AN INTERDISCIPLINARY LEARNING UNIT FOR FIRST YEAR UNDERGRADUATE STUDENTS: DYE-SENSITIZED SOLAR CELL FROM SUNLIGHT TO ELECTRICITY

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
(SCIENCE AND TECHNOLOGY EDUCATION)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2010

Thesis
entitled

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was submitted to the Faculty of Graduate Studies, Mahidol University
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ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my major advisor, Asst. Prof. Dr. Darapond Triampo, for her valuable guidance, advice, support, encouragement, and numerous opportunities that she has provided over the years throughout this research study. I also would like to thank my co-advisors, Assoc. Prof. Dr. Bhinyo Panijpan and Assoc. Prof. Dr. Wannapong Triampo, for their useful suggestions and generous supports. My special thanks go to Prof. Dr. Guozhong Cao, my wonderful mentor during my time at the Department of Materials Science & Engineering, University of Washington, USA, for his warm support, useful guidance, and encouragement. Without the brilliant supervisions from my advisors, this dissertation could not be done.

My sincere appreciation is extended to Dr. Pintip Ruengwongsa for her helpful supports and suggestions and Dr. Pisarn Soydhurum for his helpful comments and valuable time spent for serving as my chairman of the dissertation committee.

I am extremely thankful to the Institute for the Promotion of Teaching Science and Technology (IPST) for providing me a great opportunity to my doctoral study and a financial support for my study since high school.

I wish to express my deepest thank to my parents and my families for their love, care and support, and for helping me to focus on my education. Finally, I dedicate this dissertation to all meaningful people who have touched my life, particularly my parents, my families, and all of my teachers and friends.

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ABSTRACT

The research study consisted of two main research areas: scientific part and educational part. The scientific part investigated the power conversion efficiency (PCE) of hybrid nanostructured ZnO dye-sensitized solar cell (DSSC) and templated TiO_2 nanotubes hybrid solar cell. The results showed an enhancement of the PCE, which resulted from a high surface area and a direct pathway for fast electron transport of the one-dimensional nanostructures photoanode.

Some of the findings from the scientific part were used to develop an inquiry learning unit for the educational part that could help students understand the concept of energy transformation from sunlight to electrical energy and also concepts that were related to solar cells. The interdisciplinary learning unit was developed for first year undergraduate students using an inquiry learning approach. The content used in this learning unit included the concepts of electricity, light, semiconductor, energy bandgap, and solar cell. Students worked in a group throughout a set of inquiry learning activities that used questions to guide the students. The findings of this study indicated the enhancement of students' conceptual understanding and students' positive attitude toward the learning unit. This developed learning unit can be used as a guideline for developing an interdisciplinary learning unit to motivate students to learn more about science in the future.

KEY WORDS: DYE-SENSITIZED SOLAR CELL / HYBRID SOLAR CELL / POLYMER SOLAR CELL / INTERDISCIPLINARY LEARNING UNIT

87 pages

หน่วยการเรียนแบบบูรณาการ “เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง” สำหรับนักศึกษาระดับปริญญาตรีชั้นปีที่ 1

AN INTERDISCIPLINARY LEARNING UNIT FOR FIRST YEAR UNDERGRADUATE STUDENTS: DYE-SENSITIZED SOLAR CELL FROM SUNLIGHT TO ELECTRICITY

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บทคัดย่อ

การศึกษาวิจัยนี้แบ่งการศึกษาออกเป็นสองส่วน คือส่วนที่เป็นการวิจัยทางด้านวิทยาศาสตร์และด้านวิทยาศาสตร์ศึกษา โดยงานด้านวิทยาศาสตร์เป็นการศึกษาเพื่อพัฒนาประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง และเซลล์แสงอาทิตย์ชนิดไฮบริด โดยการประยุกต์ใช้เส้นใยนาโน ZnO และท่อนาโน TiO_2 เป็นขั้วไฟฟ้า ผลจากการศึกษาพบว่าประสิทธิภาพของเซลล์แสงอาทิตย์ทั้งสองชนิดเพิ่มขึ้น ซึ่งเป็นผลมาจากการมีพื้นที่ผิวที่มากพอ และมีการนำอิเล็กตรอนได้รวดเร็วของขั้วไฟฟ้าที่ทำจากเส้นใยนาโน ZnO และ ท่อนาโน TiO_2

ความรู้ที่ได้จากการศึกษาวิจัยในทางวิทยาศาสตร์บางส่วนถูกนำมาจัดทำเป็นหน่วยการเรียนการสอนแบบบูรณาการ เพื่อช่วยให้นักศึกษาระดับปริญญาตรีชั้นปีที่ 1 มีความรู้ความเข้าใจเกี่ยวกับหลักการในการเปลี่ยนพลังงานแสงอาทิตย์ให้เป็นพลังงานไฟฟ้า โดยหน่วยการเรียนการสอนแบบบูรณาการเรื่องเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง จะใช้วิธีการสอนแบบสืบเสาะหาความรู้ เนื้อหาที่เกี่ยวข้องในหน่วยการเรียนนี้ประกอบด้วยเรื่องกระแสไฟฟ้า แสง สารกึ่งตัวนำ แถบพลังงาน และหลักการทำงานของเซลล์แสงอาทิตย์ นักเรียนที่เข้าร่วมกิจกรรมจะทำงานเป็นกลุ่ม และเรียนรู้ด้วยกระบวนการสืบเสาะหาความรู้ผ่านกิจกรรมการเรียนรู้ต่างๆ โดยมีคำถามเป็นสิ่งชี้นำในการเรียน ผลจากการศึกษาผลพบว่านักเรียนมีความรู้เกี่ยวกับเรื่องเซลล์แสงอาทิตย์มากขึ้นและมีทัศนคติที่ดีต่อวิธีการสอนและหน่วยการเรียนที่สร้างขึ้น หน่วยการเรียนที่สร้างขึ้นสามารถที่จะใช้เป็นตัวอย่างในการสร้างหน่วยการเรียนการสอนแบบบูรณาการสำหรับการเรียนการสอนวิทยาศาสตร์ในอนาคต เพื่อเป็นการช่วยกระตุ้นให้นักเรียนมีความสนใจและอยากเรียนรู้วิทยาศาสตร์มากขึ้นได้

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LIST OF ABBREVIATIONS

AM	air mass
a.u.	arbitary unit
CB	conduction band
cm	centimeter
cm^2	square centimetre
DEG	diethylene glycol
DI	deionized water
DSSC	dye-sensitized solar cell
EDX	energy dispersive X-ray analysis
et at.	*et. alli* (Latin), and others
eV	electron volt
e^-	electron
e.g.	for example
FF	fill factor
FTO	fluorine doped tin oxide
g	gram
h	hour
HOMO	highest occupied molecular orbital
h^+	hole
I	current
IPST	The Institute for the Promotion of Teaching Science and Technology
ITO	indium tin oxide
I^-	iodide ion
I_3^-	triiodide ion
i.e.	*ed est* (Latin), that is

LIST OF ABBREVIATIONS (cont.)

J_{sc}	short-circuit current density
KeV	kiloelectron volt
LUMO	lowest unoccupied molecular orbital
M	molar, mol/L
mg	milligram
min	minute
mL	milliliter
mM	millimolar
mW	milliwatt
nm	nanometer
NP	nanoparticle
NR	nanorod
NRC	National Research Council
NREL	National Renewable Energy Laboratory
NT	nanotube
NW	nanowire
N3	cis-di(thiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)-ruthenium(II)
N719	cis-di(thiocyanato)-bis(2,2'-bipyridyl-4-carboxylate-4'-carboxylic acid)-ruthenium(II)
OPV	organic photovoltaic
Ox	oxidation
PCBM	Phenyl-C61-buryric acid methyl ester
PCE	power conversion efficiency
PV	photovoltaic
P3HT	Poly(3-hexylthiophene-2,5-diyl)
Red	reduction
SEM	scanning electron microscope

LIST OF ABBREVIATIONS (cont.)

TCO	transparent conducting electrode
TEM	transmission electron microscope
TiO_2	titanium dioxide
V	voltage
VB	valence band
V_{oc}	open-circuit photovoltage
XRD	X-ray diffraction
ZnO	zinc oxide
μm	micrometer
η	the power conversion efficiency
°C	degree celsius

CHAPTER I

INTRODUCTION

Overview

This chapter introduces the overall details of the research study which is separated into two parts: the scientific part and the educational part. Each part contains the background and rational of the research. The chapter ends with the outline of the organization of the thesis.

1.1 Background and Rationale of the Study

Part I: Scientific Aspect

With increasing energy-demands and environmental-concerns, more attention have been drawn to new energy systems based on renewable sources. Over the past years, significant emphasis have been put on the developing and understanding of solar light-driven charge separation in molecular systems as a method of converting solar energy to electricity. Dye-sensitized solar cells (DSSC) and organic photovoltaics (OPV), the third generation solar cell, have attracted lots of attention as they can be processed from solution and have become a promising low cost alternative to the traditional inorganic solar cell [1-8].

The key element in DSSC is the photoelectrode which consists of highly porous wide bandgap semiconductors, typically TiO_2 and ZnO network with dye molecules adsorbed onto the surface. Dye molecules capture incident photons and generate electron-hole pairs; electrons are readily injected into the conduction band of the semiconductors and transport to a charge collector. In order to achieve high power conversion efficiency, large amount of dye molecules should be adsorbed. Semicondoctor with high specific surface area is desired. The charge transfer from dye molecules to charge collector should be efficient so as to minimize or eliminate possible loss of charges through surface recombination. Based on the TiO_2

nanoparticle (NP) network, the DSSC has achieved Air Mass 1.5 (AM 1.5) solar efficiencies more than 11% [9, 10]. However, the further enhancement in power conversion efficiency (PCE) is difficult, partly due to the charge recombination process which reduces the electron transport rate through the nanocrystalline photoanodes [11]. Efforts have been made to improve the charge transport in the photoelectrode by using one-dimensional nanostructure, including ZnO nanorod (NR) and nanowire (NW), and TiO_2 nanotube (NT) arrays [11-14]. However, the PCE of such DSSC remained low, for example, ZnO NW DSSC with the NW length of 33 μm was only 2.1 % [15]. A key point which limits the PCE of the ZnO NW DSSC is the insufficient surface area for dye adsorption [11].

In the case of polymer solar cells, the key efficiency is the bulk heterojunction, which is a blend of electron-donating semiconducting polymers and electron-withdrawing fullerides. This bulk heterojunction morphology enhances the interfacial area where the photogenerated excitons, electron-hole pairs, are dissociated into charge carriers and enables holes and electrons to be transported and collected. The PCE was increased. Up to 8.13% has been recently reported in the bulk heterojunction polymer solar cells [16]. However, polymer based solar cells still suffer from low efficiencies and limited lifetime as compared to silicon-based solar cell [17]. The limited efficiency of the bulk heterojunction polymer solar cell is due to the lower charge mobility in polymer [18], the charge trapping in the conducting pathways of fullerides and polymer to the electrodes [19], and the mismatch of the absorption spectrum of the active layer and the solar emission [20, 21].

To address the intrinsic limitations of the DSSCs and the polymer solar cells, new strategies have been investigated such as developing new dye molecules, new electrolyte systems, and new morphologies of the photoelectrode (nanorods, nanowires, nanotubes, and aggregates) for DSSC [3, 22-28], and developing new polymers with a low bandgap for better match absorption of the solar spectrum and a hybrid organic/inorganic solar cells (hybrid solar cells) for polymer solar cells [29-35]. The main objective of this part was to investigate the properties and efficiencies of DSSC and hybrid solar cell using the photoelectrode made of the one-dimensional nanostructure, nanowires and nanotubes.

Part II: Educational Aspect

Science education in developing countries is widely considered to be in crisis, not because students are failing in content, but because they are not interested in or engaged by science as it is currently being taught in schools [36]. In the case of Thailand, science instruction emphasized on lecture methods to ensure that all contents needed in preparing for university entrance examination were covered [37]. Students lacked opportunities to practice skills, both in scientific and thinking processes, which are essential for science learning [38]. Another problem is that students are usually evaluated based upon what they have memorized, rather than their scientific process skills [39]. Large scale study showed “when students move to high school, many experience disappointment, because the science they are taught is neither relevant nor engaging and does not connect with their interests and experiences” [40]. A potential solution to this problem of student engagement may be the provision of a more integrated curriculum with courses and lessons that help students to understand the connections between science and the real world.

An integrated curriculum provides opportunities to work on a few cross-disciplinary objectives, to apply knowledge across the subject boundaries and to work on tasks that is meaningful and relevant, by focusing the curriculum on a problem or topic rather than on a discrete discipline. By approaching a problem or topic from the vantage point of many disciplines, students are exposed to more information and more views, providing them with the raw material needed to construct understanding [41, 42]. Some literatures claim the positive educational outcomes for students who participate in integrated curricula increases the understanding and application of general concepts [43, 44], better able to transfer knowledge to different contexts, more motivated, and more likely to learn higher order thinking skills [45]. Moreover, the content of most integrated curricula is considered to be more closely related to students’ experiences in real life outside school classroom, and hence, enhance engagement [46].

Rreformation of science education worldwide are derived from the constructivist views of teaching and learning. These reforms explicitly ask teachers to change their teaching strategies by shifting the emphasis from the traditional textbook-based, rote learning, to exploration, inquiry-based learning situated in real-world phenomena[47]. Inquiry-based science instruction is one of the most effective teaching and learning strategies for the constructivist [48], which has gained increasing attention as a way to engage students learning and help them develop deep understandings.

The aim of this part is involved in the adaptation of the research finding from the scientific part to develop a guided-inquiry learning unit, Dye-Sensitized Solar Cell from Sunlight to Electricity (DSSC learning unit), to help student understand the concept of energy transformation in the form of sunlight to electrical energy.

1.2 Research Objectives

Scientific Aspect

1) To synthesize hybrid ZnO nanostructure as photoanode for an increase DSSC efficiency

2) To synthesize TiO2 NT using ZnO NR template for an increase hybrid solar cell efficiency

Educational Aspect

1) To develop an inquiry DSSC learning unit to promote students' understanding in the concept of energy transformation from solar energy to electrical energy

2) To investigate the effectiveness of the learning unit on students' understanding

1.3 Organization of the Thesis

The thesis is divided into two main parts: scientific part and educational part. The educational part is an adaptation of the knowledge from the scientific part to develop an inquiry DSSC learning unit: The thesis is organized in six chapters as follows:

Chapter One provides the background and objectives of research study.

Chapter Two presents the literature reviews related to the study both in scientific part and educational part.

Chapter Three presents the investigation of the properties and efficiencies of DSSC using the photoelectrode made of hybrid nanostructure of NW-NP ZnO. The ZnO NWs electrode served as a direct pathway for fast electron transport which reduces the electron recombination. The crystallite ZnO NPs dispersed between ZnO NWs offerd a high surface area for dye adsorption.

Chapter Four presents investigation the properties and efficiencies of hybrid solar cell based on TiO_2 NTs infiltrated with poly(3-hexylthiophene-2,5-diyl), P3HT, and phenyl-C61-buryric acid methyl ester, PCBM. The hybrid solar cells using TiO_2 NTs have the advantages of both the bulk heterojunction (a blend of P3HT/PCBM) and ordered architectures (TiO_2 NTs). The bulk heterojunction morphology provides the sufficient interfacial area for the separation of photogenerated excitons. The ordered architectures help to reduce electron recombination and function as a direct pathway for fast electron transport to the charge collecting electrode.

Chapter Five presents the study of the educational part of the thesis: developing a guided-inquiry DSSC learning unit and the investigation of the effectiveness of the learning unit on students' understanding in the concept of energy transformation from solar energy into electrical energy.

Chapter Six presents the overall finding of the research study.

CHAPTER II
LITERATURE REVIEW

Overviews

This chapter presents the literature review of scientific and educational aspects. The scientific aspect reviews on the development of the different generation of solar cell and the essential components. The educational aspect reviews on interdisciplinary learning, followed by inquiry-based teaching and learning, and ends with the assessment in science education.

2.1 Solar Cells

Solar cell or photovoltaic, PV, is a device that converts solar energy into electricity and can be broadly categorized into three generations.

2.1.1 First Generation

The 1st generation solar cells are made of large single crystal silicon solar cell [49], p-n junction silicon based solar cell. Most of the solar cells available in today's market fall into this category [50]. They dominate in market due to their high efficiency, 24.7 % [51]. However, their fabrication is expensive. This is because several steps such as purification, crystallization, implantation, diffusion, and more are involved. This prevents any significant progress in reducing the production costs and is a problem that second generation solar cells hope to remedy [17].

2.1.2 Second Generation

The 2nd generation solar cells, thin film technology [49], have been developed to address energy requirements and production costs of the 1st generation solar cells. The 2nd generation uses glass substrates with thin films of inexpensive semiconductors compound. However, the lower manufacturing cost is offset by the of presence structural deformities which reduce the efficiency. The commercial efficiency of the 2nd generation solar cells is approximately 11-15 % [52-56].

The working mechanism of the 1st and 2nd generation solar cells is base on the p- and n-type semiconductor as shown in Figure 2.2. After illumination of the solar cell by sunlight, electron-hole pairs are generated and separated by the built-in electric field across the p-n junction, the holes are swept into the p-layer and the electrons are swept into the n-layer. Although these opposite charges attract each other, most of them can only recombine by passing through an external circuit outside the material because the internal potential energy barrier. A schematic diagram of the solar cell base on p-n junction is shown in Figure 2.1

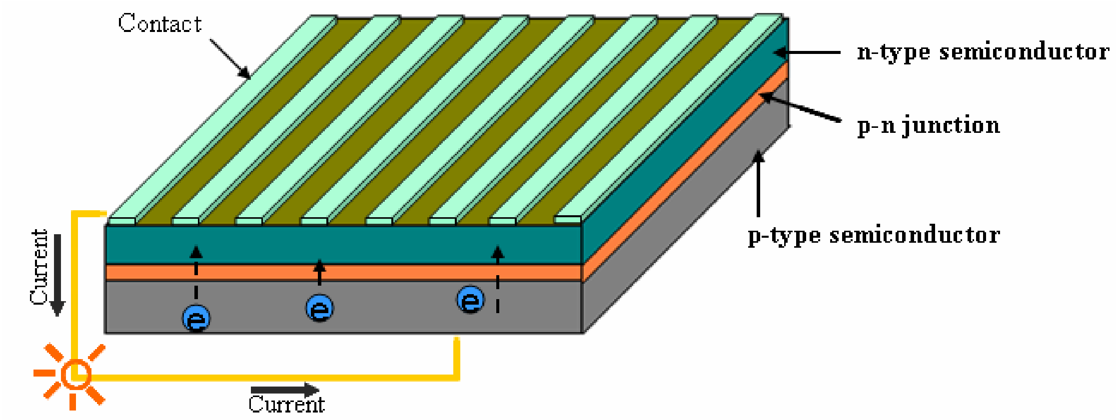


Figure 2.1 A scheme of a silicon based on p-n junction solar cell [57].

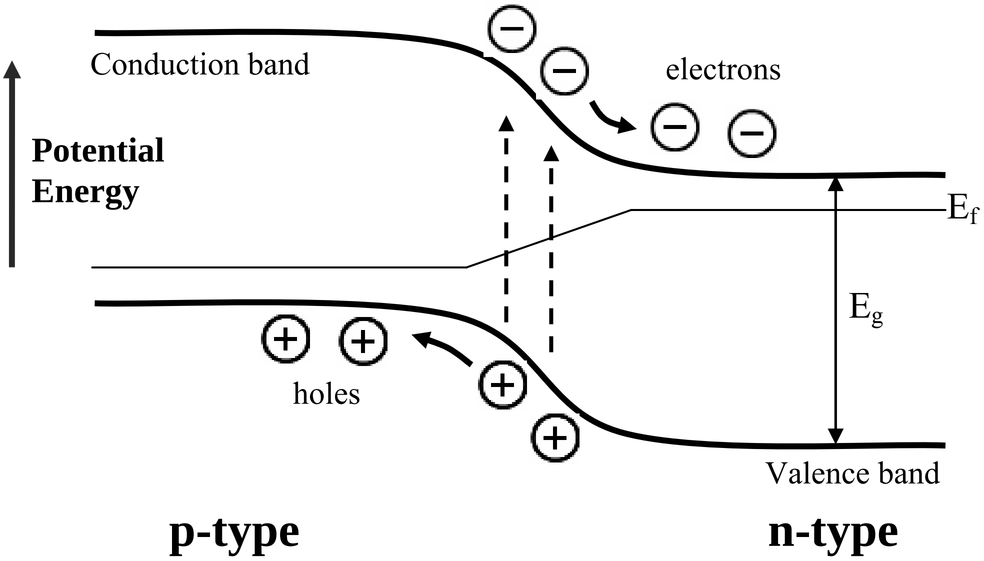


Figure 2.2 The energy band diagram of a p-n junction in solar cell [58].

