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Cerium (III) Doping as a Strategy to Improve Antimicrobial Efficiency of Zinc Sulfide Nanomaterial

by

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The undersigned certify that they have read, and recommended to the Institute of Engineering for acceptance, a thesis report entitled "Cerium (III) Doping as a Strategy to Improve Antimicrobial Efficiency of Zinc Sulfide Nanomaterial" submitted by Saugat Chapagain in partial fulfillment of the requirements for the degree of Masters in Material Science and Engineering.

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ABSTRACT

Zinc Sulphide is a wide bandgap semiconductor used in various engineering applications in the field of nanomaterials. In this work, Zinc Sulphide, 0.5 % Cerium doped Zinc Sulphide, 0.5 % Cobalt doped Zinc Sulphide and 0.25% Cobalt – 0.25% Cerium co-doped nanomaterials were prepared by coprecipitation method. The physicochemical properties of these materials were studied using FESEM/EDX. FESEM showed mostly uniform spherical agglomeration of nanoparticles formed in the range of around 30-40 nm. EDX for the Co-Ce co-doped ZnS confirmed doping of the Zinc Sulphide with Cobalt and Cerium. XRD showed no significant change in lattice structures of the samples confirming the doping of samples. Antimicrobial effects of as-prepared nanomaterials were studied by Agar well diffusion method. Results show that 0.5 % Cerium doped Zinc Sulphide enhanced the antibacterial effect significantly in case of E. coli compared to those in S. aureus and C. albicans.

Keywords: *Zinc Sulphide, Cerium, Cerium doped Zinc Sulphide, Antimicrobial effect*

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LIST OF ABBREVIATIONS

Ag	Argentum
Au	Aurum
CdS	Cadmium Sulphide
Ce	Cerium
CNT	Carbon nanotube
Co	Cobalt
Cu	Copper
DNA	Deoxyribonucleic acid
Eu	Europium
Fe_3O_4	Ferrous ferric oxide
Mn	Manganese
Ni	Nickel
NP	Nanoparticle
Pb	Lead
PbS	Lead Sulphide
ROS	Reactive oxygen species
Tb	Terbium
TiO_2	Titanium dioxide
UV	Ultraviolet
ZnO	Zinc oxide
ZnS	Zinc Sulphide

LIST OF SYMBOLS

Å	Angstrom
°C	Degree Celsius
e–	Electrons
eV	Electron volt
g	Gram
h^+	Holes
L	Liter
M	Molar
mL	Milliliter
mg	Milligram
mm	Millimeter
pH	Potential of Hydrogen
psi	Pound per square inch

CHAPTER 1: INTRODUCTION

1.1 Background

Nanomaterials are a group of substances that have individual particle size smaller than 100 nm. The advancement on nanomaterials in this 21st century has been massive. Because they occupy a small space and have a large surface area-to-volume ratio, they have unique physical, chemical, and biological properties. These unique properties due to nanoscale effects make nanoparticles very different from their bulk forms. The nano forms show greater reactivity, electron transport, optical absorption, and catalytic efficiency. Few types of nanoparticles like metal nanoparticles (Au, Ag), metal oxide nanoparticles (TiO_2, ZnO), semiconductor nanoparticles (ZnS and CdS), and carbon-based nanomaterials (carbon nanotubes, fullerene and graphene) exist (Jeevanandam et al., 2018; Madhwani & Jain, 2015). They can also be found in a variety of shapes like spheres, rods, wires, sheets, hollow structures and core-shell particles. Each shape has its own surface energies and functional behaviors. These changes have a big effect on the properties of nanomaterials like charge mobility, photocatalytic efficiency, etc. Semiconductor nanoparticles have become the basis for many new technologies, such as biosensors, photocatalysts, solar cells, and many other optoelectronic devices (Wang et al., 2013; Fang et al., 2011)

Cadmium sulfide (CdS) and Lead sulfide (PbS) are some common examples of metal sulfide nanoparticles that have been studied for their optical and electronic properties. However, their application in real life is limited because they are very toxic. CdS NPs are known to produce high levels of reactive oxygen species (ROS). This high concentration of ROS can lead to oxidative stress, cause DNA damage, and have shown cytotoxic effects in both HeLa cells and microbes (Hossain et al., 2013). Cadmium (Cd) based materials are further discouraged for use due to the environmental and health hazards it possesses (Rodríguez-Fragoso et al., 2012). PbS NPs have shown to cause inflammatory responses and oxidative damage in organs like the lungs in animals. The effect seen is greater for NPS in comparison to bulk Lead (Pb) compounds (Li et al., 2013). The negative effects due to CdS and Pbs on cells and metabolic functions make them unsuitable for biomedical or environmental applications where biocompatibility is essential and cytotoxicity is to be minimized.

Because of the various dangers on cells and human metabolic functions caused by heavy metal sulfides (CdS and PbS), there is a growing focus on finding safer alternatives. Zinc sulfide (ZnS) has been seen as a promising candidate because of the low toxicity shown by ZnS nanoparticles in comparison to that of CdS or PbS. Comparative studies of ZnS and CdS quantum dots show that ZnS has less effect on DNA, even at higher doses than that of CdS (Grzesiakowska et al., 2023). ZnS nanoparticles also have good optical properties, chemical stability, and biocompatibility. This makes ZnS an useful alternate for antimicrobial, photocatalytic and biomedical applications (Aguilar Jáuregui et al., 2022).

Among the various nanomaterials, Zinc sulfide (ZnS) is a promising semiconductor because it has a wide bandgap of around 3.6 eV, high photostability, and is an environmentally safe alternative. Zinc sulfide can be typically found in zinc blende and wurtzite structures. Both forms show good luminescence and high thermal stability (Kaur et al., 2016). On the nanoscale, we can see quantum confinement effects that modify its electronic and optical behaviors resulting in a tunable bandgap and optical properties. Scientists have studied ZnS nanostructures for more advanced uses like photocatalysis, solar energy conversion, and antimicrobial coatings (Shanmugam et al., 2014; Kwamboka et al., 2016).

Antimicrobial resistance has now become a global health problem that could set back years of progress in the field of public health and medicine. Many antibiotics have lost effect on microbial organisms and have proven ineffective in recent times. The increasing resistance of bacteria to antibiotics requires the development of alternative plans and antimicrobial strategies to cope with the antimicrobial resistance seen at present times. Nanomaterials, especially metal and semiconductor NPs show good antibacterial properties against various bacteria of gram-positive and gram-negative strains and on various Fungi as well. The formation of ROS causes oxidative stress on the bacterial surface. This results in disruption of cell membranes and causes cell destruction (Sharmin, 2021).

ZnS nanoparticles are semiconductors which can move to the surface of the microbes and generate reactive oxygen species when in contact with them which in turn damages microbial cells. But this ability can be further enhanced by doping the nanoparticles. Doping is a great way to alter the electronic structure, optical absorption, and defect density of the semiconductors. Introducing foreign atoms into the ZnS lattice can modify its electronic band structure, crystallinity of the nanoparticle, and enhance light absorption in the visible spectrum (Poornaprakash et al., 2021, de Andrade Neto et al., 2021). Transition metal dopants, particularly cobalt (Co^{2+}), can replace Zn^{2+} ions in the lattice of the Zinc Sulphide, resulting in localized states also called as luminescence centers, depending on the concentration of the dopant and the conditions under which it was synthesized (Patel et al., 2017; Weide et al., 2016).

In contrast to transition metal dopants, rare earth dopants play a unique role in optical alteration and charge carrier dynamics. Cerium (Ce^{3+}/Ce^{4+}), with its two valence states, can shift between being an electron donor and an acceptor. This process can be called a redox cycle. This makes photocatalytic performance better and makes it less likely to break down during photocatalysis. Ce doping also enhances up the defect mediated energy transfer processes, which makes ZnS efficient when it is exposed to both UV and visible light spectrum (Suganthi & Pushpanathan-2, 2019).

Recent studies indicate that Cobalt doping also enhances optoelectronic performance of the nanoparticle (Das et al., 2020; Emegha et al., 2024) and shows quantum confinement effect which may result in an improvement of the the antimicrobial ability of the doped Zinc Sulphide (Patel et al., 2016) whereas Cerium doping improves optical absorption and photocatalytic properties (Tounsi et al., 2022; de Andrade Neto et al., 2021). However, the combined effect of these dopants, namely Ce and Co on ZnS, has not been sufficiently studied, leading to a lack of understanding of how dual doping simultaneously modifies band structures and antimicrobial effectiveness of the ZnS nanoparticle. The synergistic combination of cobalt and cerium doping can offer a unique approach to enhance the antimicrobial properties of ZnS. Cobalt and Cerium co-doping is expected to improve the efficiency of ROS generation and increase the effectiveness of synthesized nanoparticles in terms of antimicrobial activity.

