Synthesis and Characterization of Zinc Oxide Nanostructures

A thesis submitted in partial fulfilment of the requirements for the award of the degree of

Master of Technology

in

Nanoscience and Technology

By

Victor Kuno (2K12/NST/22)



Under the guidance of

Dr Mohan Singh Mehata Assistant Professor DTU, New Delhi Dr Amrish Panwar Assistant Professor DTU, New Delhi

Department of Applied Physics Delhi Technological University New Delhi-110042 July 2014

Certificate

This is to certify that the work entitled "Synthesis and Characterization of Zinc Oxide Nanostructures" is submitted in partial fulfillment of the requirements for the award of degree of Master of Technology in Nanoscience and Technology at the Department of Applied Physics, Delhi Technological University. It is further certified that no part of thesis has been submitted to any university for the award of any other degree.



Dr. Mohan Singh Mehata (Supervisor)	Signature:	Date:
Dr. Amrish Panwar (Co-Supervisor)	Signature:	Date:
Prof. S.C. Sharma (Head of Dept)	Signature:	Date:

Abstract

Zinc oxide nanostructures were synthesized by a wet chemical route using precursors zinc acetate dihydrate and potassium hydroxide and capping agents ethylene glycol (EG) and ethylenediamine (EDA) in ethanol/water solvents. The nanostructures consist of nanoparticles, nanorods and nanoflowers. Structural and morphological characterization of the nanostructures was performed using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The optical properties of the synthesized nanostructures were also investigated using UV/Vis and Photoluminescence (PL) spectroscopy. Results show that the nanoparticles calcinated at 450°C deagglomerate when recalcinated at a higher temperature and the particle shape becomes spherical. The hexagonal wurtzite structure as confirmed by the XRD patterns is unchanged after the sample is recalcinated. Defects-related states are also eliminated at a higher temperature of 750°C and UV emission is observed at 359nm. The nanorods synthesized using EDA at 450°C are short with a length of around 300nm and results reveal that increasing the calcination temperature to 600°C reduces the aspect ratio. PL spectrum results show the existence of two bands, UV emission due to free excitonic recombination and blue emission due to defect states. The ZnO nanoflowers synthesized using EDA with a growth time of 6hrs consist of self-assembled bullet-shaped nanorods. The absorption spectrum shows a peak at 264nm due to the quantum confinement effect and the PL spectrum exhibits near-band edge emission at 360nm and the defectrelated band at 430nm.

Acknowledgement

I would like to express my deepest gratitude to my project supervisor Dr Mohan S Mehata, Assistant Professor, Laser-Spectroscopy Lab, DTU, New Delhi for his indispensible guidance, valuable discussions, constant support and encouragement throughout my project research and development. My supervisor has been a great source of inspiration and the many things I have learnt from him will continue to guide me further in my academic and research career.

I would like also to extend my special thanks to my co-supervisor Dr Amrish Panwar for his great support in fulfilling many requirements of this work. Great thanks also to the other Applied Physics faculty members whose mentor will positively affect me in my academic and research career. And with great pleasure to also specifically mention Mr Sandeep Mishra for the SEM and XRD measurements.

My special thanks also go to the PhD scholars in the Laser-Spectroscopy Lab, DTU, the likes of Sir. Ratnesh, Ms. Sangeeta, Miss. Nisha for their technical support in UV/Vis and PL measurements and I would also want to thank the PhD scholars in other research labs and departments the likes of Miss. Lucky, Mr. Vinay, Mr Amity.

I would like also to thank my classmates the likes of Rishibrind, Aparajita, Preeti, Rohan, Nikita and the others for creating an enjoyable learning environment.

Special thanks also to my wife, Mai Tatenda, and to my parents, relatives and friends for their encouragement and great love during my project work.

And last but not least, I would like to thank the Lord God Almighty, the Creator of all mankind for His unfailing love and unmerited favor and has been my source of inspiration

Victor Kuno 2K12/NST/22

Table of Contents

CHAPTER 1: INTRODUCTION

1.1	Background and Motivation	1
1.2	ZnO Crystal Structure	2
1.3	ZnO Physical Parameters	3
1.4	Electronic Band Structure	3
1.5	Review of Related Work	5
1.6	Applications	10
1.7	Aims and Objectives	12

