

**SYNTHESIS AND CHARACTERIZATION OF ZINC-DOPED CADMIUM
SELENIDE NANOPARTICLES FOR POSSIBLE APPLICATION
IN SOLAR CELLS**

Nimrod Gitonga

**A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Physics of Murang'a University of Technology**

August, 2025

DECLARATION

Student Declaration

I hereby declare that this thesis is my original work and to the best of my knowledge has not been presented for a degree award in this or any other university. I understand what plagiarism is and I am aware of the University's policy in this regard. I understand that any false claim in respect of this work shall result in disciplinary action in accordance with the University Anti-Plagiarism Policy.

Nimrod Gitonga

AS402/5151/2023

Date

Supervisors' Approval

The undersigned certify that they have read and hereby recommended for acceptance of Murang'a University of Technology a thesis entitled **“Synthesis and Characterization of Zinc Doped Cadmium Selenide Nanoparticles for Possible Application in Solar Cell.”**

Dr. Sharon Kiprotich,

Department of Physical and Biological Sciences,
Murang'a University of Technology.

Date

Dr. Michael Musembi,

Department of Physical Sciences,
Machakos University.

Date

DEDICATION

This research is dedicated to my beloved parents Isaac Murithi and Beth Mugure for their unwavering support, love and encouragement. To my brothers Maxwell and Malcom who have always been source of joy and inspiration.

I also dedicate this work to my friends and mentors who have offered guidance, wisdom and encouragement, and to all those who have made this journey meaningful. Without your support, this would not have been possible.

Thank you for believing in me.

ACKNOWLEDGEMENT

I am forever grateful to the almighty God for his protection, guidance, providence and care throughout my studies.

To my supervisors Dr. Sharon Kiprotich and Dr. Michael Musembi I extend my appreciation for your invaluable guidance, encouragement, and expertise throughout this research. Your insightful feedback and continuous support have been essential in shaping this work, and I am truly grateful for your patience and dedication.

I am thankful to the Department of Physical and Biological Science at Murang'a University of Technology for help with data collection, analysis and other research-related tasks.

I also wish to sincerely thanks my friends Shadrack, Nancy, Joan, James, Bethwel, Sharon, Ken, Glory, Dennis, Dessy and Mwititi. Thank you for the support and encouragement you have given me.

I am incredibly grateful to my family whose love and support have been my foundation throughout my academic journey. To my parents and siblings, thank you for your endless encouragement and belief in my potential. Thank you for your love and constant motivation.

Lastly, but not least I would like to take a moment to thank myself for the resilience, perseverance and determination to complete this thesis. The journey has been challenging at times, but my commitment to seeing through has been a testament to my personal growth and dedication.

This thesis is as a result of the collective support and encouragement of everyone mentioned above, and I am truly thankful to each one of you.

ABSTRACT

The increasing global demand for renewable energy has highlighted the need for advanced materials that can improve the efficiency and affordability of solar cells. This research focused on developing CdSe and Zn-CdSe nanoparticles through sol-gel synthesis, aiming to optimize key parameters such as doping concentration, growth temperatures, and annealing temperatures to achieve desirable structural and optical characteristics. The synthesized CdSeNPs and Zn-CdSeNPs were characterized using X-ray diffraction (XRD), Ultra-Violet visible (UV-vis), photoluminescence spectroscopy (PL) and Fourier transmission infra-red (FT-IR) spectroscopy. The XRD pattern of CdSeNPs displayed zinc blende cubic and the patterns of CdSe nanoparticles revealed additional peaks at certain growth temperatures. The cubic structure was maintained when Zn doping concentrations were varied as well as variation in the annealing temperature indicating that all dopants had occupied the interstitial sites. Growth temperature of 45°C, Zn doping concentration of 3 mol% and annealing temperature of 275°C displayed highest XRD peak intensities. This is an indication of improved crystallinity at these growth parameters. The crystallite size of nanoparticles determined using Debye-Scherrer formula were observed to generally increase with increase in growth temperature. The largest average crystallite size was obtained at a growth temperature of 75°C. When Zn doping concentration and annealing temperature was varied, it was found that the crystallite size decreased as the parameters were increased. The calculated crystallite sizes of Zn-CdSeNPs ranged from 17.72 to 28.11 nm. There was an observation of variation in the lattice strain of the synthesized nanoparticles. Optical analysis displayed changes in the absorbance as growth temperature, Zn doping concentration and annealing temperature were varied. The estimated bandgap energies of nanoparticles estimated using Tauc's plot were 1.83, 1.65, 1.71, 1.66, 1.67, 1.71 and 1.8 eV for samples prepared at a growth temperature of 25, 45, 60, 75, 90, 105 and 120°C respectively. Doping CdSe with Zn decreased the bandgap energy from 2.23 to 1.92 eV. The band gap energies obtained for samples annealed at 150, 175, 200, 225, 250, and 275°C are 2.10, 1.96, 2.24, 1.18, 2.53 and 1.23 eV respectively. All the as-prepared samples absorbed light at different wavelengths. This is confirmed by the PL results where varying emission wavelengths were observed. Maximum emission peak intensity was obtained when the samples were prepared at growth temperature of 90°C. Changes in PL emission intensity were noted with varying dopant concentrations and annealing temperatures, indicating their influence on the optical behavior of the nanoparticles. The functional groups determined using from FT-IR spectra showed the expected groups in all the samples with Cd-Se and Zn-Se bond observed at the finger print region. As the concentration of zinc dopant increased, the intensity and sharpness of the peaks increased bands appearing around 500–700 cm^{-1} . In this study, CdSe and Zn-CdSe nanoparticles were successfully synthesized using the sol-gel method. Through systematically experimentation, the optimum growth temperature, doping concentration, and annealing temperature were determined, resulting in enhanced structural and optical properties of the nanoparticles for solar cell applications.

TABLE OF CONTENTS

DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
LIST OF TABLES	ix
LIST OF FIGURES	x
ACRONYMS AND ABBREVIATIONS	xii
DEFINITION OF OPERATIONAL TERMS	xiii
CHAPTER ONE: INTRODUCTION	1
1.1 Background Information.....	1
1.2 Statement of the Problem.....	2
1.3 Research Objectives.....	3
1.3.1 General Objective	3
1.3.2 Specific Objectives	3
1.4 Research Questions.....	3
1.5 Significance of the Study	4
1.6 Scope and Limitation	4
1.7 Contributions of the Thesis	5
1.8 Organization of the Thesis	5
CHAPTER TWO: LITERATURE REVIEW	7
2.1 Introduction.....	7
2.2 Fossil Fuel.....	7
2.3 Impacts of Burning Fossil Fuels	8
2.3.1 Climate Change.....	8
2.3.2 Global Warming.....	9
2.4 Solar Cells.....	9
2.5 Nanoparticles Based Solar Cells.....	11
2.6 Cadmium Selenide Nanoparticles	12
2.7 Effects of Growth Temperature on the Structural and Optical Properties of CdSe Nanoparticles	12
2.8 Effects of Doping Semiconductors Nanoparticles	13
2.9 Dopants	14
2.9.1 Iron.....	14
2.9.2 Gallium	15
2.9.3 Zinc	15
2.10 Effects of Annealing Temperature on Nanoparticles	15
2.11 Methods Preparing Nanoparticles	16

2.11.1 Chemical Co-precipitation	17
2.11.2 Sol-gel Process	17
2.11.3 Hydrothermal Synthesis of Nanoparticles	18
2.12 Analytical Techniques used to Analyze Nanomaterials	18
2.12.1 Fourier Transform Infrared Spectroscopy	18
2.12.2 Ultraviolet-visible Spectroscopy	19
2.12.3 X-ray Diffraction	20
2.12.4 Scanning Electron Microscope (SEM)	21
2.13 Summary	22
CHAPTER THREE: MATERIALS AND METHODS	23
3.1 Introduction	23
3.2 Materials	23
3.3 Method	23
3.3.1 Preparation of Se ions	23
3.3.2 Synthesis of CdSe Nanoparticles	23
3.3.3 Synthesis of CdSe Nanoparticles at Different Growth Temperature on the Structural and Optical of CdSe	24
3.3.4 Synthesis of Different Zinc mol % Dopant Concentration on Structural and Optical Properties of CdSe Nanoparticles	24
3.3.5 Synthesis of Zinc Doped CdSe Nanoparticles Annealed at Different Growth Temperature on Structural and Optical Properties of Zn-CdSe Nanoparticles	24
3.4 Analytical Techniques	25
3.4.1 FTIR	25
3.4.2 UV-Vis Spectroscopy	26
3.4.3 X-ray Diffraction	27
3.4.4 Photoluminescence Spectroscopy	29
3.5 Summary	29
CHAPTER FOUR: RESULTS AND DISCUSSION	30
4.1 Introduction	30
4.2 Effects of Growth Temperature on the Structural and Optical Properties of CdSe Nanoparticles	30
4.2.1 Photoluminescence Spectroscopy	30
4.2.2 Optical Properties	32
4.2.3 XRD Analysis	34
4.2.4 FT-IR Analysis	38
4.3 Effects of Doping Concentrations on Material Properties of CdSe:Zn Nanoparticles	39
4.3.1 X-ray Diffraction (XRD) Analysis	39

4.3.2 Photoluminescence Spectroscopy	43
4.3.3 Optical Properties.....	44
4.3.4 FT-IR Analysis	47
4.4 Effects of Annealing Temperature on Structural and Optical Properties of CdSe:Zn Nanoparticles	48
4.4.1 X-ray Diffractions (XRD) Analysis	48
4.4.2 Optical Analysis	51
4.4.3 Photoluminescence Spectroscopy	53
4.4.4 FT-IR Analysis	55
4.5 Summary	56
CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS	57
5.1 Conclusion	57
5.2 Recommendations.....	59
5.2.1 Recommendation for policy.....	59
5.2.2 Recommendation for Future Work.....	60
REFERENCES.....	62
APPENDICES	76

LIST OF TABLES

Table 4.1: PL intensity and emission band of samples prepared at different growth temperatures	31
Table 4.2: summarizes the crystallite size, FWHM and the lattice parameters of CdSe nanoparticles prepared at different growth temperatures.	36
Table 4.3: shows the summarized crystal size, lattice constant d, a and FWHM of Zn-CdSeNPs with different Zn concentration.	42
Table 4.4: Summarized absorption peaks, edge and bandgap energy of Zn-CdSeNPs	47
Table 4.5: shows the summarized crystal size, lattice constant d, a and FWHM of Zn-CdSeNPs with different annealing temperature.	50

LIST OF FIGURES

Figure 2.1: The global production of carbon dioxide from fossil fuel (Heede, 2023).	7
Figure 2.2: Types of solar cell technologies.....	11
Figure 2.3: Stages of sol-gel method	18
Figure 2.4: FT-IR spectrum showing the main regions.....	19
Figure 2.5: UV-Vis spectra of CdSe nanoparticle (Acharya et al., 2011)	20
Figure 2.6: XRD pattern of CdSeNP's (Suresh & Arunseshan, 2014)	21
Figure 2.7: a) SEM images of CdSe NPs prepared with SeCl ₄ b) SEM images of Cd (OA) ₂ .H ₂ O 2H ₂ O (Kurtina et al., 2023)	22
Figure 3.1: Shimadzu IR spirit FT-IR model	26
Figure 3.2: Evolution one plus UV-Vis spectroscopy at Murang'a University of Technology.....	27
Figure 3.3: ARL EQUINOX 100 X-ray Diffractometer	28
Figure 3.4: SP-LF97 model PL spectroscopy at Murang'a University of Technology	29
Figure 4.1: Spectra of CdSeNPs prepared at different growth temperature	30
Figure 4.2: Shows the variation of photoluminescence intensity with temperature ..	32
Figure 4.3: UV-Vis spectra of CdSeNPs synthesized at different growth temperatures	33
Figure 4.4 Tauc's plot of CdSeNPs prepared at varying growth temperatures.....	34
Figure 4.5: XRD pattern of CdSeNPs prepared at varying growth temperatures.....	35
Figure 4.6: Relationship between crystal size, peak intensity and growth temperature	37
Figure 4.7: W-H plot for CdSeNPs synthesized at growth temperature of (a) 60 and (b) 120 °C	38
Figure 4.8: FT-IR spectra of CdSeNPs synthesized at a growth temperature of 25, 60 and 90 °C.....	39
Figure 4.9: (a) XRD spectra of Zn-CdSe and (b) enlarged XRD peak [111] of Zn-CdSe nanoparticles.....	40
Figure 4.10: Relationship between FWHM, Crystal size and Zn mol %.....	43
Figure 4.11: (a) PL emission spectra of varying concentration of Zn-CdSeNPs (b) Relationship between PL Intensity, emission wavelength and mol % of Zn dopant in CdSeNPs	44
Figure 4.12: UV-vis spectra of Zn-CdSe nanoparticles	45
Figure 4.13: Shows the Tauc's plot of different concentration of Zinc dopant	46
Figure 4.14: FT-IR spectra of Zn doped CdSe nanoparticle	48
Figure 4.15: XRD pattern depicted by Zn doped CdSe nanoparticles.....	48

Figure 4.16: Relationship between FWHM,crystallite size and annealing temperature	51
Figure 4.17: The UV-vis absorbance spectra of Zn-CdSeNPs.....	52
Figure 4.18: Tauc's plot of Zn-CdSe nanoparticles at varying % Zn mol concentrations	53
Figure 4.19: The emissions spectra of Zn-CdSe nanoparticles prepared at different annealing temperatures	54
Figure 4.20: FTIR spectra of Zn-CdSeNPs annealed at different.....	55

ACRONYMS AND ABBREVIATIONS

CAI	Climate Accountability Institute
CdSeNP	Cadmium Selenide Nanoparticles
CuONP	Copper oxide nanoparticles
DSSC	Dye Sensitized Solar Cells
eV	Electron Volts
FCCC	Framework Convention on Climate Change
FTIR	Fourier Transform Infrared spectroscopy
FWHM	Full Width at Half Maximum
GHG	Greenhouse Gases
HOMO	Highest Occupied Molecular Orbital
ICDD	International Convention Diffraction Data
LUMO	Lowest Unoccupied Molecular Orbital
NPs	Nanoparticles
NRC	National Research Center
pH	Potential of hydrogen
PL	Photo Luminescence spectroscopy
PV	Photovoltaic
SEM	Scanning electron microscope
UV-Vis	Ultra violet visible spectroscopy
XRD	X-ray diffraction

DEFINITION OF OPERATIONAL TERMS

Synthesis - The process of producing nanoparticles through chemical, physical, or biological methods to achieve desired size, shape, and composition.

Characterization - A set of analytical techniques used to determine the physical, chemical, structural, and optical properties of synthesized materials.

Doping - The intentional introduction of foreign atoms (dopants) into a material to modify its electrical, optical, or structural properties.

Annealing - A heat treatment process used to improve crystallinity, reduce defects, and enhance the physical properties of a material.

Bandgap Energy - The energy difference between the valence band and conduction band of a semiconductor; it determines the material's optical and electronic behavior.

Photoanode - A light-sensitive electrode that absorbs photons and generates electrons, typically used in solar cells or photo-electrochemical cells.

Crystal Size - The average dimension of a coherent, ordered region in a polycrystalline material, often estimated from XRD data using the Scherrer equation.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

The global transition towards renewable energy sources is imperative to mitigate climate change and secure sustainable energy for future generations. It is estimated that the power demand would increase beyond 30TW by 2050 (Roy *et al.*, 2020). Since burning fossil fuels is the traditional method of producing power, extensive research is being done to develop an efficient power production system because the rise in power requirements cannot be met. Solar energy, in particular, holds immense potential due to its abundance and environmental friendliness. Photovoltaic (PV) technology, which converts sunlight directly into electricity, plays a central role in harnessing solar energy. Numerous researchers are drawn to the II-VI group of binary semiconductors due to their broad variety of applications in solid state devices, including solar cells, opto-electronic devices, and solar selective coatings (Yadav, 2012a). CdSe is an important II-VI group semiconductor widely utilized in opto-electronic devices and photo-electrochemical solar cells. CdSe possesses a direct bandgap value 1.7eV, high absorption coefficient in the visible spectrum, and compatibility with solution-based processing techniques thus, it stands out as a suitable candidate for use in solar cell technologies (K. Sharma *et al.*, 2012).

When the CdSe material is crystalline, it typically does so in three different phases: cubic (zinc blende), hexagonal (wurtzite), or a combination of both the hexagonal and cubic phases. There has been a lot of interest in the phase change of CdSe nanostructures. The effects of annealing, doping concentration, mechanical grinding, etc., can cause such a phase shift to be seen (Yadav, 2012b). When it comes to solar cell applications, CdSe material is a more appealing option financially than the well-studied CdTe absorber material. Researchers are paying close attention to Cd-based compounds (CdSe and CdTe) solar cells even though Cd is poisonous. These compounds could be potential alternatives as compared to silicon solar cells and perovskite solar cells which are costly, less stable and rapidly degrade respectively.

Despite its favorable properties, CdSe-based solar cells face challenges that limit their efficiency and commercial viability. Chief among these challenges are carrier recombination losses and relatively low open-circuit voltage, which hamper the overall device performance. To address these limitations and further enhance the efficiency of CdSe-based solar cells, doping or co-doping with transition metal elements has emerged as a promising strategy. Dopant addition to the CdSe host lattice may change the structure and expose more active sites, which is good for catalytic, electrochemical, and photovoltaic applications (Huang *et al.*, 2020). Appropriate dopants could also regulate the conductivity and type of conduction in CdSe. Doping CdSe with transition metal ions such as zinc (Zn) offers the possibility of enhancing its optoelectronic properties for improved solar cell performance (Gong *et al.*, 2020).

This research aims at synthesizing and characterizing CdSe:Zn nanoparticles using sol-gel method of synthesis. The sol-gel method of synthesizing nanoparticles offers advantages such as facile control over composition, morphology, and size distribution, making it a suitable technique for producing semiconductor nanocrystals with tailored properties for solar cell applications.

1.2 Statement of the Problem

The amount of greenhouse gases (GHG) released into the atmosphere has been increasing since 1990 due to industrialization. According to the National Oceanic and Atmospheric Administration (NOAA) the level of man-made greenhouse gases has increased by 49%. These gases have led to global warming and climate change which has affected the lives of living organisms on planet earth. Fossil fuels are the major contributor of greenhouse gases since they emit about 34 billion tone of CO₂ into the atmosphere yearly, therefore there is need to develop alternative source of renewable or non-renewable energy to curb the utilization of fossil fuels and solar energy is a promising technology (Kabir *et al.*, 2018).

Solar energy is free, abundant, clean and does not make any kind of noise to the environment. Solar energy is green energy and can be harnessed by use of solar cells. Solar cells convert sun radiation into solar energy but their efficiency and cost limits its application. The efficiency of photovoltaic cells is currently less than 23% (Polman *et al.*, 2016), this efficiency can be improved using nanoparticles. Nanoparticles are

materials that have size range of 1-100nm. These nanoparticles can be prepared from transitional metals such as ZnO, SnO₂, CdSe, and CdO, etc. Structural and morphological properties of nanoparticles affect their efficiency in solar cells, these properties are affected by growth temperature, pH, concentration of dopant and annealing temperatures. These properties can be improved by using dopants. Doping CdSe nanoparticles with Zn ions offers a promising approach to tailor structural and optical properties for improved photovoltaic performance. Growth temperature and annealing temperature are some of the key factors that affects structural, optical and morphological properties of nanoparticles (Waweru *et al.*, 2024).

1.3 Research Objectives

1.3.1 General Objective

To synthesize and characterize CdSe:Zn nanoparticles for possible solar cell applications.

1.3.2 Specific Objectives

1. To study the effects of growth temperature on the structural and optical properties of CdSe nanoparticles.
2. To examine the effects of doping concentrations on material properties of CdSe:Zn nanoparticles.
3. To investigate the effects of annealing temperatures on the structural and optical properties of CdSe:Zn nanoparticles.

1.4 Research Questions

1. How does growth temperature affect the structural and optical properties of CdSe nanoparticles?
2. In which way does Zn mol% concentration affect the structural properties of CdSe nanoparticles?
3. What are the effects of annealing temperature on the structural and optical properties of CdSe nanoparticles?

1.5 Significance of the Study

The importance of this study lies in its possibility to advance solar cell technology, offering a pathway towards higher efficiency and sustainability. Through the synthesis and characterization of CdSe:Zn nanoparticles, this research might overcome existing limitations in solar cell performance by tailoring the properties of these materials. While elemental cadmium and selenium are toxic in their free forms, their combination into a stable compound like CdSe significantly reduces their hazardous nature. In this study, CdSe:Zn nanoparticles were used due to their stability, controlled synthesis, and promising application in solar cells. Their use supports the development of clean energy technologies, contributing to reduced dependence on fossil fuels and addressing environmental sustainability. By exploring the potential of CdSe:Zn nanoparticles, this research contributes to the development of alternative energy solutions aligned with global efforts to reduce carbon emissions and promote environmental sustainability. Moreover, the economic viability of solar energy is bolstered by the potential for low-cost production of CdSe:Zn nanoparticles using scalable synthesis methods, promising wider accessibility to solar technology. This research has implications beyond academia, extending to industrial stakeholders seeking to develop commercial solar cell technologies with improved performance and cost-effectiveness. Thus, by exploring the intricate relationship between composition, structure, and optoelectronic properties, this study offers insights that could catalyze the transition towards a cleaner and more sustainable energy in future.

1.6 Scope and Limitation

This research focused on the synthesis and characterization of zinc-doped cadmium selenide (Zn-CdSe) nanoparticles using the sol-gel method. The study involved synthesizing both pure CdSe and Zn-doped CdSe nanoparticles. The scope of optimization was limited to three key parameters: growth temperature, dopant concentration and annealing temperature.

Only zinc (Zn) was used as the dopant material. The growth temperatures investigated ranged from 25°C to 120°C, while annealing temperatures were varied between 150°C and 275°C. The doping concentration of zinc in CdSe nanoparticles was explored within the range of 1% to 15%.

The study was limited to this specific doping range due to practical challenges in maintaining crystal quality and uniform dispersion at higher dopant levels, which may lead to phase separation or structural distortion.

1.7 Contributions of the Thesis

This research contributes to the ongoing efforts in developing efficient, low-cost, and environmentally friendly photovoltaic materials by focusing on the synthesis and characterization of Zn-doped CdSe nanoparticles. The study provides the following contributions:

1. **Optimized Synthesis Protocol:** It establishes an effective sol-gel synthesis method for producing Zn-doped CdSe nanoparticles, optimizing parameters such as growth temperature, doping concentration, and annealing conditions for enhanced structural and optical performance.
2. **Doping Influence Analysis:** It provides a detailed investigation on how zinc incorporation modifies the crystallinity, particle size, and band gap energy of CdSe, thereby tuning its properties for better light absorption and charge carrier dynamics.
3. **Comprehensive Characterization:** Using FTIR, UV-Vis, XRD and PL the study delivers a clear understanding of how synthesis parameters influence structural and optical properties, which are directly relevant to solar cell applications.
4. **Band Gap Engineering for Solar Applications:** The work demonstrates how Zn doping can induce a controlled band gap shift (red or blue shift), crucial for matching solar spectrum absorption, thereby improving the suitability of CdSe-based materials as photoanodes in solar cells.
5. **Foundation for Future Device Integration:** While this study does not fabricate full solar cells, it provides fundamental knowledge and experimental data that can serve as a base for integrating Zn-CdSe nanoparticles into practical photovoltaic devices.

