



Studies of fabrication and stability of dye sensitized nanocrystalline TiO₂ solar cells

Thesis submitted
By

Ahmed Esmail Kamal Shalan
B.Sc. (Chemistry) 2008

Under the supervision of

Prof. Dr. M. S. A. Abdel-Mottaleb
Professor of Inorganic and Photochemistry
Faculty of Science, Ain Shams University

Assoc. Prof. Dr. Mohamed Mohamed Rashad
Head of Electronic and Magnetic Division, Advanced Materials
Department, Central Metallurgical Research and Development
Institute (CMRDI).

Dr. Esam Bakir
Lecturer of inorganic and Photochemistry
Faculty of Science, Ain Shams University

To
Department of Chemistry
Faculty of Science
Ain Shams University
For
THE DEGREE
M.Sc. IN CHEMISTRY
(2012)

Approval Sheet

Name of candidate: Ahmed Esmail Kamal Shalan

Degree: M.Sc. Degree in Chemistry

Thesis Title: Studies of fabrication and stability of dye sensitized nanocrystalline TiO₂ solar cells

This Thesis has been approved by:

1- Prof. Dr. M. S. A. Abdel-Mottaleb

Professor of Inorganic and Photochemistry, Faculty of Science,
Ain Shams University.

2- Assoc. Prof. Dr. Mohamed Mohamed Rashad

Head of Electronic and Magnetic Division, Advanced Materials
Department, Central Metallurgical Research and Development
Institute (CMRDI).

3- Dr. Esam Bakir

Lecturer of inorganic and Photochemistry, Faculty of Science, Ain Shams
University.

Approval

Prof. Dr. Maged Shafik
Chairman of Chemistry Department

Studies of fabrication and stability of dye sensitized nanocrystalline TiO₂ solar cells

By

Ahmed Esmail Kamal Shalan

B.Sc. (Chemistry) 2008

Under the supervision of:

1- Prof. Dr. M. S. A. Abdel-Mottaleb

Chemistry Department, Faculty of Science, Ain Shams University,
Abbassia, Cairo, Egypt

2- Assoc. Prof. Dr. Mohamed Mohamed Rashad

Head of Electronic and Magnetic Division, Advanced Materials
Department, Central Metallurgical Research and Development
Institute (CMRDI).

3- Dr. Esam Bakir

Chemistry Department, Faculty of Science, Ain Shams University,
Abbassia, Cairo, Egypt



Faculty of science
Chemistry department

Studies of fabrication and stability of dye sensitized nanocrystalline TiO_2 solar cells

A Thesis
Submitted for the Master Degree of Science
(Chemistry)
(M.Sc.)

By
Ahmed Esmail Kamal Shalan
B.Sc. (Chemistry), 2008

Department of Chemistry
Faculty of Science
Ain Shams University

2012

Dedication
To
My Dear Parents

CONTENTS

	<i>Pages No</i>
List of Figures	v
List of Tables	xv
List of Abbreviations	
Abstract	
Acknowledgement	
Goals and Scope of the Work	
Introduction	1
1. Literature survey	5
1.1. Solar energy	8
1.2. Overview of photovoltaic technologies and market	9
1.3. Photovoltaic technology (PV)	10
1.4. The Photovoltaic Principle	11
1.5. Nanotechnology for photovoltaics	11
1.6. Semiconductors	13
1.7. Titanium dioxide	16
1.8. Shapes of Titanium dioxide nanopowders	18
1.9. The dye-sensitized solar cell	20
1.9.1. Basic principle and historical background	20
1.9.2. The architecture of the dye sensitized solar cell	22
1.9.2.1. Device structure	22
1.9.2.2. Energy diagram and working principle of a dye solar cell	24
1.10. Efficiency of Photovoltaic Solar Cell	28
1.11. Synthesis of titania nanoparticles	30

1.12.	Synthetic Methods for titanium dioxide nanostructures	31
1.12.1.	Sol-Gel method	31
1.12.2.	Microemulsion method	32
1.12.3.	Hydrothermal and Solvothermal methods	33
1.12.4.	Chemical Vapor Deposition and Physical Vapor Deposition methods	36
1.12.5.	Electrodeposition method	37
1.12.6.	Organic acid precursor method	37
1.12.7.	Microwave method	38

CHAPTER II

MATERIALS AND EXPERIMENTAL PROCEDURES 40

2.1.	Materials and Reagents	40
i.	Titanium sources	40
ii.	Organic acids	40
iii.	Alkali reagents	40
vi.	Dye sensitized solar cell materials	40
2.2.	Procedure	41
2.2.1	Preparation of TiO ₂ nanorods by hydrothermal method	41
2.2.2	Preparation of TiO ₂ nanoparticles by hydrothermal method	41
2.2.3	Preparation of TiO ₂ nanoparticles by organic acid precursor method	42
2.3.	Preparation of Photoanodes	42