Enhanced antimicrobial property of the ZnS nanomaterials could make a big difference in health care, food safety, wastewater treatment and protecting the environment. These materials can be incorporated into medical devices and systems like wound healing or scaffolds preparation. They can also be used in textiles for antimicrobial coatings. They can also be incorporated in preparation of filtration membranes, and cleaning systems for wastewater treatment. They are a good alternative for scalable applications because they are safe, cheap, and generally stable. This research promotes to a sustainable and secure nanotechnology solution to combat microbial contamination, particularly in environments where conventional antibiotics are ineffective, via the synthesis of Co–Ce co-doped ZnS nanoparticles.

1.2 Problem Statement

ZnS nanoparticles are known for their potential in optoelectronics and as antimicrobial applications, but pure ZnS has some limitations like a large bandgap (about 3.6 eV), a high rate of electron-hole recombination, and reduced activity in visible light. These characteristics make it less applicable for real-world antibacterial uses. Also, pure ZnS has a low surface defect density and poor charge transfer, which makes it harder for reactive oxygen species to form and reduces antimicrobial efficiency (Suganthi & Pushpanathan-2, 2019; de Andrade Neto et al., 2021).

Several studies have attempted to overcome these limitations through single-metal doping methodologies. Transition metal dopants like Co, Mn, and Ni, have shown improvements in the photocatalytic and magnetic properties of ZnS nanoparticles (Patel et al., 2017; Lahariya & Ramrakhiani, 2020), while rare earth elements like Ce, Er enhance luminescence and optical absorption of the ZnS nanoparticles (Tounsi et al., 2022; Poornaprakash et al., 2021). However, these studies often focus on the effects of specific dopants and do not provide a systematic comparison among various types of dopants.

Cobalt doping improves visible-light responsiveness and photoactivity. However, if doping concentration goes above a certain limit, it could make recombination centers. Likewise, Cerium doping improves electron trapping and stability, but it might not be enough to make absorption go into the visible region alone. As a result, the synergistic effect of Co–Ce co-doping on ZnS nanomaterials has not been sufficiently inspected, particularly regarding the enhancement of antibacterial effectiveness.

The absence of studies investigating how co-doping influences structural, electronic, and biological properties of the synthesized ZnS nanoparticles presents a significant research gap. Understanding these relationships is crucial for designing doped semiconductor materials with optimal antimicrobial performance. Thus, there is a need to develop and evaluate Co and Ce doped ZnS nanomaterials synthesized under controlled conditions, analyze their physicochemical, antimicrobial and optical properties. The co-doped sample must be further investigated against the singly doped samples and systematically evaluated about their antimicrobial potential against pathogenic microorganisms.

1.3 Objectives

1.3.1 General Objective:

1. To synthesize pure Zinc Sulphide, Cerium, Cobalt and Cerium Cobalt co-doped Zinc Sulphide nanoparticles and evaluate their antimicrobial and antifungal performance.

1.3.2 Specific Objectives:

1. To synthesize pure Zinc Sulphide, Cerium, Cobalt and Cerium Cobalt co-doped Zinc Sulphide nanoparticles using co-precipitation method.
2. To characterize the structural, optical and antimicrobial properties of the synthesized ZnS nanomaterials.
3. To assess the performance of as-prepared nanomaterials in antimicrobial applications.

1.4 Significance of Study

This study holds significant scientific importance as it examines the synthesis and antibacterial characteristics of ZnS nanoparticles, including their cerium (Ce) and cobalt (Co) and Ce-Co co-doped forms. As microbes and fungal diseases become more common with increasing microbial resistance, there is a growing need for other antimicrobial materials that are effective, and safe for the environment. Nanomaterials like ZnS, are considered as promising alternatives because of their unique optical, electrical, and surface properties which make it easier to inhibit microbial growth through mechanisms like reactive oxygen species (ROS), and membrane disruption of microorganisms.

Doping ZnS nanoparticles with transition and rare-earth metals such as Co and Ce further enhances these intrinsic properties. This is seen because of modification in the electronic band structure, increase in the charge carrier separation efficiency, and improvement in surface reactivity of the obtained nanoparticles. Doping with Ce introduces Ce^{3+}/Ce^{4+} pairs that help redox reactions. These redox active pairs of Ce^{3+}/Ce^{4+} speed up catalytic oxidation and the reactive oxygen species (ROS) formation. Co doping, on the other hand, can introduce defect sites in the lattice of the ZnS that make it easier for electron hole mobility and impact the antibacterial performance. This dual-doping strategy may result in a superior antimicrobial and antifungal efficiency of doped nanoparticles compared to pure ZnS nanoparticles.

The findings of this study hold significance not only for materials science but also for their practical applications. Understanding how dopants change the physical, chemical, and biological properties of ZnS can help us make better antimicrobial coatings, biomedical implants, and water treatment and purification systems in the future. The study also contributes to sustainable nanotechnology by proposing ZnS based substitutes for silver or copper nanoparticles, which are more costly and toxic to the environment.

This study advances our understanding of doped semiconductor nanoparticles and provides valuable information about developing efficient, affordable, and eco-friendly antimicrobial alternatives to combat the worldwide problem of microbial resistance and pathogenic control using the synthesized NPs.

1.5 Research Scope

The study focuses on synthesizing Zinc Sulphide nanoparticles using coprecipitation method in the lab and evaluating their performance in antimicrobial and antifungal applications. The scope includes material synthesis using co precipitation method, characterization of the synthesized nanomaterials using advanced techniques such as Ultraviolet visible Spectroscopy (UV-vis), Fourier Transform Infrared spectroscopy (FTIR), Scanning electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), X-ray Diffraction (XRD), and antimicrobial testing using Agar well diffusion method.

1.6 Limitations

The synthesis of required nanoparticles can be done easily in the laboratory. Limitations of this work include the industrial scalability of the obtained nanoparticles for engineering applications. The availability of high-resolution characterization tools for further characterization of the synthesized nanoparticles remains another major limitation of this work.

1.7 Thesis Structure Overview

This report has been divided into five chapters. Chapter 1 introduces the study by presenting the background of zinc sulphide (ZnS) as a semiconductor. It discusses the need for dopant, and the motivation behind cobalt and cerium co-doping. It outlines the research problems, objectives, and significance of the study in enhancing antimicrobial properties of ZnS nanoparticles. Chapter 2 provides a detailed review of concepts on both single-doped and co-doped ZnS systems. This chapter also identifies the existing research gaps that justify the present work. Chapter 3 explains the experimental methodology used in synthesizing ZnS nanoparticles doped samples, including materials, synthesis procedures, characterization techniques (UV–Vis, FTIR, XRD, FESEM, EDX, antimicrobial test). Chapter 4 presents the experimental results obtained from structural, optical, morphological, and antimicrobial characterization and analyses the changes introduced by co-doping. Finally, Chapter 5 discusses these findings in relation to previously published literature, and summarizes the major outcomes of the study, draws conclusions, provides practical and scientific implications, and suggests directions for future research on doped ZnS and related nanomaterials.

CHAPTER 2: LITERATURE REVIEW

2.1 Nanoparticles

Nanotechnology is the study of particles below 100 nanometers in size. Thus, materials with at least one dimension below 100 nm are called nanomaterials. They have unique structural, optical, and chemical properties that come from quantum confinement and their very high surface area-to-volume ratio These properties make nanoparticles very different from their bulk forms. Optical absorption, reactivity, catalytic efficiency and Thermal resistance are some of the properties of Zinc Sulphide which are enhanced in the nanoparticles as opposed to their bulk forms (Kaur et al., 2016). Nanoparticles can be further classified as metal nanoparticles (Au, Ag, Cu, etc.), metal oxide nanoparticles (TiO_2, ZnO, Fe_3O_4, etc.), semiconductor nanoparticles (ZnS, PbS, CdS, etc.), and carbon-based nanomaterials (carbon nanotubes (CNTs), fullerenes and graphene) (Jeevanandam et al., 2018). They can also be found in shapes such as spheres, rods, wires, sheets, hollow structures, core-shell particles, and even in forms of porous architectures. Each shape has its own surface energies and functional behaviors (Choi et al., 2014). These changes have a big effect on properties of the NPs like charge mobility, photocatalytic efficiency, etc.

