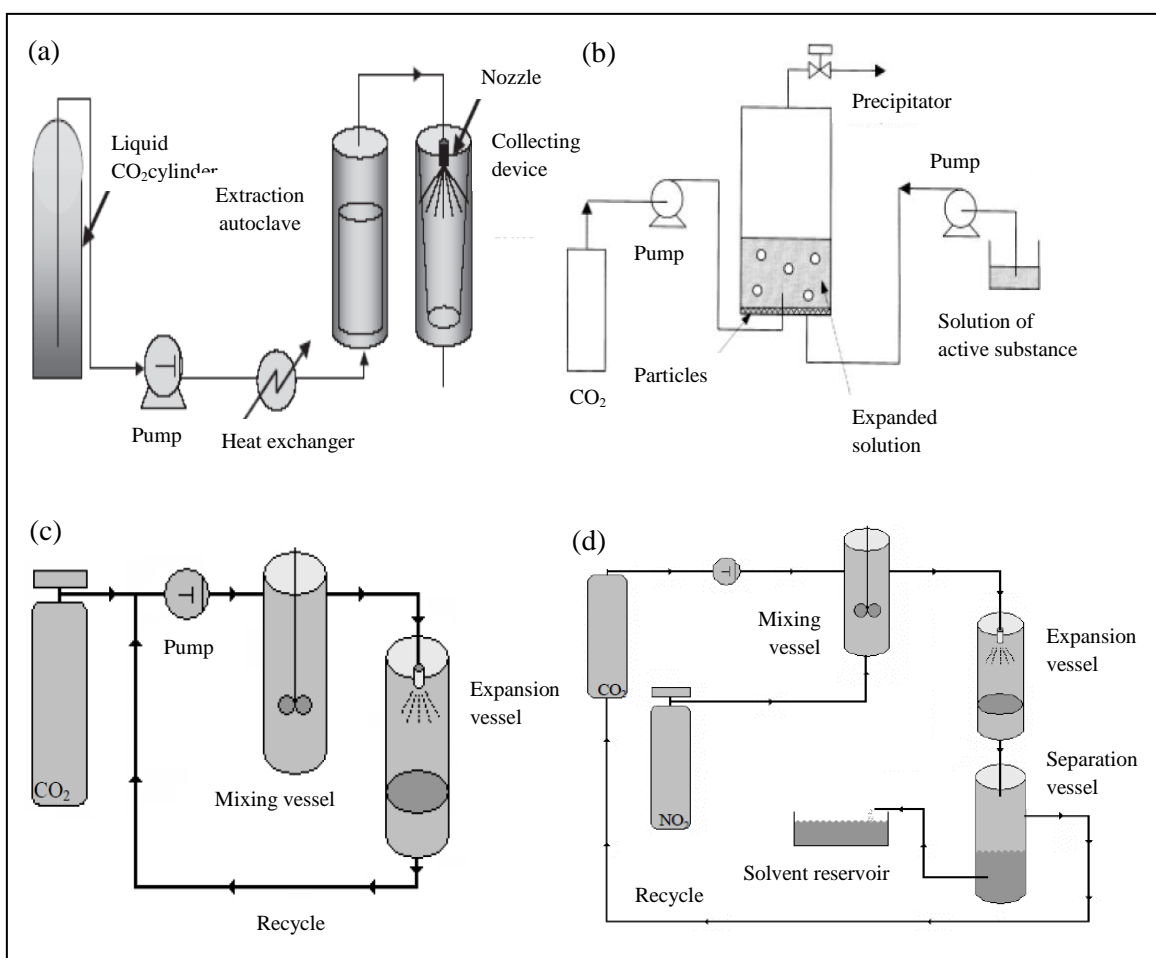


Figure 2.5: Schematic of (a) RESS, (b) SAS, (c) PGSS and (d) DELOS (Gordillo, G, & Hailey, X., 2004)

2.2.2.1 Ultrasonic process

Manipulating the physical, biological and chemical properties means TiO_2 semiconductor can be made to be better ‘sponge’ leading to higher solar cell performance. Basically, conventional methods of powder particle size reduction that can be used in this application are milling (Yamamoto, Y. *et al.*, 2011), grinding, jet milling, crushing, and air micronization. Milling, due to impact and high shear fields however produced irregular particles size and the particles might be contaminate from milling media. Therefore, new advance in processing-ultrasonic approached as it generates in liquids by implosive bubble collapse and associated shock waves as shown in Figure 2.6 below (Jin, H. B., & Suslick, K. S., 2010).

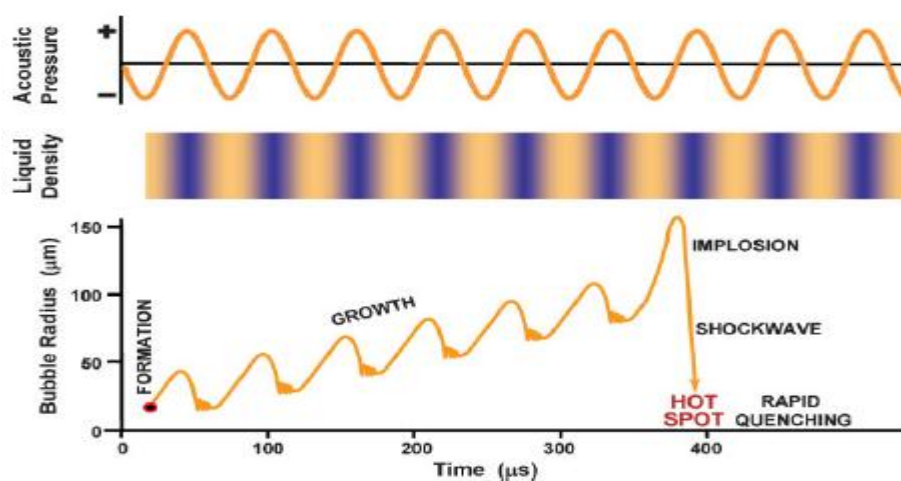


Figure 2.6: Schematic representation of transient acoustic cavitation (Jin, H. B., & Suslick, K. S., 2010)