2.1.3 Third Generation

The 3rd generation solar cells involve new materials and concepts, which many people believe will allow for substantially lower cost systems while maintaining reasonable efficiency. Systems under development now include: DSSC [59-62], organic polymer cells or polymer solar cells [5, 7, 8, 35, 63], hybrid solar cells [64-66], quantum dots solar cells [67-69], and tandem solar cells [70-72]. Figure 2.3 gives an overview of the performance of different PV systems over the last thirty years. Figure 2.4 shows where these three generations of PV cells stand against each other in terms of overall conversion efficiency and manufacturing costs.

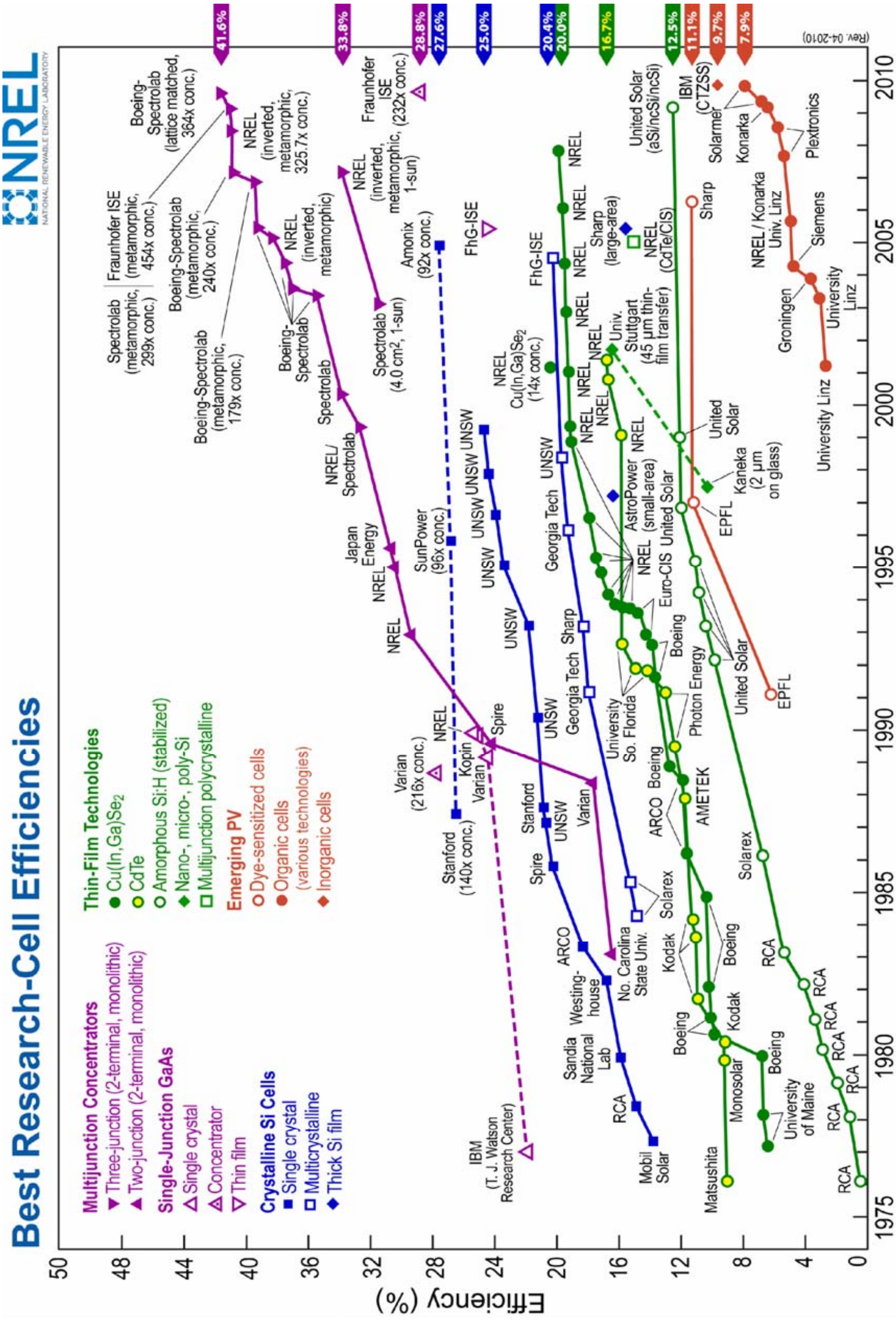


Figure 2.3 The state of different photovoltaic systems [74]

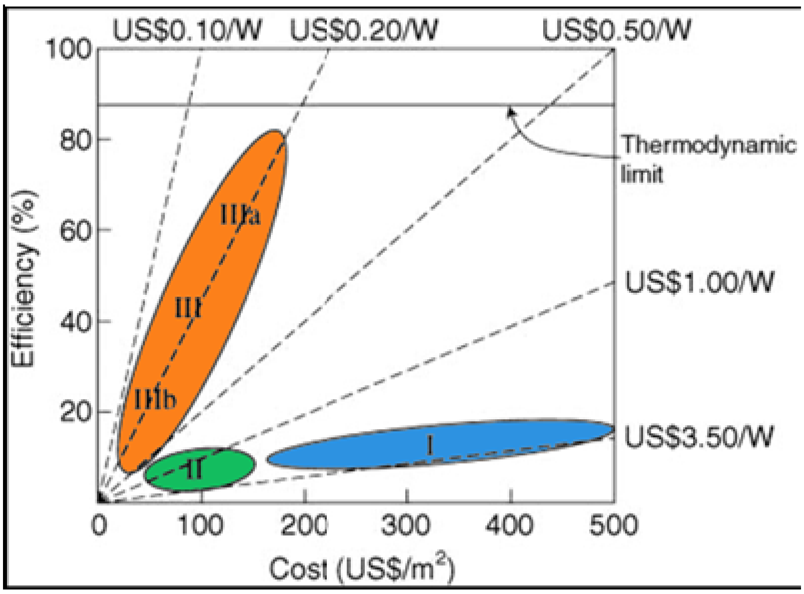


Figure 2.4 Trend in cost-performance relationship of all three generations of PV systems [75]

2.2 Dye-Sensitized Solar Cells

Among the newly developed photovoltaic technologies, the DSSC is the most promising alternative to the inorganic p-n junction based cell [1, 76]. The first DSSC was reported by Gratzel and O'Regan in 1991 [1] and had an efficiency of 7.1-7.9 % in simulated solar light. Since this initial report, DSSC efficiencies have reached ~11 % [77]. The heart of the DSSC is a high surface area TiO_2 nanoparticulate electrode, covered with a monolayer of dye molecules [1]. Upon photoexcitation of the dye, an electron is injected into the conduction band of the TiO_2 connected to a transparent conducting electrode. The reduced dye is regenerated by electron donation from the electrolyte, usually an organic solvent containing the iodide/triiodide couple. The electrolyte itself is regenerated at the counter electrode by reduction of the triiodide, the circuit being completed through and external load [78]. A schematic operation of a DSSC shows in Figures 2.5.

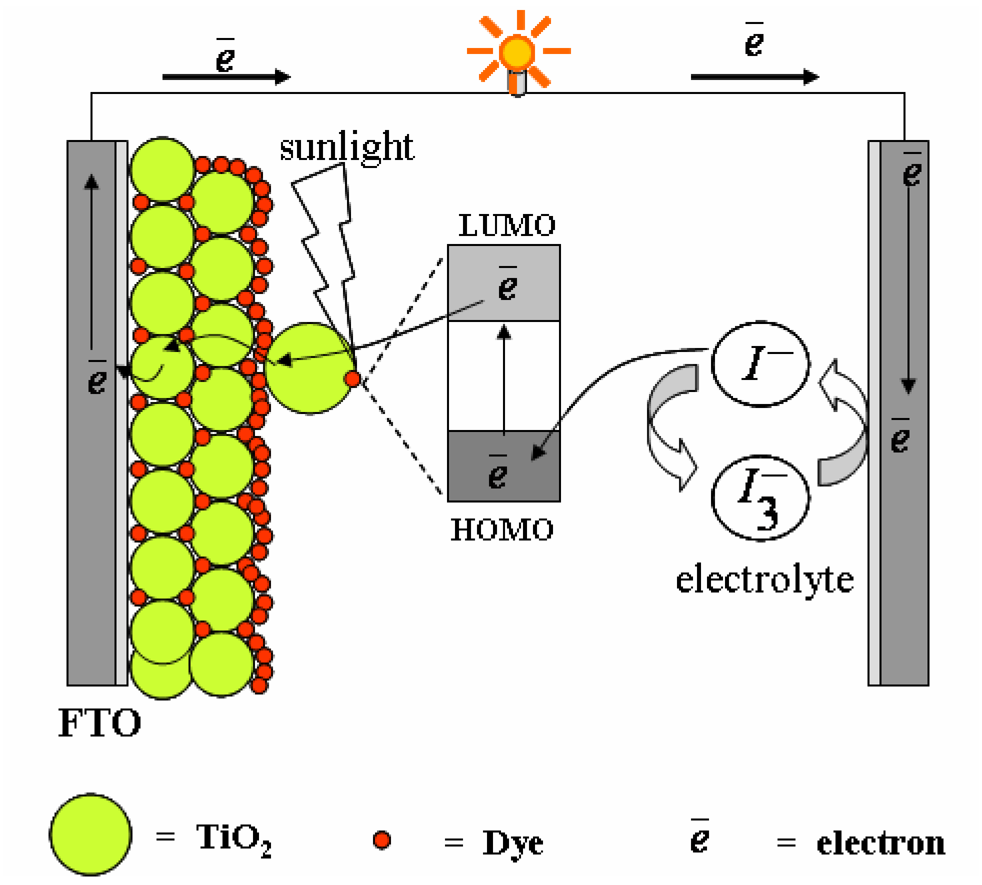


Figure 2.5 A Schematic operation diagram of a DSSC [78]

The overall solar conversion efficiency, PCE, is a product of the short-circuit current density, Jsc, the open-circuit photovoltage, Voc, and the fill factor, FF, according to [79]:

$$PCE = \frac{Jsc \ x \ Voc \ x \ FF}{P_{in}} \qquad (2.1)$$

Where P_{in} is the total solar power incident on the cell, 100 mW/cm^2 for AM 1.5

Composition of dye-sensitized solar cells

The major component of DSSC consists of 4 parts: (1) a nanocrystalline semiconductor, (2) a dye sensitizer, (3) an electrolyte, and (4) a transparent conducting electrode (TCO)

2.2.1. Nanocrystalline semiconductor

The DSSCs are based on the wide band gap nanocrystalline semiconductors [1]. The semiconductors act as the photoanode in the DSSC. One of the most promising semiconductors for DSSC is TiO_2 [80-82]. Titanium dioxide is a widely used semiconductor, due to its excellent chemical stability, optical transmittance in the visible region, and inexpensive material. The energy gap between the valence band (VB) and the conduction band (CB) of TiO_2 in the rutile phase is 3.26 eV [83, 84]. The large band gap facilitates the formation of a wide depletion layer since the semiconductor can be biased at more positive potential without causing carrier inversion. Thus the spatial separation of electrons from the oxidation dye on the surface can be enhanced. Other materials such as ZnO [3, 15, 27, 28, 62], SnO_2 [85-88], Nb_2O_5 [89-91] and CdS [92, 93] have also been researched as possible electrode materials. Although they do produce photocurrents, their efficiencies are not as high as titanium dioxide. The TiO_2 layer performs three major functions in the cell; (1) provides a surface for dye adsorption (2) accepts electrons from the excited dye, (3) conducts electrons to the TCO.

2.2.2 Dye sensitizer

The dye sensitizer is the layer which interacts with the sunlight, and therefore is a very important part of the DSSC. Upon interaction with the light, electrons from the dye molecules jump from the ground state to the excited state and get transferred onto the conduction band of TiO_2. For effective electron injection to take place, the energy levels of the sensitizer and the semiconductor should be well matched, such that the excited state of the sensitizer should lie just above the conduction band of the semiconductor. The ground state energy level should be just below that of the electrolyte and be of sufficient reduction potential to be easily reduced by the redox electrolyte [94, 95]. Figure 2.5 illustrates the ground (HOMO) and excited (LUMO) of dye sensitizer in the electron configuration diagram. The most commonly used photosensitizer is ruthenium based polypyridyl complexes. The most efficient solar cell to date prouduced is cis-Ru(2,2'-bipyridal-4,4'-dicarboxylate)$_2$(NCS)$_2$ (N3 dye) [96-98]. The chemical formula of N3 dye and N719 are shown in Figure 2.6. An important factor determining the effectiveness of a dye as a sensitizer is the spectral overlap between the absorbance of the dye and the solar radiation reaching the earth. Significant research has been done to engineer dyes that capture light throughout the visible and near infrared spectrum.

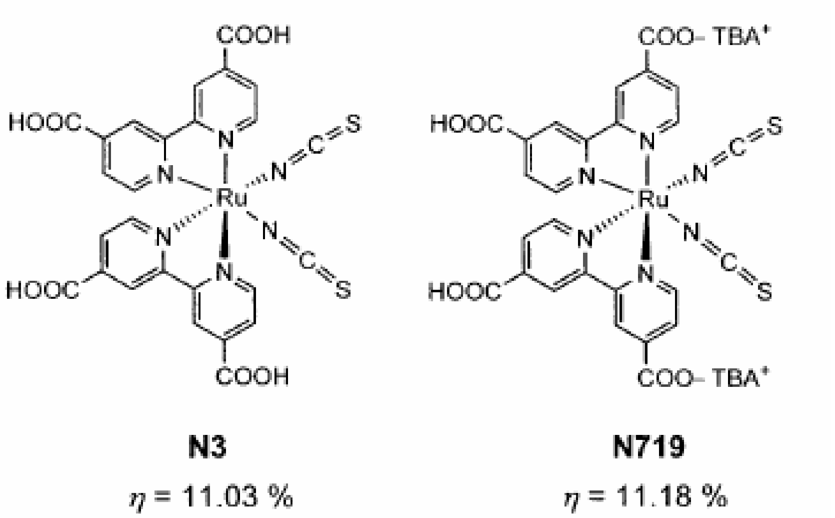


Figure 2.6 The structure of N3 and N719 dye [99].

2.2.3 Electrolyte

The electrolyte is a redox system, typically based on iodine and triiodide (I^-/I_3^-) [3, 80, 97, 100]. The iodide is the electron donor regenerating the oxidized dye and triiodide is the electron acceptor at the counter electrode. In order to have an effective electron transport, the redox potential of the electrolyte should lie between the platinum counter electrode work function and the sensitizer reduction potential. The electrolyte is the solvent based system. It degrades and evaporates at higher temperature. Therefore, the fabrication requires a perfect sealing of the cell. Lots of research are being conducted to in producing quasi-solid-state and solid state electrolytes to avoid degradation and leakage in DSSC, for example, organic hole-transport materials [101, 102], low molecular weight gels [103], ionic liquid-based gel electrolytes [104-106], polymer electrolytes [107-109], and solid polymer electrolytes [110-112]. The efficiencies obtained with these electrolytes are quite low at this stage due to the lower ionic conductivity of the electrolytes [113, 114].

2.2.4 Transparent conducting electrode

Typically, the TCO is conductive glass substrates which functions as the electrode of the cell. The TCO should have low sheet resistance and high transparency. The photoanode is usually heat treated up to 450-500 ^{o}C [80, 115-117] to calcine TiO_2 NPs, therefore, the TCO film resistance should be stable at least up to 500 ^{o}C. Most commonly used TCOs are fluorine-doped tin oxide (FTO) and indium-doped tin oxide (ITO). At higher temperature, the FTO is more stable than the ITO [118, 119].

2.3 Polymer Solar Cells

A polymer solar cell is a solar cell which uses semiconducting conjugated polymers as active components to convert solar light into electricity. It usually composed of organic semiconductors and inorganic semiconductors, integrated the unique properties of both materials. Therefore, polymer cells provide the potential to achieve high energy conversion efficiency at low-cost manufacturing. A great amount of efforts have been devoted to this area and in recent years there has been a rapid increase in the efficiency from 3% to 8.13% [16, 120-122] as shown in Table 2.1

Table 2.1 The recent PCE of polymer solar cell

Year	Efficiency	Company
2010	8.13 %	Solarmer Energy
2009	7.9 %	Solarmer Energy
2009	6.4 %	Konarka Technologies
2007	5.4 %	Plextronics
2006	3.0 %	Sharp

The key to polymer solar cells is the bulk heterojunction, which is a blend of electron-donating semiconducting polymers and electron-withdrawing fullerides. This bulk heterojunction morphology enhances the interfacial area, where the photogenerated excitons, electron-hole pairs, are dissociated into charge carriers. Once the excitons have been separated, the electrons and holes are to be transported by fullerene (electron transport material) and polymer (hole transport material), respectively, to their electrodes to generate current. The extracted current density depends largely on the device architecture. The separation of the excitons is shows in Figure 2.7. The P3HT (poly(3-hexylthiophene)) is a conjugated hole conducting polymer that is commonly used as the electron donor material because of its semicrystalline lamellar structure leading to higher hole mobilities than other conjugated polymers [123]. The C60 derivative, PCBM, ((6,6)-phenyl C61-butyric acid methyl ester), is a commonly used as the electron acceptor material because of its high electron mobility and excellent electron accepting properties [124]. Figure 2.8 shows the energy band diagram and a schematic of a polymer solar cell based on a heterojunction between thin P3HT and PCBM layers. Typically a TCO, such as, ITO is used as a contact to the donor and a low work function metal ,such as, Al or Ca is used as a contact to the acceptor [125]. In general, contact electrodes are selected such that the work function of the donor contact is lower than the HOMO of the donor, and the work function of the acceptor contact is higher than the LUMO of the acceptor [126]. Figure 2.9 shows the hybrid solar cell which use the blend of P3HT and PCBM filled in the TiO_2 NT.

