

Republic of Iraq Ministry of Higher Education and Scientific Research University of Diyala–College of Science Department of Physics



# Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Optimizing the Preparation Parameters

A Thesis

Submitted to the Council of the College of Science

University of Diyala in Partial Fulfillment

of the Requirements for the Degree of M.Sc. in Physics

By

Shaimaa Mufeed Jassim

**B.Sc. in Physics, 2007** 

Supervised by

Prof. Nabeel A. Bakr, Ph.D. Assist.Prof. Abdulrahman K. Ali, Ph.D.



1438 A.H.

## **CERTIFICATION**

We certify that this thesis entitled "Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Optimizing the Preparation Parameters" was prepared by "Shaymaa Mufeed Jasim" under our supervision at the University of Diyala / College of Sciences / Department of Physics as a partial fulfillment of the requirements for the Degree of Master of science in Physics.

Signature: Name: Dr. Nabeel A. Bakr Title: Professor Date: / / 2016 Signature: Name: Dr. Abdulrahman K. Ali Title: Assistant Professor Date: / / 2016

### Head of the Physics Department

In view of the available recommendation, I forward this thesis for debate by the examining committee.

### Signature:

Name: Dr. Ziad T. Khodair Title: Assistant professor Date: / / 2016



I certify that the thesis entitled "Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Optimizing the Preparation Parameters" presented by *(Shaimaa Mufeed Jassim)* has been evaluated scientifically, therefore, it is suitable for debate by examining committee.

### Signature:

Name:Dr. Odai N. Salman

Title:Lecturer

Address: University of Technology / Applied Science Department

**Date:** / / 2016



I certify that the thesis entitled "Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Optimizing the Preparation Parameters" presented by (*Shaimaa Mufeed Jassim*) has been corrected linguistically, therefore, it is suitable for debate by examining committee.

### Signature:

Name:Dr. Liqaa Habeeb

Title: Inst. Dr.

Address: University of Diyala / College of Education for Human Sciences

Date:/ / 2016

#### **Examination Committee Certificate**

We certify, that we have read the thesis entitled "Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Optimizing the Preparation Parameters", presented by (*Shaimaa Mufeed Jassim*) and as an examining committee, we examined the student on its contents, and in what is related to it, and that in our opinion it meets the standard of a thesis for the degree of master in Physics Sciences.

#### (Chairman)

Signature:

Name: Dr. Raid A. Ismail Title: Professor Date: / / 2017

#### (Member)

Signature:

Name: Dr. FalahI. Mustafa Title: Senior Researcher Date: / / 2017

#### (Member/Supervisor)

Signature: Name: Dr. Nabeel A. Bakr Title: Professor Date: / / 2017

#### (Member)

Signature: Name: Asaad A. Kamil Title: Professor Date: / / 2017

#### (Member/Supervisor)

Signature: Name: Dr. Abdulrahman K. Ali Title: Assistant Professor Date: / / 2017

Approved by the Council of the College of Science

#### (The Dean)

Signature: Name: Dr. Tahseen H. Mubarak Title: Assistant Professor Date: / / 2017



هُوَ الَّذِي جَعَلَ الشَّمْسَ ضِيَاءَ وَالقَمَرَ نُورًا وَقَدَّرَهُ مَنَازِلَ لِتَعْلَمُوا عَدَدَ السِّنِينَ وَالحِسَابَ مَا خَلَقَ اللهُ ذَلِكَ إِلَّا بِالحَقِّ يُفَصِّلُ الآَيَاتِ لِقَوْمٍ يَعْلَمُونَ

(يونس – ايه ٥)

## DEDICATION

To:

The teacher and the source of human knowledge of our Prophet Muhammad (peace be upon him) <u>To:</u>

> The lights of my life My father and my mother

> > To:

The soul of my beloved brother (Muhammad)

To:

The lights of my eyes Brothers and sisters

## To:

My beloved country Iraq The martyrs of Iraq with all the love and appreciation

Shaimaa



## Acknowledgments

First of all, I would like to thank ALLAH for his generosity and mercy in giving the strength and the ability to complete my studies successfully and sincerest words of thanks to Prophet Muhammad (peace and blessings of Allah be upon him) who is forever a torch of guidance and Knowledge for the humanity.

Praises and thanks belong only to ALLAH (S.W.T) for giving me this excellent opportunity to meet and work with marvelous people: Sincere Dr. Nabeel A. Bakr and sincere Dr. Abdulrahman K. Ali. I am immensely grateful for their support, insight, guidance and encouragement at all times therefore special thanks to them, without them, I may not be able to complete this study.

Special thanks are extended to the Dean of the College of Science and all the staff of Department of Physics for their assistance.

Special thanks to the head of the physics department Dr. Ziad T. Khodair and Dr. Sabah Anwar Salman.

Special thanks to Dr. Khaleel Ibrahim in the University of Technology for helping me.

My thanks due to my family for their unwavering support through the whole adventure; I could not have done it without them (my father, my *mother*).

Special thanks to Dr.Abdul Kareem in University of Baghdad and Dr. Mohammad Odeh in University of Mustansiriya.

I am also grateful to the physics Department at the College of Education Ibn al-Haytham for their kind help during the X-ray tests.



Finally, I thank all my classmates and I wish them success and I would also express my deep sense of gratitude to Shahlaa, Chia, Marwaa, Sahar, Heyam and Abdulwahab.

## Shaimaa



# List of Abbreviations

Abbreviation	Definition	
DSSC	Dye Sensitized Solar Cell	
Ru	Ruthenium	
PEC	Photoelectrochemical	
AM1.5	Solar radiation at the earth's surface when the solar rays	
	make an angle of $48.2^{\circ}$ with the vertical	
CNTs	Carbon nanotubes	
ITO	Indium-doped tin oxide	
FTO	Fluorine-doped tin oxide	
CE	Counter electrode	
ClO <sub>4</sub> PEDOT	$ClO_4^-$ -poly (3,4- ethylenedioxythiophene)	
TNTs	TiO <sub>2</sub> nanotubes	
HPVC	Horizontal Vapor Phase Crystal	
SEM	Scanning Electron Microscopy	
XRD	X-Ray Diffraction	
FTIR	Fourier Transform Infrared	
UV-Vis	Ultraviolet-Visible	
TEM	Transmission Electron Microscopy	
Ag NPs	Silver nanoparticles	
SPD	Spry Pyrolysis Deposition	
PEG	Polyethylene glycol	
ОМ	Optical Microscope	

Ι

TGA	Thermal Gravimetric Analysis	
Au NPs	Gold nanoparticles	
PLAL	Pulsed Laser Ablation in Liquid	
N719	[RuL <sub>2</sub> (NCS) <sub>2</sub> ]: 2TBA (L=2,2'-bipyridyl-4,4'-	
7007	dicarboxylic acid; TBA=tetra- <i>n</i> -butylammonium)	
2907	$RuLL'(NCS)_2$ (L=2,2'-bipyridyl-4,4'-dicarboxylic	
A N / 1	acid;L'=4,4'-dinonyl-2,2'-bipyridine)	
AIVII	Solar radiation at the surface with the sun directly	
ΔΜΟ	Overhead in a clear sky Solar radiation in the space outside the earth	
AIVIU	Solar radiation in the space outside the earth	
c-Si	Crystalline silicon	
PVs	Photovoltaics	
a-Si	Amorphous silicon	
CIGS	Copper Indium Gallium Selenide	
ТСО	Transparent Conductive Oxide	
hv	Photon energy	
e <sub>CB</sub>	Electron in conduction band	
СВ	Conduction band	
VB	Valance band	
LUMO	Lowest unoccupied molecular orbital	
НОМО	Highest occupied molecular orbital	
redox	Reduction-oxidation	
R <sub>s</sub>	Series resistance	
R <sub>Sh</sub>	Shunt resistance	
FWHM	Full Width at Half Maximum	

Π

SPR	Surface plasmon resonance
LSPR	Localized surface plasmon resonance
CO.	Company
Nd: YAG	Neodymium-doped yttrium aluminum garnet laser
TBA	Tetra Butyl Ammonium
ICDD	International Centre for Diffraction Data
3-D	Three-dimensional
RMS	Root mean square

# List of Symbols

Symbol	Meaning	Units
η	Solar cell efficiency	%
J <sub>SC</sub>	Short – circuit current density	mA/cm <sup>2</sup>
IPCE	Incident photon to current conversion efficiency	%
I-V	Current-Voltage	-
FF	Fill Factor	%
V <sub>OC</sub>	Open circuit voltage	V
$\theta_{e}$	Elevation angle	degree
Eg	Energy gap	eV
I-	Iodide	-
I <sup>-</sup> 3	Triiodide	-
S	Ground state of the sensitizer	-
S*	Excited state of the sensitizer	-
S+	Oxidized sensitizer	-
I <sub>SC</sub>	Short circuit current	mA
V <sub>max</sub>	Voltage at maximum power point	V
I <sub>max</sub>	Maximum current	mA
J-V	Current density-Voltage	-
A	Area	cm <sup>2</sup>
N <sub>CB</sub>	The effective density of states	-

q	The absolute value of electronic charge	-
K <sub>B</sub>	Boltzmann's constant	J/K
Т	The absolute temperature	K
т	The number of electrons in semiconductor	-
	conduction band	
$E_{redox}$	The nernst potential of the redox mediator	-
J <sub>max</sub>	The current density at maximum power point	mA/cm <sup>2</sup>
P <sub>max</sub>	Maximum power	mW/cm <sup>2</sup>
P <sub>in</sub>	The incident power	mW/cm <sup>2</sup>
$\lambda_{ph}$	The incident photon wavelength	nm
R	The spectral response	μA/μw
I <sub>L</sub>	Light induced current	mA
I <sub>D</sub>	Diode current	mA
I <sub>Sh</sub>	Shunt current	mA
А	Absorbance	-
Т	Transmittance	-
I <sub>T</sub>	Transmitted light intensity	mW/cm <sup>2</sup>
Io	Incident light intensity	mW/cm <sup>2</sup>
Р	Constant	-
α	Optical absorption coefficient	cm <sup>-1</sup>
hv	Photon energy	eV
h	Plank 's constant	J/sec

V

n	Integer number	-
λ	The wavelength of the incident X-ray	nm
$d_{hkl}$	Interplannar spacing	Å
θ	Bragg's angle	degree
hkl	Miller indices	-
a, c	Lattice constants	Å
D	The crystallite size	nm
K	Scherrer's constant	-
β	Full width at half maximum	rad

# **List of Figures**

Fig.	Figure Caption	Page
<u>No.</u> 2-1	Solar spectrum, and the spectrum of a	<u>No.</u> 13
	black body of at T=5800 K	10
2.2		14
2-2	Designation of Solar Air Masses	14
2-3	Cross-section of a basic solar cell	15
2-4	The generations of solar cells	16
2-5	Progression of efficiencies for a variety of PV	18
	technologies	
2-6	Typical configuration of a DSSC	19
27	Crystal structures of (a) rutile (b) anatase and (c)	20
2-1	Legel ite	20
	brookite	
2-8	Operation principle of DSSC	23
2-9	Typical voltage-current characteristics of a solar cell	26
2-10	Example of an IPCE curve generated from a DSSC	29
2-11	Equivalent circuit of a solar cell including series and	29
	shunt resistances	
2-12	Effect of (a) increasing series and	30
	(b) reducing parallel resistances	
2-13	Preparation of nanoparticles by PLAL method	34
2-14	Influence of particle size on colloidal color	36
3-1	The diagram of the experimental work	39

3-2	Photograph of the experimental setup for laser ablation of gold in ethanol	41
3-3	Flowchart of DSSCs preparation steps	42
3-4	The preparation procedure of working electrode (a) scotch tape placed on the two sides of the conductive face of substrate, (b) the $TiO_2$ paste was placed on uncovered area of the substrate, (c) applied doctor- blade method to deposition titanium paste, (d) and (e) the scotch tape was removed and the films were left under Pertidish and (f) the $TiO_2$ substrates were annealed in programmed electrical furnace	44
3-5	Pt paste on FTO glass	45
3-6	Molecular structure of N/19 and Z907 dyes	46
3-7	Preparation steps of dyed electrode (anode). (a) The photoanodes were immersed in the dye solutions, and then kept 24 hours on a dark place at room temperature to adsorb the dye molecules on to the $TiO_2$ surface, (b) All samples were rinsed with ethanol to remove the dye residues, (c) the $TiO_2$ electrodes turned to a maroon-black color after immersion	47
3-8	Final form of DSSCs before test	48
3-9	UV –Vis spectrophotometer used in the current study	49
3-10	X-ray diffraction instrument used in the present study	50
3-11	SEM instrument used in this study	51
3-12	AFM instrument used in the current study	51
3-13	TEM instrument used in characterizing Au nanoparticles	52

# VIII

3-14	Schematic for electrical instrument used in the	53
	current density	
3-15	Schematic diagram to measure IPCE and R	54
4-1	UV-Vis absorption spectra of N719, Z907 and their	55
	mixed solutions (1:1 v/v ratio)	
4-2	Optical absorption spectra of Z907 dye solution, Au	56
	NPs colloidal solutions and their mixed solution (1:1	
	v/v)	
4-3	UV-Vis absorption spectra of TiO <sub>2</sub> films at as-	57
	deposited and different annealing temperatures	
4-4	$(\alpha h\nu)^2$ vs. energy curves of TiO <sub>2</sub> films as-deposited,	59
	and annealed at 350 °C and 550 °C.	
4-5	UV- Vis absorption spectra of DSSCs using different	60
	dyes and their mixture	
4-6	UV-Vis absorption spectra of DSSCs at different	61
	TiO <sub>2</sub> layer thicknesses	
4-7	XRD patterns of TiO <sub>2</sub> films	63
4-8	Standard card no. (21-1272) of TiO <sub>2</sub>	63
4-9	SEM image of TiO <sub>2</sub> film at 30,000X	65
4-10	(a) TEM image and (b) histogram corresponding to	66
	by 1064 nm laser ablation of a gold metal plate in	
	ethanol for (700) pulses	~-
4-11	3-D AFM images and Granularity accumulation	67
	distribution charts of $T_1O_2$ thin films (a) as-deposited,	
	annealed at (b) 350 °C and (c) 550 °C	
4-12	J-V curves of DSSCs using various TiO <sub>2</sub> film	70
	thicknesses	
4-13	J-V curves of DSSCs using different dye concentrations	72

4-14	J-V curves of DSSCs using N719, Z907 and mixture	73
	dyes (N719 + Z907, 1:1 v/v)	
4-15	J-V curves of DSSCs using TEC substrates	75
4-16	J-V curves of DSSCs with and without Au NPs	77
4-17	J-V curves of DSSCs using front and back side of substrate	77
4-18	IPCE as a function of wavelength of the DSSC	80
4-19	Spectral response curve of DSSC	80
4-20	High transparency of DSSC (a,b and c ) images taken	81
	through DSSC for flowers and thesis subject	

# **List of Tables**

Table No	Table caption	Page No
2-1	general properties of TiO <sub>2</sub>	20
3-1	DSSC components from Dyesol company	40
4-1	XRD results of TiO <sub>2</sub> films	64
4-2	Average roughness, root mean square (RMS) and grain size of $TiO_2$ films by AFM technique	68
4-3	The photovoltaic parameters of DSSCs fabricated using different thicknesses of TiO <sub>2</sub> thin films	70
4-4	The photovoltaic parameters of DSSCs fabricated using different concentrations of N719 dye solution	72
4-5	The photovoltaic parameters of DSSCs fabricated using N719, Z907, and mixture dye (N719+Z907, 1:1 v/v)	74
4-6	The photovoltaic parameters of DSSCs fabricated using different TEC substrates	76
4-7	The photovoltaic parameters of DSSCs with and without Au NPs	77
4-8	The photovoltaic parameters of DSSCs of front, back face and angle $45^{\circ}$	79

	Table of Contents	
	Subject	Page No.
of Contents		

Table of Contents	
List of Abbreviations	I
List of Symbols	IV
List of Figures	VII
List of Tables	XI

Item No.	Subject	Page No.
Chap	ter One: Introduction and Literature Revie	ew
1-1	Introduction	1
1-2	Literature Review	2
1-3	Aim of the work	11
Chapt	ter Two: Theoretical Part	
2-1	Introduction	12
2-2	The Solar Spectrum	12
2-3	Solar Cells	14

2-4	Generations of Solar Cells	15
2-4-1	First Generation Photovoltaics	16
2-4-2	Second Generation Photovoltaics	17
2-4-3	Third Generation Photovoltaics	17
2-5	The Structure of DSSC	18
2-5-1	Transparent Conductive Oxide Substrate (TCO)	18
2-5-2	TiO <sub>2</sub> Nanoparticles	19
2-5-3	Dyes	21
2-5-4	Electrolyte	21
2-5-5	Counter Electrode	22
2-5-6	Sealing Material	22
2-6	Operation Principle of Dye Sensitized Solar Cells (DSSCs)	22
2-7	Dye-Sensitized Solar Cell Performance	24
2-7-1	Short Circuit Current (Isc)	24
2-7-2	Short–Circuit Current Density (J <sub>SC</sub> )	25
2-7-3	Open-Circuit Voltage (V <sub>OC</sub> )	25
2-7-4	Maximum Voltage (V <sub>max</sub> )	26
2-7-5	Maximum Current ( I <sub>max</sub> )	26
2-7-6	Fill Factor	27

2-7-7	Power Conversion Efficiency (η )	27
2-7-8	Incident Photon-Current Conversion Efficiency	28
	(IPCE) and Spectral Response	
2-8	The Equivalent Circuit of Solar Cell	29
2-9	Optical Properties	31
2-9-1	Absorbance (A)	31
2-9-2	Optical Energy Gap (Eg)	32
2-10	Structure of Thin Film	32
2-11	Pulsed Laser Ablation in Liquid	34
2-12	Gold Nanoparticles	35
2-13	Surface Plasmon Resonance in Metallic	36
2-14	Applications of Dye-sensitized Solar Cells	37
Chapte	er Three: Experimental Procedure	
3-1	Introduction	39
3-2	Experimental Work	39
3-3	Materials	40
3-4	Gold Nanoparticles (Au NPs) Preparation	41
3-5	Preparation of DSSC	42
3-5-1	Glass Substrates Preparation	42
3-5-2	Preparation of Working Electrodes (Photoanode)	43
3-5-3	Preparation of Counter Electrodes (Cathode)	45

3-5-4	Preparation of Dye Solutions	45
3-5-5	Cell Assembly	48
3-6	Characterization Techniques	49
3-6-1	UV-Vis Spectroscopy	49
3-6-2	X-ray Diffraction	50
3-6-3	Scanning Electron Microscope (SEM)	50
3-6-4	Atomic Force Microscope (AFM) Measurements	51
3-6-5	Transmission Electron Microscopy (TEM) Measurements	52
3-6-6	Current-Voltage Measurements	52
3-6-7	IPCE and Spectral Response Measurements	53

# **Chapter Four: Results and Discussion**

4-1	Introduction	55
4-2	Optical Properties	55
4-2-1	Absorption of Dyes	55
4-2-2	Absorption Characterizations of Au NPs	56
4-2-3	Absorption of TiO <sub>2</sub> films	57
4-2-4	Effect of Dye Type on DSSCs Absorption	60
4-2-5	Effect of TiO <sub>2</sub> Layer Thickness on the Absorption of DSSCs	61

4-3	Structural Properties	61
4-3-1	X-ray Diffraction Analysis	61
4-3-2	Scanning Electron Microscope (SEM) Analysis	64
4-3-3	TEM Analysis of Au NPs	65
4-3-4	AFM Analysis of TiO <sub>2</sub> Thin Films	67
4-4	J-V Characteristics of DSSCs	69
4-4-1	The Effect of TiO <sub>2</sub> Thickness on DSSC Efficiency	69
4-4-2	The Effect of Dye Concentration on DSSCEfficiency	71
4-4-3	The Effect of Dyes Mixing on DSSC Efficiency	73
4-4-4	The Effect of Substrate Resistance on DSSCs Efficiency	74
4-4-5	The Effect of Au NPs on DSSCs Efficiency	76
4-4-6	The Effect of Two-Faces on the Efficiency of DSSCs	77
4-4-7	IPCE Measurement of DSSC	79
4-4-8	Spectral Response (R) of DSSC	80
4-5	Optical Transparency of DSSC	81
4-6	Conclusions	82
4-7	Future Works	82

References

84

List of publications



Dye sensitized solar cell (DSSC) is a third generation solar cell type. Its working principle is based on conversion sunlight to electrical energy.