Farrell, K. A. (2001) studied the effect of a relatively ultrasonic upon titania grain size and phase content. Based on more research on ultrasonic process for agglomeration breakage (Chang, W. O., et al., 2004; Sumandeeep, K., 2007) which is illustrated in Figure 2.7 (Mandzy, N., Grulke, E., & Druffel, T., 2005) with different

parameters involved, Jin & Suslick (2010) summarized results showing that ultrasonic approach has more advantages over conventional methods in the synthesis of nanostructured materials such as metals, alloys, oxides, sulfides, carbides, carbons, polymers, and even biomaterials. The versatility of the ultrasonic process when performed in a solvent produces a more uniform size distribution, contributes to a higher surface area, a faster reaction time, and improved phase purity.

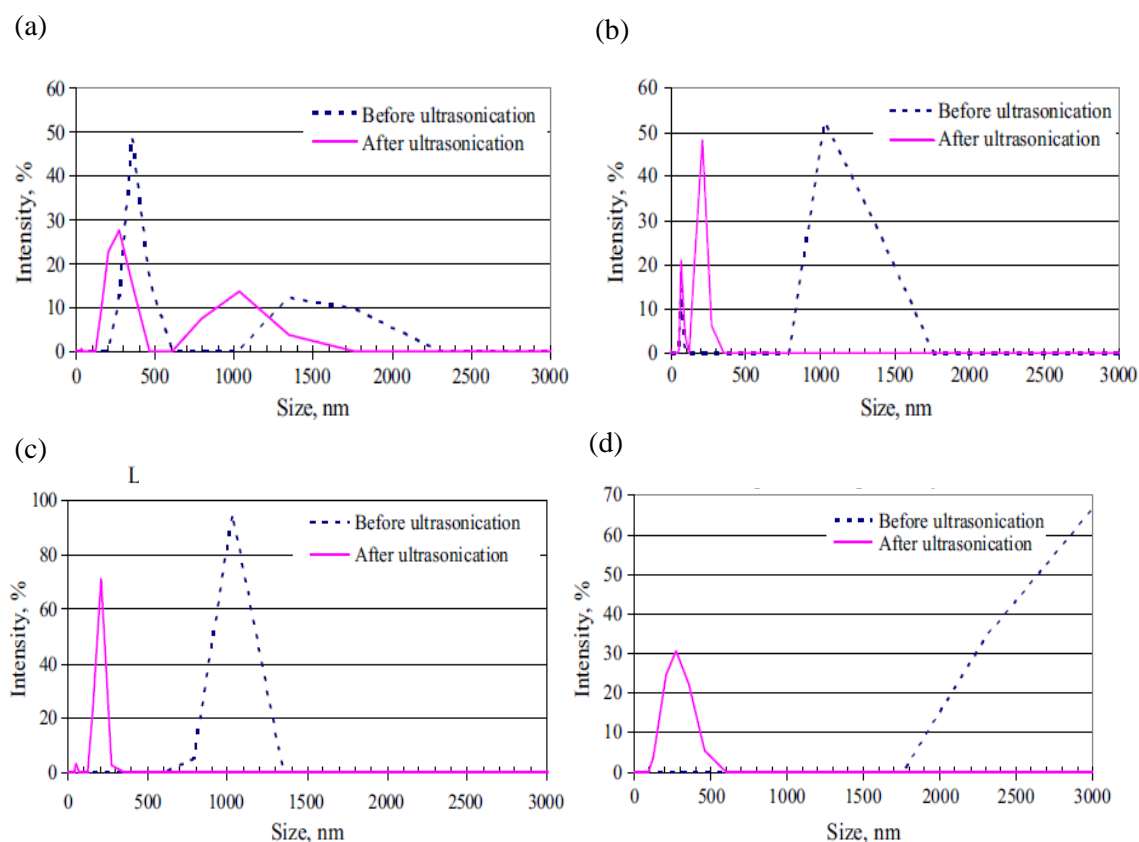


Figure 2.7: Intensity distribution for agglomerates analysis results for TiO₂ nanopowders before and after ultrasonification for commercial titania nanopowders from three suppliers: Nanostructured & Amorphous Materials, Inc. for (a) anatase and (b) rutile, (c) anatase from Degussa, and (d) titania from TAL Materials, Inc. (Mandzy, N., *et al.*, 2005).

2.3 Dye sensitizer

Dye sensitizers used in photovoltaic solar cells can be divided into two types, (1) inorganic dyes and (2) organic dyes. Inorganic dye includes metal complex, such as polypyridyl complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots (Kong et al., 2007). The three dyes shown in Figure 2.8 can be considered as the backbone of currently applied sensitizers with efficiency >10 %.