1.8 Organization of the Thesis

Chapter One begins with the introduction summarizing the Background of the Study, Statement of the Problem, Objectives of the Study, Research Questions, Significance of the Study, Justification of the Study, Scope and Limitation of the Study.

Chapter Two which is the Literature Review involves discussion on Fossil fuel, Solar cells, Nanoparticles based solar cells, Dopants, Methods of preparing nanoparticles and analytical techniques used to analyze nanoparticles.

Chapter Three involves outlining of Materials, Methods and Characterization employed in order to achieve the specific objectives.

Chapter Four involves Results and Discussion of data obtained from the various characterization techniques of the synthesized nanoparticles using X-ray diffraction (XRD), Ultra violet visible spectroscopy (UV-Vis) and Photoluminescence (PL) spectroscopy. The results have been discussed in order of the research objectives (i) Effects of growth temperature on optical and structural properties of CdSeNPs, (ii) Effects of different Zn % mol doping on CdSe nanoparticles' optical and structural properties, and (iii) Effects of annealing temperature on structural and optical properties of zinc doped cadmium selenide nanoparticles.

Chapter five involves conclusion and recommendations.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter summarizes the literature on nanoparticle application and methods that have been used by different scholars to synthesize and characterize them. It also gives details on the effects of doping nanoparticles for various application.

2.2 Fossil Fuel

Burning of fossil fuels produce harmful gases to the environment, carbon dioxide being the most prominent product (Soeder, 2021). The two key greenhouse gases(GHG) carbon dioxide and methane are produced in billions of tons annually from the burning of fossil fuel for energy and transportation (Tollefson, 2022). In 2020 the CO₂ produced was 35 billion metric tons compared to 1950 which had only 5 billion metric tons (Heede, 2023) this might have been contributed by the fast growth of industries and urbanization. Figure 2.1 shows the global production of CO₂ from fossil fuels and cement emission from 1820 to 2020 from climate accountability institute (CAI) (Heede, 2023).

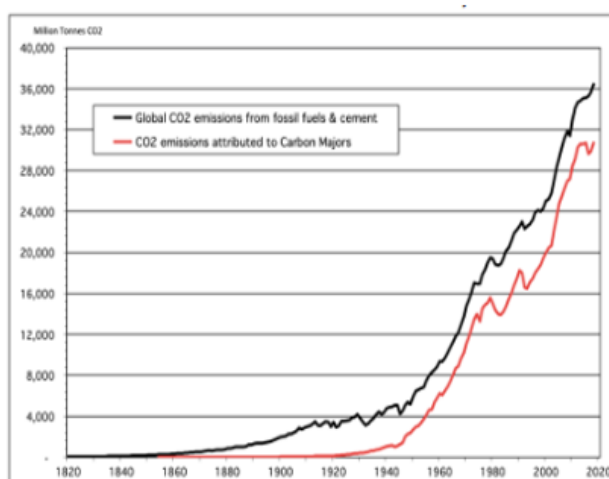


Figure 2.1: The global production of carbon dioxide from fossil fuel (Heede, 2023).

The major challenge for 21st century include the energy insecurity, anthropogenic climate change and physical inaccessibility of energy or prices that are not that competitive (Fantazzini *et al.*, 2011).

2.3 Impacts of Burning Fossil Fuels

The major environmental challenges that are associated with fossil fuels include the climate change, global warming and the greenhouse gases (GHG). These effects have been felt throughout the world as evidenced by heatwaves, rise in sea levels among other effects.

2.3.1 Climate Change

Framework Convention on Climate Change (FCCC) define climate change as “a change in climate that is attributed directly or indirectly to human activity, that alters the composition of the global atmosphere, and that is in addition to natural climate variability over comparable time period” (Söder, 2023). Climate change is a major concern in this century as evidence by high record of rainfall and heatwaves globally. Factors that influence the sun’s radiation received, which are also lost in the space affects the redistribution of energy and thus causing climate change (Change, 1996). The two major causes of climate change are anthropogenic and natural causes.

Anthropogenic causes are mainly due to human activities such deforestation. Trees utilized carbon dioxide from atmosphere and convert it through photosynthesis into living biomass (FAO 2010). Forests are referred to as carbon sinks since they take more carbon dioxide than what they produce (Haghipour & Burg, 2014). Deforestation released carbon dioxide that had accumulated in forest soil and trees. According to national research Centre (NRC) global warming is a result of: human activities which are adding heat trapping greenhouse gases such as methane, nitrous oxide and water vapor to the atmosphere. (Ellison *et al.* 2018)

of Although human activities are the major cause of climate change, there are natural causes that might have slightly contributed to it, such as variations in the sun’s intensity. Natural changes that affect the amount of solar energy reaching the Earth’s surface contribute to climate change (EPA 2010; IPCC 2018). Other natural factors include volcanic eruptions, which release large amounts of greenhouse gases and dust

particles into the atmosphere. The accumulation of dust particles, whether from natural events or anthropogenic sources, can also influence the wavelength solar radiation reaching the surface by scattering and absorbing light. This alters the spectral quality and intensity of sunlight, potentially impacting both climate patterns and optical measurements taken from the Earth's.

2.3.2 Global Warming

Global warming is one of the topics that has captured the attention of the world due to its massive impact and which cannot be ignored. Human activities such as the burning of fossil fuels and deforestation have led to increase in emission of carbon dioxide. Carbon dioxide is a good absorber of radiation from the earth surface and therefore, increasing the amount of carbon dioxide on the earth surface will act as a blanket, keeping it warmer than it could have been. Other gases such as methane from agricultural and mining activities have also increased causing global warming. If the amount of carbon dioxide emitted into the atmosphere is not regulated, the average temperature will rise by a third degree Celsius. Carbon dioxide for instance overlap with infrared on the regions they absorbed energy (2000-15000nm) thus soaks up most of the infrared radiation vibrate and re-emit half of it onto the earth as heat thus causing greenhouse effects (Florides & Christodoulides, 2009)

2.4 Solar Cells

To reduce the amount of fossil fuel being burnt for energy production, there is need for alternative renewable energy such as the utilization of naturally available solar which can be easily harnessed from the sun. Solar cell also known as photovoltaic cell (PV) is a device that converts solar energy into electrical energy directly. They are the building blocks of solar panels used to harness energy that used in various applications “The amount of solar radiation that strike the earth on one day $4.3 \times 10^{20} \text{W/m}^2$ is sufficient to meet global energy demand of one year (Lewis & Nocera, 2006)”. Solar cell is one of the device that promote creation of clean and safe energy which is renewable (Letcher, 2020).

Silicon based solar cells were the first generation of solar cells to be manufactured. The efficiency of silicon based solar cells were very low thus led to development of thin film and dye sensitized solar cell (DSSC) (Saif *et al.*, 2023) . The efficiency of

thin film and DSSC were high in comparison to silicon based solar cells. The latest type of solar cell is organic solar cells which has high efficiency compared with the rest. The development of these solar cells are hindered by their cost and efficiency (Sharma *et al.*, 2015). Efficiency of photovoltaic solar cell (photovoltaic conversion) is given as the amount of electricity that can be generated from the conversion of fraction of sun's energy. Solar panels are collection of tiny solar cells. Accumulation of dust in the atmosphere or cloud has great impact on the wavelength which in turn lowers the intensity of radiation and the capability of solar cell. In addition to dust, other pollutants that are emitted from heavy vehicles have caused air pollution which are deposited on the solar cell (Kazem & Chaichan, 2016). (Wei *et al.*, 2017) determined the efficiency of solar panel at different time of the day in four days and the largest efficiency was observed at 11:30 am having 35% at an irradiance of 391 W/m².

There are three key factors that determine the working mechanism of a solar cell: absorption of light to generate electron-hole pairs (charge carriers), dissociation and movement of these carriers to their respective electrodes, and the creation of a potential difference at the p-n junction. This potential difference arises from the diffusion of electrons and holes across the junction, forming a depletion region that establishes an internal electric field. The built-in voltage at the junction enables the flow of current when the cell is connected to an external circuit, and it can be influenced by visible light. In high power application, large and bulky solar panels are used and these solar panels will require big roof to fit in and space so that it can trap as much as possible solar radiation (Tsoutsos *et al.*, 2005). The principle of electron hole creation is widely used in modern photovoltaic technology, where each cell is composed of p and n type layers. In this principle the photon with adequate energy hit the p and n junction such that electron is released. The electron released used the absorbed energy to move from one layer to another. The p type semiconductor has more holes whereas n type semiconductor has more electrons. In solar cells, electron hole recombination takes place which leads to electric field being created in the depletion region. There are various materials that have been applied in photovoltaic solar cells such as Si, CdTe, CuInS. Depending on the material used to make photovoltaic cells, figure 2.2 below show different classes of solar cells.

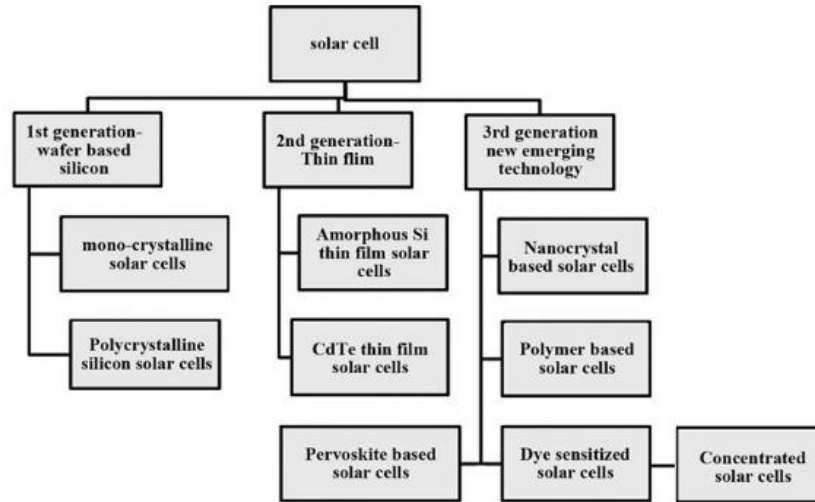


Figure 2.2: Types of solar cell technologies (Roy et al., 2020)

2.5 Nanoparticles Based Solar Cells

Nanoparticles are materials that have a size range between 1-100nm. Solar cells based on these nanoparticles constitute of semiconductors mainly from transition metal groups. As a result of advancement in technology, these nanoparticles are meant to replace semiconducting materials in the bulky state such as Si or CdTe. In conventional semiconductor solar cell, photons stimulates an electron thereby generating an electron hole (Dubey *et al.*, 2013). In nanoparticles, numerous electron-hole pairs can be formed when nanoparticles generated from the same semiconductor are strike by a photon. Two, three and seven are the major electrons holes that have been observed in some of the cases (Sethi *et al.*, 2011)

Cadmium chalcogenide(CdX, with X= S, Te and Se)have gained interest in the last decades since they have relatively small bandgap and thus can harvest photons in the observable infrared regions (Houghton, 2009) the bandgap for CdSe is 1.73eV (Peter, 2011). Varying the size of nanoparticle can help to fine tune the size of bandgap therefore it is important to consider the physics and chemistry of CdX nanoparticles. CdSe has attracted much interest from the quantum dot silicon solar cells (QDSSC) field due to its remarkable electronic properties (Choi *et al.*, 2014).

Nanomaterials are materials with low dimension (1-100nm) and have unique physical and electronic properties than the bulk materials, these nanomaterials have recently been researched for their practical uses (Ye *et al.*, 2011). CdSe is one of the strongest materials used in photodetectors due to its high absorption coefficient (Jin *et al.*, 2014).

Nanoparticles are used in solar cell to improve their electronic and optical properties, these nanoparticles can either be metallic or metal oxides, some of the oxides that have been widely used include ZnO, CuO and TiO₂ which all have thin and sizeable band gap (Sun *et al.*, 2013). The size and shape of inorganic nanoparticles can be tailored to meet specific property requirements (de Freitas *et al.*, 2010).

2.6 Cadmium Selenide Nanoparticles

Among the group 2-7 semiconductors CdSe is widely used semiconductor that crystalize in wurzite or zinc blende which is basic cubic structure. The compatibility of CdSe bandgap with solar spectrum makes it interesting in solar cells (Yadav, 2012b). When impurities are introduced to crystal structure of CdSe it affects its properties. CdSe nanopowder properties vary based on the nanostructure's morphology and dimensions. Colloidal nanocrystals of high quality and monodisperse size and shape has been used widely in industries for biological labeling reagents. The percentage of surface atoms of CdSe nanoparticles increases from 20 to 100% as the crystal size decrease from 10 to 1 nm (Gupta & Ramrakhiani, 2009).

2.7 Effects of Growth Temperature on the Structural and Optical Properties of CdSe Nanoparticles

The distinctive optical characteristics of semiconducting nanoparticles (NPs) are key factors driving significant interest from nanotechnologists and material scientists worldwide. One of the primary optical properties of semiconductor NPs is their band gap energy. Advances in nanoscience technology have enhanced the understanding of the fundamental properties and potential applications of various nanomaterials, sparking increased interest in the study of metal selenide NPs. This growing interest stems from the promising implications these nanomaterials hold for fundamental principles in physics and chemistry, which attracts researchers from a wide range of scientific fields to explore the opportunities in nanoscience and nanotechnology (Kiprotich *et al.*, 2019).

For this reason, the temperature at which CdSe nanoparticles grow is a critical factor in determining its material properties. At higher temperature large crystal sizes and improved crystal quality is observed as evidenced by more intense XRD pattern observed by (Dejene, 2022). To obtain high quality nanoparticles, growth temperature should be optimized to obtain sufficient energy required for two chemical species to collide and cause reaction (Venci *et al.*, 2023). The reported room temperature bandgap energy of CdSe nanoparticles is 1.74 eV for wurtzite structure and 1.66 eV for zinc blende structure (Ghazy *et al.*, 2020). Increasing growth temperature of ZnO from 65°C to 95°C resulted in nanorods with improved crystal quality and higher aspect ratio and thus enhanced optical properties (Abdulrahman *et al.*, 2021). These changes are important for application in electronic devices where crystallinity and morphology impacts device efficiency thus the need to obtain the optimum growth temperature of CdSe nanoparticles used in solar cells. There is limited number of published studies focusing on the influence of growth temperature on the properties of CdSe nanoparticles, therefore further research is needed in this area to bridge the knowledge gap and enhance the application of CdSeNPs in energy harvesting devices.

2.8 Effects of Doping Semiconductors Nanoparticles

The nanomaterials of group II-VI conductors are being pursued due to their ability to control their morphology and shape. CdSe material has a bandgap energy comparable with solar energy spectrum, adjustable n and p type of conductivity depending on the dopant and high absorption coefficient in visible and infrared region (Hassen *et al.*, 2020). CdSe nanoparticles degrades when exposed to sunlight for a very long time thus decreasing the efficiency of solar cells. They also have lower conversion efficiency when compared to other nanoparticles such silicon (Terricabres-Polo *et al.*, 2024). To improve CdSe nanoparticles properties for solar cells application, several factors such as method of preparation, use of dopant, growth temperature and annealing temperature are being considered.

Introducing alien element to semiconductors have tremendous effects on the optical, morphological and electronic properties. For example when (F. A. Zhao *et al.*, 2019) prepared Ag doped CdSe quantum dots, it was observed that incorporation of Ag into core region leads to metallic-like electronic properties. Several transitional metals are

used as dopants in CdSe nanoparticles to modify the optical, electronic and magnetic properties of CdSe. They include Ag, Mn, Co, and Ni. In this study zinc was used as dopant in CdSe nanoparticles used in solar cell application because Zn^{2+} has smaller ionic radius ($0.74\text{\AA}$) compared to Cd^{2+} ($0.95\text{\AA}$) thus the lattice contraction in nanoparticle obtained can lead to better crystallinity, improving charge carrier mobility in photovoltaic and optoelectronic devices (S *et al.*, 2016). Dopant are introduced via different techniques to the host for example sol-gel, microwave assisted, green synthesis and laser ablation.

Sol gel method is highly recommended in synthesis of doped nanoparticles since it is uncomplicated method with explicit control of physical properties of materials (Laurent *et al.*, 2008) green synthesis is also a rising technique that has been developed that utilizes plant extract and this method does not use toxic solvent which makes it environmental friendly (Jamkhande *et al.*, 2019). Water is mainly used to avoid using toxic solvents. In laser ablation the laser beam is irradiated onto the target surface inside a vacuum chamber which makes its to evaporate. (Menazea *et al.*, 2020) doped selenium nanoparticles in polyvinyl alcohol blend using laser ablation method.

2.9 Dopants

2.9.1 Iron

Iron has atomic number of 26 and mass number of 56. Fe based nanoparticles have been widely studied and used in various application such as Ferro fluids and magnetic cell separation (Arsalani *et al.*, 2021). (Singh & Verma, 2012) confirmed from the XRD results that Fe has a solubility limit that is less than 6% in CdSe. Iron has been doped in various metal oxide such as TiO_2 and the UV spectrum was observed to have shift to visible region when iron was added. When Fe is doped to CuO nanotubes for solar cell application it was observed that there was a notable blue shift in the band gap in contrast to undoped CuO nanotubes. This indicates that Fe is a good dopant in metal or metal oxides used in solar.

2.9.2 Gallium

Gallium is post transitional metal having atomic number of 31 and mass number of 71 (Gómez *et al.*, 2024) prepared Ga nanoparticles and used it as reflection prevention structures on solar cells, an increase by 18% of short-circuit current was observed. GaNP's limits the light that go through the device. This was observed in local surface Plasmon resonance (LSPR). This property has enabled it to be used as dopant in various semiconductors material to improve their conductivity. (Catalán-Gómez *et al.*, 2024) prepared gallium doped titanium oxide nanoparticles that was used to and it was observed that the optimum doping was 3.125% and the presence of gallium dopant had an important influence on photocatalytic activity on the production of hydrogen gas.

2.9.3 Zinc

It is a transitional element with atomic number of 30 and mass number of 66. (W. Zhao *et al.*, 2017) introduced zinc to replace lead in perovskite solar cell due to its unique properties and the observation was that the efficiency increased from 17.44 to 18.18%. Zinc nanoparticles are widely used in medical field due to its low toxicity and has been used majorly in drug delivery (Faiz *et al.*, 2015). Zinc is an excellent dopant material used to improve the properties of semiconductors metals. Zinc has atomic radius of 0.138nm which is closer to that of Cadmium with 0.154nm thus making it easier to be incorporated into the lattice sides of the Cadmium.

2.10 Effects of Annealing Temperature on Nanoparticles

Annealing temperature is one of the thermodynamic parameters that have an impact on the structural, optical, growth rate and size distribution of nanoparticles. The emission color and purity of nanoparticles are influenced by their crystallite size and size distribution. When the annealing temperature of nanoparticles is controlled, the size and size distribution of nanoparticles can be controlled to a certain extent. Good photoluminescence properties can be obtained when the surface structure of nanoparticles is controlled, and this will help in different applications of the nanoparticles (Kiprotich *et al.*, 2018) . The electrical, structural, physical, chemical and optical properties of nanoparticles depend on the size of the nanostructure due to quantum confinement effects (Lambora & Bhardwaj, 2023).

Annealing involves heating materials to a defined temperature and sustaining that temperature for a determined duration. This is necessary to alter the physical chemical and workability of material. (Kuo *et al.*, 2006) prepared Al-doped ZnO and annealed at different temperatures, the XRD pattern showed that when samples were annealed at a temperature of 850°C there was an increased in peak intensity meaning that the crystallinity of the sample was high. The time at which samples are annealed also affects the properties of materials. For example (Enriquez, 2013) annealed CdS at 400 °C at different time interval of five, fifteen, thirty, forty five and sixty minutes and the XRD pattern of the samples showed that intensity of the peaks increased with annealing time and temperature (Akylbekova *et al.*, 2024)

The structural properties of nanoparticles such as crystal size, shape and crystal structure are influenced by temperature at which they are grown. Temperature is a key factor in modifying the structural and optical characteristics of nanoparticles. (Pandey *et al.*, 2013) synthesized Ag nanoparticles at a varying growth temperature and the nanoparticles obtained were analyzed using UV vis spectroscopy. It was observed that as temperature increases, strongest absorption band shifted to a longer wavelength. This means that crystal size of Ag nanoparticles increased with an increased in growth temperature which align with what was observed with transmission electron microscope. Growth temperature is a critical parameter that shapes the structural and optical properties of zinc-doped CdSe nanoparticles. By carefully controlling this temperature, researchers have optimized crystallinity, particle size, band gap energy, and photoluminescence are the factors essential for enhancing light absorption, charge mobility, and overall efficiency in solar cell applications. Finding the ideal growth temperature allows for the creation of zinc-doped CdSe nanoparticles with tailored properties that support high-performance photovoltaic devices. (Faiz *et al.*, 2015)

2.11 Methods Preparing Nanoparticles

Nanoparticles can be prepared using several methods such as chemical co-precipitation, sol-gel method, electrochemical synthesis, hydrothermal synthesis, chemical vapor deposition and others.

2.11.1 Chemical Co-precipitation

In chemical co-precipitation it produces chalcogenides with strong compositional control. The reacting material precipitate after the reaction is complete and their solubility depends on the pH of the solvent. The reactant precipitate as a precursor in simple solvent. This method has been widely used to prepare nanoparticles for example (Sridevi *et al.*, 2019) doped CdSe with 5% and 10% Fe and it was observed that the affiliation of Fe to lattice of CdSe inhibits the reintegration of electron and hole pairs by generating impurity levels in the bandgap. Chemical co-precipitation often struggles with achieving uniform doping of elements (e.g., zinc in CdSe), which can result in phase segregation and non-uniform material properties (Lims *et al.*, 2024).

2.11.2 Sol-gel Process

Sol gel method (solution method) is widely employed as compared to any other method as a result of its distinctive properties and characteristics, it has the ability to generate nanoparticles of the same size and high quality on an industrial scale (Rahman & Padavettan, 2012). In addition to these, sol gel method produces nanoparticles with the highest purity of about 99.99% purity (Kajihara, 2013). This method involves the change of state from sol to gel by drying it to remove the solvent (Innocenzi, 2019). When the temperature is increased during the sol-gel process it will make the grains to grow and creates a microstructure that consist of coarse grains (Yang *et al.*, 2020). Figure 2.3 shows how sol-gel method of synthesizing nanoparticles is carried out.

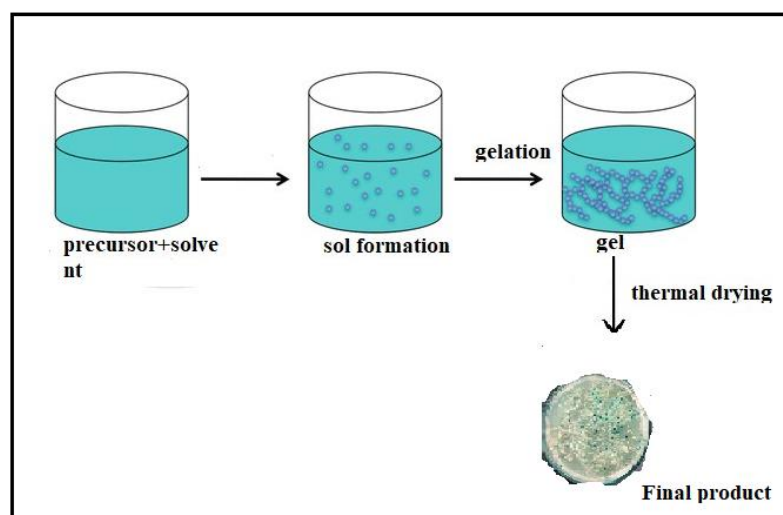


Figure 2.3: Stages of sol-gel method (Bokov et al., 2021)

2.11.3 Hydrothermal Synthesis of Nanoparticles

Hydrothermal method is a solution reaction-based approach. During this process the synthesis nanoparticles takes place at a variable temperature. Pressure variation (high or low) is used to control morphology of material being prepared. The vapor pressure of the main precursor plays a central role (Gan *et al.*, 2020). Williams *et al.*, (2007) synthesized CdSe nanoparticles using the hydrothermal method and nanoparticles displayed quantum confinement effects, as indicated by a blue shift in fluorescence. Additionally, hydrothermally produced CdSe nanoparticles—where the reaction medium is preheated before introducing the inorganic precursors—are likely to exhibit a high quantum yield.