Because these properties of NPs can be altered, they have become important in many fields. For example, semiconductor nanoparticles can be used in optoelectronics and photocatalysis, metal and metal oxide nanoparticles can be used for antimicrobial properties; and carbon-based nanomaterials can be used for energy storage, and biomedical engineering (Alivisatos, 1996). Improvements in synthesis mechanisms and nanoscale engineering keep paving new properties for nanoparticles, leading to newer applications.

2.2 Zinc Sulfide (ZnS) Nanomaterials

Zinc sulfide (ZnS) is one of the oldest and well-known II–VI semiconductor compounds. ZnS is known for its unique structural, optical, and electronic properties.

It commonly crystallizes in two polymorphic forms: the cubic zinc blende and the hexagonal wurtzite phase, both displaying wide bandgaps of roughly 3.6 eV (Fang et al., 2011; Wang et al., 2013). At the nanoscale, ZnS shows strong quantum confinement effects that change its optical and luminescent properties. These adjustable features make it very attractive for application in the fields of biomedicine, photocatalysis, and optoelectronics (Kaur et al., 2016).

Different ZnS nanomaterials synthesis routes have been used over a long time. These methods include sol-gel, hydrothermal, chemical precipitation, and microwave-assisted techniques of synthesis (Ramteke et al., 2018; Patel et al., 2017). The chemical co-precipitation method is still one of the most popular among all the methods because it is an easy to use and cheap method. Also, this method leads to nanoparticles with high purity and consistent shape and crystallinity. ZnS nanoparticles produced via co-precipitation often exhibit homogeneity, facilitating precise incorporation of dopant ions in the lattice of the ZnS (Wang et al., 2013).

The optical properties of ZnS are significantly influenced by the defect states, surface morphology, and conditions of synthesis of the nanoparticles. The particle size is found to be reduced when structure of ZnS transitions between zinc blende and wurtzite, affecting their photoluminescence properties and adsorption properties (Qadri et al., 2001). It is also evident that ZnS nanostructure arrays, such as nanowires, nanorods, and thin films, have more surface area and directional charge transport which is useful for electronic devices and catalysis (Fang et al., 2011).

In addition to its optoelectronic properties, ZnS has also shown promise as an antimicrobial agent through photocatalytic ROS production. ZnS nanoparticles exhibit antimicrobial properties against both Gram-positive and Gram-negative strains due to their ability to disrupt microbial membranes (Kwamboka et al., 2016). However, their activity is still limited by the wide bandgap, which makes it difficult to work within a visible light spectrum. Because of this, doping techniques are required to make ZnS work better in visible light and improve microbial inhibition (Suganthi & Pushpanathan, 2019).

2.3 Doping Strategies in ZnS Nanomaterials

Doping is the process of adding foreign atoms to a host lattice to change its electrical, optical, or catalytic properties. Doping ZnS can introduce impurity energy levels within the bandgap, which makes it easier for electron hole separation and extend absorption in the visible range (Poornaprakash et al., 2021).

The two main types of metal dopants commonly used are transition metals (3d series) and rare-earth elements (4f series). Researchers have investigated transition metals like Co, Mn, Ni, and Cu widely to study shallow donor or acceptor states. On the other hand, rare earth metal ions like Ce, Eu, and Tb enhance optical emission and defect stability of the nanoparticles (Tammenmaa et al., 1986).

Co-doped ZnS nanoparticles synthesized using a microwave-assisted method showed a substantial reduction in bandgap energy with increasing Co concentration (Patel et al., 2017), thereby confirming the effectiveness of transition metal ions in regulating optical transitions. Doping introduces lattice distortions and defect states that trap charges, improving photocatalytic degradation and antibacterial activity of the nanoparticles (Suganthi & Pushpanathan, 2019).

The type of dopant and concentration of dopant vastly influence the performance of ZnS nanoparticles. Excess dopant concentration leads to phase segregation or recombination centers, which reduces the efficiency of the nanoparticles (Weide et al., 2016). Thus, optimizing the concentration of dopants is essential for obtaining a balance between improved conductivity and structural integrity.

2.4 Cobalt Doping in ZnS Nanomaterials

2.4.1 Structural and Optical Modifications

Doping cobalt to ZnS changes the host crystal lattice a lot because the ionic radius of Co^{2+} is very close to that of Zn^{2+} (0.72 Å in Co^{2+} vs. 0.74 Å in Zn^{2+}). Adding Co^{2+} ions to the ZnS lattice by substitution causes small lattice strain, changes the local electrical environment, and changes the way defects are spread out in the lattice (Heiba et al., 2021).

Salem et al. (2014) studied Cobalt doped ZnS nanoparticles synthesized with a capping agent and found that Cobalt doping could change optical absorption in the visible spectrum. The bandgap increased from 3.95 eV to 4.08 eV as the quantity of Cobalt increased. This verified that Co^{2+} is involved in changing the band structure. Weide et al. (2016) stated that Co doping increases the photostability of ZnS. This stability is very critical for long-term photocatalytic and antimicrobial applications of the ZnS nanoparticles.

2.4.2 Antimicrobial and Photocatalytic Activity

Das et al. (2020) discovered that doping cobalt at low concentrations (≤3%) can enhance optoelectronic properties. Emegha et al. (2024) synthesized zinc–cobalt sulfide nanofilms, demonstrating enhanced conductivity and optical activity, suggesting potential applications in optoelectronics and antimicrobial applications.

Sharma et al. (2025) demonstrated that Co-doped ZnS quantum dots possess the capability to charge storage, thereby indicating their role in improving electronic behavior. These traits also make ZnS better at redox reactions, which are very important for oxidizing microbial cells and thus inhibiting microbial growth. So, Co doping not only reduces the optical bandgap, but it also makes antimicrobial performance better by encouraging ROS-mediated bacterial inactivation under visible light.

2.5 Cerium (Ce^{3+}/Ce^{4+}) Doping in ZnS Nanomaterials

2.5.1 Structural and Optical Effects

Cerium, a rare-earth element that can exist in two oxidation states (Ce^{3+} and Ce^{4+}), is a good dopant for controlling charge carrier dynamics. Cerium doped ZnS nanoparticles and observed a decrease in bandgap energy and an increase in luminescence intensity, which was credited to the 4f–5d electronic transitions of Ce^{3+} ions.

Tounsi et al. (2022) applied the sol–gel method to synthesize Cerium doped ZnS thin films, observing improved crystallinity and visible-light absorption of the NPs. The Ce ions created additional defect levels within the bandgap of the ZnS, which promotes efficient charge separation and improves photoactivity in the visible range of light. Suganthi & Pushpanathan (2019) observed that Ce doping affected phase stability, causing ZnS to shift from the cubic to the wurtzite phase at higher concentrations, which can be justified by the improved photocatalytic degradation performance.

Shanmugam et al. (2014) examined Ce^{3+}-doped ZnS nanostructures and detected significant luminous emission peaks which could be attributed to 5d to 4f transitions, which in turn confirms the substitution of Ce^{3+} at Zn^{2+} sites. These findings demonstrate that Ce serves as a luminescence activator while simultaneously improving energy transfer and optical responsiveness.

2.5.2 Functional and Antimicrobial Improvements

Ce-doped ZnS has enhanced antibacterial properties because of the ROS production and has better surface activity because of defects. de Andrade Neto et al. (2021) synthesized Ce–Ni co-doped ZnS nanoparticles, which showed significant improvements in antibacterial and electrical properties due to synergistic interactions between the dopants Cerium and Nickel. Suganthi & Pushpanathan (2019) also showed that Ce-doped ZnS was better at photocatalytic degradation of dyes justifying that it works well as a photocatalyst and might also work as an antibacterial agent.

The redox cycling between Ce^{3+} and Ce^{4+} helps in trapping photogenerated electrons and reduces recombination rates. These effects causes oxidative stress to rise in bacterial cells, which damages the cell wall and slows down metabolism (Tammenmaa et al., 1986; Poornaprakash et al., 2021).

2.6 Cobalt Cerium co-doping

Cobalt Cerium co-doping represents an advanced modification strategy that combines the optical and catalytic advantages of both transition metal and rare-earth dopants.

While Co introduces 3d states that enhance visible absorption, Ce contributes to charge trapping and redox cycling, altogether improving the carrier mobility and photoactivity of the nanoparticles.

Poornaprakash et al. (2021) demonstrated that co-doping ZnS with 3d and 4f elements significantly tailors its optical and magnetic properties, reducing bandgap and enhancing defect-mediated transitions. Similarly, Lahariya & Ramrakhiani (2020) investigated Mn–Ni co-doped ZnS systems and found that co-doping leads to strong luminescence and magnetic coupling, implying that similar synergistic outcomes can be expected from Co–Ce doping on ZnS.