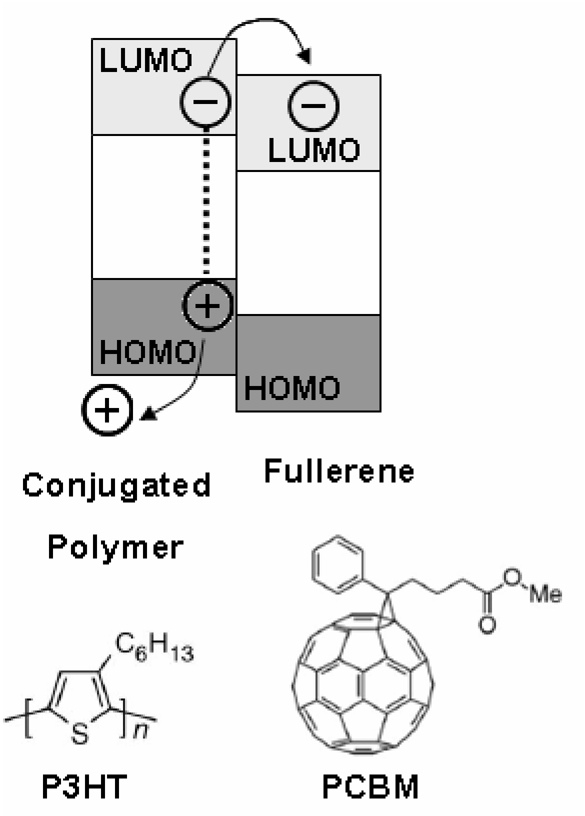


Figure 2.7 The dissociation diagram of exciton in P3HT and PCBM [127]

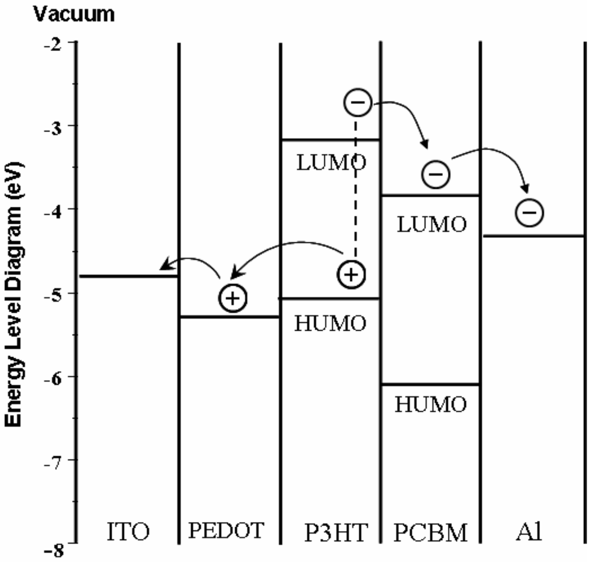


Figure 2.8 Schematic energy levels diagram of solar cell containing P3HT and PCBM [128]

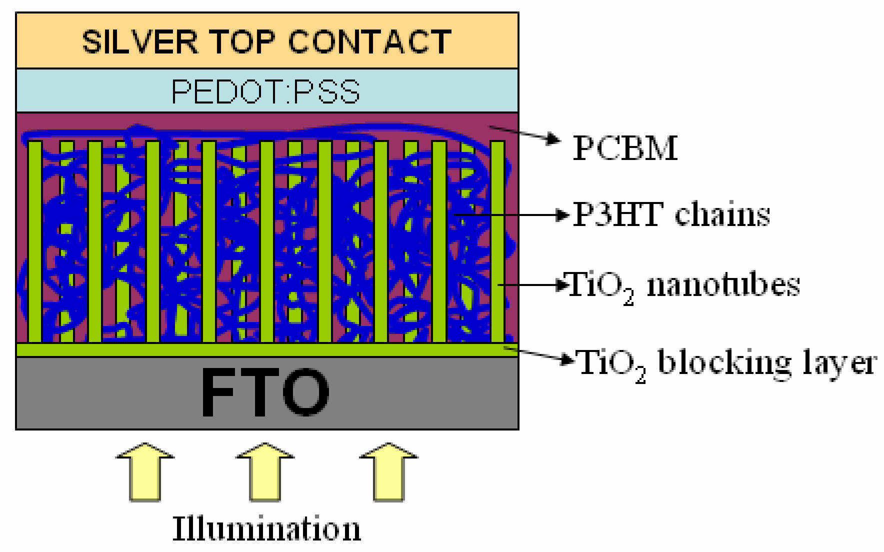


Figure 2.9 The hybrid solar cell using a blend of P3HT/PCBM filled in to TiO_2 NTs

2.4 X-ray Powder Diffraction

X-ray powder diffraction is a powerful method for the characterization of inorganic solids [129]. In this technique, a beam of x-rays which is an electromagnetic radiation of wavelength about 1 Å (10^{-10} m, about the same size as an atom) is directed at a powdered sample of the compound to be studied. When an x-ray beam hits an atom of sample, the electron around the atom start to oscillate and cause the x-ray wave interference, commonly known as x-ray diffraction. This can be both constructive and destructive interference. A constructive interference result when the incident wavelength is proportional to the lattice spacing of the crystalline sample. We can measure the distances between the planes of the atoms in the crystal structure by applying Bragg's Law.

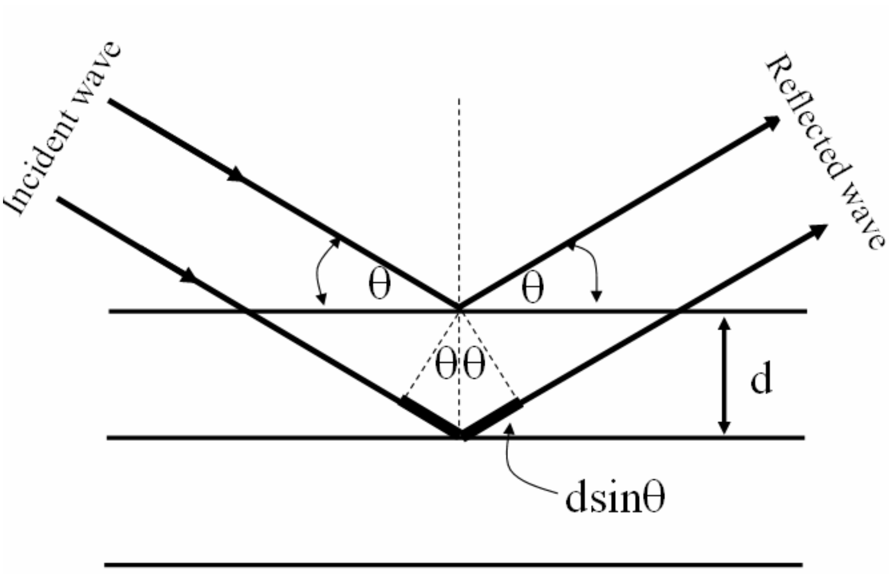


Figure 2.10 Geometrical illustration of the Braggs' law [130].

Bragg's equation:

$$n\lambda = 2d\sin\theta \tag{2.2}$$

n	is an interger
λ	is the wavelength of the x-rays
d	is the interplanar spacing generating the diffraction
θ	is the diffraction angle

The plot of the intensity of the scattered x-ray against angle is called a diffraction pattern. An example of the XRD diffraction pattern shows in Figure 2.11. The intensity of the diffraction peak is related to the quantity of diffraction planes. The position of diffraction peaks, 2θ, can be used to calculate the distance between the planes of atoms in the crystal structure, d-spacing. Each peak measures a d-spacing that represents a family of lattice planes [131].

X-ray diffraction has been used in two main areas, for the fingerprint characterization of materials and the determination of their structure. Each crystalline solid has its unique characteristic x-ray diffraction pattern which may be used as a "fingerprint" for its identification. x-ray crystallography can be used to determine its structure, i.e. how the atoms pack together in the crystal structure and what the distance or angle between atoms in crystal structure. The x-ray diffractogram can be used to determine the size and the shape of the unit cell. Moreover, the XRD diffraction data can able be used to calculate the particle size (crystallite size). The crystallite size can be calculated from the full width at half maximum (FWHM) of the diffraction peak of XRD pattern using the Debye-Scherrer equation [132].

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2.3}$$

D	is the crystallite size, Å
K	is the crystallite-shape factor = 0.9
λ	is the x-ray wavelength, 1.5418 Å for $CuK\alpha$
θ	is the observed peak angle, degree
β	is the full width at half maximum, radian

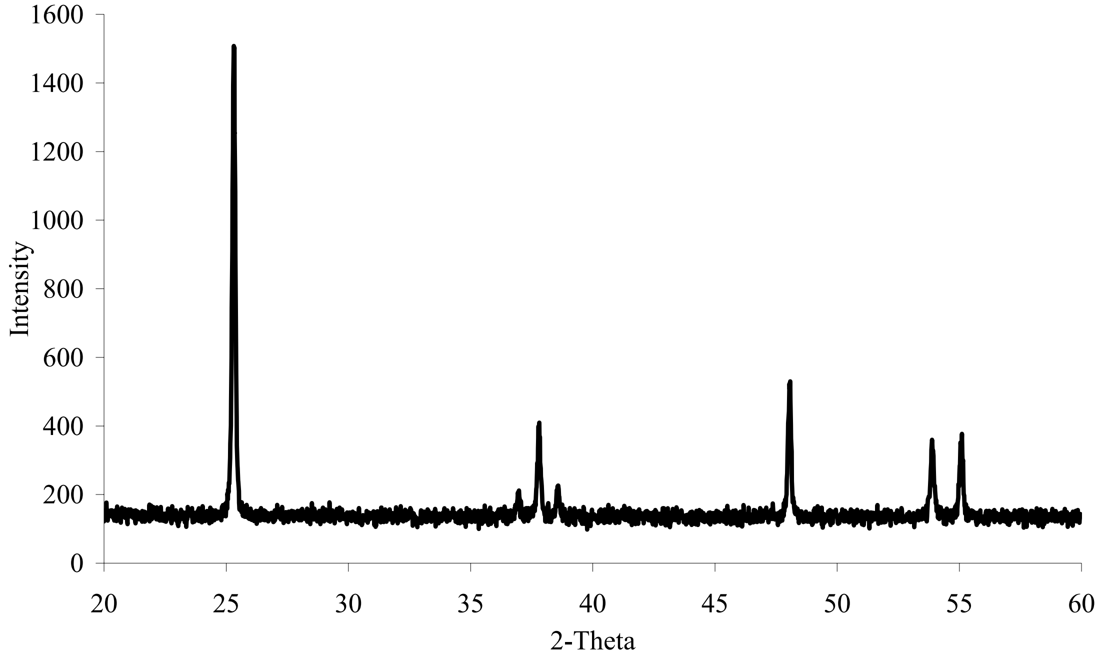


Figure 2.11 XRD diffraction pattern of TiO_2 (Degussa, P-25)

2.5 Energy Dispersive X-ray Spectroscopy

Energy-dispersive x-ray spectroscopy (EDS or EDX) is an analytical technique used for analysis of element in a sample. This technique relies on the investigation of a sample through interactions between electromagnetic radiation and matter. When a high-energy beam of charged particles such as electrons or protons hits an atom of a sample, the incident beam may excite an electron in an inner shell, ejecting it from the shell, and create an electron hole. An electron from an outer, higher-energy shell then fills the hole, and released energy in the form of an x-ray, showed in Figure 2.12. The energy of the x-rays emitted from samples can be measured by an energy-dispersive spectrometer [133].

The energy of the emitted x-rays is characteristic of the difference between the energy of two shells in the atomic structure of the element. Each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from one another.

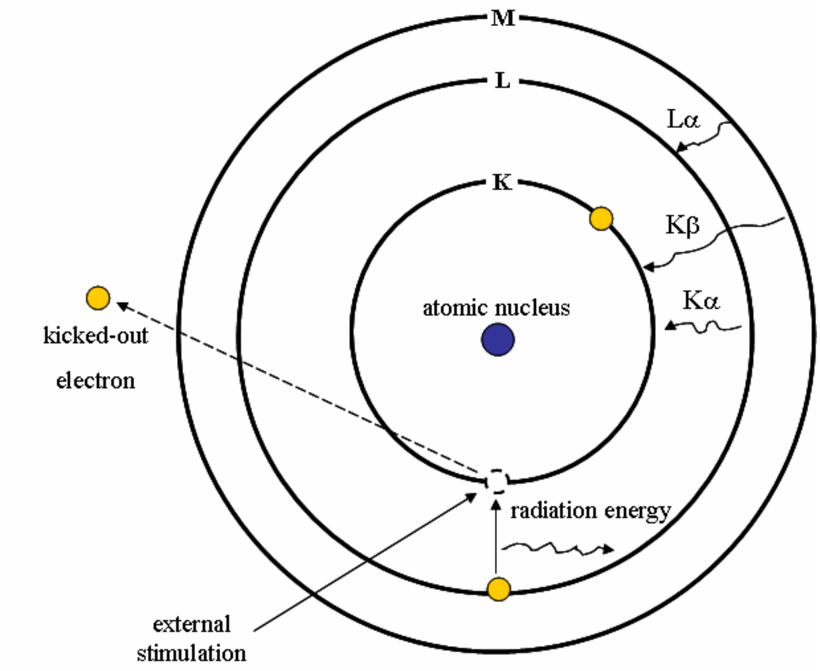


Figure 2.12 Principle of the energy dispersive x-ray spectroscopy, EDS [134]

EDX systems are usually equipped on a scanning electron microscope (SEM) or the transmission electron microscope (TEM) instruments where the imaging capability of the microscope is used to identify the samples of interest. The data generated by EDX analysis consist of spectra showing peaks corresponding to the emitted x-ray energy release by elements. An example of the EDX spectra shows in Figure 2.13.

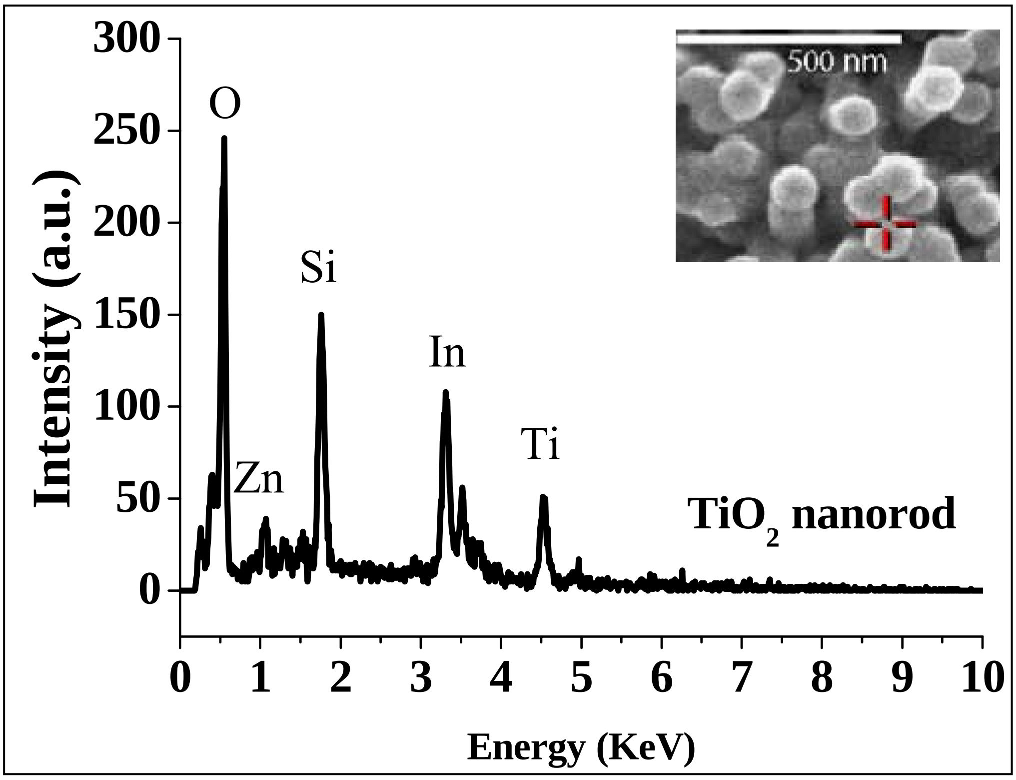


Figure 2.13 The EDX spectra of TiO_2 NR arrays prepared by using ZnO NR template; insets corresponding to an image for EDX analysis

2.6 Interdisciplinary learning

Disciplinary is a term used to describe types of knowledge, expertise, skills, etc. that are strongly associated with academic areas of study [135]. Klein defined disciplinarity as “tools, methods, procedures, exempla, concepts, and theories that account coherently for a set of objects or subjects” [136].

Interdisciplinary learning is an educational process in which the multidisciplinary, two or more disciplines, are integrated to enhance the knowledge across a central theme or topics [137]. Jacobs defined an interdisciplinary as “a knowledge view and curriculum approach that consciously applies methodology and language from more than one discipline to examine a central theme, topic, issue, problem, or work” [138]. By focusing on an issue or core theme, interdisciplinary learning encourages students to perceive the connections between seemingly unrelated knowledge, which facilitating a personalized process of organizing knowledge.

2.7 Inquiry-Based Teaching and Learning

Most recent theories of learning in science view the learners as active constructors of knowledge [139]. Often referred as constructivist in science education, these current perspectives represent a significant shift from traditional views of learners as passive receptors of knowledge, behaviourism, to learners as active meaning makers. Inquiry-based science instruction is one of the most effective teaching and learning strategies for the constructivist [48], which has gained increasing attention as a way to engage student learning and help them develop deep understanding.

National science education reforms strongly advocate the implementation of an inquiry-based learning in science classrooms [47, 140, 141]. Some science educators advocated the using of inquiry learning approach in a wide range of classrooms e.g. K-12, college students, and pre-service science teachers [142, 143].

Many evidences show benefits of inquiry-based approaches in science instruction. Dalton and Morocco found students who used an inquiry approach performed well on content assessments and developed scientific concepts regardless of ability level [144]. Yoshina and Harada stated inquiry learning encourages student learning by creating knowledge through asking questions, investigating, evaluating data, presenting organized information, and expressing personal views thus mirroring the processes real world scientists incorporate daily [145]. An inquiry-based learning environment supports students in learning by engaging them in extended investigations to pursue answers to question and solve real problems[146].

The American National Research Council (NRC) points out that inquiry is a set of skills that students need to master and as a body of understanding that students need to learn [47, 141]. NRC also notes that student’s inquiry is a multifaceted activity that involves 1) making observations, 2) posing questions, 3) examining multiple sources of information to see what is already known, 4) planning investigations, 5) reviewing what is already known in light of the student’s experimental evidence, 6) using tools to gather, analyze and interpret data, 7) proposing answers, explanations and predictions and 8) communicating the results. In addition, the NRC suggests five fundamental features of inquiry-based approaches in teaching science are:

1) Learners are engaged by scientifically oriented questions

2) Learners give priority to evidence, which allows them to develop and evaluate explanations that address scientifically oriented questions

3) Learners formulate explanations from evidence to address scientifically oriented questions

4) Learners evaluate their explanations in light of alternative explanations, particularly those reflective scientific understanding

5) Learners communicate and justify their proposed explanations.

Bybee proposed the model as 5E instruction model for inquiry teaching and learning [147]. The 5E instructional model contains five elements: engagement, exploration, explanation, elaboration and evaluation. Each "E" represents part of the process of helping students sequence their learning experiences to construct their understanding of concepts. The details of each stage described as below:

Step 1: Engagement

Activities are introduced to engage students with a problem or phenomenon. Such activities capture student's interest and enable them to make connections with what they know and can do.

Step 2: Exploration

Next, students participate in hands-on experiences through which they explore the concept further. They receive little explanation or terminology at this point because they are to define the problem or phenomenon in their own words. At this point students can help one another make sense of the concept. Students spend considerable time talking about their experiences, both to articulate their own understanding and to understand one another's point of view.

Step 3: Explanation

After students have explored the scientific concept independently, then they use the terms to describe what they have experienced and begin to examine how the explanation fits with what they already know.

Step 4: Elaboration

Students are given opportunities to apply the concept in new situations, or they are introduced to related ideas that they explore and explain with the information and experiences they have accumulated so far. Interaction between students is essential during the elaboration stage. By discussing their ideas with each other, they gain a deeper understanding of the concept.

Step 5: Evaluation

At this stage, students continue to elaborate their understanding and evaluate what they now know and what they have yet to figure out. This stage provides opportunity for teacher to evaluate student progress toward achieving the educational objectives.

Colburn (2004) listed three basic forms of inquiry learning: (a) structured inquiry, (b) guided inquiry, and (c) open inquiry [148]. Structured inquiry provides instructions for laboratory activities but it requires students to generate data tables, graphs, and conclusions. In guided inquiry, students developed the laboratory procedure as well as the requirements of a structured inquiry. Open inquiry, however, allowed students to make the majority of decisions regarding the laboratory focus. This environment placed students in a role similar to actual scientists.

2.8 Assessment in Science Education

Assessment is a process of information collection in the contexts of instruction that will be used to examine and describe student’s performance. Assessment in science education is different from other subjects. Science education assessment has been changed from paper-pencil test and now emphasizes on students’ performance of inquiry-based science instruction. National Science Education Standards of the U.S.[141] has suggested three major aspects of science assessment. These outcomes consist of conceptual understanding in science, ability to perform scientific inquiry and understandings about inquiry.

As student’s inquiry is a multifaceted activity, NRC suggests five aspects to assess the abilities of students in inquiry: 1) identifying a worthwhile and researchable question, 2) planning the investigation, 3) executing the research plan, 4) drafting the research report and 5) assessing individual student achievement [149]. In addition, the NRC suggests methods of assessment that can be used, such as, paper and pencil testing, performance testing, interviews, portfolios, performances, observing programs.

CHAPTER III

ZnO NANOPARTICLES AND NANOWIRE ARRAY HYBRID PHOTOANODES FOR DYE-SENSITIZED SOLAR CELLS

Overview

ZnO NW-NP array hybrid photoanodes for DSSC with NW arrays to serve as a direct pathway for fast electron transport and NPs dispersed between NWs to offer a high specific surface area for sufficient dye adsorption has been fabricated and investigated to improve the PCE. The overall PCE of the ZnO hybrid photoanode DSSC with the N3-sensitized has reached ~ 4.2%, much higher than both ~1.58 % of ZnO NW DSSC and ~1.31 % of ZnO NP DSSC, prepared and tested under otherwise identical conditions.

