

Synthesis of Zinc Sulfide Nanocrystals by Chemical Bath Deposition Methods

Omar M. Hameed^{1*}

¹Department of Medical Laboratory Technique, AlNoor University College, Nineveh, Iraq

Abstract: Chemical bath deposition method was used to create zinc sulfide (ZnS) nanoparticles. The CBD contained fixed components such as ZnCl₂, NH₄NO₃, and CS (NH₂)₂ and KOH. Samples were heated at 90°C in a bath with magnetic agitation. Homogeneity, high transparency, adhesion, and crystalline ZnS films were achieved using KOH (1.4 M). For structural and optical investigation, the produced nanoparticles are examined using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier Transform Infrared (FTIR) Spectroscopy, and ultraviolet-visible (UV-Vis) Absorption Spectroscopy. In XRD, the cubic crystal structure can be seen at 350nm, the UV-Vis spectrum reveals a blue peak. The absorbance and type of bonds present in samples are determined by FTIR spectra.

Keywords: Zinc sulfide nanoparticle, chemical bath deposition (CBD), X-ray diffraction (XRD), UV-visible spectroscopy, Fourier transforms infrared (FTIR), scanning electron microscopy (SEM).

1. Introduction

Zinc sulphide is the most important materials in photonics research, transparent semiconductor with a relatively broad band gap (3.8 eV). solar cells ,electroluminescent devices and other optoelectronic devices [1, 2] are all possible applications for ZnS. ZnS nanostructures in one dimension are appealing because they can be used to make electrical and optoelectronic Nano devices [3-5]. ZnS crystallizes as Zinc blende or Wurtzite, however Wurtzite is probably the most useful for technological applications due to its non-central symmetry and polar surfaces. It's a highly attractive material for detecting, modulating visible and near ultraviolet light and emitting [6,7], ZnS is one of the most promising materials for thin film electroluminescent displays[8], blue-emitting laser diodes and multilayers dielectric filters [9,10].

The ZnS preparation is interest due to their optical and optoelectronic. There are a few publications related to ZnS Nano crystals in the literature, Because there is no chemical precursor that can directly produce ZnS particles, Generating ZnS nanoparticles in porous media channels is thus a significant issue. In this research, we show how to make ZnS nanoparticles using a simple chemical approach, as well as their structural, morphological, and optical properties.

* Corresponding Author: researcherstaff06@alnoor.edu.iq

2. Experimental details

Chemical reagents: 80 ml of (1.5) M NH_4NO_3 , 80 ml of (0.02) M ZnCl_2 , 80 ml of (0.2 M) $\text{CS}(\text{NH}_2)_2$, and 200 ml of KOH (1.4 M) for the manufacture of ZnS NPS chemical baths were made individually.

The chemical solution was contained within a glass container. The container was filled with ZnCl_2 , KOH, and NH_4NO_3 . A magnetic stirrer was used to agitate the chemical solution, and a hot plate was used to heat it to 90 °c. After the temperature was reached, the container was finally filled with $\text{CS}(\text{NH}_2)_2$ (0.2 M) (thiourea), which promoted the synthesis of ZnS. To reduce evaporation losses and the resulting changes in concentration, the chemical bath was covered. The solution cooled to room temperature naturally. The product-containing solution was centrifuged and then rinsed with distilled water. The washing process was repeated ten times to eliminate contaminants from the sample. In oven at 60 °C , the resulting white product was dried for 12 hours.

The ZnS sample underwent analysis using several analytical tools. The X-ray diffraction analysis was carried out using a Siemens model D500, while SEM analysis was performed using a ZEISS model: sigma VPEDS, with mapping conducted using equipment from Oxford Instruments in the UK. For absorption spectra analysis within the 200-1100 nm range, a Shimadzu UV 1800 twin beam from Japan was used. To evaluate the composition and quality of the compound within the 4000-400 cm^{-1} range, Fourier transform infrared spectroscopy (FTIR) was conducted using a Shimadzu FT-IR8400S from Japan.

