DESIGN OF ANISOTROPIC CORE/SHELL NANOSTRUCTURES: BANDGAP ENGINEERING FOR EFFICIENT PHOTOCATALYTIC AND PHOTOVOLTAIC APPLICATIONS

SUNITA

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2014

Design of Anisotropic Core/Shell Nanostructures: Bandgap Engineering for Efficient Photocatalytic and Photovoltaic Applications

by

SUNITA

Department of Chemistry

Submitted
in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

INDIA

JANUARY 2014

CERTIFICATE

This is to certify that the thesis entitled, "**Design of Anisotropic Core/Shell Nanostructures: Bandgap Engineering for Efficient Photocatalytic and Photovoltaic Applications**", being submitted by Ms. Sunita, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Ms. Sunita has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

Date:

Professor A. K. Ganguli

Department of Chemistry

Indian Institute of Technology Delhi

New Delhi – 110016

INDIA

ACKNOWLEDGMENTS

It is a great pleasure to extend my heartfelt thanks to all those who made this thesis possible.
I am thankful to Prof. Ashok Kumar Ganguli, my thesis supervisor, for giving me the opportunity to work under his guidance.

I am also grateful to the Head, Prof. A. Ramanan, Department of Chemistry, IIT Delhi for providing me the necessary facilities in the department to carry out my research. Also I would like to thank all the faculty members of the department for their help.

I am extremely thankful to Prof. S. Ghosh and Mr. Pawan Kumar Srivastava, School of physical sciences, JNU for useful scientific discussions and also for carrying out TEM and I-V measurements. I would also like to thank Prof. A. Patra and Mr. Simanta Kundu, IACS Kolkata for I-V measurements. I am also thankful to Dr. P. H. Borse and Ms. Alka Pareek, ARCI, Hyderabad for photovoltaic measurements.

I am grateful to all supporting staff at the department, IIT Delhi for their kind help and cooperation.

I wish to express my gratitude for my colleagues, Dr. Saroj, Dr. Sonalika, Dr. Jahangeer, Dr. Menaka, Dr. Masood, Dr. Aditya, Dr. Manu Sharma, Dr. Oruganti Anjaneyulu, Dr. R. Parthasarathy, Bharat, Ashima, Akanksha, Gohil, Zeba, Nibedita, Soumen, Sandeep, Kasinath, Jayanti, for providing me an excellent and friendly working environment.

I owe everything to my parents and sister who have done everything to enable me to concentrate on my research. I am sincerely thankful to all those who have helped me in the successful completion of this work. Last, but not the least, I thank God for who gave me the grace and privilege to pursue this program and successfully complete it.

I acknowledge the financial support of Council of Scientific and Industrial Research, CSIR for a fellowship.

Sunita

ABSTRACT

With the depletion of fossil-fuel reserves, an urgent challenge confronting human beings is to seek a clean and sustainable alternative-energy source. In this regard, semiconductor photocatalysis has gained immense attention by the scientific and engineering world because of the great potential as one of clean, low cost, and environmentally friendly strategies to solve the energy crisis and environmental issues toward sustainable processes. As Fujishima and Honda first presented the concept of photo-electrochemical water splitting into H_2 and O_2 over a TiO_2 electrode, TiO_2 has and continues to be the most widely studied material for photocatalytic applications. However, recent researches on ZnO semiconductor have shown that it has the potential to be an alternative material for the photovoltaic cells and photocatalytic decomposition of organic pollutants due to its high quantum efficiency. The emergence of ZnO as an alternative is due to having a band gap similar to TiO_2 and also having much higher electron mobility than that of TiO_2 thus lowering the charge recombination. Apart from this, ZnO semiconductor can be fabricated into a variety of nanostructures and their morphology can be modified easily by using different synthetic methods. However, there are two obvious drawbacks of the ZnO as a photocatalyst. On one hand, ZnO is a wide band gap semiconductor that restricts the photoresponse of the only UV, thus significantly depressing the visible light utilization of the solar spectrum can only absorb the UV light, which accounts for only 4 % of the total sunlight. On the other hand, the quick recombination rate of photogenerated electron-hole pairs in ZnO results in low quantum efficiency of photocatalytic reactions. Also, more importantly, ZnO normally suffers from intrinsic drawback of photocorrosion, which greatly reduces its photoactivity

