



***STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF
(ZnO)_X (ZrO₂)_{1-X} NANOCOMPOSITES PREPARED BY THERMAL
TREATMENT METHOD***

HAMIDU ISHAKU MIDALA

FS 2020 18



**STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF
(ZnO)_x (ZrO₂)_{1-x} NANOCOMPOSITES PREPARED BY THERMAL
TREATMENT METHOD**

By

HAMIDU ISHAKU MIDALA

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Master of Science**

March 2020

COPYRIGHT

All material contained within the thesis, including without limitation text, logos, icons, photographs, and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



DEDICATION

I dedicated this work to my family

LATE HAMIDU YERIMA

LATE AMINA HAMIDU

AHMED HAMIDU

AISHA ADAMU

AMINA ISHAKU

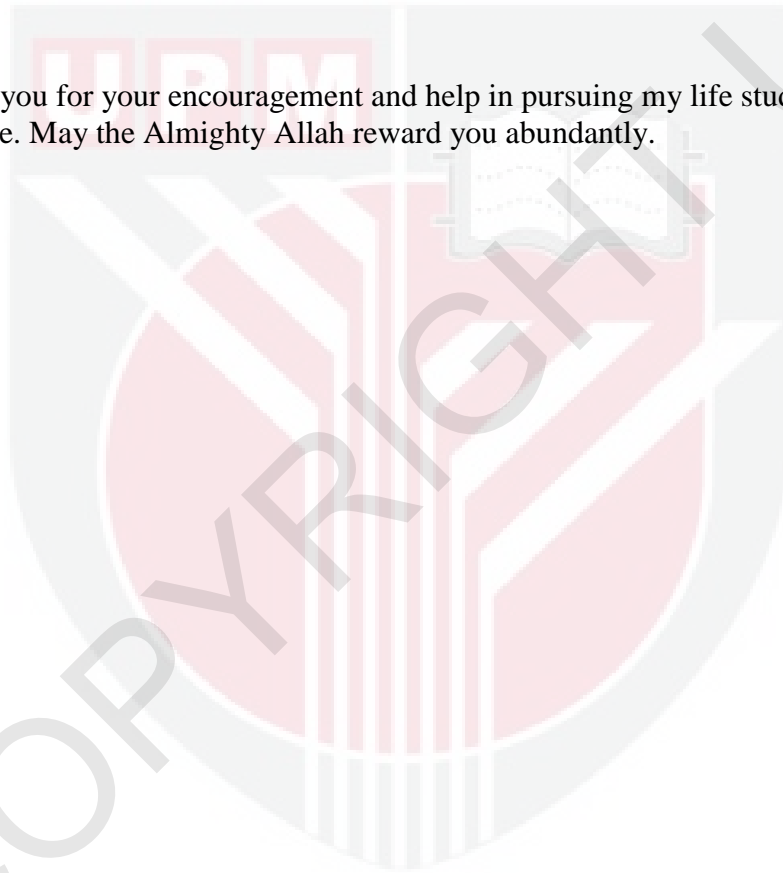
ABDULHAMEED ISHAKU

ZAINAB ISHAKU

FATIMA ISHAKU

AHMED ISHAKU

Thank you for your encouragement and help in pursuing my life studies and struggle. May the Almighty Allah reward you abundantly.



© COPYRIGHT

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

**STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF
(ZnO)_x (ZrO₂)_{1-x} NANOCOMPOSITES PREPARED BY THERMAL
TREATMENT METHOD**

By

HAMIDU ISHAKU MIDALA

March 2020

Chairman : Professor Halimah binti Mohamed Kamari, PhD
Faculty : Science

The purpose of this study was to investigate the constituents of nanomaterial that was made from zinc nitrate, zirconia nitrate and polyvinyl pyrrolidone, which is assumed as classification of novel materials. The unique product obtained through the thermal treatment process containing the zinc oxide and zirconia oxide nanocomposites as well as organic polymer. This product possesses better characteristics as compared to their nano-sizes. So, the binary oxide of the nanocomposite (Zinc oxide (ZnO))_x (Zirconia oxide (ZrO₂))_{1-x} at constant concentration of 4g polyvinylpyrrolidone (PVP) was calcined at various temperature that was produced with thermal treatment process. Zinc and Zirconium nitrates as well as PVP (capping agent) was used to produce nanocomposite materials (ZnO)_x(ZrO₂)_{1-x} s for x = 0.2, 0.5, and 0.8 molarity. To ensure the best yield, the characterization has been performed. Thermal analysis (TGA), gave the optimization of the thermal treatment technique and show the appropriate temperature to carry out the calcination process. The crystallinity of the sample was measured by using X – ray diffraction (XRD). Fourier transform infra-red (FTIR) spectroscopy analysis proved that ZnO and ZrO₂ were the original compounds for the prepared nanocomposite (ZnO)_x (ZrO₂)_{1-x}. However, the morphological characterization was determined via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and were supported by XRD results. It showed the increment of the average sample sizes from 21 – 40 nm due to the increment of calcination temperature. Ultraviolet visible spectroscopy (UV-Vis) determine the gap of optical path and decreased the values for both nanocomposite ZnO and ZrO₂. Photoluminescence (PL) displayed the increment of intensity when the particle size was increased. The study also showed the application of optical in the binary particle application with the wider nano size (ZnO)_x (ZrO₂)_{1-x} as a novel functional material. The varying calcination temperature has control over the (ZnO)_x (ZrO₂)_{1-x} particle sizes by the permission of this method, so the generation of semiconductor materials with multiple band gap is possible. Detailed wavelengths of solar energy can be captured by these materials, which can be an appropriate choice for employment of solar cell applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**SIFAT STRUKTUR, MORFOLOGI DAN OPTIK $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$
NANOKOMPOSIT YANG DISEDIAKAN DENGAN KAEDAH RAWATAN
TERMA**

Oleh

HAMIDU ISHAKU MIDALA

Mac 2020

Pengerusi : Profesor Halimah binti Mohamed Kamari, PhD
Fakulti : Sains

Kajian ini bertujuan untuk menyiasat jujuk bahan nano yang dianggap terdiri daripada zink nitrat, zirkonia nitrat dan polivinilpyrrolidon, yang dianggap sebagai klasifikasi bahan baru. Produk unik diperoleh melalui proses rawatan terma yang mengandungi nanokomposit zink oksida dan zirkonia oksida dan juga polimer organik. Produk ini mempunyai ciri-ciri yang lebih baik berbanding dengan saiz nano mereka. Oleh itu, oksida binari nanokomposit (Zink oksida $(\text{ZnO})_x$ (Zirkonia oksida ZrO_2)) $_{1-x}$ pada kepekatan malar polivinilpyrrolidone (PVP) 4g, dikalsinasi pada pelbagai suhu dihasilkan dengan cara proses rawatan terma. Zink dan Zirkonium nitrat, dengan PVP (ejen perlindungan) digunakan untuk menghasilkan bahan nanokomposit $(\text{ZnO})_x(\text{ZrO}_2)_{1-x}$ untuk $x = 0.2, 0.5,$ dan 0.8 mol. Untuk memastikan hasil yang berjaya, pencirian berikut telah dilakukan. Analisis terma (TGA) memberikan pengoptimalan teknik rawatan terma dan menunjukkan suhu yang sesuai di mana proses kalsinasi perlu dilakukan. Kehabluran sampel diukur menggunakan Belauan sinar-X (XRD). Analisis fasa spektrum FTIR mengesahkan ZnO dan ZrO_2 adalah sebatian asal bagi nanokomposit $(\text{ZnO})_x(\text{ZrO}_2)_{1-x}$ yang disediakan. Walaupun, ciri-ciri morfologi telah ditentukan dengan menggunakan Mikroskopi Pengimbasan Elektron (SEM), Transmisi Elektron Mikroskopi (TEM) yang disokong oleh keputusan XRD menunjukkan peningkatan saiz purata sampel dari 21 - 40 nm disebabkan kenaikan suhu kalsinasi. Spektrum reflektif resap UV-Vis menentukan jurang jalur optik dan didapati penurunan nilai bagi kedua-dua nanokomposit ZnO dan ZrO_2 . Spektrum foto pendarchaya (PL) menunjukkan peningkatan keamatan apabila saiz zarah meningkat. Penyelidikan ini juga melihat aplikasi optik di kalangan aplikasi binari zarah bersaiz nano $(\text{ZnO})_x(\text{ZrO}_2)_{1-x}$ yang luas sebagai bahan berfungsi baru. Suhu kalsinasi yang berbeza-beza mempunyai kawalan terhadap ukuran zarah $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ dengan menggunakan kaedah ini, maka dengan ini mungkin penghasilan bahan semikonduktor dengan jurang berbilang jalur dapat terjadi. Panjang gelombang tenaga suria yang terperinci dapat ditangkap oleh bahan-bahan ini, aplikasi sel suria menjadi pilihan yang tepat untuk digunakan.

ACKNOWLEDGEMENTS

First of all, my sincere gratitude and praise goes to Almighty Allah S.W.T for having given me courage, patience, strength and maturity to write this thesis.

My heartfelt appreciation and unique thanks go to my supervisor, Professor Dr. Halimah Mohammad Kamari for her tremendous assistance, generous advice, invaluable guidance, encouragement, moral support and collaboration during my study period. I would like to extend to my co-supervisor, Dr. Chan Kan Tim, my sincere appreciation for his advice. Also, I would like to express my deep appreciation to Dr. Naif Al – Hada for his moral support, guidance and help during my studies and thesis.