3.1 Introduction

DSSCs have attracted a lot of attention as they are low-cost third generation solar cells, potentially for wide-spread commercialization [1-3]. The key element in DSSC is the photoelectrode, which consists of highly porous wide bandgap semiconductors, typically TiO_2 and ZnO network with dye molecules adsorbed onto the surface forming a monolayer. Dye molecules capture the incident photons and generate electron-hoe pairs; electrons are readily injected into the conduction band of TiO_2 or ZnO and transported to charge collector. In order to achieve high power conversion efficiency, a large amount of dye molecules should be adsorbed, so a high specific surface area is desired. The charge transfer from dye molecules to charge collector should be efficient so as to minimize or eliminate possible loss of charges through surface recombination. Based on the TiO_2 NP network, the DSSC has achieved AM 1.5 solar efficiencies more than 10 % [9, 10]. However, the further enhancement of the PCE is difficult, partly due to charge recombination and reduced electron transport rate through the nanocrystalline photoanodes [11]. Efforts have been made to improve the charge transport in the photoelectrode, and the enhancement has been demonstrated by using one-dimensional nanostructure, including ZnO NR and NW and TiO_2 NT arrays [11-14]. However, the PCE of such DSSC remained low, for example, ZnO NW DSSC with the NW length as long as 33 μm was only 2.1 % [15] and a key point which limited the PCE of ZnO NW DSSC should be an insufficient surface area for dye adsorption [11].

The further improved the PCE of the DSSC can be expected by making the photoanodes with exhibited both a high surface area and fast electron transport. Various ZnO structures have been employed to be used as photoanode of the DSSC to improve the surface area and electron transport, including branch structure [22], tetrapod [23], nanoflower [24], and composite NW/NP [25-27]. The overall PCE of these cells were largely increased, compared to pure ZnO NP DSSC, which amounted to 1.51 %, 3.27 %, 1.9 %, and 3.2 % for branch structure, tetrapod, nanoflower, and composite ZnO NW/NP, respectively. The increase in the overall PCE is due to the enriched surface area for better dye loading and higher charge transport [27, 150]. In this work we report on the fabrication and investigation of DSSC using ZnO NP and NW array photoanode (hybrid ZnO NW-NP DSSC). The ZnO hybrid photoanode composed of ~11 μm length ZnO NW arrays to serve as a direct pathway for fast electron transport and crystallite ZnO NPs dispersed between ZnO NWs to offer a high surface area for dye adsorption.

3.2 Experimental Details

3.2.1 Synthesis of ZnO NP.

ZnO NPs were synthesized by the hydrolysis of zinc salt in diethylene glycol [28]. 2g of Zinc acetate dihydrate was added to 100 mL of diethylene glycol (DEG) with vigorous stirring. The mixture was rapidly heated at 200 °C in an oil bath. The reaction continued for about 2 h with continual stirring. The as-obtained colloidal solution was then sequentially concentrated by 1) centrifugally separating the ZnO NPs from the solvent, 2) removing the supernatant, and 3) redispersing the precipitate in 5 mL of ethanol.

3.2.2 Synthesis of ZnO NWs.

The ~100 nm thick seed layer of ZnO was first prepared on the FTO by spin-coat the 0.60 mol.l^{-1} of $Zn(CH_3COO)_2.2H_2O$ in a 2-methoxyethanol/monoethanolamine. The seed substrates were annealed at 250 ^{o}C for 10 min, and subsequent soaking in an aqueous solution of 0.015 M $Zn(NO_3)_2$ and 0.015 M hexamethylenetetramine at 95 ^{o}C for 60 h with refreshing the growth solution every 12 h.

The crystallographic characterizations of the ZnO NPs and ZnO NWs samples were performed in a Bruker D8 Focus X-ray diffractometer. The surface morphology and the fracture cross section of the specimens were obtained by scanning electron microscope (SEM, Philips, JEOL JSM7000).

3.2.3 Device fabrication and characterization.

The colloidal dispersions of ZnO NPs were spin-coated on the ZnO NWs films. After the films dried, they were washed with deionized water (DI) and annealed at 350 °C for 1 h to remove any residual organic matter from the ZnO surface. The films were then sensitized by immersing them into 0.5 mm ethanolic solution of the ruthenium complex cis-[RuL2(NCS)2] (commercially known as N3 dye) for approximately 20 min [62]. The films were then rinsed with ethanol to remove the additional dye. The electrolyte was a liquid mixture containing 0.5M tetrabutylammonium iodide, 0.1M lithium iodide, 0.1M iodine, and 0.5M 4-tert-butylpyridine in acetonitrile. The photovoltaic behavior was characterized when the cell devices were irradiated by simulated AM 1.5 sunlight with an output power of 100 mW.cm^{-2}. An Ultraviolet Solar Simulator (model 16S, Solar Light Co., Philadelphia, PA) with a 200W Xenon Lamp Power Supply (Model XPS 200, Solar Light Co., Philadelphia, PA) was used as the light source, and a Semiconductor Parameter Analyzer (4155A, Hewlett–Packard, Japan) was used to measure the current and voltage.

3.3 Results and Discussion

The SEM images of ZnO NWs prepared by varying the concentration and growth time show in Figure 3.1. This observation is consistent with the results reported in literature [151]. It was found that the length of ZnO NWs can be controlled by varying the growth time in ZnO precursor solution. Particularly, the length of ZnO NWs increases when extending the growth time, as shown in Figure 3.4 (d-f). Meanwhile, the diameter of NR is independent of the reaction time and mainly tailed by the concentration of zinc source.

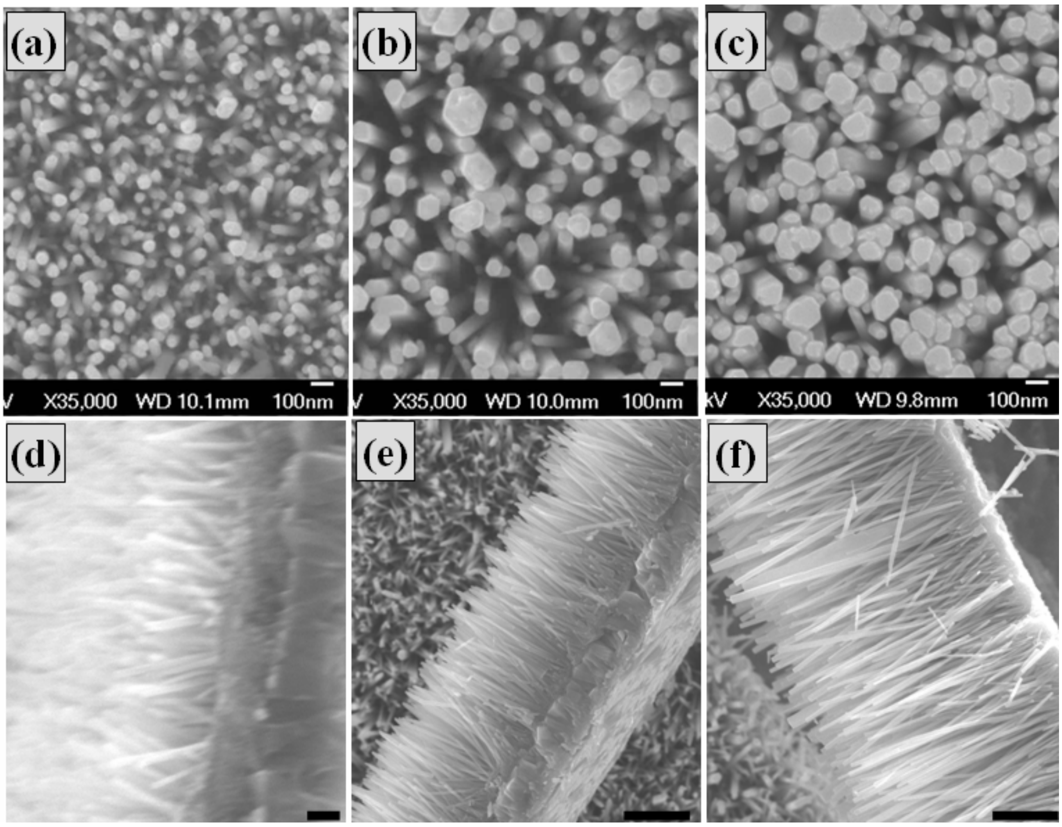


Figure 3.1 (a), (b), and (c) the top view scanning electron microscopy (SEM) images of ZnO NRs prepared by varing the concentration of $Zn(NO_3)_2$ at 0.025 M, 0.050 M and 0.100 M, respectively, (d), (e), and (f) the cross section SEM images of ZnO NRs prepared by using 0.015 M $Zn(NO_3)_2$ and varying growth time at 2 h, 6 h, and 12 h, respectively. Scale bar: (d) = 100 nm, (e) and (f) = 1 µm.

Figure 3.2 is the scanning electron microscopy (SEM) images with Figure 3.2(a) showing the top-view and Figure 3.2(b) the cross-section of ZnO NW arrays. The ZnO NWs with a diameter in the range of 40–500 nm (average ~ 116 nm) and a length of ~ 11 µm were well aligned perpendicularly to the FTO substrate. From SEM images, the density of ZnO NWs is estimated to be ~ 14 wires.μm^{-2}. By spin-coating the colloidal dispersion of ZnO NPs (synthesized in diethylene glycol at 240 ^{o}C) on the top of ZnO NW arrays, the ZnO NPs with the average diameter of about 14 nm were partly penetrated and dispersed between of the ZnO NWs but with the large fraction remained and coated on the surface of NW arrays (shown in Figure 3.2(c) and 3.2(d)). More SEM images see Appendix A.

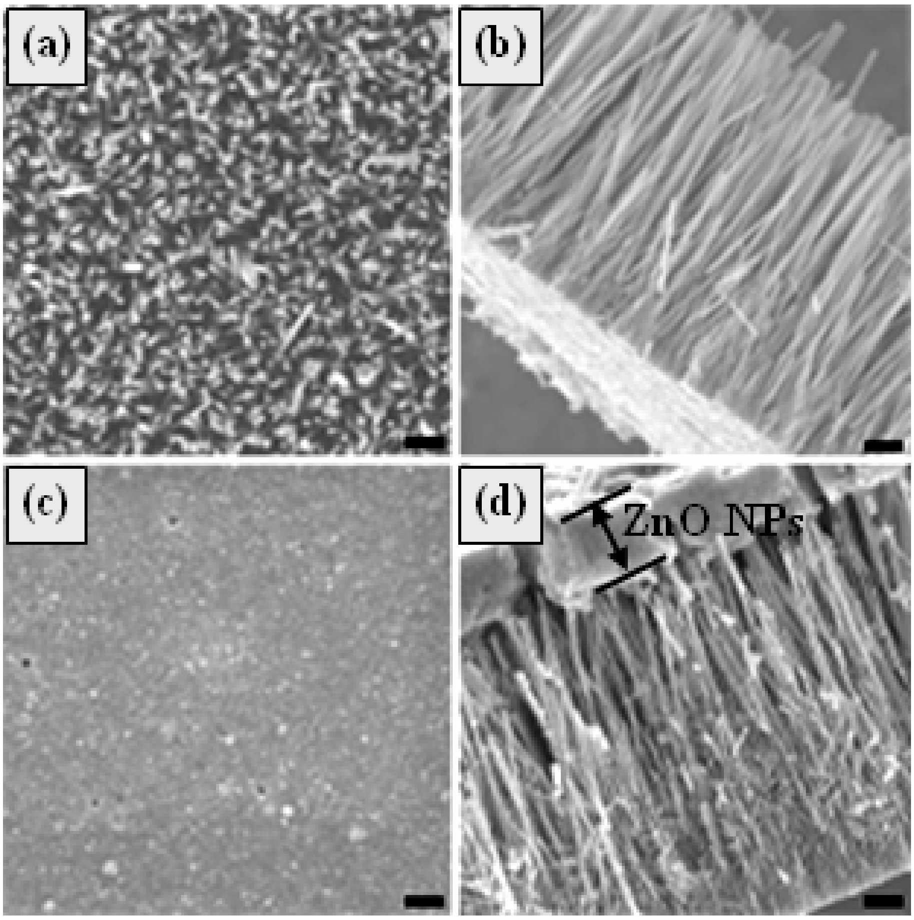


Figure 3.2 SEM images of ZnO NW arrays and hybrid ZnO NW-NP, (a) the top-view of ZnO NW arrays, (b) cross-section of ZnO NW arrays, (c) top-view of hybrid ZnO NW-NP, and (d) cross-section of hybrid ZnO NW-NP. Scale bars in (a)-(d) are 1 µm.

Figure 3.3 shows and compares the XRD patterns of the ZnO NW film and hybrid ZnO NW-NP photoanode. ZnO NW-NP film exhibited a high crystallinity with very well defined (100), (002), and (101) diffraction peaks. The (002) diffraction peak is mainly attributed to the wurtzite structure of well aligned ZnO NWs which tend to occur along the c axis [152]. The (100) and (101) diffraction peaks are resulted from the ZnO NPs [153].

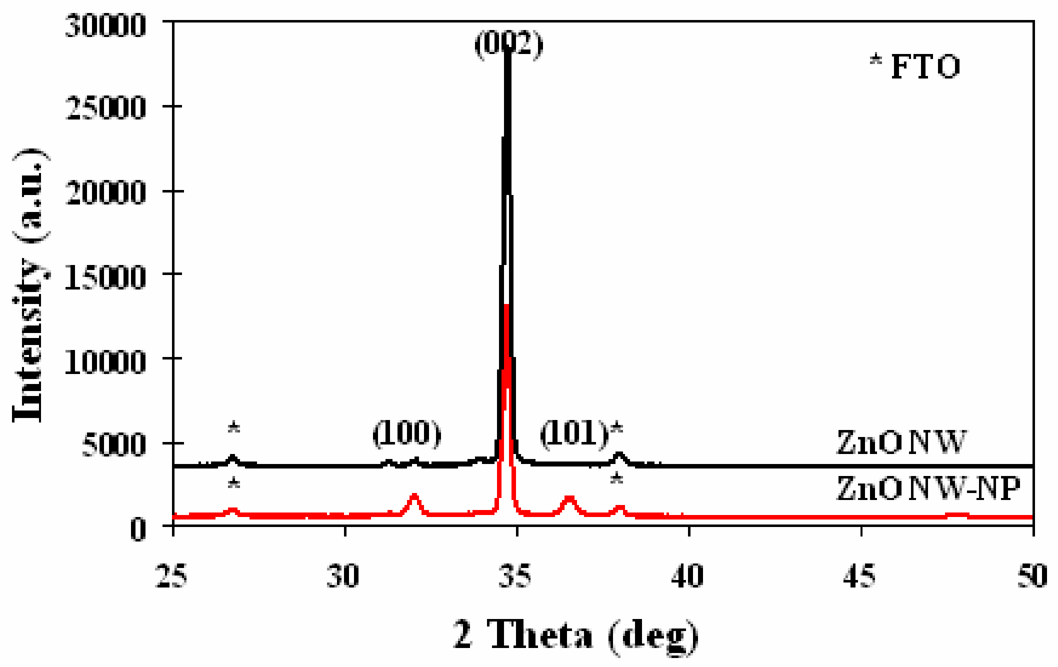


Figure 3.3 XRD patterns of ZnO NW and hybrid ZnO NW-NP

Figure 3.4 shows the photocurrent density (I)–voltage (V) characteristics for the DSSC fabricated using N3-sensitized ZnO NPs, ZnO NWs, and hybrid ZnO NW-NP. The values of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall power conversion efficiency (η), were summarized in Table 3.1. The PCE of ZnO NW DSSC with the length of ~1.7 μm, ~5.1 μm, and ~11 μm were 0.94%, 1.16%, and 1.58%, respectively. The increase of efficiency with the length of NW was the result of increase the surface area for dye absorption. However, there is no linear dependence between the PCE and the length of ZnO NWs. Such a lack of direct relationship may be partly ascribed to the fact that the density of the NWs decreases with an increased length as a result of evolution selection growth.

Reduced density of NWs would lead to a reduced surface area for dye adsorption. The obtained V_{oc} and FF of ZnO NW DSSCs are comparable to Law et al [11] and Xu et al [15]. The best overall PCE of DSSC with the ZnO hybrid photoanode has reached 4.2 % with V_{oc} of 613 mV, J_{sc} of 15.16 mA.cm^{-2}, and a fill factor of 46 %, far higher than both 1.58 % of ZnO NW DSSC, and 1.31 % of ZnO NP DSSC which prepared and tested under otherwise identical conditions.

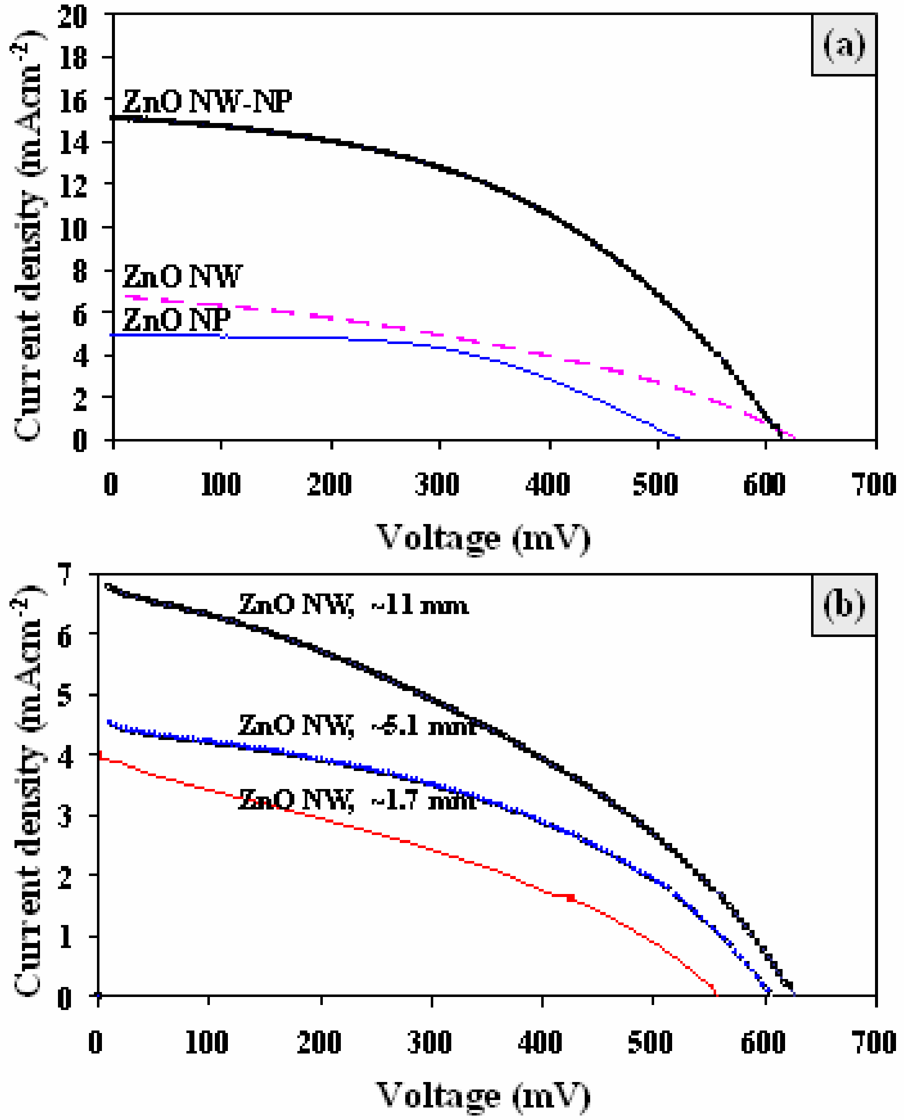


Figure 3.4 The photocurrent density-voltage curves of the N3 sensitized; (a) ZnO NP DSSC, ZnO NW DSSC, and hybrid ZnO NW-NP DSSC and (b) ZnO NW DSSC with the lengths of ~1.7µm, ~5.1 µm, and ~11 µm.