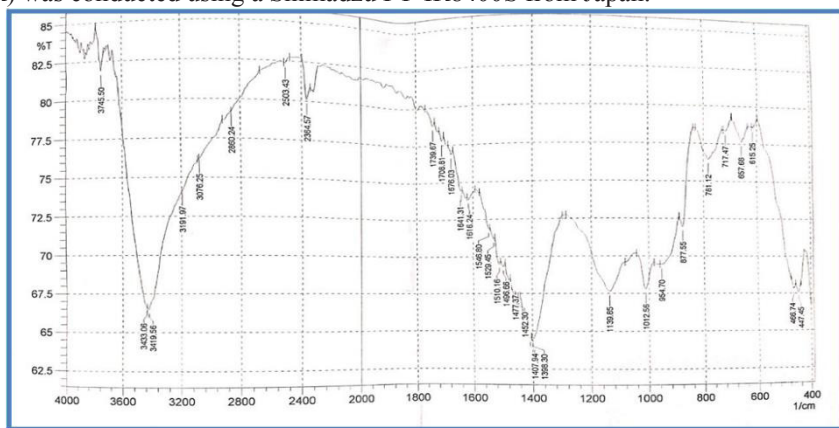


Figure 1: FTIR spectra of synthesized ZnS nanoparticles.

3. Result and discussion

FT-IR Analysis of ZnS NPS In the range 4000 to 400 cm^{-1} , Figure (1) shows how FTIR spectra are used to analyze the composition and quality of a substance. The transmission bands of ZnS samples is almost identical, as seen by their FTIR spectra. The prominent bands are located at 1012 and 657 cm^{-1} , respectively, and are caused by ZnS stretching and vibration [11]. The decreases at 1407 cm^{-1} and 1447 cm^{-1} are most likely attributable to the creation of the materials microstructure [12]. The bands around 3433-3419 cm^{-1} correspond to the frequency of hydroxyl group hydrogen stretching (OH stretching) [13]. (CO) vibrational modes derived from (CO₂) absorbed at nano crystals surface are responsible for the bands about 1630 cm^{-1} [14].

3.1. UV-VIS Analysis of ZnS nano piratical

The absorption spectra of ZnS nanoparticles within the ultraviolet and visible ranges were found to exhibit significant absorption around the 400 nm mark, representing the optical band gap. This absorption peak demonstrated a shift towards the blue at approximately 350 nm. These spectra were illustrated in Figure 2 of the study and were sourced from prior research [15, 16]. The NPS absorbance in the 345 wavelength range. [17].

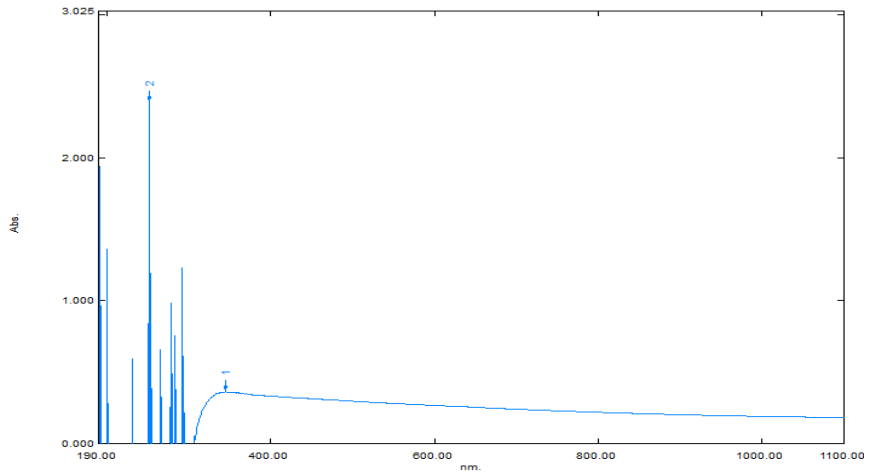


Figure 2: Absorption spectra for ZnS nanostructures.

3.2. SEM Analysis

SEM examination provides information on the objects' shapes and sizes. As can be seen, the ZnS nanoparticles had nearly homogenous spherical shapes and cural floral structure High KOH concentration caused grain aggregation due to grain development events [18]. (49.2 nm) nm is the average diameter. As illustrated in the figure (3).

