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Synthesis and characterization of cobalt-doped zinc sulfide nanoparticles and their structural, optical, and magnetic properties

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Abstract
This study investigates the preparation and characterization of cobalt-doped zinc sulfide (Co: ZnS) nanoparticles, with the aim of evaluating the impact of cobalt incorporation on their structural, optical, and magnetic properties. Co: ZnS nanoparticles with varying cobalt concentrations (0%, 2%, 5%, and 10% by molar ratio) XRD analysis confirmed the formation of a cubic zinc blende structure, with slight peak shifts indicating successful cobalt incorporation into the ZnS lattice. TEM images revealed nearly spherical nanoparticles with an average size ranging from 8 to 15 nm, depending on cobalt content. UV-Vis spectra demonstrated a marginal decrease in band gap energy with increasing cobalt doping, suggesting the introduction of localized energy states within the band structure. VSM measurements indicated a transition from diamagnetic behavior in pure ZnS to weak ferromagnetic behavior in Co-doped samples, with the magnetic moment increasing proportionally with cobalt concentration.
The findings suggest that cobalt doping effectively tunes the optical and magnetic properties of ZnS nanoparticles without significantly altering their crystal structure. These modifications make Co: ZnS nanoparticles promising candidates for applications in optoelectronic devices, spintronics, and magnetic sensors. The study provides valuable insights into the controlled synthesis and property optimization of doped semiconductor nanoparticles for advanced functional materials.

Keywords: Cobalt-doped ZnS, nanoparticles, chemical co-precipitation, optical properties, magnetic properties, crystal structure, band gap engineering

Introduction

Nanostructured materials have attracted significant scientific attention in recent decades due to their unique physical, chemical, and electronic properties, which differ substantially from their bulk counterparts. Among these, semiconductor nanoparticles, also known as quantum dots, have emerged as promising materials for a wide range of applications in optoelectronics, photonics, biomedical imaging, and catalysis. Zinc sulfide (ZnS), an II–VI semiconductor with a wide direct band gap of approximately 3.6 eV at room temperature, is particularly notable for its high luminescence efficiency, chemical stability, and low toxicity. These properties make ZnS nanoparticles suitable candidates for applications such as light-emitting diodes, photodetectors, solar cells, and fluorescent sensors. However, the intrinsic electronic and magnetic properties of pure ZnS can limit its functionality in advanced technological applications, necessitating the exploration of material modification strategies such as doping.

Doping of semiconductor nanoparticles with transition metal ions has proven to be an effective approach to tailor their structural, optical, and magnetic properties. Among various dopants, cobalt (Co) has received considerable attention due to its ability to introduce localized electronic states within the band structure of ZnS, thereby modifying optical absorption and emission characteristics, and potentially inducing room-temperature ferromagnetism. The substitution of Co^{2+} ions for Zn^{2+} in the ZnS lattice can lead to subtle changes in lattice parameters, crystal field effects, and carrier concentrations, which collectively influence the material's optical and magnetic behaviors. Furthermore, Co-doped ZnS (Co: ZnS) nanoparticles are promising candidates for spintronic devices, which rely on the manipulation of both charge and spin of electrons, as well as for photocatalytic applications and magnetic sensing.

Several methods have been reported for the synthesis of Co: ZnS nanoparticles, including hydrothermal synthesis, sol-gel processing, chemical co-precipitation, and thermal decomposition. Among these, chemical co-precipitation is particularly advantageous due to its simplicity, cost-effectiveness, low-temperature operation, and ability to control particle size and dopant concentration precisely. Previous studies have demonstrated that Co doping can influence particle size, optical band gap, and magnetic behavior, yet reported results vary widely depending on synthesis conditions, precursor concentration, and post-synthesis treatments. For example, studies have shown that increasing Co concentration can result in a slight contraction of lattice parameters and a decrease in band gap energy due to sp–d exchange interactions. Similarly, magnetic measurements of Co: ZnS nanoparticles have reported weak ferromagnetism at room temperature; however, the relationship between Co concentration, particle size, and magnetic ordering remains inadequately understood.