Table 3.1 The photovoltaic properties of ZnO DSSC

Samples	The thickness of DSSC (μm)	Jsc [mA/cm^2]	Voc [mV]	FF [%]	η [%]
ZnO NW	~1.7 (NW)	4.09	553	41	0.94
ZnO NW	~5.1 (NW)	4.55	609	41	1.16
ZnO NW	~11 (NW)	6.79	629	37	1.58
ZnO NP	~10 (NP)	4.94	521	51	1.31
Hybrid ZnO NW-NP	~11 + ~2 (NW+NP)	15.16	613	46	4.24

The remarkable improved solar cell performance of ZnO NW-NP hybrid DSSC was the results from the increase in Jsc and FF, which may be attributed to the following reasons. First, high-crystalline ZnO NPs (~14 nm) dispersed between long ZnO NW arrays (~11 μm) resulted in an increased surface area for more dye adsorption and, thus, an increased J_{sc} [25, 26, 150]. The amount of dye molecules adsorbed on ZnO NW and hybrid ZnO NW–NP photoelectrodes, by desorbing the dye molecules using a 0.1 M aqueous NaOH solution was found to be 6.39×10^{16} molecule.cm^{-2} and 7.48×10^{16} molecule.cm^{-2}, respectively. These results agree very well with the results reported by Rao and Dutta [154] and Seow et al. [155]; which showed the number of dye molecules adsorbed on the ZnO NW surface is greater than that on the ZnO NP surface. Secondly, the single crystalline ZnO NWs in the hybrid ZnO NW-NP photoanode served as direct pathways for rapid charge transfer and consequently reduce the loss of charges as suggested in the open literature [14, 27]. Schematic representation of the possible electron path way for the hybrid ZnO NW-NP DSSC shows in Figure 3.5(b). Finally, the increase of adsorbed-dyes on the ZnO NPs covered on the surface of ZnO NWs, as shown in Figure 3.5(a), provides a sufficient electron which can compensate the sacrificing electron during the electron transport and, thus, improve the FF. It is also noted that although ZnO NWs in micrometer length may serve as light scatters as reported with large aggregates [28, 62, 156] or particles [80], the significant enhancement of short circuit current density only in hybrid ZnO NW-NP photoanode DSSC is unlikely due to the scattering effect. Further experiments are under way to improve the penetration of ZnO NPs between the ZnO NWs to further enhance the power conversion efficiency.

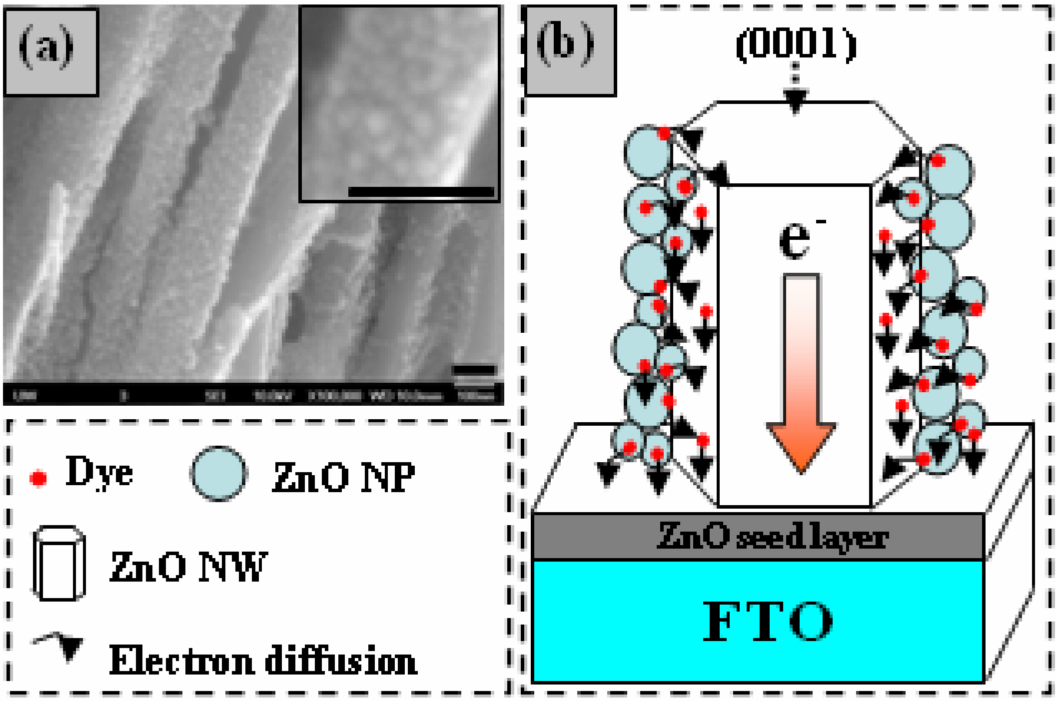


Figure 3.5 (a) the SEM image of ZnO NPs on the surface of ZnO NW in the hybrid ZnO NW-NP photoanode, scale bars 100 nm and (b) the schematic representation of the possible electron path way in the hybrid ZnO NW-NP photoanode.

CHAPTER IV

ENHANCE PHOTOVOLTAIC PERFORMANCE OF NANOSTRUCTURED HYBRID SOLAR CELL USING HIGHLY ORIENTED TiO_2 NANOTUBES

Overview

Highly oriented TiO_2 NTs have been fabricated using ZnO NR template through liquid reactive deposition on the ITO substrates. The diameter and length of TiO_2 NTs can be effectively controlled for the suitable use for a hybrid solar cell by varying the diameter and length of the ZnO NR template. A mixture of P3HT/PCBM was infiltrated into the gaps between TiO_2 NTs to form the hybrid solar cell with the double heterojunction between P3HT and TiO_2 and P3HT and PCBM. The V_{OC} , J_{sc}, fill factor and power conversion efficiency of the hybrid solar cell using highly oriented TiO_2 NTs were 646 mV, 9.95 $mA.cm^{-2}$, 51.6% and 3.32%, respectively, much higher than 1.2% of hybrid solar cell based on ZnO NRs tested under otherwise identical conditions and significantly higher than 0.7% of the same type hybrid solar cells reported in literature. The enhancement of the power conversion efficiency could be resulted from the efficient charge separation at the double heterojunction and the highly oriented TiO_2 NTs with smaller diameter and higher density for hybrid solar cells.

4.1 Introduction

The widespread use of inorganic solar cells remains limited due to the high costs of fabrication [17]. A lot of efforts are being made to develop so-called third generation of solar cells including DSSC [3, 157] and organic photovoltaics, OPVs [4, 5, 158]. OPVs or polymer based photovoltaic devices can be processed from solution and have become a promising low cost alternative to traditional inorganic solar cell [6-

8, 159]. The key of the polymer solar cells is the bulk heterojunction, which is a blend of electron-donating semiconducting polymers and electron-withdrawing fullerides. This bulk heterojunction morphology enhances the interfacial area, where the photogenerated excitons, electron-hole pairs, are dissociated into charge carriers and enables holes and electrons to be transported and collected. The PCE of up to 7.4 % have been recently reported in the bulk heterojunction polymer solar cells [160]. However, polymer based solar cells still suffer from low efficiencies and the limited lifetime as compared to silicon-based solar cell [17]. The limited efficiency of the bulk heterojunction polymer solar cell is due to the lower charge mobility in polymer [18], the charge trapping in the conducting pathways of fullerides and polymer to the electrodes [19], and the mismatch of the absorption spectrum of the active layer and the solar emission [20, 21]. To address the intrinsic limitations of polymer solar cells, new strategies have been investigated such as developing new polymers with a low bandgap for better match absorption of the solar spectrum [160], a hybrid organic/inorganic solar cells (hybrid solar cells), which are composed of an organic donor material, such as a conjugated polymer, and an *n*-type inorganic semiconductor [29-34]. These hybrid solar cells have the potential to combine the properties of physical stability and high charge mobility of inorganic materials and the potential of easy control of the active layer structure and interface morphology.

The hybrid solar cells using a vertically oriented TiO_2 NT or NR arrays filled with the blend of P3HT and PCBM have been investigated [34, 161-165], which have the advantages of both the bulk heterojunction and ordered architectures. The bulk heterojunction morphology provides the sufficient interfacial area for the separation of photogenerated excitons. The ordered architectures help to reduce the electron recombination and function as the direct path way for fast electron transport to the charge collecting electrode. In addition, when a blend of P3HT and PCBM deposited on the vertically aligned TiO_2 NTs or NRs, a double heterojunction structure is formed, and improves the charge separation at the interfaces between P3HT and PCBM, and between P3HT and TiO_2, promising higher power conversion efficiency.

Oriented or ordered TiO_2 NTs can be readily prepared by anodizing titanium foils in an acidic electrolyte. Although anodization of Ti film has several advantages and the hybrid solar cells achieved a high power conversion efficiency of

4.7% [165], a dense array, precise control of the NT configuration and a high throughput process can not be guaranteed and TiO$_2$ NT, fabricated by anodization of titanium foils is difficult to use in the micro and nano device applications [166]. More recently, Rattanavoravipa et al.[167] reported a one-step templating method to prepare highly aligned TiO$_2$ NW arrays (100-150 nm in diameter and 1 µm long), which uses ZnO NR obtained from aqueous solution route as a template. However, for the application of hybrid solar cell, these TiO$_2$ nanostructures are either too densely populated, which would prevent the effective infiltration of polymer solution, or their diameters are too large, which limit the specific surface area, leading to less efficient charge separation, and a power conversion efficiency of 0.7% has been achieved [167].

In this work, a simple fabrication method is employed for the growth of highly oriented TiO$_2$ NTs on the ITO substrates by using ZnO NRs as templates, which are formed by an aqueous solution route. The diameter and the length of TiO$_2$ NTs were carefully controlled for being used in the hybrid solar cell by varying the diameter and length of ZnO NR template. It was found that the hybrid solar cell based on these TiO$_2$ NTs infiltrated with P3HT and PCBM show an enhanced power conversion efficiency of 3.32 %, as compared to 0.7 % reported in literature [167].

4.2 Experimental Details

4.2.1 Synthesis of TiO$_2$ NTs.

The deposition was conducted via a three-step procedure: 1) Seed layers were first grown to block the injection of holes into ITO electrode. ITO substrates were cleaned by acetone/ethanol sonication. These freshly cleaned ITO glasses were used to deposit a thin layer of TiO$_2$ of thickness ~30 nm by immersing the substrate in a solution containing 0.1 M $(NH_4)_2TiF_6$ and 0.2 M H_3BO_3 for 30 min at 25 ^oC. The substrates were then spin coated by 0.60 mol.l^{-1} of $Zn(CH_3COO)_2.2H_2O$ in a 2-methoxyethanol/monoethanolamine to form ~50 nm thick seed layer of ZnO, followed by heat treatment at 300 ^oC for 10 min to obtain dense and transparent seed layers. 2) ZnO template growing. The seeded substrates were placed in an aqueous solution containing 0.015 M $Zn(NO_3)_2$ and 0.015 M hexamethylenetetramine at 95 ^oC for 2 h. Subsequently, the resultant films were thoroughly rinsed with deionized water to remove any residual salt or amino complex and dried with compressed air. 3) TiO_2 NT forming. The synthesized ZnO NR arrays on ITO were immersed in aqueous solution consisting of 0.075 M $(NH_4)_2TiF_6$ and 0.2 M H_3BO_3 at room temperature for 1.5 h. The resulting TiO_2 NTs were then dipped in a 0.5M H_3BO_3 solution for 1 h to remove any residual ZnO. The products were then rinsed with DI water and calcined in air at 400 ^oC for 1h. Crystallographic characterizations of the samples were performed in a Bruker D8 Focus X-ray diffractometer. The surface morphology and the fracture cross section of the specimens were obtained by scanning electron microscope (SEM, Philips, JEOL JSM7000) with an energy-dispersion X-ray analyzer.

4.2.2 Device fabrication and characterization.

The chlorodebenzene solution containing 20 mg mL^{-1} P3HT (Reike Metal, Sepiolid P100) and 16 mg mL^{-1} PCBM (American Dye Source Inc. ADS61BFB) was stirred inside the glovebox for overnight at 60 ˚C and then spin coated at 1,000 rpm onto the TiO_2 NT covered substrates, which were firstly air plasma treated for 15 min. The samples were then placed on a hot plate at 150 °C for 15 min to help self-organization of P3HT [168], driving away residual water and assisting the the polymer infiltration into the TiO_2 NT arrays [165], A hole-transport layer of poly(3,4-ethylene-dioxylene thiophene):poly(styrene sulfonic acid) (PEDOT:PSS, Clevios P VP Al 4083) was subsequently spin-coated with a thickness of ~50 nm outside of the glove box, filtered through a 0.45 μm filter. The films were baked at 120˚C for 10 min and then the devices were transferred into a deposition chamber inside the glovebox and 100 nm of Ag was thermally evaporated under a vaccum of 2×10^{-6} Torr. The *J-V* characteristics of solar cell were tested in air using a Keithley 2400 source measurement unit, and an Oriel Xenon lamp (450W) coupled with an AM1.5 filter. A calibrated silicon reference solar cell certificated by the National Renewable Energy Laboratory (NREL) was used to confirm the measurement conditions. A light intensity of 100 $mW.cm^{-2}$ was used in all the measurements in this study.

4.3 Results and Discussion

Figure 4.1 shows and compares the XRD patterns of the TiO_2 NT film before (Figure 4.1a) and after (Figure 4.1b) annealed at 400 ˚C for 1h in air. Before annealing, the TiO_2 NTs were an amorphous which only demonstrates the diffraction peaks from ITO glass (JCPDS Card no. 39-1058). After annealing at 400 ˚C for 1h in air, the TiO_2 NTs had anatase phase (JCPDS Card no. 84-1286) and there is no diffraction peaks indicating that ZnO templates completely removed by the final step of wet etching. Based on the XRD data, the final TiO_2 NTs were found to consist of ~19.4 nm (Scherrer equation [132]) anatase nanocrystals.

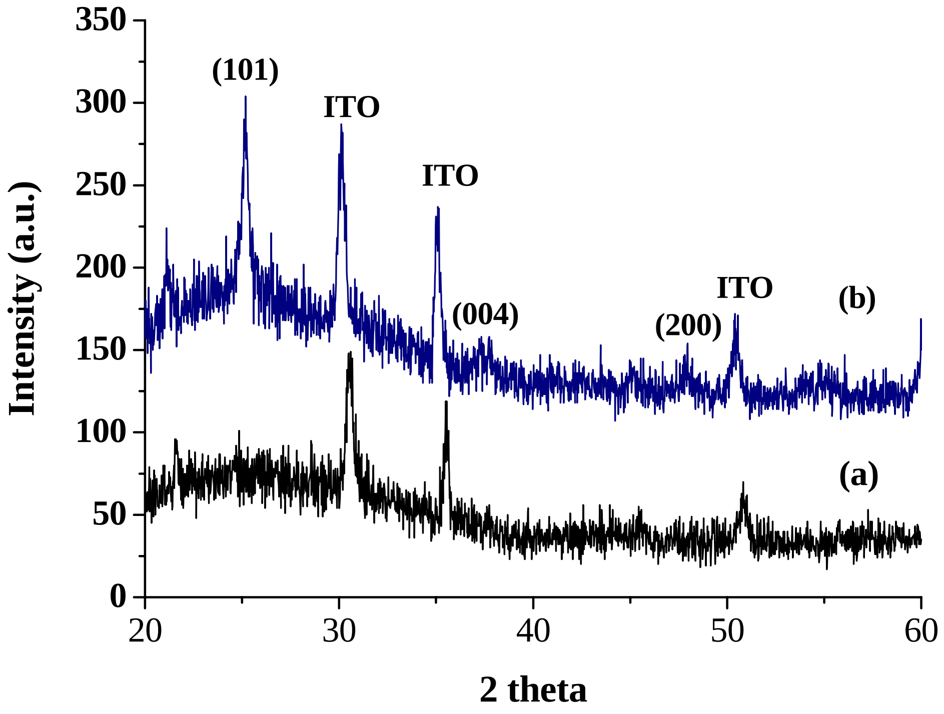


Figure 4.1 XRD patterns of the TiO_2 NT films before (a) and after (b) annealed at 450 ˚C

Apart from the XRD patterns, energy dispersive X-ray (EDX) before and after the formation of TiO_2 NTs was further used to reveal the formation of TiO_2 and elimination of the ZnO template. Figure 4.2 shows the EDX spectra, where Zn and Ti contents were analyzed on the ZnO NRs and TiO_2 NTs, respectively. The absence of a peak at ~1 keV, corresponding to Zn, of the EDX spectra taken from TiO_2 NTs indicates the removal of the ZnO NR template.

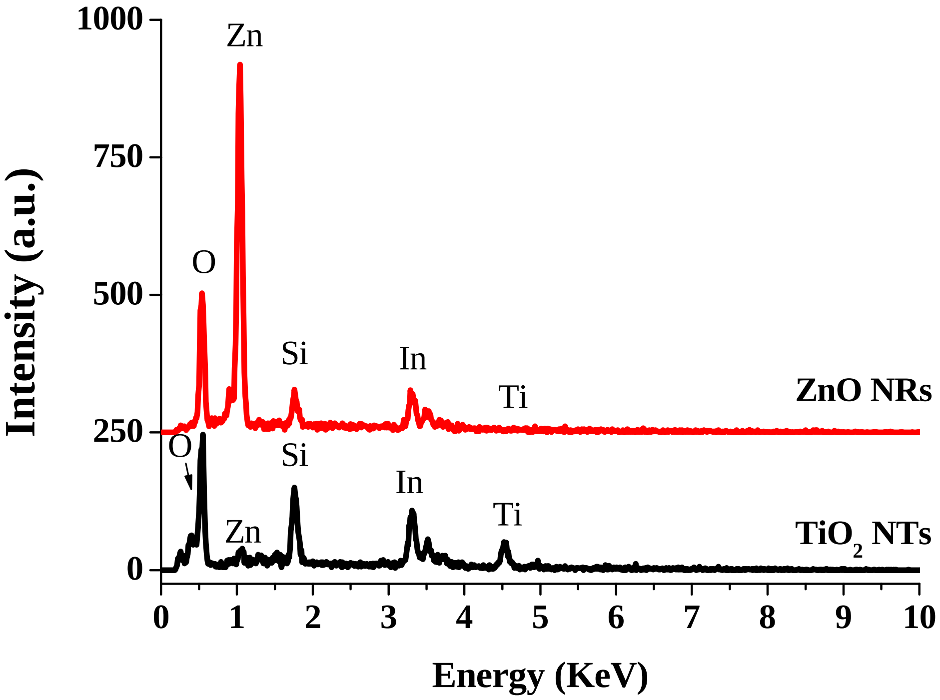


Figure 4.2 EDX spectra of ZnO NR arrays and TiO_2 NT arrays

Figure 4.3a and 4.3b show the top view SEM images of the ZnO NR and TiO_2 NT film. As shown in Figure 3a, highly uniform and well spaced arrays of ZnO NRs were successfully formed with preferential growth in the c-axis orientation (<0001>). Each NT is about 20-30 nm in diameter and ~150-200 nm in length. More SEM images see Appendix A. The structure of ZnO NRs was found to be very sensitive to the processing parameters, including the precursor concentration, growth temperature and time. These ZnO NRs were subsequently converted to TiO_2 NTs via the liquid-phase deposition in an aqueous solution consisting of $(NH_4)_2TiF_6$ and H_3BO_3. It is reasonable to assume that, under optimized conditions, the ZnO layer could be completely removed and the TiO_2 NTs retain the length and diameter of the ZnO template. The formation of TiO_2 is believed to proceed via the following equation Eq 1. [115, 169]

$$TiF_6^{2-} + 2H_2O \Leftrightarrow TiO_2 + 6F^- + 4H^+ \qquad (4.1)$$

This reaction can be shifted to the right by adding H_3BO_3 which reacts with F^- ions and form a more stable complex ions, BF_4^-, as outlined in Eq 2.

$$H_3BO_3 + 4H^+ + 4F^- \Leftrightarrow BF_4^- + H_3O^+ + 2H_2O \qquad (4.2)$$

ZnO NRs will dissolve into the solution by react with H_3O^+ and this process resulted in the formation of a TiO_2 NTs with the top-end closed.

$$ZnO + 2H_3O^+ \rightarrow Zn^{2+} + 3H_2O \qquad (4.3)$$

The deposition TiO_2 on the ZnO NR template and the removal of ZnO NRs proceed simultaneously [115]. The deposition of TiO_2 continued to fill the void space within the TiO_2 tubule and the TiO_2 NR could finally be obtained, when the deposition time is sufficiently long. The resultant TiO_2 NTs were further immersed in a H_3BO_3 solution to ensure the complete removal of any residual ZnO. The pH of the solution is very sensitive to the dissolution of ZnO NRs. The decrease in pH value of the solution accelerates the dissolution of ZnO NRs and will result in a lower array density of TiO_2 NTs [169].