2.12 Analytical Techniques used to Analyze Nanomaterials

Various analytical techniques are used to characterize nanoparticles these include Fourier transform infrared spectroscopy (FT-IR), Ultra violet Visible spectroscopy (UV-vis), X-ray diffractometer (XRD), Photoluminescence spectroscopy (PL) and Scanning electron microscopy (SEM).

2.12.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy identifies molecular structures by analyzing how they interact with infrared light. Infrared light represents wavenumbers between 12800-10 cm^{-1} in solar spectrum but its main regions that are used in IR

spectroscopy is between $4000\text{--}400\text{ cm}^{-1}$. When a sample absorbs the IR radiation its vibration energy level changes from ground state to excited state due to change in dipole moment. Every molecule has unique IR spectrum due to unique structures that connect the atoms (Ghamgosar, 2017). The intensity of the peak obtain from IR determines the amount of functional group in sample and the unique peak determine the functional group present in the sample (Beskers *et al.*, 2015). The FT-IR spectrum have the following main regions: the mid, near and far infrared regions. At a wavelength of $\geq 3000\text{ cm}^{-1}$ the major bond stretch are those of C-H, O-H and N-H, between $2000\text{--}2500\text{ cm}^{-1}$ is a triple bond stretch of acetylenes, carbenes and nitriles and between $1500\text{--}2000\text{ cm}^{-1}$ it's a region of double bond stretch for example the carbonyls C=O or alkenes C=C. the fingerprint region (less than 1500 cm^{-1}) mainly shows major compounds. The stretching vibration CdSe nanoparticles is at around $700\text{--}400\text{ cm}^{-1}$. The figure 2.4 shows the FT-IR spectrum.

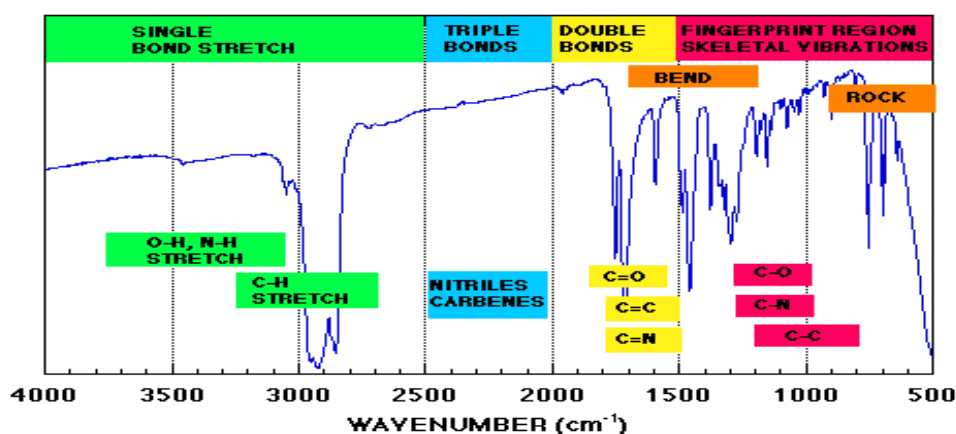


Figure 2.4: FT-IR spectrum showing the main regions (W. Zhao *et al.*, 2017)

2.12.2 Ultraviolet-visible Spectroscopy

Ultra Violet-Visible Spectroscopy is used to measure the absorbance and transmittance of light by samples. Its wavelength range from $190\text{--}900\text{ nm}$ (Asahi *et al.*, 2001).

UV-Vis has higher energy and they cause electronic transition. Short wavelength radiation has higher energy to excite electrons from high occupied molecular orbital (HOMO) to low unoccupied molecular orbital (LUMO) (Akash & Rehman, 2020). UV-Vis is used to determine the transmittance, thickness and bandgap of semiconductor which gives important information on electrical properties of material

(Grolik & Kopp, 2003). The ratio between the light intensity before and after going through the sample is called the transmittance and is given by equation 2.1.

$$T = \frac{I}{I_0} \quad (2.1)$$

Where T is transmittance, I intensity after sample and I_0 intensity before sample. Figure 2.5 below shows the UV-Vis reflectance of CdSe nanoparticles obtained by (Acharya *et al.*, 2011).

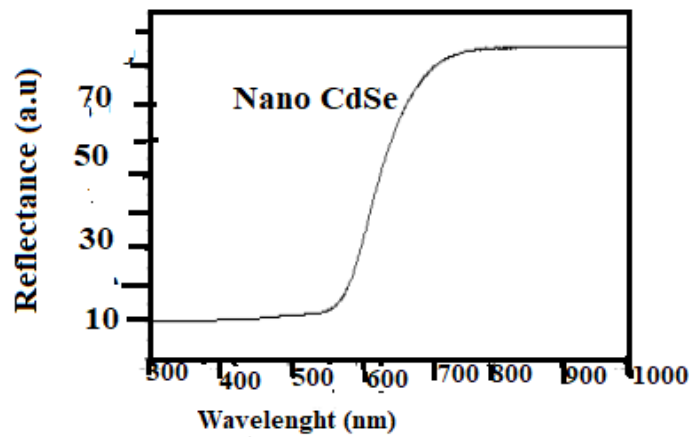


Figure 2.5: UV-Vis spectra of CdSe nanoparticle (Acharya et al., 2011)

2.12.3 X-ray Diffraction

It is a non-destructive and versatile method which is used to determine the structure, composition and texture of sample (Ermrich & Oppen., 2011). The pattern obtained from XRD is always compared to standard reference database to obtain the existing phases in sample. The reference database can be obtained from the published scientific literature prepared by centers which work professionally with XRD such as International Center of Diffraction Data (ICDD) (Ermrich & Oppen, 2011).

X-ray radiation is an electromagnetic wave which is located between Uv light and γ -rays and has an energy range of 100keV to 100eV. The X-ray radiation among electromagnetic radiation has a wavelength of 0.01 nm to 10nm. The x-ray radiation can be generated by accelerating electrons through a voltage drop and directing them

to tungsten (target material). The interaction of generated x-ray and the target sample undergo different processes such as absorption and scattering. The coherent scattered x-rays have constructive interference and this effect is used in XRD analysis described by Bragg's law in equation 2.2.

$$n\lambda = 2d\sin\theta \quad (2.2)$$

where n is an integer, d is interplanar spacing, θ is the Bragg's angle and λ is wavelength (West, 1999). Figure 2.6 below shows the XRD pattern of CdSe nanoparticles obtained by (Suresh & Arunseshan, 2014). The pattern showed that CdSeNP's formed hexagonal structure with peak (100) having the highest intensity and narrower compared with other peaks.

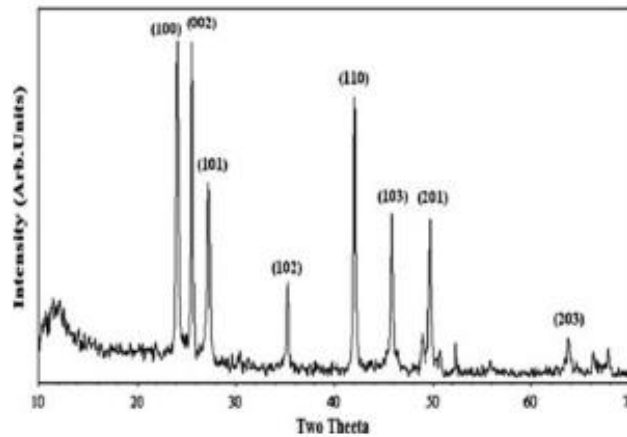


Figure 2.6: XRD pattern of CdSeNP's (Suresh & Arunseshan, 2014)

2.12.4 Scanning Electron Microscope (SEM)

Scanning Electron Microscope will be used to observe and analyze microstructural characteristics of solid samples in details as compared to optical microscopy. It uses electron beam to obtain images instead of visible light and captures images in 3 dimension like and topographical form (Goldstein *et al.*, 2003). SEM is used for both elemental and structural analysis of samples. The grain orientation of crystal and crystal structure can be determined from the structural analysis (Ghamgosar, 2017). Figure 2.7 below shows the SEM images of pure of CdSe nanoparticles prepared via hydrothermal process obtained by (Sobhani & Salavati-Niasari, 2015).

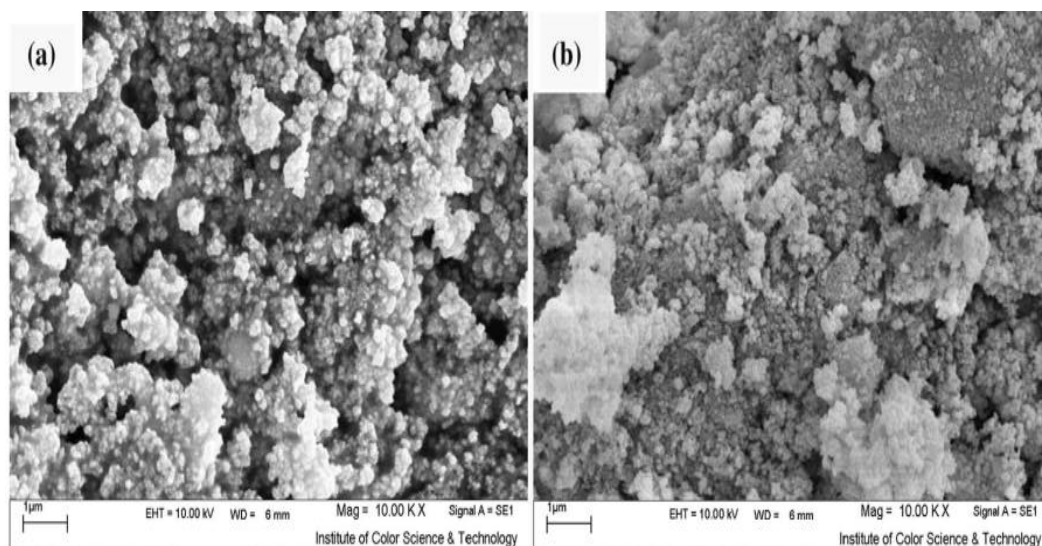


Figure 2.7: a) SEM images of CdSe NPs prepared with SeCl_4 b) SEM images of $\text{Cd}(\text{OA})_2 \cdot \text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$ (Kurtina et al., 2023)

2.13 Summary

This chapter provides a comprehensive review of literature relevant to the research. It begins by highlighting the limitations of fossil fuels and their contribution to environmental challenges such as climate change and global warming. The discussion then transitions into renewable energy, with a focus on solar cells and how nanotechnology is improving their performance. Special attention is given to cadmium selenide (CdSe) nanoparticles, discussing how growth temperature, doping (with elements like iron, gallium, and zinc), and annealing temperature influence their structural and optical properties. The chapter further explores common synthesis methods for nanoparticles, including chemical co-precipitation, sol-gel, and hydrothermal techniques. Finally, it outlines key characterization tools—FTIR, UV-Vis spectroscopy, XRD, and SEM—used to analyze the physical and chemical properties of nanomaterials.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter outlines the materials and method that was applied in the synthesis of CdSe and Zn-CdSe nanoparticles. CdSe nanoparticles were prepared at different growth temperatures, Zn doped CdSe at different dopant concentration, and Zn doped CdSe annealed at different temperatures. Sol-gel synthesis method was used to prepare nanoparticles with L-Cysteine used as a capping agent.

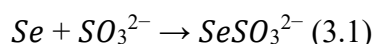
3.2 Materials

All the reagents used were of analytical grade. Anhydrous cadmium sulfite (purity >95%), cadmium chloride (anhydrous, >99%), selenium powder (purity >99%), L-Cysteine (>99%) and zinc acetate (>=99.4%). Deionized water was prepared in the Murang'a University of Technology Research Laboratory.

3.3 Method

3.3.1 Preparation of Se ions

Selenium powder (0.3 g) and 1.0 g of sodium sulphite in 100 ml of deionized water was refluxed for 8 hours at a temperature of 90°C to form sodium selenosulphate ions as shown in equation 3.1.



3.3.2 Synthesis of CdSe Nanoparticles

The synthesis of CdSe nanoparticles was adapted from the procedure reported by (Kiprotich et al., 2019) with slight modification. Initially, 0.04 g of cadmium chloride was dissolved in 50 mL of deionized water. An equivalent molar amount of L-cysteine was then added to achieve a 1:1 L-cysteine to cadmium ratio. The solution's pH was adjusted to 11 to ensure uniform dispersion of nanoparticles. This mixture was transferred into a three-necked flask and stirred continuously. Subsequently, 3 mL of reduced selenium ions were introduced, and the solution was refluxed at 95 °C for one hour to synthesize CdSe nanoparticles. After cooling to room temperature, the resulting nanoparticles were washed with excess ethanol and dried in an oven at 90 °C

for one hour. Finally, the nanoparticles underwent annealing at 250 °C for two hours using a muffle furnace.

3.3.3 Synthesis of CdSe Nanoparticles at Different Growth Temperature on the Structural and Optical of CdSe

To synthesize the nanoparticles, 0.04 g of cadmium chloride was dissolved in 50 ml of deionized water. L-cysteine was added in a quantity that maintained a molar ratio of 1:1 with cadmium. The pH of the resulting solution was adjusted to 11 to promote even dispersion of the nanoparticles. This solution was transferred into a three-necked flask and stirred continuously. Afterwards, 3 ml of reduced selenium ions were added, and the mixture was refluxed for one hour at varying temperatures of 30, 45, 60, 75, 90, 105, and 120 °C. The synthesized nanoparticles were then cooled to room temperature, thoroughly rinsed with ethanol, and dried in an oven at 90 °C for one hour. Finally, the dried samples were annealed in a muffle furnace at 250 °C for two hours.

3.3.4 Synthesis of Different Zinc mol % Dopant Concentration on Structural and Optical Properties of CdSe Nanoparticles

Using the optimal growth temperature identified above, the procedure was repeated by introducing zinc acetate in varying molar concentrations: 1%, 3%, 5%, 7%, 9%, 11%, and 15% relative to cadmium. Each solution was refluxed for 1 hour, cooled to room temperature, rinsed with ethanol, dried at 90 °C for 1 hour, and annealed at 250 °C for two hours.

3.3.5 Synthesis of Zinc Doped CdSe Nanoparticles Annealed at Different Growth Temperature on Structural and Optical Properties of Zn-CdSe Nanoparticles

Nanoparticles were synthesized using the optimal growth temperature and doping concentration identified in the previous steps. The samples were refluxed for 1 hour, cooled to room temperature, washed with ethanol, and dried at 90 °C for 1 hour. Finally, they were annealed at different temperatures: 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, and 275 °C for 2 hours each to study the effects of annealing temperature on the properties of Zn-doped CdSe nanoparticles.

3.4 Analytical Techniques

Various techniques were employed to characterize the synthesized nanoparticles for different applications. Characterization of nanoparticles involves the comprehensive analysis of their physical, chemical, and structural properties to understand their behavior, functionality, and potential applications. Given that nanoparticles possess unique properties due to their nanoscale dimensions, it is essential to use multiple analytical techniques to evaluate parameters such as size, shape, surface chemistry, crystallinity, and optical behavior. In this study, XRD was used to examine the crystal structure and estimate crystallite size, FTIR helped identify functional groups and confirm capping, UV-Vis spectroscopy was employed to determine optical absorption and band gap energy, and PL analysis was used to study emission characteristics and defect states. This multifaceted approach enabled a more accurate evaluation and optimization of the Zn-doped CdSe nanoparticles for potential application in solar cells.

3.4.1 FTIR

The FTIR spectroscopy is a powerful tool for identifying functional groups and chemical bonds within materials by measuring their infrared absorption spectra. In the context of nanoparticles, FTIR is instrumental in detecting surface modifications, capping agents, and interactions with other molecules. For instance, in green-synthesized silver and gold nanoparticles, FTIR analysis can reveal the presence of phytochemicals responsible for reduction and stabilization processes. Characteristic absorption bands, such as those around 3300–3400 cm^{-1} (O–H stretching) and 1600–1700 cm^{-1} (C=O stretching), indicate specific functional groups involved in nanoparticle synthesis and stabilization (Bahari *et al.*, 2023)

Shimadzu FT-IR was used to analyze the samples. The spectroscopy was turned on to warm up and the background scanning was performed to ensure that the spectrum that will be obtained is of the sample. The wavenumbers of the machine was set between 400–4000 cm^{-1} . The sample was loaded on the sample holder and then scanned. The spectrum obtained was analyzed to point out the functional groups in the samples. Figure 3.1 below shows Shimadzu IR spirit FT-IR model.

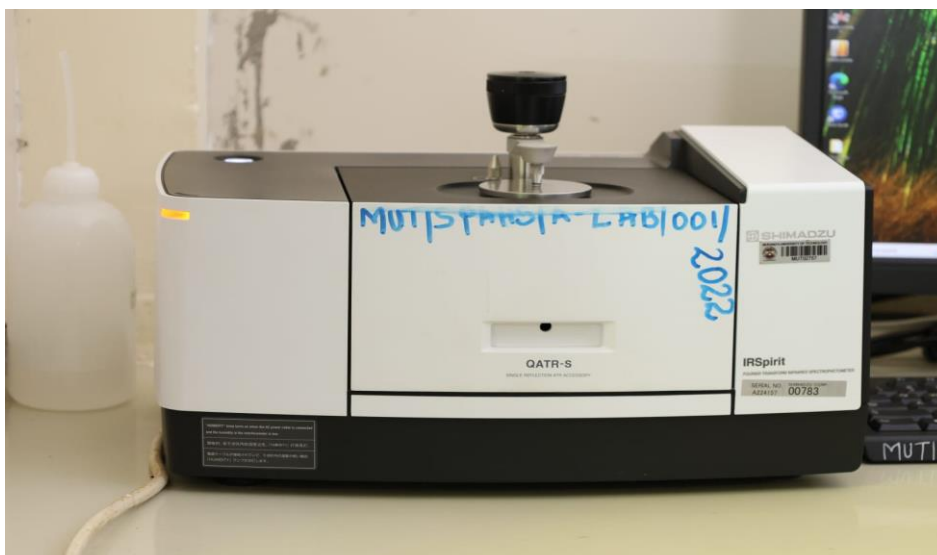


Figure 3.1: Shimadzu IR spirit FT-IR model

3.4.2 UV-Vis Spectroscopy

The UV-Vis spectroscopy examines how a sample absorbs ultraviolet and visible light, offering information about electronic transitions within nanoparticles. It is especially valuable for analyzing the optical characteristics and estimating the bandgap energies of semiconductor nanomaterials. For example, in plasmonic nanoparticles, UV-Vis analysis can detect surface plasmon resonance (SPR) peaks, which are sensitive to particle size, shape, and the surrounding environment. A blue shift in the absorption spectrum typically indicates a decrease in nanoparticle size, as observed in studies where increasing the concentration of reducing agents led to smaller nanoparticles with shifted SPR peaks (Mourdikoudis *et al.*, 2018)

The spectroscopy was turned on and calibrated using a standard reference material. Wavelength of 100-350 nm was set followed by background scanning. Samples was dissolve in ethanol then loaded into cuvette, scanned to obtain the transmittance and absorbance. Band gap of the nanoparticles was calculated using Taucs equation (Baishya *et al.*, 2018)

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3.2)$$

With A being a constant, $h\nu$ is the photon energy, E_g is the band gap and n is the 2 for indirect transmissions and $\frac{1}{2}$ for direct transmission.

Where the band gap energy (E_g) of semiconductor and ($ah\nu$) is related to photon energy ($h\nu$). Figure 3.2 shows the evolution one plus model UV-vis spectroscopy at Murang'a University of Technology.



Figure 3.2: Evolution one plus UV-Vis spectroscopy at Murang'a University of Technology

3.4.3 X-ray Diffraction

XRD is a non-destructive technique that provides information about the crystalline structure, phase composition, and crystallite size of materials. By analyzing the diffraction patterns produced when X-rays interact with a crystalline sample, researchers can determine lattice parameters and identify different crystalline phases. In nanoparticle research, XRD is used to confirm the formation of specific crystal structures and to estimate average particle sizes using the Debye-Scherrer equation. (Bamal *et al.*, 2021) used XRD to analyze biosynthesized silver nanoparticles to assess their crystallinity and phase purity. Figure 3.3 shows ARL EQUINOX 100 X-ray Diffractometer.



Figure 3.3: ARL EQUINOX 100 X-ray Diffractometer

The samples were grounded into powder and loaded to XRD sample holder. The X-ray beams was directed to the sample and the pattern obtained was used to calculate crystal size, lattice parameters and full width at maximum. Bragg's equation was used to determine the lattice spacing of nanoparticles (Doan *et al.*, 2020)

$$n\lambda = 2d\sin\theta \quad (3.3)$$

Where λ is the wavelength, θ is the incidence angle d is the interplanar spacing. the average crystal size of the nanoparticles is calculated using the Scherrer equations (Muniz et al., 2016).

$$L = \frac{K\lambda}{\beta\cos\theta} \quad (3.4)$$

Where λ is wavelength, β is the full width at half maximum and K is constant.

The lattice parameters a and c was calculated using the equation below

For a at plane (111)

$$a = \frac{\lambda}{\sin\theta\sqrt{3}} \quad (3.5)$$

and c at plane (002) is given b

$$c = \frac{\lambda}{\sin\theta} \quad (3.6)$$

3.4.4 Photoluminescence Spectroscopy

PL spectroscopy involves the excitation of electrons in a material and the subsequent emission of light as electrons return to their ground state. This technique is essential for studying the electronic structure and defect states in nanoparticles. In semiconductor nanoparticles like quantum dots, PL analysis can reveal information about bandgap energies, surface defects, and quantum confinement effects. For instance, the photoluminescence behavior of metallic nanoparticles, such as gold nanoflowers, has been studied to understand their emission properties, which are influenced by factors like shape and size (Bamal *et al.*, 2021). The samples were loaded to microscope which was operated under vacuum to ensure high quality imaging. The spectroscopy was used to determine the surface morphology and size distribution of nanoparticles. Figure 3.4 below shows SP-LF97 model PL spectroscopy at Murang'a University of Technology.



Figure 3.4: SP-LF97 model PL spectroscopy at Murang'a University of Technology

3.5 Summary

This chapter outlines the materials utilized and the procedures followed to meet the research objectives. It also presents the analytical techniques used to evaluate the synthesized samples. The nanoparticles were prepared using the sol-gel method. The characterization of the samples was carried out using techniques such as Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and Ultraviolet-Visible (UV-Vis) spectroscopy

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discusses the results obtained from FTIR, XRD, UV-vis and PL of CdSe and Zn doped CdSe nanoparticles. The results have been discussed according to the specific objectives. It entails effects of growth temperature on CdSeNPs, effects of doping concentration on Zn-CdSeNPs and effects of annealing temperature on Zn-CdSeNPs.

