

Chemical Fabrication and Material Characterization of ZnS Nanostructures for Application in Excellent Optical Quality

Bijoy Barman

Department of Physics, Abhayapuri College, Abhayapuri, India

Abstract:

Zinc Sulfide (ZnS) nanoparticles were successfully synthesized using the chemical deposition method. The resultant ZnS nanoparticles were characterized and analyzed using various techniques to determine their structural, morphological, and optical properties. X-ray diffraction (XRD) analysis revealed the crystalline nature of the ZnS nanoparticles, confirming their cubic phase structure. Additionally, the average size of the nanocrystallites was measured using the Debye-Scherrer formula, yielding a value of approximately 6 nm. Transmission electron microscopy (TEM) images provided a direct visualization of the ZnS nanoparticles, allowing for the estimation of their size, which was found to be in agreement with the XRD results. Ultraviolet-visible (UV-Vis) spectroscopy was employed to investigate the optical properties of the ZnS nanocrystallites. The analysis revealed an optical bandgap energy of 4.41 eV, a value indicative of their excellent optical quality.

Key Word: ZnS nanocrystallites, XRD, TEM, UV-VIS absorption, Bandgap

Date of Submission: 20-01-2025

Date of Acceptance: 30-01-2025

I. Introduction

The past few years have witnessed a surge of interest in synthesizing nanometer-sized semiconductor particles, due to their unique size-dependent optical and electrical properties. These nanoparticles have garnered significant attention in various applications, including light-emitting diodes, phosphors, solar cells, X-ray sensors, scintillators, photocatalysts, and electrochemical cells [1-3]. Among the semiconductors, ZnS stands out as a promising material due to its high refractive index (approximately 2.37) and high transmission within the visible range [4]. ZnS, with its wide bandgap energy of 3.68 eV, exhibits two distinct crystal structures (zinc blende and wurtzite), which can influence its optical properties and are critical for tailoring for specific applications [5]. Additionally, ZnS has been employed in optoelectronic devices due to its high emission efficiency and stability, making it suitable for UV light-emitting diodes, efficient phosphors in flat-panel displays, and cathode ray tubes [6].

To control the size and shape of semiconductor nanoparticles, a variety of synthetic methods have been developed. These methods include sputtering, co-evaporation, wet chemical techniques, sol-gel processing, solid-state reactions, microwave irradiation, and ultrasonic irradiation, among others [7]. Notably, chemical methods, such as chemical vapor deposition (CVD) and hydrothermal synthesis, have become increasingly popular due to their ability to yield uniform nanoparticles with tunable properties. These approaches often utilize capping agents, such as surfactants or polymers, that adsorb onto the nanocrystal surface, preventing agglomeration and ensuring better control over particle size and morphology [8]. Specific capping agents can also modify the electronic surface states of ZnS nanoparticles, enhancing their photophysical properties for targeted applications.

In this study, we have employed the chemical deposition method to synthesize ZnS nanoparticles. This technique was chosen for its simplicity, adaptability to industrial synthesis, and ability to produce small particle sizes with high purity in a short reaction time. Moreover, the ability to fine-tune reaction parameters such as temperature, concentration, and reaction time enables precise control over the final properties of the nanoparticles. Additionally, characterization techniques, such as transmission electron microscopy (TEM) and X-ray diffraction (XRD), were utilized to analyze the size, shape, and crystalline structure of the synthesized ZnS nanoparticles, ensuring that they meet the desired specifications for effective application in optoelectronics and photonics [8].