It has been analyzed that transition metal doping in ZnS for photovoltaic performance enhancement and concluded that multi-dopant systems can simultaneously improve electrical conductivity, carrier lifetime, and stability. Translating these findings to antimicrobial applications suggests that Co–Ce co-doped ZnS nanoparticles could achieve higher ROS production and improved antimicrobial activity.

Moreover, dual doping may stabilize both ZnS crystal phases and reduce non-radiative recombination losses. This combination enhances the durability and reactivity of the nanomaterial in biological systems, making it suitable for biomedical coatings and disinfection technologies (Emegha et al., 2024; Sharma et al., 2025).

2.7 Antimicrobial Mechanisms

Metal and metal-based nanoparticles demonstrate good antimicrobial ability via a synergy of physicochemical interactions at the cellular interface, the liberation of metal ions, and the production of reactive oxygen species (ROS). (Sharmin et al., 2021). An increasing amount of research on green-synthesized nanoparticles shows that these methods still work when plant extracts are used as reducing and capping agents to make the particles. For example, Subedee et al. (2023) made nanoparticles of copper-zinc (Cu-Zn) alloy from the stem extract of Tinospora cordifolia and found that they were very effective against both Gram-positive and Gram-negative bacteria. This may be credited to the bimetallic synergy of Cu and Zn, which enhances ion release and reactive oxygen species (ROS) production. This resulted in membrane disruption. The phytochemicals from the extract that are stuck to the surface of the nanoparticles may help them stick to the walls of microbial cells even more and cause oxidative stress in the area, which would make the bactericidal effects even stronger when extracts are used.

Parajuli et al. (2024) synthesized silver nanoparticles from the methanolic extract of Artemisia vulgaris leaves, exhibiting significant antibacterial ability. For the Artemisia derived Ag NPs, the presence of plant-based phytochemicals which allow for closer contact with microbial cells, which would increase the production of ROS and interactions between metals and biomolecules. The incorporation of nanoparticles can further refine antimicrobial performance by controlling nanoparticle dispersion, release, and surface exposure. Rajaure et al. (2024) incorporated Ag NPs into cellulose nanocrystals derived from Eulaliopsis binata leaves, noting enhanced antimicrobial activity compared to cellulose nanocrystals alone.

Across these studies, several core antimicrobial mechanisms consistently emerge like membrane disruption through physical interaction, generation of ROS and interference with intracellular signaling leading to slowed metabolism and cell death (Sharmin et al., 2021). The green-synthesized nanocomposites reported by Subedee et al. (2023), Parajuli et al. (2024), and Rajaure et al. (2024) align with this framework enhancing biocompatibility and potentially yielding synergistic antimicrobial effects. These insights are highly relevant for the design of future nanomaterials that integrate antimicrobial efficiency with environmentally sustainable synthesis methodologies and safer alternatives.

2.8 Antimicrobial Mechanisms of Doped ZnS Nanoparticles

The main things that affect how well doped ZnS nanoparticles kill bacteria are the production of reactive oxygen species (ROS), the way surface charges interact with each other, and the way they directly touch microbial membranes. Doped ZnS absorbs photons when light hits it. This moves electrons (e^-) from the valence band to the conduction band and leaves holes (h^+) behind. These charge carriers are involved in surface redox events that create reactive oxygen species (ROS) like hydroxyl radicals and superoxide ions, which kill parts of microbes (Suganthi & Pushpanathan, 2019).

These organisms kill bacterial cells by causing oxidative stress, lipid peroxidation, and DNA damage. Doping Co and Ce makes this process better by lowering recombination, making carriers live longer, and letting light absorb into the visible spectrum (Salem et al., 2014; Tounsi et al., 2022).

Also, metal ions like Co^{2+} can directly change the membranes of bacteria, making them less permeable and changing how they break down food. Cerium, on the other hand, makes redox cycling happen all the time, even when there isn't much light (de Andrade Neto et al., 2021). This dual mechanism makes doped ZnS different from regular photocatalytic systems because it works for a longer time.

There is no doubt in the literature that adding Co and Ce to ZnS separately makes its optical, catalytic, and antibacterial properties better. Nonetheless, a substantial gap remains in systematic studies of Co–Ce co-doped ZnS intended to enhance antibacterial efficacy, thereby affirming the focus of this thesis.

2.9 Research Gap

A significant amount of research has been conducted on the preparation and modification of ZnS nanomaterials, predominantly focusing on single dopant systems, such as transition metals (Co, Mn, Ni, Cu) or rare-earth elements (Ce, Eu, Tb). These studies have shown that doping can change the optical, luminescence and structural properties of ZnS greatly (Patel et al., 2017; Tounsi et al., 2022). However, the synergistic effects of dual dopants, particularly Cobalt and Cerium when co-doped have not been thoroughly examined in terms of their antibacterial potential.

Co doping can enhance the absorption of visible light and the charge separation (Weide et al., 2016; Salem et al., 2014), whereas Ce doping can increase defect management and luminescence property of the substance (Tounsi et al., 2022; Suganthi & Pushpanathan, 2019). Even so, insufficient research exists regarding the impact of Co and Ce co-doping on the optical and antimicrobial properties of ZnS nanoparticles. Thus, this study is based on the novelty of the co-doping of the Cerium and Cobalt on Zinc Sulphide and study it’s antimicrobial property.

CHAPTER 3: MATERIALS AND METHOD

3.1 Materials

- Zinc Sulphate heptahydrate ($ZnSO_4.7H_2O$) (Qualigens Fine Chemicals)
- Sodium Sulphide nonahydrate ($Na_2S.9H_2O$) (Fizmerk India Chemicals)
- Ammonium Chloride (NH_4Cl) (SRL Pvt. Ltd.)
- Ammonium Hydroxide ($NH_4(OH)$) (Fizmerk India Chemicals)
- Cerium (III) Nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) (Sigma-Aldrich)
- Cobalt Nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (Chemsynth Fine Chemicals)
- MH agar powder (Sisco research laboratories Pvt. Ltd, India)
- Methanol (Qualigens Fine Chemicals)
- Distilled water

3.2 Method

3.2.1 Research Methodology

This study is based on coprecipitation method to synthesize pure and doped zinc sulfide (ZnS) nanoparticles. The methodology consisted of synthesis of ZnS and doped ZnS nanoparticles, structural and optical characterization of the nanoparticles, preparation of microbial cultures, and finally, evaluation of antimicrobial activity.

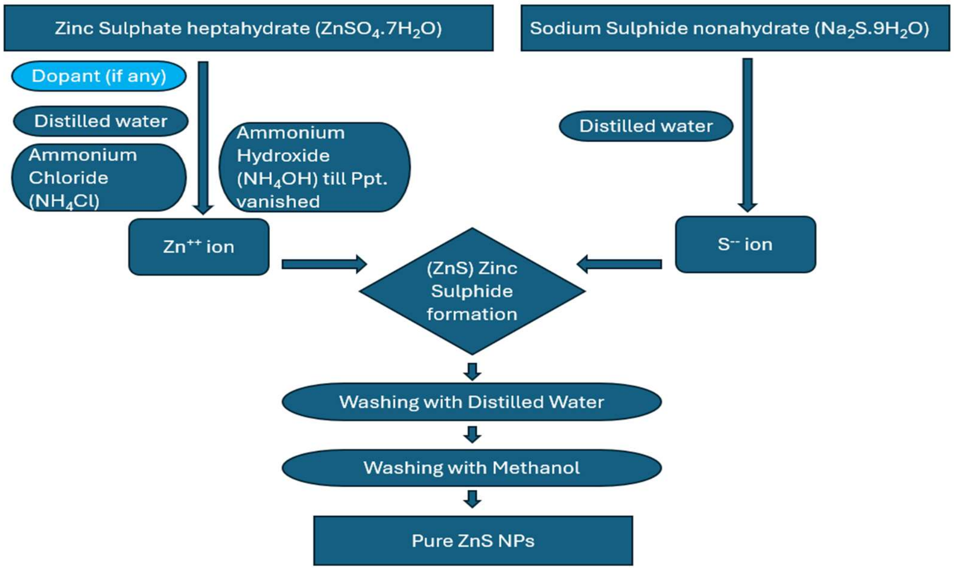


Figure 3.1: Flowchart of Synthesis of the Nanoparticles

3.2.1.1 Zinc Sulphide Preparation:

As demonstrated in Figure 3.1, Zinc Sulphide nanoparticles were synthesized in lab using coprecipitation method. Coprecipitation method is also called as wet chemical solution method of material preparation. Zinc Sulphate heptahydrate ($ZnSO_4.7H_2O$) was taken as the source of Zinc and Sodium Sulphide nonahydrate ($Na_2S.9H_2O$) was used as source of Sulphur for ZnS NPs synthesis. Firstly, a 0.1 M solution was prepared by dissolving 2.8754 g $ZnSO_4.7H_2O$ in 100 mL distilled water. Then, 0.5349 g of Ammonium Chloride (NH_4Cl) was added to it to prevent common ion effect. The addition of NH_4Cl caused an excess ion of NH_4^+ which in turn suppressed the ionization of weak base $NH_4(OH)$ to later prevent formation of $Zn(OH)_2$. This solution was stirred in a magnetic stirrer for half an hour to ensure completely uniform solution. After that, $NH_4(OH)$ was added dropwise under vigorous stirring till precipitation of $Zn(OH)_2$ was observed. $NH_4(OH)$ was added till all the white precipitate of $Zn(OH)_2$ was converted into soluble form and no precipitation was seen in the beaker. The pH was around 10, which signifies the solution was basic. This basic condition is preferred when adding sodium sulfide because it helps the Zinc ions react properly with Sulfide ions to form pure and stable Zinc Sulfide nanoparticles.