Nevertheless, my unique thanks go to my family for supporting the complexion of this study, my colleagues in particular Mrs Suzliana and my friends Waziri Ibrahim, Hayatu Sa'ad, Abdulhameed Boderel, Musa Umar who contributed directly or indirectly to the achievement of this study, all the staff of the department of physics and the graduate school for their cooperation and lastly, Tet fund for the financial support rendered.

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software

Signature: _____

Date: _____

Name and Matric No.: Hamidu Ishaku Midala, GS51564

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature: _____

Name of Chairman
of Supervisory
Committee:

Professor Dr. Halimah binti Mohamed Kamari

Signature: _____

Name of Member
of Supervisory
Committee:

Dr. Chan Kar Tim

TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	ii
ACKNOWLEDGEMENTS	iii
APPROVAL	iv
DECLARATION	vi
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xv
CHAPTER	
1 INTRODUCTION	1
1.1 General Introduction	1
1.2 Statement of the problem	3
1.3 Significant of the Study	3
1.4 Objectives of the study	4
1.5 Thesis outline	4
2 LITERATURE REVIEW	5
2.1 General introduction on metal and binary oxide nanomaterials	5
2.2 Metal Oxide Nanostructures	6
2.3 Methods for synthesis of ZrO ₂ and ZnO Nanoparticles.	7
2.3.1 Hydrothermal method	8
2.3.2 Sol-Gel Method	8
2.3.3 Micro emulsion Method	9
2.3.4 Electrochemical Method	9
2.3.5 Sonochemical Method	10
2.3.6 Chemical Vapor Deposition	10
2.3.7 Spray Pyrolysis Deposition	11
2.3.8 Solvothermal Method	11
2.3.9 Thermal treatment Method	12
2.4 Composites	14
2.4.1 Nanocomposite	14
2.5 Application of ZnO and ZrO ₂ Nanoparticles	16
2.5.1 Zinc Oxide (ZnO) Nanoparticles Applications	16
2.5.2 Zirconium Oxide (ZrO ₂) Nanoparticles Applications:	16
2.6 Metal nanoparticles	17
2.7 Zinc oxide (ZnO) nanoparticle	18
2.8 Zirconia oxide (ZrO ₂) nanoparticle	19
2.9 Hexagonal and tetragonal crystal structures of ZnO/ZrO ₂	20
2.9.1 Zinc Oxide (ZnO)	20
2.9.2 Zirconia Oxide (ZrO ₂)	20
2.10 Optical Properties of Metal Oxide nanomaterials	21
2.11 TGA results for PVP, Zinc and Zirconia nitrates	22

2.12	Tetragonal crystal system	23
3	THEORY	24
3.1	Optical properties of semiconductors	24
3.1.1	Introduction to energy bands	24
3.1.2	Energy band formation	25
3.1.3	Fundamental absorption edge	25
3.1.4	Direct and indirect band gap semiconductor materials	26
3.1.5	Excitonic absorption	27
3.1.6	Density of states and dimensions of material	28
3.1.7	Fermi energy level in semiconductor	30
3.2	Optical emission	33
3.2.1	Generation of electron-hole pairs	33
3.2.2	Recombination mechanism in semiconductor	33
3.2.2.1	Intrinsic recombination	33
3.2.2.2	Radiative band-band recombination	33
3.2.2.3	Extrinsic recombination mechanism	34
4	METHODOLOGY	36
4.1	Introduction	36
4.2	Materials	36
4.3	Nanocomposites Sample Preparation	36
4.4	Sample Characterization	37
4.4.1	Thermogravimetric Analysis / Derivative (TGA / DTG)	38
4.4.2	X-ray Diffraction (XRD)	39
4.4.3	Fourier Transform Infrared (FTIR)	41
4.4.4	Scanning Electron Microscopy (SEM)	43
4.4.5	Transmission Electron Microscopy (TEM)	45
4.4.6	Ultra Violet Visible Spectrophotometer (UV- vis)	46
4.4.7	Photoluminescence (PL)	47
4.4.8	Calculation of crystalline size using XRD	49
5	RESULTS AND DISCUSSION	50
5.1	Thermal based in aqueous metal /polymer solution	50
5.1.1	Formation of metal nanocomposites	50
5.2	TGA - DTG measurements for metal salts with PVP	51
5.3	X- Ray diffraction patterns for ZnO, ZrO ₂ nanocomposites	54
5.4	Microstructures of Nanocomposites using TEM	58
5.5	SEM micrographs of ZnO and ZrO ₂ nanocomposites	62
5.6	FTIR analysis of ZnO/ZrO ₂ nanocomposites and PVP	65
5.7	Reflectance spectrum of binary oxide (ZnO) _x (ZrO ₂) _{1-x} by UV – Vis	69
5.8	PL measurements of binary (ZnO) _x (ZrO ₂) _{1-x} nanocomposites	74
5.9	Energy band gap for ZnO and ZrO ₂	76
5.9.1	Energy band gap of (ZnO)	76
5.9.2	Energy band gap of (ZrO ₂)	77

5.9.3	Optical properties of $(\text{ZnO})_x(\text{ZrO}_2)_{1-x}$	77
5.10	Formation mechanism of binary $(\text{ZnO})_x(\text{ZrO}_2)_{1-x}$ nanocomposites	78
6	CONCLUSION AND FUTURE WORKS	79
6.1	Conclusion	79
6.2	Recommendations for future works	80
	REFERENCES	81
	APPENDICES	97
	BIODATA OF STUDENT	101
	PUBLICATION	102



© COPYRIGHT UPM

LIST OF TABLES

Table		Page
5.1	The percentage weight loss of sample 1, 2, and 3	54
5.2	Peaks for $(\text{ZnO})_{0.2} (\text{ZrO}_2)_{0.8}$	56
5.3	Peaks for $(\text{ZnO})_{0.5} (\text{ZrO}_2)_{0.5}$	57
5.4	Peaks for $(\text{ZnO})_{0.8} (\text{ZrO}_2)_{0.2}$	57
5.5	Calcination temperature and crystallite size (XRD)	58
5.6	Shows XRD and TEM results for products of the three samples at various temperatures of calcination	62
5.7	FTIR assignment of vibration mode for $(\text{ZnO})_{0.2} (\text{ZrO}_2)_{0.8}$ nanoparticles	66
5.8	FTIR assignment of vibration mode for $(\text{ZnO})_{0.5} (\text{ZrO}_2)_{0.5}$ nanocomposites	67
5.9	FTIR assignment of vibration mode for $(\text{ZnO})_{0.8} (\text{ZrO}_2)_{0.2}$	69
5.10	Energy band gap of $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ nanocomposites obtained at various calcination temperature	73
5.11	Energy band gaps of (ZnO) at various calcination temperatures	77
5.12	Energy band gaps of (ZrO_2) at various calcination temperatures	77

LIST OF FIGURES

Figure	Page	
2.1	The Wurtzite cryatal structure of zinc oxide	18
2.2	The Monoclinic structure of ZrO_2	19
2.3	ZnO hexagonal crystal structure	20
2.4	Tetragonal structure model of ZrO_2	21
2.5	Thermal degradation steps for PVP, PVA, and blend	22
2.6	TGA/DSC curves of zinc nitrate hexahydrate	22
2.7	TGA/DSC curves of zirconia YSZ burned gel	23
2.8	Body -centered tetragonal crystal structure	23
3.1	Illustration of the formation of energy bands in a Si crystal	24
3.2	(a) direct band gap semiconductor (b) indirect band gap semiconductor	26
3.3	Schematic illustration of excitonic bands for $n = 1$ and $n = 2$ in semiconductors. E_g represents the energy gap	28
3.4	The diagrams of density of states and the system dimension	30
3.5	Fermi-Dirac distribution function at $T = 0$ K and at two $T > 0$ K	31
3.6	Schematic diagram of intrinsic recombination mechanism: (a) radiative band-band recombination (b) Auger band – band recombination	34
4.1	Flow chart of the synthesis of metal oxide nanocomposites by thermal treatment method	37
4.2	Simplified representation of the TGA instrument	39
4.3	Schematic diagram of a diffractometer	40
4.4	Simplified representation of FTIR	42
4.5	Simplified representation of SEM	44
4.6	Simplified representation of TEM	45
4.7	Schematic diagram of UV-Visible Spectrophotometer	47

4.8	Simplified representation of PL measurements	48
5.1	The propose nanocomposite growth mechanism	51
5.2	Thermogravimetric analysis and thermogravimetric derivative (DTG) curves at 10 °C min ⁻¹ heating rates sample 1	52
5.3	Thermogravimetric analysis (TGA) and thermogravimetric derivative (DTG) curves a heating rate of 10 °C min ⁻¹ sample 2	53
5.4	Thermogravimetric analysis (TGA) and thermogravimetric derivative (DTG) curves at a heating rate of 10 °C min ⁻¹ sample 3	53
5.5	XRD results of binary (ZnO) _{0.2} (ZrO ₂) _{0.8} nanocomposites at (a) room temperature 30 °C and calcined at (b) 500 °C (c) 600 °C (d) 700 °C and (e) 800 °C	55
5.6	XRD results of binary (ZnO) _{0.5} (ZrO ₂) _{0.5} nanocomposites at (a) room temperature 30 °C and calcined at (b) 500 °C (c) 600 °C (d) 700 °C and (e) 800 °C	56
5.7	XRD results of binary ZnO) _{0.8} (ZrO ₂) _{0.2} nanocomposites at (a) room temperature 30 °C and calcined at (b) 500 °C (c)600 °C (d)700 °C and (e) 800 °C	57
5.8	TEM results for (ZnO) _{0.2} (ZrO ₂) _{0.8} nanocomposites and particle size distribution at calcination temperatures of (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C respectively	59
5.9	TEM results for (ZnO) _{0.5} (ZrO ₂) _{0.5} nanocomposites and particle size distribution at calcination temperatures of (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C respectively	60
5.10	TEM results for (ZnO) _{0.8} (ZrO ₂) _{0.2} nanocomposites and particle size distribution at calcination temperatures of (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C respectively	61
5.11	SEM results of (ZnO) _{0.2} (ZrO ₂) _{0.8} with calcination temperature at (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C respectively	63
5.12	SEM results of (ZnO) _{0.5} (ZrO ₂) _{0.5} with calcination temperature at (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C respectively	63
5.13	SEM results of (ZnO) _{0.8} (ZrO ₂) _{0.2} with calcination temperature at (a) 500 °C (b) 600 °C (c) 700 °C and (d) 800 °C respectively	64
5.14	Dispersive energy x-ray spectrum (EDX) for sample 1 nanocomposites calcined at 600 °C	64