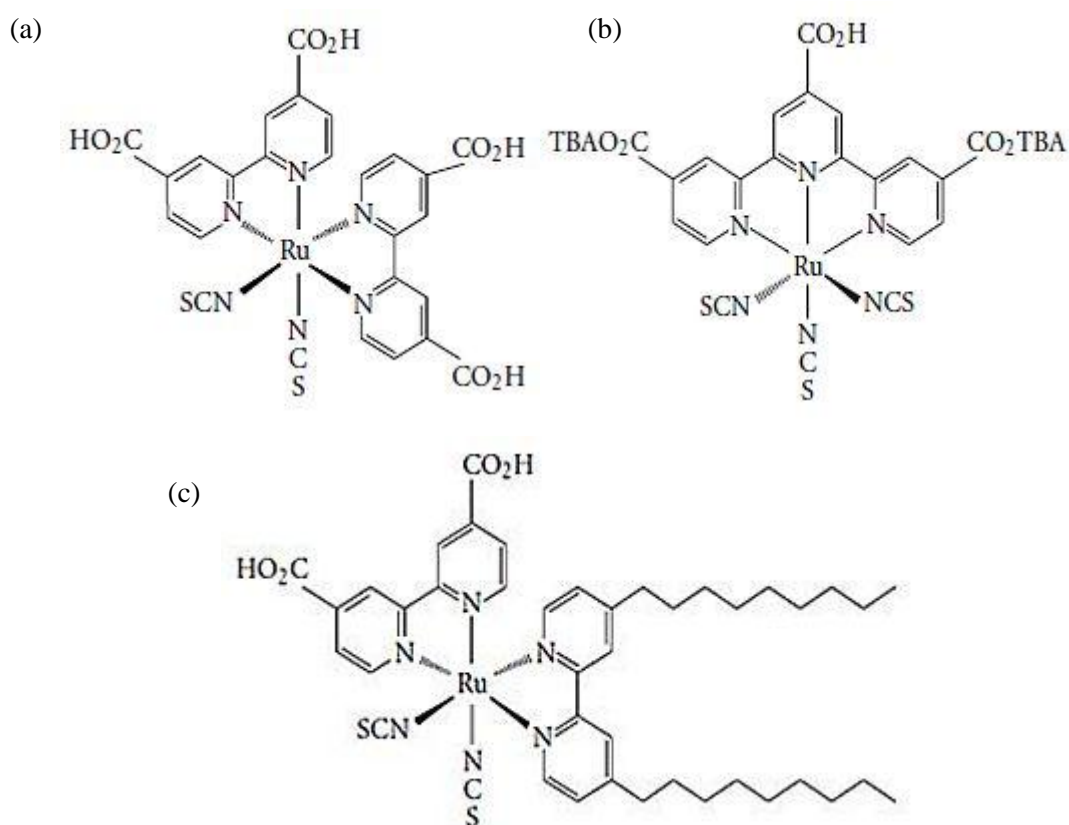


Figure 2.8: Molecular structures of three most frequently applied ruthenium polypyridyl complexes for DSSCs; (a) N-3, "red dye", (b) N-749, "black dye", and (c) Z-907 (Lenzmann, F. O. & Kroon, J. M., 2007).

Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are used as effective sensitizers due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer (MLCT) (Hao, S., 2006). However, the synthesis process of this complex is very complicated, expensive and contains heavy metals which make it unpopular from environmental value.

The use of natural stuff as sensitizing dye for the energy conversion solar cell is very interesting due to significant benefits from economical aspect as it inexpensive because they do not contain noble metals like Ru, Pt, and Os. In addition, the natural dye can be easily extracted from fruits (Tanihaha, S. L., Uranus, H. P, & Darma, J., 2010; Calogero, G., & Di Marco, G., 2008), vegetables (Chang, H. *et al.*, 2010; Chin, G. K., & Bee, J. S., 2011; Ortiz, N. M. G. *et al.*, 2010) and flowers (Khwanchit, W., Vissanu, M., & Sumaeth, C., 2007) which mostly contains chlorophyll and anthocyanins (glycosylated polyhydroxy derivatives of 2-phenylbenzo pyrylium salts) as solar cell dye sensitizer.

Moreover, a wide variety of structures can be obtained thus provides possibilities for molecular design and thus allow for easy control of their absorption spectra as refer to Figure 2.9. With the general structure of Donor (D)- π conjugation bridge- acceptor (A), this organic dyes have high molar absorption coefficients ($30\ 000$ - $100\ 000\ \text{M}^{-1}\ \text{cm}^{-1}$) relative to those of Ru-complex sensitizers, owing to intramolecular π - π^* transitions. Hence, enhance the photovoltaic performance of DSSC based on organic dye sensitizers (Luque, A., & Hegedus, S., 2003; Rani, S., Shishodia, P. K., & Mehra, R. M., 2010).