Figure 3.2 : Formation of Zinc Sulphide Nanoparticles

In another beaker, 2.4018 g of $Na_2S.9H_2O$ was taken and dissolved in 100 mL of distilled water to prepare a 0.1 M solution. This solution was stirred for a few minutes in a magnetic stirrer and stored in an airtight container to prevent oxidation. Freshly prepared sodium sulphide solution was taken for each time to ensure oxidation has not turned it into other compounds like sodium thiosulphate ($Na_2S_2O_3$) or sodium sulphate (Na_2SO_4). This ensures enough Z^+ ions are available for reaction to form ZnS nanoparticles. This solution was added dropwise to the beaker containing Zinc Sulphate as shown in Figure 3.2 using a burette, to form ZnS NPs. Slow addition of Sodium Sulphide was done with vigorous stirring to minimize local supersaturation which ensures even mixing and uniform particle size formation. The prepared ZnS NPs were washed with distilled water for a few times and then rinsed with methanol to remove any ions remaining with the NPs. The ZnS was then left to dry in an oven at 50°C. The Nanoparticles obtained were then ground in a mortar pestle and stored safely in a vile for future use.

3.2.1.2 *<u>Doped Sample Preparation:</u>*

The process of doped sample preparation is very similar to that of pure ZnS nanoparticle formation. The dopant concentration was kept at 0.5 atomic weight percentage of the total concentration. The dopant was added in the solution of Zinc Sulphate initially before the addition of Ammonium Chloride. This ensures the homogeneous doping on the prepared Zinc Sulphide nanoparticles. For Cobalt doped Zinc Sulphide (Co:ZnS) preparation, 0.01455 g of Cobalt Nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and 2.86102 g Zinc Sulphate heptahydrate ($ZnSO_4.7H_2O$) was taken in a beaker and added with 0.5349 g of Ammonium Chloride (NH_4Cl). Rest of the process was identical to that of pure ZnS nanoparticles formation.

Figure 3.3 : All Prepared Samples

For Cerium doped Zinc Sulphide (Ce:ZnS) preparation, 0.02171 g of Cerium Nitrate hexahydrate ($Ce(NO_3)_3\cdot6H_2O$) was taken. And for co-doped sample (CoCe:ZnS), 0.00728 g Cobalt Nitrate hexahydrate ($Co(NO_3)_2\cdot6H_2O$) and 0.01086 g Cerium Nitrate hexahydrate ($Ce(NO_3)_3\cdot6H_2O$) was taken. All the doped samples, namely Co:ZnS, Ce:ZnS and CoCe:ZnS were prepared and stored safely in vile for future use as shown in Figure 3.3.

3.2.2 Physicochemical Characterization:

UV-vis Spectroscopy:

UV spectrophotometer (Shimadzu corporation) (Pulchowk Campus) was used for UV-vis spectroscopy of the samples. UV-vis spectroscopy is done to analyze the peak shift caused by doping on the samples. 10 mg of the samples were each taken in a test tube and dissolved in 10 mL distilled water and then sonicated for about 10 minutes. This was then tested in the spectrophotometer against distilled water in the range 800 nm to 200 nm.

FTIR:

FTIR Spectrometer (Perkin Elmer) (Amrit Campus) was used for Fourier transform infrared spectroscopy (FTIR). FTIR was done to characterize functional groups present in the samples. FTIR was done for the solid samples on the spectral range of 4000cm^{-1} to 400 cm^{-1}.

XRD:

Diffractometer system (XPERT-PRO) (Jeonbuk National University) was used for X-ray diffraction spectroscopy (XRD) to characterize composition and crystallinity of the Nanoparticles.

FESEM/EDX:

FESEM (JNBU Curf EM lab.) (Jeonbuk National University) was used for surface morphology study of the samples whereas EDX (Oxford Instruments) (Jeonbuk National University) was used for elemental composition identification.

3.2.3 Antimicrobial and Antifungal analysis:

3.2.3.1 Preparation of Antimicrobial Culture Media:

13 g of liquid broth (LB) powder (Sisco research laboratories Pvt. Ltd, India) was taken and dissolved in 1 L of distilled water to prepare a liquid broth media for the growth of bacteria and fungi. The broth media was heated in an autoclave at 121 °C for 25 minutes keeping the pressure at 15 psi to sterilize it. The media was cooled down to around 50 °C and transferred into 15 mL centrifuge tubes keeping 5 mL in each tube for testing. These tubes were used to co-culture bacterial seeds after being incubated for a day.

3.2.3.2 Preparation of MH Media Plates:

39 g of MH agar powder (Sisco research laboratories Pvt. Ltd, India) was taken and dissolved in 1 L of distilled water to prepare Mueller-Hinton Agar (MHA) plates for antibiotic susceptibility testing. The MHA was heated in an autoclave at 121 °C for 25 minutes keeping the pressure at 15 psi to sterilize it. The media was cooled down to around 50 °C and transferred into sterilized petri dishes of 90 mm diameter keeping 25 mL in each Petri dish for testing.

3.2.3.3 Antimicrobial Testing Procedure:

The media plates prepared were labeled with sample names for the antimicrobial tests and 100 µL of freshly cultured bacterial cells were applied to the media plate surface. Wells of 9 mm diameter and 3 mm depth were created on the surface of media plates to load sample, standard and negative control. 100 mg/mL concentration of sample was prepared in dimethyl sulfoxide (DMSO) and 100 µL of that solution was loaded in the wells. Other wells were loaded with standard and negative control DMSO solutions. For positive control (c+), kanamycin antibiotic of concentration 3 mg/mL was used as for antibacterial zone of inhibition (ZOI) study whereas Itraconazole of 20 mg/mL concentration was used for antifungal ZOI study.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Results

This chapter discusses the expected outcomes from the synthesis, characterization, and antimicrobial testing of ZnS, Co:ZnS, Ce:ZnS, and CoCe:ZnS nanoparticles.

4.2 UV-vis Spectroscopy

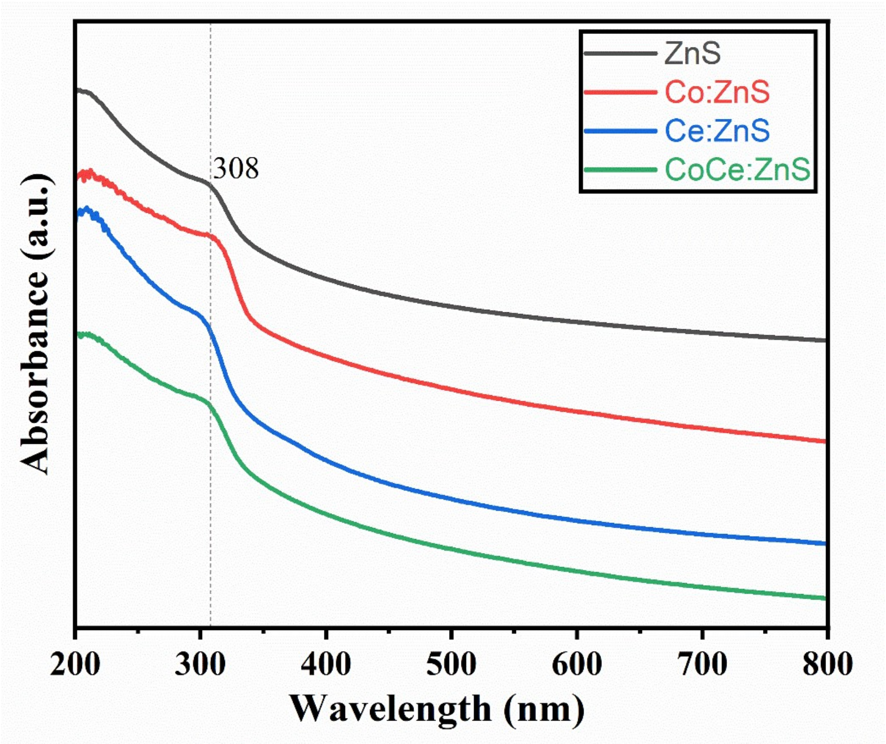


Figure 4.1 : UV-vis spectroscopy of ZnS, Co:ZnS, Ce:ZnS and CoCe:ZnS

The UV-Vis spectra of ZnS, Co:ZnS, Ce:ZnS and CoCe:ZnS are portrayed in fig. 4.1. The spectra reveal the inflation in the UV absorbance at around 308 nm. Cobalt doping exhibited a slight red shift which can be compared with similar results (Gawai & Dole, 2017). while cerium doping exhibited a blue shift of absorption edge. This blue shift is due to quantum confinement. Similar results were observed in others report too (Tounsi et al., 2022). The Ce and Co co-doping sample exhibited a slight blue shift.

