

Ain Shams University
University College of Women
(Arts, Science and Education)
Physics Department



**Synthesis, Characterization of ZnO Nanoparticles
Using Wet Chemical Technique for Dye Sensitized
Solar Cells**

By
Hussam Subri Musleh
For

Ph.D. Degree in Science (solid state physics)

A thesis submitted

To

Physics Department

**University College of Women (Arts, Science and Education)
Ain-Shams University**

Under supervision of :

Prof.Dr. Hamdia Abd- El hamed Zayed

**Professor of Solid State, Physics Dept., University College of Women
(Arts, Science and Education)- Ain-Shams University**

Prof.Dr. Naji M. Al-Dahoudi

**Professor of material Science, Physics Dept., Al-Azhar University-
Gaza**

Dr. Hassan Tamous

**Assistance Professor of Physical Chemistry, Chemistry Dept., Al-
Azhar University-Gaza**

2018



Physics Department

APPROVAL SHEET

Name: *Hussam Subri Musleh*

Scientific Degree: Ph.D. in science (solid state physics)

Title: Synthesis, Characterization of ZnO Nanoparticles

Using Wet Chemical Technique for Dye Sensitized Solar Cells

Supervisors

Prof. Dr.
Hamdia Abd El-
Hamid Zayed

Prof. of Solid State Physics,
Physics Department -
Women's College for Arts,
Science, and Education
Ain Shams University

Prof. Dr.
Naji M. Al-
Dahoudi

Prof. of material
Science, Physics
Dept., Al-Azhar
University
Gaza

Dr.
Hassan M. Tamous

Assistance Professor of
Physical Chemistry,
Chemistry Dept., Al-
Azhar University-Gaza

(2018)

بسم الله الرحمن الرحيم

(انا كل شيء خلقتاه بقدر)

القمر 49

Acknowledgment

In the name of ALLAH the most compassionate all praise be to ALLAH, the lord of the worlds; and prayers and peace be upon Prophet MOHAMMED.

Firstly, I must acknowledge my limitless thanks to ALLAH; the Ever-Thankful, for help and bless.

My deepest appreciation and sincere gratitude to my supervisors professor Prof. Dr. Hamdia Abd El-Hamid Zayed, Prof. Dr. Naji M. Al-Dahoudi and Dr. Hassan M. Tamous.

I am greatly indebted to them for all the efforts they have put in for the successful completion of this thesis.

I would also, like to thank my friend Mohamed Musleh, for his encouragement. I also extend my profound thanks to Physics Department Women's College Ain Shams University- Cairo, the department of physics and department of chemistry in Al-Azhar university- Gaza Palestine. Finally, I would like to express my sincere gratitude to Dr. Ahmed Ramzy, National Research Center- Cairo, for his kind help in EDX characterization.

Dedication

I dedicate my thesis to:
My parents who kept supporting me
throughout the process,
My loving wife
who stood by me in my difficult time,
My Kids, Balssam, Sabri, Bassant and
Bayaan
My Brothers, sisters and uncles who
encouraged and supported me.