CHAPTER 2: EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

2.1	The Sol-Gel process	13
2.2	Characterization Techniques	16
2.2.1	Structural and Morphological Characterization	16
2.2.1.1	X-Ray Diffraction (XRD)	16
2.2.1.2	Scanning Electron Microscope (SEM)	
2.2.2	Optical Characterization	
2.2.2.1	UV/Vis spectroscopy	21
2.2.2.2	Photoluminescence (PL) spectroscopy	
	References	27

CHAPTER 3: STUDY ON THE EFFECT OF RECALCINATION AT A HIGHER TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZnO NANOPARTICES

3.1	Introduction	32
3.2	Experimental Procedure	33
3.3	Results and Discussion	34

3.4	Conclusion	.39
	References	.40

CHAPTER 4: TEMPERATURE DEPENDENCE GROWTH OF ZnO NANOCAPSULES USING DIRECTIONAL AGENT EDA

4.1	Introduction	43
4.2	Experimental Procedure	44
4.3	Results and Discussion	45
4.4	Conclusion	48
	References	49

CHAPTER 5: GROWTH OF SELF-ASSEMBLED ZnO NANOFLOWERS BY THE SOL-GEL PROCESS

5.1	Introduction	
5.2	Experimental Procedure	
5.3	Results and Discussion	54
5.4	Conclusion	
	References	

List of Figures

Figure 1.1. ZnO crystal structures	2
Figure 1.2. ZnO band diagram	4
Figure 1.3. The effect of high pressure deagglomeration on TiO ₂ particles	5
Figure 1.4. FESEM diagram of the synthesized nanorods by S.K.Patra [13]	6
Figure 1.5. SEM images of ZnO nanoflowers by Chakraborty et al [17]	8
Figure 1.6. Schematics of nanorods growth with increasing temperature	9
Figure 2.1. Simplified sol-gel downstream processes	13
Figure 2.2. Schematic representation of the different routes of the sol-gel technology	14
Figure 2.3. X-Ray Diffraction in accordance with Bragg's law	17
Figure 2.4. Bruker D8 ADVANCE X-Ray Diffractometer at DTU	18
Figure 2.5. Schematic diagram of the SEM	19
Figure 2.6. Different types of particles emitted in an SEM	20
Figure 2.7. HITACHI S-3700N SEM at DTU	21
Figure 2.8. Schematic diagram of the UV/Vis spectrophotometer	22
Figure 2.9. PerkinElmer Lambda 750 UV/Vis/NIR spectrophotometer at DTU	24
Figure 2.10. Typical experimental set-up for PL measurements	25
Figure 2.11. HORIBA Jobin Yvon Fluorolog 3 (FL3-22) spectrofluorometer at DTU	26
Figure 3.1. Flowchart of the zinc oxide nanoparticles synthesis process	34
Figure 3.2. XRD spectra of zinc oxide nanoparticles calcinated at 450°C	.34
Figure 3.3. XRD spectra of zinc oxide nanoparticles recalcinated at 750°C	.35
Figure 3.4. SEM images of zinc oxide nanoparticles calcinated at 450°C	.36
Figure 3.5. SEM images of zinc oxide nanoparticles recalcinated at 750°C	.36
Figure 3.6. Absorption spectra of the zinc oxide nanoparticles	.37

Figure 3.7. Fluorescence spectra of the zinc oxide nanoparticles at $\lambda_{exc} = 320$ nm
Figure 4.1. Flowchart of the zinc oxide nanocapsules synthesis process
Figure 4.2. SEM images of the zinc oxide nanocapsules synthesized at 450°C45
Figure 4.3. SEM images of the zinc oxide nanocapsules synthesized at 600°C46
Figure 4.4. EDX spectra of the zinc oxide nanocapsules synthesized at 450°C46
Figure 4.5. Absorption spectra of zinc oxide nanocapsules
Figure 4.6. PL spectra of the zinc oxide nanocapsules at $\lambda_{exc} = 320$ nm
Figure 5.1. Flowchart of the zinc oxide nanoflowers synthesis process
Figure 5.2. SEM images of the zinc oxide nanoflowers
Figure 5.3. XRD of the zinc oxide nanoflowers
Figure 5.4. EDX spectra of the zinc oxide nanoflowers
Figure 5.5. Absorption spectra of the synthesized zinc oxide nanoflowers
Figure 5.6. PL spectra of the zinc oxide nanoflowers at $\lambda_{exc} = 320$ nm

List of Tables

Table 1.1. ZnO physical parameters	3
Table 1.2. Information of the synthetic conditions and ZnO particles obtained	7
Table 3.1. Summary of comparison of the properties.	38