and photostability. As a result, it still posts a long-standing challenge to resolve these fundamental disadvantages for diverse aspects of photocatalytic applications. To solve these problems, research activities have been proliferated to reinforce the photocatalytic properties by manipulating nanostructures or morphologies of ZnO including polymer passivation, surface doping with non-metallic/metallic elements or semiconductor oxides and surface deposition of the metal nanoparticles. In these cases, of particular note is the coupling of ZnO nanostructures covered with a mid/narrow band gap sensitizers such as CdS, PbS, Bi_2S_3, CdSe, Ag_2S, CdTe to form the so-called core/shell nanostructures which not only chemically passivates surface-related trapping sites, but also retards the electron-hole pairs recombination. To further suppress the electron-hole pair recombination, the idea of forming type-II band alignment in the core/shell nanostructures is explored, which results in electron wavefunction mainly residing in one semiconductor and the hole wavefunction in other semiconductor, leading to efficient separation of photogenerated charge carriers at the core/shell interface and enhancing the photocatalytic efficiency of ZnO based core/shell nanostructures in the visible region.

The motivation of the present research originated from the idea that the coupling of wide band gap semiconductor with the mid/narrow band gap semiconductor (which acts as sensitizer) forms an efficient heterostructure for the separation of photogenerated charge carriers and makes it a good candidate for visible-light photocatalysis and photovoltaics.

Thus, the present thesis is aimed to shift the optical absorption of ZnO from UV to the visible spectral range and improve its photocatalytic activity under visible light irradiation by using the core/shell geometry with mid/narrow band gap sensitizers.

In the current study, we have synthesized anisotropic ZnO core/shell nanostructures using a facile surface-functionalization method. These core/shell nanostructures were synthesized using citric acid as the surface functionalizing agent. The fabricated core/shell nanostructures exhibited efficient light harvesting with high photocatalytic and photovoltaic efficiency due to their wide range of light absorption and type-II band alignment. We have investigated the mechanism of the photodegradation of RhB and MB to elucidate the efficiency enhancement of the ZnO based core/shell nanostructures. The thesis deals with the synthesis, characterization and band gap engineering of type-II ZnO based core/shell nanostructures for photocatalytic and photovoltaic applications.

Chapter 1 A brief overview of research in the area of photocatalysis and band gap engineering of semiconductor metal oxides using core/shell morphology with a sensitizer is discussed. Of particular interest is type-II band alignment, a highly desirable property for photocatalytic and photovoltaic applications which is discussed in detail in this introduction chapter. Synthetic methodologies for obtaining core/shell nanostructures and the motivation behind the present study have been outlined.

Chapter 2 Core/shell nanorods of ZnO/CdS have been synthesized with varying shell thickness and their shell thickness dependent photocatalytic and photovoltaic properties have been investigated. The optical absorption of the nanorods can be tuned to cover almost the entire visible region of the solar spectrum through the effects of shell thickness. The photocatalytic studies confirmed that the ZnO/CdS core/shell nanorods exhibit improved degradation efficiency compared to bare ZnO and CdS under simulated solar radiation. The core/shell nanorods having shell (CdS) thickness of 30 nm

(ZnO/CdS3) displays the highest photocatalytic efficiency for the degradation of Rhodamine B under simulated solar radiation, indicating efficient separation of electron-hole pairs. These nanorods having CdS shell of 30 nm (ZnO/CdS3) are also superior in charge separation as well as carrier transport, thus exhibiting a 14-fold increment of short-circuit current density for a conversion efficiency (η) enhancement of 232-fold as compared to bare ZnO nanorods. We have discussed the importance of the core/shell geometry and the effect of shell thickness on the light harvesting performance for photocatalysis and photovoltaic cells in this chapter.