Hussam Musleh

Contents

	<i>Acknowledgments</i>	<i>III</i>
	<i>Deduction</i>	<i>IV</i>
	<i>Contents</i>	<i>V</i>
	<i>List of figures</i>	<i>IX</i>
	<i>List of tables</i>	<i>XIV</i>
	<i>List of symbols</i>	<i>XVI</i>
	<i>Abstract</i>	<i>1</i>
	<i>Introduction</i>	<i>4</i>
<i>1-</i>	<i>Nanotechnology</i>	<i>4</i>
<i>2-</i>	<i>Solar cells</i>	<i>5</i>
	CHAPTER I Literature Review	
<i>1-1</i>	<i>Literature review</i>	<i>8</i>
<i>1-2</i>	<i>Aim of this work</i>	<i>17</i>
	CHAPTER II Theoretical Aspects	
<i>2-1</i>	<i>Materials of DSSC</i>	<i>18</i>
<i>2-1-1</i>	<i>Electrodes</i>	<i>18</i>
<i>2-1-1-1</i>	<i>Front electrode (FTO substrate)</i>	<i>18</i>
<i>2-1-1-2</i>	<i>Back electrode (Platinum counter electrode)</i>	<i>19</i>
<i>2-1-2</i>	<i>Sensitizing dyes</i>	<i>19</i>
<i>2-1-2-1</i>	<i>Ruthenium complex</i>	<i>20</i>
<i>2-1-2-2</i>	<i>Metal-free organic dyes</i>	<i>21</i>
<i>2-1-3</i>	<i>Electrolyte</i>	<i>22</i>
<i>2-1-4</i>	<i>Operational principle of DSSC</i>	<i>24</i>
<i>2-3</i>	<i>The simple electrical model of a solar cell</i>	<i>26</i>
<i>2-3-1</i>	<i>The parameters of solar cell</i>	<i>27</i>
<i>2-4</i>	<i>X-ray diffraction studies (XRD)</i>	<i>30</i>
<i>2-5</i>	<i>Transmission electron microscopy (TEM)</i>	<i>32</i>
<i>2-6</i>	<i>UV–VIS absorption spectroscopy</i>	<i>33</i>
<i>2-6-1</i>	<i>Determination of optical band gap</i>	<i>34</i>
<i>2-7</i>	<i>Photoluminescence spectroscopy (PL)</i>	<i>35</i>

	CHAPTER III Materials & Experimental Techniques	
3-1	<i>Materials used in ZnO nanoparticle synthesis</i>	36
3-2	<i>Materials used in DSSCs fabrication</i>	36
3-3	<i>Techniques of preparation</i>	37
3-3-1	<i>simple preparations techniques</i>	37
3-3-2	<i>Reflux technique</i>	39
3-3-3	<i>Sol gel technique</i>	41
3-3-4	<i>Combustion technique</i>	44
3-4	<i>DSSC preparation</i>	47
3-4-1	<i>Cleaning of the FTO substrate</i>	47
3-4-2	<i>Preparation of ZnO electrode (FTO/ZnO/dye)</i>	47
3-4-3	<i>Preparation of redox</i>	48
3-4-4	<i>Assembly of DSSC</i>	48
3-5	<i>Investigation of the prepared DSSCs</i>	50
3-5-1	<i>X-ray diffraction studies (XRD)</i>	50
3-5-2	<i>Electron dispersive x-ray analysis (EDX)</i>	50
3-5-3	<i>High resolution transmission electron microscopy (HRTEM) analysis</i>	51
3-5-4	<i>UV-VIS absorption spectra</i>	52
3-5-5	<i>Photoluminescence analysis</i>	53
3-5-6	<i>J-V measurements of DSSC</i>	54
	Chapter IV Results and Discussion	
4-1	<i>Absorption spectra of Eosin B, Eosin Y and Rhodamine B Dyes</i>	55
4-2	<i>Pure ZnO Synthesized using Simple precipitation technique</i>	56
4-2-1	<i>Synthesis of ZnO NPs at different aging time</i>	56
4-2-1-1	<i>Structural Identification</i>	56
4-2-1-1-1	<i>Energy Dispersive X-ray Analysis (EDX)</i>	56
4-2-1-1-2	<i>X –ray diffraction studies</i>	57
4-2-1-1-3	<i>HRTEM analysis of pure ZnO</i>	61
4-2-1-2	<i>Optical studies</i>	63
4-2-1-2-1	<i>UV-VIS absorption studies of pure ZnO</i>	63
4-2-1-2-2	<i>Photoluminescence spectroscopy</i>	65