5.15	FTIR spectra of $(\text{ZnO})_{0.2}(\text{ZrO}_2)_{0.8}$ nanocomposites in the scope of $280 - 4000 \text{ cm}^{-1}$ at (a) $30 \text{ }^\circ\text{C}$, (b) $500 \text{ }^\circ\text{C}$, (c) $600 \text{ }^\circ\text{C}$, (d) $700 \text{ }^\circ\text{C}$, and (e) $800 \text{ }^\circ\text{C}$ respectively	66
5.16	FTIR spectra of $(\text{ZnO})_{0.5}(\text{ZrO}_2)_{0.5}$ nanocomposites in the scope $280 - 4000 \text{ cm}^{-1}$ at (a) $30 \text{ }^\circ\text{C}$, (b) $500 \text{ }^\circ\text{C}$, (c) $600 \text{ }^\circ\text{C}$, (d) $700 \text{ }^\circ\text{C}$ and (e) $800 \text{ }^\circ\text{C}$ respectively	67
5.17	FTIR spectra of $(\text{ZnO})_{0.8}(\text{ZrO}_2)_{0.2}$ nanocomposites in the scope of $280 - 4000 \text{ cm}^{-1}$ at (a) $30 \text{ }^\circ\text{C}$, (b) $500 \text{ }^\circ\text{C}$, (c) $600 \text{ }^\circ\text{C}$, (d) $700 \text{ }^\circ\text{C}$, and (e) $800 \text{ }^\circ\text{C}$ respectively	68
5.18	Graph of reflectance versus wavelength of $(\text{ZnO})_{0.2}(\text{ZrO}_2)_{0.8}$ nanocomposites calcined at various temperatures $500 \text{ }^\circ\text{C}$, $600 \text{ }^\circ\text{C}$, $700 \text{ }^\circ\text{C}$ and $800 \text{ }^\circ\text{C}$	70
5.19	The energy band gap of binary $(\text{ZnO})_{0.2}(\text{ZrO}_2)_{0.8}$ nanocomposites at calcination temperatures of (a) $500 \text{ }^\circ\text{C}$, (b) $600 \text{ }^\circ\text{C}$, (c) $700 \text{ }^\circ\text{C}$ and (d) $800 \text{ }^\circ\text{C}$ respectively	71
5.20	The energy band gap of binary $(\text{ZnO})_{0.5}(\text{ZrO}_2)_{0.5}$ nanocomposites at calcination temperatures of (a) $500 \text{ }^\circ\text{C}$, (b) $600 \text{ }^\circ\text{C}$, (c) $700 \text{ }^\circ\text{C}$ and (d) $800 \text{ }^\circ\text{C}$ respectively	72
5.21	The energy band gap of binary $(\text{ZnO})_{0.8}(\text{ZrO}_2)_{0.2}$ nanocomposites at calcination temperatures of (a) $500 \text{ }^\circ\text{C}$, (b) $600 \text{ }^\circ\text{C}$, (c) $700 \text{ }^\circ\text{C}$ and (d) $800 \text{ }^\circ\text{C}$ respectively	73
5.22	PL spectra of $(\text{ZnO})_{0.2}(\text{ZrO}_2)_{0.8}$ nanocomposites calcinated at different temperatures: (a) $500 \text{ }^\circ\text{C}$ (b) $600 \text{ }^\circ\text{C}$ (c) $700 \text{ }^\circ\text{C}$ and (d) $800 \text{ }^\circ\text{C}$ respectively	74
5.23	PL spectra of $(\text{ZnO})_{0.5}(\text{ZrO}_2)_{0.5}$ nanocomposites calcinated at different temperatures: (a) $500 \text{ }^\circ\text{C}$ (b) $600 \text{ }^\circ\text{C}$ (c) $700 \text{ }^\circ\text{C}$ and (d) $800 \text{ }^\circ\text{C}$ respectively	75
5.24	PL spectra of $(\text{ZnO})_{0.8}(\text{ZrO}_2)_{0.2}$ nanocomposites calcinated at different temperatures: (a) $500 \text{ }^\circ\text{C}$ (b) $600 \text{ }^\circ\text{C}$ (c) $700 \text{ }^\circ\text{C}$ and (d) $800 \text{ }^\circ\text{C}$ respectively	76
5.25	A proposed mechanism of the interaction of the metallic ions and PVP for $(\text{ZnO})_x(\text{ZrO}_2)_{1-x}$ nanocomposites	78

LIST OF ABBREVIATIONS

ZnO	Zinc Oxide
ZrO ₂	Zirconia Oxide
NPs	Nanoparticles
PVP	Polyvinyl Pyrrolidone
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetric
XRD	X- Ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform infrared
UV – Vis	Ultraviolet Visible
PL	Photoluminescence
HMT	Hexamethylenetetramine
CVD	Chemical Vapor Deposition
ITO	Indium Tin Oxide
UVA	Ultraviolet A
UVB	Ultraviolet B
CTAB	Cetyltrimethylammonium bromide
FTO	Fat mass and obesity
ITO	Indium tin oxide
MOFs	Metal organic frameworks
K or P	Momentum
hkl	Denotes a plane that intercepts the three points a_1/h , a_2/k and a_3/l
FWHM	Full-width at half maximum
KM	Kubelka-Munk
nm	Nanometer
λ	Wavelength
λ_{max}	maximum absorbance wavelength
a	Lattice parameter
°C	Degree Celsius
θ	Bragg

CHAPTER 1

INTRODUCTION

1.1 General Introduction

An advancing field of science that study particles of nanoscale ranging from (0 -100 nm) materials with very tiny sizes is referred to Nanoscience. It is a Greek term, Nano mixture, from the Greek "Nanos" (or Latin "Nanos") meaning "Dwarf" and the significance of wisdom is the term "science." Indeed, it is an interdisciplinary field that seeks to bring about mature technology that focuses on the junction of areas such as physics, chemistry, biology, engineering and computer science. Nanoscience is the study of phenomena on a nanoscale or could be anything which has a measurement less than 100 nm (Ali, 2015). The terms, science and technology have to do with a nanoscale nature, meaning the understanding and restrained manipulation of nanoscale-dimensional structures and phenomena.

Nevertheless, it can be said that it is a revolutionized way of creating materials and products aimed to exploit their functionalities and hence producing things that are lighter, smaller and stronger. Scientists and engineers are therefore very interested in this increasing sector. To that end, expect innovative transformations from this rapidly growing field years ahead. A significant aspect of nanoscience is the determination of nanomaterial physical characteristics such as colour, optical, electrical and magnetic behaviour. Nowadays, many technological applications of nanomaterials are produced in the fields of optics, optoelectronics and photonics.

Research linked to the nanoparticle's region is on the increase as the result of nanoscale size, different from the bulk sample. This aspect of nanoparticles made the industrial and commercial applications interesting because of its distinctive property; uncommon absorptive characteristics, wide surface area, defects, and rapid diffusivity. Hence promotes scientists to investigate these characteristics from different fields and areas (Kamari et al., 2017). As a consequence, many methods have enabled modern structures, nanoplatforms, systems, or gadgets used in various applications and areas (Varughese et al., 2014; Zhang et al., 2017). This made it possible to study its significance for application in biodegradable, biocompatible and as functioned material (Kamari et al., 2017; Varughese et al., 2014). The use of hexagonal ZnO and monoclinic ZrO₂ semiconductor nanomaterials is one of the main problems perceived independently or compositionally by many research studies because of the unmatched properties. Hexagonal ZnO is part of the group II-VI composites of the metallic chemical element zinc (II) and non-metallic chemical element oxygen (VI). This showed the accessibility of the remarkable features of many ZnO semiconductor materials and endorsed many applications due to the advantage of hexagonal crystal structure. A n-type semiconductor with range of 2.16 - 3.19 eV direct band gaps is grouped into the framework regarded as the normal hexagonal shape (Varughese et al., 2014). Such properties will benefit from the unique characteristics of ZnO

nanomaterials obtained in a recognizable manner and nanoscale particle measurements for application and experimental use (Zhang et al., 2017).

ZrO₂ (Zirconia) is a sample of good natural color, high strength, resilience to transformation, high strength to corrosion, chemical and microbial tolerance, and high chemical stability. The characteristics that qualified it as a useful catalyst include: increased ability to exchange ions and redox operations, as well as wide band gap p – type semiconductor form with abundant oxygen vacancies (Singh and Nakate, 2014). ZrO₂ is used as a transistor insulator for future non- electrical (Kremer, 1996). Nicollian and Brews, (1982) identified the potential for replacing silicon oxide (SiO₂) in advance metal oxide semiconductor (MOS) devices and optical applications because of its dielectric property. Recognition has been acquired for the implementation of ZrO₂ nanoparticles in powerful oxide, fuel cells (Seungdoo Park, 2000), sensor nitrogen oxide and oxygen gas (Subbarao and Maiti, 1988). For instance, in a scheme with elevated temperature power conversion frameworks, engineering and medicine appreciated for its elevated oxygen particle transport capacity and long-turn stability, it can also be used.