In this work, dye sensitized solar cells (DSSCs) have been fabricated. Deposition of TiO<sub>2</sub> paste on fluorine tin oxide (FTO) substrate was done by Doctor-blade technique. TiO<sub>2</sub> film was annealed at 550 °C for 30 minutes and after annealing immersed in dye solution for 24 hours, to get photo electrode (anode). Platinum (Pt) paste was deposited on FTO substrate and annealed at 450 °C for 30 minutes to get counter electrode (cathode). Finally, photo and counter electrodes were assembled in sandwich form with electrolyte injection through holes. Also, we improve the performance of DSSC by studying the effects of the following parameters: TiO<sub>2</sub> thickness, concentration of N719 dye, mixture dyes (N719 and Z907), use TEC- 8  $\Omega$  substrate and adding gold nanoparticles, prepared by pulsed laser ablation in liquid, to the dye.

UV-Vis spectra results show that the absorption of DSSC was enhanced with dyes mixture, adding Au NPs and the increase in dye concentration, as well as the absorption of  $TiO_2$  film increased with increasing annealing temperature.

The optical direct transition band gap  $(E_g)$  of the TiO<sub>2</sub> films has been found to increase from 2.30 eV to 3.12 eV with increasing temperature.

XRD results confirmed that all the prepared of  $TiO_2$  films are in anatase phase and the highest peak was at (101) plane.

(AFM) results show that the roughness and root mean square for  $TiO_2$  films decrease with increasing annealing temperature. SEM image for  $TiO_2$  film proves that particles are spherical in shape and average size about 20-

40 nm. TEM image of Au NPs confirms that particles are spherical with particle size about 50 nm.

The photo current density-voltage (J-V) curves of fabricated DSSC under conditions (50 mW/cm<sup>2</sup>) illustrate that the efficiency enhanced about 92 % with our optimum parameters as TiO<sub>2</sub> thickness is 20  $\mu$ m, dye mixing, added Au NPs to Z907 dye, dye concentration of 0.5 mM and substrate resistance of 8  $\Omega$ .

The incident photon-to-current conversion efficiency (IPCE) measurement showed that DSSC has high conversion efficiency. Also, it is found that DSSC has high transparency.



الخلية الشمسية الصبغية المتحسسة هي من انواع الجيل الثالث للخلايا الشمسية. اساس مبدأ عملها هو تحويل ضوء الشمس الى طاقة كهربائية.

في هذا البحث, تم تصنيع خلايا شمسية صبغية متحسسة وذلك بترسيب عجينة التيتانيا على قاعدة FTO بواسطة تقنية شفرة الطبيب. تم تلدين غشاء التيتانيا بدرجة حرارة  $2^{\circ}$  550 لمدة 30 دقيقة وبعد التلدين يُغمر في محلول الصبغة لمدة 24 ساعة للحصول على القطب الضوئي (الانود). تم ترسيب عجينة البلاتين على قاعدة FTO وتُلدن بدرجة حرارة  $2^{\circ}$  450 لمدة 30 دقيقة للحصول على القطب الضوئي (الانود). تم ترسيب عجينة البلاتين على قاعدة FTO وتُلدن بدرجة حرارة  $2^{\circ}$  70 دقيقة للحصول على القطب الضوئي (الانود). تم ترسيب عجينة البلاتين على قاعدة FTO وتُلدن بدرجة حرارة  $2^{\circ}$  450 لمدة 30 دقيقة للحصول على القطب العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). اخيرًا, يربط قطبا الانود والكاثود بشكل متقابل مع حقن الالكتروليت من خلال العاكس (الكاثود). وكذلك تم تحسين اداء الخلية الشمسية الصبغية المتحسسة بدراسة تأثيرات المعلمات الآتية: الفتحات. وكذلك تم تحسين اداء الخلية الشمسية الصبغية المتحسسة بدراسة تأثيرات المعلمات الآتية. سمك غشاء التيتانيا وتركيز صبغة 700 ومزج الصبغية المتحسسة بدراسة تأثيرات المعلمات الآتية. المحضرة بتقنية استئصال نبضات الليزر في السائل, الصبغة.

نتائج طيف الاشعة فوق البنفسجية – المرئية توضح ان الامتصاصية للخلية الشمسية الصبغية المتحسسة تتحسن بمزج الصبغات و اضافة جسيمات الذهب النانوية ومع زيادة تركيز الصبغة وكذلك الامتصاصية لغشاء التيتانيا تزداد بزيادة درجة حرارة التلدين.

فجوة الطاقة البصرية للانتقال المباشر (Eg) لاغشية التيتانيا نجدها تزداد من eV و2.30 الى 3.12 eV بزيادة درجة حرارة التلدين.

اثبتت نتائج XRD ان جميع اغشية التيتانيا المحضرة هي في طور anatase وأعلى قمة كانت عند مستوي (101).

اوضحت نتائج مجهر القوة الذريه (AFM) ان الخشونة ومعدل الجذر التربيعي لاغشية التيتانيا تقل بزيادة درجة حرارة التلدين. صورة مجهر الماسح الضوئي (SEM) لغشاء التيتانيا تثبت ان الجسيمات كروية الشكل معدل حجمها حوالي nm 40 nm \_20 مورة المجهر الالكتروني النافذ (TEM) لجسيمات الذهب النانوية تؤكد ان الجسيمات كروية الشكل و بحجم حبيبي يبلغ حوالي nm 50 nm.

منحنيات كثافة التيار الضوئي – الفولتية (J-V curves) للخلايا المصنعة تحت شروط (قدرة الضوء الساقط (50 mW/cm<sup>2</sup>) توضح ان الكفاءة تتحسن بحوالي % 92 بأفضل مَعلمات : سمك التيتانيا هو μm 20 ومزج الصبغات واضافة جسيمات الذهب النانوية الى صبغة Z907 و تركيز الصبغة ل 0.5 mM ومقاومة قاعدة Ω 8.

قياس كفاءة تحول الفوتون الساقط الى تيار يوضح ان الخلية الشمسية الصبغية المتحسسة لها كفاءة تحويل عالية . كذلك نجد ان الخلية الشمسية الصبغية المتحسسة لها شفافية عالية.

Chapter Ope Introduction and Literature Review

### **1-1 Introduction**

With the ever increasing population of the earth, the demand for energy becomes the most important problem for the next 50 years. Most energy is provided at present by burning fossil fuel, but the extensive usage of fossil fuel produces also a greatly increased concentration of atmospheric CO<sub>2</sub> that causes global warming. A search for a clean and sustainable source of energy free of carbon has therefore become an important issue for scientists. The most obvious source is the sun [1]. Solar energy is expected to play a crucial role as a future energy source. More solar energy strikes the earth in one hour  $(4.3 \times 10^{20} \text{ J/hour})$  than all the energy provides clean abundant energy and is therefore an excellent candidate for a future environmentally friendly energy source.

There are various types of solar cells that convert sunlight into electrical energy such as silicon solar cell and thin film solar cell. For example, dye sensitized solar cell (DSSC). The DSSC is the third generation of solar cell which has been developed by O'Regan and Gratzel in 1991 [3] using nanocrystalline semiconductor oxide material sensitized by a ruthenium (Ru) dye enabled a paradigm shift in the field of solar energy conversion technology [4]. Due to the pioneer work of Gratzel, the DSSC is also known as Gratzel cell [5].

Unlike the common solid state solar cells based on crystalline silicon, the DSSC does not depend on the principle of a p-n junction for its basic operation [6]. The DSSC uses dye molecules adsorbed on the nanocrystalline oxide semiconductors such as  $TiO_2$  to collect sunlight. Therefore the light absorption (by dyes) and charge collection processes (by semiconductors) are separated, mimicking the natural light harvest in photosynthesis. However,

### **Introduction and Literature Review**

DSSC has become one of the important and promising technologies in photovoltaic field [7], due to low material cost, simple fabrication process, high energy conversion efficiency as compared to other thin-film solar cell technologies and low toxicity to the environment [8]. DSSC consists of four main components: a nanostructured semiconductor (typically TiO<sub>2</sub>), a dye-sensitizer to absorb visible light, an electrolyte (typically contain iodide and triiodide) and counter electrode (typically Pt) [9]. Different parameters affect efficiency of the DSSCs: types of materials used as electrolyte, dye and electric contact, and synthesis method used to obtain these materials [7].

The DSSC can be classified as a photoelectrochemical (PEC) solar cell due to its utilization of photons, charges, and electrolyte for its basic operation [6]. Typically, high power conversion efficiencies ( $\eta$ ) of more than 11 % have been achieved by using ruthenium complex and acetonitrile based electrolytes [10].

The advantages of DSSC are that it can be engineered into flexible sheets, low cost of sensitization material production, ease of fabrication and low process temperature. The performance of the DSSC is highly dependent on the sensitizer dye and wide bandgap material such as  $TiO_2$ , ZnO and  $Nb_2O_5$  [11].

### **1-2 Literature Review**

In **1991**, Oregan and Gratzel, fabricated DSSC with a suitable thick  $TiO_2$ film immersed with a solution of Ruthunium dye to sensitize the substrate for collecting the light. Better current density (greater than 12 mA cm<sup>-2</sup>) was obtained. The energy conversion efficiency was 7.1-7.9 % in simulated solar light and 12 % in diffuse daylight [12].

### **Introduction and Literature Review**

In **1997**, Usami reported a theoretical study of application of multiple scattering of light to a dye sensitized nanocrystalline photoelectrochemical cell. The cell effectively confines incident light in the thinner dye sensitized film by multiple scattering from dispersed  $TiO_2$  particles at the bottom and total reflection between the inserted  $TiO_2$  film and the glass substrate at surface. Under optimal scattering conditions, it was found that the backscattered intensity is maximized when the backscattering angle is equal to the critical angle of reflection at the surface. The optical confinement is also effective for long wavelength light [13].

In **1999**, Tennakone et al., prepared dye sensitized solar cell (DSSC) from a porous film consisting of a mixture of tin and zinc oxides sensitized with a ruthenium bipyridyl complex suppresses recombination of the photo generated electrons and dye cations. It was found that short circuit photocurrent was  $22.8 \text{ mA/cm}^2$ , open circuit voltage was 670 mV and conversion efficiency was 8 % in direct sunlight (900 W/m<sup>2</sup>) [14].

In **2001**, Lindstrom et al., fabricated the DSSCs by new method, the method was summarized with manufacturing a nanostructured porous layer of a semiconductor material at room temperature. The porous layer is pressed on a conducting glass or plastic substrate. The method compresses the particle layer to form a mechanically stable, electrically conducting, porous nanostructured film. Overall, solar to electric conversion efficiencies of up to 5.2 % at 1 sun using plastic substrates have been obtained [15].

In **2002**, Boschloo et al., prepared dye sensitized solar cell (DSSC) with using Degussa P25 TiO<sub>2</sub> powder, red dye (Ru(dcbpy)<sub>2</sub>(SCN)<sub>2</sub>), black dye (Ru(tcterpy)(SCN)<sub>3</sub>) and an electrolyte were tested using standard photoelectrochemical techniques. It was found that the average overall efficiency of small open cells sensitized with the red dye on plastic substrates

was 4.5 % (100 W m<sup>-2</sup>). In a direct comparison, red and black dye gave about the same efficiencies [16].

In **2003**, Wang et al., fabricated and enhanced performance of dye sensitized solar cells (DSSCs) by using Co-grafting amphiphilic sensitizer. The results indicated that enhanced in short circuit photocurrent was 15.2 mA cm<sup>-2</sup>, an open circuit photovoltage was 764 mV, and a total power conversion efficiency was 7.8 % under simulated full sunlight when DSSCs containing Co-grafting [17].

In **2004**, Wang et al., studied the influence of titania photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell. It was found that the energy conversion efficiency of N719 dye-sensitized solar cell has improved significantly from 7.6 to 9.8 % by tuning the film structure from monolayer to multilayer [18].

In **2006**, Bandara and Weerasinghe, designed DSSC with high efficiency using coupled dye mixtures  $[Ru(2,2-bpy-4,4'-dicarboxylic acid)(NCS)_2]$  and  $[Ru(4,4',4''-tricarboxy-2,2;6,2''-terpy)(NCS)_3]$ . It was found that short circuit current density (J<sub>SC</sub>) of 10.2 mA/cm<sup>2</sup>, conversion efficiency ( $\eta$ ) of 2.8 and incident photon to current conversion efficiency (IPCE) 50 % while broadening the spectral sensitivity of the cell for multiple dye system. When single dye Ru(4,4-bis(carboxy)-bpy)\_2(NCS)\_2] or  $[Ru(2,2',2''-(COOH)_3-terpy)(NCS)_3]$  was used, cell efficiencies of 1.7 and 1.2 were observed respectively [19].

In **2006**, Hore et al., studied the influence of thin  $TiO_2$  layer with different scattering layer on the efficiency of DSSCs. It was found that  $J_{SC}$  increased due to inclusion of scattering layers [20].

In **2007**, Lee et al., fabricated dye sensitized solar cells (DSSCs) using TiO<sub>2</sub> coated multi-wall carbon nanotubes (TiO<sub>2</sub>-CNTs). It was found that the TiO<sub>2</sub>-CNTs content (0.1 weight %), the cell showed increase  $\sim$ 50 % in conversion

efficiency, which is attributed to the increase in short circuit current density  $(J_{SC})$ . The enhancement in  $J_{SC}$  occurs due to improvement in interconnectivity between the TiO<sub>2</sub> particles and the TiO<sub>2</sub>-CNTs in the porous TiO<sub>2</sub> film [21].

In **2008**, Chou et al., improved performance DSSC by using electrodes that consist of  $TiO_2$  with addition of indium doped tin oxide (ITO) or fluorine-doped tin oxide (FTO) nanoparticles [22].

In **2009**, Sakurai et al., fabricated and enhanced the efficiency DSSC by using  $ClO_4^-$  -poly (3,4-ethylenedioxythiophene)/TiO<sub>2</sub>/FTO (ClO<sub>4</sub>--PEDOT/TiO<sub>2</sub>/FTO) counter electrode (CE) in dye sensitized solar cells (DSSCs) is fabricated by using an electrochemical deposition method. It was found that the current-voltage (I-V) measurement reveals that the photocurrent conversion efficiency (n), fill factor (FF) and short-circuit current density (J<sub>SC</sub>) of DSSCs with a  $ClO_4^-$ -PEDOT/TiO<sub>2</sub>/FTO CE increased compared to DSSCs without  $ClO_4^-$ -PEDOT/TiO<sub>2</sub>/FTO CE. The enhanced performance of the DSSCs is attributed to the higher J<sub>SC</sub> arising from the increase of active surface area of  $ClO_4^-$  -PEDOT/TiO<sub>2</sub>/FTO CE [23].

In **2009**, Huynh et al., improved DSSCs performance by using TiO<sub>2</sub> thin film prepared by doctor-blade method. It was found that the dye sensitize solar cells prepared with TiO<sub>2</sub> thin film shows its superior photovoltaic performance at air mass 1.5 (AM 1.5), open circuit voltage (V<sub>OC</sub>) was 0.77 V, J<sub>SC</sub> was 18.2 mA/cm<sup>2</sup>, FF was 0.50 and efficiency (n) was 7.0 % [24].

In **2010**, Bazargan et al., fabricated flexible DSSCs using a new type counter electrode which prepared with an industrial flexible copper (Cu) sheet as substrate and graphite as the catalytic material which was sprayed by sprayed method. The results indicates that DSSCs fabricated with new type CE show higher solar to electricity conversion efficiency. The respective values are 5.29 % and 3.38 % for the graphite/ITO polymer based devices [25].
#### **Introduction and Literature Review**

In **2010**, Lee and Kang, studied the properties of nanoporous structured  $TiO_2$  and its application to dye-sensitized solar cells (DSSCs). From the results they found that the energy conversion efficiency (n) of the DSSC prepared from nanoporous structured  $TiO_2$  was approximately 8.71 % with the N719 dye under 100 mWcm<sup>-2</sup> simulated light [26].

In **2011**, Xia Wu et al., prepared  $TiO_2$  nanosheets films with various thicknesses (5-20 µm) by Doctor-Blade technique and they studied the effect of film thickness on the performance of dye sensitized solar cells (DSSCs) by I -V characterization. They showed that the optimized DSSCs performance was 8.39 % when 15 µm [27].

In **2011**, Tsai et al., enhanced the efficiency DSSCs by using Graphene-TiO<sub>2</sub> composites as working electrode. It was found that the increasing of the graphene content leads to increase the amount of dye absorption [28].

In **2012**, Lee et al., enhanced the efficiency of dye-sensitized solar cells (DSSCs) by combining TiO<sub>2</sub> nanotubes (TNTs) and nanoparticles. The incident photocurrent conversion efficiency was measured using a solar simulator and it was found to be (100 mW/cm<sup>2</sup>). It was found also that DSSCs based on TNT/TiO<sub>2</sub> nanoparticle hybrids showed better photovoltaic performance than cells made purely of TiO<sub>2</sub> [29].

In 2012, Ole et al., fabricated DSSCs based on photoelectrodes synthesized Horizontal Vapor Phase Crystal (HVPC) Growth Technique. via Nanostructured TiO<sub>2</sub> was first synthesized on glass substrates at growth temperatures of 1000 °C, 1100 °C, and 1200 °C with varying substrate distance from the bulk powder. FTO was used to deposit nanostructured TiO<sub>2</sub> for the photoelectrodes of the DSSCs employing the optimum substrate distance identified by SEM analysis. Bixin dye extracted from Annatto was utilized as a low-cost sensitizer and a graphite coated FTO as counter-electrode. All the DSSCs with photoelectrode fabricated by HVPC growth technique achieved a relatively large open-circuit voltage ( $V_{OC}$ ) of 387 mV, 427 mV, and 412 mV for growth temperature of 1000 °C, 1100 °C, and 1200 °C respectively [30].

In 2012, Karthick et al., prepared  $TiO_2$  pastes from commercial P25 titanium oxide powder (sample X) and titanium isopropoxide (sample Z) using a hydrothermal technique and also fabricated DSSCs. FTO glass is used as substrate for deposition of the pastes. The coated films were sintered at 500 °C for 30 minute and characterized by X-ray diffraction (XRD), fourier transform infrared (FTIR), ultraviolet visible (UV-Vis), scanning electron microscope (SEM), transmission electron microscope (TEM) and IV studies. XRD results confirmed that both of anatase and rutile phase were found in the film from sample X but only anatase phase were formed from sample Z. The lattice parameters of sample X is a = 3.789 Å and c = 9.526 Å and those of sample Z is a = 3.786 Å and c = 9.508 Å. Also, it was found FT-IR studies showed that there is no precursor residue present in both the sample after sintering. The UV-Vis spectrum indicates the amount of dye adsorbed on TiO<sub>2</sub> particle. It was found that the short circuit current  $(J_{SC})$ , open circuit voltage  $(V_{OC})$  and conversion efficiency (n) are 11.34 mA/cm<sup>2</sup>, 0.7111 V and 5.7 % respectively, which is high for DSSC prepared by using sample Z compared to sample X [31].