4-2-1-3	<i>Photovoltaic studies</i>	68
4-2-1-3-1	<i>FTO / ZnO / Eosin B, / Pt</i>	68
4-2-1-3-2	<i>FTO / ZnO / Eosin Y, Rhodamine B / Pt</i>	71
4-2-2	<i>Pure zinc oxide at different pH value</i>	73
4-2-2-1	<i>Structural identification</i>	73
4-2-2-1-1	<i>X-Ray diffraction studies</i>	73
4-2-2-1-2	<i>HRTEM analysis of pure ZnO</i>	77
4-2-2-2	<i>Optical studies</i>	79
4-2-2-2-1	<i>UV-VIS absorption studies of pure ZnO</i>	78
4-2-2-2-2	<i>Photoluminescence spectroscopy</i>	81
4-2-2-3	<i>Photovoltaic studies</i>	83
4-2-2-3-1	<i>FTO / ZnO / Eosin B / Pt</i>	83
4-2-2-3-2	<i>FTO / ZnO / Eosin Y, Rhodamine B/ Pt</i>	86
4-2-3	<i>Pure ZnO NPs heated at 160 oC for different heating time in autoclave</i>	88
4-2-3-1	<i>Structural identification ZnO NPs</i>	88
4-2-3-1-1	<i>X-ray diffraction studies</i>	88
4-2-3-1-2	<i>HRTEM analysis of pure ZnO</i>	91
4-2-3-2	<i>Optical studies of ZnO NPs</i>	92
4-2-3-2-1	<i>UV-VIS absorption studies</i>	92
4-2-3-2-2	<i>Photoluminescence spectroscopy of pure ZnO NPs</i>	95
4-2-3-3	<i>Photovoltaic parameters</i>	97
4-2-3-3-1	<i>FTO / ZnO / Eosin B / Pt</i>	97
4-2-3-3-2	<i>FTO / ZnO / Eosin Y, Rhodamine B / Pt</i>	99
4-2-3-3-3	<i>Open circuit voltage decay</i>	101
4-2-3-3-4	<i>Dye uploading</i>	105
4-3	<i>Pure and Cu doped zinc oxide synthesized using Reflux technique</i>	106
4.3.1	<i>Structural identification</i>	106
4.3.1.1	<i>Energy dispersive X-ray analysis (EDX)</i>	106
4.3.1.2	<i>X-Ray diffraction studies</i>	106

4.3.1.3	<i>HRTEM analysis of pure ZnO using reflux technique</i>	112
4-3-2	<i>Optical studies</i>	112
4-3-2-1	<i>UV-VIS absorption studies of ZnO:Cu</i>	112
4-3-2-2	<i>Photoluminescence spectroscopy</i>	115
4-3-3	<i>Photovoltaic parameters</i>	117
4-3-3-1	<i>FTO / ZnO / Eosin B / Pt</i>	117
4-3-3-2	<i>FTO / ZnO / Eosin Y, Rhodamine B / Pt</i>	119
4-4	<i>Pure ZnO NPs using sol gel technique</i>	122
4.1.1	<i>Structural Identification</i>	122
4.1.1.1	<i>Energy Dispersive X-ray Analysis (EDX)</i>	122
4.1.1.2	<i>X –ray diffraction studies</i>	123
4-4-1-3	<i>HRTEM analysis of ZnO NPs</i>	126
4-4-2	<i>Optical studies</i>	127
4-4-2-1	<i>UV-VIS absorption studies</i>	127
4-4-2-2	<i>Photoluminescence spectroscopy</i>	130
4-4-3	<i>Photovoltaic parameters</i>	132
4-4-3-1	<i>FTO / ZnO / Eosin B / Pt</i>	132
4-4-3-2	<i>FTO / ZnO / Eosin Y, Rhodamine B / Pt</i>	135
4-5	<i>Pure ZnO synthesized using combustion technique</i>	137
4-5-1	<i>Structural identification</i>	137
4-5-1-1	<i>Energy dispersive X-ray analysis (EDX)</i>	137
4-5-1-2	<i>X-Ray diffraction studies</i>	138
4-5-1-3	<i>HRTEM analysis of pure ZnO</i>	141
4-5-2	<i>Optical studies</i>	143
4-5-2-1	<i>UV–VIS absorption spectroscopy</i>	143
4.5.2.2	<i>Photoluminescence spectroscopy</i>	145
4-5.3	<i>Photovoltaic parameters</i>	148
4-5-3.1	<i>FTO/ ZnO / Eosin B / Pt</i>	148
4.5.3.2	<i>FTO/ ZnO / Eosin Y, Rhodamine B / Pt</i>	150
	<i>Conclusion</i>	152
	<i>References</i>	154
	<i>Arabic abstract</i>	1