Zirconia oxide (ZrO₂) exist as namely cubic(c-ZrO₂), monoclinic (m-ZrO₂) and tetragonal (t-ZrO₂), at ordinary atmospheric and diverse temperatures (Madfa et al., 2014; Channu et al; 2011). The m-ZrO₂ is stable up to 1100 °C, t-ZrO₂ and the cubic phase is above 2370 °C (Tan et al., 2011). Some reported techniques for synthesising zirconia nanoparticles such as sol/gel method were carried by (Kul'met'eva et al; 2009), vapor phase method (Heshmatpour and Aghakhanpour, 2011), pyrolysis (Moravec et al., 2017), spray pyrolysis (Baqer et al., 2017) hydrolysis (Adamski et al., 2006), hydrothermal (Espinoza-González et al., 2011) and microwave pals (Tada and Iwasawa, 2003). These method, however, have some setback characteristics which include complicated procedures, longer reaction time, high reaction temperature, toxic reagents, high production costs and product use.

These set-backs do not encourage synthesis of zirconia NPs on a large scale. Nevertheless, supplementary features anticipated from ZnO – ZrO₂ composite have many optical properties in oxide semiconductors that have the potential to exhibit separate structure compared to their bulk aspects of semiconductor parts (Scholz, 2017; Salem et al., 2017).

Synthesis of industrial scale ZnO – ZrO₂ nano powder using the following techniques; heavy weight solution (Kolodziejczak-Radzimska and Jesionowski, 2014), sol – gel method (Sahoo et al., 2012; heat decomposition (Kakhaki et al., 2015), solvothermal method (Division, 1985), and heat evaporation (Karim et al., 2009). For instance, faced constraints owing to the difficulty of the synthesis method, lengthy reaction period, toxic reagents, elevated temperature, and product manufacturing outflow. None of these techniques in binary or powder form produced the material.

Through thermal treatment process, these aforementioned disadvantages can be overcome by concentrating on synthesis of thermal treatment process to yield no parallel waste $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ samples. Indeed, the highlights are going to be attractive for various mechanical-scale jobs. According to these highlights, it showed that no hazardous or ecologically harmful side-effects are produced by the current approach. In this thesis, a parallel approach that produces $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ nano powder primarily and exclusively is discussed. The prepared technique used heat-treatment synthesis therapy to harmonize $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ and to study its impact on morphological, fundamental and optical characteristics. Heat treatment method used a solution with metallic nitrate particles as a background and Polyvinylpyrrolidone (PVP) as a capping agent, thus, desirable products were obtained as the result of conducted calcinations. Various methods have been used to study the product's morphology and crystallinity. Furthermore, the work also examined the product's optical properties.

1.2 Statement of the problem

In opting method for synthesis of materials, one has to bear in mind the first requirement of its novel study. In fact, the current challenge for the synthesis of oxide nanoparticles is the development of systematic studies. The creation of $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ Nanocomposite powders has received relatively little research attention, with most research effects aimed at $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ films. With the advancement of technology, synthesis of metal oxide nanocomposite was encouraged. Thus, this approach provides numerous advantages over more pre-described techniques; the material can be manufactured with good performance, low financial outlay, high adaptability and less handling complexity, and these advantages form the basis for current research motivation. Notwithstanding, the application of $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ nanocomposite powders obtained through this method as observed from their optical properties is another factor for this research work.

1.3 Significant of the Study

Method of heat treatment created the sample in binary or powder form. It does not produce any parallel waste $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ samples. The product is environmentally friendly, (Kamari et al., 2019). The synthesis is concentrated on producing with a better quality, higher cleanliness, particle size control, high adaptability, minimal effort, and use by power products, a two way leading supplier of two way radio chargers and a two way radio accessories for motorola (Al-Hada et al., 2016).

1.4 Objectives of the study

The overall objective of this study is to use the thermal treatment method for binary synthesis $(\text{ZnO})_x (\text{ZrO}_2)_{1-x}$ nanocomposites with the PVP acting as a capping agent. The main objectives of the study are as follows:

1. To synthesize ZnO/ZrO_2 nanocomposite powder using thermal treatment method.
2. To determine the impact of calcination temperature on the sample's structure and morphology.
3. To determine the optical properties of $\text{ZnO} / \text{ZrO}_2$ nanocomposites.

1.5 Thesis outline

This section is numbered chapters 1- 6, Chapter 1 is the general introduction and problem statements on metal nanocomposites. This section also describes the significant and goals of the study. Chapter 2 presents the prior research and reviews of nanocomposites ZnO and ZrO_2 prepared using distinct methods. In addition, the processing and characterization method for Zn and Zr nanoparticles is also evaluated. Chapter 3 The structural, optical properties of products at bulk and nanoform studied. Chapter 4 shows nanocomposite sample preparation and characterization using suitable tool. Chapter 5 Discussion of all specimens used and measurements conducted using Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), Electron Microscopy transmission (TEM), Fourier Transform Infrared (FTIR), Electron Microscopy scanning (SEM), UV- Spectroscopy visible and Photoluminescence (PL). Finally, current work and some suggestions for future studies are summarized in Chapter 6

REFERENCES

- Adam, J., and Rogers, M. D. (1959). The crystal structure of ZrO_2 and HfO_2 . *Acta Crystallographica*, 12(11), 951-951.
- Adamski, A., Jakubus, P., and Sojka, Z. (2006). Synthesis of nanostructured tetragonal ZrO_2 of enhanced thermal stability. *Nukleonika*, 51(SUPPL. 1), 27–33.
- Ahmad, M., and Zhu, J. (2011). ZnO based advanced functional nanostructures: Synthesis, properties and applications. *Journal of Materials Chemistry*, 21(3), 599–614.
- Al-Hada, N. M., Mohamed Kamari, H., Abdullah, C. A. C., Saion, E., Shaari, A. H., Talib, Z. A., and Matori, K. (2017). Down-top nanofabrication of binary $(CdO)_x (ZnO)_{1-x}$ nanoparticles and their antibacterial activity. *International Journal of Nanomedicine*, Volume 12, 8309–8323.
- Al-Hada, N. M., Saion, E. B., Shaari, A. H., Kamarudin, M. A., Flaifel, M. H., Ahmad, S. H., and Gene, S. A. (2014). A facile thermal-treatment route to synthesize ZnO nanosheets and effect of calcination temperature. *PLoS ONE*, 9(8), 2–10.
- Al-Hada, N. M., Saion, E., Kamari, H. M., Flaifel, M. H., Shaari, A. H., Talib, Z. A., and Kharazmi, A. (2016). Structural, morphological and optical behaviour of PVP capped binary $(ZnO)_{0.4} (CdO)_{0.6}$ nanoparticles synthesised by a facile thermal route. *Materials Science in Semiconductor Processing*, 53, 56–65.
- Aladpoosh, R., and Montazer, M. (2015). The role of cellulosic chains of cotton in biosynthesis of ZnO nanorods producing multifunctional properties: mechanism, characterizations and features. *Carbohydrate Polymers*, 126, 122-129.
- Alagiri, M., Ponnusamy, S., and Muthamizhchelvan, C. (2012). Synthesis and characterization of NiO nanoparticles by sol–gel method. *Journal of Materials Science: Materials in Electronics*, 23(3), 728-732.
- Al-Gaashani, R., Radiman, S., Tabet, N., and Daud, A. R. (2011). Effect of microwave power on the morphology and optical property of zinc oxide nano-structures prepared via a microwave-assisted aqueous solution method. *Materials Chemistry and Physics*, 125(3), 846-852.
- Al-Saleh, M. H., Al-Anid, H. K., Husain, Y. A., El-Ghanem, H. M., & Jawad, S. A. (2013). Impedance characteristics and conductivity of CNT/ABS nanocomposites. *Journal of Physics D: Applied Physics*, 46(38), 385305.
- Ali, S. (2015). Why Nanoscience and Nanotechnology ? What is there for us ? Why Nanoscience and Nanotechnology ? What is there for us ?, (January).