4.3 FTIR Spectroscopy

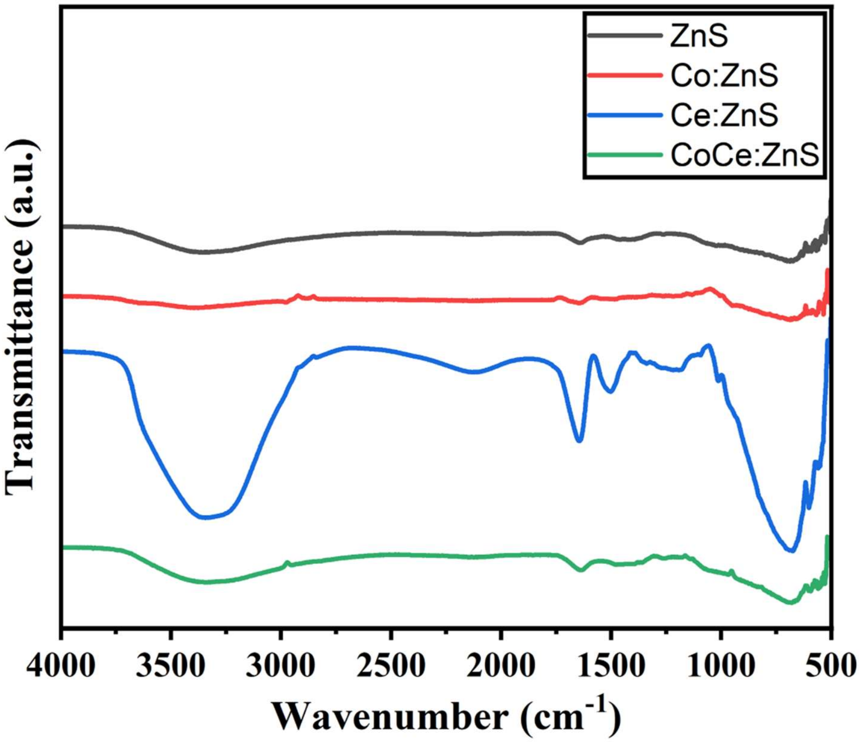


Figure 4.2 : FTIR spectroscopy of ZnS, Co:ZnS, Ce:ZnS and CoCe:ZnS

Presence of functional groups on the nanoparticles were studied in terms of FTIR. The FTIR of the ZnS and Ce-doped ZnS, Co-doped ZnS and CeCo-codoped ZnS are shown in fig. 5. The FTIR spectra show the significant absorption band at ~671 cm^{-1} along with an absorption band at ~554 cm–1 confirming the ZnS formation. In addition, there is a conspicuous absorption band at around 3200-3400 cm^{-1} which is attributed to the –OH group on the surface of ZnS. Similar results were observed in the work of Ananda et al. (Anand et al., 2010).

4.4 XRD

The degree of crystallinity of the ZnS, Ce:ZnS, CeCoZnS were studied in terms of x-ray diffraction. The XRD spectra is shown in Figure 4.3. All these NPs exhibit three conspicuous peaks at 29°, 48.9° and 57.3° corresponding to (102), 101) and (200) plane, respectively (Suganthi and Pushpanathan, 2018). These observed peaks match the hexagonal phase. No additional impurity peaks were observed confirming the absence of cobalt and cerium oxides.