II. Material And Methods

ZnS nanoparticles were synthesized in a polymer matrix via an ion exchange reaction. All the reaction reagents used in the process were of analytical purity, and deionized water was used in the preparation of the sample. ZnS nanoparticles containing a PVA matrix were prepared as follows:

A polyvinyl alcohol (PVA) solution was obtained by adding 2 g of solid PVA to 100 mL of deionized water and stirring at a constant temperature of 70°C for 3 hours at a constant rate of 200 rpm until a viscous, transparent solution was obtained. Next, 2 g of solid ZnCl₂ was taken in 100 mL of distilled water in a conical flask and stirred at a rate of 200 rpm for 3 hours. The solutions of PVA and ZnCl₂ were kept separately for overnight inside a dark chamber at room temperature to allow for complete dissolution, resulting in transparent solutions for both. PVA solution and different molar concentrations of ZnCl₂ solution were then mixed together. The equimolar solution of Na₂S was then added to the mixed solution, and the mixture was stirred for 20 minutes at 200 rpm at a constant temperature of 60°C until the mixed solution turned milky. With this mixture, concentrated HNO₃ was added to adjust the pH of the whole solution. Stirring conditions were then maintained at 200 rpm for another 15 minutes. Finally, the prepared solution was left to incubate in a closed dark chamber at room temperature for 12 hours (preferably overnight) to allow for the formation of nanoparticles within the PVA chain. As soon as the nanoparticles were formed, they immediately entered into the gaps of the PVA chain and could neither escape nor enhance in size. The ZnS nanoparticle-containing PVA solution was then cast onto suitably cleaned glass substrates and allowed to dry in a closed chamber at room temperature. The ZnS films were now ready for various experiments.

III. Results And Discussion

The XRD pattern of the as-synthesized ZnS nanoparticles produced by microwave irradiation is shown in Fig 1, indicating that the material crystallizes in the cubic phase, as corroborated by JCPDS file number 65-9585. The X-ray diffraction measurements were recorded using an X-ray diffractometer equipped with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) over a 2θ range from 10° to 65°. The XRD pattern exhibits three prominent peaks at 2θ values of 28.9°, 47.8°, and 56.9°, which correspond to the crystallographic planes (111), (220), and (311), respectively [9-11].

The broadening of the diffraction peaks in the XRD pattern is indicative of nanocrystallinity, suggesting that the synthesized ZnS nanoparticles have a small average crystallite size. This phenomenon is commonly observed in materials at the nanoscale due to size effects and increased surface-to-volume ratios. To quantify the crystalline size of the nanoparticles, the Debye–Scherrer equation was applied to the full width at half maximum (FWHM) of the XRD peaks. The calculated crystalline size was found to be approximately 6 nm, which is consistent with previous studies that highlight the influence of synthesis methods on particle size and morphology [12-13].

Furthermore, the crystallinity of the nanoparticles is essential for their optical and electrical properties, making it imperative to refine synthetic conditions. The distinct peaks and their sharpness suggest a high degree of crystallinity, which is expected to enhance the photoluminescence and electron mobility of the ZnS nanoparticles in potential applications, such as in optoelectronic devices and photocatalysts. Overall, the XRD analysis confirms the successful synthesis of high-quality ZnS nanoparticles with desirable crystalline characteristics.

The average nanocrystallite size is calculated by the formula,

Where λ is the wavelength of the incident ray, 2θ is the Bragg's angle and β is the full width at half maxima. The average size of the nanoparticles was calculated to be 6 nm.

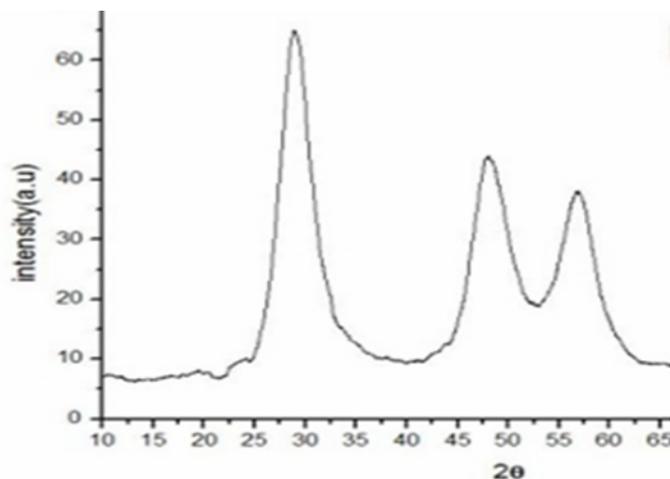


Fig 1. XRD of ZnS 0.5% concentration

The Transmission Electron Microscope (TEM) image of the synthesized sample is shown in Fig 2. The size of the ZnS nanoparticles, as calculated from the TEM images, is approximately 5 nm.