As indicated in Figure 4.3b, it is observed that the diameter of TiO_2 NTs is in the range of ~20-35 nm, which provides a large specific surface area, and thus allows efficient charge separation at the double heterojunction. The length of TiO_2 NTs was controlled to be typically 150-200 nm for an optimal hybrid photovoltaic device performance as there is a tradeoff between the distance that charge carriers need to travel to reach respective collection layer and the maximized light absorption [31]. In addition, it is noticed that the TiO_2 NT film possessed a very porous structure, i.e., the NTs are well separated from one another, which allows the efficient infiltration of polymer solution. Figure 4.3c shows the schematic process involving the growth of barrier TiO_2 layer, the ZnO seed layer, ZnO NRs, and the deposition of TiO_2 NTs and simultaneous ZnO dissolution.

Since the work function of ITO (4.5–4.7 eV) is intermediate between the work function of HOMO and LUMO of P3HT, ITO can collect either electrons or holes. The compact TiO_2 layer at the bottom of the NTs will function as a hole blocking layer to prevent the holes reaching to the transparent conductive ITO substrates [170]. Figure 4.3d shows the cross-section image of TiO_2 NTs hybrid solar cell: Ag/PEDOT:PSS/blend of P3HT:PCBM/TiO_2 NRs/ITO.

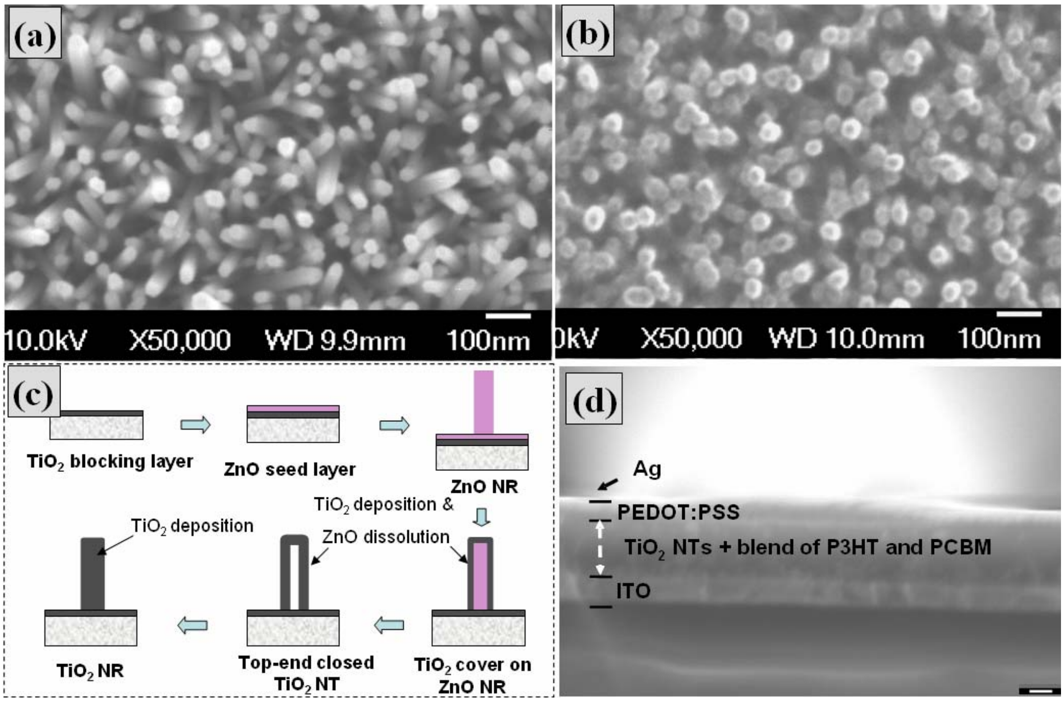


Figure 4.3 (a), (b) the top view scanning electron microscopy (SEM) images of ZnO NRs and TiO_2 NTs, respectively, (c) the schematic process of preparing TiO_2 NTs, and (d) the cross section of hybrid solar cell photoelectrode using TiO_2 NTs, scale bar is 100 nm

Figure 4.4 shows the current density - voltage curves of the hybrid solar cells based on the TiO_2 NTs infiltrated with a blend of P3HT and PCBM. For a better comparative study, the hybrid solar cell using ZnO NRs was prepared under identical processes. The values of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall power conversion efficiency (η), were summarized in Table 4.1. One approach to improve the performance of hybrid solar cell is to manipulate the dimensions of TiO_2 NTs, which is determined by ZnO NR template. It was found that the typical maximum efficiency was obtained when growing TiO_2 NTs with about 25-35 nm in diameter and ~150-200 nm in length. With too short and/or too small TiO_2 NTs, the cells showed much lower performance and vice verse. As demonstrated in Figure 4.4, the highest performed hybrid solar cells was achieved with

V_{oc}=646 mV, J_{sc}=9.96 mA.cm^{-2}, FF=51.6%, PCE=3.32% for the TiO_2 NTs annealed at 400 °C in conjunction with P3HT/PCBM. The PCE of 3.32% achieved in this work is significantly higher than 0.7% of the same type structured hybrid solar cells reported in literature [167].

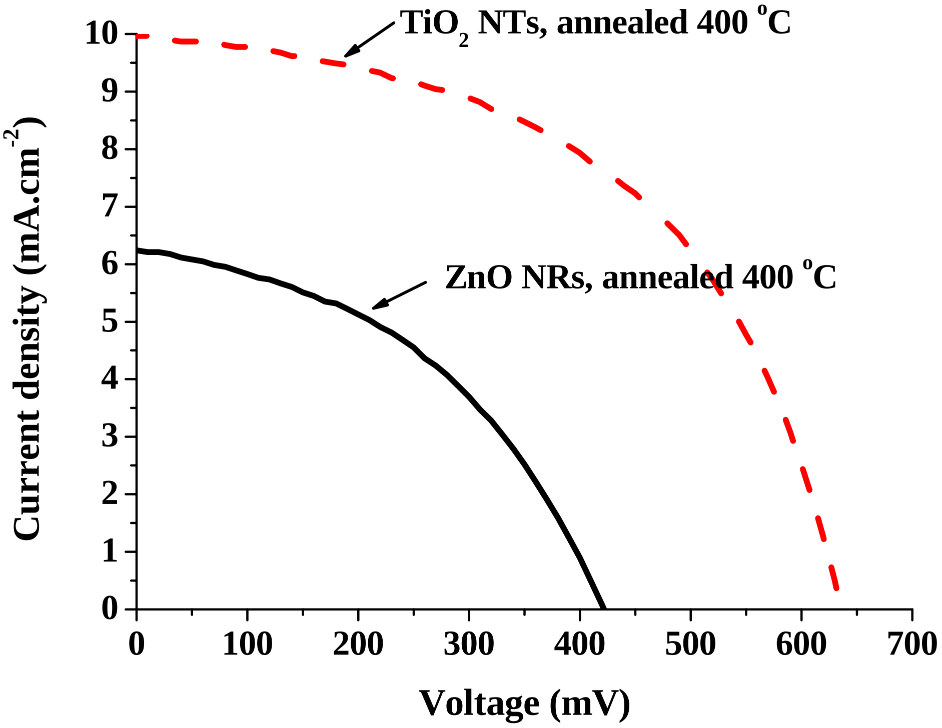


Figure 4.4 The current density-voltage curves of the hybrid solar cells of the ZnO NRs and TiO_2 NTs infiltrated with a blend of P3HT and PCBM

Table 4.1 Performances of the solar cells with the electrode made of ZnO NRs and TiO_2 NTs

Samples	Voc [mV]	Jsc [mA/cm^2]	FF [%]	η [%]
ZnO NRs, annealed 350 °C for 1h	432	6.28	43.76	1.19
TiO_2 NTs, annealed 400 °C for 1h	646	9.95	51.60	3.32

Charge separation in our hybrid solar cell occurs both at the interface between P3HT and PCBM and the interface between P3HT and TiO_2, a double heterojunction structure as shown in Figure 4.5. These double heterojunctions help improve the charge separation and TiO_2 NTs help to reduce the electron recombination and function as the direct path way for fast electron transport to the charge collecting electrode, promising better power conversion efficiency.

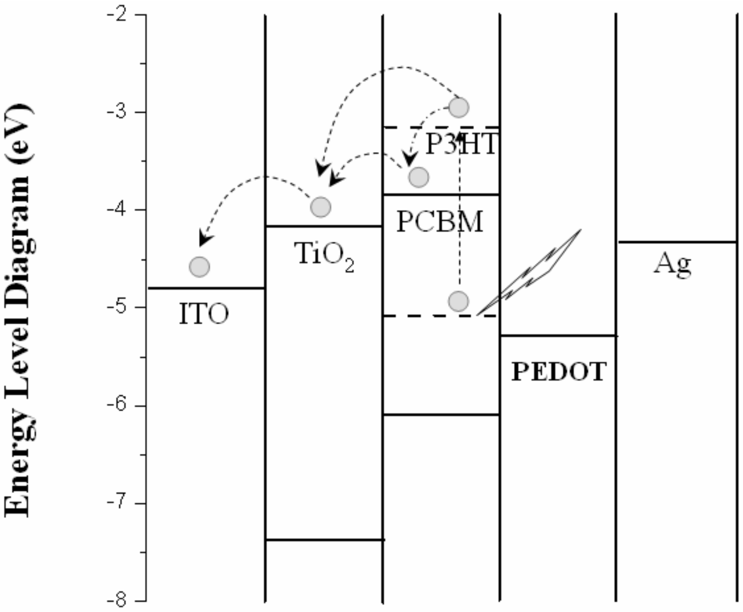


Figure 4.5 Schematic representation energy diagram of double heterojunction photovotaic device, ITO/TiO_2/blend P3HT:PCBM/PEDOT/Ag

The barrier layer of TiO_2 at the bottom keeps the holes from touching the ITO substrates so as to increase the charge collection. As a result, the short circuit current density and open circuit voltage were remarkably enhanced. On the other hand, the hybrid solar cells based on ZnO NR/ P3HT/PCBM exhibited V_{oc} of 432 mV, J_{sc} of 6.28 mA.cm^{-2}, FF of 43.76%, PCE of 1.19%, respectively, which are comparable to 1.16 % reported by Rattanavoravipa et al [171]. Obviously, the V_{oc}, $J_{sc,}$ and FF of the DSSC using ZnO NRs are significantly lower than that of TiO_2 NTs.

It should be noted that the enhanced power conversion efficiency in this hybrid solar cells could be attributed to: (1) the efficient charge separation at the double heterojunction, (2) the suitable oriented TiO_2 NTs for the hybrid solar cell, excitron diffusion length, and (3) the oriented TiO$_2$ NTs reduced the electron recombination by provided a direct path way for fast electron transport to the charge collecting electrode. In addition, the further improved the PCE could be with the consideration of the following factors: (1) ideal TiO$_2$ NTs grown perpendicular to the ITO substrates via manipulating the densities of TiO$_2$ NT. (2) Interface modification and better infilltration of polymer into TiO$_2$ NTs to improve charge separation and reduce electron recombination by tuning the polymer blend concentration, the ratio of P3HT to PCBM, spin-coat process, and polymer annealing treatment [172].

CHAPTER V
AN INTERDISCIPLINARY LEARNING UNIT: DYE-SENSITIZED SOLAR CELL FROM SUNLIGHT TO ELECTRICITY

Overview

The study of this part is involved in the adaptation of the research finding from the scientific part to develop an inquiry DSSC learning unit to promote student understanding in the concept of energy transformation in the form of sunlight into electrical energy and the concepts related to solar cells i.e., electricity, light, semiconductor, atomic structure, and energy bandgap. The findings of this study show an enhancement of the students’ conceptual understanding about the solar cells and related concepts. In addition, the students have positive attitude toward the learning unit.

5.1 Introduction

Science education in developing countries is widely considered to be in crisis, not because students are failing in content, but because they are not interested in or engaged by science as it is currently being taught in schools [36]. In the case of Thailand, science instruction emphasized on lecture methods to ensure that all contents needed in preparing for university entrance examination were covered [37]. Students lacked opportunities to practice skills, both in scientific and thinking processes, which are essential for science learning [38]. Another problem is that students are usually evaluated based upon what they have memorized, rather than their scientific process skills [39]. Large scale study showed “when students move to high school, many experience disappointment, because the science they are taught is neither relevant nor engaging and does not connect with their interests and experiences”[40]. A potential solution to this problem of student engagement may be the provision of a more integrated curriculum with courses and lessons that help students to understand the connections between science and the real world.

An integrated curriculum provides opportunities to work on a few cross-disciplinary objectives, to apply knowledge across the subject boundaries and to work on tasks that is meaningful and relevant, by focusing the curriculum on a problem or topic rather than on a discrete discipline. By approaching a problem or topic from the vantage point of many disciplines, students are exposed to more information and more views, providing them with the raw material needed to construct understanding [41, 42]. Some literatures claim the positive educational outcomes for students who participate in integrated curricula increases the understanding and application of general concepts [43, 44], better able to transfer knowledge to different contexts, more motivated, and more likely to learn higher order thinking skills [45]. Moreover, the content of most integrated curricula is considered to be more closely related to students’ experiences in real life outside school classroom, and hence, enhance engagement [46].

Science education reform worldwide are derived from the constructivist views of teaching and learning. These reforms explicitly ask teachers to change their teaching strategies by shifting the emphasis from the traditional textbook-based, rote learning, to exploration, inquiry-based learning situated in real-world phenomena [47, 173]. Inquiry-based science instruction is one of the most effective teaching and learning strategies for the constructivist [48], which has gained increasing attention as a way to engage students learning and help them develop deep understandings.

The aim of this part is involved in the adaptation of the research finding from the scientific part to develop an inquiry DSSC learning unit.

5.2 Research Objectives

5.2.1 To develop an inquiry DSSC learning unit to promote students' understanding in the concept of energy transformation from solar energy to electrical energy

5.2.2 To investigate the effectiveness of the learning unit on students' understanding

5.3 Context of the Study

Twenty participating students were first year undergraduate students, majored in science education, at a public university in northeastern Thailand. They were volunteered to enroll in this class. The total number of students in the class was 80. The research was a 3 weeks class (180 minute per class) and taught by the researcher. The class conducted as an extra class project in which students were not obligated to any curriculum constraints.

5.4 Research Design

The research design of this study involved two main stages. The details of each step describe as followed:

Step 1: Development of the learning unit based on an inquiry approach

The development of the learning unit include; studying and considering related documents for developing the learning unit, which include the Thai National Science Education Standards, the curriculum design, solar cells, inquiry-based approaches, assessment strategies in science instruction; writing a draft of the learning unit e.g. learning activities, learning tools, experiments, and assessment tools.

The procedure to develop the learning unit was adapted from Jacobs (1989), shown in Figure 5.1

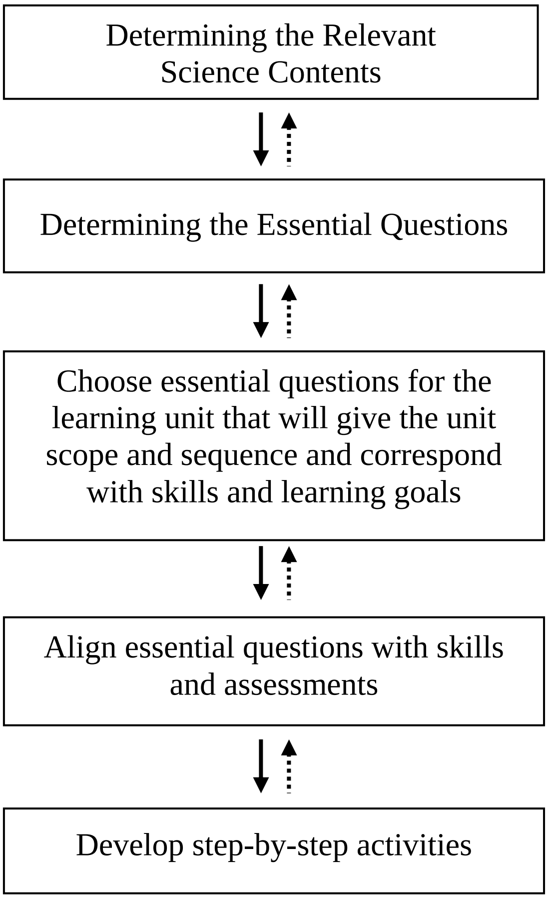
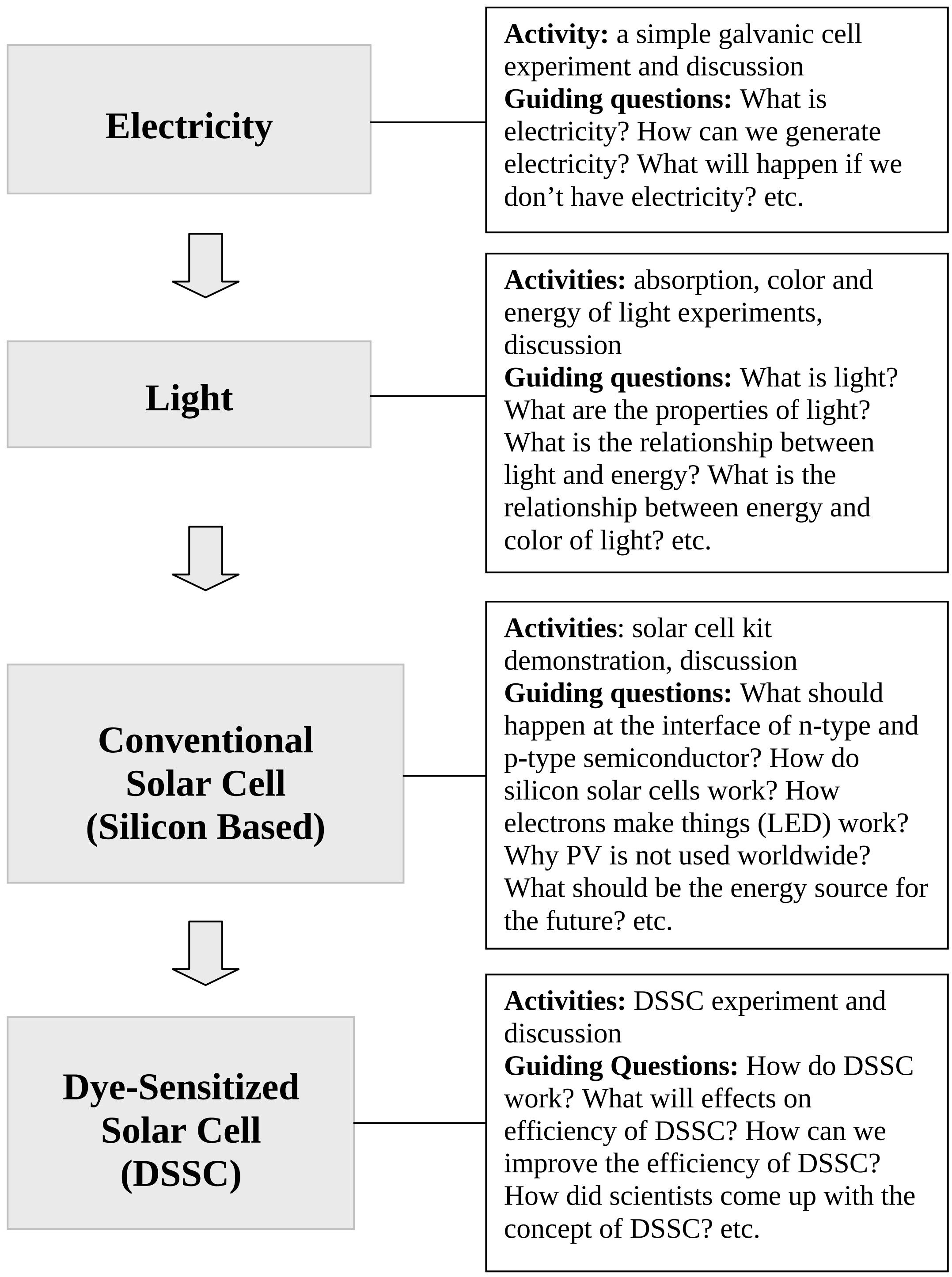


Figure 5.1 Research design for the development of the learning unit

This learning unit was designed as an introduction course. The main concept of our learning unit was about energy transformation from solar energy to electricity. The device that can help us to convert solar energy to electricity energy is solar cells. To help students to understand the whole idea of this topic (solar cell technology), we design our learning unit which compose of 4 sub-concepts: electricity, light, conventional solar cell, and DSSC. Activities of the concept of electricity, light and conventional solar cell will help students to learn how the solar cells work. The DSSC activities will help student understand and know about the ongoing research of solar cells. The flow chart and the model of the learning process of the learning unit show in Figure 5.2 and Figure 5.3, respectively.