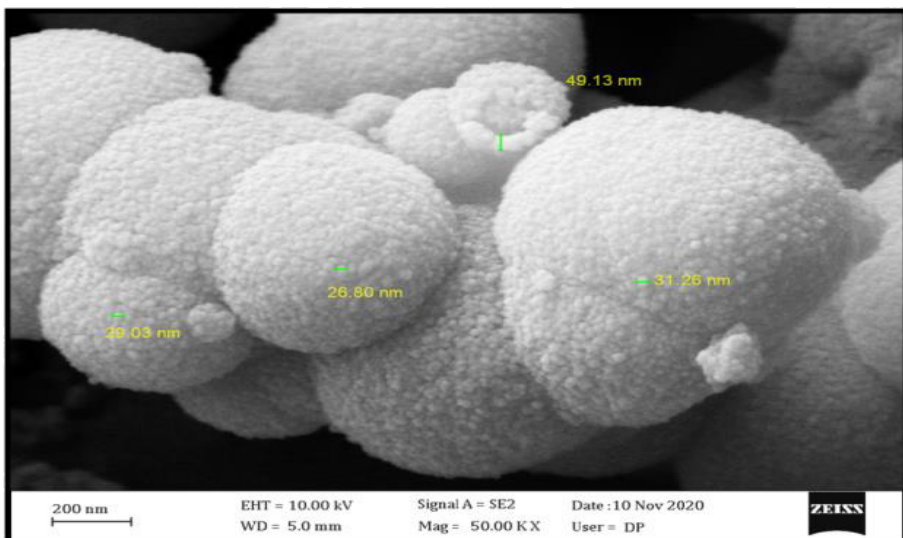


Figure 3: The SEM of ZnS NPs.

3.3. XRD analysis

The XRD data suggest that the ZnS nanoparticles were obtained in powder form, as illustrated in Figure (4). The peaks indicate the production of tiny crystallites of ZnS nanostructures, as seen in the XRD model.

The diffraction peaks of ZnS nanoparticles at 2 Theta locations 29.01 °, 48.03 °, and 57.02 ° correspond to the diffraction planes (111), (220) respectively (311). The results obtained are consistent with those found in reference [24].

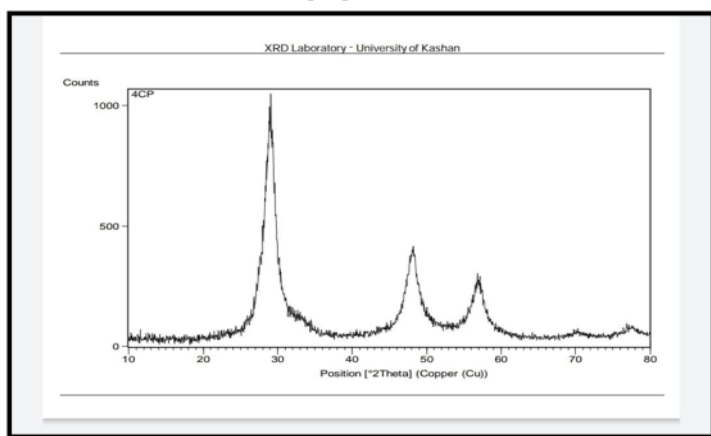


Figure 4: XRD plot of Zinc Sulfide nanoparticles

In which, λ is the wavelength of X-rays (1.54 Å) by (Cu $K\alpha$), D is the size of the crystallites, β is the full width at half maximums (FWHM) of the diffraction peak (in radians) and is the diffraction angle and K is the geometric factor (0.9) [19,20].

$$(d_{hkl} = n \lambda / 2\sin\theta) \tag{1}$$

Table 1: X-ray diffraction pattern parameters of ZnS nanoparticles.

Sample	Nkl	2θ(degree)	Fwhm (2θ)	D-spacing (nm)	Particle size (nm)
1.4M	111	28.98	0.787	0.3077	10.45
	220	48.2	0.885	0.1885	9.85
	311	57.01	0.590	0.1616	15.45

4. Conclusion

At a temperature of 90°C, the chemical bath deposition method was utilized to effectively synthesize nano-crystalline ZnS. Analysis using X-ray diffraction demonstrated that the synthesized particles had a cubic zinc blende structure with an average crystallite size of 11.9 nm and individual particle sizes ranging from 9.85 nm to 15.45 nm. The absorption spectra obtained from ultraviolet and visible ranges revealed a blue peak at a wavelength of 345 nm.