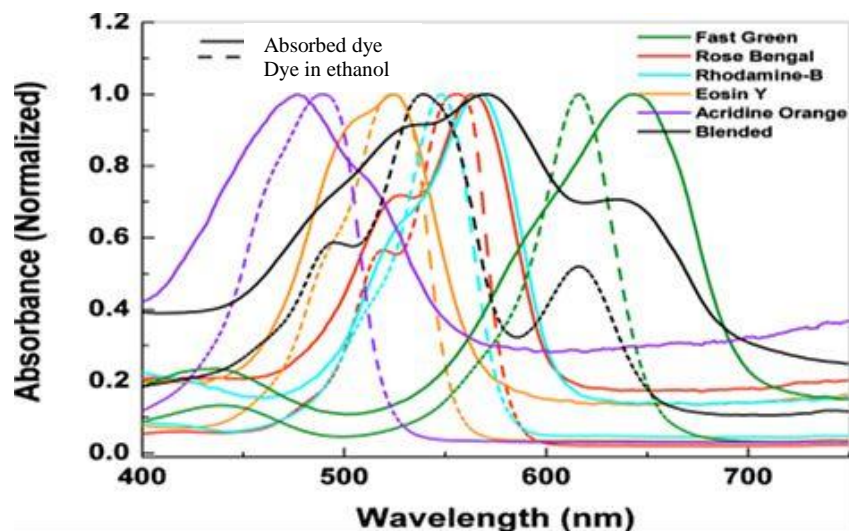


Figure 2.9: Normalized absorbance vs wavelength spectra of six dyes Rose Bengal (1 X C), Eosin- Y (1 X C), Rhodamine- B (1 X C), Acridine Orange (1 X C), Fast Green (1 X C), and blended dye (1 X C: 2 X C: 3 X C: 2 X C: 1 X C) in ethanol solution and adsorbed on ZnO electrodes (Rani, S., Shishodia, P. K., & Mehra, R. M., 2010).

2.3.1 Anthocyanin

The anthocyanin derivatives as shown in Figure 2.10, most prominent among the flavonoids (a large class of phenolic compounds) which commonly refer to natural dyes are responsible for the color in the red-blue range of the fruits, flowers and leaves of plants. Therefore, from aforementioned, it is significantly shows that anthocyanin from various plants gave different sensitizing performances.

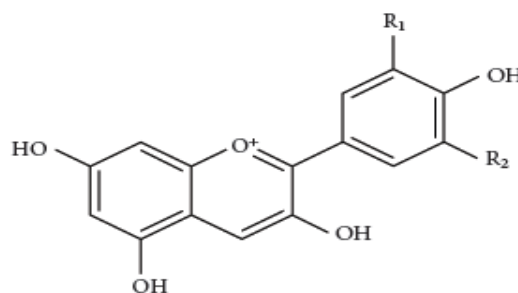


Figure 2.10: Structural formula of anthocyanidins. Cyanin, R1 = OH, R2 = H; delphinidin, R1 = R2 = OH; peonidin, R1 = OCH3, R2 = H; petunidin, R1 = OCH3, R2 = OH; malvidin, R1 = R2 = OCH3 (Konczak, I., & Zhang, W., 2004).

As far as noted, there is no evidence of study that has been conducted on the anthocyanin pigment in *Senduduk*'s fruit for dye sensitizer of photovoltaic solar cell application. The closest been reported is for anthocyanins's stability in petals at different stages of *Senduduk*'s flower development by Janna, O. A. et. al. (2005).She noted that the highest anthocyanins been found in S3 stage that is when the petals are fully formed but the flower is not yet opened for the production of new food coloring material. Years later, Koay, S. S. (2008) suggested induction and establishment of callus culture from *Senduduk*'s leaves for the production of anthocyanin.

However in 2009, Vankar, P. S., & Tiwari, V. developed a method for natural dyeing of cotton fabric using *Senduduk*'s fruit in conjunction with metal mordant under sonication. This has shown marked enhancement for cotton dyed fabric (as refer to Figure 2.11) since it reducing specific water and contribute to energy consumption. As aforementioned, anthocyanin in *Senduduk* not only serves as food and fabric dyed, it is also being studied in biomedical science (Susanti, D. *et al.*, 2008).



Figure 2.11: Cotton fabrics dyed with *Senduduk* (Vankar, P. S., & Tiwari, V, 2009)

2.4 Electrolyte

Between the two glass substrates, a typical electrolyte is encapsulated whereby functionalize as to reduce the dye cation and following electron injection hence completing the cycle of electron in DSSC. Roughly, an electrolyte can be divided into

three types; liquid electrolyte, quasi-solid state electrolyte (Wu, J. et al., 2008) and solid-state electrolyte. For liquid electrolyte, it also can be split into two; organic solvent electrolyte (acetonitrile, ethylene carbonate, and etc.,) and ionic liquid electrolyte.