2.4	Fabrication of DSSCs	43
2.5.	Equipment and Instrumentations	44
Characterization Techniques		
i.	X- Ray diffraction analysis (XRD)	44
ii.	Brunauer–Emmett–Teller (BET) measurements	45
OPTICAL CHARACTERIZATION		46
iii.	UV-Vis Transmittance Spectrophotometer	
iv.	Infrared spectroscopy	48
v.	Scanning electron microscope (SEM)	48
vi.	Transmission electron microscopy (TEM) and High Resolution Transmission electron microscopy (HRTEM)	49
vii.	Dye sensitized solar cells current-voltage (I-V) characterization	49
viii.	Sun simulator Setup	50
ix.	IPCE setup	51

CHAPTER III

RESULTS AND DISCUSSIONS 53

3.1.	Preparation of Titanium Dioxide (TiO ₂) nanopowders	53
3.1.1.	Preparation of Titanium Dioxide nanopowders using hydrothermal method	54
3.1.1.1.	Using titanium trichloride	54
i.	XRD patterns	55
ii.	Microstructure	58
iii.	Optical properties	61

v.	Photovoltaic Performance	65
3.1.1.2.	Using titanium isopropoxide	69
i.	XRD patterns (crystal structure)	69
ii.	Microstructure	72
iii.	Brunauer–Emmett–Teller (BET) measurements	76
v.	Optical properties	78
vi.	Photovoltaic Performance	81
3.1.1.3.	Effect of modifier and addition	86
i.	crystal structure	86
ii.	Microstructure	87
iii.	Optical properties	89
v.	Photovoltaic Performance	93
3.3.	Preparation of Titanium Dioxide nanopowders	
using organic acid precursor method		96
i.	Crystal structure	96
ii.	Microstructure	97
iii.	Specific Surface area S_{BET}	99
v.	Optical properties	101
vi.	Photovoltaic Performance	103
REFERENCES		108
SUMMARY AND CONCLUSIONS		
APPENDICES		
ARABIC SUMMARY		

LIST OF FIGURES

No.	Figure name	Page No.
Fig. (1)	Per-capita energy consumption by sectoral end use in (A) the developed world and (B) the developing world.	8
Fig. (2)	Current best photovoltaic research-cell efficiencies [figure by L. Kazmerski, National Renewable Energy Laboratory (NREL)].	10
Fig. (3)	Band positions of several SC and its corresponding band gaps.	15
Fig. (4)	Rutile and anatase unit cells, both showing octahedral titanium coordination. Grey and red atoms correspond to Ti^{4+} and O^{2-} , respectively.	17
Fig. (5)	Describes the TiO_2 photoanodes consisting of the NPs and NRs in the configuration of DSSCs.	20
Fig. (6)	Architecture of a dye solar cell. The nanoporous semiconductor (TiO_2) and the redox-electrolyte are located between two glass plates, coated with transparent conducting oxide (TCO). The TiO_2 is covered with a monolayer of dye and the counter electrode is coated with a thin platinum layer.	

- Fig. (7)** Chemical structure of the N719 dye molecule: $\text{RuL}_2(\text{NCS})_2$ with $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid. 24
- Fig. (8)** Chemical structure of propyl-methyl-imidazolium iodide (PMII): a room temperature molten salt (ionic liquid). 24
- Fig. (9)** Energy scheme and electron transfer paths of a dye solar cell. D is the ground state of the dye and D^* the excited state. E_{CB} and E_{VB} are the energy of the conduction band and valence band of the TiO_2 , respectively. E_{F}^{n} is the quasi-fermi level of the electrons in the conduction band of TiO_2 . E_{REDOX} is the redox energy of the redox electrolyte, with redox couple I^-/I_3^- . 25
- Fig. (10)** Schematic representation of the J-V curve for a DSSC. 29
- Fig. (11)** Dye Sensitized Solar Cell fabricated using sealing technique. 44
- Fig. (12)** Typical I-V curve of a solar cell. The important electrical parameters are the short-circuit current density j_{SC} , the open-circuit voltage V_{OC} and the maximum power point P_{MAX} with its corresponding current-density and voltage (J_{MP} , V_{OC}). 50