References

1. D'Amico, P., Calzolari, A., Ruini, A., & Catellani, A. (2017). New energy with ZnS: novel applications for a standard transparent compound. *Scientific reports*, 7(1), 1-9. Doi: 10.1038/s41598-017-17156-w.
2. Altiokka, B. (2019). Effects of inhibitor on ZnS thin films fabricated by electrodeposition. *Journal of Electronic Materials*, 48(4), 2398-2403.
3. Wei, A., Liu, J., Zhuang, M., & Zhao, Y. (2013). Preparation and characterization of ZnS thin films prepared by chemical bath deposition. *Materials Science in Semiconductor Processing*, 16(6), 1478-1484. Doi.org/10.1016/j.mssp.2013.03.016
4. D'Amico, P., Calzolari, A., Ruini, A., & Catellani, A. (2017). New energy with ZnS: novel applications for a standard transparent compound. *Scientific reports*, 7(1), 1-9. Doi: 10.1038/s41598-017-17156-w.
5. Rodríguez, G. S., Torres, R. C. C., Zeferino, R. S., & Ramos, M. E. Á. (2019). Stabilized blue emitting ZnS@ SiO₂ quantum dots. *Optical Materials*, 89, 396-401. doi: 10.1016/j.optmat.2019.01.057.
6. Sung, Y. J., Kim, J. Y. H., Choi, H. I., Kwak, H. S., & Sim, S. J. (2017). Magnetophoretic sorting of micro droplets with different microalgal cell densities for rapid isolation of fast growing strains. *Scientific reports*, 7(1), 1-11. Doi: 10.1038/s41598-016-0028-x.
7. Altiokka, B. (2019). Effects of inhibitor on ZnS thin films fabricated by electrodeposition. *Journal of Electronic Materials*, 48(4), 2398-2403. Doi: 10.1007/s11664-019-06950-z.
8. Charinpanitkul, T., Chanagul, A., Dutta, J., Rungsardthong, U., & Tanthapanichakoon, W. (2005). Effects of cosurfactant on ZnS nanoparticle synthesis in microemulsion. *Science and Technology of Advanced Materials*, 6(3-4), 266. doi:10.1016/j.stam.2005.02.005.
9. Yu, L., Ruan, H., Zheng, Y., & Li, D. (2013). A facile solvothermal method to produce ZnS quantum dots-decorated graphene nanosheets with superior photoactivity. *Nanotechnology*, 24(37), 375601. Doi:10.1088/0957-4484/24/37/375601.
10. Tounsi, A., Talantikite-Touati, D., Khalfi, R., Merzouk, H., & Haddad, H. (2017, November). Optical and structural properties of ZnS: La thin films elaborated by sol-gel method. In *International Symposium on Materials and Sustainable Development* (pp. 44-51). Springer, Cham.
11. Ashwini, K., & Pandurangappa, C. (2014). Solvothermal synthesis, characterization and photoluminescence studies of ZnS: Eu nanocrystals. *Optical Materials*, 37, 537-542.
12. Ummartyotin, S., Bunnak, N., Juntaro, J., Sain, M., & Manuspiya, H. (2012). Synthesis and luminescence properties of ZnS and metal (Mn, Cu)-doped-ZnS ceramic powder. *Solid State Sciences*, 14(3), 299-304. doi.org/10.1016/j.solidstatesciences.2011.12.005.
13. Goswami, N., & Sen, P. (2004). Water-induced stabilization of ZnS nanoparticles. *Solid state communications*, 132(11), 791-794. doi.org/10.1016/j.ssc.2004.09.022
14. Qadri, S. B., Skelton, E. F., Hsu, D., Dinsmore, A. D., Yang, J., Gray, H. F., & Ratna, B. R. (1999). Size-induced transition-temperature reduction in nanoparticles of ZnS. *Physical Review B*, 60(13), 9191. DOI:https://doi.org/10.1103/PhysRevB.60.9191
15. Lee, S. Y., Shin, Y. H., Kim, Y., Kim, S., & Ju, S. (2011). Thermal quenching behavior of emission bands in Eu-doped ZnS nanowires. *Journal of luminescence*, 131(7), 1336-1339. doi.org/10.1016/j.jlumin.2011.03.026
16. Devi, R., Raveendran, R., & Vaidyan, A. V. (2007). Synthesis and characterization of Mn²⁺-doped ZnS nanoparticles. *Pramana*, 68(4), 679-687.

17. Jaiswal, J. K., Mattoussi, H., Mauro, J. M., & Simon, S. M. (2003). Long-term multiple color imaging of live cells using quantum dot bioconjugates. *Nature biotechnology*, 21(1), 47-51.
18. Dheeb, B. I., Al-dujayli, S. M., Ibrahim, I. M., Abbas, Q. A., Ali, A. H., Ramizy, A & Hussain, A. F. (2019, February). Study the antifungal activity of ZnS: Mn nanoparticles against some isolated pathogenic fungi. In *Journal of Physics: Conference Series* (Vol. 1178, No. 1, p. 012008). IOP Publishing.
19. Bera, K., Saha, S., & Jana, P. C. (2018). Temperature Dependent Synthesis of Zinc Sulfide Nanocrystal. *Oriental Journal of Chemistry*, 34(3), 1665.
20. A. Abd AL-Zahra, Alsammarraie, A. M. A(2021) Hydrothermal synthesis and characterization of zinc sulfide nanoparticles .*Eurasian Chemical Communication*. 3 606-613 DOI:10.22034/ecc.2021.293399.1196.