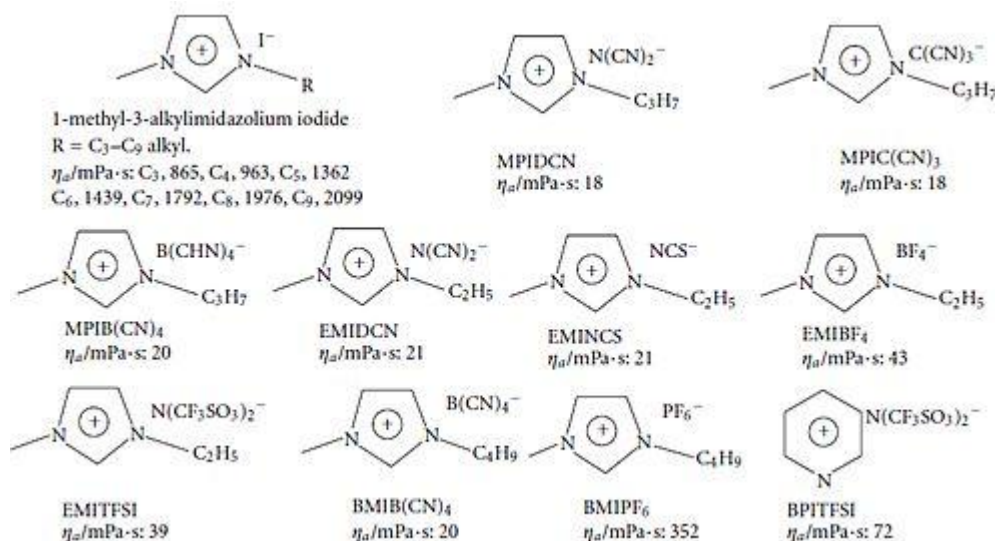


Figure 2.12: Structure and the viscosity of several ionic liquids (Kong, F. T. *et al.*, 2007).

In complex system of DSSC, one of crucial part for electron transport is the rate of the electron injection from the electrolyte to the oxidized dye sensitizer. Yip, C. T. (2010) in his thesis state that the faster the rate of reaction, the less recombination of electrons, and thus, the more chance for the electrons to leave the ‘sponge like’ TiO₂ thin film and contribute to photocurrent. When unmatched redox couple, I/I_3^- is used, counter electrolyte, nitrogen- containing heterocyclic such as 4-*ter*-butylpyridine (TBP) are needed. Different counter electrolyte or additive gives different optimization of the photovoltaic performance. However, only small amount of additive is required or it will jeopardize the system performance (Wu, J. *et al.*, 2008).

2.5 Counter electrode

The function of the counter electrode is to transfer electrons from the external circuit back to the redox electrolyte. The plain Indium Tin Oxide (ITO) layer does this rather poorly. Therefore, platinum (Pt.) mostly being used as counter electrode. As Ru complexes, Pt. would be replaced by other alternative catalyst as it is expensive for mass production. Furthermore, Pt. was found to diminish on exposure to dye solution and dissolve in the electrolyte by oxidation and complex formation with I/I_3^- . Therefore, a low cost alternative, porous carbon from graphite powder was proposed (Kay, A., & Gratzel, M., 1996). Figure 2.13 below shows the I-V curves with various mixtures of Carbon black and graphite for counter electrode. Yang, S.C.*et al.*, (2007) reported that as the ratio of Carbon black in counter electrode increased, the short-circuit current and the open-circuit voltage get improved. This is due to the larger area/volume ratio and better adhesion of carbon black than the graphite.

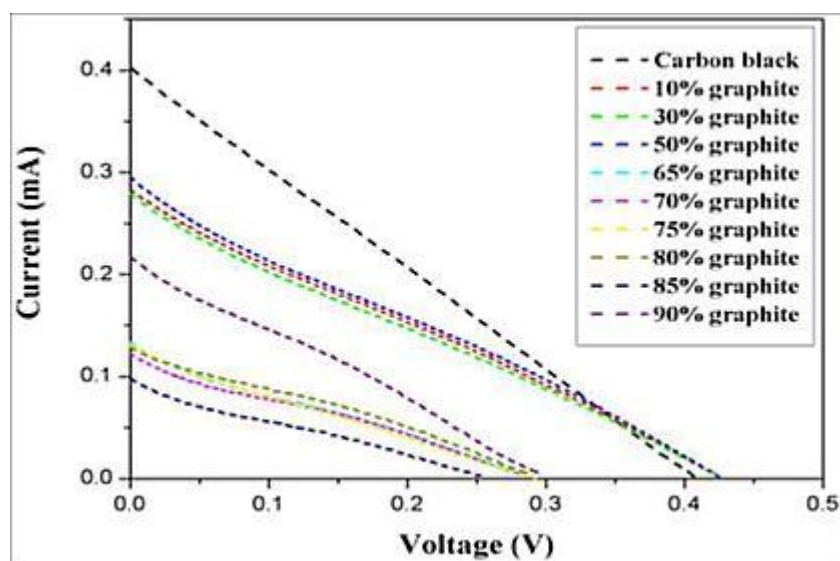


Figure 2.13: I-V curve of counter electrode with various mixing carbon ratios(Yang, S.C. *et al.*, 2007).

2.6 Dye Sensitized Solar Cell

Dye sensitized solar cell (DSSC) is a tunneling point in solar cell revolutionary where taking the nature working mechanism into account. This photovoltaic cell resembling the photosynthesis in plant in two respects: (1) it uses an organic dye like chlorophyll or anthocyanin to absorb light and produce a flow of electrons, and (2) it uses multiple layers to enhance both the light absorption and electron transportation. Therefore, due to this similarity, a truly sustainable energy source according to Ali, S. (2007) can be achieved. In 1991, O'Regan and Gratzel reported 7% efficiency of DSSCs by expanding the surface area by utilizing nanosized TiO_2 and by employing new Ru-complex sensitizers capable of absorbing in the wide visible and near-IR region from 400 to 800 nm. Since then, by optimizing the structure of nanoporous electrode, that of Ru-complex dyes, and composition of electrolytes, the efficiency has been improved to more than 11 %.(Luque, A., & Hegedus, S., 2003; Gratzel, M., 2005)

2.6.1 Basic operating theory

A schematic presentation of the operating principles of DSSC is given in Figure 2.14. The conversion of light into electric starts when the light (photon) hits the surface of electrode and absorbed by the dye molecules which is attached to the high surface area, a sponge like oxide thin film. As a results, the dye is been oxidized (D^*) and photoexcitation occurs. Photoexcitation is the state where the electron from the valence band injected to the conduction band of the oxide, leaving a hole (D^+) behind. Excited state conduction band electrons and valence band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the

surrounding electrical double layer of the charged particles (Hoffmann, M. R. *et al.*, 1995).