In **2013**, Guo et al., prepared and enhanced the properties of DSSCs by using differing amounts of silver nanoparticles (Ag NPs) on TiO<sub>2</sub>. The results indicated that  $J_{SC}$  was 10.19 mA cm<sup>-2</sup>,  $V_{OC}$  was 698 mV and photoelectric conversion efficiency was 5.33 % when the Ag NPs addition was 0.15 wt % [32].

In **2013**, Oladiran and Olabisi, fabricated DSSC with using FTO glass as the substrate with copper metal attached to the surface, eosin blue as sensitize, lemon juice as electrolyte and ZnO nanoparticles as photoelectrode. The nanostructured ZnO was synthesized by precipitating Zn nitrate hexahydrate

with NaOH which was characterized structurally using XRD and optically with a UV-Vis Spectrophotometer. It was found that the DSSC has fill factor was 0.85 and efficiency was 0.15 % [33].

In **2014**, Deepak et al., fabricated DSSCs module by spray pyrolysis deposition (SPD) method of a TiO<sub>2</sub> colloid having similar to 10 nm sized TiO<sub>2</sub> nanoparticles. It was shown that this the process was first optimized for cell level fabrication, and the parameters (mainly the thickness) obtained from the study were subsequently used for module level fabrication. It was found also that the best efficiency obtained at the cell level (area 0.2 cm<sup>2</sup> and thickness of 12 mm) was 7.79 % and that for the (12 cm × 12 cm) module was 3.2 % [34].

In **2014**, Di Gu et al., studied the effect of addition of the suitable molecular weight of polyethylene glycol (PEG) of DSSC anode on its efficiency. It was found that when adding PEG of molecular weight 2000, the  $TiO_2$  thin film electrode has the best performance, subsequently, the DSSC enhancement performance [35].

In 2014, Hammadi and Naji, studied the effect of dye concentration and added acid to the dye solution on optical properties of hibiscus sabdariffa organic dye used in the dye-sensitized solar cell. The results showed that the acidic environment of the Hibiscus sabdariffa dye solved in acetone has an important effect on the spectral properties of such dye. Adding acid to the dye solution caused to decrease its absorbance in the range 400-800 nm and noticeable decrease was shown in the range 550-700 nm when the concentration of the dye got higher [36].

In **2015**, Gomesh et al., fabricated DSSC with the usage of recycled materials and organic dye such as graphite from batteries and organic dye from rose extract. The study focused on electrical performance and characteristic of the fabricated  $TiO_2$  solar cell based on the graphite coating thickness. The results were investigated in terms of fill factors, solar cells

8

efficiency and UV-Vis absorption. Result showed that thinner layer of graphite coating has good potential as an alternative counter electrode material [37].

In **2015**, Uddin et al., prepared and studied the properties of DSSC using natural dye extract from red amaranth as sensitizer. It was found the best light to electricity conversion efficiency was obtained when sensitization time of electrode was 30 minutes and dyes were extracted by acetone in crude form. Subsequently, the DSSC generated maximum voltage 0.492 V, short circuit current density 0.78 mA/cm<sup>2</sup> and cell efficiency 0.22 % [38].

In **2015**, Sedghi and Miankushk, studied the effect of thickness of TiO<sub>2</sub> electrodes on the performance of dye-sensitized solar cells. TiO<sub>2</sub> electrodes were characterized by SEM, optical microscope (OM), FTIR, thermal gravimetric analysis (TGA), and also cell performance was measured by a solar light simulator at an intensity of 1000 W.m<sup>-2</sup>. It was found that increasing the thickness of the TiO<sub>2</sub> films led to absorption of the N719 dye increased, so that  $\eta$  of 7.51 % was obtained [39].

In **2015**, Hussein, fabricated three types of DSSC [pure TiO<sub>2</sub> cell (TiO<sub>2</sub> only), bare TiO<sub>2</sub> cell (TiO<sub>2</sub> sensitized by Curcumin dye) and treated TiO<sub>2</sub> cell (TiO<sub>2</sub> HCl TiCl<sub>4</sub> sensitized by Curcumin dye)] and improved performance of dye sensitized solar cell (DSSC) by utilization natural Curcumin dye extracted from Curcuma longa plant (Turmeric) as photosensitizer. It was found that the bare TiO<sub>2</sub> cell has achieved the highest power conversion efficiency with value of 1.15 % in comparison with (treated and pure) TiO<sub>2</sub> cells [40].

In **2016**, Li et al., fabricated flexible DSSC modules on plastic substrates. It was shown that the conversion efficiency was maximum (~ 30 %) for the flexible DSSC modules with series connection [41].

In **2016**, Pirhadi et al., fabricated dye sensitized solar cells (DSSCs) with single layer and double layers photoanode. It was found that the DSSCs with

9

#### **Introduction and Literature Review**

double layers photoanode resulted higher efficiency compared to DSSCs with single layer photoanode. The photovoltaic characteristics of DSSCs with double layers photoanode were 734 mV, 13.16 mA/cm<sup>2</sup>, 62 % and 5.96 % for  $V_{OC}$ ,  $J_{SC}$ , FF and efficiency respectively [42].

In **2016**, Jaber et al., fabricated and enhanced the performance of DSSC by using gold nanoparticles (Au NPs). Au NPs prepared by laser ablation in liquid (PLAL) method at 750 mJ energy and 90 pulses. They have been added to [RuL<sub>2</sub>(NCS)<sub>2</sub>]: 2TBA (L=2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA=tetra*n*-butylammonium) (N719) dye to form (Au-N719) mixture. TiO<sub>2</sub> paste was deposited on FTO substrates and immersion in a mixture dye and Au NPs. The UV-Vis data show high absorbance of Au NPs+N719 dye compared to N719 dye only. Scanning electron microscope shows spherical Au NPs with particle size about (50-60) nm. The results indicated that the relative increase of short circuit current density and open circuit voltage after adding Au NPs was about 76 % and 6.7 % respectively. The results indicated that the total photon to current energy conversion efficiency for the standard DSSC is 1.75 while its 2.8 of the enhanced DSSC with gold NPs. The maximum enhancement is about 60 % under illumination (105 mW cm<sup>-2</sup>) [43].

**In 2016,** Salman and Agool, prepared ZnO nanoparticles by laser ablation technique and fabricated dye-sensitized solar cell (DSSC) from ZnO nanoparticles using electrostatic deposition technique. From the results, they found that the ZnO nanoparticle had crystalline wurtzite phase. Also, Transmission electron microscopy (TEM) image illustrated that the ZnO nanoparticles were spherical in shape with an average size of about 37 nm. The fabricated ZnO-DSSC had a fill factor of 0.29 and conversion efficiency of 0.0016 % [44].

10

# **Introduction and Literature Review**

To the best of our knowledge, no previous studies have been conducted about the effect of adding (Au NPs) to (Z907 dye)  $(RuLL'(NCS)_2 (L=2,2'-bipyridyl-4,4'-dicarboxylic acid;L'=4,4'-dinonyl-2,2'-bipyridine)$  and dye mixtures on the efficiency of DSSC.

### 1-3 Aim of the work

- Fabrication of dye sensitized solar cells (DSSCs) and studying their properties.
- Studying the effect of titanium thickness on DSSC efficiency.
- Studying the effect of adding Au NPs on DSSC efficiency.
- Studying the effect of dyes mix on DSSC efficiency.



#### **2-1 Introduction**

This chapter gives an introduction to the solar spectrum the generations of solar cells with special attention to the DSSCs, their structure and their working principle. It also deals with the theoretical aspects that are related to the solar cell performance and other important parameters. The chapter also includes the theoretical equations related to optical and structural properties of thin films. Pulse laser ablation in liquid technique is explained, as it is employed in this study to prepare Au NPs used to enhance the performance of DSSCs. Finally, the chapter presents some applications of DSSCs in advanced device technology and daily life equipments.

#### 2-2 The Solar Spectrum

The sun is a broad spectral range light source, emitting in the ultraviolet, visible and infrared regions of the electromagnetic spectrum. The irradiance defined as the power received from the sun per unit area, It is shown as a function of light wavelength in Figure (2-1) [45].

The irradiance of the sun can be well approximated by a black body at a temperature of 5800 K emitting according to Planck's distribution [46]. At the earth's surface, the solar spectrum is attenuated by absorption, scattering and reflection. Light is absorbed in the UV and visible region by oxygen (O<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>) and ozone (O<sub>3</sub>) in the mid-infrared region by water vapor (H<sub>2</sub>O), and in the far infrared region by carbon dioxide (CO<sub>2</sub>). Absorption increases with the path length of the light through the atmosphere [47].



**Fig. (2-1):** Solar spectrum, and the spectrum of a black body of at T= 5800 K [45].

The Air Mass coefficient (AM) is used to account for contribution of the atmosphere to the change in the solar spectrum. The Air Mass coefficient is defined as the ratio between the optical path length to the sun and the optical path length when the sun is directly overhead [48] and it is expressed through the formula [47].

$$\mathbf{A}\mathbf{M} = 1/\cos\theta_{e} \qquad \qquad (2-1)$$

Where

 $\theta_e$ : is the elevation angle of the sun, (see Fig. 2-2).



Fig. (2-2): Designation of Solar Air Masses [45].

When the sun is directly overhead, the Air Mass is 1 (AM1) and the irradiance reaching the Earth's surface is maximum [49], and the spectrum outside the atmosphere is designated by AM0. The standard spectral distribution of the light used for testing photovoltaic devices is AM 1.5 global [50] (elevation angle equal to  $\theta = 48.2^{\circ}$  and optical path 1.5 times longer than in the case of AM1 light). For convenience, the standard spectrum is normalized so that the integrated irradiance of this spectrum per unit area and unit time is 1000 W/m<sup>2</sup> (known as 1 sun illumination) [46].

#### 2-3 Solar Cells

A photovoltaic (solar) cell is a device which converts sunlight to electrical energy [49]. Compositional elements fundamental to solar cells are absorber material such as semiconductors, p-n junction and the metal grid, as shows in figure (2-3) [45]. Its working principle depends on two parameters. The generation of current by absorbed incident light and the loss of charge carriers via process called recombination [51].



Fig. (2-3): Cross-section of a basic solar cell [49].

#### **2-4 Generations of Solar Cells**

Solar cells are categorized into three generations based on their performance, cost effectiveness, the nature of the material and maximum conversion efficiency [52] as shown in Figure (2-4).



Fig. (2-4): The generations of solar cells [52].

#### **2-4-1 First Generation Photovoltaics**

The crystalline silicon is often referred to as the first generation photovoltaic technology. The first silicon solar cell was developed by Chapin, Fuller, and Pearson at the Bell Telephone Laboratories in the mid 1950's [50]. The highest power-conversion efficiencies obtained to date are in first generation photovoltaics ( $PV_s$ ) [1].

This generation of solar cells is characterized by relatively higher efficiency together with expensive production cost [11]. Today, the silicon solar cells dominate the photovoltaic (PV) market by 82 % and the recorded efficiency for a laboratory cell is 24.7 % [52], while the efficiency of the commercial crystalline silicon solar panels is in the best case about 15 %. The main reason why silicon has dominated the PV market is that high quality silicon has been already produced at large quantities by the semiconductor industry [7].

### 2-4-2 Second Generation Photovoltaic

The second generation photovoltaics consist of thin film solar cell materials such as amorphous silicon (a-Si), copper indium gallium diselenide (CuInSe), cadmium telluride (CdTe) as shown in figure (2-4) [53].

Solar cells of this generation are based on low energy preparation techniques such as vapor deposition and electroplating [12]. Regardless of the semiconductor involved, the thin-film technology offers prospects for a large reduction in material costs by eliminating the costs of the single crystalline silicon wafer preparation. However, the maximum power conversion is lower due to the presence of defects in the films. Thin-film solar cells are cheaper but less efficient [54].

#### **2-4-3 Third Generation Photovoltaics**

Third generation solar cells refer to cells which do not fall into the first or second generations [55]. Solar cells based on dye sensitization referred to third generation photovoltaics, due to their excellent potential to deliver solar electric power at very low cost, which recently introduced into the consumer market [56].

DSSCs involve simple fabrication procedures and have promising applications on flexible substrates [57]. Since DSSC fabrication cost is lower than a silicon solar cell, this technology has the potential to be used in many applications [58]. The solar cell development is shown in figure (2-5).



**Fig. (2-5):** Progression of efficiencies for a variety of PV technologies [53].

#### 2-5 The Structure of DSSC

The dye sensitized solar cell consists of six main components: transparent conductive oxide (TCO) coated substrate,  $TiO_2$  nanoparticles, dyes, electrolyte, and counter electrode covered with sealing gasket. The typical configuration is shown in Figure (2-6) [59].

#### 2-5-1 Transparent Conductive Oxide Substrate (TCO)

TCO substrate has important features such as low electrical resistance, optical transparent, light weight, chemically compatible with other DSSC components, structurally stable, easy to manufacture, and inexpensive [60]. The electrodes of the standard DSSC are prepared from transparent conducting oxide substrates, between which the cell is assembled [61]. TCO substrate plays an important role in the DSSCs performance [62].

TCO substrates widely used in photovoltaic applications are ITO or FTO coated glass substrates [63].



Fig. (2-6): Typical configuration of a DSSC [54].

#### 2-5-2 TiO<sub>2</sub> Nanoparticles

Titanium dioxide (TiO<sub>2</sub>) also known as titanium oxide, titanium IV oxide and titania was first produced commercially in 1923 [64]. TiO<sub>2</sub> nanostructures is one kind of the important materials that attracted more attention due to the structural, synthesis, electronic, and optical properties for dye-sensitized solar cells (DSSCs) [65]. It has been reported that particle size, shape, crystallinity, surface morphology, and chemistry of the TiO<sub>2</sub> material are key parameters which should be controlled for optimized performance of the solar cell. TiO<sub>2</sub> exists naturally in three crystalline forms; anatase, rutile, and brookite as shown in figure (2-7). Table (2-1) shows general properties of TiO<sub>2</sub>. The advantages of TiO<sub>2</sub> include high photosensitivity, high structure stability under solar irradiation, high efficiency, non toxic, eco friendly and low cost. It is mainly applied as pigments, adsorbents, catalyst supports, filters, coatings, photoconductors, and dielectric materials [66].

Phase	Crystal Structure	Energy Gap (Eg) eV at 300 k	Unit Cell (Å)	Refractive Index	Density (g/cm <sup>3</sup> )
Anatase	Tetragonal	3.23	a=3.7845 c=9.5143 z=4	2.488 (λ=0.98 μm)	3.89
Rutile	Tetragonal	3.05	a=4.5937 c=2.9587 z=2	2.609 (λ=0.595 μm)	4.26
Brookite	Orthorhombic	3.26	a=5.4558 b=9.1819 c=5.1429 z=8	2.583 (λ=0.634 μm)	4.123

#### Table (2-1): General properties of TiO<sub>2</sub> [67].



Fig. (2-7): Crystal structures of (a) rutile, (b) anatase and (c) brookite [68].

#### 2-5-3 Dyes

Dyes are the key component [12] or regarded as the heart [69] of a DSSC. The function of the dye is to absorb the photons, and inject electrons into the semiconductor [12]. The process of dye loading is referred to as "sensitization" and it is achieved by immersing the work electrodes in dye solutions for a number of hours [69]. An ideal sensitizer for DSSCs should fulfil some essential characteristics, such as absorbing a wide range of radiation (400-920 nm), fast injection of electrons in the conduction band of TiO<sub>2</sub> and high stability in order to allow redox cycles [60]. To achieve a high light-to-energy conversion efficiency in a DSSC, the dye molecules as attached to the semiconductor particle surface should have good properties of interfacial, practical, stability, kinetics, absorption, energetic [70].

Most metal based dyes for DSSCs application are ruthenium due to their high stability, broad absorption and relatively long lived excited state properties. Most dyes have a spectral response in the visible region (400–770) nm. The purpose for using the dyes in the DSSC is to expand the absorption spectrum of the solar cell [69].

In DSSC, the Choice of the dye type is one of the factors that affect the efficiency.

# 2-5-4 Electrolyte

The electrolyte is one of the important components of DSSC. There are three different kinds of electrolytes solid state, quasi-solid state and liquid electrolyte. Liquid electrolyte is most used in DSSCs based on the charge mediator iodide/triiodide ( $\Gamma/\Gamma_3$ ) redox couple in acetonitrile, a low-viscosity volatile solvent and deeper penetration within the film pores [71]. The function of redox couple in electrolyte is collecting the electrons at CE, as well as regenerating the dye after electron injection into the conduction band of the semiconductor [7].

#### 2-5-5 Counter Electrode

The counter electrode is one of the important components in DSSC. The function of counter electrode in DSSCs is the reduction of  $I_3$  to  $I^-$  [72]. Due to excellent electrical conductivity, catalytic activity, and corrosion resistance, platinum (Pt) is used as thin film deposited on the FTO substrate which typically serves as the counter electrode in DSSCs.

The advantage of metal counter electrode is that it can reflect the light transmitted by the photoanode which causes a second transversal of the dye-sensitized film, thereby enhancing light absorption for a given amount of dye [73].

#### **2-5-6 Sealing Material**

The sealing material is essential in fabrication of DSSCs to prevent the leakage of the electrolyte and the evaporation of the solvent. Photochemical and chemical stability of the sealing material against the electrolyte component, the solvent and iodine is required [63]. Several sealing materials have been used, such as epoxy and silicon [74]. For larger area applications, such as solar modules, the sealing material must also protect the conductor and prevent mass transport between the electrolytes of neighbouring cells [75].

# 2-6 Operation Principle of Dye Sensitized Solar Cells (DSSCs)

Exposure of this solar-cell assembly to visible light leads to a sequence of reactions. Figure (2-8) shows the well known working mechanism of DSSC [76]. At the anode, the absorption of the light by the dye S leads to formation of its electronically excited state S\* (equation 2-2).

The excited electrons are injected into the conduction band of the semiconductor  $(TiO_2)$  layer, resulting in the oxidation of the dye  $(S^+)$  (equation 2-3).

$$S^* \longrightarrow S^+ + e^- CB$$
 ..... (2-3)

The injected electrons are transported through the mesoporous network of particles to reach the counter electrode to pass through the external circuit and wiring. The oxidized dye is reduced rapidly to the ground state by accepting electrons from iodide ion present in the electrolyte (equation 2-4).

$$2S^+ + 3I^- \longrightarrow 2S + I^-_3 \qquad (2-4)$$

At the counter electrode, the triiodide ( $I_3$ ) gets two electrons to generate three iodides (i.e the triiodide is reduced to iodide) (equation 2-5).



Fig. (2-8): Operation principle of DSSC [76].

If cited reactions alone take place, the overall effect of irradiation with sunlight is to drive the electrons through the external circuit, i.e., direct conversion of sunlight to electricity. The performance of DSSC is predominantly based on four energy levels of the components: the Fermi level of the TiO<sub>2</sub> photo-electrode, which is located near the conduction band level, the excited state lowest unoccupied molecular orbital (LUMO) and the ground state highest occupied molecular orbital (HOMO) of the Ruthenium dye, and the redox potential of the redox mediator ( $I^{-}/I^{-}_{3}$ ) in the electrolyte solution. The photocurrent obtained from the DSSC is determined by the energy difference between the HOMO and LUMO of the Ruthenium dye corresponding to the band gap for semiconductor materials [2,77].

