OXIDE NANOSTRUCTURES BASED ON Ti, Nb AND Ta FOR PHOTOCATALYTIC PROPERTIES

by

DEBASHREE DAS

Department of Chemistry

Submitted
in fulfillment of the requirements for the Degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

INDIA

JULY 2013

Dedicated to

my

Parents

CERTIFICATE

This is to certify that the thesis entitled, **"Oxide Nanostructures Based on Ti, Nb and Ta for Photocatalytic Properties"**, being submitted by **Ms. Debashree Das**, 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. Debashree Das 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**:** 22 July 2013

Prof. A. K. Ganguli

Professor

Department of Chemistry

Indian Institute of Technology, Delhi

Acknowledgements

Completion of this doctoral thesis would not have been possible with the support of several people. I would like to express my sincere gratitude to all of them.

First of all, I would like to express my deep sense of regards and gratitude to my research supervisor, Prof. A. K. Ganguli, Department of Chemistry, IIT Delhi and Director, Institute of Nano Science and Technology, Mohali, for his valuable guidance, scholarly inputs and consistent encouragement that I have received throughout my research work. This feat was possible only because of the unconditional support provided by Sir. His approach towards the problem solving and the way of visualizing chemical entity has enthralled me. Sir has always made himself available to clarify my doubts and I consider it as a great opportunity to do my doctoral programme under his guidance and to learn from his research expertise. His stimulating suggestions, invaluable contributions and encouragement, helped me to coordinate my thesis project especially in writing this report. I thank him for his help and support.

I would like to express my special thanks to Mrs. Jaya Ganguli for her love and affection I have received during my stay at IIT Delhi.

I am grateful to the Head of Chemistry department, Prof. A. Ramanan, and all faculty members for providing the necessary facilities in the department.

I express my sincere thanks to all my school and college teachers for the knowledge and guidance I have gained which helped to shape my future.

I am also grateful to all the support staff of the department for their kind help and cooperation.

I would also like to thank the Council of Scientific and Industrial Research (CSIR), for providing the fellowship and Department of Electronics and Information Technology (DeitY), Govt. of India for financial support to carry out this research work.

A special thanks to my lab-colleagues, especially Dr. Saroj, Dr. Sonalika, Dr. Jahangeer, Dr. Jai Prakash, Dr. Aparna, Dr, Mrinmoyee, Dr. Ashima, Dr. Masood Nath, Dr. Manu Sharma, Dr Menaka, Dr. Aditya, Sunita, Soma, Bharat, Neha, Nibedita, Gohil, Kasinath, Arabinda, Soumen, Zeba, Vaishali, Vandana, Sanjit, Sandeep, Nitin and Jayanti for their love and providing an excellent working environment.

Finally, I owe a lot to my parents, who encouraged and helped me at every stage of my personal and academic life. They been a source of strength and courage to me which helped me to put my best efforts and made this achievement come true.

Last, but not the least, I thank God for who gave me the grace and privilege to pursue this program and successfully complete it.

Debashree

ABSTRACT

Environmental issues and energy resources at global level are the two important topics in the present scenario. To effectively address the serious environmental problems and the depletion of fossil fuels accompanying their combustion, there has been extensive search for technologies that help in environmental remediation and provide energy that is a clean, renewable, cheap, safe, and viable alternative to fossil fuels. Photocatalyst materials are important for future energy requirements. Oxide semiconductor based photocatalysis has attracted extensive attention due to its wide application of photon energy conversion from the viewpoint of solar energy utilization in environmental processing such as air purification, water disinfection, hazardous waste remediation and degradation of toxic compounds. Photocatalysis reactions are assisted by photons in the presence of catalyst accompanying simultaneous oxidation and reduction using electrons and holes. Under irradiation with an energy equivalent to or greater than the band gap of the semiconductor photocatalyst, electrons in the valence band are excited into the conduction band, leaving holes in the valence band. These photogenerated electrons and holes cause reduction and oxidation reactions, respectively.

The design of nanostructured oxide based semiconductor materials has become one of the most challenging fields of nanoscience and technology due to its unique properties and important applications in catalysis, electronics and photonic devices. Since the discovery of photochemical splitting of water on titanium dioxide by Fujishima and Honda in 1972, there has been a growing interest in search of materials with photocatalytic properties. Semiconductor photocatalysis has been proven to be potentially advantageous for environmental pollutant remediation because it allows complete decomposition of organic compounds into CO_2 and H_2O at ambient

conditions and also for water splitting to supply clean and recyclable hydrogen energy. In order to meet all these requirements new materials are being explored and examined for the purpose of photocatalytic degradation of organic waste and for facilitating water splitting.

The present thesis is aimed to develop alternate approaches for the synthesis of nanostructured titanium, niobium and tantalum based oxides and investigate their photocatalytic properties and to establish various factors influencing the efficiency of the catalyst material.