Next, the excited electron are transported by diffusion along the oxide thin film network toward the external conducting glass and consequently reach the platinum counter electrode through the external load (Kee, E. L. *et al.*, 2009). At the time being, the oxidized dye (D^+) back to its normal state (D) as it received electron from the electrolyte which is usually containing a redox system an iodide/ triiodide couple. In turn, the electrolyte is regenerated via the electron from the external load.

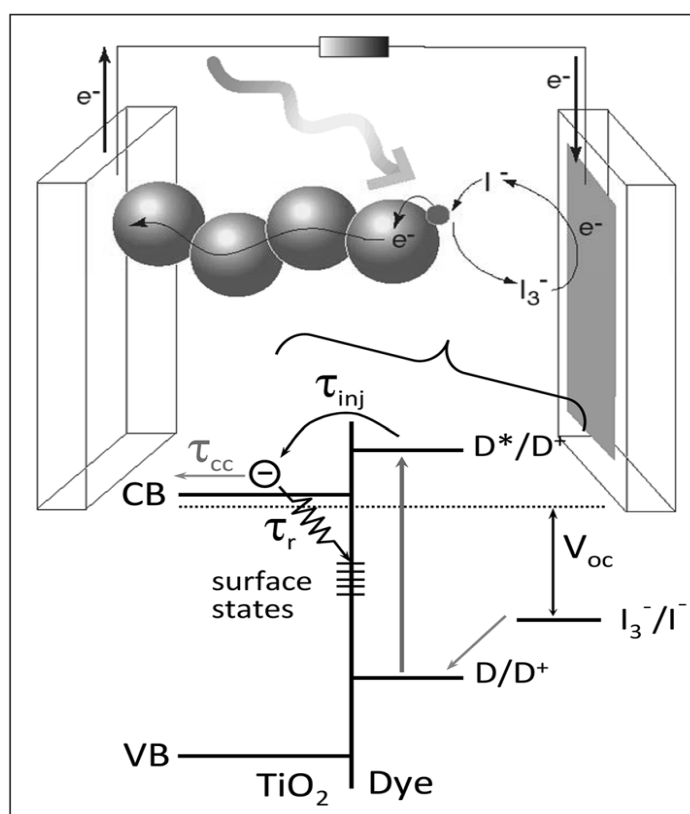
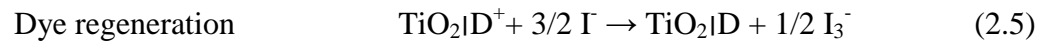
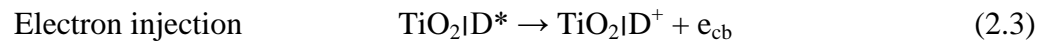
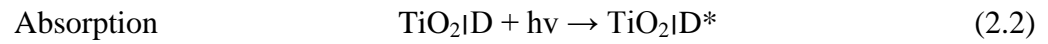


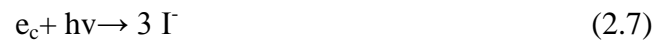
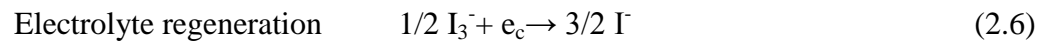
Figure 2.14: (Top) DSSC structure consisting of nanoparticulate TiO_2 film, dye, redox electrolyte and Pt counter electrode. (Bottom) Energetics of DSSC and working principle showing electron excitation, electron injection, charge transport and dye regeneration (Park, N. G., 2010).

The operating cycle due to schematic diagram above can be simplified as follows:

Anode:



Cathode:



CHAPTER 3

METHODOLOGY

3.1 Introduction

A single cell of natural dye sensitized photovoltaic metal oxide was fabricated by using a doctor blading technique including the preparation of engineering grade >99 % metal oxide with and without via sonochemical ultrasonic process treatment. Meanwhile, the natural dye, Melastoma Malabathricum's fruit was collected somewhere around Parit Raja area (at the roadside, bushes and etc.). The materials, apparatus and equipment being used in this experiment are listed in Table 3.1 and Figure 3.1 respectively in this section. As to ensure the quality and safety while carrying out this experiment, some safety rules should be taken and herein, flowcharts in Figure 3.1 as guideline of the research.