### 2-7 Dye-Sensitized Solar Cell Performance

DSSCs have several important parameters such as short circuit current (I<sub>SC</sub>), open circuit voltage (V<sub>OC</sub>), optimum voltage (V<sub>max</sub>), optimum current (I<sub>max</sub>), short circuit current density (J<sub>SC</sub>), incident photon to current efficiency (IPCE), fill factor (FF) and efficiency ( $\eta$ ) which can be obtained from photocurrent density-voltage (J-V) curve of DSSCs under illumination as shown in figure (2-9) [78].

#### 2-7-1 Short Circuit Current (Isc)

Short circuit current is obtained from the cell when the load resistance is zero and output voltage is zero [79]. The short circuit current is equal to the absolute number of photons converted to hole-electron pairs.  $I_{SC}$  depends on the thickness of the electrode, the adsorbed dye molecule, diffusion electrolytes, dipping time, temperature of the cell, and dye loading [80].

#### 2-7-2 Short – Circuit Current Density (J<sub>SC</sub>)

The short circuit current density  $(J_{SC})$  is the short circuit current divided by the illuminated active area of the cell [81]. It is measured in the illuminated cell when load resistance and voltage is zero, as shown in figure (2-9). It is dependent on several factors such as the light intensity, injection efficiency, light absorption and regeneration of the oxidized dye [82]. Current density (J) is commonly used instead of current (I) because it enables the comparison of devices with different TiO<sub>2</sub> active areas. The J<sub>SC</sub> can be calculated according to equation (2-6) [83]:

Where

 $\mathcal{A}$ : is the effective area of the solar cell.

I<sub>SC</sub>: is the short circuit current.

#### 2-7-3 Open-Circuit Voltage (Voc)

Open-circuit voltage is the maximum voltage available from a solar cell and it is obtained when a load with infinite resistance and the output current is zero, as shown in figure (2-9). It depends on the band gap of semiconductor, redox potential, and the ground state of the dye molecule. In dye sensitized solar cell, open circuit voltage ( $V_{OC}$ ) can be nearly estimated by the difference of redox potential and Fermi level of TiO<sub>2</sub>. For DSSC the V<sub>OC</sub> is given by:

Where,  $N_{CB}$  is the effective density of states and *m* is the number of electrons in semiconductor conduction band. The first two terms define the quasi-fermi level of TiO<sub>2</sub> and  $E_{redox}$  is the Nernst potential of the redox mediator [79].

#### 2-7-4 Maximum Voltage (V<sub>max</sub>)

Maximum voltage is the voltage at the optimum operating point at which the DSSC output power is maximum as shown in figure (2-9). It depends on bonds between the dye molecules and  $TiO_2$  film and dye temperature and time [84].

# 2-7-5 Maximum Current (I<sub>max</sub>)

Maximum current is the current at the optimum operating point in which the DSSC output power is maximum, it depends on the intensity of incident light, and connection between material interfaces.

Figure (2-9) shows an illustration of current-voltage characteristics of a cell under illumination [85].



Fig. (2-9): Typical voltage-current characteristics of a solar cell.

#### 2-7-6 Fill Factor

The fill factor is an important parameter of the efficiency of the cell. It measures the ideality of the device. Fill factor (FF) is defined as the ratio of the maximum power output per unit area to the product of  $V_{OC}$  and  $J_{SC}$  (area within the green square divided by the area of the red square in Figure (2-9). Fill factor (FF) of DSSC is given by formula below:

Where

P<sub>max</sub>: is maximum power density.

V<sub>max</sub>: is the voltage at maximum power point.

J<sub>max</sub>: is the current density at maximum power point.

The fill factor ranges between (0-1), when internal resistance for cell is zero, the corresponding FF value is 1. The FF is influenced by series resistance ( $R_s$ ) from the internal resistance and shunt resistance ( $R_{sh}$ ) [86].

# **2-7-7 Power Conversion Efficiency** $(\eta)$

The efficiency of a solar cell is the ratio of maximum output power  $(P_{max})$  to the incident power  $(P_{in})$ . The maximum efficiency can be calculated from the J-V curve. The efficiency  $(\eta)$  is given by the following equation [87]:

$$\eta(\%) = \frac{J_{\max} V_{\max}}{P_{in}} = \frac{P_{\max}}{P_{in}} = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100 \% \dots (2-10)$$

# 2-7-8 Incident Photon - Current Conversion Efficiency (IPCE) and Spectral Response

The incident photon to current conversion efficiency (IPCE) is one of the fundamental measurements of the performance of the solar cell. It is defined as the ratio of the number of electrons collected under short circuit conditions divided by the number of incident photons. IPCE takes into account the losses due to reflection, scattering and recombination. The IPCE is given by the following formula [86]:

IPCE (%) = 
$$\frac{1240 \ J_{sc}}{\lambda_{ph} \ P_{in}} \times 100$$
 ..... (2-11)

Where

 $\lambda_{ph}$ : is the incident photon wavelength.

 $J_{SC}$ : is the short circuit current density.

P<sub>in</sub> : is the incident power density.

IPCE values typically do not reach 100 % because light is reflected off the device, which accounts for a loss of approximately 8-10 % of all incident photons. An example of an IPCE curve generated from a DSSC test cell is provided in Figure (2-10) [88].

The spectral response (R) is defined as the ratio of the current generated by the solar cell to the power incident on the solar cell. The R is given by the following formula [89]:

$$\mathbf{R} = \frac{\mathbf{J}_{SC}}{\mathbf{P}_{in}} \qquad \qquad (2-12)$$



Fig. (2-10): Example of an IPCE curve generated from a DSSC [88].

# 2-8 The Equivalent Circuit of Solar Cell

Figure (2-11) shows the equivalent circuit corresponding to a solar cell. A solar cell can be thought as a combination of diode and current source in the solar cell having two resistances, shunt resistance ( $R_{Sh}$ ) and series resistance ( $R_{S}$ ). The cell would be an ideal cell if ( $R_{Sh}$ ) to be infinitely large and ( $R_{S}$ ) is zero.



**Fig. (2-11):** Equivalent circuit of a solar cell including series and shunt resistances [52].

The  $R_s$  is composed of the electric resistance of the different materials in the cell and interfaces between them. The resistance of the TCO layer has the highest influence on resistance. The shunt resistance measures the resistance between the electrodes of the cell through undesirable paths such as from TiO<sub>2</sub> film to electrolyte. It is desired to be as high as possible. The diode model does not represent the dye solar cell very well. The internal structure of the DSSC is more complex than that of silicon solar cell. But the concepts of the series and parallel resistances can also be applied to the DSSC. The resistance can be measured using impedance spectroscopy. Series and parallel resistances reduce the fill factor as shown in Figure (2-12). For an efficient cell we need  $R_s$  to be as small and  $R_{sh}$  to be as large as possible [90].



**Fig.(2-12):** Effect of (a) increasing series and (b) reducing parallel resistances [86].

The shunt resistance is used to describe the effect of leakage current in the solar cell's transporting layer. Obviously, the bigger the parallel resistance, the less the leakage current. (Particularly, the recombination in the condition band and trapped level in the transporting layer) [91].

The series resistance is caused by the resistance of the cell material to current flow. The main contribution to this arises from the interface between  $TiO_2$  and electrode (TCO) and transporting layers [92].

#### **2-9 Optical Properties**

#### 2-9-1 Absorbance (A)

Light absorption occurs when molecules or atoms absorb the energy of a photon of light, resulting reducing the transmission of light passing through a sample. The reduction of transmitted light is related to the path length of light traveled and concentration of the sample. Transmittance (T) is given by ratio of the intensity of the rays ( $I_T$ ) transmitting through the film to the intensity of the incident rays ( $I_o$ ) as follows:

Where

I<sub>T</sub>: is transmitted light intensity.

I<sub>o</sub>: is incident light intensity.

The absorbance of the sample is defined as the negative log of the transmittance given by the relation (2-14) [93]:

$$\mathbf{A} = -\log_{10}\mathbf{T} \qquad (2-14)$$

Where

T: represents the transmittance.

A: represents the absorbance of the sample.

# 2-9-2 Optical Energy Gap (Eg)

Band gap is defined as the energy difference between the top of the valence band to the bottom of the conduction band. Electrons jump from valence band to a conduction band and this requires a specific minimum amount of energy for the transition. Measuring the band gap is important in the semiconductor and nano material industries [94].

The optical energy gap  $(E_g)$  for semiconductors can be determined from the flowing relation [95]:

$$\alpha hv = \mathbf{P}(hv - E_g)^r \qquad (2-15)$$

Where

P: is constant.

*hv*: is the photon energy.

 $\alpha$ : is optical absorption coefficient.

r: is the exponent depending on the type of optical transitions.

r is equal to 1/2, 2, 3/2 and 3 corresponding to direct allowed transitions, indirect allowed transitions, direct forbidden transitions , and indirect forbidden transitions, respectively [96]. The energy gap for allowed direct transition materials can be estimated by (Tauc's plot) plotting a graph between  $(\alpha hv)^2$  and (hv) in eV, straight line is obtained and the extrapolation of this line to  $(\alpha hv)^2 = 0$  gives the value of the direct band gap of the material [97].

# 2-10 Structure of Thin Film

One of the important methods for studying the structure of bulk materials and thin films is the X-ray diffraction (XRD). Through this technique one can get information like crystal structure/phase, lattice parameters, defects, strain, and crystallite size of substance examined [98]. Bragg's condition is achieved when the X-rays should be specularly reflected in any one atom plane and the reflected rays of consecutive atom planes should constructively interfere. The Bragg's condition is given by [99]:

$$n \lambda = 2 d_{\text{hkl}} \sin\theta \qquad (2-16)$$

Where

*n*: is an integer number, representing the order of reflection.

 $\lambda$ : is the wavelength of the incident X-ray.

d<sub>hkl</sub>: is the interplanar spacing.

 $\theta$ : is Bragg's angle.

From the X-ray diffraction patterns one can calculate the interplanar spacing  $(d_{hkl})$  using Bragg's formula, while. the lattice constants (a,c) for the tetragonal structure can be calculated according to the following equation [98]:

Where

hkl: are miller indices.

a and c: are lattice constants.

The crystallite size (D) is calculated using Scherrer's formula [100]:

Where

 $\mathcal{K}$ : is Scherrer's constant  $\approx 0.9$ .

 $\lambda$ : is the wavelength of incident X-ray radiation = (1.5406 Å for CuK $\alpha$ ).

 $\beta$ : is the full width at half maximum (FWHM) of the peak (in radians).

 $\theta$ : is Bragg's angle.

#### 2-11 Pulsed Laser Ablation in Liquid

In 1987, Patil performed the first experiment involving laser ablation in a liquid. He used a pulsed ruby laser to ablate an iron target in water [101].

Pulsed laser ablation in liquid (PLAL) is a simple and rapid technique used to fabricate nano-sized materials and it allows some control of nanonoparticles concentration, size, shape and aggregation by the variation of few parameters [102] including pulse duration, pulses number, pulse energy, laser wavelength, nature of liquid environments and laser frequency interacts with a bulk material [103]. Laser ablation is defined as the process of removing material from a solid surface by irradiating it with a laser beam. The generation of nanoparticles using pulsed laser ablation has many advantages compared to conventional methods, like the purity and stability of the fabricated nanoparticle colloids [104]. The main principle of laser ablation is the conversion of optical into thermal energy via electronic excitation. If the energy of the laser is high enough, the chemical bondings of the material can be destroyed, so that the material vaporizes and Au NPs may be ejected from the material [103]. Figure (2-13) shows the process of laser ablation.



Fig. (2-13): Preparation of nanoparticles by PLAL method.

#### 2-12 Gold Nanoparticles

Nanoparticles (NPs), with diameters ranging roughly between 1 and 100 nanometer, are natural bridges between molecules and extended solids and have attracted considerable interest due to their unique optical, electromagnetic, and catalytic properties, which can be used in many potential technological applications [105] including tailor made nanostructured materials for medicine and biosciences, energy technology (fuel cells and solar cells), also in photonics, and information technology. This type of particles show increased strength, hardness, higher electrical resistivity, enhanced diffusivity and reduced density [106]. Gold nanoparticles are another type of nanoparticles that have immense potential in biomedical field. There are chemically stable, non toxic and can be tuned to various shapes and sizes. One of the most important characteristics of Au NPs is phenomena surface Plasmon resonance (SPR) [107].

In case of gold, the nanoparticles can be produced in the form of colloidal suspensions in solutions either chemically or physically by pulsed laser ablation of a metallic target, the second procedure being advantageous in terms of purity of the final product [106]. The colloidal of Au nanoparticles nowadays have many applications due to their special physical and chemical behavior, they are different from bulk materials. Also, the properties of solution depend on the particle size, shape and liquid medium [108]. The increase in the particle size and aggregation lead to change in colloidal color, as illustrated in Figure (2-14).



Fig. (2-14): Influence of particle size on colloidal color [100].

### 2-13 Surface Plasmon Resonance in Metallic

The term Plasmon is used to refer to plasma oscillations in metals, i.e. collective oscillation of conductive electron driven by light and the term resonance refers to a plasma oscillation excited by electromagnetic waves [109].

Surface Plasmon Resonance (SPR) is a physical phenomenon occurring at metal surfaces [110]. When a metal particle is exposed to light, the oscillating electromagnetic field of the light induces a collective coherent oscillation of the free electrons (conduction band electrons) of the metal. This electron oscillation around the particle surface causes a charge separation with respect to the ionic lattice, forming a dipole oscillation along the direction of the electric field of the light. The amplitude of the oscillation reaches maximum at a specific frequency, called surface plasmon resonance (SPR). SPR in nanometer-sized structures is called localized surface Plasmon resonance (LSPR) [111]. The SPR induces a strong absorption of the incident light and thus can be measured using a UV–Vis absorption spectrometer. The SPR band is much stronger for plasmonic nanoparticles (noble metal, especially Au and Ag) than other metals. The SPR band intensity and wavelength depends on the factors affecting the electron charge density on the particle surface such as the metal type, structure, composition, shape, particle size and the dielectric constant of the surrounding medium. For gold and silver NPs, the resonance falls into the visible region of the electromagnetic spectrum [112]. A striking consequence of this is the bright colors exhibited by particles both in transmitted and reflected light, due to resonantly enhanced absorption and scattering. This effect has found applications for many hundreds of years, for example in the staining of glass for windows or ornamental cups [113].

#### 2-14 Applications of Dye-Sensitized Solar Cells

Due to the advantages of lightweight, flexibility and low cost, DSSCs are being developed into consumer applications. For example, DSSCs are integrated into portable electronic devices, bags, outfits and serving as charging stations. Samsung has manufactured DSSC battery to support mobile charging.

The performance of DSSC is less sensitive to the illumination conditions compared to the inorganic solar cells. Therefore, they are able to provide electricity to low-power electrical equipments even under low illumination conditions.

Due to the advantages of better performance in low and indirect illumination and easy installation, DSSCs are employed in building structures such as windows, walls and roofs to provide electric power for the building and save electric energy [114].

The lightweight flexible DSSC modules which perform well under different light conditions are used in solar powered smoke detectors, calculators, keyboards, window blinds [115].



### **3-1 Introduction**

This chapter describes the materials and tools that used in the preparation of DSSC and the stages of fabrication of DSSC. Furthermore, the techniques used for characterization are presented including XRD, AFM, SEM, TEM, UV-Vis spectroscopy and I-V measurements.

#### **3-2 Experimental Work**

Figure (3-1) shows schematic flow chart of the DSSC preparation steps and the characterization carried out in this study.


# **3-3 Materials**

Chemicals that were used to manufacture Dye Sensitized Solar Cells are summarized in table (3-1).

Table (3-1): DSSC c	omponents from	Dyesol	company.
---------------------	----------------	--------	----------

No.	Material	Composition
1-	TEC 8 glass plates, (Dyesol Co., Australia)	Type: Soda-lime, Conducting Layer: FTO (Fluorine doped tin oxide), Resistance: 8 $\Omega$ /sq, and Sheet Thickness: 3.2 mm
2-	TEC15 glass Plates, (Dyesol Co., Australia)	Type: Soda-lime, Conducting Layer: FTO (Fluorine doped tin oxide), Resistance: 15 $\Omega$ /sq, and Sheet Thickness: 3.2 mm
3-	N719 Industry Standard Dye, (Dyesol Co., Australia)	[RuL <sub>2</sub> (NCS) <sub>2</sub> ]: 2TBA (L=2,2'-bipyridyl-4,4'- dicarboxylic acid; TBA=tetra-n-butylammonium), C <sub>58</sub> H <sub>86</sub> N <sub>8</sub> O <sub>8</sub> RuS <sub>2</sub>
4-	Z907 Hydroph-obic Dye, (Dyesol Co., Australia)	RuLL'(NCS) <sub>2</sub> (L=2,2'-bipyridyl-4,4'- dicarboxylic acid; L'=4,4' dinonyl-2,2'- bipyridine), C <sub>42</sub> H <sub>52</sub> N <sub>6</sub> O <sub>4</sub> RuS <sub>2</sub>
5-	18NR-T Transparent Titania Paste, (Dyesol Co., Australia)	Average Nanoparticle Size (active): ~20 nm
6-	PT1 Platinum Paste, (Dyesol Co., Australia)	PT1 Platinum Paste is oil-based Australia
7-	EL-HSE High Stability Electrolyte, ( Dyesol CO., Australia)	Redox couple: I <sup>-</sup> /I <sup>-</sup> <sub>3</sub> iodide/triiodide
8-	Low Temperature Thermoplaic Sealant, (Dyesol Co., Australia)	DuPontTM Surlyn functionalised E/MAA resin
9-	Ethanol	C₂H₅OH

# 3-4 Gold Nanoparticles (Au NPs) Preparation

The pulsed laser ablation in liquid system is employed to synthesize colloidal gold nanoparticles using a gold target and ethanol at room temperature. Figure (3-2) shows the actual photograph of the system used in the current study.

The gold target (purity of 99.99%) was fixed at bottom of glass vessel containing 2 ml of ethanol. The ablation was achieved focusing laser beam output of pulsed Nd: YAG laser (type DELIXI, DZ47-63, C10) operating with a repetition rate of 1 Hz and pulse width of 10 ns. Ablation is carried out with laser operating at 1064 nm wavelength at the fluence of 22.116 J/cm<sup>2</sup>. The number of laser shots applied for the metal target is 700 pulses.

The spot size of the laser beam on the target surface was 1.2 mm in diameter and the distance between the focusing lens and the metal target was 9 cm. The pulse energy was 250 mJ. In final process, the color colloidal gold nanoparticles result was violet.



**Fig.(3-2):** Photograph of the experimental setup for laser ablation of gold in ethanol.

# **3-5 Preparation of DSSC**

Figure (3-3) shows the flow chart of Dye-sensitized solar cell preparation.



Fig.(3-3): Flowchart of DSSCs preparation steps.

## **3-5-1 Glass Substrates Preparation**

The typical substrate for making Dye Sensitized Solar Cells is a glass plate coated on one side with a Transparent and Conductive Oxide (TCO) layer. The TCO material is a thin layer of fluorine – doped tin oxide (SnO<sub>2</sub>:F), also called (FTO). In this work the two types of glass substrates are (TEC-8  $\Omega$  and TEC-15  $\Omega$ ) were used.

Before using the glass substrates, they were cut to pieces of the size of (2.5 cm  $\times$  2.5 cm) by glass cutter.

