



Preparation of Some Photoactive and Thermal Conductive Nanomaterials and its Applications in Photocatalysis and Solar Collectors

Thesis submitted

By

Mostafa Hussein El-Noss

B.Sc. (Chemistry&Biochemistry) 2007

To

CHEMISTRY DEPARTMENT

FACULTY OF SCIENCE

AIN-SHAMS UNIVERSITY

For

THE DEGREE

M.Sc. IN CHEMISTRY

(2011)

Thesis Advisors

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

Professor of Inorganic and Photochemistry

Faculty of Science, Ain Shams University

Dr. Mohamed Said

Lecturer of inorganic and Photochemistry

Faculty of Science, Ain Shams University

Dr. Esam Bakir

Lecturer of inorganic and Photochemistry

Faculty of Science, Ain Shams University

Approval Sheet

Name of candidate: Mostafa Hussein El-Noss

Degree: M.Sc. Degree in Chemistry

Thesis Title: Preparation of Some Photoactive and Thermal Conductive Nanomaterials and its Applications in Photocatalysis and Solar Collectors

This Thesis has been approved by:

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

2- Dr. Mohamed Said

3- Dr. Esam Bakir

Approval

Prof. Dr.Maged Shafik
Chairman of Chemistry Department

Preparation of Some Photoactive and Thermal Conductive Nanomaterials
and its Applications in Photocatalysis and Solar Collectors

By

Mostafa Hussein El-Noss

B.Sc. (Chemistry&Biochemistry) 2007

Under the supervision of:

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

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

2- Dr. Mohamed Said

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

3- Dr. Esam Bakir

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

ACKNOWLEDGEMENTS

I would like to thank many people for their kind help during my work.

First of all, I would like to express my sincerest appreciation to **Prof. SabryAbdel-Mottaleb** for his support and suggesting the point of research. The best times i have enjoyed here comprise those for working on research and discuss life. Your serious attitude, insightful view, and persistent pursuing in science strongly impress me, leading me on the way towards a scientific researcher. It also inspires me with the courage to fight for my dreams.

I have learned a lot from you.

It's really my pleasure to work with the nice members of the prof.Abel-Mottaleb's group (**Dr.Mohamed said** and **Dr.Esambakir**), who joined the group before me, I appreciate your helping me start my experiments.

The financial support of STDF (project #1372) should be acknowledged.

Thank you Mom and Dad for the encouragement and support in my life.

Thanks regards

Mostafa Hussein

CONTENTS

CONTENTS

PART I

1	Introduction	1
1.1	Nanotechnology	1
1.1.1	What is nanotechnology	1
1.1.2	Nanotechnology products and applications	3
1.1.2.1	Sporting Goods	3
1.1.2.2	Car Paint and Car Waxes	3
1.1.2.3	Antibacterial Cleansers	4
1.1.2.4	Medical Bandage	4
1.1.2.5	Apparel Industry	4
1.1.2.6	Sunscreens and Cosmetics	5
1.1.2.7	Organic Light-Emitting Displays or OLEDs	5
1.1.2.8	Titanium Dioxide and Clean Air	5
1.2	Nanocatalysts	6
1.3	Nanotechnology and the Environment	7
1.3.1	Water pollution	8
1.3.2	Treatment of Textile Waste Water	11
1.4	Advanced Oxidation Processes	13
1.4.1	Homogeneous Advanced Oxidation Processes	15
1.4.1.1	The O ₃ /UV Process	16
1.4.1.2	The H ₂ O ₂ /UV Process	16
1.4.1.3	UV Fenton's Processes	18
1.4.2	Heterogeneous Photocatalysis	19
1.4.2.1	Photocatalytic process	21
1.4.2.2	Photocatalytic Semi-conductor	22
1.5	Titanium dioxide	25
1.5.1	Historical Background of TiO ₂	25
1.5.2	Titanium dioxide structure	28
1.5.3	Titanium Degussa	29
1.5.4	Titanium dioxide Photocatalysis	30
1.5.5	Enhancement of photocatalytic activity	34
1.5.5.1	Composite Semi-conductors	36

1.5.6	Practical Application of TiO ₂ Photocatalyst	39
1.6	Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution	42
1.6.1	Introduction	42
1.6.2	Experimental techniques used for studying dye degradation	46
1.6.3	Principles of photocatalysis and mechanistic pathways	47
1.6.3.1	Direct photocatalytic pathway	49
1.6.3.2	Indirect photocatalytic mechanism	52
1.6.4	Effect of operational parameters	52
1.6.4.1	Effect of pH	52
1.6.4.2	Effect of the dose of semiconductor	53
1.6.4.3	Effect of the initial concentration of dye	54
1.6.4.4	Effect of additives	54
1.6.4.5	Effect of temperature	58
1.7	Literature Review	61
	 CHAPTER 2 Experimental Techniques and Methods	66
2.1	Materials	66
2.2	Materials synthesis	67
2.3	Instrumentation	67
2.3.1	UV-VIS Measurements	67
2.3.2	XRD Measurements	67
2.3.3	TEM Measurements	68
2.3.4	Photo illumination Setup	68
2.3.5	Centrifuge	68
2.3.6	pH meter	69
2.4	Preparations and General Procedures	69
2.4.1	Photodegradation of Dyes	69