- Allam, N. K., and Grimes, C. A. (2007). Formation of vertically oriented TiO₂ nanotube arrays using a fluoride free HCl aqueous electrolyte. *Journal of Physical Chemistry C*, 111(35), 13028–13032.
- ANANDAN, K. (2008). Studies on the magnetic and optical properties and photocatalytic activity of Nickel oxide Zirconium oxide Chromium sesquioxide and Tin oxide nanomaterials synthesized by the wet chemical method.
- Arico, A. S., Bruce, P., Scrosati, B., Tarascon, J. M., and Van Schalkwijk, W. (2011). Nanostructured materials for advanced energy conversion and storage devices. In *Materials for sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group* (pp. 148-159).
- Asamoto, M., Miyake, S., Sugihara, K., and Yahiro, H. . 1. (2009). Improvement of Ni/SDC anode by alkaline earth metal oxide addition for direct methane– solid oxide fuel cells. *Electrochemistry Communications*, (7), 1508-1511.
- Auer, E., Freund, A., Pietsch, J., and Tacke, T. (1998). Carbons as supports for industrial precious metal catalysts. *Applied Catalysis A: General*, 173(2), 259-271.
- Bakhshi, A. K., and Bhalla, G. (2004). Electrically conducting polymers: Materials of the twenty first century.
- Baruah, S., and Dutta, J. (2009). pH-dependent growth of zinc oxide nanorods. *Journal of Crystal Growth*, 311(8), 2549-2554.
- Baqer, A. A., Matori, K. A., Al-Hada, N. M., Shaari, A. H., Kamari, H. M., Saion, E., Abdullah, C. A. C. (2018). Synthesis and characterization of binary (CuO)_{0.6}(CeO₂)_{0.4} nanoparticles via a simple heat treatment method. *Results in Physics*, 9, 471–478.
- Baqer, A. A., Matori, K. A., Al-Hada, N. M., Shaari, A. H., Saion, E., and Chyi, J. L. Y. (2017). Effect of polyvinylpyrrolidone on cerium oxide nanoparticle characteristics prepared by a facile heat treatment technique. *Results in Physics*, 7, 611–619.
- Bechir, M. B., Karoui, K., Tabellout, M., Guidara, K., and Rhaiem, A. B. (2014). Electric and dielectric studies of the [N(CH₃)₃H]₂CuCl₄ compound at low temperature. *Journal of alloys and compounds*, 588, 551-557.
- Bengisu, M. (2001). Applications of Ceramic Materials. In *Engineering Ceramics* (pp. 407-445). Springer, Berlin, Heidelberg.
- Birkby, I., and Stevens, R. (1996). Applications of zirconia ceramics. In *Key Engineering Materials* (Vol. 122, pp. 527-552). Trans Tech Publications Ltd.

- Bordoloi, N., Sharma, A., Nautiyal, H., and Goel, V. (2018). An intense review on the latest advancements of Earth Air Heat Exchangers. *Renewable and Sustainable Energy Reviews*, 89, 261-280.
- Bradbury, S., Joy, D. C., and Ford, B. J. (2011). Transmission electron microscope (TEM). *Encyclopedia Britannica*.
- Brown, A. (1970). *X-ray Powder Diffraction with Guinier-Hägg Focusing Cameras* (No. AE--409). AB Atomenergi.
- Bunaciu, A. A., UdrișTioiu, E. G., and Aboul-Enein, H. Y. (2015). X-ray diffraction: instrumentation and applications. *Critical reviews in analytical chemistry*, 45(4), 289-299.
- Cao, B., Cai, W., Zeng, H., and Duan, G. (2006). Morphology evolution and photoluminescence properties of ZnO films electrochemically deposited on conductive glass substrates. *Journal of applied physics*, 99(7), 073516.
- Cao, Z., Koukharenko, E., Tudor, M. J., Torah, R. N., and Beeby, S. P. (2013). Screen printed flexible Bi₂Te₃-Sb₂Te₃ based thermoelectric generator. In *Journal of Physics: Conference Series* (Vol. 476, No. 1, p. 012031). IOP Publishing.
- Caruso, F. (2001). Nanoengineering of particle surfaces. *Advanced materials*, 13(1), 11-22.
- Caruso, R. A., and Antonietti, M. (2001). Sol– gel nanocoating: an approach to the preparation of structured materials. *Chemistry of materials*, 13(10), 3272-3282.
- Casasola, R., Rincón, J. M., and Romero, M. (2012). Glass–ceramic glazes for ceramic tiles: a review. *Journal of Materials Science*, 47(2), 553-582.
- Castro, M. E. (2006). Miguel E. Castro, The UniVersity of Puerto Rico at Mayaguez JA059899G 10.1021/ja059899g. *Organic Reaction Mechanisms*, 11315–11316.
- Chaim, R., Silberman, I., and Gal- Or, L. (1991). Electrolytic ZrO₂ coatings II. microstructural aspects. *Journal of the Electrochemical Society*, 13(7), 1942–1946.
- Chandrasekaran, R., Gnanasekar, S., Seetharaman, P., Keppanan, R., Arockiaswamy, W., and Sivaperumal, S. (2016). Formulation of Carica papaya latex-functionalized silver nanoparticles for its improved antibacterial and anticancer applications. *Journal of Molecular Liquids*, 219, 232-238.
- Channu, V. R., Kalluru, R. R., Schlesinger, M., Mehring, M., and Holze, R. (2011). Synthesis and characterization of ZrO₂ nanoparticles for optical and electrochemical applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 386(1-3), 151-157.

- Chen, J., Liu, X., Wang, C., Yin, S. S., Li, X. L., Hu, W. J., and Peng, X. X. (2015). Nitric oxide ameliorates zinc oxide nanoparticles-induced phytotoxicity in rice seedlings, *297*, 173-182.
- Cheng, A. J., Tzeng, Y., Xu, H., Alur, S., Wang, Y., Park, M., and Wang, D. (2009). Raman analysis of longitudinal optical phonon-plasmon coupled modes of aligned ZnO nanorods. *Journal of applied physics*, *105*(7), 073104. Chong, F., Zhen-An, T., & Jun, Y. (2012). A novel CMOS device capable of measuring near-field thermal radiation. *Chinese Physics Letters*, *29*(3), 038502.
- Cox, E. G. (1951). Structural inorganic chemistry. *Nature*, *168*(4279), 756–757.
- Cullity, B. D. (1978). Elements of X-ray diffraction, Addison. *Wesley Mass.*
- Daniel, M., and Astruc, D. (2004). ISA - Congresses | Conferences | Meetings | Workshops | Seminars on Sociology and Social Sciences.
- Dev, A., Kar, S., Chakrabarti, S., and Chaudhuri, S. (2006). Optical and field emission properties of ZnO nanorod arrays synthesized on zinc foils by the solvothermal route. *Nanotechnology*, *17*(5), 1533.
- Devi, V., Joshi, B. C., Kumar, M., and Choudhary, R. J. (2014). Structural and optical properties of Cd and Mg doped zinc oxide thin films deposited by pulsed laser deposition. In *Journal of Physics: Conference Series* (Vol. 534, No. 1, p. 012047). IOP Publishing.
- Dhandapani, P., Siddarth, A. S., Kamalasekaran, S., Maruthamuthu, S., and Rajagopal, G. (2014). Bio-approach: ureolytic bacteria mediated synthesis of ZnO nanocrystals on cotton fabric and evaluation of their antibacterial properties. *Carbohydrate Polymers*, *103*, 448-455.
- Dillon, A. C., Mahan, A. H., Deshpande, R., Parilla, P. A., Jones, K. M., and Lee, S. H. (2008). Metal oxide nano-particles for improved electrochromic and lithium-ion battery technologies. *Thin Solid Films*, *516*(5), 794-797.
- Division, M. (1985). The Theory of Ostwald Ripening. *Journal of Statistical Physics*, *38*(1), 231–252.
- Sanchez-Dominguez, M., Pemartin, K., and Boutonnet, M. (2012). Preparation of inorganic nanoparticles in oil-in-water microemulsions: A soft and versatile approach. *Current Opinion in Colloid & Interface Science*, *17*(5), 297-305.
- Dou, S., Tao, L., Huo, J., Wang, S., and Dai, L. (2016). Etched and doped Co₉S₈/graphene hybrid for oxygen electrocatalysis. *Energy and Environmental Science*, *9*(4), 1320-1326.
- Durrant, A. (2000). Quantum Physics of matter. CRC Press.

- Elumalai, K., Velmurugan, S., Ravi, S., Kathiravan, V., and Ashokkumar, S. (2015). green synthesis of zinc oxide nanoparticles using *Moringa oleifera* leaf extract and evaluation of its antimicrobial activity.
- Espinoza-González, R. A., Diaz-Droguett, D. E., Avila, J. I., Gonzalez-Fuentes, C. A., and Fuenzalida, V. M. (2011). Hydrothermal growth of zirconia nanobars on zirconium oxide. *Materials Letters*, 65(14), 2121–2123.
- Feng, L., Zhang, Y., Xi, J., Zhu, Y., Wang, N., Xia, F., and Jiang, L. (2008). Petal effect: a superhydrophobic state with high adhesive force. *Langmuir*, 24(8), 4114-4119.
- Fernandez-Garcia, M., Martinez-Arias, A., Hanson, J. C., and Rodriguez, J. A. (2004). Nanostructured oxides in chemistry. *Characterization and Properties. Chemical Reviews*, 104(9), 4063–4104.
- Fernández- García, M., and Rodriguez, J. A. (2011). Metal oxide nanoparticles. In *Encyclopedia of inorganic and bioinorganic chemistry*.
- Fernández, M. R., Casanova, E. Z., and Alonso, I. G. (2015). Review of display technologies focusing on power consumption. *Sustainability*, 7(8), 10854-10875.
- Fujimori, A. (1983). Correlation effects in the electronic structure and photoemission spectra of mixed-valence cerium compounds. *Physical Review B*, 28(8), 4489.
- Gairola, P., Purohit, L. P., Gairola, S. P., Bhardwaj, P., and Kaushik, S. (2019). Enhanced electromagnetic absorption in ferrite and tantalum pentoxide based polypyrrole nanocomposite. *Progress in Natural Science: Materials International*, 29(2), 170–176.
- Gao, J., Lee, D., Yang, Y., Holdcroft, S., and Frisken, B. J. (2005). Self-assembly of surface-charged latex nanoparticles: a new route to the creation of continuous channels for ion conduction. *Macromolecules*, 38(14), 5854-5856.
- Gao, Y. P., Sisk, C. N., and Hope-Weeks, L. J. (2007). A sol–gel route to synthesize monolithic zinc oxide aerogels. *Chemistry of Materials*, 19(24), 6007– 6011.
- Giannelis, E. P., Krishnamoorti, R., and Manias, E. (1999). Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes. In *Polymers in confined environments* (pp. 107-147). Springer, Berlin, Heidelberg.
- Gfroerer, G. T., Netka, M. W., and Souraty, M. J. (2000). *U.S. Patent No. 6,152,648*. Washington, DC: U.S. Patent and Trademark Office.
- Grätzel, M. (2003). Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C:Photochemistry Reviews*, 4(2), 145-153.