Chapter 3 deals with the efficient and environmentally benign one-dimensional ZnO/In_2S_3 core/shell nanostructures to be used as a photocatalyst to overcome the drawback of low photocatalytic efficiency brought by electron-hole recombination and narrow photoresponse range. The photocatalytic activity under visible light to degrade Rhodamine B (RhB) was enhanced by these core/shell nanostructures due to the formation of heterojunctions, which prolongs the separation of photogenerated electrons and holes. We have also investigated the reusability of these core/shell nanostructures for degradation of RhB.

Chapter 4 This chapter deals with the design and synthesis of environmentally benign ZnO/Ag_2S core/shell nanorods for photocatalytic applications and compared with ZnO/CdS core/shell nanorods. Compared to bare ZnO and ZnO/CdS nanorods, ZnO/Ag_2S core/shell nanorods exhibit considerably higher photocatalytic efficiency for the degradation of MB dye due to its improved visible light harvesting properties owing to the incorporation of narrow band gap sensitizer Ag_2S. Through this work, we demonstrate ZnO/Ag_2S as an efficient photocatalyst that has the potential to replace Cd-based sensitizers for eco-friendly applications.

Chapter 5 In this chapter we have tuned the absorption of ZnO nanorods using PbS nanoparticles as the sensitizer. ZnO/PbS core/shell nanorods show the improved light-harvesting performance compared to the individual counterparts. Compared with the bare ZnO nanorods, the light absorption ability of the ZnO/PbS core/shell nanostrcutures is significantly enhanced due to the shift of the absorption spectrum to the visible-light region (maxima at 485 nm). Photodegradation performance of the core/shell nanorods on the organic dye methylene blue (MB) under visible light irradiation, shows that these core/shell nanorods could utilize the visible light to decompose MB with considerable efficiency. We have discussed that the core/shell architectures offer the possibility of bandgap engineering through the combination of different semiconductor materials and provide efficient light-harvesting medium which extends the control over the spatial localization of charge carriers.

Chapter 6 In this chapter we have designed the band gap tailored ZnO/CuS core/shell nanorods to enhance the photocatalytic efficiency of bare ZnO nanorods. One-dimensional ZnO/CuS core/shell heteroarchitectures with high visible-light photocatalytic activity has been successfully obtained by surface functionalization method. Compared with the pure ZnO nanorods, the obtained ZnO/CuS heterostructures showed enhancement of the visible-light photocatalytic activity to degrade methylene blue (MB) because of the formation of heterojunctions, which might improve the separation of photogenerated electrons and holes derived from the coupling effect of ZnO and CuS heterostructures. Moreover, these core/shell nanostructures could be reused for degradation of MB during a three-cycle experiment without significant decrease in the photocatalytic activity which is very important for these ZnO/CuS core/shell nanorods to be of practical use in environmental applications.

Chapter 7 We outline the major results of our studies on enhancing the photocatalytic and photovoltaic efficiencies by introducing core/shell morphology. These core/shell nanorods provide a facile and compatible frame for potential applications in nanorod-based solar cells and as efficient photocatalysts. Our achievements indicate that the core/shell nanorods guarantee efficient charge separation and are truly promising components for future photocatalysts and photovoltaic devices. We also suggest future directions to be pursued which may lead to further enhancement in photocatalytic and photovoltaic properties.

In these regards, it is expected that an introduction of a narrower band-gap sensitizer to the current core/shell heterostructures could bring more red-shifts in the absorption threshold and boost the overall efficiency. Efforts are underway to demonstrate a multi-sensitizing system for more improved photoconversion efficiency.

TABLE OF CONTENTS

CERTIFICATE		i
ACKNOWLEDGEMENTS		ii
ABSTRACT		iv
LIST OF FIGURES		x
LIST OF TABLES		xviii
ABBREVIATIONS AND SYMBOLS		xx
Chapter 1	**Introduction**	
1.1	Advanced Oxidation Processes	1
1.2	Semiconductor Photocatalysis	2
1.3	Fundamental Principles of Semiconductor Photocatalysis	3
1.4	Materials for Photocatalysis	4
1.5	Band Gap Engineering in Nanostructures	5
1.5.1	Band Gap Engineering in Nanostructures by Size and Shape	7
1.5.2	Band Gap Engineering in Nanostructures by Composition (Alloying and Impurity Doping)	9
1.5.3	Band Gap Engineering in Nanostructures by Surface Passivation	11
1.5.4	Band Gap Engineering in Nanostructures by Core/Shell Formation	13