List of Figures

	CHAPTER I	
Fig. 1-1.	Three kinds of ZnO crystal structure, black and gray spheres denote Zn and O atoms respectively. (a) Wurtzite, (b) Rocksalt and (c) Zinc blende.	8
	CHAPTER II	
Fig. 2-1	Schematic design of free metal organic dyes (top), some examples of dyes building blocks (down).	21
Fig. 2-2	Operation principle of a dye-sensitized solar cell	25
Fig. 2-3	The assembly of the dye-sensitized solar cell	25
Fig. 2-4	Equivalent circuit of solar cell	27
Fig. 2-5	The typical J-V characteristics of a solar cell, in the dark and under illumination	28
Fig. 2-6	X-ray Diffraction in accordance with Bragg's Law	31
Fig. 2-7	Schematic for a double beams UV-VIS spectrophotometer	34
	CHAPTER III	
Fig. 3-1	Flow chart of ZnO NPs synthesized using simple precipitation technique	39
Fig. 3-2	Flow chart of pure and Cu doped ZnO nanoparticle synthesis using reflux technique.	41
Fig. 3-3	Some steps of ZnO nanoparticles synthesis using sol gel technique	43
Fig. 3-4	The flow chart of ZnO synthesis using sol gel technique	43
Fig. 3-5	Flow chart of pure ZnO nanoparticle synthesized using combustion technique	45
Fig. 3-6	The changing of fluffy foam color of ZnO synthesized using combustion technique at different urea concentration	46
Fig. 3-7	Assembling the dye sensitized solar cell	49

Fig. 3-8	Philips Expert, X-ray diffraction (XRD) setup.	50
Fig. 3-9	Field Emission Scanning Electron Microscope setup	51
Fig. 3-10	High resolution transmission electron microscopy: (JEM-2100), JEOL	52
Fig. 3-11	Shimadzu UV-1601 PC, UV-VIS spectrophotometer	53
Fig. 3-12	Spectrofluorometer model SPF-200 Setup	53
Fig. 3-13	J-V measurement setup	54
	CHAPTER IV	
Fig. 4-1	The absorption spectrum of the used dyes dissolved in pure ethanol	55
Fig. 4-2	EDX spectrum of pure ZnO NPs	56
Fig. 4-3	X-ray diffraction pattern for S1, S2, S3 and S4 of pure ZnO NPs	59
Fig. 4-4	HRTEM micrograph of (S3) ZnO Nps sample (a) micrograph image, (b) diffraction patterns and (c) selected electron diffraction area and (d) histograms	62
Fig. 4-5	UV-VIS. Spectra for S1, S2, S3 and S4 of pure ZnO NPs	64
Fig. 4-6	$(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for S1, S2, S3 and S4 of pure ZnO NPs	64
Fig. 4-7	Variation of the E_g for S1, S2, S3 and S4 of pure ZnO NPs	65
Fig. 4-8	PL spectra for S1, S2, S3 and S4 of pure ZnO NPs	67
Fig. 4-9	Schematic energy level diagram showing the possible radiative transition for S1, S2, S3 and S4 of pure ZnO NPs	67
Fig. 4-10	J-V curves of the DSSCs for S1, S2, S3 and S4 of pure ZnO NPs	69
Fig. 4-11	P-V curves of the DSSCs for S1, S2, S3 and S4 of pure ZnO NPs	70
Fig. 4-12	J-V curves of the DSSCs S3 of pure ZnO NPs, using different dyes	72
Fig. 4-13	P-V curves of the DSSCs S3 of pure ZnO NPs, using different dyes	72