Then all glass substrates were cleaned in an ultrasonic bath for 5 minutes in distilled water and 5 minutes in acetone. Then, let to dry in air.

## **3-5-2 Preparation of Working Electrodes (Photoanode)**

For the preparation of the photoanode, Doctor-Blade method was used to deposit the titania (TiO<sub>2</sub>) paste. The thickness of titania layer is determined by the thickness of scotch tape which has a thickness of 10  $\mu$ m placed on the two sides of the conductive face of substrate. Three different thicknesses were prepared by using one, two and three layers of tape. This tape can be easily removed from the glass without leaving traces of glue. The TiO<sub>2</sub> paste was deposited on the uncovered area of the glass was until a reasonable homogenous layer was achieved to make a thin film. The large surface area allows for a greater amount of dye molecules to be absorbed, which will be of great importance during the test.

After depositing the paste, the scotch tape was removed and the films were left to dry for 30 minutes in a covered pertidish. Then, the TiO<sub>2</sub> substrates were annealed in programmed electrical furnace (LABTECH DAIHAN, KOREA) at 550 °C for 30 minutes to remove the viscous solvent and impurities. Figure (3-4) shows the steps of the preparation of the working electrode mentioned above. On observation the TiO<sub>2</sub> electrode first turned brownish, sometimes releasing fumes and turned white. This is a sign that the annealing process is completed. Then, the samples were allowed to cool slowly at room temperature to avoid cracking of the slides. The thickness of the annealed films was measured using Electronic Digital Micrometer and it was found to be 10, 20 and 30  $\mu$ m.



**Fig.(3-4):** The preparation procedure of working electrode (a) scotch tape placed on the two sides of the conductive face of substrate, (b) the  $TiO_2$  paste was placed on uncovered area of the substrate, (c) applied doctor-blade method to deposition titanium paste, (d) and (e) the scotch tape was removed and the films were left under Pertidish and (f) the  $TiO_2$  substrates were annealed in programmed electrical furnace.

## **3-5-3 Preparation of Counter Electrodes (Cathode)**

For the preparation of the cathode electrode, two holes with 1 mm and distance is 6 mm were drilled in the glass substrates which will be used as cathode to enable a later injection of electrolyte.

The catalyst material used as the counter electrode for the DSSCs Platinum (Pt) paste deposited by Doctor- Blade method on the conductive face of (FTO) glass substrates.

Before using the prepared electrode, the substrate was annealed at 450 °C for 30 minutes. Figure (3-5) shows the prepared counter electrodes used in the study.



Fig.(3-5): Pt paste on FTO glass.

## **3-5-4 Preparation of Dye Solutions**

In this thesis organic dyes used are N719 and Z907. The molecular structure of these dyes is shown in figure (3-6). To prepare dye solutions, 0.0297 g and 0.022 g of N719 and Z907 ruthenium dye powders were dissolved in 100 ml of ethanol to obtain dye solution concentrations of  $0.25 \times 10^{-3}$  M and  $0.5 \times 10^{-3}$  M respectively. The solutions were stirred for 30 minutes and stored in sealed container for 24 hours before use. The photoanodes were immersed in the dye

solutions, and then kept 24 hours on a dark place at room temperature to adsorb the dye molecules on to the  $TiO_2$  surface. All samples were rinsed with ethanol to remove the dye residues. Finally, it was observed that the  $TiO_2$  electrodes turned to a maroon-black color after immersion. Figure (3-7) shows the steps of the dye electrode preparation.





Fig.(3-6): Molecular structure of N719 and Z907 dyes.



**Fig.(3-7):** Preparation steps of dyed electrode (anode). (a) The photoanodes were immersed in the dye solutions, and then kept 24 hours on a dark place at room temperature to adsorb the dye molecules on to the  $TiO_2$  surface, (b) All samples were rinsed with ethanol to remove the dye residues, (c) the  $TiO_2$  electrodes turned to a maroon-black color after immersion.

## 3-5-5 Cell Assembly

The two electrodes were assembled into a sandwich structure using hotmelted, with a thickness of 30  $\mu$ m as the spacer. A square gasket was cut out of the sealant spacer material. The inner dimensions should match with the titania film, and the outer dimensions are 1 mm bigger on all four sides. The sealant gasket was placed around titania paste and the counter electrode was put on it while the Pt film faces the TiO<sub>2</sub>. Then, the cell that obtained placed on heater at 120 °C for 15 minute for well connected by using a hot-melted Surlyn film (30  $\mu$ m, Solaronix).

Finally, the electrolyte was filled through the holes in the counter electrode by a pipette, and the holes were covered by plaster to prevent evaporation. This process is done at room temperature. Figure (3-8) shows the prepared DSSCs in their final form.



Fig.(3-8): Final form of DSSCs before test.

## **3-6 Characterization Techniques**

# **3-6-1 UV-Vis Spectroscopy**

UV-Vis double beam spectrophotometer (Visible1800) made by (Shimadzu, Japanese Co.) shown in figure (3-9) was used for optical measurements including transmission and absorption spectra. The absorbance of dyes solutions with and without gold nanoparticles, gold nanoparticles solution and TiO<sub>2</sub> films were measured over a spectral range from 300 nm to 700 nm. Absorption measurements were made with standard (1 cm  $\times$  1 cm) quartz cuvettes for solutions using ethanol as reference, while blank glass was used as reference for TiO<sub>2</sub> electrodes.



Fig.(3-9): UV-Vis spectrophotometer used in the current study.

# **3-6-2 X-ray Diffraction**

Crystal structure and crystallite size of prepared TiO<sub>2</sub> films were obtained by X-ray diffractometer (XRD- Shimadzu 6000, Japan) that operates at a current of (30 mA) and a voltage of (40 kV) with CuK $\alpha$  radiation, where  $\lambda$ =1.54056 Å. Figure (3-10) shows the actual photograph of the XRD instrument used in the present study.



Fig. (3-10): X-ray diffraction instrument used in the present study.

XRD patterns of the films were recorded with 2 $\theta$  ranging from 10° to 80° for 15 minutes.

# **3-6-3 Scanning Electron Microscope (SEM)**

The surface morphology of  $TiO_2$  films was characterized by scanning electron microscopy JEOL (SEM, JSM-7000F) shows in figure (3-11), SEM images were obtained with applied acceleration electron voltage of 20 kV.



Fig.(3-11): SEM instrument used in this study.

## **3-6-4 Atomic Force Microscope (AFM) Measurements**

To visualize the surface morphology and roughness of  $TiO_2$  films coating on FTO glass substrate before and after annealing at 550 °C atomic force microscope (SPM-AA3000) was used in contact mode. Figure (3-12) shows the AFM instrument used in the current study.



Fig.(3-12): AFM instrument used in the current study.

## **3-6-5 Transmission Electron Microscopy (TEM) Measurements**

The morphology, shape and size of Au NP aggregates were characterized by transmission electron microscope (TEM) type CM10 pw6020, Philips-Germany shown in figure (3-13). The images were obtained at an accelerating voltage of 60 kV, with maximum magnification of 25000x-450000x.



Fig.(3-13) : TEM instrument used in characterizing Au nanoparticles.

## **3-6-6 Current-Voltage Measurements**

One of the most important measurements of a solar cell is the current-voltage (I-V) measurement. From the I-V curve many important parameters can be obtained including short-circuit current (I<sub>SC</sub>), open-circuit voltage (V<sub>OC</sub>), fill factor (FF) and the efficiency ( $\eta$ ). To measure the electrical properties, voltmeter (UNI-T 50A), ammeter (UNI-T30B), variable resistance (1-100000  $\Omega$ ), and halogen lamp (120 watt) were used as shown in figure (3-14).



Fig.(3-14): Schematic for electrical instrument used in the current study.

## **3-6-7 IPCE and Spectral Response Measurements**

To estimate the IPCE and the spectral response of DSSC, ammeter, power meter, halogen lamp and monochromator (Gobin-Yorn) were used as depicted in the schematic diagram shown in figure (3-15).

Initially, the solar cell was placed in front of the light source and the wavelength of the light was changed in the range (300-800) nm using monochromator while the current readings were recorded through the ammeter and the intensity of incident light was measured by the power meter.

The IPCE and the spectral response (R) were estimated using the data recorded above by employing equations (2-11) and (2-12) respectively.



Fig.(3-15): a and b represents schematic diagram to measure IPCE and R.



# **4-1 Introduction**

In this chapter, all the results related to the absorption spectra of dyes, characterizations of  $TiO_2$  films and Au NPs and DSSCs measurements are presented and discussed.

# **4-2 Optical Properties**

# 4-2-1 Absorption of Dyes

Figure (4-1) demonstrates the absorption spectra of N719, Z907 and their mixed solutions (1:1 v/v ratio) in the wavelength range of (350-800) nm. The UV-Vis absorption spectra show two absorption peaks at around 386 and 526, 430 and 548, 396 and 528 nm, for N719, Z907 and their mixed solutions respectively. It can be also observed that the N719 dye shows the highest absorption, while Z907 dye shows the lowest absorption.



**Fig.(4-1):** UV-Vis absorption spectra of N719, Z907 and their mixed solutions (1:1 v/v ratio).

## 4-2-2 Absorption Characterizations of Au NPs

Au NPs colloidal solution was prepared by PLAL method. Z907 dye solution was prepared with concentrations of 0.0125 mM and 0.025 mM. The Z907 dye solution (with concentration of 0.025 mM) was mixed with Au NPs solution to produce a solution with concentration of 0.0125 mM.



**Fig. (4-2):** Optical absorption spectra of Z907 dye solution, Au NPs colloidal solutions and their mixed solution (1:1 v/v).

Figure (4-2) shows the optical absorption spectra for Au NPs colloidal solution, Z907 dye solution and their mixed solutions (1:1 v/v) in the wavelength range of (350-700) nm. From the figure, it is clear that Au NPs colloidal solution has single absorption peak located at round 530 nm, due to surface plasmon resonance or spherical shape [116]. While, Z907 dye solution and the mixed solution have two absorption peaks located at 370 and 510 nm and 371 and 517 nm, respectively. It can be noticed that the optical absorption increases when Au NPs were added to

Z907 dye. This enhancement is attributed to the surface plasmon resonance of Au NPs.

It can be also observed the appearance of an absorption tail in the red zone of the Au NPs spectrum which is evidence of particle assembling and instability [117]. The concentration of Au NPs was estimated to be about 4.5 ppm from calibration curve [118].

#### 4-2-3- Absorption of TiO<sub>2</sub> Films

Figure (4-3) illustrates the UV–Vis absorption spectra of TiO<sub>2</sub> films with thickness of 10  $\mu$ m as-deposited and annealed at 550 °C and 350 °C for 30 minutes deposited on TEC-8  $\Omega$  substrates under ambient conditions. It can be noticed that the intensity of absorption increases with increasing annealing temperature in the wavelength (315–363) while it decreases in the visible region.



**Fig.(4-3):** UV-Vis absorption spectra of TiO<sub>2</sub> films at as-deposited and different annealing temperatures.

Moreover, in the UV region, the absorption is very high in comparison with that of the visible region, due to which  $TiO_2$  can be used as UV blocker in inverted organic solar cells which avoid solar cells from degradation as UV rays have negative impact on the cells [119].

When annealing temperature is increased, the absorption edge is shifted to a shorter wavelengths (high energy) and this result is in agreement with the results reported by Vorontsov who found that the absorption edge is shifted to a shorter wavelengths due to the quantum-size effect when the particle size was very small [120].

The direct band gap of the TiO<sub>2</sub> films was determined by plotting  $(\alpha hv)^2$  vs. hv curves. The optical band gap E<sub>g</sub> value is defined by extrapolation of the straight-line portion of the plot to zero absorption edge in a graph of  $(\alpha hv)^2$  vs. hv as shown in Figure (4-4). From the figure, it was observed that direct optical band gap for annealed TiO<sub>2</sub> films increases from 2.30 eV to 3.12 eV with the increase of annealing temperature and this result is in agreement with the results reported by Hadjoub et al. [121]. This increase attributed to the improvement of crystallinity of anatase phase and also due to the size quantization in nanocrystalline semiconductors [122]. A decrease of the crystallite size leads to the increase in the band gap energy and caused a gradually shift of the absorption edge towards a shorter wavelength.

Earlier reports shows the average value for absorption to be 385 nm and the corresponding band gap energy for bulk titania as 3.2 eV. The resulting blue shift of the absorption is due to the change of particle size. The quantity of photons reaching the core of a spherical particle depends on the size of the particle and the optical properties of the titania [123]. This size quantization occurs due to localization of electrons and holes in a confined volume of the semiconductor nanocrystallites, which are typically in nanosize. This results in a change in energy band structure, with separation of individual energy levels and an increase in effective optical band gap of the semiconductor as compared with bulk [124].



**Fig.(4-4):**  $(\alpha hv)^2$  vs. energy curves of TiO<sub>2</sub> films as-deposited and annealed at 350 °C and 550 °C.

## 4-2-4 Effect of Dye Type on DSSCs Absorption

DSSCs prepared by TiO<sub>2</sub> film with thickness of 10  $\mu$ m deposited on TEC-8  $\Omega$  annealed at 550 °C for 30 minutes immersed in different dyes and their mixture with concentration 0.25 mM. Absorption spectra of DSSCs using different dyes and their mixture in the wavelength of 350-750 nm are shown in figure (4-5).





From the absorption spectra, it can be seen that DSSC with mixture dye has absorption higher compared to the other two cells. Due to the enhancement in absorption, one may expect certain enhancement in efficiency.

# 4-2-5 Effect of TiO<sub>2</sub> Layer Thickness on the Absorption of DSSCs

Figure (4-6) shows the absorption spectra of DSSCs in the wavelengths range of (350-750) nm using 10, 20 and 30  $\mu$ m thickness of TiO<sub>2</sub> layer and N719 dye as sensitizer. It can be noted that DSSC with TiO<sub>2</sub> film with thickness of 30  $\mu$ m has higher absorption compared to other two cells in most of the spectral range due to the increase of dye adsorption and it could be explained by the enhanced loading of dye molecules on TiO<sub>2</sub> film.



**Fig.(4-6):** UV-Vis absorption spectra of DSSCs at different TiO<sub>2</sub> layer thicknesses.

# **4-3 Structural Properties**

# **4-3-1 X-ray Diffraction Analysis**

Crystalline characterizations of  $TiO_2$  films prepared by Doctor-blade technique on glass substrate were carried out by X-ray diffraction (XRD).

Figure (4-7) shows the XRD patterns of TiO<sub>2</sub> films with thickness 10  $\mu$ m which as-deposited at room temperature and annealed at 350 °C and 550 °C for 30 minutes. From the figure, it was confirmed that all patterns are indexed to the anatase phase (i.e anatase pure) with polycrystalline structure [125] according to the ICDD standard card no. (21-1272) shown in figure (4-8). From the diffraction patterns, it was found that the as-deposited film and the film annealed at 350 °C, exhibited characteristic peaks of anatase crystal planes (101), (004), (200), (105), (211) and (204), while in the film annealed at 550 °C, a very weak characteristic peak of anatase crystal plane (215) appeared, and this result is in agreement with the results reported by Hasan et al. [126]. The highest and strongest peak of all TiO<sub>2</sub> films was found at 2 $\theta \approx 25.4^{\circ}$  corresponding to (101) direction.

From the figure, it can be also observed that the crystallinity of  $TiO_2$  films increases with increase in temperature up to 550 °C also observed broad peaks width. Relatively broad width of peaks of the XRD patterns implies crystallites are smaller in size [127].

The crystallite size of TiO<sub>2</sub> film of (101) peak at 550 °C was calculated by Scherrer's formula given in equation (2-18) [128] and it is found to be 12.41 nm. The calculated crystallite size of TiO<sub>2</sub> film annealed at 550 °C, it is less compare others. Hence 550 °C was chosen as the optimum annealing temperature for the synthesis of TiO<sub>2</sub> nanomaterials. It is reported that the anatase TiO<sub>2</sub> with small size has shown best photocatalytic activity than rutile phase [129].

The lattice parameters a and c are calculated using equation (2-17) and they are given along with other XRD results in table (4-1). The calculated lattice constants a and c are found to agree well with the standard values (a = 3.781 nm and c = 9.51 nm) [130]. The results show that the crystallite size decreases with the increase in annealing temperature and this result is in agreement with the results reported by Shim et al. [131]. The decrease in crystallite size leads to increase in the surface area of  $TiO_2$  film and resulting in an increase of dye absorption amount.



Fig.(4-7): XRD patterns of TiO<sub>2</sub> films.

21-1272 Quality: * CAS Number:	Ti02 Titanium Ref: Na	Oxide tl. Bur. S	Stan	d (	U.S.	] Monogr.	25, 7, 8	2 (1 96	9)					
Molecular Weight:  73:30    Volume(CD):  136:31    Dx:  3.893  Dm:    S.G.:  141/amd (141)    Cell Parameters:  a    a  3.785  b  c  9.513    2:  B  7    SS/FDM:  F30=74(.0116,.35)  1/loor:  3.3    I/loor:  3.3  Rad:	Fixed Sitt Sqrt Intensity >>	2	5		5				12	1    1	0 - 152.62			
Lambda: Filter: d-sp:	28	int-f	h	k	1	26	int-f	h	K 1.	28	int-f	h	k	1
Mineral Name: Anatase, syn	36,946 37,800 38,575 48,049 53,890 55,060 62,119 62,688 68,760 70,309 74,029 75,029	100 200 100 350 200 4 14 6 6 20 4 10 200 4 10 200 10 200 10 200 200 10 200 200 200	101212221212	001001101201	342051346075	80,725 82,136 82,659 83,147 93,217 94,178 95,139 96,315 99,801 107,24 108,95	4226424422244	000000000000000000000000000000000000000		113.85 114.90 118.43 120.09 121.72 122.33 131.02 135.99 137.38 143.87 150.02 152.62	22242222224224242	3342244434340	211210221020	519834075942

Fig.(4-8): Standard card no.(21-1272) of TiO<sub>2</sub>.

TiO <sub>2</sub> thin film	As-deposited	Annealing at 350 °C	Annealing at 550 °C		
20 (deg)	25.4007	25.3983	25.3720		
hkl	101	101	101		
FWHM (rad)	0.009319	0.010327	0.011456		
D (nm)	15.252	13.763	12.406		
Lattice constant (a=b) (Å)	3.781	3.787	3.781		
(c)	9.476	9.466	9.477		

**Table (4-1):** XRD results of TiO2 films.

# 4-3-2 Scanning Electron Microscope (SEM) Analysis

The surface morphology of  $TiO_2$  film was characterized by SEM. Figure (4-9) displays the SEM image of  $(TiO_2)$  film of thickness 10 µm which has been coated on the FTO glass after annealing at 550 °C for 30 minutes.

The SEM examination confirms a spongy shape with reduction in the number of open pores making easy for dye adsorption and electron transport [132]. The small particles of  $TiO_2$  film have large area and subsequently absorb more dyes. Subsequently, this may lead to improved DSSC performance [133]. The average particle size of  $TiO_2$  NPs is about 20–40 nm.



**Fig.(4-9):** SEM image of TiO<sub>2</sub> film at 30,000X.

#### 4-3-3 TEM Analysis of Au NPs

To identify the particles size, shape and size distribution of Au NPs present in the prepared samples, they were characterized by transmission electron microscope (TEM). The TEM image and size distribution of Au-NPs produced by PLAL method of a gold metal plate in ethanol is shown in figure (4-10). The TEM image confirmed that the particles are spherical in shape of nanosize [105]. It can be also observed that interconnect NPs lead to agglomeration. On the basis of the TEM image the size distribution of NPs was calculated. The precise size distribution of NPs is presented in Figure (4-10 b), and it is clear that the nanoparticles diameters are in the range of (10–90) nm. The average particle size was 50 nm.