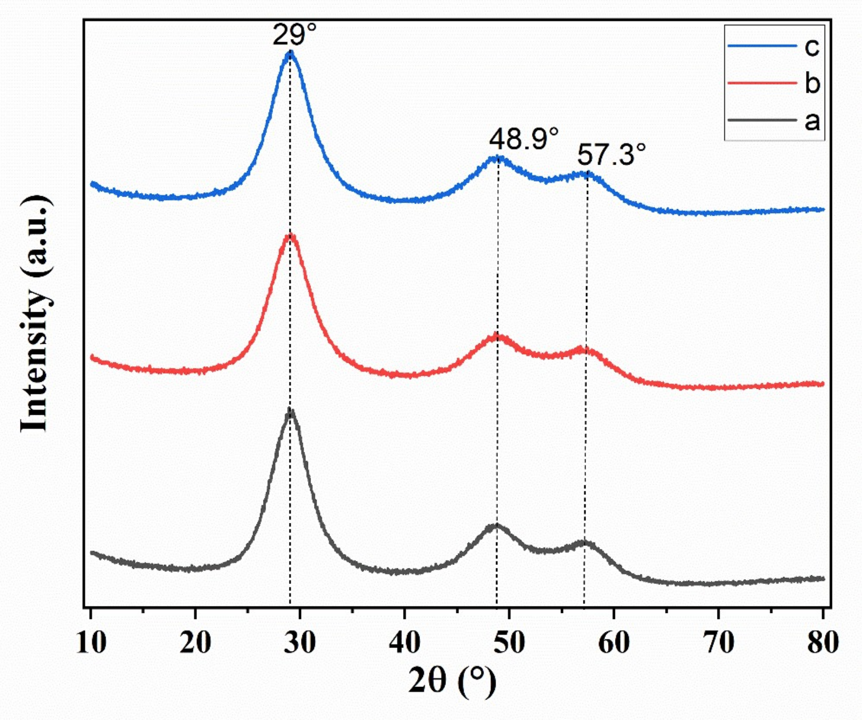


Figure 4.3 : XRD pattern of (a) Ce:ZnS, (b) ZnS and (c) CeCo:ZnS

4.5 FESEM / EDX Analysis

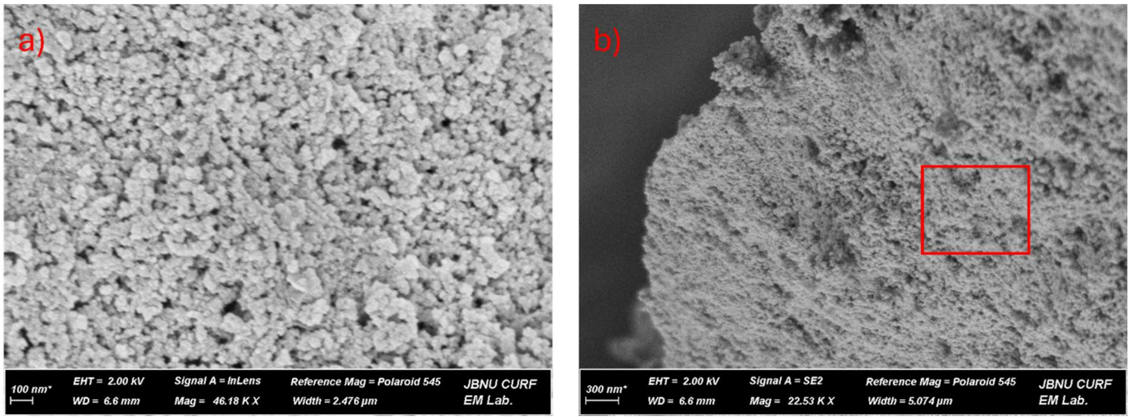


Figure 4.4 : FESEM of (a) ZnS at 100 nm, (b) ZnS at 300nm

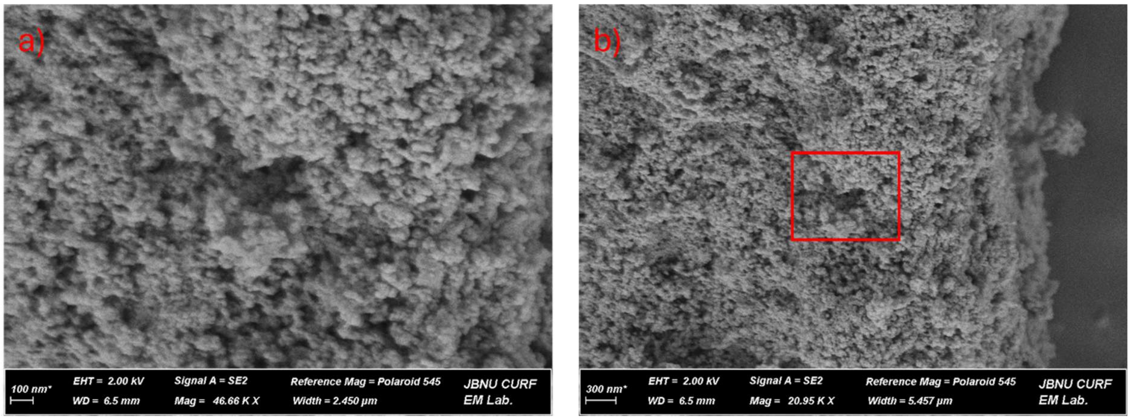


Figure 4.5 : FESEM of (a) Ce:ZnS at 100 nm, (b) Ce:ZnS at 300nm

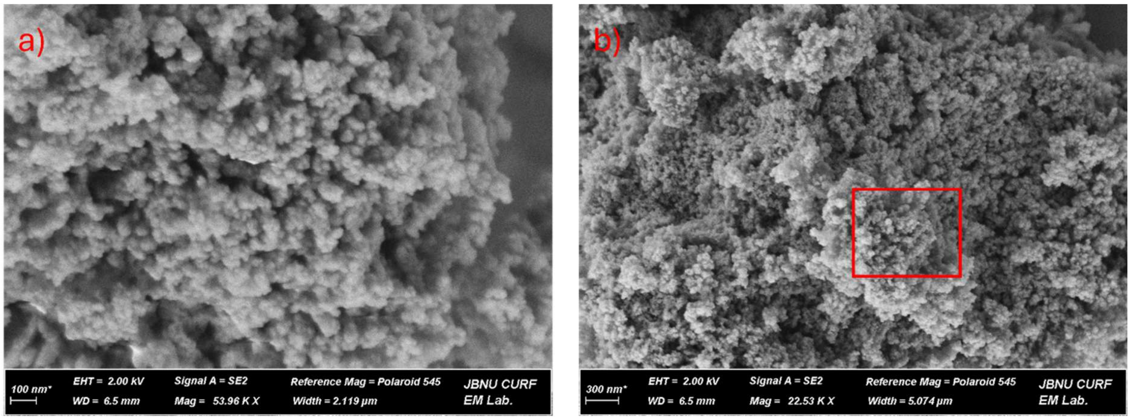


Figure 4.6 : FESEM of (a) Co:ZnS at 100 nm, (b) Co:ZnS at 300nm

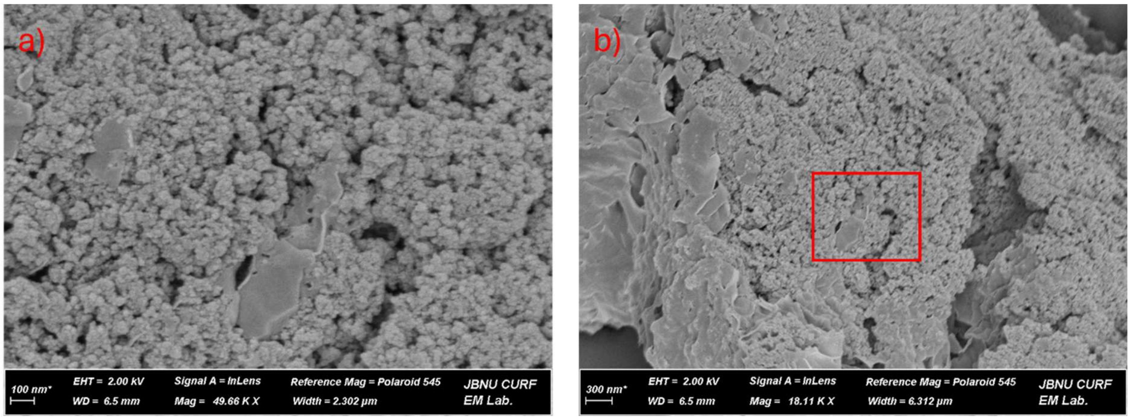
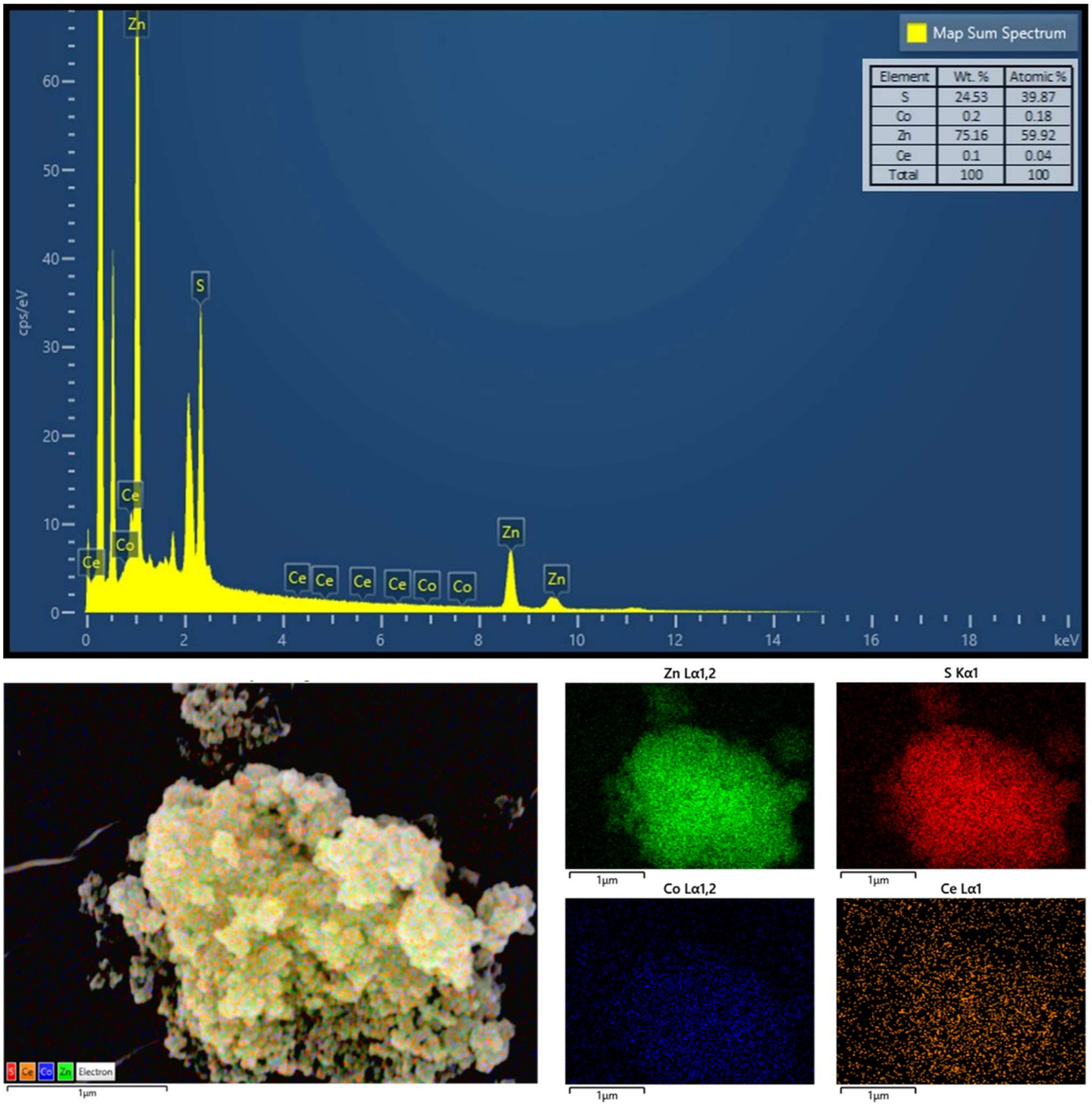


Figure 4.7 : FESEM of (a) CoCe:ZnS at 100 nm, (b) CoCe:ZnS at 300nm

The FESEM images for the ZnS sample are shown in Figure 4.4 (a) and (b) on magnification scale 100 nm and 300 nm respectively. The images clearly show the formation of particles in the range of around 40 nm. The morphology of the formed substances is seen to be rounded, and more uniform particles are seen. The FESEM images for ZnS:Ce sample are shown in Figure 4.5 (a) and (b), Co:ZnS sample are shown in Figure 4.6 (a) and (b) and for CoCe:ZnS are shown in Figure 4.7 (a) and (b). All these images clearly verify the formation of particles in the nanometer range, but more surface defects are seen for the doped samples than that of pure ZnS sample especially on the CoCe:ZnS sample. This may have been caused due to the synergistic effects of Cerium and Cobalt on the Zinc Sulphide lattice.