Fig. 4-14	The structural parameters of ZnO NPs synthesized at different pH value	75
Fig. 4-15	HRTEM micrograph of (pH14) ZnO NPs sample (a) micrograph image, (b) Diffraction patterns and (c) selected electron diffraction area and (d) histograms	78
Fig. 4-16	UV-VIS. Spectra for pH8, pH10, pH12 and pH14 of pure ZnO NPs	80
Fig. 4-17	$(\alpha h\nu)^2$ versus the photon energy ($h\nu$) of ZnO at different pH values	80
Fig. 4-18	Variation of energy gape with different pH value	81
Fig. 4-19	PL spectra of pure ZnO NPs samples at different pH value	82
Fig. 4-20	Schematic energy level diagram showing the possible radiative transition of ZnO NPs synthesized at different pH values	83
Fig. 4-21	J-V curves of DSSC of ZnO NPs synthesized at different pH values	84
Fig. 4-22	P-V curves of the DSSC of ZnO NPs synthesized at different pH values	85
Fig. 4-23	J-V curves for the DSSCs of pH14 ZnO sample, using different dyes	86
Fig.4.24	P-V curves for the DSSCs of pH14 ZnO sample, using different dyes	87
Fig. 4.25	X-ray diffraction pattern of ZnO NPs heated at 160 °C for different heating time.	89
Fig. 4.26	HRTEM micrograph of (C2) ZnO nanoparticles sample (a) micrograph image, (b) Diffraction patterns and (c) selected electron diffraction area and (d) histograms	92
Fig. 4-27	UV-VIS. Spectra for C1, C2, C3 and C4 of pure ZnO NPs	93
Fig. 4-28	$(\alpha h\nu)^2$ versus the photon energy ($h\nu$) of C1, C2, C3 pure ZnO NPs	94
Fig. 4-29	Variation of energy gape for C1, C2, C3 and C4 of pure ZnO NPs	94
Fig. 4-30	Photoluminescence studies for C1, C2, C3 and C4 of pure ZnO NPs	96
Fig. 4-31	Schematic energy level diagram showing the possible radiative transition for C1, C2, C3 and C4 of pure ZnO NPs	96

Fig. 4-32	<i>J-V characteristic curves of the DSSCs for C1, C2, C3 and C4 of pure ZnO NPs</i>	98
Fig. 4-33	<i>P-V characteristic curves of the DSSCs for C1, C2, C3 and C4 of pure ZnO NPs</i>	99
Fig.4-34	<i>J-V characteristic curves of the DSSCs C2 of pure ZnO NPs, using different dyes</i>	100
Fig. 4-35	<i>P-V characteristic curves of the DSSCs C2 of pure ZnO NPs, using different dyes</i>	101
Fig. 4-36	<i>Open circuit voltage V_{oc} decay of the solar cell based on (C2) ZnO NPs using Eosin B as a photosensitizer</i>	103
Fig. 4-37	<i>Open circuit voltage V_{oc} decay of the solar cell based on (C2) ZnO NPs sample using Eosin Y as a photosensitizer</i>	103
Fig. 4-38	<i>Open circuit voltage V_{oc} decay of the solar cell based on (C2) ZnO NPs sample using Rhodamine B as a photosensitizer</i>	104
Fig. 4-39	<i>Absorption spectra of Eosin B, Eosin Y, Rhodamine B dyes were desorbed from ZnO semiconductor layer</i>	105
Fig. 4-40	<i>EDX spectrum of pure ZnO NPs</i>	106
Fig. 4-41	<i>X-ray diffraction pattern of Cu- doped ZnO, 1:0.0% Cu, R2: 1% Cu, R3:3%Cu, and R4:5% Cu</i>	108
Fig. 4-42	<i>HRTEM micrograph of (R3) ZnO nanoparticles sample (a) micrograph image, (b) Diffraction patterns and (c) selected electron diffraction area and (d) histograms</i>	111
Fig. 4-43	<i>UV-VIS. spectra of Cu- doped ZnO NPs, R1:0.0% Cu, R2: 1% Cu, R3:3%Cu, and R4:5% Cu</i>	113
Fig. 4-44	<i>$(\alpha h\nu)^2$ versus the photon energy ($h\nu$) of Cu-doped ZnO NPs, R1:0.0% Cu, R2: 1% Cu, R3:3%Cu, and R4:5% Cu</i>	114
Fig. 4-45	<i>Variation of the energy of pure and Cu-doped ZnO NPs</i>	114
Fig. 4-46	<i>PL spectra showing the emission mechanism of pure and Cu-doped ZnO Nps., R1:0.0% Cu, R2: 1% Cu, R3:3%Cu, and R4:5% Cu</i>	116
Fig. 4-47	<i>Schematic energy level diagram showing the possible radiative transition in pure and Cu-doped</i>	116