4.2 Effects of Growth Temperature on the Structural and Optical Properties of CdSe Nanoparticles

4.2.1 Photoluminescence Spectroscopy

Figure 4.1 shows the emissions spectra of CdSe nanoparticles prepared at different growth temperatures. The analysis were carried out at ambient temperature at an excitation wavelength of 400 nm. The PL analysis revealed that emission properties were strongly dependent on growth temperature. The sample synthesized at 25°C showed negligible or no emission, which can be attributed to poor crystallinity and incomplete nucleation due to the low thermal energy at room temperature. At such conditions, the nanoparticles likely remained amorphous or poorly crystalline, not showing good photoluminescence properties (Venci *et al.*, 2023).

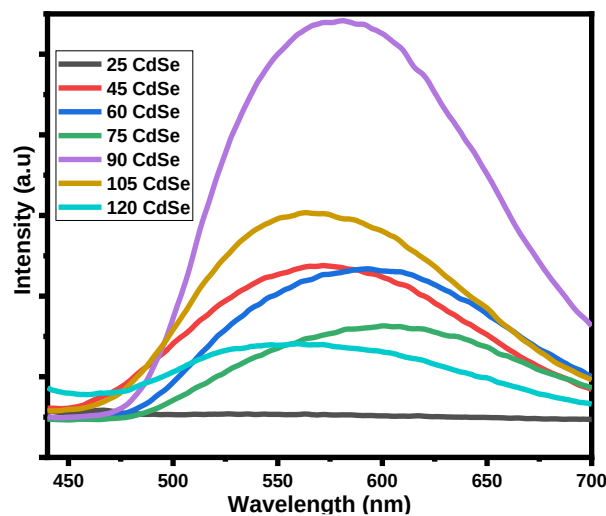


Figure 4.1: Spectra of CdSeNPs prepared at different growth temperature

As the growth temperature increased, the crystallinity of the nanoparticles improved, leading to enhanced PL intensity and observable near-band-edge emissions. However, the PL peaks are broad and asymmetric, indicating the presence of defect-related states. These defects, arising from vacancies or surface states, contribute to the overall emission and are responsible for the non-symmetric shape of the spectra. The variation in intensity and peak positions with temperature suggests a change in both the defect density and crystalline quality

Blue shift emission was observed for samples prepared at 45, 105 and 120 °C. The emission band shift to a higher wavelength from 45 to 75 then decrease from 90 to 120 as shown in Table 4.1. The blueshift observed is associated with increase in defect densities and small crystal size at lower synthesis temperature, at high synthesis temperature the crystallinity of nanoparticles is enhanced and defect densities are reduced. Similar results has been reported by (Shafeeq *et al.*, 2020)

Table 4.1: PL intensity and emission band of samples prepared at different growth temperatures

Sample (°C)	PL intensity	Emission band (nm)
CdSe 25	1.00	-
CdSe 45	4.75	571
CdSe 60	4.69	593
CdSe 75	3.25	601
CdSe 90	10.82	580
CdSe 105	6.00	570
CdSe 120	2.79	565

Figure 4.2 shows the variation of photoluminescence intensity with temperature, maximum intensity was observed at sample prepared at a growth temperature of 90 °C. The intensity tend to decrease at higher temperatures, this result from increase in defect level since at higher temperature the stabilizer molecules are decomposed and they agglomerate causing surface defects (Sumaya et al., 2023). This can also be related to the fact at the density of trapping centres is high at low temperature (Delice *et al.*, 2018). More number of carriers are liberated from photon light when light fall on the sample. These carriers move from the valence band to the conduction band when excited therefore an increase in PL intensity (Vogel & Kilin, 2015) . But after a temperature higher than 90 °C the number of trapping centres become less since some

of the trapping states are converted to recombination centres (Dejene, 2022). Non radiative recombination and scattering effects are majorly observed at high temperature thus low PL intensity. Therefore, temperatures higher than 90°C are not recommended to obtained luminescence properties of CdSe nanoparticles. To obtain good quality CdSe nanoparticles with superior photoluminescence properties, a growth temperature of 90°C is suitable. Similar results were also observed by (Handique *et al.*, 2021).

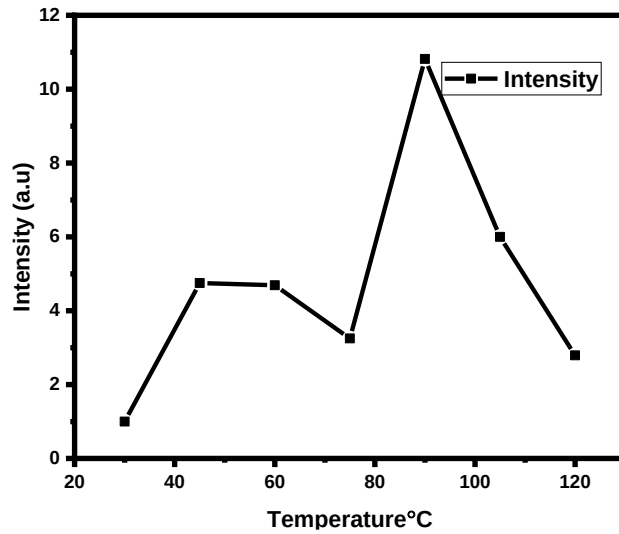


Figure 4.2: Shows the variation of photoluminescence intensity with temperature

4.2.2 Optical Properties

The analysis using ultraviolet-visible spectroscopy covered wavelengths from 200 to 800 nanometers. Bulk CdSe has a band gap energy of 1.74 eV, thus absorbed at around 700 nm absorption edge. Figure 4.3 shows the absorption edge for all the samples and were less than 700nm. This blue shift result from quantum confinement effect on the samples which causes discrete energy levels instead of continuous energy level like in bulk material. Samples prepared at 25, 60, 75 and 90°C absorbed in the visible range and had lower energy. At higher temperatures of 105 and 120 °C the absorption peaks shift to UV region.

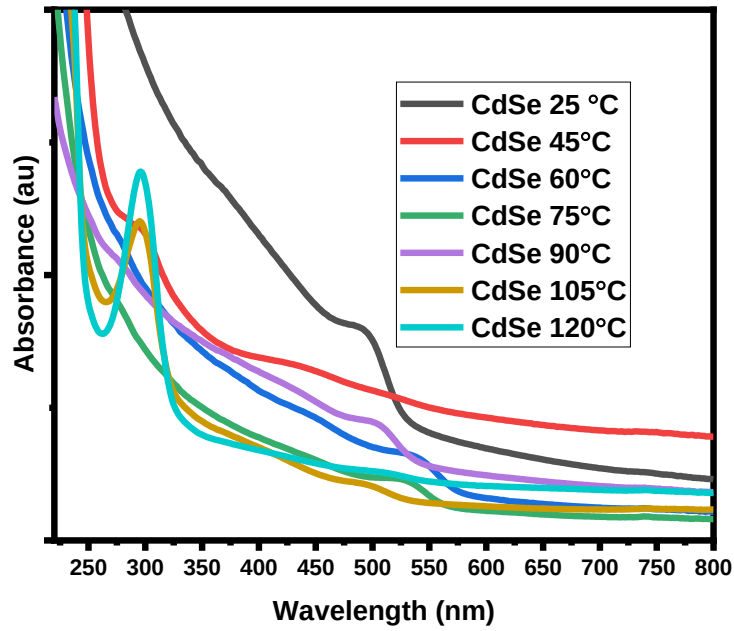


Figure 4.3: UV-Vis spectra of CdSeNPs synthesized at different growth temperatures

The optical bandgap energy was estimated by plotting Tauc's equation (Gakuru *et al.*, 2024) as shown in equation 4.1

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \quad (4.1)$$

Where the bandgap of the synthesized nanoparticles is E_g , $h\nu$ is the energy of the synthesized photon where h is plank's constant and ν photon's frequency, the coefficient of absorption is α . Gamma (γ) can be $\frac{1}{2}$ or 2 if they are indirect and direct allowed transition respectively (Vogel & Kilin, 2015). Direct transition happens without any change in momentum of electron in conduction band and photon in valence band. The band gaps are estimated by plotting energy ($h\nu$) versus $(\alpha h\nu)^2$. The graph is then extrapolated to obtain the band gap energy. The Tauc's plot for samples synthesized at different growth temperature are shown in figure 4.4. The band gap energies obtained are 1.83, 1.65, 1.71, 1.66, 1.67, 1.71 and 1.8 eV for samples prepared at a growth temperature of 25, 45, 60, 75, 90, 105 and 120°C respectively. Samples prepared at low temperature had high band gap energy. At higher temperatures above 90°C the band gap energy increase as crystal size decreases due to structural defects as observed in the photoluminescence properties of CdSe

nanoparticles. Similar results has been reported by (Ravi *et al.*, 2021). Figure 4.4 a and b shows the Tauc's plot of CdSe prepared at varying growth temperatures.

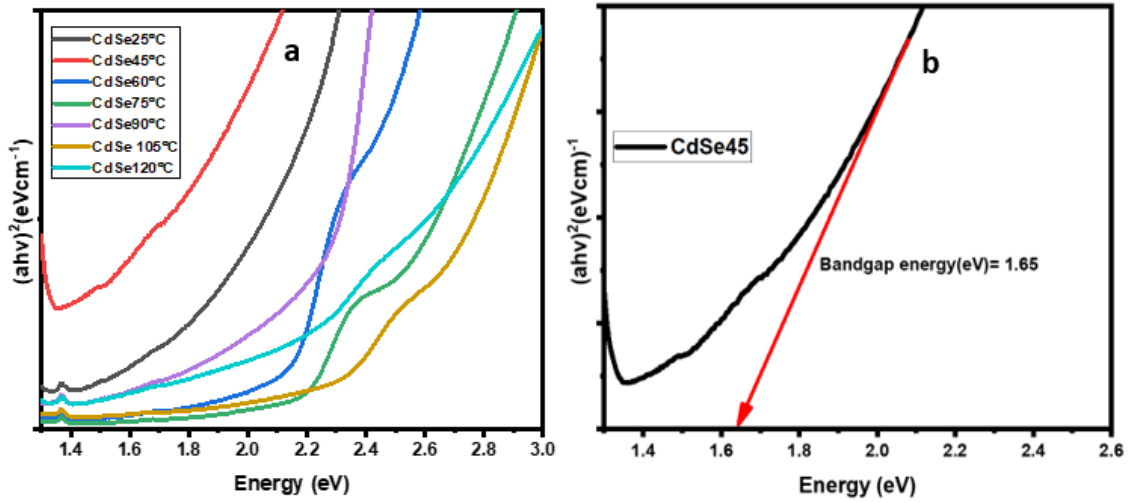


Figure 4.4 Tauc's plot of CdSeNPs prepared at varying growth temperatures

4.2.3 XRD Analysis

The X-ray diffraction patterns of CdSe nanoparticles synthesized at a growth temperature of 25, 45, 60, 75, 90, 105 and 120°C is shown in Figure 4.5. The patterns depict zinc blende cubic structure which matches with JCPDS card number 19-0191 with prominent diffraction plane at (111), (220) and (311). Preferred growth orientation of CdSe nanoparticles occur in plane (111), similar results were also obtained by (Rivera-Marquez *et al.*, 2020). As observed in Figure 4.5 the existence of other peaks marked with (*) at $2\theta = 33.72$, 31.72 , 30.16 and 30.25 for sample synthesized at a growth temperature of 105, 90, 60 and 25°C respectively, indicates structural imperfections and possible formation of secondary phases. Notably, the peak near $2\theta \approx 30.3^\circ$ corresponds to the (101) plane of hexagonal selenium, as identified by ICCD Card no. 86-2244 (Kotkata *et al.*, 2009). This suggests that elemental selenium may have formed unintentionally during synthesis. Since sodium selenosulfite (Na_2SeSO_3) and cadmium chloride (CdCl_2) were used as precursors, it is likely that under certain synthesis conditions, Na_2SeSO_3 partially decomposed, releasing selenium species that did not completely react with cadmium ions. These unreacted species may have reduced to elemental Se, particularly at lower temperatures where reaction rates are slower. The presence of these selenium-related peaks points to

incomplete incorporation of Se into the CdSe crystal lattice and emphasizes the importance of optimizing growth conditions to ensure phase purity.

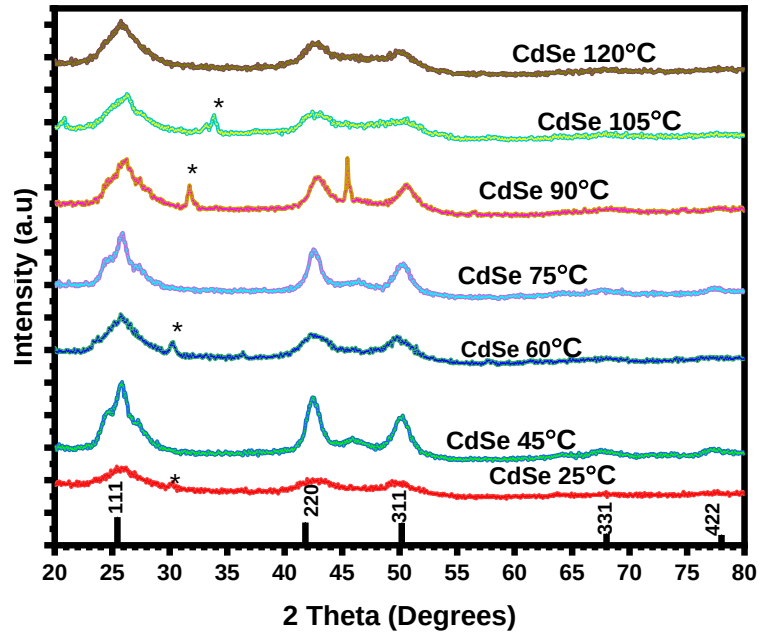


Figure 4.5: XRD pattern of CdSeNPs prepared at varying growth temperatures

The average crystal size of nanoparticles were calculated using Debye Scherrer (Ravi *et al.*, 2021) formula equation 4.2

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (4.2)$$

Where K is the 0.9 constant, the diffraction angle is θ , D is the crystal size, λ is the wavelength of X-ray diffraction used that is 0.15406 nm for Cu K α used and β is the FWHM of each peak. The maximum crystal size was observed at a growth temperature of 75°C. As the temperature increased, the crystal size also grew up to an optimal point, likely due to improved crystal stability and accelerated nucleation. Beyond this temperature, the size began to decrease. CdSe synthesized at a growth temperature of 120 °C had the smallest average crystal size. Bragg's equation (4.3) was used to calculate the lattice parameter of CdSe nanoparticles.

$$n\lambda = 2d\sin\theta \quad (4.3)$$

The X-ray wavelength λ used was of Cu K α = 1.5406 Å, n is an integer 1, d is the interplanar spacing and θ is the diffraction angle from XRD pattern. The lattice parameters a=b=c for cubic structure and lattice parameter a was obtained using cubic planar relation shown in equation 4.4

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (4.4)$$

Table 4.2: summarizes the crystallite size, FWHM and the lattice parameters of CdSe nanoparticles prepared at different growth temperatures.

Sample	Plane (hkl)	2 θ (°)	FWHM (°)	Crystal size (nm)	d _{hkl} (Å)	Lattice parameter a (Å)
CdSe 25	111	26.16	3.1755	25.6815	3.4037	5.8955
	220	42.25	3.0788	27.6597	2.1373	6.0451
	311	49.72	1.7948	48.7787	1.8323	6.0770
CdSe 45	110	25.73	2.8489	28.6009	3.4596	5.9924
	220	42.52	1.3594	62.7016	2.1244	6.0087
	311	50.10	1.8298	47.9196	1.8193	6.0339
CdSe 60	111	25.78	3.1005	26.2826	3.4530	5.9809
	220	42.74	2.6404	32.3059	2.1139	5.9790
	311	49.80	2.0701	42.3054	1.8295	6.0677
CdSe 75	111	25.75	2.7554	29.5726	3.4570	5.9879
	220	42.60	1.2049	70.7608	2.1206	5.9979
	311	50.20	1.9154	45.7968	1.8159	6.0226
CdSe90	111	26.08	2.8671	28.4393	3.4140	5.9133
	220	42.99	1.9072	44.7638	2.1022	5.9459
	311	50.53	1.8276	48.0619	1.8048	5.9860
CdSe 105	111	25.99	3.0899	26.3839	3.4256	5.9335
	220	42.85	2.3146	36.8670	2.1088	5.9645
	311	49.43	2.7512	31.7846	1.8424	6.1105
CdSe 120	111	25.87	3.3911	24.0386	3.4412	5.9709
	220	42.79	1.8705	45.6108	2.1116	5.9725
	311	49.68	4.4253	19.7803	1.8337	6.0816

The trend of crystal size and peak intensity was directly proportional, at a growth temperature of 45 °C the sample obtained had the highest intensity of 538 in XRD plane (111) and relatively large average crystal size of 46.41 nm. At low temperature 25 °C and high temperature 120 °C the intensity of the peaks at XRD plane (111) was low. This shows that at this plane the crystals of samples prepare at 25 and 120 °C tend

to align less along this direction as compared to other growth temperatures. CdSeNPs synthesized at a growth temperature of 45 °C exhibit superior structural properties as compared to other growth temperatures as indicated by enhanced XRD peak intensity and improved crystallinity. This suggests that 45 °C provide an optimal condition for orderly crystal growth and phase purity. Figure 4.6 shows the variation in crystal size, peak intensity and growth temperature of CdSe nanoparticles at XRD plane (111).

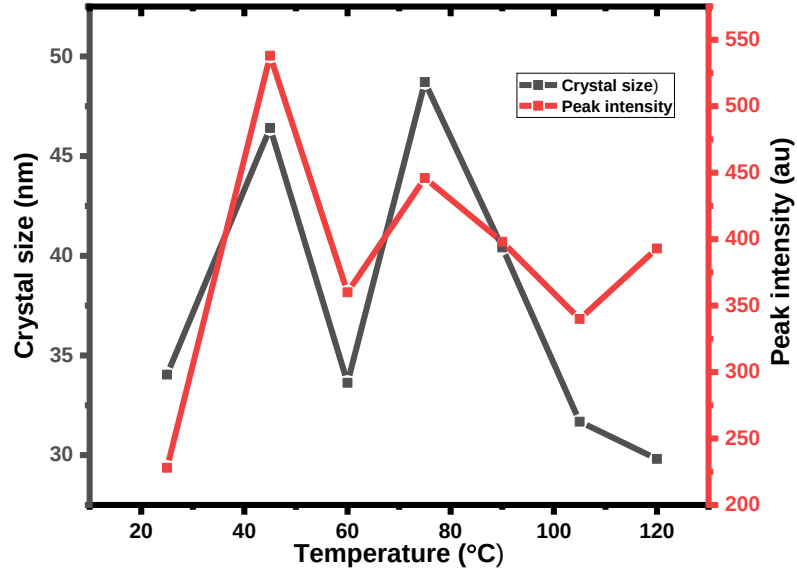


Figure 4.6: Relationship between crystal size, peak intensity and growth temperature

The broadening in the XRD peak of CdSe nanoparticles result from structural defects and strain (Nath *et al.*, 2020). Williamson-Hall was used to distinctly estimate the strain where by total broadening in nanoparticle is a sum of broadening due to strain and broadening due to crystal size. Equation 4.5 is used to calculate broadening due to strain.

$$\beta_{\varepsilon} = 4\varepsilon \tan \theta \quad (4.5)$$

Where ε is the strain, θ is the peak position and β_{ε} is broadening due to strain. The Williamson-Hall equation (4.6) (Jepngetich *et al.*, 2025) can be used to obtain both crystal size and strain.

$$\beta_T \cos \theta = \varepsilon (4 \sin \theta) + \frac{k\lambda}{D} \quad (4.6)$$

Equation (4.5) represent a straight line, in which ε is the slope of the line and the y-intercept is $\frac{k\lambda}{D}$. A plot of $4 \sin \theta$ on x-axis and $\beta_T \cos \theta$ on y-axis shows a straight line by linear fitting as shown in figure 4.7 a and b. The strain of nanoparticle is obtained from the slope, the data obtained showed that sample prepared at a growth temperature of 120°C had the lowest strain. At lower temperature the nanoparticle had more strain

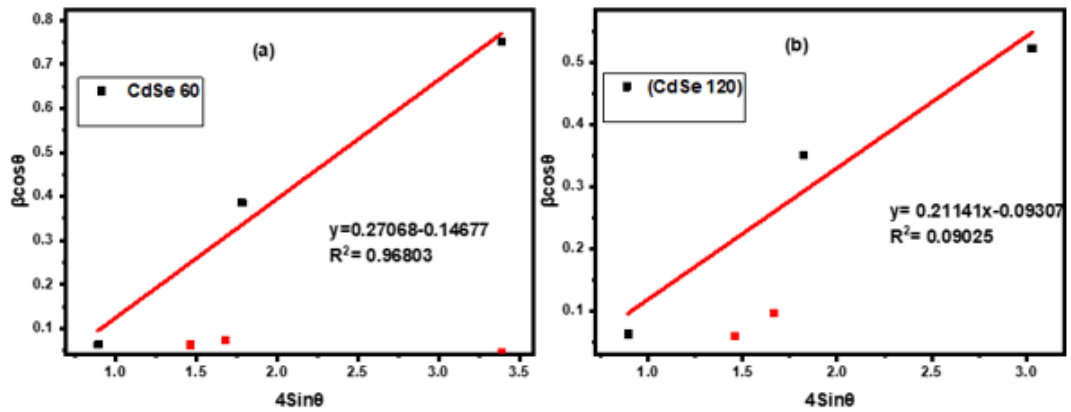


Figure 4.7: W-H plot for CdSeNPs synthesized at growth temperature of (a) 60 and (b) 120 °C

4.2.4 FT-IR Analysis

Figure 4.8 presents the FT-IR spectra of CdSe nanoparticles synthesized at growth temperatures of 25, 60, and 90 °C. These spectra were analyzed to determine the functional groups present in the samples. The results indicate that all samples exhibited absorption bands in both the fingerprint and functional group regions. Notably, a strong peak around 840 cm^{-1} was observed in the samples prepared at the lower temperatures of 25 and 60 °C. This peak correspond to metal- selenium bond vibration. In the functional group regions intense peaks were observed at 1365 and 1574 cm^{-1} this peaks C-N and N-H bending vibration respectively (Emori *et al.*, 2022). The amine group observed in this region are residual from the L-cysteine used as capping agents. Two peaks at 2008 and 2164 cm^{-1} was observed in all the samples but were intense at 30 °C, these peaks are associated with overtones (Thirugnanam &

Govindarajan, 2016). The high intensity of peaks at 25 °C suggest that at lower growth temperature the nanoparticles had better surface functionalization. At a higher wavelength of 3247 cm^{-1} a less intense peak was observed for CdSe nanoparticles prepared at a growth temperature of 60 °C, which correspond to O-H stretching vibration (Enders *et al.*, 2021).