- Fig. (13)** Sun simulator used for I-V characterization curves in Solar Cells lab, Centre de Investigacio en Nanociencia I Nanotecnologia (Cin2, CSIC), ETSE, Campus UAB, Bellaterra (Barcelona), Spain. 51
- Fig. (14)** QE/IPCE measurement system from Oriel in Solar Cells lab, Centre de Investigacio en Nanociencia I Nanotecnologia (Cin2, CSIC), ETSE, Campus UAB, Bellaterra (Barcelona), Spain. 52
- Fig. (15)** XRD patterns of (a) the prepared TiO_2 nanoparticles at 36h (b) the prepared TiO_2 nanoparticles at 24h (c) the prepared TiO_2 nanoparticles at 12h (d) the prepared TiO_2 nanoparticles at 6h. 55
- Fig. (16)** XRD patterns of (a) the prepared TiO_2 nanoparticles at 500°C (b) the prepared TiO_2 nanoparticles at 400°C (c) the prepared TiO_2 nanoparticles at 300°C . 56
- Fig. (17)** XRD patterns of (a) the prepared TiO_2 nanoparticles at 100°C (b) the prepared TiO_2 nanoparticles at 200°C (c) the prepared TiO_2 nanoparticles at 300°C (d) the prepared TiO_2 nanoparticles at 400°C (e) the prepared TiO_2

- nanoparticles at 500°C. 57
- Fig. (18)** SEM micrographs of the produced powders (a) the prepared TiO₂ nanoparticles at 100°C (b) TiO₂ nanoparticles annealed at 200°C (c) TiO₂ nanoparticles annealed at 300°C (d) TiO₂ nanoparticles annealed at 400°C (e) TiO₂ nanoparticles annealed at 500°C. 60
- Fig. (19)** TEM micrographs of the produced powders (a) the prepared TiO₂ nanoparticles at 100°C (b) TiO₂ nanoparticles annealed at 300°C (c) TiO₂ nanoparticles annealed at 500°C. 61
- Fig. (20)** UV–visible transmittance spectrum T% of as-prepared of TiO₂ nanopowders(a) the prepared TiO₂ nanoparticles at 100°C (b) annealed at 200°C (c) annealed at 300°C (d) annealed at 400°C (e) annealed at 500°C. 63
- Fig. (21)** Band gap spectrum of (a) the prepared TiO₂ nanoparticles at 100°C (b) annealed at 200°C (c) annealed at 300°C (d) annealed at 400°C (e) annealed at 500°C. 64

- Fig. (22)** FT-IR spectra of (a) the prepared TiO₂ nanoparticles at 100°C (b) the prepared TiO₂ nanoparticles at 200°C (c) the prepared TiO₂ nanoparticles at 300°C (d) the prepared TiO₂ nanoparticles at 400°C (e) the prepared TiO₂ nanoparticles at 500°C. **65**
- Fig. (23)** I–V characteristics of DSSCs made from (a) the prepared TiO₂ nanoparticles at 100°C (b) TiO₂ nanoparticles annealed at 200°C (c) TiO₂ nanoparticles annealed at 300°C (d) TiO₂ nanoparticles annealed at 400°C (e) TiO₂ nanoparticles annealed at 500°C. **68**
- Fig. (24)** IPCE of DSSCs made from (a) the prepared TiO₂ nanoparticles at 100°C (b) TiO₂ nanoparticles annealed at 200°C (c) TiO₂ nanoparticles annealed at 300°C (d) TiO₂ nanoparticles annealed at 400°C (e) TiO₂ nanoparticles annealed at 500°C using N719 ruthenium dye. **68**
- Fig. (25)** XRD patterns of (a) P25, (b) the prepared TiO₂ nanoparticles and (c) the prepared TiO₂ nanorods. **70**
- Fig. (26)** XRD patterns of (a) the prepared TiO₂ nanoparticles at 36h (b) the prepared TiO₂ nanoparticles at 24h (c) the prepared TiO₂ nanoparticles at 12h (d) the prepared TiO₂ nanoparticles at 6h. **71**

- Fig. (27)** XRD patterns of (a) the prepared TiO₂ nanoparticles at 500°C (b) the prepared TiO₂ nanoparticles at 400°C (c) the prepared TiO₂ nanoparticles at 300°C. 71
- Fig. (28)** SEM micrographs of the produced powders (a) P25 Degussa spheres particles, (b, c) as-prepared TiO₂ nanorods mixed with irregular shapes and clusters of TiO₂ (d) as-prepared TiO₂ nanoparticles. 74
- Fig. (29)** TEM micrographs of the produced powders (a),(b),(c) as-prepared TiO₂ nanorods, (d) HRTEM image of TiO₂ nanorods shows diffraction patterns and lattice spacing , which corresponds to the (101) plane of anatase, (e) as-prepared TiO₂ nanoparticles (f) EDX spectrum of the TiO₂ nanopowders product. 75
- Fig. (30)** (a) N₂ adsorption–desorption isotherms Surface area and (b) corresponding pore size distribution of the produced TiO₂ nanorods synthesized hydrothermally at low temperature and P25 Degussa commercial paste. 77
- Fig. (31)** UV–visible transmittance spectrum T% of (a) as-prepared of TiO₂ nanorods, (b) TiO₂ nanoparticles and (c) P25 Degussa. 79