Element	Wt. %	Atomic %
S	24.53	39.87
Co	0.2	0.18
Zn	75.16	59.92
Ce	0.1	0.04
Total	100	100

Figure 4.8 : EDX of CoCe:ZnS

According to the EDX spectrum as shown in Figure 4.8, the sample is primarily composed of zinc (75.16%) and sulfur (24.53%), which is confirmation of the formation of ZnS. Cobalt (0.2%) and cerium (0.1%) present in trace amounts indicate that the dopants were successfully incorporated onto the ZnS lattice. Overall EDX data confirms the successful formation of CoCe:ZnS sample without any external contamination.

4.6 Antimicrobial Performance

Table 4.1 : ZOI of Samples

Strain	**Reference culture**	**Type**	**Positive control (c+) cm**	**Co:ZnS (1)**	**CoCe:ZnS (2)**	**Ce:ZnS (3)**	**ZnS (4)**
Escherichia coli	ATCC8739	Gram -ve	1.9	1.2	1.4	1.5	1.3
Staphylococcus aureus	ATCC6538P	Gram +ve	2.1	1.3	1.3	1.3	1.3
Candida albicans	ATCC2091	Fungi	1.8	1.2	1.4	1.4	1.4

The diameter (cm) of the zone of inhibition (ZOI) has been mentioned for positive control (c+) in table 4.1 which can also be verified through Figure 4.9. The Ce:ZnS sample showed largest inhibition zone (1.5 cm) for gram negative strain (E. coli) compared to pure ZnS (1.3 cm), CoCe:ZnS (1.4 cm) and Co:ZnS (1.2 cm) which signifies that Cerium doped sample can have a greater antibacterial potential than the other samples. Co:ZnS sample showed negative effects on the antimicrobial inhibition which was also the case for Patel et al. (2016) where it was tested against E. coli.

All the ZnS based samples showed similar inhibition zones (1.3 cm) for gram positive strain (staphylococcus aureus). A study by Qi et al. (2020) stated that spherical shaped Cerium Oxide showed good antimicrobial properties against gram-negative bacteria but showed very limited antibacterial property against gram-positive bacteria. Similar observation could be made in case of Cerium doped zinc sulphide.

For Fungi (Candida albicans), Ce:ZnS and CoCe:ZnS produced the highest zones of inhibition (1.4 cm each) which is greater than Co:ZnS (1.2 cm). This indicates that Ce:ZnS showed the best results among all the doping variants of Zinc Sulphide. Negative control (c-) data has been omitted because it did not show any significant change.

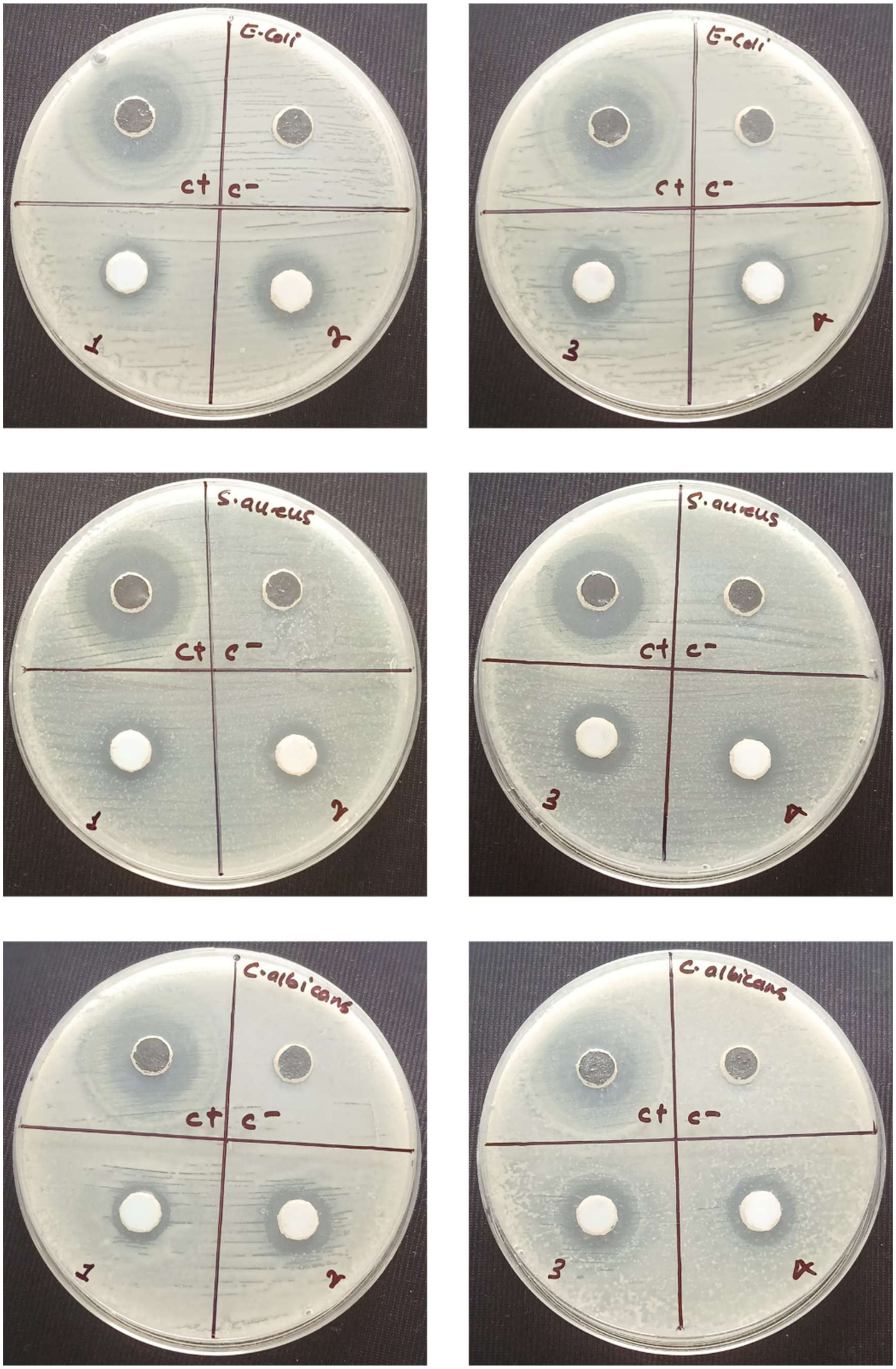


Figure 4.9 : Antimicrobial test (ZOI) of All Samples

CHAPTER 5: CONCLUSION

This thesis offers an extensive examination of the antimicrobial performance of Zinc Sulphide and Cerium, Cobalt and Cerium Cobalt co-doped ZnS nanomaterials. The morphology of the sample when confirmed by FESEM clearly showed formation of nanoparticles around a size 40 nm. Pure ZnS nanoparticles showed good uniform distribution of particles whereas more surface defects were seen on doped samples. Cerium Cobalt co-doped sample showed most surface defects probably due to the synergistic effects of Cerium and Cobalt. The sample is predominantly composed of Zinc and Sulphur as seen in the EDX claiming the successful formation of ZnS from coprecipitation method. EDX also confirmed the successful doping of the nanoparticles with Cerium and Cobalt which could be seen in trace amounts. XRD showed no extra significant peaks confirming that no other oxides were formed causing lattice deformation but instead were incorporated in the original ZnS lattice.

By checking the antimicrobial and antifungal capacity of the prepared nanomaterial, we can conclude Ce:ZnS showed a greater inhibition zone (1.5 cm) and proved to be more effective in case of gram-negative bacteria (E. coli). The samples Ce:ZnS and CoCe:ZnS both showed the highest inhibition zone (1.4 cm each) for Fungi (Candida albicans). This indicates that Ce:ZnS showed the best results among all the doping variants of Zinc Sulphide. This Ce:ZnS nanomaterial can be further be tailored to be used in wastewater treatment and environment conservation due to its property of microbial inhibition. It may also have biomedical applications such as scaffolds and antimicrobial bandages and wound healing.

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