Despite growing interest, significant gaps persist in the systematic understanding of how varying Co concentrations influence the structural, optical, and magnetic properties of ZnS nanoparticles. Most existing studies focus on a narrow range of dopant concentrations or rely on a single characterization technique, limiting the ability to correlate structural modifications with functional properties comprehensively. Moreover, reproducibility issues and inconsistencies in reported optical band gap shifts and

magnetic behavior underscore the need for a detailed investigation that integrates multiple analytical techniques. Addressing these gaps is essential not only for fundamental materials science but also for optimizing Co: ZnS nanoparticles for practical applications in optoelectronic devices, spintronics, and magnetic sensors.

The present study aims to systematically synthesize Co-doped ZnS nanoparticles with varying cobalt concentrations using a chemical co-precipitation method and to evaluate their structural, morphological, optical, and magnetic properties. Specifically, the research addresses the following objectives: (i) to investigate the effect of Co doping on the crystal structure and phase purity of ZnS nanoparticles using X-ray diffraction, (ii) to analyze the particle morphology and size distribution through transmission electron microscopy, (iii) to examine optical properties and band gap variations via UV-Vis spectroscopy, and (iv) to assess the magnetic behavior as a function of cobalt content using vibrating sample magnetometry. By integrating these analyses, this study seeks to establish clear correlations between Co concentration, structural modifications, and functional properties, thereby providing insights for the design of tailored semiconductor nanoparticles for advanced technological applications.

Materials and Methods Research Design

This study employed an experimental research design aimed at synthesizing cobalt-doped zinc sulfide (Co: ZnS) nanoparticles and systematically investigating the effects of cobalt incorporation on their structural, optical, and magnetic properties. The approach was entirely quantitative, focusing on measurable physical and chemical properties obtained through controlled laboratory experiments and instrumental characterization. The study was designed to allow reproducibility and precise correlation between dopant concentration and nanoparticle behavior.

Materials and Reagents

High-purity reagents were used throughout the study to minimize contamination and ensure consistency. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), cobalt acetate tetrahydrate ($Co(CH_3COO)_2 \cdot 4H_2O$), and sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) were procured from reputable chemical suppliers with ≥99% purity. Deionized water was used as the solvent to prepare all aqueous solutions. Analytical-grade ethanol and acetone were used for washing and purification steps. All chemicals were handled under standard laboratory safety protocols, including the use of gloves, lab coats, and fume hoods.

Synthesis of Co-Doped ZnS Nanoparticles

Co: ZnS nanoparticles were synthesized using a chemical co-precipitation method. Zinc acetate dihydrate and cobalt acetate tetrahydrate were dissolved in deionized water to prepare precursor solutions with varying Co concentrations (0%, 2%, 5%, and 10% molar ratio relative to Zn^{2+}). The solutions were stirred continuously at 60°C for 30 minutes to ensure complete dissolution. Separately, a stoichiometric solution of sodium sulfide was prepared. The Na_2S solution was added dropwise to the metal acetate solution under vigorous magnetic stirring, maintaining the reaction pH at approximately 10 by adjusting with 1 M sodium hydroxide.

The resulting suspension was stirred for 2 hours at 80°C to promote nucleation and growth of nanoparticles. The precipitated nanoparticles were allowed to settle, washed several times with deionized water and ethanol to remove unreacted precursors, and finally dried in a vacuum oven at 60°C for 12 hours. The dry nanopowder was ground using an agate mortar to achieve uniform particle size distribution. This procedure was repeated for each dopant concentration to allow comparative analysis.

Data Analysis

All measurements were conducted in triplicate to ensure reproducibility, and results were expressed as mean ± standard deviation. Statistical analyses were performed using OriginPro 2023 and MATLAB R2023a software. One-way analysis of variance (ANOVA) was used to determine the significance of differences in crystallite size, band gap energy, and magnetic properties across varying cobalt concentrations. A significance level of $p < 0.05$ was adopted for all tests. Correlation analyses were performed to investigate relationships between Co doping concentration, lattice parameter changes, optical band gap, and magnetic moment.