	CHAPTER 3 Results and Discussion	71
3.1	Methods of Data Analysis	71
3.1.1	The kinetic Rate Laws	71
3.1.2	Adsorption and Photodegradation Kinetics	73
3.2	XRD analysis	76
3.3	Data Analysis and Handling	77
3.3.1	Statistical and Data Handling Package	77
3.4	Catalyst characterization	77
3.4.1	Crystal properties and morphology	77
3.4.1.1	XRD	77
3.4.1.2	TEM	80
3.4.2	Optical properties	82
3.5	Photocatalytic degradation of Dyes 1 and 2	83
3.5.1	Photocatalytic activity	83
3.5.2	Kinetic studies	85
3.5.3	Synergistic Photocatalytic Activity	88
3.6	Enhancement of Photocatalytic activity of TiO₂	92
	Summary and conclusion of part I	97
	References of part I	101

PART II	151
CHAPTER 4 INTRODUCTION	157
CHAPTER 5 EXPERIMENTAL TECHNIQUES AND METHODS	
5.1 Experimental and Methods	157
5.1.1 Reagents and Chemicals	157
5.1.2 Preparation of nanofluids	157
5.1.2.1 Preparation of TiO ₂ nanofluids	157
5.1.2.2 Preparation of CuO nanofluids	158
5.1.2.3 Preparation of ZnO nanofluids	159
5.1.2.4 Preparation of Fe ₃ O ₄ nanofluids	159
5.2. Instrumentation	160
5.2.1 XRD Measurements	160
5.2.2 TEM Measurements	160
5.2.3 Description of Thermal Conductivity Measurements Set-Up used	161
5.3 Experiment	163
5.4 Measurements of the thermal conductivity	163
CHAPTER 6 RESULTS AND DISCUSSION	
6.1 Characterization of nanoparticles	165
6.2 Thermal analysis	169
Summary and conclusion of part I	177
Appendix	178

References of part II
Arabic summary

181

LIST OF FIGURES

1.1.	Schematic representation of the “band gap model.”	21
1.2.	Energies for various semi-conductors in aqueous electrolytes at pH=1.	25
1.3.	Bulk structure of rutile and anatase.	28
1.4.	Schematic diagram of photocatalytic process initiated by photon acting on the semi-conductor.	31
1.5.	Steps in heterogeneous photocatalytic reaction.	33
1.6.	Excitation steps using dye molecule sensitizer.	36
1.7.	Photo excitation in composite semi-conductor photo catalyst.	37
1.8.	Major Areas of activity in titanium dioxide Photocatalysis.	40
1.9.	Thin-film-fixed-bed reactor.	41
1.10.	Super-hydrophilicity.	42
1.11.	Schematic diagram showing the generation of oxidative species in a photocatalytic study.	46
1.12.	Langmuir–Hinshelwood plot in the case of Coomassie Blue degradation.	51
3.1.	XRD pattern of a , b where [a: pure TiO₂ nanocrystal, b: TiO₂– Cds nanocomposite).	78
3.2.	XRD pattern of pure TiO₂ nanocrystal and TiO₂–CdS nanocomposite	79
3.3.	TEM image of a, b, c where [a: pure TiO₂ nanocrystal, b: CdS nanocatalyst, c: TiO₂–CdS nanocomposite].	81

3.4. Normalized absorbance spectrum of TiO_2 (Degauss) and it's doped with 2% wt of nano CdS. (solid line TiO_2 and dash line CdS– TiO_2).	83
3.5. (a) The visible-absorption spectra of aqueous solutions of dyes 1 and 2 (b) Effect of catalyst in dark (line 2) showing significant adsorption of the dye on the catalyst and effect of catalyst/UV-VIS at different time intervals (lines 3 – 7).	84
3.6. Comparison between the first order linear plots of decolonization of Dye 1 [2.0×10^{-5} M] a] and Dye 2 [2.0×10^{-4} M] b] by CdS/ TiO_2 under UV-Vis and under visible light. ($\lambda_{\text{analytical}} = 490$ nm).	86
3.7. (a) A sketch of an Energy level diagram illustrating the coupling of CdS/ TiO_2 , in which electron transfer occurs from the visible light-activated CdS to the nonactivated TiO_2 . (b) Energy level diagram showing the coupling of CdS and TiO_2 , in which movement of both the electrons and holes is possible leading to synergistic e-/h+ production and separation.	91
4.1. Growth of publications by the nanofluidscommunity.	154
5.1. The combined parabolic solar collector [CPSC].	162
6.1. TEM image of TiO_2	165
6.2. TEM image of Fe_3O_4	166
6.3. TEM image of CuO	166
6.4. TEM image of CuO	167
6.5. TEM image of ZnO	167

6.6. XRD pattern of TiO_2	168
6.7. XRD pattern of ZnO	168
6.8. XRD pattern of Fe_3O_4	169
6.9. Thermal conductivity enhancement with particles concentration for TiO_2/mono ethylene glycol nanofluids.	171
6.10. Thermal conductivity enhancement particles concentration for CuO/mono ethylene glycol nanofluids.	172
6.11. Thermal conductivity enhancement particles concentration for Fe_3O_4/mono ethylene glycol nanofluids.	173
6.12. Thermal conductivity enhancement with particles concentration for ZnO/mono ethylene glycol nanofluids.	173
6.13. Enhancement of Thermal conductivity % with the best particles concentration for ZnO, TiO_2, Fe_3O_4 and CuO/mono ethylene glycol nanofluids.	174

LIST OF TABLES