References

- Ahmad, M. K., Halid, M. L. M., Rasheid, N. A., Ahmed, A. Z., Abdullah, S., & Rusop, M., Effect of Annealing Temperatures on Surface Morphology and Electrical Properties of Titanium Dioxide Thin Films Prepared by Sol Gel Method, *Journal of Sustainable Energy & Environment* 1 (2010) 17-20.
- Ali, S., Biomimicry in Solar Energy Conversion with Natural Dye-Sensitized Nanocrystalline Photovoltaic Cells, Oberlin College, Ohio(Spring 2007): Master Thesis.
- Attaf, B. (Ed.), Advances in Composite Materials for Medicine and Nanotechnology, InTech, (April 2011), ISBN: 978-953-307-235-7.
- Calogero, G., & Marco, G. D., Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells, *Solar Energy Mater. & Solar Cells* (2008), 92, 1341-1346.
- Chang, H., Wu, H. M., Chen, T. L., Huang, K. D., Jwo, C. S., & Lo, Y. J., Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea, *J. Alloys and Com.* 495 (2010), 606-610.
- Chang, W. O., Gun, D. L., Seong, S. P., Chang, S. J., & Seong, S. H., Synthesis of Nanostructured TiO₂ Particles via Ultrasonic Irradiation and Their Photocatalytic Activity, *React. Kinet. Catal. Lett.* Vol. 85, No. 2, (2004) pg. 261-268.
- Charles, C. S., Sunao, S., & Janusz, N., (Eds), Materials for energy conversion devices, CRC Press; 1st Edition Nov. 2005.
- Chin, G. K., & Bee, J. S., Seaweed Chlorophyll on the Light-electron Efficiency of DSSC, *J. Chin. Chem. Soc.*, (2011), Vol. 58, No. 2.

Davidson, M. W., Diode Lasers, The Florida State University, (2006), Retrieved from: <http://micro.magnet.fsu.edu/primer/java/lasers/diodelasers/index.html>

Diebold, U., The surface science of titanium dioxide, *Surface Science Reports* 48,(2002), 53 – 229.

Farrell, K. A., Synthesis Effects on Grain Size and Phase Content in the anatase-rutile TiO₂ system, Worcester Polytechnic Institute (2001): Master Thesis.

Gimenez, S., Sero I. M., Macor, L., Guijarro, N., Villarreal, T. L., Gomez, R., Diguna, L. J., Shen, Q., Toyoda, T., & Bisquert, J., Improving the performance of colloidal quantum-dot-sensitized solar cells, *Nanotechnology* 20 (2009) 295204 (6pp).

Giusti, M. M., & Wrolstad, R. E., *Current Protocols in Food Analytical Chemistry* F1.2.1-F1.2.13, Copyright © 2001 by John Wiley & Sons, Inc

Gordillo, G., & Hailey, X., Nanopowder production: A Comparison of Several Methods, NSF-REU Summer 2004: Project Report.

Gratzel, M., Solar Energy Conversion by Dye Sensitized Photovoltaic Cells, *Inorg. Chem.* 2005, 44, 6841-6851.

Han, L., Obata, T., & Inoue, Y., Photoelectric Material Using Organic Photosensitising Dyes and Manufacturing Method Thereof, (2000), U.S. Patent 6, 043, 428.

Halme, J., Dye-sensitized nanostructured and organic photovoltaic cells: technical review and preliminary tests, Helsinki University of Technology (2002): Master Thesis

Hao, S., Wu, J., Huang, Y., & Lin, J., Natural dyes as photosensitizers for dye-sensitized solar cell, *Sol. Ener.* 80 (2006), 209-214.

- Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W., Environmental Applications of Semiconductor Photocatalysis, *Chem. Rev.* (1995), 69-96.
- Janna, O. A., Khairul, A., Maziah, M., & Mohd, Y., Flower pigment analysis of *Melastoma Malabathricum*, *Afr. J. Biotechnol.*, Vol. 5 (2), (2006), pp.170-174.
- Jin, H. B., & Suslick, K. S., Applications of Ultrasonic to The Synthesis of Nanostructured Materials, *Adv. Mater.* (2010), 22, 1039-1059, doi: 10.1002/adma.200904093.
- Kay, A., & Gratzel, M., Low Cost Photovoltaic Modules Based on Dye Sensitized Nanocrystalline Titanium Dioxide and Carbon Powder, *Sol. Energy Mater. Sol. Cells* 44, (1996), 99-117.
- Kee, E. L., Charbonneau, C., Shan, G., P. Demopoulos, G., & Gauvin, R., Nanocrystalline TiO₂ Thin Film Electrodes for DSSC Applications, Materials in clean power systems – Research Summary, (2009)
- Khwanchit, W., Vissanu, M., & Sumaeth, C., Dye-Sensitized Solar Cell Using Natural Dye Extracted from Rosella and Blue Pea Flowers, *J. Sol. Mat.* (2007), 11, 005
- Koay, S. S., Establishment of cell suspension culture of *Melastoma Malabathricum* L. for the production of anthocyanin, Universiti Sains Malaysia (2008): PhD thesis.
- Konczak, I., & Zhang, W. (Eds), Anthocyanin- more than nature's colour, *Journal of Biomedicine and Biotechnology*, 5 (2004) 241-247.
- Kong, F. T., Dai, S. Y., & Wang, K. J., Review of Recent Progress in Dye-Sensitized Solar Cells, *Advances in OptoElectron.* Vol. (2007), Article ID 75384, doi:10.1155/2007/75384

Lenzmann, F. O. & Kroon, J. M., *Advances in Optoelectronics*, Hindawi Publishing Corporation, doi: 10.1155/2007/65073.