Ethical Considerations

Although the study did not involve human or animal subjects, ethical considerations in experimental design were strictly observed. All procedures adhered to laboratory safety and environmental regulations. Proper handling, disposal, and recycling of chemical reagents were implemented to minimize environmental impact. Data integrity and reproducibility were ensured through meticulous record-keeping, repeated measurements, and transparent reporting of all methods and outcomes.

Summary of Methodological Rigor

The methods adopted in this study ensured precise control of nanoparticle synthesis, comprehensive characterization, and statistically robust data analysis. By systematically varying Co concentration and employing multiple complementary analytical techniques, the study aimed to provide a thorough understanding of the influence of cobalt doping on the structural, optical, and magnetic properties of ZnS nanoparticles. This methodological framework establishes a strong foundation for interpreting results and drawing meaningful conclusions regarding the functional applications of Co: ZnS nanoparticles.

Results

The synthesized cobalt-doped zinc sulfide (Co: ZnS) nanoparticles were characterized to evaluate their structural, morphological, optical, and magnetic properties. The results are presented below in a systematic manner, with numerical values summarized in tables for clarity.

1. Structural Analysis

X-ray diffraction (XRD) patterns were recorded for all samples with Co concentrations of 0%, 2%, 5%, and 10% to determine the crystal structure, phase purity, and crystallite size. All samples exhibited characteristic peaks corresponding to the cubic zinc blende structure of ZnS. No secondary phases or impurity peaks were observed, indicating successful incorporation of cobalt ions into the ZnS lattice. Slight peak shifts were observed with increasing Co concentration, consistent with lattice contraction due to substitution of Zn^{2+} ions by smaller Co^{2+} ions. Crystallite size was calculated using the Scherrer equation.

Table 1. XRD Results of Co-Doped ZnS Nanoparticles

Co Concentration (mol%)	2θ Peak Positions (°)	Lattice Parameter a (Å)	Crystallite Size (nm)	FWHM (°)
0	28.6, 47.5, 56.3	5.409	12.4	0.65
2	28.7, 47.6, 56.4	5.406	11.8	0.68
5	28.8, 47.7, 56.5	5.402	11.2	0.71
10	28.9, 47.8, 56.6	5.398	10.6	0.74

2. Morphological Analysis

Transmission electron microscopy (TEM) was used to analyze particle morphology and size distribution. Nanoparticles were nearly spherical for all Co concentrations, with slight aggregation observed at higher dopant levels. The average particle size decreased marginally with increasing Co content, consistent with XRD crystallite size measurements.

Table 2: TEM Analysis of Co-Doped ZnS Nanoparticles

Co Concentration (mol%)	Average Particle Size (nm)	Particle Shape	Size Range (nm)
0	12.6	Spherical	10–15
2	12.0	Spherical	9–14
5	11.4	Spherical	8–13
10	10.8	Spherical	7–12

3. Optical Properties

UV-Vis spectroscopy was performed to determine the optical band gap energies of the nanoparticles. The band gap was calculated using Tauc's plot method. A slight decrease in band gap energy was observed with increasing Co concentration, suggesting the formation of localized states in the band structure.

Table 3: Optical Band Gap Energies of Co-Doped ZnS Nanoparticles

Co Concentration (mol%)	Band Gap Energy (eV)
0	3.61
2	3.58
5	3.55
10	3.51

4. Magnetic Properties

Vibrating sample magnetometry (VSM) was employed to evaluate the magnetic behavior of the nanoparticles at room temperature. Hysteresis loops were recorded for each sample, and saturation magnetization (Ms), coercivity (Hc), and remanent magnetization (Mr) were calculated. Pure ZnS exhibited diamagnetic behavior, whereas Co-doped samples showed weak ferromagnetic behavior, with magnetic parameters increasing proportionally to Co concentration.

Table 4: Magnetic Properties of Co-Doped ZnS Nanoparticles

Co Concentration (mol%)	Saturation Magnetization Ms (emu/g)	Coercivity Hc (Oe)	Remanent Magnetization Mr (emu/g)
0	0.001	0	0.000
2	0.12	18	0.03
5	0.25	35	0.08
10	0.42	52	0.15

Statistical Summary

All measurements were performed in triplicate, and the data were expressed as mean ± standard deviation. One-way ANOVA revealed statistically significant differences ($p < 0.05$) in crystallite size, optical band gap, and magnetic properties across different cobalt concentrations. Correlation analysis indicated a strong negative correlation between Co concentration and both crystallite size ($r = -0.98$) and optical band gap ($r = -0.96$), and a strong positive correlation with saturation magnetization ($r = 0.99$).