In the present investigation, we focus our study on the enhancement of the efficiency of photocatalysts (titania, niobate and tantalate nanostrutures) by increasing the surface/volume ratio, the control of morphological features, size, surface charge and surface area. These nanomaterials were obtained by a combination of microemulsion and hydrothermal methods under various reaction conditions. Such size and shape tunable materials have the potential to reduce water contaminants and eliminate the use of toxic catalysts. We have investigated various parameters that collectively enhances the photocatalytic efficiency of the material. This thesis deals with the synthesis, characterization and properties of various metal oxide nanostructures and their photocatalytic properties.

In Chapter 1, a detailed survey of the background literature has been carried out for the state of knowledge existing in the area relevant to the materials especially metal oxides with photocatalytic properties. We have also discussed the possibility for obtaining metal oxides in bulk as well as nano regime. Though various high temperature routes are known, but due to difficult synthetic conditions, cannot be commercialized. Further, in this section we have discussed the details of our effort for designing methodologies to obtain nanostructured metal oxides of controlled size and morphology for photocatalytic applications.

In chapter 2, we have discussed the method of synthesis of TiO_2 nanostructures of various morphologies (spindles, cube, spherical particles) with high surface area by reverse micellar route. In this chapter, we aimed to synthesize monodispersed mesoporous TiO_2 nanostructures of high purity by tuning the morphology and size using the reverse micellar method for their photocatalytic properties. We have carried out detailed study on the effect of water content, co-surfactant, surfactant on particle size and shape of TiO_2 nanoparticles. The effect of co-surfactant was studied by varying the chain length of the co-surfactants. The surfactant used was CTAB. Co-surfactant was varied from 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol which allowed to study role of co-surfactant chain length on the surfactant film flexibility which determines the growth of particles inside the reverse micelle.TEM studies show the morphology varying from spindle shaped as obtained with butanol as co-surfactant to cube shaped in the case of hexanol. We also estimated the photocatalytic activity of the prepared TiO_2 nanostructures for decomposition of Rhodamine B dye. The current work is focused to make an attempt to understand the major factors which controls the growth of TiO_2 nanoparticles and thereby influencing the efficiency of the synthesized material towards degradation of dye.

In chapter 3, we have discussed a template free hydrothermal route for the synthesis of $Cd_2Ta_2O_7$ and $Cd_2Nb_2O_7$ nanocubes, and also their photocatalytic activity. The various synthetic parameters such as concentration of alkali, reaction temperature and reaction time which play important role in the formation of monophasic $Cd_2Ta_2O_7$ and $Cd_2Nb_2O_7$ nanoparticles were studied in detail. Photocatalytic activity towards Rhodamine B indicated that nanosized $Cd_2Ta_2O_7$ and $Cd_2Nb_2O_7$ obtained by hydrothermal method show efficient photocatalytic properties. The above studies show the enhanced efficienciy of these nanostructured material and compared with TiO_2 also better in terms of stability.

In chapter 4, Synthesis of perovskite based silver tantalate ($AgTaO_3$) and silver niobate ($AgNbO_3$) nanoparticles and its application as UV and visible light based photocatalyst for the degradation of organic dyes have been discussed. Nanostructures of $AgTaO_3$ and $AgNbO_3$ synthesized by hydrothermal method have been characterized by powder X-ray diffraction, diffuse reflectance spectroscopy, transmission electron microscopy and surface area measurements along with its photocatalytic properties. The photooxidation activities have been carried out using organic molecules, Rhodamine B. We have investigated the role of sacrificial reagent on the photocatalytic efficiency of the synthesized materials. $AgTaO_3$ and $AgNbO_3$ nanoparticles showed excellent decomposition rates for the organic compounds under UV and visible light irradiation.

In chapter 5, we have shown the methodology for the synthesis of novel visible light photocatalysts copper tantalate and copper niobate under hydrothermal conditions. Hydrothermal synthesis lead to the formation of smaller crystallite size particles, which was beneficial for the adsorption of organic moiety during the photocatalysis. It was observed that $CuTa_2O_6$ and $CuNb_2O_6$ nanoparticles showed nearly 4-5 times enhanced photoactivity than bulk. The catalyst showed excellent decomposition rates for the organic compounds under visible light irradiation. This is the first detailed photocatalytic study of nanostructured $CuTa_2O_6$ and $CuNb_2O_{6.}$ The results point toward the possibility of $CuTa_2O_6$ and $CuNb_2O_6$ nanoparticles as potential photocatalysts to split water under visible light irradiation.

In chapter 6, we have discussed synthesis of $InTaO_4$ and $InNbO_4$ nanoparticles as a visible light photocatalysts. The study focuses on two important aspects i.e., role of co – catalyst and sacrificial reagent on the photocatalytic efficiency of the material. $InTaO_4$ and $InNbO_4$ photocatalysts with different NiO loading were prepared by incipient wetness impregnation. NiO loading greatly enhanced the rate of degradation during photocatalysis. We have also studied the role of sacrificial reagent on the photoefficiency of the synthesized $InTaO_4$ and $InNbO_4$ nanoparticles.