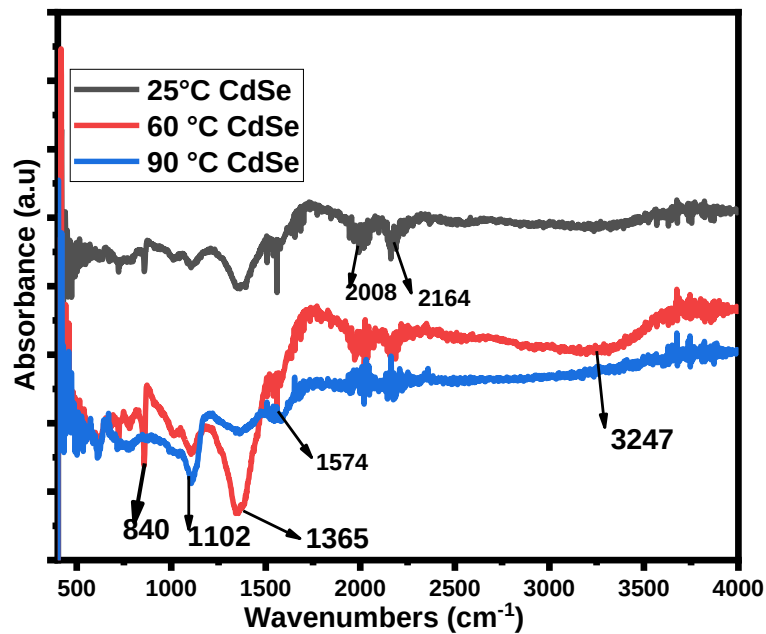


Figure 4.8: FT-IR spectra of CdSeNPs synthesized at a growth temperature of 25, 60 and 90 °C

4.3 Effects of Doping Concentrations on Material Properties of CdSe:Zn Nanoparticles

4.3.1 X-ray Diffraction (XRD) Analysis

The XRD pattern depicted by pure and Zn 1% mol dopant concentration on CdSe nanoparticles is shown in Figure 4.9(a). The peaks obtained matches those in JCPDS card no 19-0191 associated with zinc blende cubic structure.

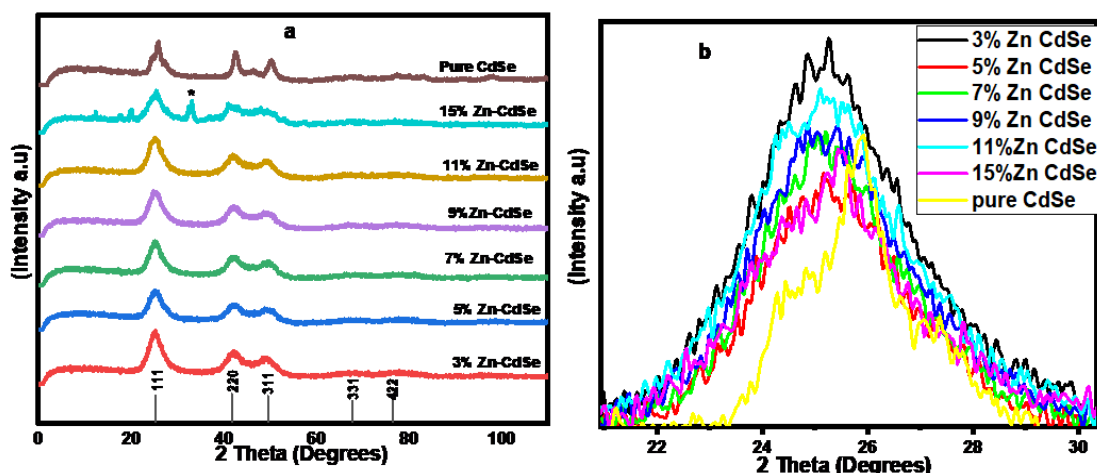


Figure 4.9: (a) XRD spectra of Zn-CdSe and (b) enlarged XRD peak [111] of Zn-CdSe nanoparticles

Doping CdSe with Zn affects its physical, chemical and crystal size properties as demonstrated by color change from dark brown to reddish brown for doped samples. A peak was observed at $2\theta = 33.48$ (marked with *) for 15% Zn doped CdSe nanoparticles. High concentration of dopant causes clustering as shown by peak broadening based on crystal size obtained of (16.99 nm) for 15% at plane (111). 3% Zn-CdSe had the highest intensity and 5% Zn-CdSe nanoparticles had the lowest intensity at peak (111) as shown in Figure 4.9(b). This means that at 3% Zn doped the nanoparticles were highly crystalline. Doping CdSeNPs increases its crystallinity, similar results has been reported when Zinc oxide was doped with magnesium and the XRD pattern showed sharper peaks, indicating better crystal quality (S et al., 2016).

The intensity of the peaks decreased with increased in Zn dopant concentration, this may be attributed by factors such as increased in micro strain, introduction of lattice distortion or partial transformation of material to amorphous phase. This observation is uniform with findings reported by (Akl *et al.*, 2020) who stated that as disorder increases, the peak intensity decreases reflecting a reduced ability of the crystal lattice to diffract X-rays coherently. Crystal defects occur when Zn is used as dopant in CdSe, this changes the stoichiometry as result of charge imbalance arising from this defects (Pradeev Raj *et al.*, 2018).

The crystal size of nanoparticles was determined using Debye-Scherrer equation. The equation is given in equation 4.7 (S *et al.*, 2016)

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (4.7)$$

D is the crystal size, K is the constant equals to 0.9, the wavelength of the radiation denoted by λ is 1.54960 Å for copper K α radiation, full width at half maximum (β_{hkl}) and θ is the peak position. The average crystal size of CdSeNPs decreased when doped with Zn, with 15% Zn doped CdSe nanoparticles having a crystal size of 17.72 nm, 3% had 17.60 nm and pure CdSeNPs had a crystal size of 24.67 nm. This decrease in crystal size with increasing Zn concentration is associated with the fact that Zn limits the agglomeration of CdSeNPs and improves its surface area (Gakuru *et al.*, 2024). It is also possible that Zn²⁺ can substitute Cd²⁺ ions in the lattice of CdSe. Given that the ionic radius of Zn²⁺ (0.74 Å) is smaller than the ionic radius of Cd²⁺ (0.92 Å), this disparity causes a decrease in lattice parameters leading to a smaller crystallite size and more compact crystal structure (Asere & Laing, 2020). The FWHM decreased when doped with 7 % Zn, this indicates an improvement in crystallinity and an increase in crystal size of nanoparticles (Kiprotich *et al.*, 2016) as observed from the data obtained 7% zinc doped CdSe nanoparticles had an average crystal size of 20.31 nm.

Table 4.3: shows the summarized crystal size, lattice constant d, a and FWHM of Zn-CdSeNPs with different Zn concentration.

Sample	Plane (hkl)	2 θ (°)	FWHM (°)	Crystal size (nm)	d _{hkl} (Å)	Lattice parameter a (Å)
Pure CdSe	111	25.3301	4.1701	19.5339	3.5133	6.0854
	220	43.0449	5.1811	16.4810	2.0997	5.9388
	311	49.7662	2.3049	37.9906	1.8307	6.0717
3%Zn-CdSe	111	25.3155	4.4933	18.1190	3.5153	6.0889
	220	42.2967	5.3559	15.9025	2.1351	6.0389
	311	49.0760	4.6436	18.8048	1.8548	6.1516
5%Zn-CdSe	111	25.3566	4.6050	17.6809	3.5097	6.0792
	220	42.3925	4.8942	17.4083	2.1305	6.0259
	311	49.1552	4.5034	19.3964	1.8520	6.1423
7%Zn-CdSe	111	25.3242	4.4466	18.3101	3.5141	6.0868
	220	42.3163	3.6046	23.3163	2.1341	6.0360
	311	49.3325	4.5323	19.2863	1.8458	6.1218
9%Zn-CdSe	111	25.3243	4.6273	17.5946	3.5141	6.0868
	220	42.3661	5.3129	16.0349	2.1317	6.0293
	311	49.0800	4.6065	18.9566	1.8547	6.1513
11%Zn-CdSe	111	25.2688	4.6884	17.3636	3.5217	6.0999
	220	42.3543	6.1273	13.9031	2.1323	6.0310
	311	49.1973	4.2726	20.4476	1.8505	6.1373
15%Zn-CdSe	111	25.1208	4.7884	16.9959	3.5283	6.1114
	220	41.8514	3.4913	24.3591	2.1567	7.9998
	311	48.0237	7.3671	11.8040	1.8930	6.2783

The lattice constant d was calculated using the Bragg's equation

$$n\lambda = 2d_{hkl}\sin\theta \quad (4.8)$$

For Zinc blende cubic structure a=b=c therefore lattice constant a was calculated using equation 4.9

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (4.9)$$

A plot of FWHM against crystal size (D) showed that they were inversely proportional as shown in Figure 4.10. Smaller crystals have large grain boundaries which broadens the peaks in XRD.

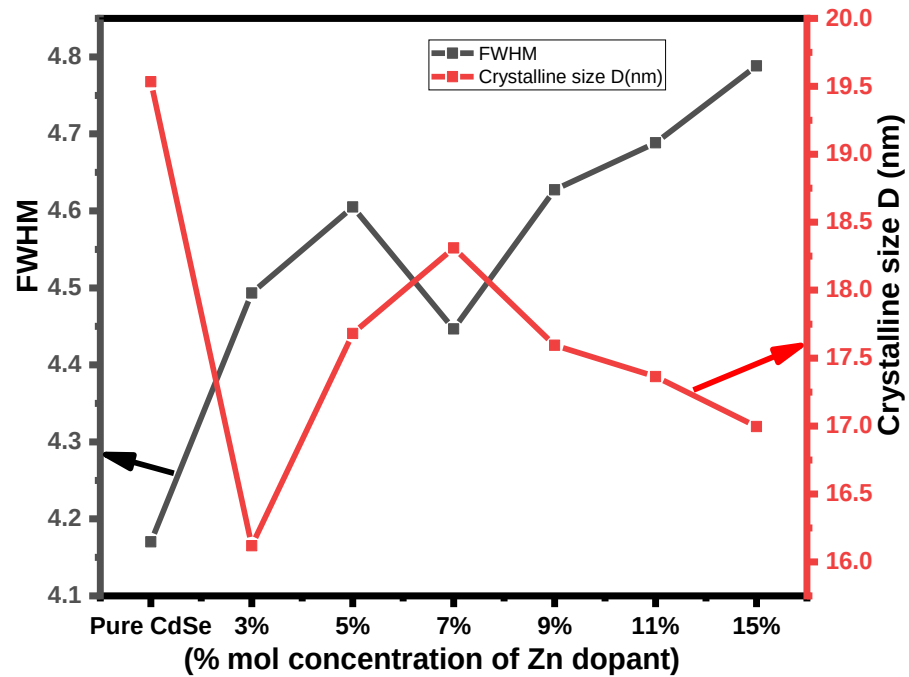


Figure 4.10: Relationship between FWHM, Crystal size and Zn mol %

4.3.2 Photoluminescence Spectroscopy

The photoluminescence properties of Zn-CdSe nanoparticles were carried out at an ambient temperature at an excitation wavelength of 400 nm to determine the luminescence properties of Zn-CdSe nanoparticles and their defects. The photoluminescence properties of CdSe were found to be dopant concentration dependant. Figure 4.11 shows how different concentration of Zn dopant affects the FWHM, peak position and intensity of peak in PL.

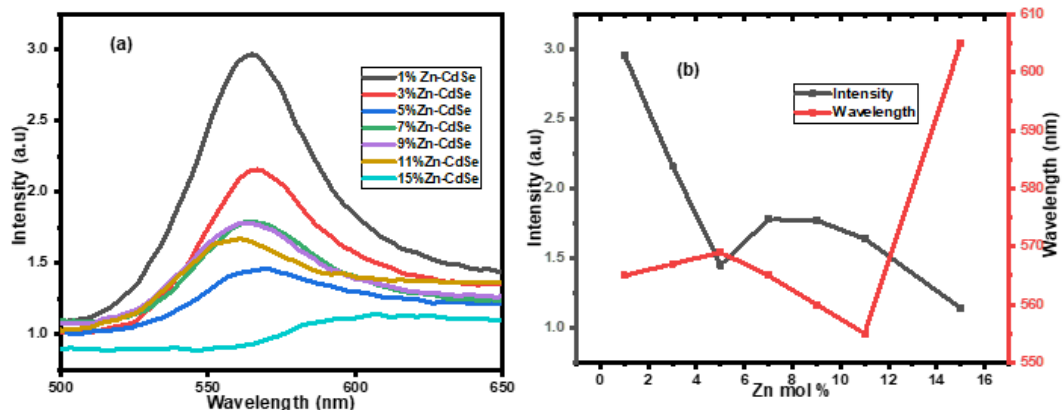


Figure 4.11: (a) PL emission spectra of varying concentration of Zn-CdSeNPs (b) Relationship between PL Intensity, emission wavelength and mol % of Zn dopant in CdSeNPs

The photoluminescence intensity decreased as the dopant concentration increased, showing higher intensity at lower dopant concentrations. This is associated with the fact that highly doped nanoparticles excite electrons which can return to ground state without emitting photons (non-radiative recombination) (Thirugnanam & Govindarajan, 2016). 1% Zn-CdSe nanoparticles had the highest PL intensity and 15% Zn-CdSe nanoparticle had the lowest PL intensity. At high dopant concentration the emission wavelength shift to longer wavelength (redshift) as a result of lattice strain or dopant induced defects (Asere & Laing, 2020). Blueshift was observed when low dopant concentration was used, due to quantum confinement effects that occurs when the crystal size decrease the energy gap between conduction band and emission band increase (Hamizi et al., 2018). The dimension of FWHM of PL spectra of samples reflects the distribution of particle size, this can be an efficient method to study size focusing. The FWHM range from 80 to 100nm and decreases with increased in dopant concentration. Narrow FWHM of the PL spectra reflects narrow particle size distribution and this can be used to investigate the size focusing (Zaini *et al.*, 2020)

4.3.3 Optical Properties

The bandgap energy (E_g) of semiconductor materials suspended in a liquid with a known coefficient is typically determined using UV-Vis absorption spectroscopy. The UV-Vis absorbance spectra for the Zn-CdSe nanoparticles is illustrated in figure 4.12.

The nanoparticles absorbed at different wavelength depending on the amount of dopant used. Highly doped Zn-CdSeNPs (15%) absorbed at higher wavelength (550 nm), high concentration of dopant modifies the electronic properties of nanoparticles due to defects that result from stress, strain, interstitial and vacancies defects (Zhu *et al.*, 2015). Bulk CdSe absorbed at a wavelength of 690 nm, the shift towards the shorter wavelength confirms the formation of nanoparticles. Pure CdSe nanoparticle had the lowest absorption band and it absorbed at the lowest wavelength. Similar results were observed by (Ca et al., 2020).

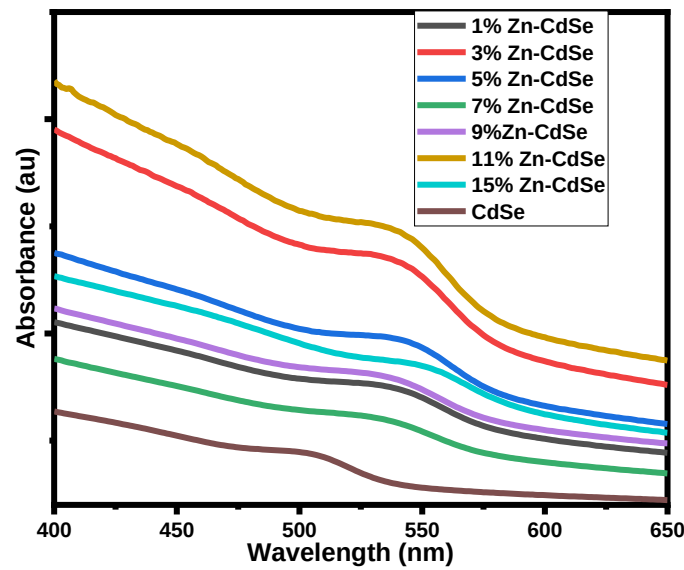


Figure 4.12: UV-vis spectra of Zn-CdSe nanoparticles

To obtain the bandgap energy of nanoparticles Tauc's equation 4.10 (Asere & Laing, 2020) was used to estimate the values and a graph plotted.

$$(\alpha h\nu)^\gamma = A h\nu - A E_g \quad (4.10)$$

Where E_g is the bandgap energy, A is constant, $h\nu$ is the photon energy, α is absorption coefficient and γ is direct or indirect allowed transition from valence band to conduction band. When γ is 2 it is indirect and when $\frac{1}{2}$ it is direct allowed transition. The plot obtained was extrapolated to intersect the $h\nu$ axis to obtain the bandgap energy. Figure 4.13 a and b shows the Tauc's plot of different concentration of Zinc dopant.

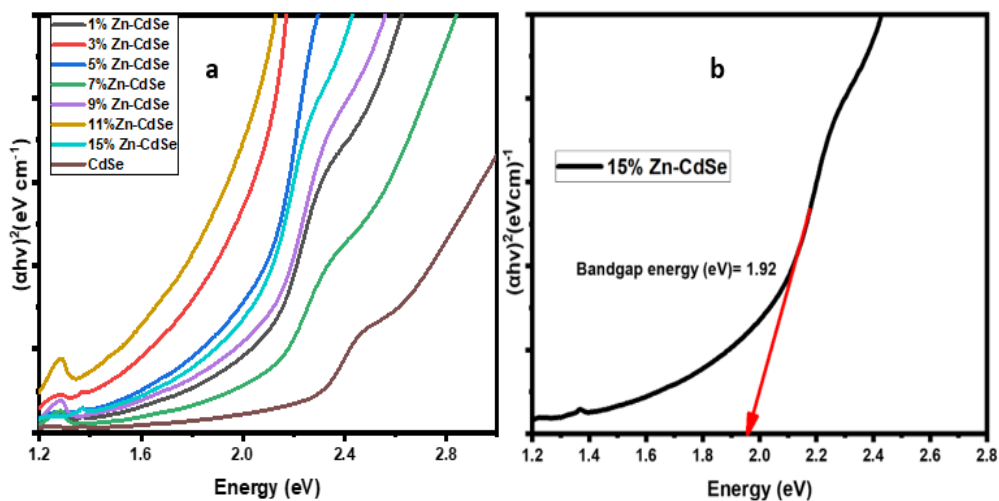


Figure 4.13: Shows the Tauc's plot of different concentration of Zinc dopant

Table 4.4 shows the bandgap energy obtained when Tauc's plot was extrapolated. The optical properties of CdSe nanoparticles can be tuned by varying the dopant concentration. The bandgap energy was the same for samples prepared with 1 and 15% Zn dopant (1.92 eV). Increase in bandgap energy at 1% zinc dopant is observed as a results of Zn substituting Cd in CdSe to form $\text{Cd}_x\text{Zn}_x\text{Se}$ nanoparticle. The bandgap energy of ZnSe is 2.7 eV (Imran *et al.*, 2018) which is higher compared with 1.74 eV of bulk CdSe, therefore the alloy form has intermediate properties. When high concentration of dopant is added the lattice strain and defects influence the optical properties of nanoparticles thus affecting its bandgap energies. Doping CdSe with Zn

decrease the bandgap energy from 2.23 to 1.92 eV. For solar cells applications where the band gap energy required should be lower than the bulk material for ease transition of photons from valence band to conduction band doping CdSe nanoparticle with 11% zinc gives the optimum conditions. Table 4 summarizes the absorption peak and absorption edge for each concentration of dopant

Table 4.4: Summarized absorption peaks, edge and bandgap energy of Zn-CdSeNPs

Zn _x -CdSeNPs	Absorption peak (nm)	Absorption edge (nm)	Optical bandgap (eV)
X=0	505	529	2.23
X=1	544	567	1.92
X=3	538	574	1.5
X=5	545	571	1.80
X=7	534	569	2.04
X=9	537	569	1.8
X=11	533	559	1.35
X=15	550	579	1.92

4.3.4 FT-IR Analysis

To determine the functional groups present in the synthesized Zn-CdSe nanoparticles, samples were analyzed with FT-IR spectra. Figure 4.14 shows the FT-IR spectra of Zn-doped CdSeNPs (7, 9, 11, 15 and pure CdSeNPs). The spectra showed that the sample absorbed in both the fingerprint and functional group region. The peak observed at 3280 cm^{-1} in Zn-CdSeNPs is assigned to O-H group present in the sample (Jepngetich *et al.*, 2025), pure CdSeNPs did not absorb in the functional group regions. The intensity of this peak increased with an increase in zinc dopant concentration. The prominent peak in the doped samples at 1556 cm^{-1} is assigned to stretching vibration of C=O (Yao & Huang, 2022) present in the zinc acetate solution used as precursor of dopant and some from L-cysteine used as capping agent. The peaks observed at 1382 and 1294 cm^{-1} correspond to COO^- stretching vibration (Yao & Huang, 2022). The peak at 1294 cm^{-1} was observed for sample doped with 15 % zinc only, this might have resulted from higher concentration of zinc acetate used which contains large concentration of organic compounds. At 1060 cm^{-1} both capped and pure samples absorbed, this peak corresponds to stretching vibration of C-N present in the L-cysteine used as capping agents (Slavov *et al.*, 2024). In the fingerprint region (shown in the inset) a stretching vibration of Cd-Se and Zn-Se is observed, as the concentration of zinc dopant increases the intensity and sharpness of the peaks increased. This suggests that incorporation of zinc into the CdSe nanoparticle alters the surface chemistry and can modify the structure of the nanoparticle obtained.

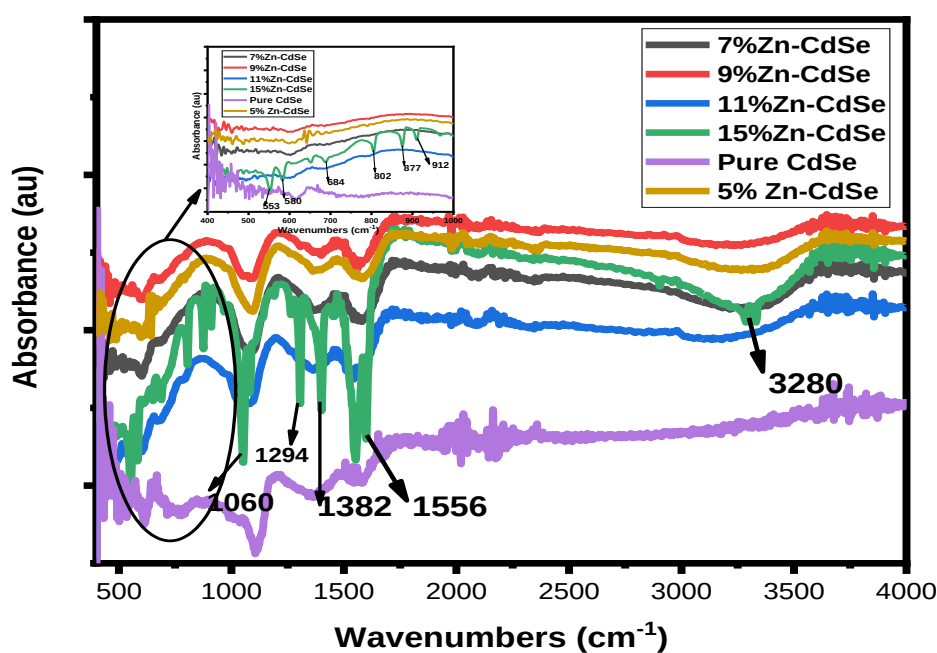


Figure 4.14: FT-IR spectra of Zn doped CdSe nanoparticle

4.4 Effects of Annealing Temperature on Structural and Optical Properties of CdSe:Zn Nanoparticles

4.4.1 X-ray Diffractions (XRD) Analysis

The XRD pattern depicted by Zn doped CdSe nanoparticles is shown in Figure 4.15 (a). The analysis aimed to determine the changes in lattice parameters, crystallinity, or peak shifting arising from annealing Zn doped CdSe nanoparticles.