Activity: a simple galvanic cell experiment and discussion
Guiding questions: What is electricity? How can we generate electricity? What will happen if we don’t have electricity? etc.

Activities: absorption, color and energy of light experiments, discussion
Guiding questions: What is light? What are the properties of light? What is the relationship between light and energy? What is the relationship between energy and color of light? etc.

Activities: solar cell kit demonstration, discussion
Guiding questions: What should happen at the interface of n-type and p-type semiconductor? How do silicon solar cells work? How electrons make things (LED) work? Why PV is not used worldwide? What should be the energy source for the future? etc.

Activities: DSSC experiment and discussion
Guiding Questions: How do DSSC work? What will effects on efficiency of DSSC? How can we improve the efficiency of DSSC? How did scientists come up with the concept of DSSC? etc.

Figure 5.2 A flow chart of the DSSC learning unit

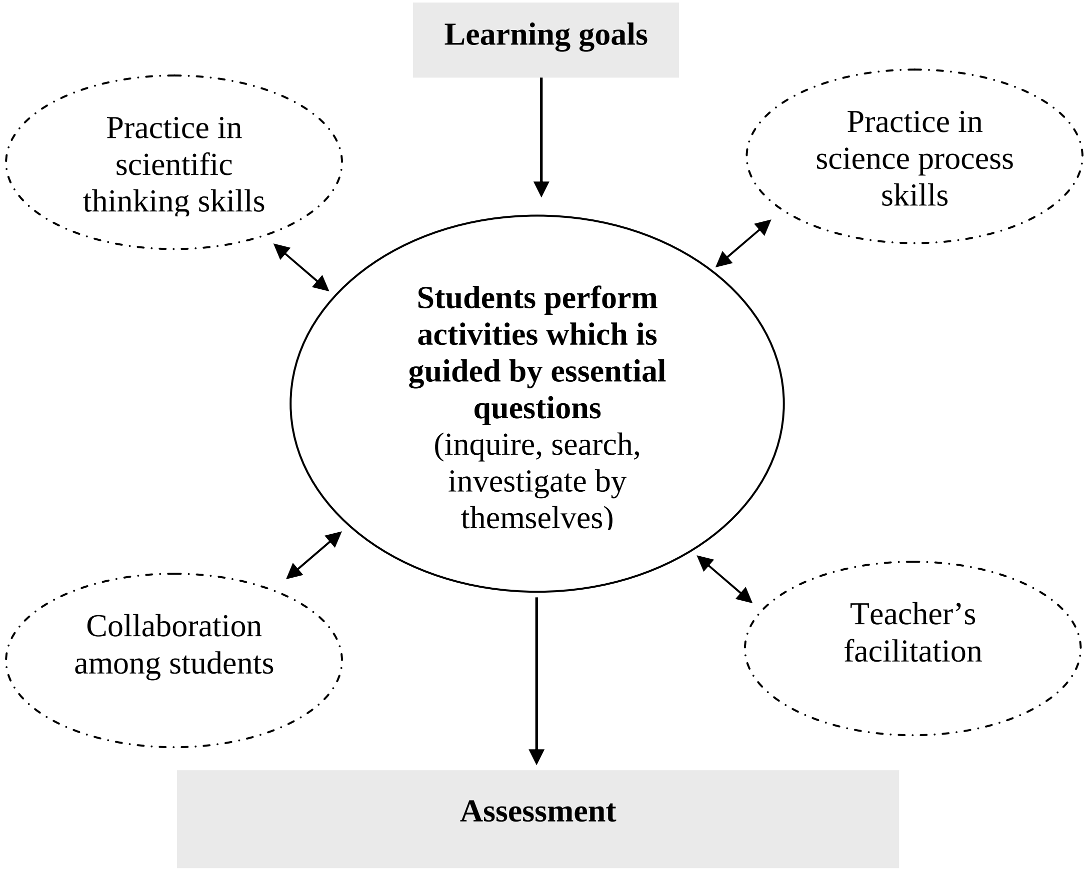
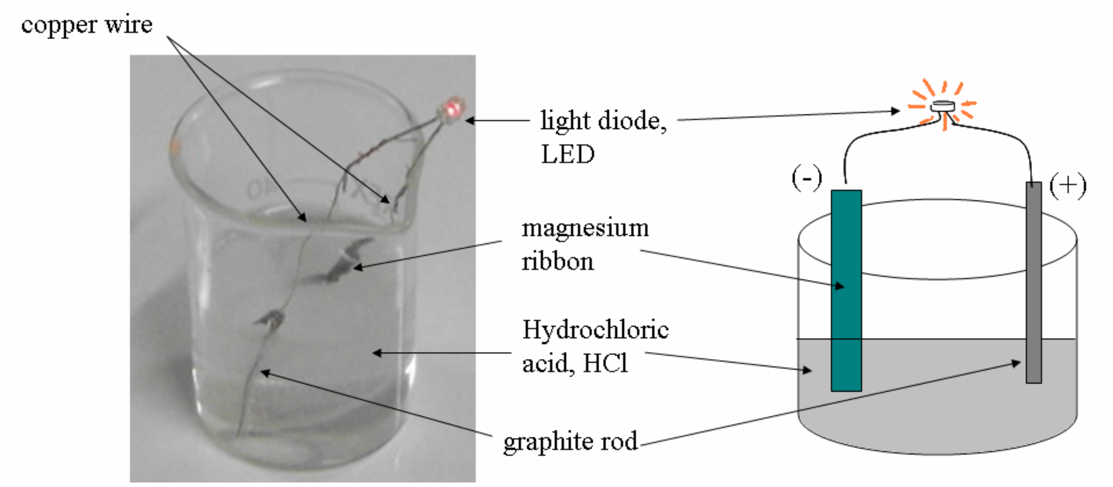


Figure 5.3 A model of the learning process in the DSSC learning unit

The learning activities: Before we get electricity from sunlight, first student have to know what electricity is. Second what light is. After they know the relationship between electricity and light, then they will be ready to learn how solar cells work. To understand the concept of electricity, we have a simple galvanic cell experiment for them to investigate. This simple galvanic cell will help student to get a clear understanding about electricity, the flow of electron. In the teaching methods of this experiment, we used predict-observe-explain (POE) and we had guiding questions to guide them to learn, i.e. what happen at the magnesium ribbon when put it into an acid? What happen at the magnesium and graphite rod electrode? Why? What happen if we use different LED color? Figure 5.4 show a simple galvanic cell.



Figrue 5.4 A simple galvanic cell

From the galvanic cell experiment, students will know that electricity is the flow of electron. We want the electricity from sunlight. So, what is light? How can we get electron from sunlight? About this concept, we have to know light has energy and also they should know about other properties and applications of light. To let them know about the energy of light, we asked them; what happen when you stand in the rice field in the middle of daytime, felt hot or burn. The examples of guiding question of this learning concept are: What is light? How can we see thing? What is absorption? What is the relationship between color of light and energy or wavelength? etc.

After students know about electricity and light, the next concept students have to know is the concept about the solar cell materials. In this concept, student have to know some content that relate to materials which are semiconductor, atomic structure, energy bandgap, doping; p-type, n-type semiconductor, p-n junction, and photoelectric effect. Some of our teaching methods were lectures and extra reading. In the lectures, mostly we used discussion to discuss and predict thing what will happen. After students know the concepts they are able to predict what the properties should be for p-type and n-type semiconductors, and what will happen at the interface between p-type and n-type semiconductor, etc.

After students learned the 3 main concepts: electricity, light, and conventional solar cell, then we discuss about the advantage and disadvantage of the conventional solar cell. After that we let students to learn about the ongoing research of solar cell. Our sample of ongoing research was DSSC.

To learn about DSSC, we had the DSSC experiment for student. In this experiment, students made the DSSC cell by themselves, working in a group. We provided a simple direction lab for student. The step to make the DSSC show in Figure 5.5.

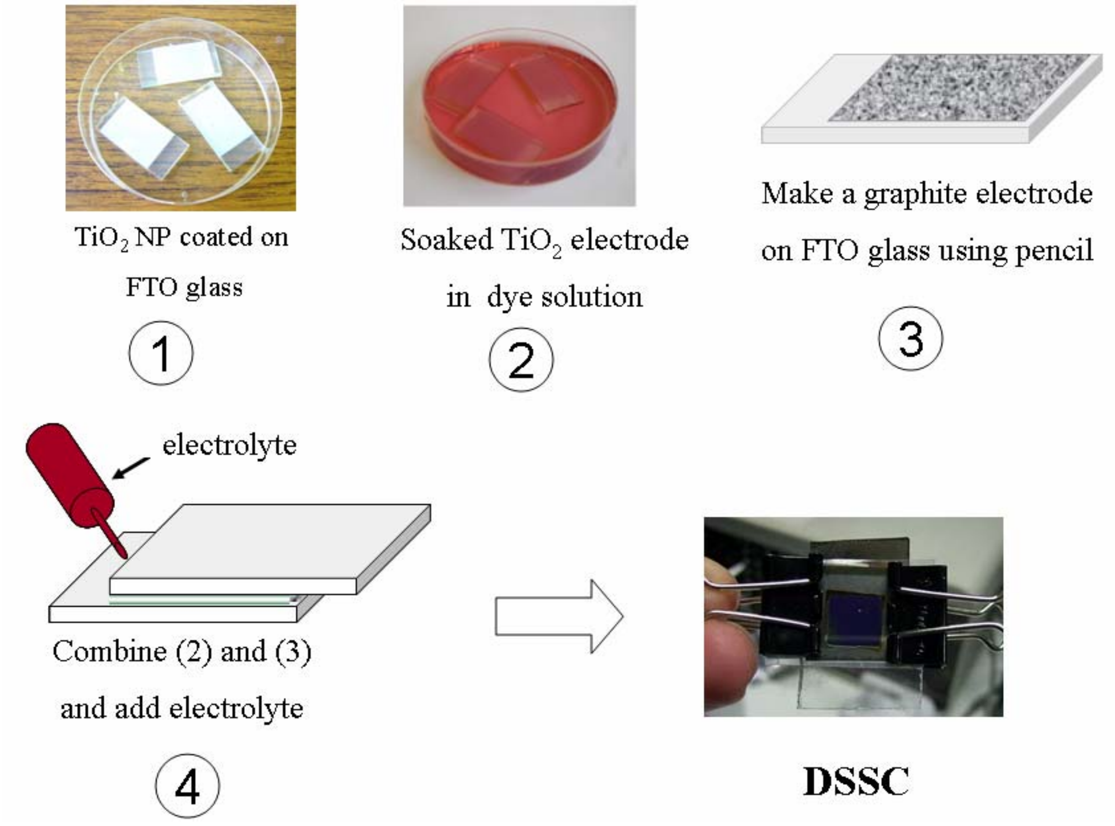


Figure 5.5 Steps to make DSSC

The first step is making a TiO_2 working electrode, and then soaking the TiO_2 electrode in dye solution. The choices of dye can be anything from plants that have color. Another electrode can be made by rubbing a pencil lead on to the FTO glass. The pencil lead serves the graphite as catalyst. To make the DSSC, clipped the TiO_2 electrode and the graphite electrode together and add the electrolyte into the gap between the two electrodes (between the two electrodes used filter paper as a spacer to prevent the direct contact between the two electrodes). The solar cell efficiency can be tested using a multimeter. The voltage obtained is about 0.6 V. The current depends on the type of dye molecule.

Step 2: Implementation of the learning unit

The interdisciplinary DSSC learning unit was implemented in a public university in Northeastern Thailand. Students took the pre-test prior to an instruction. They were designed to work in a group. Each group had 5 students. During the class activities, students were required to be active learner and the teacher’s role was to be a facilitator. Students were encouraged to think, inquire and integrate their knowledge with the provided activities. After completion of the learning unit, all of the students took the post-test, the journal writing. One of the students in each group volunteered to do an interview for their opinion towards the learning unit.

5.5 Data Collection and Analysis

Students’ conceptual understanding and perception of the DSSC learning unit were collected and summarized. Students’ conceptual understanding data, pre- and post-test scores, were processed statistically. Qualitative data including journal writing, interviews, and students’ suggestions or difficulties in doing each activity were used to describe students’ perception and used to support the statistical findings.

5.6 Results

5.6.1 The DSSC Learning Unit

The DSSC learning unit was developed as an interdisciplinary learning unit which integrated two main disciplines, Physics and Chemistry. The learning unit was designed as the introduction course. The learning unit involved many concepts such as electricity, light, semiconductor, atomic structure, band energy, p-type and n-type semiconductor, p-n junction, redox reaction, and properties of nanomaterials. The learning process of this learning unit is based on an inquiry approach which used questions to guide students to the learning goals. The role of the teacher (researcher) was to be a facilitator that is to provide students with learning tools and activities. The keys of this learning unit were the simple activities, group discussion, and the guiding questions that allow students to practice both scientific thinking and science process skills.

5.6.2 Students' Conceptual Understanding and Students' Perception of the DSSC learning unit

The effectiveness of the learning unit on the student's conceptual understanding as well as their perception and preferences were investigated. The effect of the Learning unit on students' conceptual understanding was evaluated using the pre-test and post-test. The perception and preferences were investigated using journal writing and interviews.

Table 5.1 T-test results of the Pre- and Post-test scores of the DSSC learning unit

Topic	**Mean**		**t-test**	**p-value**
	Pre-test	**Post-test**		
Electricity	1.38 ± 0.80	2.28 ±0.75	3.80	.001
Light	0.49 ±0.33	0.88 ±0.28	4.32	.000
Conventional Solar cell	0.56 ± 0.51	2.38 ±1.01	6.72	.000
Dye-Sensitized Solar Cell	0.64 ±0.54	1.46 ±0.57	5.49	.000
Total	3.07 ±1.31	6.98 ±1.36	10.63	.000

*total score = 12

The paired-samples t-test was used to test the significant difference of the gained scores. The mean pre-test scores of the students are lower than the mean post-test scores. The t-test results of mean pre- and post-test scores of the students in both topics showed that the difference of mean pre- and post-test scores were of significant at the 0.05 level. This indicates the enhancement of students' conceptual understanding.

The perception and preferences were investigated using journal writing and interviews. The journal notes were coded to identify themes. Results were shown in Table 5.2.

Table 5.2 Students' journal writing on the DSSC learning unit

Topic	Answers from students (%)
1. The learning unit is interesting and meaningful.	75
2. The learning activities help me understand more about solar cells and related concepts.	85
3. The learning unit is a bit difficult because mostly they are new concepts which was never learnt before.	15
4. I want to learn more or research in this topic.	25

***** N=20

The results in Table 5.2 show the percentage of the coded theme from the students' journal which were collected after the implementation of the learning unit; 75 % of students thought the learning unit was interesting and meaningful, 85 % of them agreed that the learning unit helped them to understand more about solar cells and related concepts.

Regarding to the investigation of the perception about the learning unit, four students were interviewed. They were asked to express their opinions towards the learning unit. Results of the interview data showed that students had positive attitude regarding adopting the DSSC learning unit. Their responses showed their positive attitudes: 1) students explained that the learning activities provided an opportunity for them to refine their understanding of some science concepts; 2) students learned what they had never known before; 3) the learning activities were simple but interesting and meaningful because of it is related to real life; 4) the learning activities allowed them think and come up with new ideas by themselves;

and 5) most of the students said that they are able to learn science better because they have to think more, and conduct experiments by themselves.

5.7 Discussion

The DSSC learning unit was developed and implemented. The findings of this study showed an enhancement of the conceptual understanding about solar cells and related concepts. In addition, the students had positive attitude toward the learning unit.

In regarding to students' conceptual understanding, the mean pre-test scores of the students were lower than post-test scores. The p-value ,of pre- and post-test scores showed that the mean pre- and post-tests scores of the students were of significant difference at the 0.05 level. This indicates the enhancement of the students' conceptual understanding. The advantage of an inquiry instructional approach on the enhancement of the student understanding was similar to those reported by references [174-177]. Hofstein & Lunetta and Tobin pointed out that the significant benefits of providing students' opportunity to perform hands-on laboratory investigations can promote students' understanding of complex concepts as well as enhance their interest and motivation [178, 179]. Stohr-Hunt claimed that students who did hands-on activities once or twice a week gained more standard test scores than students who did hands-on activities 2-3 weeks a time [180].

The students who did activities through the learning unit had positive attitude toward the learning unit. This resulted from the learning approaches used in this learning unit. The keys instructional approaches of the learning unit are the class discussion about the events or simple demonstrations. The information of the discussion will be drawn from what students already know. The purpose of the discussion was to make students come up with knowledge or ideas by themselves. These situations which allowed students actively build their own knowledge based on their current and prior knowledge support the constructivist learning [181-183] and make the meaningful learning to students, affected on the student's attitude and also enhance the student's conceptual understanding.

Moreover, the developed learning unit not only provides an opportunity for students to perform hands-on activities, but also let them practice scientific thinking skill through a group or class discussion using guiding questions. The discussions help students to understand the connections between science and the real world and better able to transfer knowledge to different contexts [45]. Additionally, the content of the learning unit “solar cells” which is about alternative energy source is considered to be more closely related to students’ experiences in real life outside their classroom, and hence, enhance engagement which will effect students’ attitude [46].

5.8 Limitation of the Study

The implementation of the learning unit was conducted without comparing student outcomes with a control group. The results in this study are only preliminary and should be confirmed with other teachers and other groups of students with larger number of participants. However, the overall findings, enhancement of student’s conceptual understanding and student’s positive attitude toward the learning unit, indicate the successfulness of the learning unit implementation. This learning unit can be used as a guideline for developing other interdisciplinary learning unit to motivate and help students to learn science.

5.9 Recommendations

1. This study was a preliminary research. There were only 20 participants involved. To ensure the effectiveness of the learning unit with reliability, additional group of larger number of students in different school and areas should be included in the future study.

2. This interdisciplinary learning unit was developed as an introduction course for first year undergraduate students with a general concept. The future study can adapt this learning unit as an interdisciplinary learning unit for high school student to help encourage or motivate student to learn science.

3. The interdisciplinary learning unit not only can enhance the students' conceptual understanding but also reflect the nature of problem in everyday life, which requires an integration of all information or knowledge to get the best solution for future situations and problems. From document searching, there are only few examples of an interdisciplinary learning unit. The teachers and science educators could develop more interdisciplinary leaning unit to help students to learn science, get more experience, and prepare them for lifelong learning.

4. To increase the effectiveness of interdisciplinary learning unit, teachers should be well trained for teaching both knowledge and pedagogy, as well as, teaching method and environment to help students develop their understanding.

CHAPTER VI

CONCLUSION

Overview

This chapter concludes the main findings of the research. It is divided into two parts: scientific part and educational part.

6.1 Scientific Aspect

6.1.1 ZnO NW-NP hybrid nanostructured photoanodes for DSSC

The hybrid ZnO NW-NP photoanode for DSSC has been fabricated and investigated to improve the power conversion efficiency. The hybrid nanostructured photoanode composed of ~11 μm length ZnO NW arrays to serve as a direct pathway for fast electron transport and ZnO NPs (7-10 nm) dispersed and filled the gaps between ZnO NWs to offer a high surface area for sufficient dye adsorption. The overall power conversion efficiency of DSSC with the N3-sensitized ZnO hybrid nanostructured photoanode has reached ~ 4.2%, with V_{oc} of ~613 mV, J_{sc} of ~15.2 mA/cm^2, and a fill factor of ~ 46%, far higher than ~1.58 % of ZnO NW DSSC, and ~1.31 % of ZnO NP DSSC, prepared and tested under otherwise identical conditions and all without chemical modification nor antireflection coating. The remarkably improved solar cell performance is attributed mainly to the improvement in J_{sc} which can be explained by the high surface area and fast electron transport of ZnO hybrid nanostructured photoanodes.