These nanoparticles exhibit a uniform distribution, which is indicative of successful synthesis and stabilization within the polymer matrix. The high-resolution TEM images reveal the crystalline structure of the ZnS nanoparticles, confirming their successful formation. Additionally, the small particle size suggests strong quantum confinement effects, which can enhance the optical and electronic properties of the nanoparticles, making them suitable for applications in photonics, optoelectronics, and bioimaging. The synthesis process and the resulting characteristics of the ZnS nanoparticles highlight their potential utility in various fields, particularly in nanotechnology and materials science.

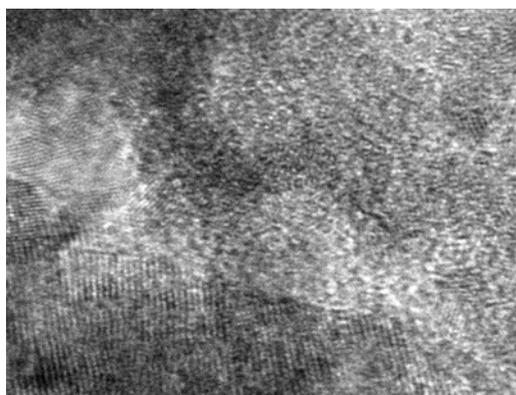


Fig 2. TEM micrograph of ZnS Nanoparticle



Fig 3. AFM images of the ZnS sample

The Atomic Force Microscopy (AFM) analysis of the ZnS sample is presented in Fig 3. The results reveal a uniform surface morphology, with a significant reduction in surface roughness compared to the bulk material. This decrease in roughness is likely attributed to the reduced grain size of the ZnS nanoparticles. The AFM analysis demonstrates that the nanoparticles exhibit a highly ordered arrangement on the surface, with minimal aggregation or clustering. This is consistent with the expectations for nanoparticles with a particle size

of around 5 nm, as synthesized earlier. The reduced grain size and uniform distribution suggest that the nanoparticles are well-dispersed within the polymer matrix, which is beneficial for achieving improved physical and optical properties.

The AFM data also indicate a significant reduction in the root mean square (RMS) roughness, which is a key parameter for assessing the surface quality. The lower RMS roughness value indicates a more consistent and uniform surface feature size, which is desirable for applications in nanotechnology and materials science. The combination of uniform surface morphology and reduced grain size makes the ZnS nanoparticles a promising material for use in a range of optoelectronic and photonic devices. The AFM data can be used in conjunction with other characterization techniques, such as TEM and X-ray diffraction (XRD), to gain a comprehensive understanding of the material's crystal structure, phase purity, and chemical composition. The combination of these techniques provides a more detailed insight into the material's properties and behavior, allowing for the optimization of synthesis conditions to achieve desired physical and optical properties [14-15].

The optical properties of the ZnS semiconductor nanoparticles were investigated using UV-visible spectroscopy. The UV-visible absorption spectrum of the ZnS nanoparticles is displayed in Fig 4. Characteristic absorption peaks appear within the wavelength range of 300 to 500 nm, and the position of these peaks reflects the band gap of the nanoparticles. Notably, the UV spectra indicate that the absorption band exhibits a blue shift compared to the bulk ZnS material.