	ZnO Nps., R1:0.0% Cu, R2: 1% Cu, R3:3% Cu, and R4:5% Cu	
Fig. 4-48	<i>J-V characteristic curves for DSSC of Cu doped ZnO NPs</i>	118
Fig. 4-49	<i>P -V characteristic curves for DSSC of Cu doped ZnO NPs</i>	118
Fig. 4-50	<i>J-V characteristic curves for DSSC of Cu doped ZnO NPs based on (R3) ZnO NPs using different photosensitizer</i>	120
Fig. 4- 51	<i>P- V characteristic curves for DSSC of Cu doped ZnO NPs based on (R3) ZnO NPs using different photosensitizer</i>	121
Fig. 4-52	<i>EDX spectrum of synthesized ZnO NPs</i>	122
Fig . 4-53	<i>X-ray diffraction pattern of ZnO NPs synthesized at different annealing temperature: (O1) 350 °C, (O2) 400 °C, (O3) 500 °C and (O4) 550 °C</i>	124
Fig. 4-54	<i>HRTEM micrograph of (O2) ZnO NPs sample (a) micrograph image, (b) Diffraction patterns (c) selected electron diffraction area and (d) histograms</i>	127
Fig. 4-55	<i>UV-VIS. spectra of pure ZnO for O2, O3, and O4 of pure ZnO NPs</i>	129
Fig. 4-56	<i>$(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for O2, O3, and O4 of pure ZnO NPs</i>	129
Fig. 4-57	<i>Variation of the energy gap of ZnO NPs synthesized using different annealing temperature</i>	130
Fig. 4-58	<i>PL spectra of pure ZnO at different annealing temperature</i>	131
Fig. 4-59	<i>Schematic energy level diagram showing the possible radiative transition in ZnO NPs synthesized using different annealing temperature</i>	132
Fig. 4-60	<i>J-V characteristic curves of pure ZnO NPs synthesized at different annealing temperature</i>	133
Fig. 4-61	<i>P-V characteristic curves of pure ZnO NPs synthesized at different annealing temperature</i>	134
Fig. 4-62	<i>J-V characteristic curves for DSSC of pure ZnO NPs based on (O3) ZnO Ps using different photosensitizer</i>	136

Fig. 4-63	<i>P-V characteristic curves for DSSC of pure ZnO NPs based on (O3) NPs using different photosensitizer</i>	136
Fig. 4-64	<i>EDX spectrum of synthesized ZnO NPs</i>	137
Fig. 4-65	<i>X-ray diffraction pattern for U1, U2, U3 and U4 of pure ZnO NPs</i>	139
Fig. 4-66	<i>HRTEM micrograph of (U4) ZnO NPs sample (a) micrograph image, (b) Diffraction patterns and (c) selected electron diffraction area and (d) histograms</i>	142
Fig. 4-67	<i>UV-VIS. Spectra for U1, U2, U3 and U4 of pure ZnO NPs</i>	144
Fig.4-68	<i>$(\alpha hv)^2$ versus the photon energy ($h\nu$) for U1, U2, U3 and U4 of pure ZnO NPs</i>	144
Fig. 4-69	<i>Variation of the E_g for U1, U2, U3 and U4 of pure ZnO NPs</i>	145
Fig. 4-70	<i>PL spectra for U1, U2, U3 and U4 of pure ZnO NPs</i>	174
Fig. 4-71	<i>Schematic energy level diagram showing the possible radiative transition in U1, U2, U3 and U4 of pure ZnO NPs</i>	147
Fig. 4-72	<i>J-V characteristic curves of the DSSCs for U1, U2, U3 and U4 of pure ZnO NPs</i>	149
Fig. 4-73	<i>P- V characteristic curves of the DSSCs for U1, U2, U3 and U4 of pure ZnO NPs</i>	149
Fig. 4-74	<i>J-V characteristic curves for DSSC of pure NPs cell based on (U4) ZnO NPs using different dyes as a photosensitizer</i>	151
Fig. 7-75	<i>P-V characteristic curves for DSSC of pure NPs cell based on (U4) ZnO NPs using different dyes as a photosensitizer</i>	151