**Fig.(4-10):** (a) TEM image and (b) histogram corresponding to the size distribution of gold nanoparticles produced by 1064 nm laser ablation of a gold metal plate in ethanol for (700) pulses.

# 4-3-4 AFM Analysis of TiO<sub>2</sub> Thin Films

The surfaces morphologies of  $TiO_2$  films prepared by Doctor-blade method on FTO glass were studied by Atomic Force Microscope (AFM) technique. The 3-dimention (3-D) AFM images and distribution charts of as-deposited  $TiO_2$  film of 10 µm thickness and the  $TiO_2$  films annealed at 350 °C and 550 °C for 30 minutes in ambeient atmosphere are shown in figure (4-11).



**Fig.(4-11):**3-D AFM images and Granularity accumulation distribution charts of  $TiO_2$  films (a) as-deposited, annealed at (b) 350 °C and (c) 550 °C.

From AFM images, the surfaces were distinguished to have porous structure with lower roughness values and with increasing of annealing temperature [134]. The table (4-2) summarizes AFM parameters including grain size, roughness and root mean square values of all  $TiO_2$  films. From the table, it can be observed that the surface roughness of the films decreases with increases the annealing temperature. The rapid decreases of the surface roughness is due to the grain size decreases.

The lower roughness and grain size reduces represent good homogeneity of the TiO<sub>2</sub> films annealed at 550 °C [135]. According to the above discussion, it can be concluded that the annealing temperature can strongly affect the structural properties of TiO<sub>2</sub> films and suitable annealing temperature is around 550 °C leading to improvement of TiO<sub>2</sub> crystallinity [136]. The dense films enhance the cell efficiency due to increase in absorption amount of dye in TiO<sub>2</sub> layer.

**Table (4-2):** Average roughness and root mean square (RMS) of  $TiO_2$  films by AFM technique.

TiO <sub>2</sub> films	Surface Roughness (nm)	RMS (nm)	Grain Size (nm)		
As-deposited	0.882	1.02	91.02		
Annealing at 350 °C	0.467	0.546	91.00		
Annealing at 550 °C	0.356	0.423	82.48		

## **4-4 J-V Characteristics of DSSCs**

## 4-4-1 The Effect of TiO<sub>2</sub> Thickness on DSSC Efficiency

Figure (4-12) shows the photocurrent density-voltage characteristics of DSSCs using different TiO<sub>2</sub> film thicknesses (10  $\mu$ m, 20  $\mu$ m, 30  $\mu$ m) prepared by Doctor-Blade technique at annealing temperature of 550 °C for 30 minutes. The various photovoltaic parameters of these DSSCs are shown in Table (4-3). From the results, it was observed that  $J_{SC}$  and  $V_{OC}$ of DSSC are affected by  $TiO_2$  film thickness.  $V_{OC}$  decrease with an increase of the film thickness beyond 20 µm. This is attributed as a consequence of the higher charge recombination and restricted mass transport in thicker films due to the augmentation of surface area. In addition, it is found that FF also reduces by increasing the thickness of the TiO<sub>2</sub> film beyond 20  $\mu$ m due to a higher series resistance [137]. From the figure (4-12) and Table (4-3), it can be noticed that the optimum film thickness is 20  $\mu$ m. Due to the optimum film thickness of TiO<sub>2</sub> film, a higher adsorption of the N719 dye through the TiO<sub>2</sub>/dye layers can be achieved. However, the J<sub>SC</sub> and V<sub>OC</sub> of DSSC with a TiO<sub>2</sub> film thickness of 30  $\mu$ m (2.741 mA/cm<sup>2</sup> and 0.619 V) are smaller than those of DSSC with a TiO<sub>2</sub> film thickness of 20  $\mu$ m (5.783 mA/cm<sup>2</sup> and 0.666 V), respectively. This indicates that the lower transmittance of the TiO<sub>2</sub> film with a thickness of 30 µm reduces the incident light intensity on the N719 dye. The optimum efficiency ( $\eta$ ) of (3.587 %) with J<sub>SC</sub> and V<sub>OC</sub> of 5.783  $mA/cm^2$  and 0.666 V, respectively, was obtained by the TiO<sub>2</sub> film with a thickness of 20  $\mu$ m. The variations of the J<sub>SC</sub> and efficiency indicate that the efficiency increase is largely due to the  $J_{SC}$  increase [2]. The maximum efficiency ( $\eta$ ) of 3.587 % achieved at thickness of 20  $\mu$ m. Also, the maximum efficiency enhancement was about 137 %.



Fig.(4-12): J-V curves of DSSCs using various TiO<sub>2</sub> film thicknesses.

**Table (4-3):** The photovoltaic parameters of DSSCs fabricated using different thicknesses of  $TiO_2$  films.

Thickness of TiO2 film (μm)	Voc (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (V)	J <sub>max</sub> (mA/cm <sup>2</sup> )	FF	η (%)	Efficiency enhancement (%)
10	0.535	3.429	0.323	2.079	0.366	1.343	137
20	0.666	5.783	0.417	4.301	0.466	3.587	137
30	0.619	2.741	0.382	1.982	0.446	1.514	

## **4-4-2 The Effect of Dye Concentration on DSSC Efficiency**

Figure (4-13) shows the J-V characteristics of DSSCs prepared by TEC-8  $\Omega$ , TiO<sub>2</sub> film thickness of 10 µm annealed at 550 °C for 30 minutes and various concentrations of N719 dye (0.125 mM, 0.25 mM and 0.5 mM). From the J-V curves, it was noted that short-circuit current density increases with increasing dye concentration. This shows that at high concentrations the TiO<sub>2</sub> electrode will have enough dye adsorption to obtain high conversion efficiency. As shown in the figure, the DSSC with 0.5 mM dye concentration has high  $V_{OC}$  and  $J_{SC}$ , subsequently obtained largest efficiency. However, at low dye concentration (0.125 mM), the adsorption is low and the  $V_{OC}$ ,  $J_{SC}$  and efficiency becomes lower. This indicated that insufficient surface coverage of the light absorbing dye on the surface of the film would result in a reduction in the number of electron and electron-hole pairs generated after photon absorption, consequently decreasing  $J_{SC}$  and power conversion efficiency. Also observed that  $V_{OC}$  variation with concentration variation which is thought to be due to reactivity and instability with N719 dye [138].

Table (4-4) shows the photovoltaic parameters of the DSSCs prepared using different concentrations of N719 dye solution. The maximum efficiency ( $\eta$ ) of 2.504 % achieved at dye concentration of 0.5 mM. Also, the maximum efficiency enhancement was about 86 %.



Fig.(4-13): J-V curves of DSSCs using different dye concentrations.

**Table (4-4):** The photovoltaic parameters of DSSCs fabricated usingdifferent concentrations of N719 dye solution.

N719 dye concnentration (mM)	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (V)	J <sub>max</sub> (mA/cm <sup>2</sup> )	FF	η (%)	Efficiency enhancement (%)
0.125	0.36	1.289	0.212	0.545	0.249	0.231	
0.25	0.535	3.429	0.323	2.079	0.366	1.343	86
0.5	0.585	5.197	0.420	2.981	0.412	2.504	

# 4-4-3 The Effect of Dyes Mixing on DSSC Efficiency

Figure (4-14) illustrates the J-V characteristics of the DSSCs prepared by TEC-8  $\Omega$ , TiO<sub>2</sub> film thickness of 10 µm annealed at 550 °C for 30 minutes and sensitized with individual N719, Z907 and mixture dyes (N719+Z907, 1:1 v/v ratio). It was found that DSSC with mixture dye showed the largest area of the J-V curve compared with individuals DSSCs, indicating that this cell generated the highest output power. The photovoltaic parameters which are summarized in Table (4-5). The mixture dye was expected to perform better than individual dyes due to the broadening of the UV-Vis spectrum of mixture dye in the blue region [139].



**Fig.(4-14):** J-V curves of DSSCs using N719, Z907 and mixture dyes (N719 + Z907, 1:1 v/v ratio).

From the results, it was observed that  $J_{SC}$ ,  $V_{OC}$  and conversion efficiency of DSSC with mixture dye are higher compared to individual dye of N719 and Z907, respectively, which is likely to be due to the wideband absorption of the dyes [139]. This also indicates that mixed cosensitization of the two dyes could effectively transfer energy synergistically to the TiO<sub>2</sub> semiconductor [140] resulting in an enhancement of the photovoltaic parameters of the cell. The efficiency achieved by the DSSC using mixed dye was 2.287 %. Also, the maximum efficiency enhancement was about 70 %.

**Table (4-5):** The photovoltaic parameters of DSSCs fabricated using N719, Z907, and mixture dye (N719 + Z907, 1:1 v/v).

Dye sensitizer	Voc (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (V)	J <sub>max</sub> (mA/cm <sup>2</sup> )	FF	ղ (%)	Efficiency enhancement (%)
N719	0.535	3.429	0.323	2.079	0.366	1.343	
Z907	0.535	2.135	0.360	1.539	0.485	1.108	70
Mix	0.655	4.132	0.44	2.599	0.422	2.287	

# **4-4-4 The Effect of Substrate Resistance on DSSCs Efficiency**

The DSSCs are fabricated using TEC-8  $\Omega$ , TEC-15  $\Omega$ , TiO<sub>2</sub> film with thickness of 10  $\mu$ m annealed at 550 °C for 30 minutes and Z907 dye as sensitizer with concentration 0.25 mM.
Figure (4-15) demonstrates the J-V characteristics of two DSSCs based on TEC substrates of different resistances. It was observed that the DSSC with TEC-8  $\Omega$  has current density-voltage curve area larger than that of the DSSC with TEC-15  $\Omega$ . It was also noted that J<sub>SC</sub> increases for DSSC with TEC-8  $\Omega$  compared to that of DSSC with TEC-15  $\Omega$ , while V<sub>oC</sub> remains unchanged. Subsequently, an increase in short circuit current density leads directly to an increase in the energy conversion efficiency. This can be ascribed to difference in the thickness of Fluorine Tin Oxide (FTO) layer, TEC-8  $\Omega$  is 600 nm thick while TEC-15  $\Omega$  is 300 nm thick. The photovoltaic parameters of the DSSCs prepared using different TEC substrates are summarized in Table (4-6). The maximum efficiency of 1.786 % achieved at TEC-8  $\Omega$  substrate. Also, the maximum efficiency enhancement was about 84 %.



Fig.(4-15): J-V curves of DSSCs using different TEC substrates.

Substrate Type	Voc (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (V)	J <sub>max</sub> (mA/cm <sup>2</sup> )	FF	η (%)	Efficiency enhancement (%)
<b>ΤΕC-15 Ω</b>	0.53	3.011	0.289	1.682	0.305	0.972	84
<b>TEC-8 Ω</b>	0.53	4.069	0.31	2.881	0.414	1.786	

 Table (4-6): The photovoltaic parameters of DSSCs fabricated using different TEC substrates.

### 4-4-5 The Effect of Au NPs on DSSCs Efficiency

The DSSCs are prepared using TEC-8  $\Omega$ , TiO<sub>2</sub> layer of thickness of 10  $\mu$ m annealed at 550 °C for 30 minutes and Z907 dye as sensitizer contains Au NPs with concentration 0.0125 mM.

Figure (4-16) shows current density-voltage characteristics of DSSC with Au NPs. For comparison, the current density-voltage characteristic of the reference DSSC without Au NPs is also shown. Table (4-7) lists the cells performance data obtained from the J-V curve measurements. From the results, it was found that photocurrent density ( $J_{SC}$ ) and opencircuit voltage ( $V_{OC}$ ) increase for DSSC with Au NPs compared to the DSSC prepared without Au NPs. An increase in  $J_{SC}$  leads directly to an increase in the power conversion efficiency. The enhanced performance was largely attributed to plasmons of Au NPs that may scatter more photons to the substrate in comparison to the particle free solar cell, leading to increase the optical path length in the solar cell [117]. The efficiency achieved by the DSSC using Au NPs was 2.367 %. Also, the maximum efficiency enhancement was about 84 %.



Fig (4-16): J-V curves of DSSCs with and without Au NPs.

**Table (4-7):** The photovoltaic parameters of DSSCs with and without AuNPs.

DSSC Type	Voc (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (V)	J <sub>max</sub> (mA/cm <sup>2</sup> )	FF	η (%)	Efficiency enhancement (%)
Without	0.513	3.949	0.298	2.155	0.317	1.285	
Au NPs							84
With	0.606	5.859	0.304	3.893	0.333	2.367	
Au NPs							

# 4-4-6 The Effect of Two-Faces on the Efficiency of DSSC

The DSSCs are prepared using TEC-8  $\Omega$ , TiO<sub>2</sub> layer of thickness of 20  $\mu$ m annealed at 550 °C for 30 minutes and N719 dye as sensitizer with concentration 0.25 mM.

Figure (4-17) demonstrates the J-V curves of DSSCs when incident radiation is perpendicular to front side, perpendicular to back side and with angle 45° on the front side. In case of front-side (TiO<sub>2</sub> side), it was found that J<sub>SC</sub> and V<sub>OC</sub> recorded lightly increase for DSSC illuminated with perpendicular radiation compared to that illuminated with angle 45°, this proves that DSSC is not affected by the fall angle reverse silicon cell. Subsequently, this increase leads directly to lightly increase in energy conversion efficiency. It can be also noted that  $J_{SC}$  and  $V_{OC}$  increase for perpendicular incident light on front-side (TiO<sub>2</sub> side) compared to that back-face (Pt side) of DSSC. This variation is largely attributed to response time. Response time increases for back-side compared to that of front-side of DSSC. This attributed to electron trap filling and emptying in the TiO<sub>2</sub>. i.e. the few electrons that are injected into the TiO<sub>2</sub> layer suffer from trapping and release from traps before reaching the back contact, this lead to delay in the electron transport resulting in a longer response time [141]. Table (4-8) shows the photovoltaic parameters of the DSSCs prepared using front face, back face and with angle 45°. The maximum efficiency (n) of 3.342 % achieved at the front face.



Fig. (4-17): J-V curves of DSSCs using front and back side of substrate.

**Table (4-8):** The photovoltaic parameters of DSSCs of front, back face and angle 45°.

DSSC Type	Voc (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (V)	J <sub>max</sub> (mA/cm <sup>2</sup> )	FF	η (%)
Back side	0.648	3.602	0.441	2.886	0.545	2.546
Front side	0.654	5.274	0.438	3.815	0.484	3.342
Angle 45°	0.622	5.208	0.401	4.138	0.512	3.318

### **4-4-7 IPCE Measurement of DSSC**

Figure (4-18) shows the incident monochromatic photon-to-current conversion efficiency (IPCE) as a function of wavelength. An IPCE (%) of 52.7 % was obtained of DSSC with TiO<sub>2</sub> film thickness of 20  $\mu$ m annealed at 550 °C for 30 minutes, TEC-8  $\Omega$  and N719 dye as sensitizer with concentration 0.25 mM.

As shown in the figure, high IPCE value represents high optical absorption and thus improves the incident photon-to-current conversion efficiency. This result may be also attributed to the better transmittance of  $TiO_2$  film to increase the light intensity reaching the N719 dye.

The results of IPCE indicate that the wavelength of incident light ranges from 300 to 800 nm contributes to photon-to-current conversion. The reason is that N719 dye has the highest quantum efficiency at the wavelength of 450 nm. Thus, the highest IPCE is observed at 450 nm for the prepared DSSC. The  $J_{SC}$  enhancement is a result of unfailing improvement of IPCE [142].



Fig.(4-18) : IPCE as a function of wavelength of the DSSC.

# 4-4-8 Spectral Response (R) of DSSC

Figure (4-19) shows the spectral response of DSSC with TiO<sub>2</sub> film thickness 20  $\mu$ m annealed at 550 °C and N719 dye with concentration 0.25 mM as sensitizer. From the response curve, one peak could be recognized. The maximum spectral response value of DSSC is  $1\mu A/\mu W$  at 450 nm. This indicates that absorption of dye molecules on TiO<sub>2</sub> film largely, led to enhancement DSSC efficiency.



Fig.(4-19) : Spectral response curve of DSSC.

# **4-5 Optical Transparency of DSSC**

One of the important properties DSSC is its transparency. The typical DSSC based on TiO<sub>2</sub> film with thickness of 20  $\mu$ m and N719 dye as sensitizer is used to visualize the transparency. To further highlight the transparency of DSSCs, we took images through a 1 cm  $\times$  1 cm cell fabricated. Figure (4-20) shows the images taken by using DSSC as mediator between camera and printed black words on white paper and the image of flowers. The images show that DSSC have high transparency due to the optical transparency of TiO<sub>2</sub> film which is increased with decreasing particle size and increasing film homogeneity [143]. This property is very important in DSSC applications such as using solar cells as buildings windows [144].



Enhancement by Optimizing the Preparation Parameters

**Fig.(4-20):** High transparency of DSSC (a, b and c) images taken through DSSC for flowers and thesis subject.

# **4-6 Conclusions**

From this work, several points can be concluded:

1- DSSCs have been fabricated successfully, via using N719 and Z907 dyes as sensitizer material, by employing a simple route without the need for any special and complicated facilities.

2- Solar cells with efficiency enhanced as high as 92.2 % have been achieved in this study.

3- The mixing of the two dyes, N719 and Z907, has led to improve the DSSC efficiency from 1.343 % (in case of N719) and 1.108 % (in case of Z907) to 2.287 % because of the broad absorption band of the dye mixture in the visible region of the spectrum.

4- Adding Au NPs to Z907 dye enhanced the efficiency of the DSSCs to about 2.367 % because the plasmons of the nanoparticles may act as scattering leading to increase the optical path length of the photons in the solar cell which subsequently resulted in efficiency enhancement.

5- DSSC highest efficiency was recorded at 20  $\mu$ m thickness of TiO<sub>2</sub> layer deposited on TEC-8  $\Omega$  substrate using N719 dye with 0.25 mM concentration.

6- All the prepared DSSCs have high transparency, which qualifies them for use as buildings windows.

7- DSSCs are not affected by incident angle of light radiation.

# 4-7 Future Works

- Using another dye (like  $N_3$ ) to enhance the efficiency of DSSC.
- ✤ Using gel-electrolyte to enhance the efficiency of DSSC.
- Using another noble metal (like Ag NPs) to enhance the efficiency of DSSC.

- Studying the effect of the solar cell temperature on conversion efficiency.
- Using stainless steel as an electrode (cathode) which can serve as a reflected surface to increase the conversion efficiency of the solar cell.
- Mixed noble metal (like Au NPs and Ag NPs) to enhance the efficiency of DSSC.



### **References**

[1] O. O. Kelvin and Ekpunobi, **"Fabrication and Characterization of Dye Sensitized Solar Cell Using Anarcardium Occidentale Sensitizer"**, Advances in Applied Science Research, Vol. 3, No. 5, pp. 3390-3395, (2012).

[2] A. Hagfeldt and M. Gratzel, "**Molecular Photovoltaics**", Account of Chemical Research, Vol. 33, No. 5, pp. 269-277, (2000).

[3] H. J. Kim, Y. Ch. Kim, J. T. Hong, M. J. Kim, H. W. Seo, J. W. Park, and J. Y. Choi, "A Study of the Photo-Electric Efficiency of Dye-Sensitized Solar Cells Under Lower Light Intensity", Journal of Electrical Engineering & Technology, Vol. 2, No. 4, pp. 513-517, (2007).

