Dedicated to My Beloved Parents

Late Mrs. Batula Bibi

Late Mr. Habibur Rahaman

DECLARATION

I, Hasimur Rahaman, hereby declare that the thesis entitled "**Synthesis, Characterization and Physicochemical Properties of Size and Shape-Selective Manganese Oxides and their Composites**" has not been submitted either in whole or in part previously to any other institution for the award of any degree or qualification and does not contain any previously published material or written by another person, except where due reference is made in the text.

Place: Silchar Hasimur Rahaman

Date: 05.09.2016

Acknowledgements

At first, I would like to express my sincere thanks and deep sense of gratitude to Dr. S. K. Ghosh, my supervisor, whose thoughtful suggestions and guidance always support me in carrying out this research work. Without his constant supervision, motivation and inspiration at every step, perhaps this work could not have been matured up to the present level.

I would like to express my gratitude to Prof. P. C. Pal, the Head, Department of Chemistry and Ex. Heads, Prof. N. V. S. Rao and Prof. C. R. Bhattacharjee for their constant support and help during the research work.

I would like to thank Dr. Sk. Jasimuddin for providing facilities for cyclic voltammetry measurements. I would like to offer my gratitude to Prof. S. B. Paul, Dr. P. Mondal, Dr. M. K. Paul, Dr. D. Sengupta, Dr. H. Acharya, Dr. S. Choudhury, Dr. T. Sanjoy Singh and Dr. R. Panchadhayee for their moral support and help during the course of this research work. I would also like to remember Prof. M. R. Islam for providing his laboratory at the initial stage to start this work.

I would like to thank Dr. Nikhil R. Jana, IACS, Kolkata for providing fluorescence microscopic facilities; Dr. Dilip Kumar Maiti, University of Calcutta, Kolkata for providing me lab facilities for some parts of experiments; Dr. Achintya Singh, Bose Institute, Kolkata for Raman measurements; SAIF, NEHU, Shillong for providing electron microscopic facilities; Dr. Susmita Kundu, CSIR-Central Glass & Ceramic Research Institute for providing us gas sensing measurements facilities; Dr. Mahuya Sengupta, Department of Biotechnology, Assam University, Silchar for providing us biological experimental facilities and Dr. Soumen Basu, Thapar University for characterization of some of the materials.

I would like to convey my thanks to Mr. P. R. Ramesh, Mr. S. Bhattacharjee, Mr. B. Nath, Mr. Jahangir Alom Barbhuiya, Mr. Jamil Ahamed Barbhuiya, Mr. L. Hmar, Mr. Rajib Kurmi, Mr. Sanjib Bagdi and all other office staffs for their valuable help during my Ph. D. programme.

I am grateful to my labmates, Dewan Da, Ali Da, Hirak, Sudip and Dorothy for their unwavering support during my Ph. D. work. They were not only the people I worked with, but also my friends in need. I express my sincere thanks to all the Research Scholars (Golam Mohiuddin, Nazma Begum, Ram Krishna Laha, Shubhenjit Hazra, Barun Ghosh, Samiran Garain and Radah M. Laha) of the Department of Chemistry Assam University, Silchar for their constant help and support during my Ph. D. work.

I express my sincere thanks to all other Research Scholars of the Department of Chemistry, for their active co-operation and friendship that made me enjoyable during this research work.

I also thanks my all brothers (Hasibur Rahaman, Hafizur Rahaman and Hamidur Rahaman) and my six sisters, specially my elder sister Moniza Sultana and brother-in law Md. Barkatullah for inspiring and accompanying me throughout the tenure of my Ph. D. work.

I acknowledge Department of Chemistry, Assam University, Silchar, and funding agencies, DST, DBT and UGC, New Delhi for providing infrastructures and financial support.

At last but not the least, I acknowledge and express my heartiest regards to my father, Late Mr. Habibur Rahaman and mother, Late Mrs. Batula Bibi, for their constant affection, motivation, inspiration and help. Without them, I would not been the person what I am today. I would like to thank all my family members for their constant support, encouragements and eagerness throughout my career.

Hasimur Rahaman

TABLE OF CONTENTS

Applications in Electrocatalysis and Cytotoxicity Studies

Preface

The aim of this work is to exploit the unique physicochemical properties of manganese oxide and their composites molecules and other different semiconductor material near various sizes and shapes of metal nanostructures Metallic particles in the nanometer size regime display widely interesting size-dependent optical, electronic, magnetic, catalytic and chemical properties. With such applications on the horizon, new synthetic routes for quickly and reliably rendering magnetic nanoparticle surfaces have become an increasingly important focus. Different shape and size-selective change of physicochemical properties of manganese oxides and their composites. For this purpose, the present Ph. D. thesis entitled **"Synthesis, Characterization and Physicochemical Properties of Size and Shape-Selective Manganese Oxides and their Composites"** has been chosen. This thesis includes the synthesis of different manganese oxides (like Mn_3O_4, Mn_2O_3 and MnO) nanoparticles of various sizes and shapes (spherical, nanorods, microdendelions shape nanostructures), formation of noble metal-manganese oxide nanocomposites (like Au-Mn_3O_4, Ag-Mn_3O_4) and their photophysical properties based on catalysis (both organic and photocatalysis), electrocatalysis and selective sensing measurements and also formation of more interesting system such as dual metal oxides and triple semiconductor nanocomposites. Moreover, size selective manganese oxide nanoparticles-semiconductor assembly and their various physicochemical properties have been studied using microscopic (transmission electron microscopy, scanning electron microscopy) and spectroscopic (UV-visible spectroscopy, diffuse reflectance spectroscopy, Raman spectroscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, X-ray diffraction, and selected area electron diffraction) techniques. The complete work of the thesis has been divided into seven chapters