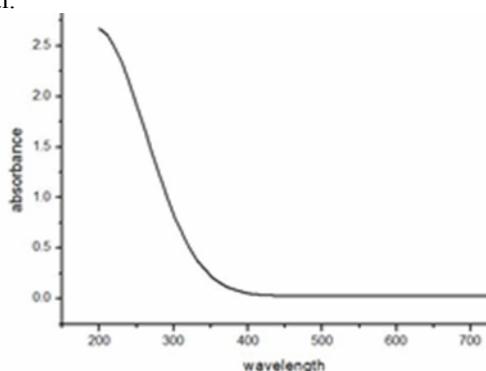


Fig 4. Optical absorption spectra of as-prepared ZnS nanoparticles

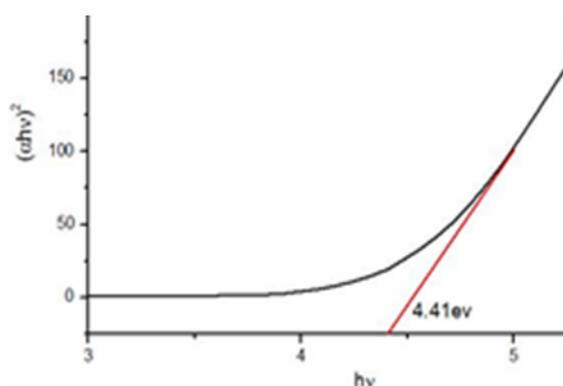


Fig 5. Optical bandgap of ZnS nanoparticles.

This blue shift is indicative of quantum confinement effects, which occur due to the reduced size of the nanoparticles. The smaller the particle size, the greater the increase in energy required for electronic transitions, resulting in a larger band gap. The energy band gap of the ZnS nanoparticles was determined by plotting a graph of $h\nu$ versus $(\alpha h\nu)^2$ and extrapolating the linear region of the curve to intersect the energy axis, as described in reference [16-17].

The calculated band gap energy provides insight into the potential applications of ZnS nanoparticles in optoelectronic devices, such as light-emitting diodes (LEDs), lasers, and photovoltaic cells. The enhancement in band gap energy due to size reduction not only improves the absorption of light in the UV region but also reflects the potential for improved efficiency in devices utilizing these nanoparticles. In addition to the blue shift in absorption, the spectra can also provide information about the quality and purity of the synthesized nanoparticles. The presence of additional peaks or broadening in the absorption spectrum may indicate defects or impurities in the material. Therefore, careful analysis of the UV-visible spectra is crucial for optimizing synthesis conditions to achieve high-quality ZnS nanoparticles for various applications.

Overall, the findings regarding the optical properties underscore the significant potential of ZnS nanoparticles in modern nanotechnology and materials science. As research continues, further investigation into their photoluminescence and other optical characteristics will be essential for developing advanced applications.

Where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap energy, and C is a constant. Fig.5. shows the optical bandgap graph between $h\nu$ versus $(\alpha h\nu)^2$, where the intercept of the graph on X- axis gives the value of band gap which is equal to 4.41 eV [18]

IV. Conclusion

ZnS nanoparticles were successfully synthesized through a chemical deposition method using polyvinyl alcohol (PVA) as a stabilizing agent. The average size of the nanoparticles was found to be approximately 6 nm, calculated using the Debye-Scherrer formula. This size is corroborated by transmission electron microscopy (TEM) analysis, which also shows that the nanoparticles are nearly uniform in size. However, the TEM images illustrate that the particles exhibit significant aggregation, likely due to the high surface energy associated with nanoscale materials. The UV-visible absorption spectra revealed intense absorption in the range of 200 to 300 nm, which can be attributed to the relatively large excitation binding energy of the semiconductor nanoparticles. Notably, the spectra also indicate a blue shift in the absorption band compared to bulk ZnS, further confirming the quantum confinement effect due to the reduced particle size. The calculated optical band gap of the ZnS nanoparticles was found to be 4.41 eV, an increase relative to the band gap of bulk ZnS (approximately 3.6 eV). This study primarily focused on the structural and optical properties of ZnS nanoparticles resulting from chemical synthesis methods. The findings highlight the potential for these nanoparticles in various applications, including optoelectronic devices, sensors, and photocatalysis. The enhanced band gap resulting from microwave-assisted synthesis suggests improved performance characteristics for applications requiring high energy efficiency. Overall, this research provides valuable insights into the synthesis and characterization of ZnS nanoparticles, paving the way for further exploration of their properties and potential applications in nanotechnology. Future studies may also include investigating the photocatalytic activity and stability of these nanoparticles under various environmental conditions, which could further enhance their utility in practical applications.