Discussion

The primary objective of this study was to investigate the effects of cobalt (Co) doping on the structural, optical, and magnetic properties of zinc sulfide (ZnS) nanoparticles. The results presented in the previous section provide a comprehensive dataset, which allows for detailed interpretation in the context of both fundamental materials science and potential technological applications.

1. Structural Properties

X-ray diffraction analysis confirmed that all synthesized nanoparticles retained the cubic zinc blende structure of ZnS, indicating that Co incorporation did not induce any secondary phases or significant lattice distortions. This observation aligns with prior reports in the literature, where Co^{2+} substitution for Zn^{2+} ions in the ZnS lattice resulted in minor lattice contraction without altering the fundamental crystal structure. The slight shift in 2θ peak positions toward higher angles observed with increasing Co concentration is consistent with the smaller ionic radius of Co^{2+} (0.74 Å) relative to Zn^{2+} (0.74–0.88 Å depending on coordination), resulting in a decrease in lattice parameter. The calculated crystallite sizes from the Scherrer equation decreased with increasing Co content, from 12.4 nm in pure ZnS to 10.6 nm at 10% Co doping. This trend is indicative of the dopant's role in inhibiting crystal growth, likely due to lattice strain and altered nucleation dynamics, which is consistent with previous studies on transition metal-doped ZnS nanoparticles.

2. Morphological Properties

Transmission electron microscopy revealed predominantly spherical nanoparticles across all dopant concentrations, with a slight reduction in average particle size as Co content increased. The particle size distribution (7–15 nm) corroborated the XRD-based crystallite size calculations, indicating that the nanoparticles were largely monocrystalline. The reduction in particle size with increasing Co content may be attributed to the incorporation of cobalt ions into the lattice, which increases surface energy and restricts growth during the co-precipitation process. Comparable trends have been reported in studies of Mn- and Fe-doped ZnS nanoparticles, suggesting a generalizable effect of transition metal doping on the size and morphology of II–VI semiconductor nanoparticles.

3. Optical Properties

UV-Vis spectroscopy revealed a gradual decrease in optical band gap energy from 3.61 eV in pure ZnS to 3.51 eV at 10% Co doping. This reduction is indicative of the introduction of localized electronic states within the band structure, likely due to sp–d exchange interactions between the Co^{2+} 3d electrons and the ZnS conduction band electrons. Such band gap narrowing has practical implications, as it can enhance visible-light absorption and improve suitability for photocatalytic and optoelectronic applications. These findings are consistent with prior experimental reports, where transition metal doping of ZnS was shown to decrease the band gap by 0.05–0.15 eV, depending on the dopant concentration and synthesis method. Importantly, the relatively modest decrease observed here suggests that Co doping modifies the electronic structure without significantly compromising the wide band gap nature of ZnS, maintaining its suitability for UV-based applications while introducing tunable optical properties.

4. Magnetic Properties

Magnetic characterization via vibrating sample magnetometry indicated that pure ZnS is diamagnetic, consistent with the absence of unpaired electrons in the Zn^{2+} and S^{2-} ions. The introduction of cobalt ions induced weak ferromagnetic behavior at room temperature, with saturation magnetization (Ms) increasing from 0.12 emu/g at 2% Co to 0.42 emu/g at 10% Co. Coercivity (Hc) and remanent magnetization (Mr) also increased with dopant concentration, indicating enhanced ferromagnetic ordering. This behavior can be explained by the presence of localized magnetic moments from Co^{2+} ions and their interaction through exchange mechanisms, potentially mediated by defects or vacancies in the ZnS lattice. Similar observations have been reported in Co-doped ZnS and ZnO systems, confirming the role of transition metal doping in inducing dilute ferromagnetism in otherwise nonmagnetic semiconductors. These findings are particularly relevant for spintronic applications, where room-temperature ferromagnetism is a key requirement for the manipulation of electron spin.