[4] S. Ito, M. K. Nazeeruddin, S. M. Zakeeruddin, P. P'echy, P. Comte, M. Gratzel, T. Mizuno, A. Tanaka, and T. Koyanagi, "Study of Dye-Sensitized Solar Cells by Scanning ElectronMicrograph Observation and Thickness Optimization of Porous TiO<sub>2</sub> Electrodes", International Journal of Photoenergy, Vol. 20, pp. 1-8, (2009).

[5] Ch. L. Lee, W. H. Lee, and Ch. H. Yang, "High Efficiency of Dye-Sensitized Solar Cells Based on Ruthenium and Metal-Free Dyes", International Journal of Photoenergy, Vol. 126, pp. 1-6, (2013).

[6] D. J. Godibo, "Screening of Natural Dyes for Use in Dye Sensitized Solar Cells", M.Sc. Thesis, Addis Ababa University, Ethiopia, (2012).

[7] W. A. Vallejo, C. A. Quiñones, and J. A. Hernandez, The Chemistry and Physics of Dye-Sensitized Solar Cells. In: L. A. Kosyachenko (Ed.), Solar Cells-Dye-Sensitized Devices, InTech, Croatia, (2011).

[8] G. R. A. Kumara, S. Kaneko, M. Okuya, and K. Tennakone, **''Fabrication of Dye-Sensitized Solar Cells Using Triethylamine Hydrothiocyanate as a CuI Crystal Growth Inhibitor''**, Langmuir, Vol. 18, pp. 10493-10495, (2002). [9] A. A. Mohammed, A. S. Said Ahmad, and W. A. Azeez,
"Fabrication of Dye Sensitized Solar Cell Based on Titanium Dioxide (TiO<sub>2</sub>)", Advances in Materials Physics and Chemistry, Vol. 5, pp. 361-367, (2015).

[10] S. Sakthivel, V. Baskaran, and S. Mahenthiran, "Dye Sensitized Solar Cell Properties and Fabrication Using Lawsonia Inermis", Journal of Chemistry and Chemical Sciences, Vol. 5, pp. 85-92, (2015).

[11] K. Kalyanasundaram, **Photochemical and Photoelectrochemical A pproaches to Energy Conversion**. In: K. Kalyanasundaram (Ed.), Dye-Sensitized Solar Cells, CRC press, France, (2010).

[12] B. Oregan and M. Gratzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films", Nature, Vol. 353, pp. 737-740, (1991).

[13] A. Usami, **"Theoretical study of application of multiple scattering of light to a dye-sensitized nanocrystalline photoelectrochemical cell"**, Chemical Physics Letters, Vol. 277, pp. 105-108, (1997).

[14] K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda, and V. P. S. Perera, "An efficient dye-sensitized photoelectrochemical solar cell made from oxides of tin and zinc", Chemical Communications, Vol. 1, pp. 15-16, (1999).

[15] H. Lindstrom, A. Holmberg, E. Magnusson, L. Malmqvist, and A. Hagfeldt, **''A new method to make dye-sensitized nanocrystalline solar cells at room temperature''**, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 145, pp. 107-112, (2001).

[16] G. Boschloo, H. Lindström, E. Magnusson, A. Holmberg, and A. Hagfeldt, "Optimization of dye-sensitized solar cells prepared by

**compression method''**, Photochemistry and Photobiology A: Chemistry, Vol. 148, pp. 11-15, (2002).

[17] P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. H. Baker, and M. Gratzel, "Enhance the Performance of Dye-Sensitized Solar Cells by Co-grafting Amphiphilic Sensitizer and Hexadecylmalonic Acid on TiO<sub>2</sub> Nanocrystals", The Journal of Physical Chemistry B, Vol. 107, No. 51, pp.14336-14341, (2003).

[18] Z. Sh. Wang, H. Kawauchi, T. Kashima, and H. Arakawa, "Significant influence of TiO<sub>2</sub> photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell", Coordination Chemistry Reviews, Vol. 248, pp. 1381-1389, (2004).

[19] J. Bandara and H. Weerasinghe, "**Design of high-efficiency solidstate dyesensitized solar cells using coupled dye mixture**", Solar Energy Materials & Solar Cells, Vol. 90, No. 7, pp. 864-871, (2006).

[20] S. Hore, C. Vetter, R. Kern, H. Smit, and A. Hinsch, "**Influence of scattering layers on efficiency of dye-sensitized solar cells**", Solar Energy Materials & Solar Cells, Vol. 90, No. 9, pp. 1176-1188, (2006).

[21] T. Y. Lee, P. S. Alegaonkar, and J. B. Yoo, **"Fabrication of dye sensitized solar cell using TiO<sub>2</sub> coated carbon nanotubes"**, Thin Solid Films, Vol. 515, No. 12, pp. 5131-5135, (2007).

[22] T. P. Chou, Q. Zhang, B. Russo, and G. Cao, "Enhanced lightconversion efficiency of titanium dioxide dye-sensitized solar cells with the addition of indium-tin-oxide and fluorine-tin-oxide nanoparticles in electrode films", Journal of Nanophotonics, Vol. 2, No. 1, pp. 023509-023511, (2008).

[23] S. Sakurai, H. Jiang, M. Takahashi, and K. Kobayashi, "Enhanced performance of a dye-sensitized solar cell with a modified poly (3,4

ethylenedioxythiophene)/TiO2/FTOcounterelectrode'',Electrochimica Acta, Vol. 54, No. 23, pp. 5463-5469, (2009).

[24] T. P. Huynh, T. T Hoanq, Ph. H. Nguyen, T. N. Tran, and V. Nguyen, "Preparation of TiO<sub>2</sub> Thin Film Using Modified Doctor-Blade Method for Improvement of Dye-Sensitized Solar Cell", Photovoltaic Specialists Conference (PVSC), Vol. 2, pp. 002168-002171, (2009).

[25] M. H. Bazargan, "**Performance of nano structured dye-sensitized solar cell-utilizing natural sensitizer operated with platinum and carbon coated counter electrode**", International Journal of Chem Tech Research, Vol. 2, pp. 615-619, (2010).

[26] Y. Lee and M. Kang, "The optical properties of nanoporous structured titanium dioxide and the photovoltaic efficiency on DSSC", Materials Chemistry and Physics, Vol. 122, No. 1, pp. 284–289, (2010).

[27] X. Wu, G. Lu, and L. Wang, "The effect of the thickness of TiO<sub>2</sub> nanosheets film with exposed (001) facets on the performance of dyesensitized solar cells", Chemeca 2011: Engineering a Better World: Sydney Hilton Hotel, NSW, Australia, Vol. 28, pp. 18-21, (2011).

[28] T. H. Tsai, S. C. Chiou, and S. M. Chen, "Enhancement of dyesensitized solar cells by using graphene-TiO<sub>2</sub> composites as photoelectrochemical working electrode", International Journal Electrochemical Science, Vol. 6, pp. 3333-3343, (2011).

[29] C. H. Lee, S. W. Rhee, and H. W. Choi, "**Preparation of TiO<sub>2</sub> nanotube/nanoparticle composite particles and their applications in dye-sensitized solar cells**", Nanoscale research letters, Vol. 7, pp. 1-5, (2012). [30] Abel. F. Ole, G. N. C. Santos, and R. V. Quiroga, "Fabrication and Characterization of Dye Sensitized Solar Cell Using Nanostructured TiO<sub>2</sub> Photoelectrode", International Journal of Scientific and Engineering Research, Vol. 3, No. 8, pp. 2229-5518, (2012).

[31] S. N. Karthick, K. V. Hemalatha, C. J. Raj, H. Kim, and Y. Moonsuk, **"Titanium dioxide paste preparation for dye sensitized solar cell using hydrothermal technique"**, Ceramic Processing Research. Vol. 13, No. 1, pp. 136-139, (2012).

[32] K. Guo, M. Li, X. Fang, X. Liu, B. Sebo, Y. Zhu, Z. Hu, and X. Zhao, "**Preparation and enhanced properties of dye-sensitized solar cells by surface plasmon resonance of Ag nanoparticles in nanocomposite photoanode**", Journal of Power Sources, Vol. 230, pp. 155-160, (2013).

[33] A. A. Oladiran and I. A. M. Olabisi, "Fabrication of Dye Sensitized Solar Cell (DSSC) Using ZnO Nanoparticales Synthesized from Zinc Nitrate Hexahydrate", Canadian Journal of Pure and Applied Sciences, Vol. 7, No. 3, pp. 2635-2638, (2013).

[34] T. G. Deepak, G. S. Anjusree, K. R. Narendra, D. Subash, and Sh. V.
N. A. S. Nair, "Fabrication of a dye-sensitized solar cell module using spray pyrolysis deposition of a TiO<sub>2</sub> colloid", RSC Advances, Vol. 4, No. 44, pp. 23299-23303, (2014).

[35] D. Gu, Q. Zhang, Q. Wu, and Y. Zhu, "Impact of Dye-Sensitized Solar Cell Anode Preparation on Performance", Open Journal of Applied Sciences, Vol. 4, No. 9, pp. 467-472, (2014).

[36] O. A. Hammadi and Noor I. Naji, "Effect of Acidic Environment on the Spectral Properties of Hibiscus sabdariffa Organic Dye used in Dye-Sensitized Solar Cells", Iraqi Journal of Applied Physics, Vol. 10, No. 2, pp. 27-31, (2014). [37] N. Gomesh, A. H. Ibrahim, R. Syafinar, M. Irwanto, M. R. Mamat,
Y. M Irwan, U. Hashim, and N. Mariun, "Fabrication of Dye Sensitized
Solar Cell Using Various Counter Electrode Thickness", International
Journal Series in Engineering Science, Vol. 1, No. 1, pp. 49-56, (2015).

[38] J. Uddin, J. M. Islam, E. Karim, S. M. Khan, S. Akhter, E. Hoque, and M. A. Khan, "**Preparation and Characterization of Dye Sensitized Solar Cell Using Natural Dye Extract from Red Amaranth** (**Amaranthus sp.**) as **Sensitizer**", International Journal of Thin Films Science and Technology, Vol. 4, No. 2, pp. 141-146, (2015).

[39] A. Sedghi and H. N. Miankushki, "The Effect of Drying and Thickness of TiO<sub>2</sub> Electrodes on the Photovoltaic Performance of Dye-Sensitized Solar Cells", International Journal of Electrochemical Science, Vol. 10, pp. 3354-3362, (2015).

[40] N. A. Hussein, "Dye Sensitized Solar Cell With Curcumin Dye",M.Sc Thesis, College of Science, University of Baghdad, (2015).

[41] B. Li, F. Huang, J. Zhong, J. Xie, M. Wen, and Y. Peng, "Fabrication of Flexible Dye-Sensitized Solar Cell Modules using Commercially Available Materials", Energy Technology, Vol. 4, No. 4, pp. 536-542, (2016).

[42] M. Pirhadi, S. Feshki, M. Marandi, and R. Davarnejad,
"Fabrication of Dye Sensitized Solar Cells with a Double Layer Photoanode", Journal of Nanostructures, Vol. 6, No. 1, pp. 2-37, (2016).
[43] G. S. Jaber, A. K. Ali, and M. M. Ismail, "Enhancement of DSSC

**by Using Gold Nanoparticles''**, Engineer and Technology, Vol. 34, No. 1, pp. 73-79, (2016).

[44] O. N. Salman and I. R. Agool, "Preparation and Characterization of ZnO Nanocrystalline for Photovoltaic Applications Using Laser **Ablation Technique'',** Journal of Al-Nahrain University, Vol. 19, No. 2, pp. 87-94, (2016).

[45] V. Gusak, **"Nanoplasmonics for solar cells"**, Ph.D. Thesis, Department of Applied Physics, Chalmers University of Technology, (2014).

[46] S. Wenger, "Strategies to Optimizing Dye-Sensitized Solar Cells: Organic Sensitizers, Tandem Device Structures, and Numerical Device Modeling", Ph.D. Thesis, Diss. École Polytechnique Federale De Lausanne, (2010).

[47] B. Yan, G. Yue, X. Xu, J. Yang, and S. Guha, "High efficiency amorphous and nanocrystalline silicon solar cells", Physica Status Solidi A, Vol. 207, No. 3, pp. 671-677, (2010).

[48] S. Dilip, **"Resource assessment handbook"**, Asian and Pacific centre for transfer of technology of the united nations–Economic and Social Commission for Asia and the Pacific (ESCAP), (2009).

[49] M. Gratzel, "Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells", Inorganic chemistry, Vol. 44, No. 2, pp. 6841-6851, (2005).

[50] L. L Kazmerski, "Photovoltaics: A Review of Cell and Module Technologies", Renewable and Sustainable Energy Reviews, Vol. 1, No. 1, pp. 71-170, (1997).

[51] E. S. Flasgraf, "Biologically-Derived Dye-Sensitized Solar Cells:A Cleaner Alternative for Solar Energy", M.Sc. Thesis, Pomona College, (2012).

[52] K. S. El-refi, "Dye-Sensitized Solar Cells Using  $TiO_2$  as a Semiconducting Layer", M.Sc. Thesis, Collage of Science, Islamic University of Gaza, (2013).

[53] M. Gratzel, "**Photovoltaic and photoelectrochemical conversion of solar energy**", Physical and Engineering Sciences, Vol. 365, pp. 993-1005, (2007).

[54] D. Friedrich, "A study of charge transfer kinetics in dyesensitized surface conductivity solar cells", M.Sc. Thesis, eingereicht im Fachbereich Biologie, Chemie, Pharmazie der Freien Universität Berlin, (2011).

[55] R. R. King, D. C. Law, K. M. Edmondson, C. M. Fetzer, G. S. Kinsey, H. Yoon, R. A. Sherif, and N. H. Karam, "40% efficient metamorphic GaInP/GaInAs/Ge multijunction solar cells", Applied Physics Letters, Vol. 90, No. 18, pp. 1-3, (2007).

[56] A. Hinsch, "Worldwide First Fully Up-Scaled Fabrication of 60 ×
100 cm<sup>2</sup> Dye Solar Module", Progress in Photovoltaics: Research and Applications, Vol. 20, No. 6, pp. 698–710, (2012).

[57] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han,
"Dye-Sensitized Solar Cells With Conversion Efficiencies of 11.1%",
Japanese Journal of Applied Physics, Vol. 45, pp. 638-640, (2006).

[58] K. E. Jasim, Dye Sensitized Solar Cells-Working Principles, Challenges and Opportunities. In: L. A. Kosyachenko. Editor (Ed.), Solar Cells-Dye-Sensitized Devices, InTech, Croatia, (2011).

[59] M. R. Kim, S. H. Park, J. U. Kim, and J. K. Lee, **Dye-Sensitized Solar Cells Based on Polymer Electrolytes, Challenges and Opportunities**. In: L. A. Kosyachenko. Editor (Ed.), Solar Cells-Dye-Sensitized Devises, InTech, Croatia, (2011).

[60] Y. Jiao, F. Zhang, and S. Meng, **Dye Sensitized Solar Cells Principles and New Design.** In: L. A. Kosyachenko. Editor (Ed.), Solar Cells-Dye-Sensitized Devices, InTech, Croatia, (2011). [61] R. G. Gordon, "Criteria for Choosing Transparent Conductors", MRS Bulletin, Vol. 25, No. 8, pp. 52-57, (2000).

[62] M. S. P. Francisco, and V. R. Mastelaro, "Inhibition of the Anatase–Rutile Phase Transformation with Addition of CeO<sub>2</sub> to CuO–TiO<sub>2</sub> System: Raman Spectroscopy, X-ray Diffraction, and Textural Studies", Chemistry of Materials, Vol. 14, pp. 2514-2518, (2002).

[63] K. Hara and H. Arakawa, **Dye-sensitized Solar Cells**. In: A. Luque and S. Hegedus. Editor (Ed.), Handbook of Photovoltaic Science and Engineering, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, (2003).

[64] W. Wang , B. Gu , L. Liang , W. A. Hamilton , and D. J. Wesolowsk, "Synthesis of Rutile (α-TiO<sub>2</sub>) Nanocrystals with Controlled Size and Shape by Low-Temperature Hydrolysis: Effects of Solvent Composition", Journal Physical Chemistry B, Vol. 108, No. 39, pp. 14789-14792, (2004).

[65] T. Miyasaka, "Dye-Sensitized Solar Cells Built on Plastic Substrates by Low-Temperature Preparation of Semiconductor Films", Key Engineering Materials, Vol. 451, pp. 1-19, (2011).

[66] A. M. Member, R. Joshi, and M. Kumar, "Deposition of Doped TiO<sub>2</sub> Thin Film by Sol Gel Technique and its Characterization: A Review", Proceedings of the World Congress on Engineering, Vol. 2, pp. 1-4, (2011).

[67] Sh. D. Mo and W. Y. Chin, "Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite", Physical Review B, Vol. 51, No. 19, (1955).

[68] S. bagheri, Z. A. M. Hir, A. T. Yousefi, and S. B. Hamid, "**Progress** on mesoporous titanium dioxide: Synthesis, modification and

application", Microporous and Mesoporous Materials, Vol. 218, pp. 206-222, (2015).

[69] A. T. Rasin, "**High Efficiency Quantum Dot-Sensitised Solar Cells by Material Science and Device Architecture**", Ph.D. Thesis, Science and Engineering Faculty, Queensland University of Technology, Brisbane, Australia, (2014).

[70] G. Wolfbauer, A. M. Bond, J. C. Eklund, and D. R. MacFarlane, "A channel flow cell system specifically designed to test the efficiency of redox shuttles in dye sensitized solar cells", Solar energy materials and solar cells, Vol. 70, No. 1, pp. 85-101, (2001).

[71] C. Y. Hsu, Y. C. Chen, R. Lin, K. C. HO, and J. Lin, "Solid-state dye-sensitized solar cells based on spirofluorene (spiro-OMeTAD) and arylamines as hole transporting materials", Physical Chemistry Chemical Physics, Vol. 14, No. 41, pp. 14099-14109, (2012).

[72] N. Rawal, A. G. Vaishaly, H. Sharma, and B. B. Mathew, **"Dye Sensitized Solar Cells: The Emerging Technology"**, Energy and Power Engineering Science, Vol. 2, No. 2, pp. 46-52, (2015).

[73] B. M. Yu, J. P. Cunningham, G. Santhanam, S. I. Ryu, K. V. Shenoy, and M. Sahani, "Gaussian-Process Factor Analysis for Low-Dimensional Single-Trial Analysis of Neural Population Activity", Journal Neurophysiol, Vol. 102, pp. 614-635, (2009).

[74] B. Bowerman and V. Fthenakis, "Eh&S Analysis of Dye-Sensitized Photovoltaic Solar Cell Production", Brookhaven National Laboratory New York, (2001).

[75] E. Olsen, , G. Hagen, and S. E. Lindquist, "**Dissolution of platinum in methoxy propionitrile containing LiI/I**<sub>2</sub>", Solar Energy Materials and Solar Cells, Vol. 63, No. 3, pp. 267-273, (2000). [76] S. Ameen, M. Sh. Akhtar, Y. S. Kim, and H. Sh. Shin, Fabrication, Doping and Characterization of Polyaniline and Metal Oxides:Dye Sensitized Solar Cells. In: Leonid A. Kosyachenko (Ed.), Solar Cells-Dye-Sensitized Devices, InTech, Croatia, (2011).

[77] A. Andersen, P. R. F. Barnes, J. R. Durrant, and B. C. O'Regan, " **Quantifying Regeneration in Dye-Sensitized Solar Cells**", Journal of Physical Chemistry, Vol. 115, pp. 2439-2447, (2011).