- Hajibeygi, M., Maleki, M., and Shabaniyan, M. (2018). The effects of poly (amide-imide) coating on the thermal, combustion and mechanical properties of polyvinyl chloride ZnO nanocomposites. *Progress in Organic Coatings*, 122, 96-106.
- Han, T. (2008). Optical Properties of Low Dimensional semiconductor materials. Royal Institute of Technology, Stockholm, Sweden.
- Henrich, V. E., and Cox, P. A. (1994). The surface chemistry of metal oxides. *Cambridge University Press: Cambridge, UK*.
- Heshmatpour, F., and Aghakhanpour, R. B. (2011). Synthesis and characterization of nanocrystalline zirconia powder by simple sol-gel method with glucose and fructose as organic additives. *Powder Technology*, 205(1–3), 193–200.
- Horrocks, A. R., Price, D., and Price, D. (Eds.). (2001). *Fire retardant materials*. woodhead Publishing.
- Huang, H., Kelder, E. M., and Schoonman, J. (2001). Graphite–metal oxide composites as anode for Li-ion batteries. *Journal of Power Sources*, 97, 114–117.
- Huang, J., Liu, Y., Hou, H., and You, T. (2008). Simultaneous electrochemical determination of dopamine, uric acid and ascorbic acid using palladium nanoparticle-loaded carbon nanofibers modified electrode. *Biosensors and Bioelectronics*, 24(4), 632-637.
- Izaki, M., and Omi, T. (1996). Transparent zinc oxide films prepared by electrochemical reaction. *Applied Physics Letters*, 68(17), 2439-2440.
- Jiang, D., Hulbert, D. M., Kuntz, J. D., Anselmi-Tamburini, U., and Mukherjee, A. K. (2007). Spark plasma sintering: A high strain rate low temperature forming tool for ceramics. *Materials Science and Engineering: A*, 463(1-2), 89-93.
- Jin, S., Fallgren, P. H., Morris, J. M., and Chen, Q. (2007). Removal of bacteria and viruses from waters using layered double hydroxide nanocomposites. *Science and Technology of Advanced Materials*, 8(1-2), 67.
- Johan, M. R., Suan, M. S. M., Hawari, N. L., and Ching, H. A. (2011). Annealing effects on the properties of copper oxide thin films prepared by chemical deposition. *International Journal of Electrochemical Science*, 6(12), 6094–6104.
- John P. Dakin, R. B., Michel Digonnet, K. S. (2006). Hand book of optoelectronics. Taylor and Francis group, New York.
- Jung, S. H., Oh, E., Lee, K. H., Yang, Y., Park, C. G., Park, W., and Jeong, S. H. (2007). Sonochemical preparation of shape-selective ZnO nanostructures. *Crystal Growth and Design*, 8(1), 265-269.

- Kachynski, A. V., Kuzmin, A. N., Nyk, M., Roy, I., and Prasad, P. N. (2008). Zinc oxide nanocrystals for nonresonant nonlinear optical microscopy in biology and medicine. *Journal of Physical Chemistry C*, 112(29), 10721–10724.
- Kai, W., Hirota, Y., Hua, L., and Inoue, Y. (2008). Thermal and mechanical properties of a poly (ϵ - caprolactone)/graphite oxide composite. *Journal of Applied Polymer Science*, 107(3), 1395-1400.
- Kakhaki, Z. M., Youzbashi, A., and Naderi, N. (2015). Optical properties of zinc oxide nanoparticles prepared by a one-step mechanochemical synthesis method. *Journal of Physical Science*, 26(2), 41–51.
- Kamari, H., Al-Hada, N., Saion, E., Shaari, A., Talib, Z., Flaifel, M., and Ahmed, A. (2017). Calcined Solution-Based PVP Influence on ZnO Semiconductor Nanoparticle Properties. *Crystals*, 7(2), 2.
- Kamari, H. M., Al-Hada, N. M., Baqer, A. A., Shaari, A. H., and Saion, E. (2019). Comprehensive study on morphological, structural and optical properties of Cr₂O₃ nanoparticle and its antibacterial activities. *Journal of Materials Science: Materials in Electronics*.
- Kaneti, Y. V., Jiang, X., and Yu, A. (2013). Controllable Synthesis of ZnO Nanoflakes with. exposed (1010) for enhanced gas sensing performance. *Journal of Physical Chemistry C*, 117(25), 13153-13162.
- Karim, S., Maaz, K., Ali, G., and Ensinger, W. (2009). Diameter dependent failure current density of gold nanowires. *Journal of Physics D: Applied Physics*, 42(18).
- Kevan, S. D., and Gaylord, R. H. (1987). High-resolution photoemission study of the electron structure of the noble-metal (111) surfaces. *Physical Review B*, 36(11), 5809–5818.
- Keiteb, A. S., Saion, E., Zakaria, A., and Soltani, N. (2016). Structural and optical properties of zirconia nanoparticles by thermal treatment synthesis. *Journal of Nanomaterials*, 2016.
- Khalim Khafidz, N. Z. A., Yaakob, Z., Timmiati, S. N., Lin, K. S., and Lim, K. L. (2019). Hydrogen sorption of magnesium oxide carbon nanofibre composite. *Malaysian Journal of Analytical Sciences*, 23(1), 60–70.
- Kim, D. C., Kong, B. H., and Cho, H. K. J. (2008). Morphology control of 1D ZnO nanostructures grown by metal-organic chemical vapor deposition. *Journal of Materials Science: Materials in Electronics*, 19(8-9), 760-763.
- Kittel, C. (2005). Introduction to solid state physics (8th ed.): Wiley.

- Koebel, M. M., Jones, L. C., and Somorjai, G. A. (2008). Preparation of size-tunable, highly monodisperse PVP-protected Pt-nanoparticles by seed-mediated growth. *Journal of Nanoparticle Research*, 10(6), 1063-1069.
- Kolodziejczak-Radzimska, A., and Jesionowski, T. (2014). Zinc oxide-from synthesis to application: A review. *Materials*, 7(4), 2833–2881.
- Kremer, F. (1996). The dielectric properties of proteins. *Dielectrics Newsletter*, 31, 2–3.
- Krunk, M., Dedova, T., and Açık, I. O. (2006). Spray pyrolysis deposition of zinc oxide nanostructured layers. *Thin Solid Films*, 3(515), 1157-1160.
- Krupa, A. N. D., and Vimala, R. (2016). Evaluation of tetraethoxysilane (TEOS) sol-gel coatings, modified with green synthesized zinc oxide nanoparticles for combating microfouling. *Materials Science and Engineering: C*, 61, 728–735.
- Kul'met'eva, V. B., Porozova, S. E., Krasnyi, B. L., Tarasovskii, V. P., and Krasnyi, A. B. (2009). Preparation of zirconia ceramics from powder synthesized by a sol-gel method. *Refractories and Industrial Ceramics*, 50(6), 438–440.
- Kumar, K. D., Narayana, K., and Rao, K. A. (2018). Green Synthesis of Zinc Oxide Nanoparticles using Extracts of Ocimum Tenuiflorum and its Characterization. *Journal of Nanoscience Nanoengineering and Applications*, 8(1), 9-19.
- Kumar, R., Al-Dossary, O., Kumar, G., and Umar, A. (2015). Zinc oxide nanostructures for NO₂ gas-sensor applications: A review. *Nano- Micro Letters*, 7(2), 97–120.
- Kumari, B., Sharma, S., Singh, N., Verma, A., Satsangi, V. R., Dass, S., and Shrivastav, (2014). ZnO thin films, surface embedded with biologically derived Ag/Au nanoparticles, for efficient photoelectrochemical splitting of water. *International Journal of Hydrogen Energy*, 39(32), 18216-18229.
- Kung, H. H. (1989). T. metal oxides: surface chemistry and catalysis (Vol. 45). E. (1989). No Title Transition metal oxides: surface chemistry and catalysis. Elsevier., Vol. 45.
- Lanje, A. S., Sharma, S. J., Pode, R. B., and Ningthoujam, R. S. (2010). Synthesis and optical characterization of copper oxide nanoparticles. *Library*, 1(2), 36–40.
- Law, M., Greene, L. E., Radenovic, A., Kuykendall, T., Liphardt, J., and Yang, P. (2006). ZnO– Al₂O₃ and ZnO– TiO₂ core– shell nanowire dye- sensitized solar cells. *The Journal of Physical Chemistry B*, 110(45), 22652-22663.
- Lee, G. H., Park, J. G., Sung, Y. M., Chung, K. Y., Cho, W. I., and Kim, D. W. s., 295205. (2009). Enhanced cycling performance of an Fe₀/Fe₃O₄