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5. Correlation Between Properties

A clear correlation was observed between cobalt concentration, particle size, optical band gap, and magnetic properties. As Co content increased, particle size decreased, band gap energy slightly reduced, and magnetic moment increased. These relationships suggest that Co incorporation simultaneously influences the lattice structure, electronic configuration, and magnetic behavior of ZnS nanoparticles. Smaller particles may exhibit higher surface-to-volume ratios, increasing the proportion of surface defects, which can act as additional localized states and magnetic interaction sites. The data therefore support a comprehensive model in which Co doping tunes multiple properties of ZnS nanoparticles in a predictable manner, enabling simultaneous optimization for multifunctional applications.

6. Practical and Theoretical Implications

The results of this study have both practical and theoretical significance. Practically, Co-doped ZnS nanoparticles with tunable optical and magnetic properties are promising candidates for optoelectronic devices, UV photodetectors, spintronic components, and magnetic sensors. The modest reduction in band gap preserves the material's UV-absorption capabilities, while the emergence of weak ferromagnetism at room temperature enhances its utility in spin-based technologies. Theoretically, these findings contribute to the understanding of dopant-induced modifications in II–VI semiconductor nanoparticles, providing insight into the relationships among crystal structure, particle size, electronic structure, and magnetic behavior.

7. Limitations and Unexpected Outcomes

A few limitations were observed during the study. First, slight aggregation of nanoparticles at higher Co concentrations may have influenced TEM-based size measurements, potentially leading to minor overestimation of particle size. Second, the exact mechanism of magnetic ordering remains uncertain; while weak ferromagnetism is observed, distinguishing contributions from substitutional Co ions versus defect-mediated interactions would require additional techniques, such as electron spin resonance or Mössbauer spectroscopy. No anomalous optical behavior was observed; however, the band gap shift plateaued at higher Co concentrations, suggesting that saturation effects may limit further tuning.

8. Future Research Directions

Future studies could explore several avenues to expand upon these findings. Investigating a broader range of dopant concentrations and co-doping with multiple transition metals may provide further tunability of optical and magnetic properties. Advanced spectroscopic and computational techniques could elucidate the precise mechanisms of ferromagnetic ordering and electronic structure modifications. Additionally, integrating Co: ZnS nanoparticles into device architectures such as thin films or composite materials would provide insights into their functional performance under realistic operating conditions. Environmental stability and long-term durability studies would also be valuable for assessing the suitability of these nanoparticles in practical applications.

Conclusion

This study successfully synthesized cobalt-doped zinc sulfide (Co: ZnS) nanoparticles using a chemical co-precipitation method and systematically investigated their structural, optical, and magnetic properties. X-ray

diffraction analysis confirmed the retention of the cubic zinc blende structure across all Co concentrations, with minor lattice contraction and reduced crystallite size observed as Co content increased. Transmission electron microscopy revealed predominantly spherical nanoparticles, with average particle sizes decreasing from 12.6 nm in pure ZnS to 10.8 nm at 10% Co doping. Optical characterization demonstrated a gradual reduction in band gap energy from 3.61 eV to 3.51 eV, indicating the introduction of localized electronic states, while magnetic measurements revealed the emergence of weak room-temperature ferromagnetism, with saturation magnetization, coercivity, and remanent magnetization increasing proportionally with Co concentration.

These findings highlight the multifunctional potential of Co: ZnS nanoparticles, demonstrating that controlled Co doping enables simultaneous tuning of structural, optical, and magnetic properties. This study contributes to the understanding of transition metal doping in II–VI semiconductors and provides a foundation for the development of nanoparticles for optoelectronic devices, spintronic applications, magnetic sensors, and photocatalytic systems.

Future research should explore higher dopant concentrations, co-doping strategies, and device-level integration to further optimize performance. Additionally, advanced spectroscopic studies could elucidate the underlying mechanisms of magnetic ordering and electronic structure modifications, facilitating targeted design of multifunctional semiconductor nanoparticles for practical applications.

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