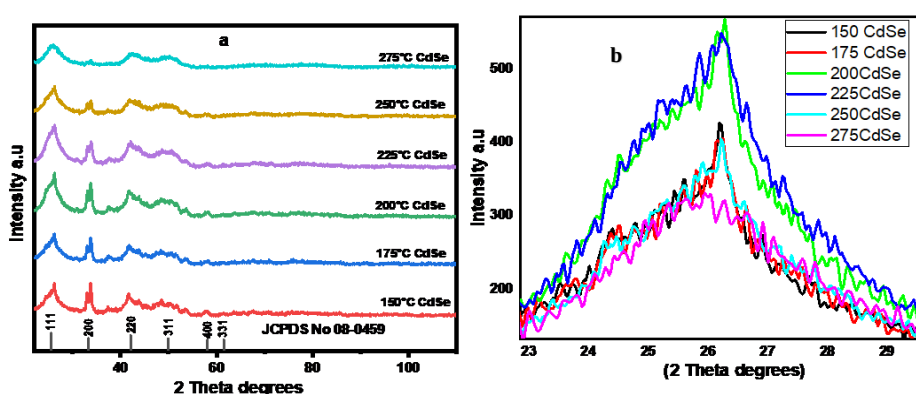


Figure 4.15: XRD pattern depicted by Zn doped CdSe nanoparticles

The diffraction peaks of the Zn-doped CdSe nanoparticles were analyzed at different annealing temperatures ranging from 150°C to 275°C. The results confirmed that the synthesized samples retained the cubic structure of CdSe. This indicates that the dopant was successfully incorporated into the CdSe lattice. It reveals that the peaks at scattering angle (2θ) 25.80°, 42.20° and 48.50°, corresponds to (111), (200) and (220) reflection planes, for CdSe. In this, they have matched XRD peaks with Joint Committee on Powder Diffraction Standards file No 08-0459 for CdSe. Zn-CdSe synthesized at 225°C had the highest intensity and Zn-CdSe synthesized at 275°C had the lowest intensity at peak (111) shown in Figure 4.15(b).

At first, the peak intensity rose as the nanoparticles were annealed up to 225 °C, but then it decreased at higher annealing temperatures. Overall, annealing promotes grain growth within the crystal lattice because atoms at specific lattice planes gain higher energy, leading to a more orderly atomic arrangement (Alagarasan *et al.*, 2021). This means that at 225 °C the nanoparticles were highly crystalline.

The crystal size of the nanoparticles was determined using the Debye-Scherrer equation, shown in equation 4.11

$$D = \frac{K\lambda}{\beta_{hkl} \cos\theta} \quad (4.11)$$

Here, D represents the crystal size, K is a constant valued at 0.9, λ is the wavelength of the X-ray radiation (1.54960 Å for copper K α radiation), (β_{hkl}) is the full width at half maximum (FWHM) of the peak, and θ is the diffraction angle. Analysis of the XRD data reveals that the crystallite size increases with annealing temperature, ranging from 150°C to 225°C, where it attains a maximum size of 28.11 nm. This growth in particle size with higher annealing temperatures suggests that grain boundary diffusion leads to the coalescence of smaller grains into larger ones during the annealing process (Mahato *et al.*, 2015). At 250 °C, the crystallite size decreases to 27.12 nm, and at 275 °C, it further decreases to 24.34 nm. This decrease at higher temperatures may be attributed to sintering effects, where the nanoparticles agglomerate or undergo a phase transition that results in smaller effective crystallite sizes. High temperatures could also introduce more defects or lead to dopant diffusion, disrupting crystal growth and reducing the crystallite size. It is also possible that Zn²⁺

can substitute Cd^{2+} ions in the lattice CdSe given that the ionic radius of Zn^{2+} (0.74 Å) is smaller than the ionic radius of Cd^{2+} (0.92 Å), this disparity causes a decrease in lattice parameters leading to a smaller crystallite size and more compact crystal structure (Asere & Laing, 2020).

Table 4.5: shows the summarized crystal size, lattice constant d, a and FWHM of Zn-CdSeNPs with different annealing temperature.

Sample	Plane (hkl)	$2\theta(^{\circ})$	FWHM ($^{\circ}$)	Crystal size (nm)	d_{hkl} (Å)	Lattice parameter a (Å)
Zn-CdSe 150	111	25.7425	2.9050	28.0490	3.4595	5.9922
	200	33.5457	1.2307	67.4131	2.6693	5.3386
	220	42.4199	4.8558	17.5478	2.1291	6.0219
Zn-CdSe 175	110	25.7939	2.9586	27.5436	3.4512	5.9778
	200	33.5744	1.1940	69.4928	2.6671	5.3342
	220	42.4843	4.6895	18.1737	2.1261	6.0135
Zn-CdSe 200	111	25.8140	2.9063	28.0412	3.4486	5.9733
	200	33.5685	1.2507	66.3386	2.6675	5.3350
	220	42.0411	2.4430	34.8345	2.1475	6.0740
Zn-CdSe 225	111	25.9091	2.8992	28.1148	3.4361	5.9517
	200	33.6020	1.3775	60.2395	2.6650	5.3300
	220	42.8153	4.4559	19.1483	2.1104	5.9691
Zn-CdSe 250	111	25.8859	3.0053	27.1213	3.4391	5.9569
	200	33.5326	1.3348	62.1521	2.6703	5.3406
	220	42.2610	3.5043	24.3021	2.1367	5.6568
Zn-CdSe 275	111	25.9731	3.3494	24.3392	3.4277	5.9371
	200	33.7633	0.4233	196.1184	2.6526	5.3052
	220	42.8376	2.7512	20.9355	2.1094	5.9662

The lattice constant d was calculated using the Bragg's equation

$$n\lambda = 2d_{hkl}\sin\theta \quad (4.12)$$

For Zinc blende cubic structure $a=b=c$ therefore lattice constant a was calculated using equation 4.13

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (4.13)$$

A plot of FWHM against crystal size (D) showed that they were inversely proportional as shown in Figure 4.16. Smaller crystals have large grain boundaries which broadens the peaks in XRD

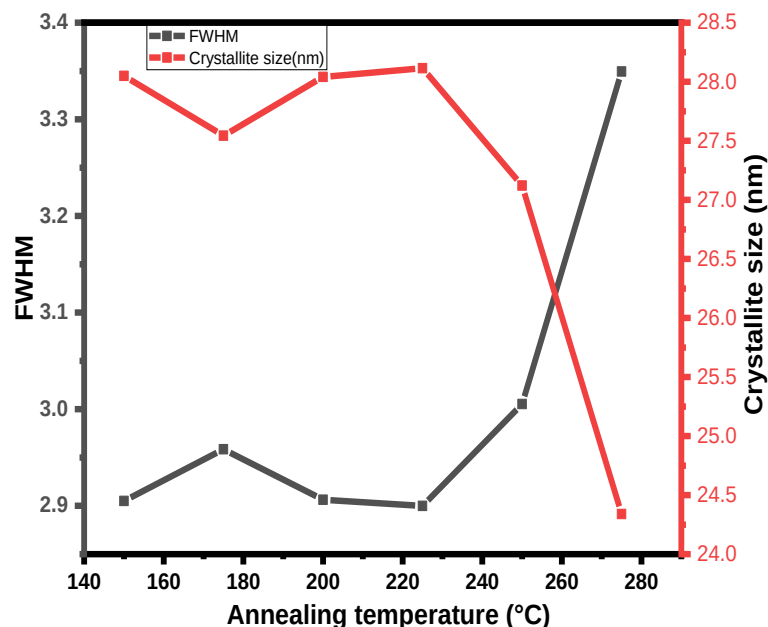


Figure 4.16: Relationship between FWHM,crystallite size and annealing temperature

4.4.2 Optical Analysis

The UV-Vis absorption spectra of Zn-doped CdSe nanoparticles annealed at temperatures ranging from 150 °C to 275 °C show distinct variations in absorbance intensity and spectral features, indicating the influence of annealing temperature on the optical and structural properties of the material. All samples exhibit prominent absorption peak within the UV region (around 300–320 nm). The intensity of absorption increases with annealing temperature, peaking for the Zn-CdSe 275 °C sample. This indicates enhanced light absorption capability due to improved crystallinity or increased particle size. The Zn-CdSe 250 °C sample shows the lowest absorbance, possibly indicating higher structural disorder or reduced optical activity at that annealing condition. The UV-vis absorbance spectra of Zn-CdSeNPs are shown in figure 4.17. With increasing annealing temperature up to 275 °C, the absorption edge shows a red-shift, suggesting increased crystallite size and reduced quantum

confinement (Zhu et al., 2015). This trend is in agreement with the XRD analysis, which showed a decrease in FWHM and an increase in crystallite size with temperature up to a certain point (around 225 °C) beyond which crystallite size decreased and FWHM increased, likely due to thermal-induced lattice distortion or defect formation. The optical bandgap energy was estimated by plotting Tauc's equation as shown in equation 4.14

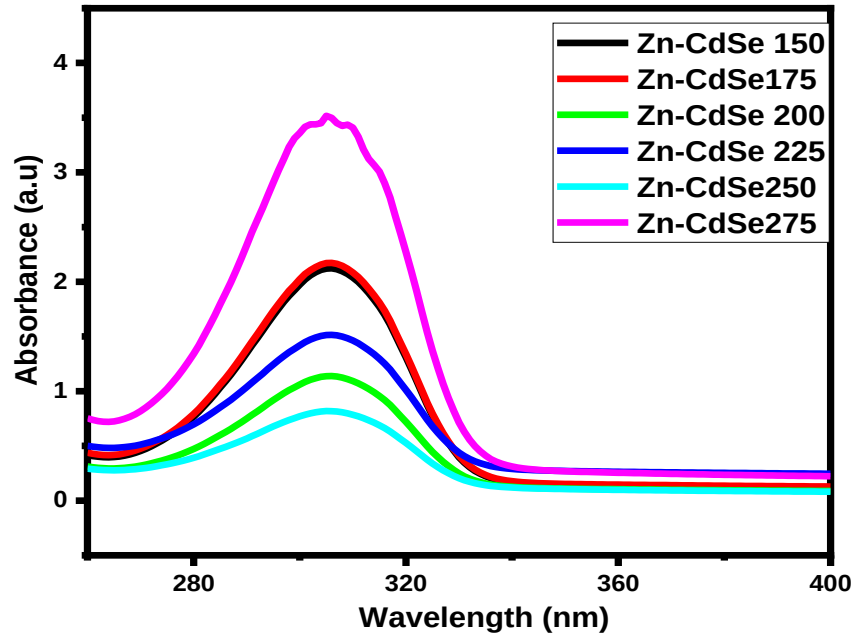


Figure 4.17: The UV-vis absorbance spectra of Zn-CdSeNPs

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \quad (4.14)$$

Where the bandgap of the synthesized nanoparticles is E_g , $h\nu$ is the energy of the synthesized photon where h is plank's constant and ν photon's frequency, the coefficient of absorption is α . Gamma (γ) can be $\frac{1}{2}$ or 2 if they are indirect and direct allowed transmission respectively (Jepngetich *et al.*, 2025). Direct transition happens without any change in momentum of electron in conduction band and photon in valence band. The band gaps are estimated by plotting energy ($h\nu$) versus $(\alpha h\nu)^2$.

Figure 4.18 a and b shows the Tauc's plot of Zn-CdSe annealed at different annealing temperature. The graph is then extrapolated to obtain the band gap energy. The band gap energies obtained are 2.10, 1.96, 2.24, 1.18, 2.53 and 1.23 eV for samples annealed at 150, 175, 200, 225, 250, and 275 °C respectively.

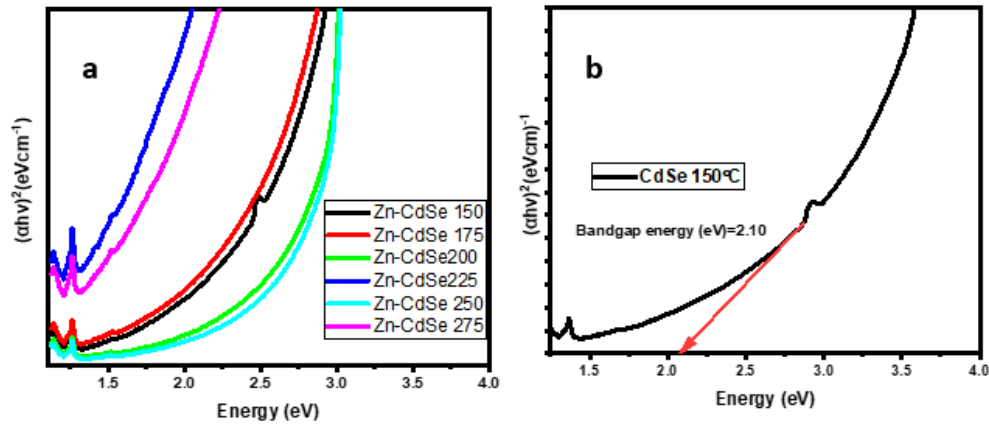


Figure 4.18: Tauc's plot of Zn-CdSe nanoparticles at varying % Zn mol concentrations

The observed bandgap of 1.18 eV at 225 °C could indicate significant grain growth at this temperature, reducing quantum confinement. However, the subsequent increase to 2.53 eV at 250 °C suggests a possible reduction in crystallite size or the formation of new phases with higher bandgap energies. Such behavior has been reported in CdSe thin films, where annealing at higher temperatures led to decreased bandgap energies due to increased crystallite size and reduced defects (Hussain, *et al.*, 2021).

4.4.3 Photoluminescence Spectroscopy

The photoluminescence properties and defects in CdSeNPs synthesized at different annealing temperature were analyzed using Infitek SP-LF97 PL spectroscopy. The emissions spectra of Zn-CdSe nanoparticles prepared at different annealing temperatures are shown in figure 4.19. The analysis were carried out at ambient temperature at an excitation wavelength of 340 nm. The photoluminescence properties of CdSeNPs were found to be annealing temperature dependent. The PL spectra of

Zn-doped CdSe nanoparticles annealed at various temperatures revealed a distinct increase in emission intensity with rising annealing temperature, peaking at 275 °C.

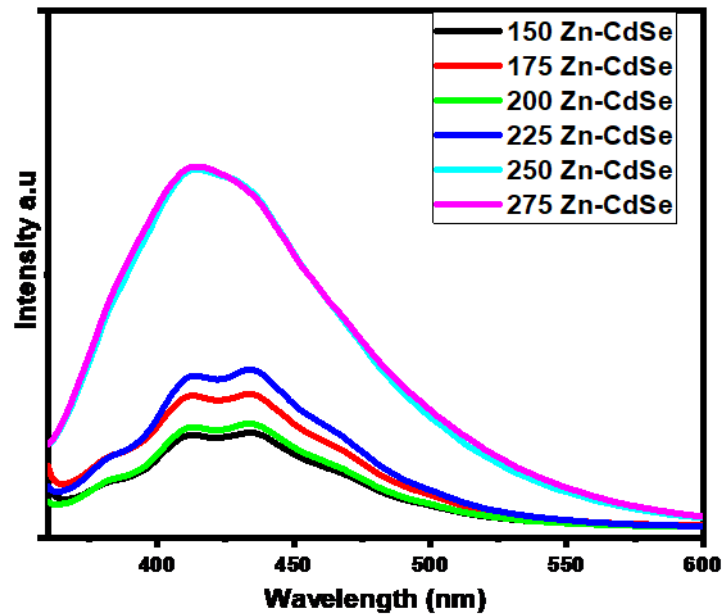


Figure 4.19: The emissions spectra of Zn-CdSe nanoparticles prepared at different annealing temperatures

This enhancement is attributed to improved crystallinity and reduced structural defects resulting from thermal treatment. Similar findings have been reported by (Kim, *et al.*, 2012), who observed that annealing CdS quantum dots at 100 °C significantly improved crystal quality and quantum efficiency—from 1 % to 29 %. The reduced density of non-radiative recombination centers due to defect relaxation enables more efficient radiative recombination, thus enhancing PL intensity. As annealing temperature increases, a redshift in the PL emission peaks is commonly observed. This phenomenon is primarily due to the growth of nanoparticle size resulting from enhanced atomic mobility at elevated temperatures. Larger nanoparticles exhibit reduced quantum confinement effects, leading to a decrease in bandgap energy and, consequently, a shift of emission to longer wavelengths.

4.4.4 FT-IR Analysis

Fourier Transform Infrared (FTIR) spectroscopy was employed to investigate the surface chemistry and functional groups present in Zn-CdSe nanoparticles subjected to annealing at varying temperatures (150 °C, 175 °C, and 225 °C). The FTIR spectra, as depicted in Figure 4.20, reveal distinct absorption bands corresponding to various vibrational modes, providing insights into the chemical modifications induced by thermal treatment.

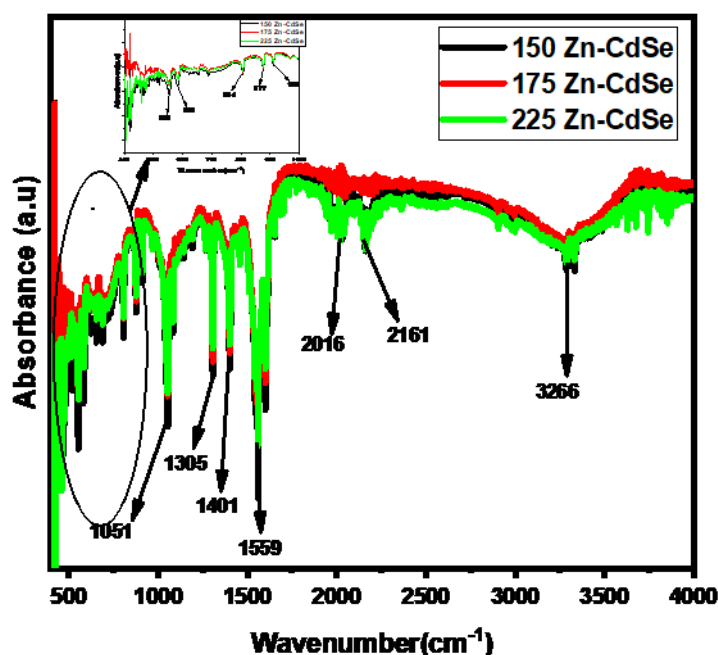


Figure 4.20: FTIR spectra of Zn-CdSeNPs annealed at different

All samples showed a broad absorption peak around 3400 cm⁻¹, attributed to O-H stretching vibrations, which indicates the presence of hydroxyl groups and adsorbed moisture on the nanoparticle surfaces. The intensity of this peak decreases as the annealing temperature rises, suggesting gradual elimination of surface hydroxyl groups and water through thermal desorption (Hussain *et al.*, 2021). Additionally, absorption bands in the range of 2850–2950 cm⁻¹ correspond to C–H stretching vibrations from aliphatic compounds. These bands are most intense in the sample annealed at 150 °C, likely due to residual zinc acetate dopant precursor and L-cysteine

capping agent. With increasing annealing temperature, the reduction in band intensity indicates the breakdown or evaporation of organic residues. (Chen *et al.*, 2019).

A prominent absorption band near 1700 cm^{-1} is observed, which is characteristic of C=O stretching vibrations from carbonyl or carboxylate groups. The position and intensity of this band exhibit slight variations with annealing temperature, suggesting alterations in the coordination environment of these groups. Such changes may be indicative of the transformation of surface-bound carboxylates or the formation of metal–selenium bond (Kurtina *et al.*, 2023). In the lower wavenumber region, bands appearing around $500\text{--}700\text{ cm}^{-1}$ are associated with metal–oxygen (M–O) and metal–selenium (M–Se) stretching vibrations. Specifically, the band near 680 cm^{-1} can be attributed to Zn–O stretching modes, while bands in the vicinity of 600 cm^{-1} may correspond to Cd–Se vibrations. The presence and evolution of these bands with annealing temperature provide evidence of changes in the bonding environment and crystallinity of the nanoparticles (Dejene, 2022).

4.5 Summary

The results presented in this chapter clearly demonstrate that the structural and optical properties of CdSe and Zn-doped CdSe nanoparticles are significantly influenced by growth temperature, dopant concentration, and annealing temperature. Growth temperature was found to affect the crystallinity and photoluminescence intensity of the nanoparticles, with optimal emission observed at moderate synthesis temperatures due to enhanced crystal quality. Varying the Zn dopant concentration revealed that moderate doping improved optical absorption and reduced bandgap energy, likely due to improved crystallinity and reduced defect density, with 11% Zn emerging as the optimum concentration. Additionally, annealing temperature was shown to impact particle size, structural ordering, and emission intensity, with $225\text{ }^{\circ}\text{C}$ identified as the optimal condition that balanced thermal energy for crystallization without causing significant grain growth. Overall, the findings confirm that careful tuning of synthesis parameters can significantly enhance the properties of nanoparticles for potential application in solar cells.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Nanoparticles of CdSe and Zn-CdSe were successfully synthesized using solgel method. Growth temperature, different mol % of Zinc dopant and annealing temperatures had enormously affected the properties of nanoparticles. Preferred growth orientation of CdSe nanoparticles occur in plane (111). The XRD pattern of CdSeNPs displayed zinc blende cubic and the patterns of CdSe nanoparticles revealed additional peaks at certain growth temperatures, which are attributed to the incomplete incorporation of selenium into the CdSe lattice. Crystal size calculated from Debye Scherrer equation showed that the crystal size increase with an increase in temperature up to an optimum level due to stabilization of crystal size and high rate of nucleation at higher temperature, then decrease. The largest crystal size was obtained at a growth temperature of 75°C and CdSe synthesized at a growth temperature of 120 °C had the smallest average crystal size.

When CdSeNPs were doped with varying concentration of zinc, the zinc blende cubic structure of CdSe was maintained. 3% Zn-CdSe had the highest intensity and 5% Zn-CdSe nanoparticles had the lowest intensity at peak (111). This means that at 3% Zn doped the nanoparticles were highly crystalline. Doping CdSeNPs increases its crystallinity. The intensity of the peaks decreased with increase in Zn dopant concentration. This is attributed by factors such as increase in micro strain, introduction of lattice distortion or partial transformation of material to amorphous phase. The average crystal size of CdSeNPs decrease when doped with Zn, with 15% Zn doped CdSe nanoparticles having a crystal size of 17.72 nm, 3% had 17.60 nm and pure CdSeNPs had a crystal size of 24.67 nm. This is because Zn^{2+} can substitute Cd^{2+} ions in the lattice of CdSe given that the ionic radius of Zn^{2+} (0.74 Å) is smaller than the ionic radius of Cd^{2+} (0.92 Å). This disparity causes a decrease in lattice parameters leading to a smaller crystallite size and more compact crystal structure.

On the effects of annealing temperature, Zn-CdSe synthesized at 225 °C had the highest intensity and Zn-CdSe synthesized at 275°C had the lowest intensity at peak (111). This means that at 225 °C the nanoparticles were highly crystalline.

The crystallite size increases as the annealing temperature rises from 150°C to 225 °C, reaching a maximum size of 28.11 nm at 225 °C which indicates to the diffusion of grain boundaries of smaller grains to form larger grains on annealing.