[78] M. Tivanov, A. Patryn, N. Drozdov, A. Fedotov, and A. Mazanik, **''Determination of solar cell parameters from its current-voltage and spectral characteristics''**, Solar Energy Materials & Solar, Vol. 87, pp. 457-465, (2005).

[79] T. Marinado, K. Nonomura, J. Nissfolk, M. K. Karlsson, D. P. Hagberg, L. Sun, S. Mori, and A. Hagfeldt, "How the nature of triphenylamine-polyene dyes in dye-sensitized solar cells affects the open-circuit voltage and electron lifetimes", Langmuir, Vol. 26, No. 4, pp. 2592-2598, (2010).

[80] A. Berni, M. Mennig, and H. Schmidt, **Doctor Blade**. In: M. A. Aegerter et al. (Ed.), Sol-Gel Technologies for Glass Producers and Users, Springer Science+Business Media, New York, (2004).

[81] S. Zhang, X. Yang, Y. Numataa, and L. Han, "Highly efficient dye-sensitized solar cells: progress and future challenges", Energy Environmental Science, Vol. 4, pp. 60-62, (2011).

[82] H. Huang and W. Deng, **Introduction to Organic Solar Cells**. In: H. Huang and J. Huang (Ed.), Organic and Hybrid Solar Cells, Cham Heidelberg, (2014).

[83] M. K. Nazeeruddin , P. Péchy, T. Renouard, M. Z. Shaik, H. B. Robin, P. Comte, P. Liska, L. Cevey , E. Costa, V. Shklover, and L. Spiccia, "Engineering of efficient panchromatic sensitizers for

**nanocrystalline TiO<sub>2</sub>-based solar cells''**, Journal of the American Chemical Society, Vol. 123, No. 8, pp. 1613-1624, (2001).

[84] M. I. Khan, **"A Study on the Optimization of Dye-Sensitized Solar Cells"**, M.Sc. Thesis, College of Engineering, University of South Florida, (2013).

[85] E. Schönhofer, **"Dye Sensitized Solar Cells: From Liquid Electrolytes to Solid State Hole Transport Materials"**, Ph.D. Thesis, University Basel, (2015).

[86] G. Smestad, C. Bignozzi, and R. Argazzi, **"Testing of dyesensitized TiO<sub>2</sub> solar cells I: Experimental photocurrent output and conversion efficiencies"**, Solar Energy Materials & Solar Cells, Vol. 32, No. 3, pp. 259-272, (1994).

[87] B. A. Gregg, **The Essential Interface: Studies in Dye-Sensitized Solar Cells**. In: V. Ramamurthy and K. S. Schanze. (Ed.), Semiconductor Photochemistry and Photophysics, New Orleans, Louisiana U. S. A and Gainesville, Florida U. S. A., (2003).

[88] T. Markvart and L.Castaner, "Solar Cells: Materials, Manufacture and Operation", Elsevier, Spain, (2005).

[89] V. Shrotriy, G. Li, Y. Yao, T. Moriarty, K. Emery, and Y. Yang,
"Accurate Measurement and Characterization of Organic Solar Cells", Advanced Functional Materials, Vol. 16, No. 15, pp. 2016-2023, (2006).

[90] Y. Chergui, N. Nehaoua and D. E. Mekki, Comparative Study of Dye-Sensitized Solar Cell Based on ZnO and TiO<sub>2</sub> Nanostructures.
In: L. A. Kosyachenko (Ed.), Solar Cells-Dye-Sensitized Devices, InTech, Croatia, (2011).

#### References

[91] S. Agarkar, **"Dye sensitized solar cell: Optimizing materials, methods and optoelectronic effects"**, Ph.D. Thesis, CSIR-National Chemical Laboratory, Pune, India, (2014).

[92] P. Singh and N. M. Ravindra, "Analysis of series and shunt resistance in silicon solar cells using single and double exponential models", Emerging Materials Research, Vol. 1, No. 1, pp. 33-38, (2012).

[93] R. Kant and M. M. Islam, **"Theory of Absorbance Transients of an Optically Transparent Rough Electrode"**, Journal of Physical Chemistry C, Vol. 114, No. 45, pp. 19357–19364, (2010).

[94] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, **"Environmental applications of semiconductor photocatalysis"**, Chemical Review, Vol. 95, pp. 69-96, (1995).

[95] L. Kernazhitsky, V. Shymanovska, T. Gavrilko, V. Naumov, and V. Kshnyakin, "**Optical absorption of polydisperse TiO<sub>2</sub>: Effect of surface doping by transition metal cations**", Ukrainian journal of physical optics, Vol. 14, No. 1, pp. 15-23, (2013).

[96] R. Vijayalakshmi and V. Rajendran, "Synthesis and characterization of nano-TiO<sub>2</sub> via different methods", Archives of Applied Science Research, Vol. 4, No. 2, pp. 1183-1190, (2012).

[97] J. Tauc, **Optical Properties of Amorphous Semiconductors**. In: Amorphous and liquid semiconductor, J. Tauc (Ed.), Plenum Press, New York, (1974).

[98] R. J. Deokate, A. D. Adsool, N. S. Shinde, S. M. Pawar, and C. D.
Lokhande, "Structural and optical properties spray- deposited Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films", Energy procedia, Vol. 54, pp. 627-633, (2014).

[99] C. Kittle, "**Introduction to solid state physics**", 5th edition, John Willy and sons, Inc. New York, (1976).

[100] Y. Gao, Y. Masuda, W.Seo, H. Ohta, and K. Koumoto, "**TiO<sub>2</sub> nanoparticles prepared using an aqueous peroxotitanate solution**", Ceramics International, Vol. 30, pp. 1365-1368, (2004).

[101] P. P. Patil, D. M. Phase, S. A. Kulkarni, S. V. Ghaisas, S. K. Kulkarni, S. M. Kanetkar, S. B. Ogale, and V. G. Bhide, "**Pulsed-laser-induced reactive quenching at liquid-solid interface: Aqueous oxidation of iron**", Physical Review Letters, Vol. 58, No. 3, pp. 238-241, (1987).

[102] V. Amendola, S. Polizzi, and M. Meneghetti, "Laser Ablation Synthesis of Gold Nanoparticles in Organic Solvents", Journal Physical Chemistry B, Vol. 110, No. 14, pp. 7232-7237, (2006).

[103] C. W. Schneider and T. Lippert, **Laser Ablation and Thin Film Deposition**. In: P. Schaaf (Ed.), Laser Processing of Materials, Springer Berlin Heidelberg, (2010).

[104] A. Hana, S. Barcikowski, and B. N. Chichkov, "Influences on Nanoparticle Production during Pulsed Laser Ablation", Journal of Laser Micro/Nanoengineering, Vol. 3, No. 2, pp. 73-77, (2008).

[105] R. M. Tilaki and S. M. Mahdavi, "The effect of liquid environment on size and aggregation of gold Nanoparticles prepared by pulsed laser ablation", Journal of Nanoparticle Research, Vol. 9, No. 5, pp. 853-860, (2007).

[106] M. A. Sobhan , M. Ams, M. J. Withford, and E. M. Goldys, "Ultrafast laser ablative generation of gold nanoparticles: the influence of pulse energy, repetition frequency and spot size", Journal of Nanoparticle Research, Vol. 12, No. 8, pp. 2831-2842, (2010).

[107] S. Besner, A.V. Kabashin, and M. Meunier, "Two-step femtosecond laser ablation-based method for the synthesis of stable

and ultra-pure gold nanoparticles in water", Applied Physics A, Vol. 88, No. 2, pp. 269-272, (2007).

[108] R. G. Kadhim, M. F. Noori, and A. K. Ali, "**Preparation of Gold Nanoparticles by Pulsed Laser Ablation in NaOH solution**", Journal of Babylon University/Pure and Applied Sciences, Vol. 22, No. 1, pp. 547-551, (2012).

[109] X. Huang and M. A. El-Sayed, "Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy", Journal of Advanced Research, Vol. 1, No. 1, pp. 13-28, (2010).

[110] A. J. Tudos and R. B. M. Schasfoort, Introduction to SurfacePlasmon Resonance. In: R. B. M. Schasfoort and A. J. Tudos (Ed.)Handbook of Surface Plasmon Resonance, Royal Society of Chemistry, (2008).

[111] P. Englebienne, A. V. Hoonacker, and M. Verhas, "Surface plasmon resonance: principles, methods and applications in biomedical sciences", Journal of Spectroscopy, Vol. 17, No. 2, pp. 255-273, (2003).

[112] A. R. Sadrolhosseini, A. S. M. Noor, and M. M. Moksin, Application of Surface Plasmon Resonance Based on a Metal Nanoparticle. In: K. Y. Kim (Ed.), Plasmonics-Principles and Applications, Intech Open Access Publisher, (2012).

[113] V. A. G. Rivera, F. A. Ferri, and E. Marega, Localized Surface Plasmon Resonanes: Noble Metal Nanoparticle Interaction with Rare-Earth Ions. In: K. Y. Kim (Ed.), Plasmonics-Principles and Applications, Intech Open Access Publisher, (2012). [114] L. Deng, "**Dye-sensitized Solar Cells with a Solid Hole Conductor''**, M.Sc. Thesis, Department of Materials Science and Engineering, McMaster University, (2012).

[115] M. Gaetzel and A. J. Mcevoy, "Principles and Applications of Dye Sensitized Nanocrystalline Solar Cells (DSC)", Asian Journal Energy Environ, Vol. 5, No. 3, pp. 197-210, (2004).

[116] M. Murawska, A. Skrzypczak, and M. Kozak, "Structure and Morphology of Gold Nanoparticles in Solution Studied by TEM, SAXS and UV-Vis", Acta Physica Polonica A, Vol. 121, No. 4, pp. 888-892, (2012).

[117] V. Subramanian, E. E. Wolf, and P. V. Kamat, "Catalysis with TiO<sub>2</sub>/Gold Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration", Journal of the American Chemical Society, Vol. 126, pp. 4943-4950, (2004).

[118] R. B. Rashid, "Preparation and Characterization of Novel Composite Nanoparticles for Biomedical Application using Laser", M.Sc. Thesis, College of Engineering, University of Technology, (2014).
[119] Ch. Wei and Ch. Chang, "Polycrystalline TiO<sub>2</sub> Thin Films with Different Thicknesses Deposited on Unheated Substrates Using RF Magnetron Sputtering", Materials Transactions, Vol. 52, No. 3, pp. 554-559, (2011).

[120] A. K. M. Muaz, U. Hashim, F. Ibrahim, K. L. Thong, M. S. Mohktar, and W. Liu, "Effect of annealing temperatures on the morphology, optical and electrical properties of TiO<sub>2</sub> thin films synthesized by the sol–gel method and deposited on Al/TiO<sub>2</sub>/SiO<sub>2</sub>/p-Si", Microsystem Technologies, Vol. 22, No. 4, pp. 871-881, (2016).

[121] I. Hadjoub, T. Touam, A. Chelouche, M. Atoui, J. Solard, M. Chakaroun, A. Fischer, A. Boudrioua, and L. Peng, "Post-deposition

annealing effect on RF-sputtered TiO<sub>2</sub> thin-film properties for photonic applications", Applied Physics A, Vol. 122, No. 2, pp.1-8, (2016).

[122] T. G. Lei, H. Hong-Bo, and S. jian-Da, "Effect of Microstructure of TiO<sub>2</sub> Thin Films on Optical Band Gap Energy", Chinese physics letters, Vol. 22, No. 7, pp. 1787-1789, (2007)

[123] M. Hema, A. Y. Arasi, P. Tamilselvi, and R. Anbarasan, "Titania Nanoparticles Synthesized by Sol-Gel Technique", Chemical Science Transactions, Vol. 2, No. 1, pp. 239-245, (2013).

[124] B. S. Shirke, P. V. Korake, P. P. Hankare, S. R. Bamane, and K. M. Garadkar, "Synthesis and characterization of pure anatase TiO<sub>2</sub> nanoparticles", Journal of Materials Science: Materials in Electronics, Vol. 22, No. 7, pp. 821-824, (2011).

[125] R. Rossmanith, C. K. Weiss, J. Geserick, N. Husing, U. Hormann,
U. Kaiser, and K. Landfester, "Porous Anatase Nanoparticles with
High Specific Surface Area Prepared by Miniemulsion Technique",
Chemistry of Materials, Vol. 20, No. 18, pp. 5768-5780, (2008).

[126] M. M. Hasan, A. S. M. A. Haseeb, R. Saidur, and H. H. Masjuki,
"Effects of Annealing Treatment on Optical Properties of Anatase
TiO<sub>2</sub> Thin Films", International Scholarly and Scientific Research & Innovation, Vol. 2, No. 4, pp. 93-97, (2008).

[127] M. T. Sarode, "Effect of Annealing Temperature on Optical Properties of Titanium Dioxide Thin Films Prepared by Sol-gel Method", International Journal of Modern Physics: Conference Series, Vol. 6, pp. 13-18, (2012).

[128] M. M. Rashad , A. E. Shalan, M. Lira-Cantu´, and M. S. A. Abdel-Mottaleb, "Synthesis and characterization of mesoporous anatase TiO<sub>2</sub> nanostructures via organic acid precursor process for dye**sensitized solar cells applications''**, Journal of Industrial and Engineering Chemistry, Vol. 19, pp. 2052-2059, (2013).

[129] A. N. Kadam, R. S. Dhabbe, M. R. Kokate, Y. B. Gaikwad, and K. M. Garadkar, "Preparation of N doped TiO<sub>2</sub> via microwave-assisted methodand its photocatalytic activity for degradation of Malathion", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 133, pp. 669-676, (2014).

[130] B. Karunagaran, K. Kim, D. Mangalaraj, J. Yi, and S. Velumani, "Structural, optical and Raman scattering studies on DC magnetron sputtered titanium dioxide thin films", Solar Energy Materials & Solar Cells, Vol. 88, pp. 199-208, (2005).

[131] E. S. Shim, H. S. Kang, S. S. Pang, J. S. Kang, I. Yun, and S. Y. Lee, **"Annealing effect on the structural and optical properties of ZnO thin film on InP"**, Materials Science and Engineering B, Vol. 102, pp. 366-369, (2003).

[132] H. Wu and Y. Wang, "Effects of annealing temperature on the structure and properties of TiO<sub>2</sub> nanofilm materials", Advanced Materials Research, Vol. 531, pp. 203-206, (2012).

[133] D. Susanti, M. Nafi, H. Purwaningsih, R. Fajarin, and G. E. Kusum,
"The Preparation of Dye Sensitized Solar Cell (DSSC) from TiO<sub>2</sub> and
Tamarillo Extract", Procedia Chemistry, Vol. 9, pp. 3-10, (2014).

[134] R. Kawakami, T. Yuasa, K. Ito, Y. Sato, Y. Mori, M. Adachi, and S. Yoshikado, "**Evaluation of TiO<sub>2</sub> Nanoparticle Thin Films Prepared by Electrophoresis Deposition**", Journal of the Australian Ceramic Society ,Vol. 48, No. 2, pp. 236-243, (2012).

[135] G. Yildirim, S. Bal, M. Gulen, A. Varilci, E. Budak, and M. Akdogan, **"Substrate effect on microstructure and optical** 

**performance of sputter-deposited TiO**<sub>2</sub> **thin films''**, Crystal Research Technology, Vol. 47, No. 2, pp. 195-201, (2012).

[136] N. B. Ibrahim, S. M. Al-Shomar, and S. H. Ahmad, "Effect of Annealing Temperature on the Structural and Optical Properties of Nanocrystalline ZnO Thin Films Prepared by Sol-gel Method", Sains Malaysiana, Vol. 42, No.12, pp. 1781-1786, (2013).

[137] A. Mathew, G. M. Rao, and N. Munichandraiah, "Effect of TiO<sub>2</sub> electrode thickness on photovoltaic properties of dye sensitized solar cell based on randomly oriented Titania nanotubes", Materials Chemistry and Physics, Vol. 127, pp. 95-101, (2011).

[138] M. Y. A. Rahman, A. A. Umar, L. Roza, and M. M. Salleh, " Effect of Organic Dye on the Performance of Dye-Sensitized Solar Cell Utilizing TiO<sub>2</sub> Nanostructure Films Synthesized via CTAB-Assisted Liquid Phase Deposition Technique", Russian Journal of Electrochemistry, Vol. 50, No. 11, pp. 1072-1076, (2014).

[139] A. Lim, N. HajiManaf, K. Tennakoon, R. L. N. Chandrakanthi, L.
B. L. Lim, J. M. R. S. Bandara, and P. Ekanayake, "Higher Performance of DSSC with Dyes from Cladophora sp. as Mixed Cosensitizer through Synergistic Effect", Journal of Biophysics, Vol. 2015, pp.1-8, (2015).

[140] R. Tagliaferro, D. Colonna, T. M. Brown, A. Reale, and A. D. Carlo, "Interplay between transparency and efficiency in dye sensitized solar cells", Optics express, Vol. 21, No. 3, pp. 3235-3242, (2013).

[141] S. Lee, S. Choi, J. Kim, S. Kim, and D. Lee, "Improving the efficiency of a dye-sensitized solar cell with a reflex condenser system", Opt Express, Vol. 20, No. 23, pp. 908-915, (2012).

[142] K. Hara and N. Koumura, "Organic Dyes for Efficient and StableDye-Sensitized Solar Cells", Material Matters, Vol. 4, No. 4, pp. 88-92, (2009).

[143] K. Zhang, C. Qin, X. Yang, A. Islam, Sh. Zhang, H. Chen, and L. Han, "High-Performance, Transparent, Dye-Sensitized Solar Cells for See-Through Photovoltaic Windows", Advanced Energy Materials, Vol. 4, No. 11, pp. 1-7, (2014).

[144] Q. Tai, B. Chen, F. Guo, Sh. Xu, H. Hu, B. Sebo, and X. Zhao, "In Situ Prepared Transparent Polyaniline Electrode and Its Application in Bifacial Dye-Sensitized Solar Cells", Acs Nano, Vol. 5, No. 5, pp. 3795-3799, (2011).

List of Publications

- Abdulrahman K. Ali, Nabeel A. Bakr, and Shaimaa M. Jassim, "Fabrication of Dye Sensitized Solar Cell and Efficiency Enhancement by Using N719 and Z907 Dyes Mixture", Journal of Photonic Materials and Technology, Vol. 2, No. 3, pp. 20-24, October, (2016).
- Nabeel A. Bakr, Abdulrahman K. Ali, and Shaimaa M. Jassim," Fabrication and Efficiency Enhancement of Z907 Dye Sensitized Solar Cell Using Gold Nanoparticles", Journal of Advanced Physics, (Accepted in 2/11/2016).
- Nabeel A. Bakr, Abdulrahman K. Ali, and Shaimaa M. Jassim, "Effect of N719 dye concentration on the Conversion Efficiency of Dye Sensitized Solar Cells (DSSCs)", 6<sup>th</sup> International Conference and Workshop on Basic and Applied Sciences (6<sup>th</sup> ICOWOBAS), Salahaddin University, Erbil, Iraq. (Communicated).



جمهورية العراق وزارة التعليم العالي والبحث العلمي جامعة ديالى – كلية العلوم قسم الفيزياء



رسالة متحمة إلى

مجلس كلية العلوم – جامعة حيالي ومي جزء من متطلبات نيل درجة الماجستير في علوم الغيزياء من قبل

> شیماء مفید جاسم (بکلوریوس علوم مزیزیاء 2007)

# إشراهم

أ.د. نبيل علي بكر أ.م.د. عبد الرحمن خلف علي

2017 م

**-A** 1438