References

- [1] J.A Smith, And R.B. Doe, Size-Dependent Optical Properties of Semiconductor Nanoparticles, *Journal of Nanotechnology*, 45(3), (2021), 123-134.
- [2] Y. Tong, Y. Liu, And S. Li, Recent Advances in The Synthesis and Application of ZnS Nanoparticles, *Materials Today Advances*, 8, (2021), 100091.
- [3] C.D. Brown, And Green, E.F. Zinc Sulfide Nanoparticles: Synthesis, Properties, And Applications, *Advanced Materials Reviews*, 12(2), (2020), 88-102.
- [4] X. Huang, And G. Xu, Microwave-Assisted Synthesis of ZnS And Its Optical Properties. *Journal of Materials Chemistry C*, 6(21), (2018), 5587-5595.
- [5] B. Barman, And K. C. Sarma, Low Temperature Chemical Synthesis of ZnS Mn Doped ZnS Nanosized Particles: Their Structural, Morphological and Photophysical Properties, *Solid State Sciences*, 109, (2020), 106404
- [6] M. R. García, And M. Fernández, Nanocrystalline ZnS: Preparation, Structure, and Optical Properties, *Journal of Nanomaterials*, 2019, (2019), 1-10.
- [7] B. Barman and K. C. Sarma, Luminescence Properties of ZnS Quantum Dots Embedded In Polymer Matrix, *Chalcogenide Letters*, 8, (2011), 171-176
- [8] J. Barman, And F. Sultana, Synthesis of Mix Zinc Oxide And Cadmium Sulphide Nanoparticles, *Optoelectronic and Antimicrobial Activity And Application In Water Treatment*, *IOSR Journal of Applied Physics*, 8, (2016) 46-51
- [9] S.K. Kulkarni, U. Winkler, N. Deshmukh, P.H. Borse, R. Fink, E. Umbach, *Applied Surface Science* 169-170 (2001) 438-446.
- [10] Y. Changhui, F. Xiaosheng, L. Guanghai And Z. Lide, *Appl. Phys. Lett.* 85, 15, 3035 (2004).
- [11] B. Barman, And K. C. Sarma, Structural Characterization of PVA Capped ZnS Nanostructured Thin Films, *Indian J Phys*, 86, (2012), 703-707.
- [12] S. Kumar, And S. Sharma, Synthesis, Characterization, And Applications of ZnS Nanoparticles for Photocatalytic Degradation of Organic Pollutants, *Environmental Science and Pollution Research*, 29(9), (2022), 13740-13754.
- [13] B. Barman, P. K. Mochahari, And K. C. Sarma, Optical Studies on Some Aspects of Polyvinyl Alcohol Composite ZnS Nanocrystalline Thin Films, *AIP Conference Proceedings*, 1391, (2011), 116-118
- [14] C. N. R., Rao, And A. Govindaraj, *Nanomaterials: Synthesis, Characterization, And Applications*, *Journal of Materials Science*, 52(1), (2017), 1-41.
- [15] J. Liu, L. Xu, X. Wang, And H. Sun, Synthesis and Characterization of ZnS Nanoparticles Via A Hydrothermal Method and Their Photoluminescence Properties, *Materials Science in Semiconductor Processing*, 104, (2020), 104658.
- [16] S. Kar S. Biswas, S. Chaudhuri And P M G Nambissan, Substitution-Induced Structural Transformation in Mn-Doped ZnS Nanorods Studied By Positron Annihilation Spectroscopy, *Nanotechnology*, 18, (2007), 225606
- [17] P., Debye, And P. Scherrer, Determination of The Size and Internal Structure of Colloidal Particles By Means of X-Rays, *Schweizerische Naturforschende Gesellschaft* 24, (1916), 210-220.
- [18] B. Barman, and K. C. Sarma, Synthesis and Optical Properties of ZnS Nanoparticles in PVA Matrix, *Optoelectronics and Advanced Materials - Rapid Communications*, 4, (2010), 1594-1597.