Lund, H., Nilsen, R., Salomatova, O., Skare, D., & Riisem, E., *Solar Cells*, (2008),
retrieved from <http://org.ntnu.no/solarcells/pages/generations.php>

Luque, A., & Hegedus, S., *Handbook of Photovoltaic Science and Engineering*,
Wiley, P674 (2003). from:
http://books.google.com.my/books?id=sLMkCsde1u4C&pg=PT691&dq=DSSC&hl=en&ei=1_YTuOuPMaHrAfIkJTPDQ&sa=X&oi=book_result&ct=result&resnum=1&ved=0CC4Q6AEwAA#v=snippet&q=DSSC&f=true

Mandzy, N., Grulke, E., & Druffel, T., Breakage of TiO₂ agglomerates in electrostatically stabilized aqueous dispersions, *Powder Technology* 160 (2005) 121-126.

Murali, S., *Towards Low Temperature Sintering Methods for DSSC*, The State University of New Jersey (2011): Ph.D Thesis.

Ortiz, N. M. G., Maldonado, I. A. V., Espadas, A. R. P., Rejon, G. J. M., Barrios, J. A. A. Oskam, G., Dye-sensitized solar cells with natural dyes extracted from achiote seeds, *Sol. Ener. Mat. & Sol. Cells* 94 (2010), 40-44.

Park, N. G., Dye-Sensitized Metal Oxide Nanostructures and Their Photoelectrochemical Properties, *Journal of the Korean Electrochemical Society* Vol. 13, (2010), No. 1, 10-18.

Rani, S., Shishodia, P. K., & Mehra, R. M., Development of a dye with broadband absorbance in visible spectrum for an efficiency dye-sensitized solar cell, *J. Renewable Sustainable Energy* 2, (2010).043103

- Razykov, T. M., Ferekides, C. S., Morel, D., Stefanakos, E., Ullal, H. S., & Upadhyaya, H. M., Solar Photovoltaic Electricity: Current Status and Future Prospects, *Sol. Energy*, doi:10.1016/j.solener.2010.12.02
- Sastrawan, R., Photovoltaic modules of dye solar cells, Albert-Ludwigs University (2006, June): PhD Thesis.
- Sumandeep. K., Light Induced Oxidative Degradation Studies of Organic Dyes and Their Intermediates, Thapar University (2007): PhD Thesis
- Sundström, V. (Ed.), Solar Energy Conversion, *Dalton Trans.*, (2009), issue 45.
- Susanti, D., Sirat, M. H., Ahmad, F., & Ali, M. R., Bioactive Constituents from The Leaves of *Melastoma Malabathricum* L., *Jurnal Ilmiah Farmasi*, Vol.5 No.1 Tahun 2008.
- Takechi, K., Muszynski, R., & Kamat, P. V., Fabrication Procedure of Dye-Sensitized Solar Cells, Retrieved on Feb (2009), from http://world_wide_web.nd.edu/~pkamat/pdf/solarcell.pdf
- Tanihaha, S. L., Uranus, H. P., & Darma, J., Fabrication and Characterization of Dye-sensitized Solar Cell using Blackberry Dye and Titanium Dioxide Nanocrystals, 2010 *Second International Conference on Advances in Computing, Control, and Telecommunication Technologies*.
- Tholvanen, A., Characterization and manufacturing technique of dye-sensitized solar cell. Helsinki University of Technology (2003, Dec): Master Thesis.
- Vankar, P. S., Tiwari, V., Singh, L. W., Potsangbam, L., "Sonicator dyeing of cotton fabric and chemical characterization of the colorant from *Melastoma malabathricum*", *Pigment & Resin Technology*, Vol.38 Iss: 1, (2009), pp.38-42
- Wolf, E. L., Quantum Nanoelectronics, 2nd Edition, Copyright © 2009 WILEY-

VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN: 978-3-527-40749-1.

- Wongcharee, K., Meeyoo, V., & Chavadej, S., Dye-sensitized Solar Cell using Natural Dyes Extracted from Rosella and Blue Pea Flowers, *Sol. Energy Mater. Sol. Cells*, (2007), 91, 566-571
- Wu, J., Lan, Z., Hao, S., Li, P., Lin, J., Huang, M., Fang, L., & Huang, Y., Progress on the electrolytes for dye-sensitized solar cells, *Pure Appl. Chem.*, Vol. 80, No. 11, pp. 2241-2258, (2008), Doi: 10.1351/pac200880112241 © 2008 IUPAC.
- Yamamoto, Y., Aoyama, Y., Shimizu, S., Kano, J., Saito, F., & Ito, S., Influence of Titania Dispersivity on the Conversion Efficiency of Dye-Sensitized Solar Cells, *International Journal of Photoenergy*, Vol. (2011), doi:10.1155/2011/234931.
- Yang, S. C., Jing, N. L., Sheng, Y. T., Chen, C. T., Manufacture of Dye-Sensitized Nano Solar Cells and their I-V Curve Measurements, *Proceedings of ICAM2007*, Nov. 26-28, (2007), Tainan, Taiwan.
- Yip, C. T., Effect of morphologies and electronic properties of metal oxide nanostructure layer on dye sensitized solar cells, The University of Hong Kong (2010): PhD. Thesis
- Zhou, H., Wu, L., Miao, Q., Xin G., & Ma, T., DSSC using Natural Dyes as Sensitizers, 978-1-4244-3544-9/10\$25.00 ©2010 IEEE.