- nanocomposite electrode for lithium-ion batterie. *Nanotechnology*, 20(29) 136-791.
- Li, X., Zheng, W., He, G., Zhao, R., and Liu, D. (2013). Morphology control of TiO₂ nanoparticle in microemulsion and its photocatalytic property. *ACS Sustainable Chemistry and Engineering*, 2(2), 288-295.
- Liang, Z., Susha, A., and Caruso, F. (2003). Gold nanoparticle-based core– shell and hollow spheres and ordered assemblies thereof. *Chemistry of materials*, 15(16), 3176-3183.
- Lu, C. H., and Yeh, C. H.). (1997). Emulsion precipitation of submicron zinc oxide powder. *Materials Letters*, 33(3-4), 129-132.
- Maaz, K., Karim, S., Mashiatullah, A., Liu, J., Hou, M. D., Sun, Y. M., and Chen, Y. F. (2009). Structural analysis of nickel doped cobalt ferrite nanoparticles prepared by coprecipitation route. *Physica B: Condensed Matter*, 404(21), 3947-3951.
- MacDiarmid, A. G. (2001). Nobel Lecture: “Synthetic metals”: A novel role for organic polymers. *Reviews of Modern Physics*, 73(3), 701.
- Madfa, A. A., Al-Sanabani, F. A., Al-Qudami, N. H., Al-Sanabani, J. S., and Amran, A. G. (2014). Use of Zirconia in Dentistry: An Overview. *The Open Biomaterials Journal*, 5(1), 1–7.
- Mahata, P., Aarthi, T., Madras, G., and Natarajan, S. (2007). Photocatalytic degradation of dyes and organics with nanosized GdCoO₃. *Journal of Physical Chemistry C*, 111(4), 1665–1674.
- Mansir, N., Taufiq-Yap, Y. H., Rashid, U., and Lokman, I. M. (2017). Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. *Energy Conversion and Management*, 141, 171-182.
- Mariammal, R. N., Ramachandran, K., Renganathan, B., and Sastikumar, D. (2012). On the enhancement of ethanol sensing by CuO modified SnO₂ nanoparticles using fiber-optic sensor. *Sensors and Actuators B: Chemical*, 169, 199-207.
- Marignier, J. L., Belloni, J., Delcourt, M. O., and Chevalier, J. P. (1985). Microaggregates of non-noble metals and bimetallic alloys prepared by radiation-induced reduction. *Nature*, 317(6035), 344-345.
- McCullough, J. T., and Trueblood, K. N. (1959). The crystal structure of baddeleyite (monoclinic ZrO₂). *Acta Crystallographica*, 12(7), 507-511.
- Menczel, J. D., and Prime, R. B. (Eds.). (2009). *Thermal analysis of polymers: fundamentals and applications*. John Wiley and Sons.

- Mitra, S., Patra, P., Pradhan, S., Debnath, N., Dey, K. K., Sarkar, S., and Goswami. (2015). Microwave synthesis of ZnO@mSiO₂ for detailed antifungal mode of action study: understanding the insights into oxidative stress. *A. Journal of Colloid and Interface Science*, 444, 97-108.
- Mohammed, M. K., Ahmed, D. S., and Mohammad, M. R. (2019). Studying antimicrobial activity of carbon nanotubes decorated with metal-doped ZnO hybrid materials. *Materials Research Express*, 6(5), 055404.
- Mohanty, B. C., Choi, H. R., and Cho, Y. S. (2011). Fluctuations in global surface scaling behaviour in sputter-deposited ZnO thin films. *EPL (Europhysics Letters)*, 93(2), 26003.
- Moravec, P., Smolík, J., Keskinen, H., Mäkelä, J. M., and Levdansky, V. V. (2017). Vapor Phase Synthesis of Zirconia Fine Particles from Zirconium Tetra-Tert-Butoxide. *Aerosol and Air Quality Research*, 7(4), 563–577.
- Mui, S. C., Trapa, P. E., Huang, B., Soo, P. P., Lozow, M. I., Wang, T. C., ... Sadoway, D. R. (2002). Block copolymer-templated nanocomposite electrodes for rechargeable lithium batteries. *Journal of the Electrochemical Society*, 149(12), 1610–1615.
- Nassau, K., McClure, S. F., Elen, S., and Shigley, J. E. (1997). Synthetic moissanite: A new diamond substitutes. *Gems and Gemology*, 33(4), 260-275.
- Nicollian, E. H., & Brews, J. R. (1982). MOS/metal oxide semiconductor/physics and technology. *New York, Wiley-Interscience*, 1982. 920 p.
- Niu, H., Yang, Q., and Tang, K. (2006). A new route to copper nitrate hydroxide microcrystals. *Materials Science and Engineering: B*, 135(2), 172-175.
- Nogueira, J. R., and Cavalcanti, J. C. (1996). Pricing network services: The Case of the Internet. *Available at SSRN 1581*.
- Pang, S., Xie, T., Zhang, Y., Wei, X., Yang, M., Wang, D., and Du, Z. 18417-18422. (2007). Research on the effect of different sizes of ZnO nanorods on the efficiency of TiO₂-based dye-sensitized solar cells. *The Journal of Physical Chemistry C*, 111(49).
- Papis, E., Rossi, F., Raspanti, M., Dalle-Donne, I., Colombo, G., Milzani, A., ... Gornati, R. (2009). Engineered cobalt oxide nanoparticles readily enter cells. *Toxicology Letters*, 189(3), 253–259.
- Pavia, D. L., Lampman, G. M., and Kriz, G. S. (2001). Introduction to Spectroscopy, Thomson Learning. Inc., USA, 24-29.
- Peulon, S., and Lincot, D. (1996). Cathodic electrodeposition from aqueous solution of dense or open-structured zinc oxide films. *Advanced Materials*, 8(2), 166–170.

- Piconi, C., and Maccauro, G. (1999). Zirconia as a ceramic biomaterial. *Biomaterials*, 20(1), 1-25.
- Poizot, P. L. S. G., Laruelle, S., Grugeon, S., Dupont, L., and Tarascon, J. M. (2000). Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature*, 407(6803), 496.
- Pyrz, W. D., and Buttrey, D. J. (2008). Particle size determination using TEM: a discussion of image acquisition and analysis for the novice microscopist. *Langmuir*, 24(20), 11350- 11360.
- Rashid, M. I., Shahzad, T., Shahid, M., Ismail, I. M., Shah, G. M., and Almeelbi, T. (2017). Zinc oxide nanoparticles affect carbon and nitrogen mineralization of Phoenix dactylifera leaf litter in a sandy soil. *Journal of Hazardous Materials*, 324, 298-305.
- Ratke, L., and Voorhees, P. W. (2013). *Growth and coarsening: Ostwald ripening in material processing*. Springer Science and Business Media.
- Razeghi, M. (2009). *Fundamentals of solid state engineering* (3rd ed.). Springer.
- Reich, S., Thomsen, C., and Maultzsch, j. (2004). *Carbon nanotubes: basic concepts and physical properties*. Wiley- VCH.
- Rein, S. (2005). *Lifetime Spectroscopy: A Method of Defect Characterization in Silicon for Photovoltaic Applications*: Springer.
- Reddy, N. K., Ahsanulhaq, Q., and Hahn, Y. B. (2008). Fabrication of zinc oxide nanorods based heterojunction devices using simple and economic chemical solution method. *Applied Physics Letters*, 93(8), 083124.
- Resa, S., Orte, A., Miguel, D., Paredes, J. M., Puente- Muñoz, V., Salto, R., and Crovetto, L. (2015). New dual fluorescent probe for simultaneous biothiol and phosphate bioimaging. *Chemistry—A European Journal*, 21(42), 14772-14779.
- Roucoux, A. (2005). Stabilized Noble Metal Nanoparticles: An Unavoidable Family of Catalysts for Arene Derivative Hydrogenation. In *Surface and Interfacial Organometallic Chemistry and Catalysis*.
- Sahoo, S., Barik, S. K., Gaur, A. P. S., Correa, M., Singh, G., Katiyar, R. K., and Katiyar, R. S. (2012). Microwave Assisted Synthesis of ZnO Nano-Sheets and Their Application in UV-Detector. *ECS Journal of Solid State Science and Technology*, 1(6), Q140–Q143.
- Salem, Aeshah, Saion, E., Al-Hada, N. M., Kamari, H. M., Shaari, A. H., and Radiman, S. (2017). Simple synthesis of ZnSe nanoparticles by thermal treatment and their characterization. *Results in Physics*, 7, 1175–1180.

- Saravanan, R., Karthikeyan, N., Gupta, V. K., Thirumal, E., Thangadurai, P., Narayanan, V., and Stephen, A. J. M. S. (2013). ZnO/Ag nanocomposite: an efficient catalyst for degradation studies of textile effluents under visible light. *Materials Science and Engineering: C*, 33(4), 2235-2244.
- Sassaroli, A., and Fantini, S. (2004). Comment on the modified Beer–Lambert law for scattering media. *Physics in Medicine and Biology*, 49(14), N255.
- Schärtl, W. (2000). Crosslinked spherical nanoparticles with core–shell topology. *Advanced Materials*, 12(24), 1899-1908.
- Schelling, P. K., Phillpot, S. R., and Wolf, D. (2001). Mechanism of the cubic- to-tetragonal phase transition in zirconia and yttria- stabilized zirconia by molecular- dynamics simulation. *Journal of the American Ceramic Society*, 84(7), 1609-1619.
- Scholz, F. (2017). *Compound semiconductors: Physics, technology, and device concepts*. *Compound Semiconductors: Physics, Technology, and Device Concepts*.
- Schultze, J. W., and Karabulut, H. (2005). Application potential of conducting polymers. *Electrochemical Acta*, 50(7-8), 1739-1745.
- Seungdo Park, J. M. V. and R. J. G. (2000). Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature*, 404(6775), 265–267.
- Schelling, P. K., Phillpot, S. R., and Wolf, D. (2001). Mechanism of the cubic- to-tetragonal phase transition in zirconia and yttria- stabilized zirconia by molecular- dynamics simulation. *Journal of the American Ceramic Society*, 84(7), 1609-1619.
- Singh, A. K., and Nakate, U. T. (2014). Microwave synthesis, characterization, and photoluminescence properties of nanocrystalline zirconia. *The Scientific World Journal*, 2014.
- Singh, S. C. (2013). Zinc Oxide Nanostructures; Synthesis, Characterizations and Device Applications. *Journal of Nanoengineering and Nanomanufacturing*, 3(4), 283-310.
- Singh, S. C., Singh, D. P., Singh, J., Dubey, P. K., Tiwari, R. S., and Srivastava, O. N. (2008). Metal Oxide Nanostructures; Synthesis, Characterizations and Applications. *Plasma Science and Technology*, (May 2014).
- Singh, J. (2006) *Optical properties of condensed matter and applications*. John Wiley and sons.
- Snaith, H. J., and Schmidt- Mende, L. (2007). Advances in liquid- electrolyte and solid- state dye- sensitized solar cells. *Advanced Materials*, 19(20), 3187-3200.