6.1.2 Enhanced photovoltaic performance of hybrid solar cell using highly oriented TiO_2 NTs

Highly oriented TiO_2 NTs have been fabricated using ZnO NR template through liquid reactive deposition on ITO substrates. The diameter and length of TiO_2 NTs can be effectively controlled for the suitable use in a hybrid solar cell by varying the diameter and length of the ZnO NR template. A mixture of P3HT/PCBM was infiltrated into the gaps between TiO_2 NTs to form the hybrid solar cell with the double heterojunction between P3HT and TiO_2 and P3HT and PCBM. The presence of P3HT-TiO_2 heterojunction provides an additional interface as compared to conventional polymer-based photovoltaics, so as to increase the J_{sc}. The V_{OC} , J_{sc}, fill factor and power conversion efficiency of the hybrid solar cell using highly oriented TiO_2 NTs were 646 mV, 9.95 $mA.cm^{-2}$, 51.6% and 3.32%, respectively, much higher than 1.2% of ZnO NRs based hybrid solar cell, tested under otherwise identical conditions, and significantly higher than 0.7% of the same type hybrid solar cells reported in literature [167]. Such an enhancement in power conversion efficiency is attributed to smaller diameter of TiO_2 NTs with high density, yet well spaced for efficient penetration of polymer solution. Further improvement in device performance can be achieved by growing vertically oriented TiO_2 NT array and/or by organic/inorganic interface modification.

6.2 Educational Aspect

The DSSC learning unit was developed to promote student understanding about the concept of energy transformation in the form of sunlight into electrical energy and the concepts related to solar cells i.e., electricity, light, semiconductor, atomic structure, and band energy. The learning unit was developed based on an inquiry learning approach. The key instructional approach of the learning unit was the class discussion which using guiding questions as guideline. The DSSC learning unit not only provide an opportunity for students to perform hands-on activities, but also let them practiced scientific thinking skill through group or class discussion. The finding of this study showed a significant improvement from the pre-test to the post-test. The p-value scored from the pre-test and post-test of the students were of significant difference at the 0.05 level. This indicated the enhancement of the students' conceptual understanding. In addition, students' journal writing and students' interview showed that the students have positive attitude toward the learning unit.

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APPENDIX

Experimental Data: SEM images of ZnO and TiO_2

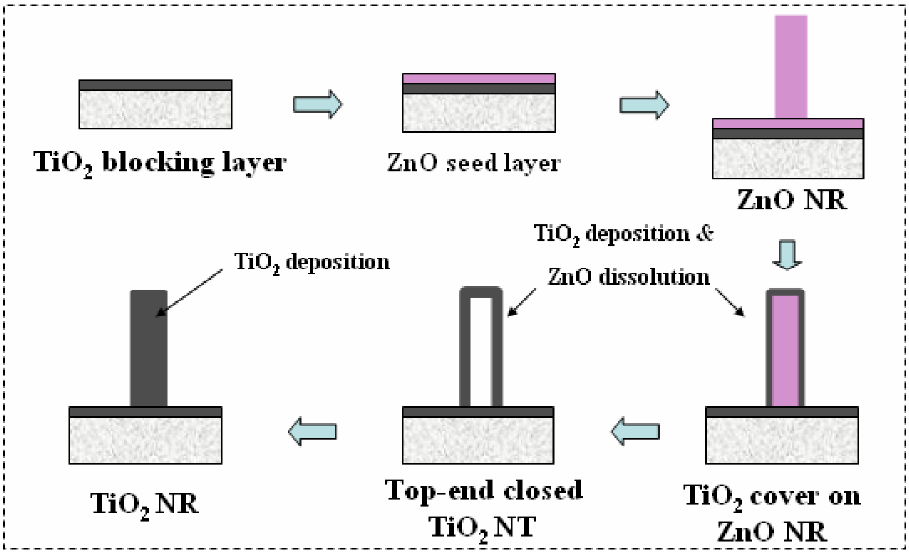

Figure A.1 The step to prepare TiO_2 NTs using ZnO NR template

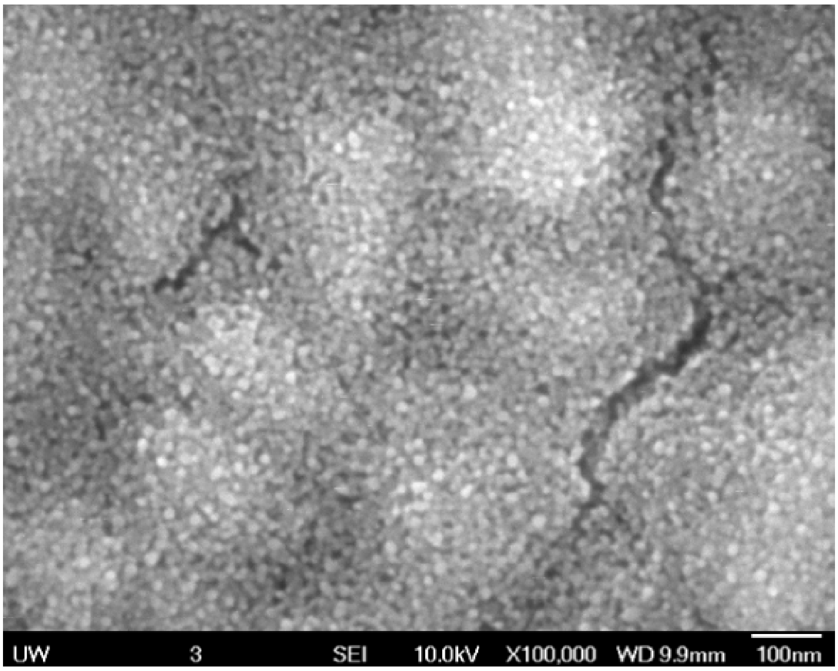

Figure A.2 SEM image of ZnO seed layer

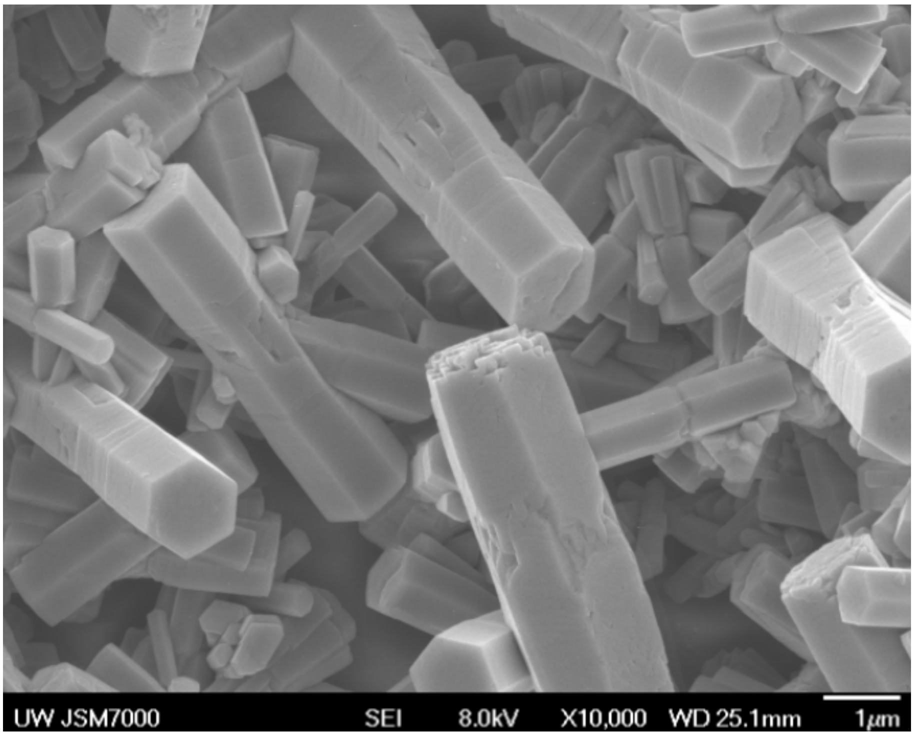

Figure A.3 SEM image of ZnO NRs grown without ZnO seed layer

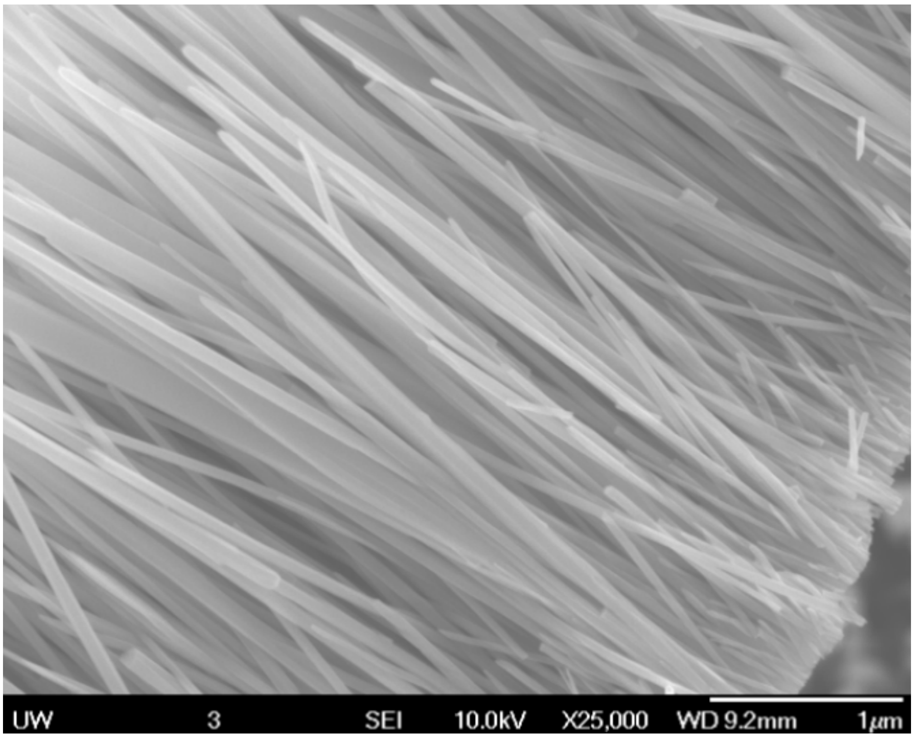

Figure A.4 SEM image of ZnO NRs grown with ZnO seed layer

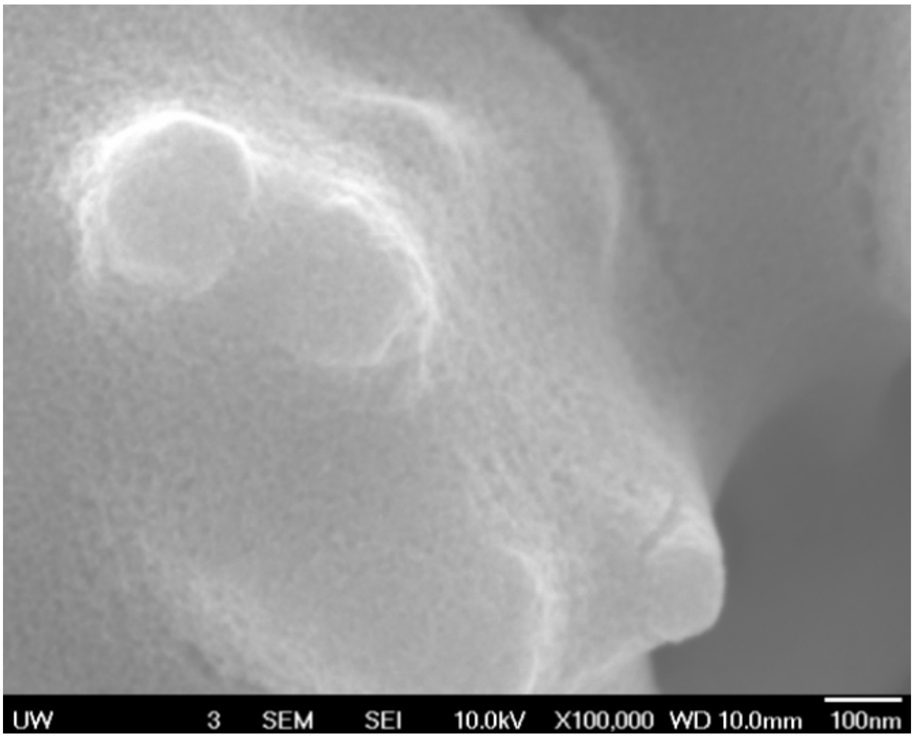

Figure A.5 SEM image of ZnO NPs cover on the surface of ZnO NWs

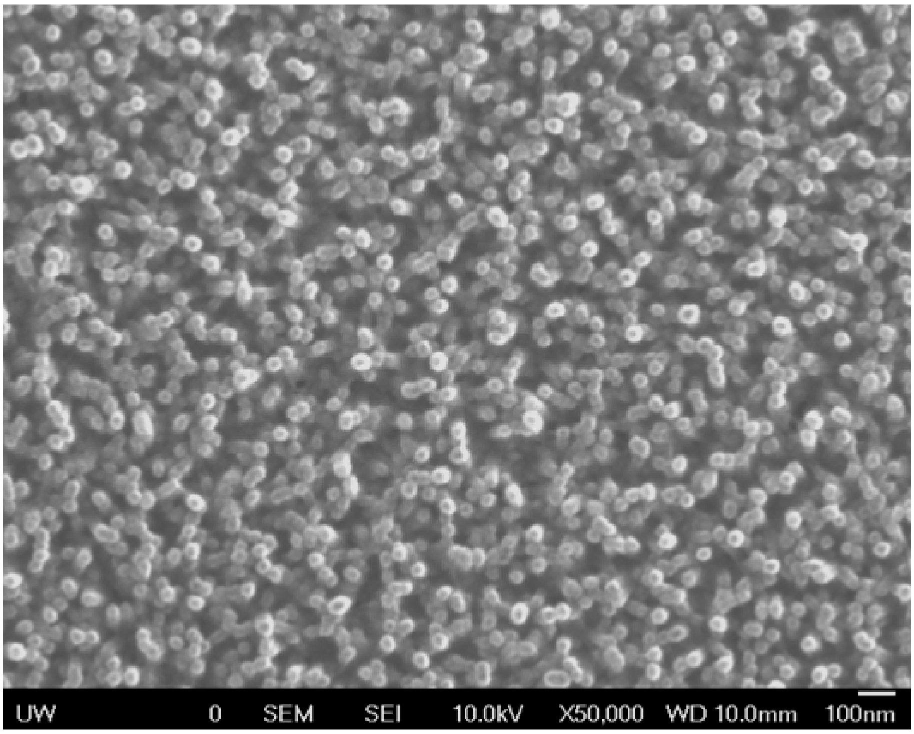

Figure A.6 SEM image of small diameter TiO_2 NTs

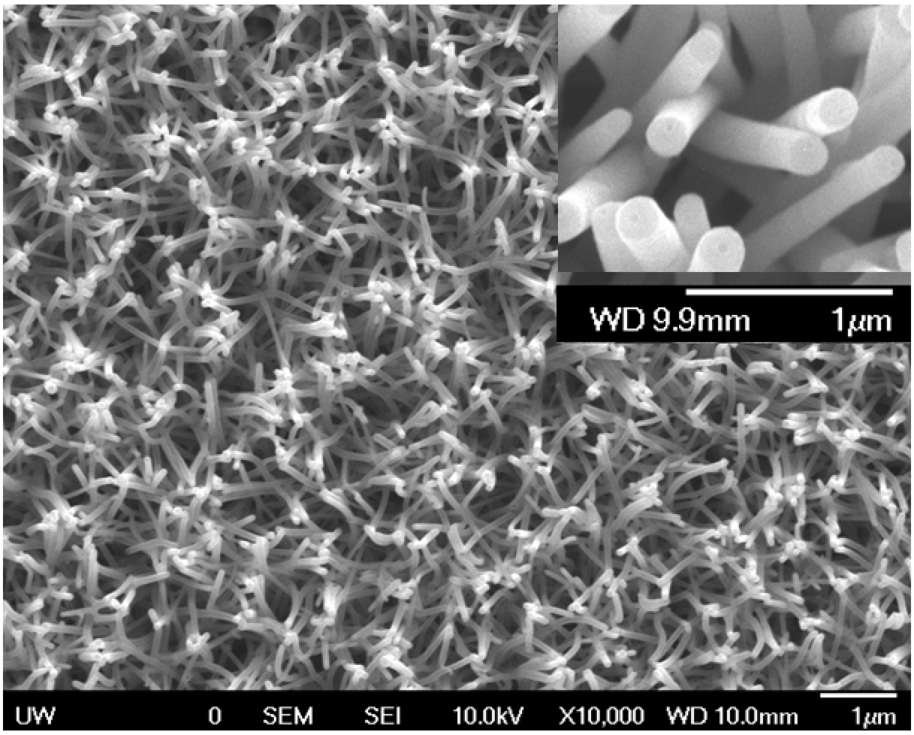

Figure A.7 SEM image of top-end close TiO_2 NTs

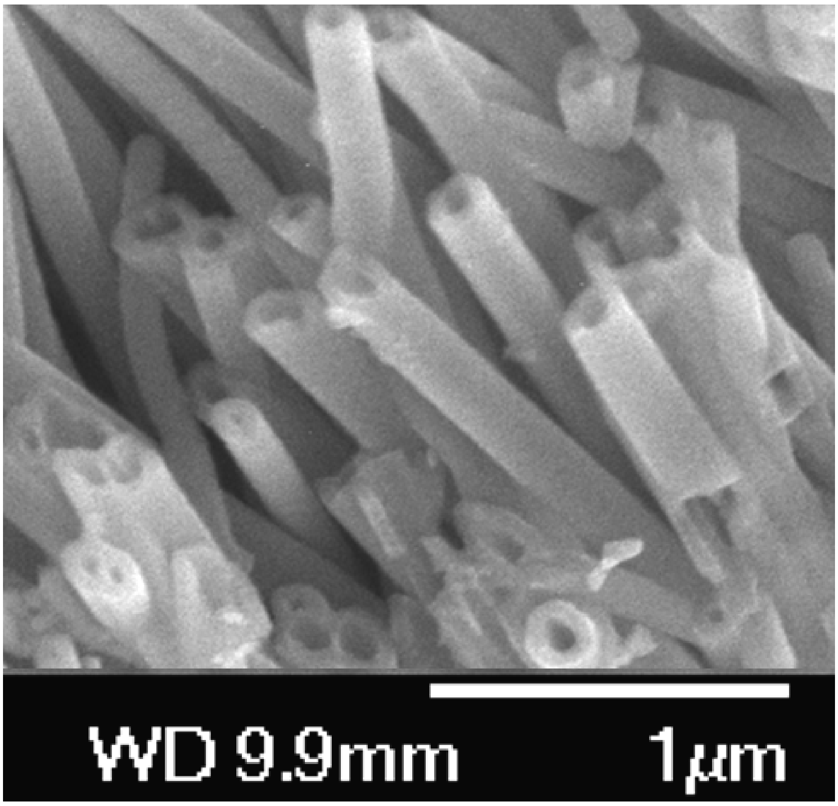

Figure A.8 SEM image of TiO_2 NTs

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PUBLICATIONS/PRESENTATION

1. **Yodyingyong, S**.; Panijpan, B.; Triampo, W.; Triampo, D., An Inexpensive Furnace for Calcination: Simple TiO_2 Synthesis. *Journal of Chemical Education* **2009,** 86, (8), 950-952. **(cover page)**
2. **Yodyingyong, S**.; Zhang, Q.; Park, K.; Dandeneau, C. S.; Zhou, X.; Triampo, D.; Cao, G., ZnO nanoparticles and nanowire array hybrid photoanodes for dye-sensitized solar cells. *Applied Physics Letters* **2010,** 96, (7), 073115-3.
3. **Yodyingyong, S**.; Zhou, X.; Zhang, Q.; Triampo, D.; Xi, J.; Park, K.; Limketkai, B.; Cao, G., Enhanced photovoltaic performance of nanostructured hybrid

solar cell using highly oriented TiO2 nanotubes. *The journal of physical chemistry C.* **(accepted)**

4. **Yodyingyong,S**.; Panijpan, B., & Dahsah, C. (2007, 6-9 November). Teaching an instrumental overview of gas chromatograph (GC) based on guided-inquiry approach. In Proceeding from ICASE Asian Symposium 2007. Pattaya, Thailand. (Proceeding)
5. **Yodyingyong, S.**; Zhang, Q.; Park, K.; Dandeneau, C. S.; Zhou, X.; Triampo, D.; Cao, G. (2010, 21-25 April). ZnO composite photoelectrodes for dye-sensitized solar cells with high power conversion efficiency. Paper presented at the 239th ACS National Meeting and Exposition, San Francisco, USA.