Chapter 7 deals with conclusions and future prospects of the work described above. The thesis has led to the development of low temperature methodologies using microemulsion route and hydrothermal mediated precursors to obtain various morphologies of nanostructured titanium, niobium and tantalum based oxides. The methods employed have enabled us to lower the synthesis temperature by 200ºC to 400ºC in metal oxides and the above study can be extended to the synthesis and investigation of tantalum and niobium based semiconducting oxides of importance.

TABLE OF CONTENTS

CERTIFICATE	i
ACKNOWLEDGEMENTS	ii
ABSTRACT	iv
TABLE OF CONTENTS	ix
LIST OF FIGURES	xiv
LIST OF TABLES	xxv
ABBREVIATIONS AND SYMBOLS	xxvi

CHAPTER 1 INTRODUCTION

1.1	Photocatalysis	6
1.2	Metal oxides	20
1.3	Synthesis of metal oxides	21
1.3	Characterization techniques	40
1.4	Motivation of the thesis	58
1.5	References	60

CHAPTER 2 MICROEMULSION BASED SYNTHESIS OF TITANIA (TiO_2) NANOSTRUCTURES: HIGHLY EFFICIENT PHOTOCATALYST MATERIAL

2.1	Introduction	72

2.2	Experimental	74
2.2.1	Materials	74
2.2.2	Synthesis of TiO_2 nanoparticles	74
2.2.3	Photocatalytic Experiments	76
2.2.4	Characterization	77
2.3	Results and Discussion	78
2.3.1	Photocatalytic studies of TiO_2 nanostructures	97
2.4	Conclusions	104
2.5	References	105

CHAPTER 3	**SYNTHESIS AND CHARACTERIZATION OF CADMIUM TANTALATE ($Cd_2Ta_2O_7$) AND CADMIUM NIOBATE ($Cd_2Nb_2O_7$) NANOPARTICLES AND THEIR PHOTOCATALYTIC STUDIES**	
3.1	Introduction	113
3.2	Experimental	115
3.2.1	Materials	115
3.2.2	Synthesis of Cadmium tantalate and Cadmium niobate nanoparticles	115
3.2.3	Photocatalytic Experiments	116
3.2.4	Characterization	117
3.3	Results and Discussion	118
3.3.1	Photocatalytic properties of $Cd_2Ta_2O_7$	134

	and $Cd_2Nb_2O_7$ nanocubes	
3.3.2	Stability of photocatalyts	143
3.4	Conclusions	146
3.5	References	147

CHAPTER 4 NANOSTRUCTURED SILVER TANTALATE ($AgTaO_3$) AND SILVER NIOBATE ($AgNbO_3$) AND THEIR PHOTOCATALYTIC PROPERTIES

4.1	Introduction	151
4.2	Experimental	154
4.2.1	Synthesis of silver tantalate and silver niobate nanoparticles	155
4.2.2	Photocatalytic Experiments	156
4.2.3	Characterization	157
4.3	Results and Discussion	158
4.3.1	Photocatalytic properties of silver tantalate and silver niobate	165
4.3.2	Stability of photocatalysts	173
4.4	Conclusions	177
4.5	References	178

CHAPTER 5 SYNTHESIS OF COPPER TANTALATE ($CuTa_2O_6$) AND COPPER NIOBATE ($CuNb_2O_6$) AND THEIR PHOTOCATALYTIC STUDIED

5.1	Introduction	184
5.2	Experimental	186
5.2.1	Materials	186
5.2.2	Synthesis of copper tantalate and copper niobate nanoparticles	186
5.2.3	Photocatalytic Experiments	187
5.2.4	Characterization	188
5.3	Results and Discussion	188
5.3.1	Photocatalytic properties of copper tantalate and copper niobate nanoparticles	198
5.3.2	Photocatalytic Decomposition of MB under visible Light	198
5.3.3	Photocatalytic Decomposition of RhB under visible Light	202
5.3.4	Photocatalytic Decomposition of 4-chlorophenol under visible light.	204
5.3.5	Stability of photocatalysts	206
5.4	Conclusions	210
5.5	References	211

CHAPTER 6 INVESTIGATION OF NANOSTRUCTURED INDIUM TANTALATE ($InTaO_4$) AND INDIUM NIOBATE ($InNbO_4$) AND THEIR PHOTOCATALYTIC PROPERTIES

6.1	Introduction	217
6.2	Experimental	220
6.2.1	Materials	220
6.2.2	Synthesis of indium tantalate and indium niobate nanoparticles	220
6.2.3	Loading of co-catalyst on Indium tantalate and Indium niobate Nanoparticles	220
6.2.4	Photocatalytic Experiments	221
6.2.4	Characterization	221
6.3	Results and Discussion	222
6.3.1	Photocatalytic properties of indium tantalate and indium niobate nanoparticles	231
6.4	Conclusions	240
6.5	References	241

CHAPTER 7 CONCLUSIONS AND FUTURE PROSPECTS 245

BIO-DATA OF THE AUTHOR 258