1.6	Visible Light Type-II Core/Shell Heterostructures	16
1.7	Synthesis of Type-II Core/Shell Heterostructures	18
1.7.1	Chemical Vapour Deposition	18
1.7.2	Chemical Deposition Method	19
1.7.3	Electrochemical Deposition	19
1.7.4	Ion exchange method	20
1.7.5	Successive Ionic Layer Adsorption and Reaction	20
1.7.6	Solvothermal/Hydrothermal Method	20
1.8	Characterization of Core/Shell Nanostructures	21
1.9	Motivation of the thesis	22
1.10	References	26
Chapter 2	**Thickness Dependent Photovoltaic and Photocatalytic Properties of ZnO/CdS Core/Shell Nanorods**	
2.1	Introduction	34
2.2	Experimental	36
2.2.1	Preparation of ZnO Nanorods	36
2.2.2	Preparation of CdS Nanoparticles	36
2.2.3	Preparation of ZnO/CdS Core/Shell Nanorods	37
2.2.4	Characterization	38
2.2.5	Photovoltaic experiments	39
2.2.6	Photocatalytic experiments	40
2.2.7	Analysis of hydroxyl radicals (OH•)	41

2.3	Results and discussion	41
2.3.1	Photocatalytic mechanism	60
2.4	Conclusions	64
2.5	References	65
Chapter 3	**Band Gap Tuning of ZnO Nanorods using In_2S_3 Shell for Enhanced Visible-Light-Driven Photocatalysis**	
3.1	Introduction	70
3.2	Experimental	72
3.2.1	Preparation of ZnO Nanorods	72
3.2.2	Preparation of In_2S_3 Nanoparticles	72
3.2.3	Preparation of ZnO/In_2S_3 Core/Shell Nanorods	73
3.2.4	Characterization	73
3.2.5	I-V and Photoconductivity measurements	75
3.2.6	Photocatalytic experiments	75
3.2.7	Analysis of hydroxyl radicals (OH•)	76
3.3	Results and discussion	77
3.3.1	Photocatalytic mechanism	88
3.4	Conclusions	96
3.5	References	97

Chapter 4	**Light Harvesting and Environmentally Benign ZnO/Ag_2S Core/Shell Nanorods for Enhancement of Visible-Light-Driven Photocatalysis : A Comparison with ZnO/CdS Core/Shell Nanorods**	
4.1	Introduction	102
4.2	Experimental	105
4.2.1	Preparation of ZnO Nanorods	105
4.2.2	Preparation of ZnO/Ag_2S Core/Shell Nanorods	105
4.2.3	Characterization	105
4.3	Results and discussion	108
4.4	Conclusions	121
4.5	References	122
Chapter 5	**Band Gap Engineering of ZnO using Core/Shell Geometry with PbS Nanoparticles for Light Harvesting**	
5.1	Introduction	125
5.2	Experimental	126
5.2.1	Preparation of ZnO Nanorods	126
5.2.2	Preparation of PbS Nanoparticles	127
5.2.3	Preparation of ZnO/PbS Core/Shell Nanorods	127
5.2.4	Characterization	128

5.2.5 Photocatalytic experiments 129

5.3 Results and discussion 130

5.4 Conclusions 140

5.5 References 141

Chapter 6 **Band Gap Tailored ZnO/CuS Core/Shell Nanorods : An approach to Enhance Photocatalytic Efficiency**

6.1 Introduction 144

6.2 Experimental 146

6.2.1 Preparation of ZnO Nanorods 146

6.2.2 Preparation of CuS Nanoparticles 146

6.2.3 Preparation of ZnO/CuS Core/Shell Nanorods 146

6.2.4 Characterization 147

6.2.5 Photocatalytic experiments 148

6.3 Results and discussion 149

6.4 Conclusions 163

6.5 References 164

Chapter 7 **Conclusions and Future Prospects** 165

BIO-DATA OF THE AUTHOR 169