Absorption spectra were obtained when samples were characterized using UV-Vis spectroscopy. The samples were dissolved in ethanol and scan at a wavelength of 200 to 800 nm. Tauc's equation was plotted to obtain the bandgap energies of nanoparticles. Samples prepared at low temperature had high band gap energy. At higher temperatures above 90°C the band gap energy increase as crystal size decreases due to structural defects. Doping CdSe with Zn decreased the bandgap energy from 2.23 to 1.92 eV. The band gap energies obtained for samples annealed at 150, 175, 200, 225, 250, and 275°C are 2.10, 1.96, 2.24, 1.18, 2.53 and 1.23 eV respectively. Zn-CdSe annealed at 225°C had the smallest bandgap of 1.18 eV as compared to 2.23 eV of pure CdSeNPs.

PL spectra was used to determine electronic and defects in CdSe and Zn-CdSeNPs. The spectra of the samples were obtained at room temperature at an excitation energy of 400 nm. The photoluminescence properties of CdSeNPs were found to be growth temperature dependent. Sample prepared at room temperature (25 °C) did not emit when excited at a wavelength of 400 nm, this might have resulted from poor crystallinity due to slower growth rate. Maximum photoluminescence intensity was observed at sample prepared at a growth temperature of 90 °C. The intensity tends to decrease at higher temperatures, this result from increase in defect level since at higher temperature the stabilizer molecules are decomposed and they agglomerate causing surface defects. 1% Zn-CdSe nanoparticles had the highest PL intensity and 15% Zn-CdSe nanoparticle had the lowest PL intensity. At high dopant concentration the emission wavelength shift to longer wavelength (redshift) as a result of lattice strain or dopant induced defects. The PL intensity of Zn-doped CdSe nanoparticles increased with rising annealing temperature.

FT-IR spectra confirms the presence of functional groups in both pure and doped CdSe nanoparticles. At lower temperature intense peak at 840 cm^{-1} was observed for samples synthesized at a temperature of 25 and $60\text{ }^{\circ}\text{C}$. This peak correspond to metal- selenium bond vibration. At a higher wavelength of 3247 cm^{-1} a less intense peak was observed for CdSe nanoparticles prepared at a growth temperature of $60\text{ }^{\circ}\text{C}$, which correspond to O-H stretching vibration. The peak observed at 3280 cm^{-1} in Zn-CdSeNPs is assigned to O-H group present in the sample. Pure CdSeNPs did not absorbed in the functional group regions. The intensity of this peak increased with an increased in zinc dopant concentration. The prominent peak in the doped samples at 1556 cm^{-1} is assigned to stretching vibration of C=O present in the zinc acetate solution used as precursor of dopant and some from L-cysteine used as capping agent. The peaks observed in at 1382 and 1294 cm^{-1} correspond to COO^- stretching vibration.

5.2 Recommendations

5.2.1 Recommendation for policy

Based on the synthesis and characterization of Zn-CdSeNPs the following recommendations are suggested to help these nanoparticles become more applicable in solar cells.

To enhance the performance and quality of Zn-doped CdSe nanoparticles, a comprehensive characterization approach is essential. Techniques such as X-ray diffraction (XRD) should be employed to confirm the crystallinity and phase composition, while UV-Vis spectroscopy is useful for determining bandgap energy. Photoluminescence (PL) analysis helps assess electron-hole recombination dynamics, and Fourier Transform Infrared Spectroscopy (FTIR) is important for identifying surface functional groups and bonding characteristics.

Surface modification plays a critical role in minimizing surface defects. The use of appropriate capping agents not only improves nanoparticle stability and photoluminescence efficiency but also helps prevent oxidation and enhances dispersibility in various media.

Optimization of the synthesis process should focus on precise control of parameters such as dopant concentration, growth temperature, and annealing temperature. Zinc concentration should be carefully regulated to fine-tune the optical and electronic properties of the nanoparticles while avoiding the introduction of crystal defects caused by excessive doping. Doping with 11% zinc has been found to yield optimum results, while a growth temperature of 90 °C is recommended for producing high-quality CdSe nanoparticles with enhanced photoluminescence. The sol-gel method is particularly suitable for this purpose due to its ability to yield nanoparticles with uniform morphology and narrow size distribution.

Proper annealing conditions are crucial in enhancing structural and optical properties. Annealing temperatures between 200 °C and 250 °C significantly improve crystallinity and minimize structural defects by reducing non-radiative recombination centers. However, annealing above 275 °C may cause agglomeration and deterioration of the crystal structure and should therefore be avoided.

Lastly, the doping strategy must ensure uniform incorporation of zinc ions to maintain consistent material properties. Controlled doping technique, such as sol-gel is recommended to achieve a homogeneous distribution of zinc within the CdSe matrix.

5.2.2 Recommendation for Future Work

Future studies should investigate alternative dopants beyond zinc to assess their influence on the structural and optical properties of CdSe nanoparticles. Dopants such as manganese (Mn), copper (Cu), or iron (Fe) could offer enhanced performance depending on the intended application. Exploring and comparing these alternatives may reveal more efficient doping strategies.

Surface functionalization of Zn-CdSe nanoparticles could also be explored to tailor them for specific applications such as biosensing or medical imaging. Functional modification can enhance the compatibility, selectivity, and stability of the nanoparticles in different environments.

Testing the performance of Zn-doped CdSe nanoparticles in real devices, particularly in solar cells, is essential to evaluate their practical viability. Such studies would help transition the materials from laboratory development to industrial or commercial applications.

Reproducibility and scalability are critical for practical deployment. Future research should aim to standardize synthesis protocols to ensure consistent quality. The sol-gel technique, due to its cost-effectiveness and simplicity, shows promise for scale-up if optimized appropriately for batch-to-batch consistency.

Additionally, advanced characterization techniques such as transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and time-resolved photoluminescence (TRPL) should be employed to gain deeper insights into the nanoparticles' morphology, chemical states, and emission lifetimes. These would provide a more comprehensive understanding of the materials and guide further optimization.

applicable. Furthermore, Zn-doped CdSe nanoparticles should be tested in practical solar cell prototypes to evaluate their real-world performance and commercial viability, bridging the gap between laboratory research and practical application.

REFERENCES

- Abdulrahman, A. F., Ahmed, S. M., Hamad, S. M., & Barzinjy, A. A. (2021). Effect of Growth Temperature on Morphological, Structural, and Optical Properties of ZnO Nanorods Using Modified Chemical Bath Deposition Method. *Journal of Electronic Materials*, 50(3), 1482–1495. <https://doi.org/10.1007/s11664-020-08705-7>
- Acharya, A., Sahu, S., Balamurgan, S., & Roy, G. S. (2011). Effect of doping on nano cadmium-selenide (CdSe)-assessment through UV-VIS spectroscopy. *Lat. Am. J. Phys. Educ. Vol*, 5(1), 134.
- Akash, M. S. H., & Rehman, K. (2020). Ultraviolet-Visible (UV-VIS) Spectroscopy. In M. S. H. Akash & K. Rehman, *Essentials of Pharmaceutical Analysis* (pp. 29–56). Springer Nature Singapore. https://doi.org/10.1007/978-981-15-1547-7_3
- Akl, A. A., El Radaf, I. M., & Hassanien, A. S. (2020). Intensive comparative study using X-Ray diffraction for investigating microstructural parameters and crystal defects of the novel nanostructural ZnGa₂S₄ thin films. *Superlattices and Microstructures*, 143, 106544. <https://doi.org/10.1016/j.spmi.2020.106544>
- Akylbekova, A., Dauletbekova, A., Baimukhanov, Z., Vlasukova, L. A., Usseinov, A., Saduova, N., Akilbekov, A. T., Pankratov, V. A., & Popov, A. I. (2024). Annealing Effect on Structural, Optical and Electrophysical Properties of ZnSe Nanocrystals Synthesized into SiO₂/Si Ion Track Template. *Materials*, 17(16), 4149. <https://doi.org/10.3390/ma17164149>
- Alagarasan, D., Varadharajaperumal, S., Arun Kumar, K. D., Naik, R., Arunkumar, A., Ganesan, R., Hegde, G., & El Sayed Massoud, E. (2021). Optimization of different temperature annealed nanostructured CdSe thin film for photodetector applications. *Optical Materials*, 122, 111706. <https://doi.org/10.1016/j.optmat.2021.111706>
- Arsalani, S., Loewa, N., Kosch, O., Radon, P., Baffa, O., & Wiekhorst, F. (2021). Magnetic separation of iron oxide nanoparticles to improve their application for magnetic particle imaging. *Physics in Medicine & Biology*, 66(1), 015002. <https://iopscience.iop.org/article/10.1088/1361-6560/abcd19/meta>

- Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., & Taga, Y. (2001). Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science*, 293(5528), 269–271. <https://doi.org/10.1126/science.1061051>
- Asere, T. G., & Laing, G. D. (2020). Zn-doped CdSe nanoparticles: Impact of synthesis conditions on photocatalytic activity. *Environmental Technology & Innovation*, 20, 101126. <https://doi.org/10.1016/j.eti.2020.101126>
- Bahari, N., Hashim, N., Abdan, K., Md Akim, A., Maringgal, B., & Al-Shdifat, L. (2023). Role of Honey as a Bifunctional Reducing and Capping/Stabilizing Agent: Application for Silver and Zinc Oxide Nanoparticles. *Nanomaterials*, 13(7), 1244. <https://doi.org/10.3390/nano13071244>
- Baishya, K., Ray, J. S., Dutta, P., Das, P. P., & Das, S. K. (2018). Graphene-mediated band gap engineering of WO₃ nanoparticle and a relook at Tauc equation for band gap evaluation. *Applied Physics A*, 124(10), 704. <https://doi.org/10.1007/s00339-018-2097-0>
- Bamal, D., Singh, A., Chaudhary, G., Kumar, M., Singh, M., Rani, N., Mundlia, P., & Sehrawat, A. R. (2021). Silver Nanoparticles Biosynthesis, Characterization, Antimicrobial Activities, Applications, Cytotoxicity and Safety Issues: An Updated Review. *Nanomaterials*, 11(8), 2086. <https://doi.org/10.3390/nano11082086>
- Beskers, T. F., Hofe, T., & Wilhelm, M. (2015). Development of a chemically sensitive online SEC detector based on FTIR spectroscopy. *Polymer Chemistry*, 6(1), 128–142. <https://pubs.rsc.org/en/content/articlehtml/2014/py/c4py01043d>
- Bokov, D., Turki Jalil, A., Chupradit, S., Suksatan, W., Javed Ansari, M., Shewael, I. H., Valiev, G. H., & Kianfar, E. (2021). Nanomaterial by Sol-Gel Method: Synthesis and Application. *Advances in Materials Science and Engineering*, 2021(1), 5102014. <https://doi.org/10.1155/2021/5102014>
- Ca, N. X., Van, H. T., Do, P. V., Thanh, L. D., Tan, P. M., Truong, N. X., Oanh, V. T. K., Binh, N. T., & Hien, N. T. (2020). Influence of precursor ratio and dopant concentration on the structure and optical properties of Cu-doped ZnCdSe-alloyed quantum dots. *RSC Advances*, 10(43), 25618–25628. <https://doi.org/10.1039/D0RA04257A>
- Catalán-Gómez, S., Castellano, E. M., Schwarz, M., Bajo, M. M., Vargas, L. D., Gonzalo, A., Redondo-Cubero, A., Carro, A. G., Hierro, A., & Ulloa, J. M.

- (2024). Gallium nanoparticles as antireflection structures on III-V solar cells. *Solar Energy Materials and Solar Cells*, 265, 112632. <https://www.sciencedirect.com/science/article/pii/S0927024823004531>
- Change, I. C. (1996). The science of climate change. *Second Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge.
- Chen, Y.-A., Chou, K.-H., Kuo, Y.-Y., Wu, C.-Y., Hsiao, P.-W., Chen, P.-W., Yuan, S.-H., & Wu, D.-S. (2019). Formation of ZnO/Zn_{0.5}Cd_{0.5}Se Alloy Quantum Dots in the Presence of High Oleylamine Contents. *Nanomaterials*, 9(7), 999. <https://doi.org/10.3390/nano9070999>
- Choi, H., Radich, E. J., & Kamat, P. V. (2014). Sequentially Layered CdSe/CdS Nanowire Architecture for Improved Nanowire Solar Cell Performance. *The Journal of Physical Chemistry C*, 118(1), 206–213. <https://doi.org/10.1021/jp410235s>
- de Freitas, J. N., Grova, I. R., Akcelrud, L. C., Arici, E., Sariciftci, N. S., & Nogueira, A. F. (2010). The effects of CdSe incorporation into bulk heterojunction solar cells. *Journal of Materials Chemistry*, 20(23), 4845–4853. <https://pubs.rsc.org/en/content/articlehtml/2010/jm/c0jm00191k>
- Dejene, F. B. (2022). Characterization of low-temperature-grown ZnO nanoparticles: The effect of temperature on growth. *Journal of Physics Communications*, 6(7), 075011. <https://doi.org/10.1088/2399-6528/ac8049>
- Delice, S., Isik, M., & Gasanly, N. M. (2018). Characterization of trap centers in Gd₂O₃ nanoparticles by low temperature thermoluminescence measurements. *Optik*, 158, 237–242. <https://doi.org/10.1016/j.ijleo.2017.12.102>
- Doan, N. S., Huh, J., Mac, V. H., Kim, D., & Kwak, K. (2020). Probabilistic Risk Evaluation for Overall Stability of Composite Caisson Breakwaters in Korea. *Journal of Marine Science and Engineering*, 8(3), 148. <https://doi.org/10.3390/jmse8030148>
- Dubey, S., Sarvaiya, J. N., & Seshadri, B. (2013). Temperature dependent photovoltaic (PV) efficiency and its effect on PV production in the world—a review. *Energy Procedia*, 33, 311–321. <https://www.sciencedirect.com/science/article/pii/S1876610213000829>

- Ellison, D. (2018). Forests and Water. *Background Analytical Study*, 2. https://www.researchgate.net/profile/David-Ellison-5/publication/324685224_From_Myth_to_Concept_and_Beyond_-_The_BioGeoPhysical_Revolution_and_the_Forest-Water_Paradigm/links/5adc6de6a6fdcc29358a3b41/From-Myth-to-Concept-and-Beyond-The-BioGeoPhysical-Revolution-and-the-Forest-Water-Paradigm.pdf
- Emori, W., Ogunwale, G. J., Louis, H., Agwamba, E. C., Wei, K., Unimuke, T. O., Cheng, C.-R., Ejiofor, E. U., Asogwa, F. C., & Adeyinka, A. S. (2022). Spectroscopic (UV–vis, FT-IR, FT-Raman, and NMR) analysis, structural benchmarking, molecular properties, and the in-silico cerebral anti-ischemic activity of 2-amino-6-ethoxybenzothiazole. *Journal of Molecular Structure*, 1265, 133318. <https://doi.org/10.1016/j.molstruc.2022.133318>
- Enders, A. A., North, N. M., Fensore, C. M., Velez-Alvarez, J., & Allen, H. C. (2021). Functional Group Identification for FTIR Spectra Using Image-Based Machine Learning Models. *Analytical Chemistry*, 93(28), 9711–9718. <https://doi.org/10.1021/acs.analchem.1c00867>
- Enriquez, J. P. (2013). effect of annealing time and temperature on structural, optical and electrical properties of cds films deposited by cbd. *Chalcogenide Letters*, 10(2). <https://search.ebscohost.com/login.aspx?direct=true&profile=ehost&scope=site&authtype=crawler&jrnl=15848663&AN=88425922&h=UMc4enmkix20%2FDwibLWVoPMktr2i7tgP9unTvuSWX6fGov0XbXT9GMidqhR0c25dNg7G8uqKFI3FzhT7nEAiRg%3D%3D&crl=c>
- Ermrich, M., & Oppen, D. (2011). X-Ray powder diffraction. *XRD for the Analyst, Getting Acquainted with the Principles*, 63–85. https://malvern-panalytical.promoshops.nu/media/602045_HR.pdf
- Faiz, H., Zuberi, A., Nazir, S., Rauf, M., & Younus, N. (2015). Zinc oxide, zinc sulfate and zinc oxide nanoparticles as source of dietary zinc: Comparative effects on growth and hematological indices of juvenile grass carp (Ctenopharyngodon idella). *International Journal of Agriculture and Biology*, 17(3). https://www.researchgate.net/profile/Muhammad-Rauf-8/publication/315825652_Zinc_Oxide_Zinc_Sulfate_and_Zinc_Oxide_Nano

particles_as_Source_of_Dietary_Zinc_Comparative_Effects_on_Growth_and_Hematological_Indices_of_Juvenile_Grass_Carp_Ctenopharyngodon_idella/links/58ebd239aca272bd2875f95c/Zinc-Oxide-Zinc-Sulfate-and-Zinc-Oxide-Nanoparticles-as-Source-of-Dietary-Zinc-Comparative-Effects-on-Growth-and-Hematological-Indices-of-Juvenile-Grass-Carp-Ctenopharyngodon-idella.pdf

- Fantazzini, D., Höök, M., & Angelantoni, A. (2011). Global oil risks in the early 21st century. *Energy Policy*, 39(12), 7865–7873. <https://www.sciencedirect.com/science/article/pii/S0301421511007245>
- Florides, G. A., & Christodoulides, P. (2009). Global warming and carbon dioxide through sciences. *Environment International*, 35(2), 390–401. <https://doi.org/10.1016/j.envint.2008.07.007>
- Gakuru, S., Kiprotich, S., & Waithaka, P. (2024). Structural and Optical Properties of Fe Doped TiO_2 Nanoparticles: Investigation of Effects of Different Doping Concentration. *Advances in Materials*, 13(2), 20–30. <https://doi.org/10.11648/j.am.20241302.11>
- Gan, Y. X., Jayatissa, A. H., Yu, Z., Chen, X., & Li, M. (2020). Hydrothermal synthesis of nanomaterials. *Journal of Nanomaterials*, 2020, 1–3. <https://www.hindawi.com/journals/jnm/2020/8917013/>
- Ghamgosar, P. (2017). *Advanced Metal Oxide Semiconductors for Solar Energy Harvesting and Solar Fuel Production* [PhD Thesis, Luleå University of Technology]. <https://www.diva-portal.org/smash/record.jsf?pid=diva2:1144392>
- Ghazy, A., Safdar, M., Lastusaari, M., & Karppinen, M. (2020). Amorphous-to-crystalline transition and photoluminescence switching in guest-absorbing metal–organic network thin films. *Chemical Communications*, 56(2), 241–244. <https://doi.org/10.1039/C9CC08904G>
- Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Lyman, C. E., Lifshin, E., Sawyer, L., Michael, J. R., Goldstein, J. I., & Newbury, D. E. (2003). Special topics in scanning electron microscopy. *Scanning Electron Microscopy and X-Ray Microanalysis: Third Edition*, 195–270. https://link.springer.com/chapter/10.1007/978-1-4615-0215-9_5

- Gong, H., He, Y., Yin, J., Liu, S., Qing, M., Peng, Q., Huo, C.-F., Wang, H., Yang, Y., & Wen, X.-D. (2020). Electronic effects of transition metal dopants on Fe(100) and Fe₅ C₂ (100) surfaces for CO activation. *Catalysis Science & Technology*, 10(7), 2047–2056. <https://doi.org/10.1039/C9CY02428J>
- Grolik, B., & Kopp, J. (2003). Optical properties of thin semiconductor films. *October, 31st*, 1–11.
- Gupta, P., & Ramrakhiani, M. (2009). Influence of the particle size on the optical properties of CdSe nanoparticles. *The Open Nanoscience Journal*, 3(1). <https://benthamopen.com/ABSTRACT/TONANOJ-3-15>
- Haghipour, N., & Burg, J.-P. (2014). Geomorphological analysis of the drainage system on the growing Makran accretionary wedge. *Geomorphology*, 209, 111–132. <https://www.sciencedirect.com/science/article/pii/S0169555X13006168>
- Hamizi, N. A., Johan, M. R., Chowdhury, Z. Z., Wahab, Y. A., Al-Douri, Y., Saat, A. M., & Pivezhzani, O. A. (2018). Optical structure modification induced by lattice strain in Mn-doped CdSe QDs. *Optical Materials*, 86, 441–448. <https://doi.org/10.1016/j.optmat.2018.10.041>
- Handique, K. C., Siboh, D., Nanung, Y., Barman, B., & Kalita, P. K. (2021). Effect of temperature on the optical properties of chemically synthesized CdSe nanostructures. *Materials Today: Proceedings*, 46, 6312–6317. <https://doi.org/10.1016/j.matpr.2020.05.444>
- Hassen, M., Riahi, R., Laatar, F., & Ezzaouia, H. (2020). Optical and surface properties of CdSe thin films prepared by sol-gel spin coating method. *Surfaces and Interfaces*, 18, 100408. <https://doi.org/10.1016/j.surfin.2019.100408>
- Heede, R. (2023). *History of Eni emissions 1953-2022 and attributed climate reparations*. <https://www.greenpeace.org/static/planet4-italy-stateless/2024/01/163d12b1-history-of-eni-emissions-1953-2022-and-attributed-climate-reparations-heede.pdf>
- Houghton, J. (2009). *Global warming: The complete briefing*. Cambridge university press. <https://books.google.com/books?hl=en&lr=&id=oUbWnWfnaJ4C&oi=fnd&>

pg=PR17&dq=%5D+Global+warming:+the+complete+briefing+J+Houghton
&ots=0PSibyZ_1T&sig=1w3vUbgrF1OGEEPryZ3yUCWqTqo

- Huang, J., Jiang, Y., An, T., & Cao, M. (2020). Increasing the active sites and intrinsic activity of transition metal chalcogenide electrocatalysts for enhanced water splitting. *Journal of Materials Chemistry A*, 8(48), 25465–25498. <https://doi.org/10.1039/D0TA08802A>
- Hussain, S., Iqbal, M., Khan, A. A., Khan, M. N., Mehboob, G., Ajmal, S., Ashfaq, J. M., Mehboob, G., Ahmed, M. S., Khisro, S. N., Li, C.-J., Chikwenze, R., & Ezugwu, S. (2021). Fabrication of Nanostructured Cadmium Selenide Thin Films for Optoelectronics Applications. *Frontiers in Chemistry*, 9, 661723. <https://doi.org/10.3389/fchem.2021.661723>
- Imran, M., Saleem, A., Khan, N. A., Khurram, A. A., & Mehmood, N. (2018). Amorphous to crystalline phase transformation and band gap refinement in ZnSe thin films. *Thin Solid Films*, 648, 31–38. <https://doi.org/10.1016/j.tsf.2018.01.010>
- Innocenzi, P. (2019). *The Sol-to-Gel Transition*. Springer International Publishing. <https://doi.org/10.1007/978-3-030-20030-5>
- Jamkhande, P. G., Ghule, N. W., Bamer, A. H., & Kalaskar, M. G. (2019). Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. *Journal of Drug Delivery Science and Technology*, 53, 101174. <https://www.sciencedirect.com/science/article/pii/S1773224718308189>
- Jepngetich, J., Njoroge, P. W., Opiyo, S., & Kiprotich, S. (2025). Synthesis and characterization of Ag-ZnO using citrus reticulata peel extract. *Materials Research Express*, 12(5), 055003. <https://doi.org/10.1088/2053-1591/adda91>
- Jin, W., Gao, Z., Zhou, Y., Yu, B., Zhang, H., Peng, H., Liu, Z., & Dai, L. (2014). Novel graphene–oxide–semiconductor nanowire phototransistors. *Journal of Materials Chemistry C*, 2(9), 1592–1596. <https://pubs.rsc.org/en/content/articlehtml/2014/tc/c3tc32123a>
- Kabir, E., Kumar, P., Kumar, S., Adelodun, A. A., & Kim, K.-H. (2018). Solar energy: Potential and future prospects. *Renewable and Sustainable Energy Reviews*, 82, 894–900.