Chapter 1

This chapter describes the general introduction about the current literature related to the research work presented on manganese oxide nanomaterials, their composites and physicochemical properties of the nanostructures.

Chapter 2

This chapter presents a brief description about the chemicals and reagents used and various techniques and analytical instruments used for the characterisation for the synthesised manganese oxides and other related materials.

Chapter 3

This chapter describes the synthesis of different shape and size selective manganese oxide nanoparticles using soft-template strategy and synthesized materials used in photocatalysis and selective organic catalytic oxidations reactions. This chapter consists of two sub-sections:

Chapter 4

This chapter describes the synthesis of different shape and size selective gold-manganese oxides and silver-manganese nanocomposites using non-toxic binary solvents mixture as soft-template and synthesized materials used in electrocatalytic water oxidation/oxygen reduction reaction and in sensing of VOCs. This chapter consists of two sub-sections:

Chapter 5

This chapter includes the new types of metal oxides-manganese oxides di-oxides nanocomposites. Here we have synthesized iron oxide-manganese oxide (Fe_3O_4-Mn_3O_4 NCs) and nickel oxide-manganese oxide (NiO-Mn_3O_4 NCs) nanocomposites by facile hydrothermal treatment. This chapter consists of two sub-sections. In first section we have discussed the synthesized reduced magnetic material (Fe_3O_4-Mn_3O_4 NCs) are used biological applications and in the other we have discussed the most important part of this thesis, room-temperature, neutral pH water splitting by NiO-Mn_3O_4 NCs.

Chapter 6

In this chapter, a new type of nanocomposites have been synthesized using three different semiconductor materials in a unit system. Typical triple semiconductor nanocomposites here report for first time as best of our knowledge. Here we studied the photocatalysis application and band-gap tenability of synthesized MnO-ZnO-CdO triple semiconductor.

Chapter 7

The important outcomes of the completed research are summarized and the future scopes of the work are mentioned in this chapter.

List of Figures

List of Schemes

List of Tables

Abbreviations

AFM	Atomic Force Microscopy
aq	Aqueous
4-ATP	4 - Aminothiophenol
BET	Brunauer–Emmett–Teller
CV	Cyclicvoltametry
CdSe	Cadmium Selenide
dil	Dilute
DC	Direct Current
DF-STEM	Dark Field Scanning Tunneling Electron Micrograph
DLS	Dynamic light scattering
EDX	Energy Dispersive X-ray
FTIR	Fourier Transformed Infrared
HRTEM	High Resolution Transmission Electron Microscopy
LSV	Linear Sweep Voltammetry
mg	Miligram
mL	Mililiter
NCs	Nanocomposites / Nanoclusters
nm	Nanometer
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
PBS	Phosphate Buffer Saline
PXRD	Powder X-ray Diffractometer
QDs	Quantum Dots
SAED	Selected Area Electron diffraction
SEM	Scanning Electron Microscopy
SPR	Surface Plasmon Resonance
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscopy
UV-vis	Ultraviolet and visible
VSM	Vibrating-Sample Magnetometer
XRD	X-ray Diffractometer

Symbols

2D	two dimensional	3D	three dimensional
Å	angstrom	A_e	surface area of ellipsoidal tip-head
c	velocity of light	°C	celsius
cm	centimeter	C	concentration
E_g	band gap	eV	electron volt
E_{pc}	cathodic potentials	E_{pa}	anodic potentials
E_{ET}	energy transfer efficiency	E_F	Fermi energy level
ΔE_P	potential difference	ϵ_m	real dielectric of the medium
Φ	quantum yield	*fcc*	face-centered cubic
h	hour	hν	photon energy
i_{pa}	anodic peak current	i_{pc}	cathodic peak current
I_0	intensity of the exciting source beam	k	solvent interaction energy parameter
K	kelvin	k_T	energy transfer rate
kDa	kilodalton	kV	kilovolt
K_{SV}	Stern-Volmer constant	K_{cat}	catalytic rate constant
k_F	Fermi wave-vector	λ_{ex}	excitation wavelength
λ_{max}	maximum wavelength	λ_{abs}	maximum absorption wavelength
λ_{em}	maximum emission wavelength	M	molar
mM	millimolar	mL	milliliter
meV	millielectron volt	min	minutes
N	numbers of nanoparticles per milliliter	nm	nanometer
		nM	nanomolar
N_A	Avogadro’s number	η	refractive index
µM	micromolar	µA	microampere
µ	dipole moment	R	average radii of the particles