- Soltani, A., Haghjoo, F., and Shahrtash, S. M. (2012). Compensation of the effects of electrical sensors in measuring partial discharge signals. *IET Science, Measurement and Technology*, 6(6), 494-501.
- Stankic, S., Suman, S., Haque, F., and Vidic, J. (2016). Pure and multi metal oxide nanoparticles: synthesis, antibacterial and cytotoxic properties. *Journal of nanobiotechnology*, 14(1), 73.
- Subbarao, E. C., and Maiti, H. S. (1988). Science and technology of zirconia. *Advances in Ceramics*, 24, 731-737.
- Sujinnapram, S., Termsuk, U., Charoentam, A., and Sutthana, S. (2013). Synthesis and Characterization of Nanocrystalline ZnO Powders by a Direct Thermal Decomposition Route Using Zinc Nitrate Hexahydrate. In *Advanced Materials Research* (Vol. 770, pp. 68-71). Trans Tech Publications Ltd.
- Suzuki, K., Murayama, K., and Tanaka, N. (2015). Enhanced luminescence in Eu-doped ZnO nanocrystalline films. *Applied Physics Letters*, 107(3), 1-5.
- Switzer, J. A. (1986). The n-Silicon/Thallium (III) Oxide Heterojunction Photoelectrochemical Solar Cell. *Journal of the Electrochemical Society*, 133(4), 722-728.
- Rao, V., Latha, P., Ashokan, P. V., and Shridhar, M. H. (1999). Thermal Degradation of Poly (N-vinylpyrrolidone)-Poly (vinyl alcohol) Blends. *Polymer journal*, 31(10), 887-889.
- Tada, M., and Iwasawa, Y. (2008). Supported catalysts from chemical vapor deposition and related techniques. *Handbook of Heterogeneous Catalysis: Online*, 539-555.
- Tada, M., and Iwasawa, Y. (2003). Approaches to design of active structures by attaching and molecular imprinting of metal complexes on oxide surfaces. *Journal of Molecular Catalysis A: Chemical*, 204, 27-53.
- Takami, S., Hayakawa, R., Wakayama, Y., and Chikyow, T. (2010). Continuous hydrothermal synthesis of nickel oxide nanoplates and their use as nanoinks for p-type channel material in a bottom-gate field-effect transistor. *Nanotechnology*, 21(13), 134009.
- Talam, S., Karumuri, S. R., and Gunnam, N. (2012). Synthesis, characterization and spectroscopic properties of ZnO nanoparticles. *ISRN Nanotechnol* 2012: 1-6.
- Tan, D., Lin, G., Liu, Y., Teng, Y., Zhuang, Y., Zhu, B., and Qiu, J. (2011). Synthesis of nanocrystalline cubic zirconia using femtosecond laser ablation. *Journal of Nanoparticle Research*, 13(3), 1183-1190.

- Tang., C. L. (2005). *Fundamentals of quantum mechanics: for solid state electronics and optics*. Cambridge University Press, New York, USA.
- Tomov, R. I., Krauz, M., Jewulski, J., Hopkins, S. C., Kluczowski, J. R., Glowacka, D. M., and Glowacki, B. A. (2010). Direct ceramic inkjet printing of yttria-stabilized zirconia electrolyte layers for anode-supported solid oxide fuel cells. *Journal of Power Sources*, 195(21), 7160-7167.
- Uárez, B. H., García, P. D., Golmayo, D., Blanco, A., and Lopez, C. (2005). ZnO inverse opals by chemical vapor deposition. *Advanced Materials*, 17(22), 2761–2765.
- Umar, A., Lee, S., Im, Y. H., and Hahn, Y. B. (2005). Flower-shaped ZnO nanostructures obtained by cyclic feeding chemical vapour deposition: structural and optical properties. *Nanotechnology*, 16(10), 2462.
- Valden, M., Lai, X., and Goodman, D. W. (1998). Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science* 281(5383),1647-1650.
- Van den Rul, H., Mondelaers, D., Van Bael, M. K., and Mullens, J. (2006). Water-based wet chemical synthesis of (doped) ZnO nanostructures. *Journal of Sol-Gel Science and Technology*, 39(1), 41–47.
- Varughese, G., K.T, U., and A.S, K. (2014). Characterisation and band gap energy of wurtzite ZnO nanocrystallites, *Journal of Material Sceince*,3(3), 133– 136.
- Vitor, G., Palma, T. C., Vieira, B., Lourenço, J. P., Barros, R. J., and Costa, M. C. (2015). Start-up, adjustment and long-term performance of a two- stage bioremediation process, treating real acid mine drainage, coupled with biosynthesis of ZnS nanoparticles and ZnS/TiO₂ nanocomposites. *Minerals Engineering*, 75, 85-93.
- Voutou, B., Stefanaki, E. C., and Giannakopoulos, K. (2008). Electron microscopy: The basics. *Physics of advanced materials winter school*, 1(11).
- Wang, X., Hanson, J. C., Rodriguez, J. A., Belver, C., and Fernández-García, M. (2005). The structural and electronic properties of nanostructured Ce_{1-x-y}Zr_xTb_yO₂ ternary oxides: Unusual concentration of Tb³⁺ and metal↔oxygen↔metal interactions. *Journal of Chemical Physics*, 122(15).
- Wang, X., Hu, P., Fangli, Y., and Yu, L. (2007). Preparation and characterization of ZnO hollow spheres and ZnO– carbon composite materials using colloidal carbon spheres as templates. *The Journal of Physical Chemistry C*, 111(18), 6706-6712.
- Wang, Y., Wang, J. J., Wang, W. Y., Mei, Z. G., Shang, S. L., Chen, L. Q., and Liu, Z. K. (2010). A mixed-space approach to first-principles calculations of

phonon frequencies for polar materials. *Journal of Physics: Condensed Matter*, 22(20), 202201.

Wang, Y., Zhang, X., Wang, A., Li, X., Wang, G., and Zhao, L. (2014). Synthesis of ZnO nanoparticles from microemulsions in a flow type microreactor. *Chemical Engineering Journal*, 235, 191-197.

Wen, X., Wang, S., Ding, Y., Lin Wang, Z., and Yang, S. (2005). Controlled growth of large-area, uniform, vertically aligned arrays of α -Fe₂O₃ nanobelts and nanowires. *Journal of Physical Chemistry B*, 109(1), 215–220.

West, A. R. (1984). Solid state chemistry and its applications. John Wiley and Sons: Chichester.

Wu, W., Liu, Z., Jauregui, L. A., Yu, Q., Pillai, R., Cao, H., and Pei, S. S. (2010). Wafer-scale synthesis of graphene by chemical vapor deposition and its application in hydrogen sensing. *Sensors and Actuators B: Chemical*, 150(1), 296-300.

Xia, Y., Gates, B., Yin, Y., and Lu, Y. (2000). Monodispersed colloidal spheres: old materials with new applications. *Advanced Materials*, 12(10), 693- 713.

Xiao-Xia, T., Shao-Bo, Q., Hong-Liang, D., Ye, L., and Zhuo, X. (2012). Effects of (Lice) co-substitution on the structural and electrical properties of CaBi₂Nb₂O₉ ceramics. *Chinese Physics B*, 21(3), 037701.

Xiong, H. M., Xu, Y., Ren, Q. G., and Xia, Y. Y. (2008). Stable aqueous ZnO@ polymer core– shell nanoparticles with tunable photoluminescence and their application in cell imaging. *Journal of the American Chemical Society*, 130(24), 7522-7523.

Zhang, H., Wu, J., Zhai, C., Du, N., Ma, X., and Yang, D. (2007). From ZnO nanorods to 3D hollow microhemispheres: solvothermal synthesis, photoluminescence and gas sensor properties. *Nanotechnology*, 18(45), 455604.

Zhang, Q. P., Xu, X. N., Liu, Y. T., Xu, M., Deng, S. H., Chen, Y. and Xiong, G. (2017). A feasible strategy to balance the crystallinity and specific surface area of metal oxide nanocrystals. *Scientific Reports*, 7, 1–12.

Zhang, S., Yao, L., Sun, A., and Tay, Y. (2019). Deep learning-based recommender system: A survey and new perspectives. *ACM Computing Surveys (CSUR)*, 52(1), 1-38.

Zhao, J., Wu, T., Wu, K., Oikawa, K., Hidaka, H., and Serpone, N. (1998). Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/TiO₂ dispersions under visible light irradiation: Evidence for the need of substrate adsorption on TiO₂ particles. *Environmental Science and Technology*, 32(16), 2394–2400

Zuniga-Perez, J., Consonni, V., Lymperakis, L., Kong, X., Trampert, A., Fernandez-Garrido, S., and Wagner, M. R. (2016). Polarity in GaN and ZnO: Theory, measurement, growth, and devices. *Applied Physics Reviews*, 3(4), 041303.