- Kajihara, K. (2013). Recent advances in sol–gel synthesis of monolithic silica and silica-based glasses. *Journal of Asian Ceramic Societies*, 1(2), 121–133. <https://doi.org/10.1016/j.jascer.2013.04.002>
- Kazem, H. A., & Chaichan, M. T. (2016). Experimental analysis of the effect of dust's physical properties on photovoltaic modules in Northern Oman. *Solar Energy*, 139, 68–80.
- Kiprotich, S., Dejene, F. B., & Onani, M. O. (2019). Structural and optical properties of novel CdSe nanoparticles produced via a facile synthetic route: Studies on the effects of cadmium sources. *Surface and Interface Analysis*, 51(7), 722–732. <https://doi.org/10.1002/sia.6643>
- Kiprotich, S., Dejene, F. B., Ungula, J., & Onani, M. O. (2016). The influence of reaction times on structural, optical and luminescence properties of cadmium telluride nanoparticles prepared by wet-chemical process. *Physica B: Condensed Matter*, 480, 125–130. <https://doi.org/10.1016/j.physb.2015.08.062>
- Kiprotich, S., Onani, M. O., & Dejene, F. B. (2018). High luminescent L -cysteine capped CdTe quantum dots prepared at different reaction times. *Physica B: Condensed Matter*, 535, 202–210. <https://doi.org/10.1016/j.physb.2017.07.037>
- Kotkata, M. F., Masoud, A. E., Mohamed, M. B., & Mahmoud, E. A. (2009). Structural characterization of chemically synthesized CdSe nanoparticles. *Physica E: Low-Dimensional Systems and Nanostructures*, 41(4), 640–645. <https://doi.org/10.1016/j.physe.2008.10.019>
- Kuo, S.-Y., Chen, W.-C., Lai, F.-I., Cheng, C.-P., Kuo, H.-C., Wang, S.-C., & Hsieh, W.-F. (2006). Effects of doping concentration and annealing temperature on properties of highly-oriented Al-doped ZnO films. *Journal of Crystal Growth*, 287(1), 78–84. <https://www.sciencedirect.com/science/article/pii/S0022024805011693>
- Kurtina, D. A., Grafova, V. P., Vasil'eva, I. S., Maksimov, S. V., Zaytsev, V. B., & Vasiliev, R. B. (2023). Induction of Chirality in Atomically Thin ZnSe and CdSe Nanoplatelets: Strengthening of Circular Dichroism via Different Coordination of Cysteine-Based Ligands on an Ultimate Thin Semiconductor Core. *Materials*, 16(3), 1073. <https://doi.org/10.3390/ma16031073>

- Lambora, S., & Bhardwaj, A. (2023). Morphology Transition with Temperature and its Effect on Optical Properties of Colloidal MoS₂ Nanostructures. *ACS Omega*, 8(30), 27725–27731. <https://doi.org/10.1021/acsomega.3c03478>
- Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Vander Elst, L., & Muller, R. N. (2008). Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications. *Chemical Reviews*, 108(6), 2064–2110. <https://doi.org/10.1021/cr068445e>
- Letcher, T. M. (2020). *Future energy: Improved, sustainable and clean options for our planet*. Elsevier.
- Lewis, N. S., & Nocera, D. G. (2006). Powering the planet: Chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences*, 103(43), 15729–15735. <https://www.pnas.org/doi/abs/10.1073/pnas.0603395103>
- Lims, S. C., Jose, M., Aswathappa, S., Dhas, S. S. J., Kumar, R. S., & Pham, P. V. (2024). Co-precipitation synthesis of highly pure and Mg-doped CdO nanoparticles: From rod to sphere shapes. *RSC Advances*, 14(31), 22690–22700. <https://doi.org/10.1039/D4RA03525A>
- Mahato, S., Shakti, N., & Kar, A. K. (2015). Annealing temperature dependent structural and optical properties of electrodeposited CdSe thin films. *Materials Science in Semiconductor Processing*, 39, 742–747. <https://doi.org/10.1016/j.mssp.2015.06.019>
- Menazea, A. A., Ismail, A. M., Awwad, N. S., & Ibrahim, H. A. (2020). Physical characterization and antibacterial activity of PVA/Chitosan matrix doped by selenium nanoparticles prepared via one-pot laser ablation route. *Journal of Materials Research and Technology*, 9(5), 9598–9606. <https://www.sciencedirect.com/science/article/pii/S2238785420314782>
- Mourdikoudis, S., Pallares, R. M., & Thanh, N. T. K. (2018). Characterization techniques for nanoparticles: Comparison and complementarity upon studying nanoparticle properties. *Nanoscale*, 10(27), 12871–12934. <https://doi.org/10.1039/C8NR02278J>
- Muniz, F. T. L., Miranda, M. R., Morilla dos Santos, C., & Sasaki, J. M. (2016). The Scherrer equation and the dynamical theory of X-ray diffraction. *Acta*

- Crystallographica Section A: Foundations and Advances*, 72(3), 385–390.
<https://scripts.iucr.org/cgi-bin/paper?S205327331600365X>
- Nath, D., Singh, F., & Das, R. (2020). X-ray diffraction analysis by Williamson-Hall, Halder-Wagner and size-strain plot methods of CdSe nanoparticles- a comparative study. *Materials Chemistry and Physics*, 239, 122021.
<https://doi.org/10.1016/j.matchemphys.2019.122021>
- Pandey, S. K., Pandey, S. K., Mukherjee, C., Mishra, P., Gupta, M., Barman, S. R., D'Souza, S. W., & Mukherjee, S. (2013). Effect of growth temperature on structural, electrical and optical properties of dual ion beam sputtered ZnO thin films. *Journal of Materials Science: Materials in Electronics*, 24(7), 2541–2547. <https://doi.org/10.1007/s10854-013-1130-5>
- Peter, L. M. (2011). The Grätzel Cell: Where Next? *The Journal of Physical Chemistry Letters*, 2(15), 1861–1867. <https://doi.org/10.1021/jz200668q>
- Polman, A., Knight, M., Garnett, E. C., Ehrler, B., & Sinke, W. C. (2016). Photovoltaic materials: Present efficiencies and future challenges. *Science*, 352(6283), aad4424. <https://doi.org/10.1126/science.aad4424>
- Pradeev Raj, K., Sadaiyandi, K., Kennedy, A., Sagadevan, S., Chowdhury, Z. Z., Johan, Mohd. R. B., Aziz, F. A., Rafique, R. F., Thamiz Selvi, R., & Rathina Bala, R. (2018). Influence of Mg Doping on ZnO Nanoparticles for Enhanced Photocatalytic Evaluation and Antibacterial Analysis. *Nanoscale Research Letters*, 13(1), 229. <https://doi.org/10.1186/s11671-018-2643-x>
- Rahman, I. A., & Padavettan, V. (2012). Synthesis of silica nanoparticles by sol-gel: Size-dependent properties, surface modification, and applications in silica-polymer nanocomposites—a review. *Journal of Nanomaterials*, 2012, 8–8. <https://www.hindawi.com/journals/jnm/2012/132424/abs/>
- Ravi, P., Kumaravel, D. K., Subramanian, D., Thoondyaiah, D., Rao, V. N., Venkatakrisnan, S. M., & Sathish, M. (2021). Temperature-Driven Morphology Control on CdSe Nanofractals and Its Influence over the Augmented Rate of H₂ Evolution: Charge Separation via the S-Scheme Mechanism with Incorporated Cu₃P. *ACS Applied Energy Materials*, 4(12), 13983–13996. <https://doi.org/10.1021/acsaem.1c02790>
- Rivera-Marquez, J. A., Contreras-Rascón, J. I., Lozada-Morales, R., Díaz-Reyes, J., Castillo-Palomera, R., Alvarez, M. E., Meléndez-Lira, M., & Zelaya-Angel, O.

- (2020). Raman spectroscopy study of the wurtzite-zinc blende phase transition of bare CdSe nanoparticles. *Materials Science and Engineering: B*, 260, 114621. <https://doi.org/10.1016/j.mseb.2020.114621>
- Roy, P., Kumar Sinha, N., Tiwari, S., & Khare, A. (2020). A review on perovskite solar cells: Evolution of architecture, fabrication techniques, commercialization issues and status. *Solar Energy*, 198, 665–688. <https://doi.org/10.1016/j.solener.2020.01.080>
- S, R., J, S., M, K., A, A., & M, J. (2016). Studies on Different Doped Zn Concentrations of CdSe Thin Films. *Journal of Powder Metallurgy & Mining*, 05(01). <https://doi.org/10.4172/2168-9806.1000143>
- Saif, O. M., Elogail, Y., Abdolkader, T. M., Shaker, A., Zekry, A., Abouelatta, M., Salem, M. S., & Fedawy, M. (2023). Comprehensive Review on Thin Film Homojunction Solar Cells: Technologies, Progress and Challenges. *Energies*, 16(11), 4402. <https://doi.org/10.3390/en16114402>
- Sethi, V. K., Pandey, M., & Shukla, M. P. (2011). Use of nanotechnology in solar PV cell. *International Journal of Chemical Engineering and Applications*, 2(2), 77. <http://www.ijcea.org/papers/79-A555.pdf>
- Shafeeq, K. M., Athira, V. P., Kishor, C. H. R., & Aneesh, P. M. (2020). Structural and optical properties of V2O5 nanostructures grown by thermal decomposition technique. *Applied Physics A*, 126(8), 586. <https://doi.org/10.1007/s00339-020-03770-5>
- Sharma, K., Al-Kabbi, A. S., Saini, G. S. S., & Tripathi, S. K. (2012). Determination of dispersive optical constants of nanocrystalline CdSe (nc-CdSe) thin films. *Materials Research Bulletin*, 47(6), 1400–1406.
- Sharma, S., Jain, K. K., & Sharma, A. (2015). Solar cells: In research and applications—a review. *Materials Sciences and Applications*, 6(12), 1145–1155. <https://scirp.org/journal/PaperInformation?PaperID=62181>
- Singh, J., & Verma, N. K. (2012). Synthesis and Characterization of Fe-Doped CdSe Nanoparticles as Dilute Magnetic Semiconductor. *Journal of Superconductivity and Novel Magnetism*, 25(7), 2425–2430. <https://doi.org/10.1007/s10948-012-1631-0>
- Slavov, D., Tomaszewska, E., Grobelny, J., Drenchev, N., Karashanova, D., Peshev, Z., & Bliznakova, I. (2024). FTIR spectroscopy revealed nonplanar

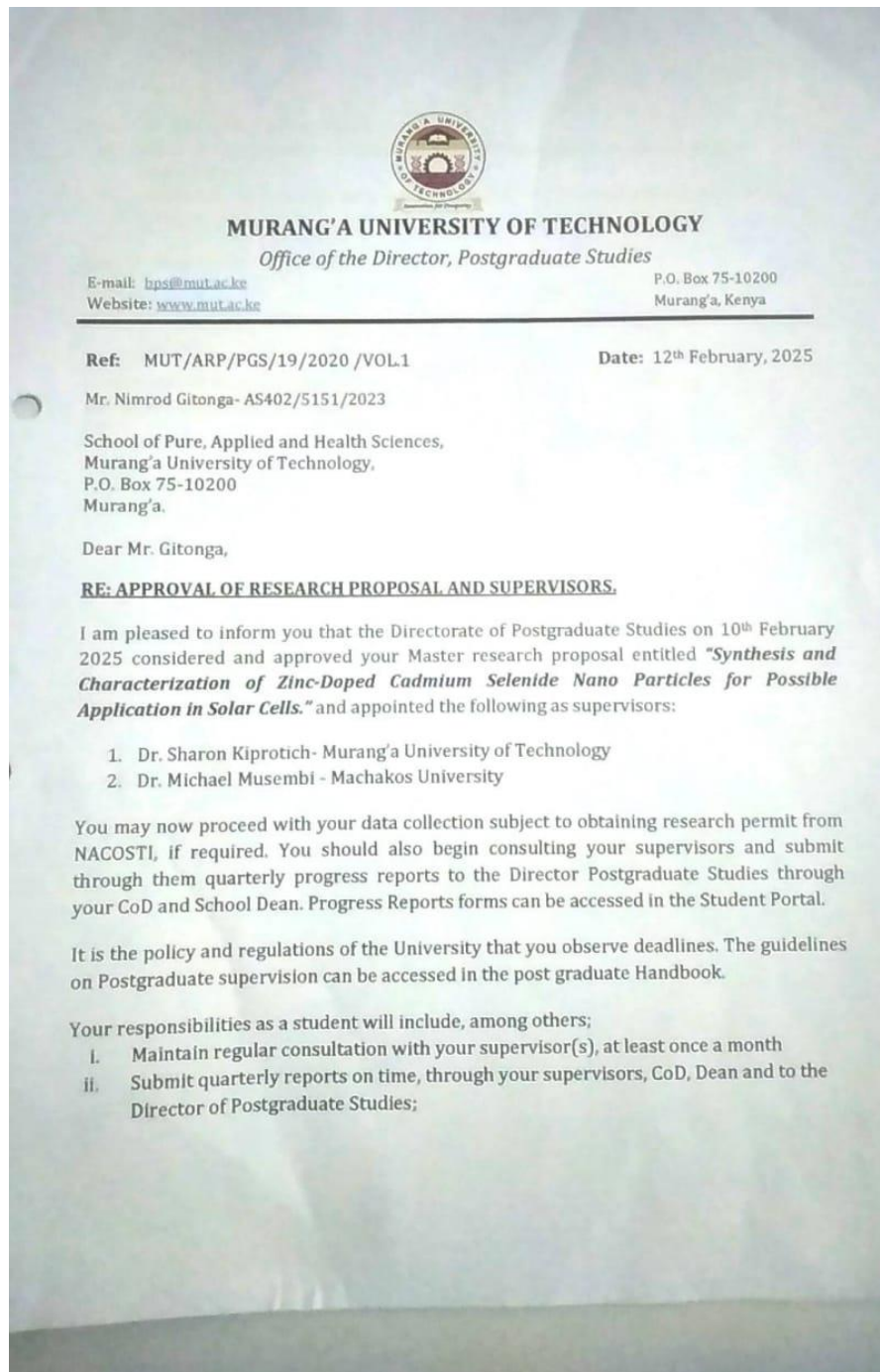
- conformers, chain order, and packaging density in diOctadecylamine- and octadecylamine-passivated gold nanoparticles. *Journal of Molecular Structure*, 1314, 138827. <https://doi.org/10.1016/j.molstruc.2024.138827>
- Sobhani, A., & Salavati-Niasari, M. (2015). CdSe nanoparticles: Facile hydrothermal synthesis, characterization and optical properties. *Journal of Materials Science: Materials in Electronics*, 26(9), 6831–6836. <https://doi.org/10.1007/s10854-015-3297-4>
- Söder, R. (2023). Climate change, security and military organizations: Changing notions in the Swedish armed forces. *Earth System Governance*, 15, 100169. <https://doi.org/10.1016/j.esg.2023.100169>
- Soeder, D. J. (2021). Fossil Fuels and Climate Change. In D. J. Soeder, *Fracking and the Environment* (pp. 155–185). Springer International Publishing. https://doi.org/10.1007/978-3-030-59121-2_9
- Sridevi, D. V., Sundaravadivel, E., & Kanagaraj, P. (2019). Influence of Fe doping on structural, physicochemical and biological properties of CdSe nanoparticles. *Materials Science in Semiconductor Processing*, 101, 67–75. <https://www.sciencedirect.com/science/article/pii/S1369800119308935>
- Sumaya, M. U., Maria, K. H., Toma, F. T. Z., Zubair, M. A., & Chowdhury, M. T. (2023). Effect of stabilizer content in different solvents on the synthesis of ZnO nanoparticles using the chemical precipitation method. *Heliyon*, 9(10), e20871. <https://doi.org/10.1016/j.heliyon.2023.e20871>
- Sun, S., Zhang, X., Zhang, J., Wang, L., Song, X., & Yang, Z. (2013). Surfactant-free CuO mesocrystals with controllable dimensions: Green ordered-aggregation-driven synthesis, formation mechanism and their photochemical performances. *CrystEngComm*, 15(5), 867–877. <https://pubs.rsc.org/en/content/articlehtml/2013/ce/c2ce26216a>
- Suresh, S., & Arunseshan, C. (2014). Dielectric Properties of Cadmium Selenide (CdSe) Nanoparticles synthesized by solvothermal method. *Applied Nanoscience*, 4(2), 179–184. <https://doi.org/10.1007/s13204-012-0186-5>
- Terricabres-Polo, R., De Bruin, T. A., Kaul, A., Van Sark, W. G. J. H. M., & Donega, C. D. M. (2024). Durable Quantum Dot-Based Luminescent Solar Concentrators Enabled by a Photoactive Block Copolymer. *Advanced Energy Materials*, 14(48), 2402375. <https://doi.org/10.1002/aenm.202402375>

- Thirugnanam, N., & Govindarajan, D. (2016). Aqueous synthesis and characterization of Ni, Zn co-doped CdSe QDs. *International Nano Letters*, 6(2), 105–109. <https://doi.org/10.1007/s40089-015-0175-2>
- Tollefson, J. (2022). *Scientists raise alarm over ‘dangerously fast’ growth in atmospheric methane.* Nature Publishing Group. <https://www.sciencenovate.com/articles/d41586-022-00312-2.pdf>
- Tsoutsos, T., Frantzeskaki, N., & Gekas, V. (2005). Environmental impacts from the solar energy technologies. *Energy Policy*, 33(3), 289–296. <https://www.sciencedirect.com/science/article/pii/S0301421503002416>
- Venci, X., George, A., Rahul, S., Dhayal Raj, A., Albert Irudayaraj, A., Josephine, R. L., John Sundaram, S., & Kaviyarasu, K. (2023). Investigation on the formation of self-assembled CdSe dendrite structures and their photocatalytic efficiency. *Inorganic Chemistry Communications*, 148, 110309. <https://doi.org/10.1016/j.inoche.2022.110309>
- Vogel, D. J., & Kilin, D. S. (2015). First-Principles Treatment of Photoluminescence in Semiconductors. *The Journal of Physical Chemistry C*, 119(50), 27954–27964. <https://doi.org/10.1021/acs.jpcc.5b06434>
- Waweru, G., Kiprotich, S., & Waithaka, P. (2024). *Effects of Growth Temperature on the Structural and Optical Properties of Synthesized Titanium Dioxide Nanoparticles.* <https://idl-bnc-idrc.dspacedirect.org/bitstreams/1e065307-334f-44fa-9559-d21854b73e9d/download>
- Wei, N. T. J., Nan, W. J., & Guiping, C. (2017). Experimental study of efficiency of solar panel by phase change material cooling. *IOP Conference Series: Materials Science and Engineering*, 217(1), 012011. <https://iopscience.iop.org/article/10.1088/1757-899X/217/1/012011/meta>
- West, A. R. (1999). Basic solid state chemistry. (No Title). <https://cir.nii.ac.jp/crid/1130282269181478528>
- Williams, J. V., Adams, C. N., Kotov, N. A., & Savage, P. E. (2007). Hydrothermal Synthesis of CdSe Nanoparticles. *Industrial & Engineering Chemistry Research*, 46(13), 4358–4362. <https://doi.org/10.1021/ie061413x>
- Yadav, A. A. (2012a). Synthesis and characterization of Fe doped cadmium selenide thin films by spray pyrolysis. *Journal of Alloys and Compounds*, 543, 129–134. <https://doi.org/10.1016/j.jallcom.2012.07.097>

- Yadav, A. A. (2012b). Synthesis and characterization of Fe doped cadmium selenide thin films by spray pyrolysis. *Journal of Alloys and Compounds*, 543, 129–134. <https://www.sciencedirect.com/science/article/pii/S092583881201314X>
- Yang, W., Liu, J., Wang, Y., & Gao, S. (2020). Experimental study on the thermal conductivity of aerogel-enhanced insulating materials under various hygrothermal environments. *Energy and Buildings*, 206, 109583. <https://www.sciencedirect.com/science/article/pii/S037877881931549X>
- Yao, G., & Huang, Q. (2022). Theoretical and experimental study of the infrared and Raman spectra of L-lysine acetylation. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 278, 121371. <https://doi.org/10.1016/j.saa.2022.121371>
- Ye, Y., Gan, L., Dai, L., Dai, Y., Guo, X., Meng, H., Yu, B., Shi, Z., Shang, K., & Qin, G. (2011). A simple and scalable graphene patterning method and its application in CdSe nanobelt/graphene Schottky junction solar cells. *Nanoscale*, 3(4), 1477–1481. <https://pubs.rsc.org/en/content/articlehtml/2011/nr/c0nr00999g>
- Zaini, M. S., Ying Chyi Liew, J., Alang Ahmad, S. A., Mohmad, A. R., & Kamarudin, M. A. (2020). Quantum Confinement Effect and Photoenhancement of Photoluminescence of PbS and PbS/MnS Quantum Dots. *Applied Sciences*, 10(18), 6282. <https://doi.org/10.3390/app10186282>
- Zhao, F. A., Xiao, H. Y., Bai, X. M., & Zu, X. T. (2019). Effects of Ag doping on the electronic and optical properties of CdSe quantum dots. *Physical Chemistry Chemical Physics*, 21(29), 16108–16119. <https://doi.org/10.1039/C9CP02433F>
- Zhao, W., Yang, D., Yang, Z., & Liu, S. (Frank). (2017). Zn-doping for reduced hysteresis and improved performance of methylammonium lead iodide perovskite hybrid solar cells. *Materials Today Energy*, 5, 205–213. <https://doi.org/10.1016/j.mtener.2017.06.009>
- Zhu, Z., Shao, H., Dong, X., Li, N., Ning, B.-Y., Ning, X.-J., Zhao, L., & Zhuang, J. (2015). Electronic Band Structure and Sub-band-gap Absorption of Nitrogen Hyperdoped Silicon. *Scientific Reports*, 5(1), 10513. <https://doi.org/10.1038/srep10513>

APPENDICES

Appendix 1: Research authorization



- iii. Ensure quality work all through;
- iv. Present your research findings at 2-3 seminars/conferences prior to thesis examination.
- v. Publish one article from your research findings in a refereed journal prior to thesis examination.

For any further clarification please contact the undersigned.

Yours Sincerely,

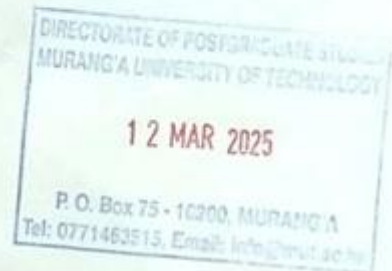


Prof. Geoffrey Muchiri, PhD
Director, Postgraduate Studies

GM/HBK

Copy to:

1. Registrar – Academics and Students Affairs
2. Dean, School of Pure, Applied and Health Sciences



Appendix 2: Publication

This thesis has produced the following publication:

Gitonga, N., Kiprotich, S., & Musembi, M. (2025). Structural, photoluminescence and optical properties of CdSe:Zn nanoparticles: Effects of doping concentrations. *American Journal of Condensed Matter Physics*, 14(1), 1–7.