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Assessment of Antimicrobial Activity of Chemical Bath Deposited Zinc Sulfide Thin Films

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Abstract: *The unique structural, electronic, and optical characteristics of semiconductor nanocrystals resulting from their high surface to volume (S/V) ratio and the quantum confinement effect have attracted a lot of attention. Due to its stability, affordability, and low toxicity in electroluminescent applications, cubic ZnS, a semiconductor with a broad band gap, has drawn a lot of interest. The creation of zinc sulfide nanoparticles and their antimicrobial activity against topical skin pathogen, pathogens growing on food containers and Antifungal activity against fungus growing on walls are demonstrated in the current study. At room temperature, chemical bath deposition is used to create ZnS thin films. It is fast, innovative, and environment friendly synthesis method for zinc sulfide (ZnS) nanoparticles. Zinc Sulfide an important semiconductor material in the II-VI group with direct and significant band gap energy is 3.63–3.92 eV. Different characteristics of ZnS crystal include the massive ionization transition and phase that are stable in conditions of a normal atmosphere. Several physiochemical methods, including X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Visible spectroscopy, Energy Dispersive X-ray (EDX), and Transmission Electron Microscopy (TEM), were used to analyze the as-prepared ZnS thin films.*

Keywords: ZnS thin films, Chemical Bath Deposition, Antimicrobial activity, Antifungal Activity

I. INTRODUCTION

Thin films as an antibacterial agent has attracted attention in the recent rea being its application in various food industries to control the growth of the pathogenic and nonpathogenic bacteria. Various materials are used for the synthesis of thin films which includes Zinc, nickel, iron etc. Majority of the metals shows either bacteriostatic or bactericidal effects as the metals and their oxides inhibits the growth of microorganisms by interfering with the cell membrane, cell wall or microbial growth[1]. The ease of thin films in preparation, its wide area, thermal resistance, has increased its application in the packaging of the food material [2]. Also thin films can be used in the treatment of infections in medical field[3]. In the present research zinc sulfide thin films are used to evaluate their antimicrobial potential against Gram positive and Gram negative bacteria and also against fungal pathogens.

The tool for designing, producing, characterizing and using nanostructured materials is nanotechnology. In at least one dimension, it typically deals with structures with a size between 1 and 100 nanometers. It has emerged as a field that is expanding and changing quickly and offers potential chances to develop better materials and products [5]. The size of nanoparticles has a significant impact on their characteristics[4]. They are highly chemically reactive due to their high specific surface area. The quantum size effect, which is also a result of their smaller size, causes an increase in band-gap energy [5]. Several techniques have been used to create ZnS thin films, including the hydrothermal method, chemical vapor deposition, chemical bath deposition, chemical precipitation, chemical co-precipitation,microwave irradiation route, sonochemical method, sol-gel technique and the solvothermal method[6]. In the current paper, we used the straightforward and user-friendly chemical bath deposition method. Antimicrobial activity is one of the many uses for gold and silver nanoparticles in the food and healthcare industries, among other uses for nanotechnology. Zinc sulfide is a semiconductor belonging to the II-IV group with a wide band gap energy of 3.68 eV, making it suitable for

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biosensors, fluorescent, chemical, and other widely researched and compared sulfide and oxide materials for antimicrobial applications. ZnS is an inorganic substance that has a variety of practical uses [7].

Because of its excellent optical, electrical, luminescence, and photochemistry properties, ZnS semiconductor films are extensively investigated in a variety of nanoelectronics fields. ZnS NPs have a wide range of potential applications in optoelectronics, ultraviolet light-emitting diodes, sensors, field emitters, injection lasers, infrared windows, flat-panel displays, thin films electroluminescent devices, photo catalytic activities, and antimicrobial activity [8]. Many diseases still have bacterial infections as their main cause, and they can even be fatal. The development of new bactericidal techniques is required in response to the rising concern regarding multidrug resistant bacterial strains. According to this perspective, the development of microbial resistance against the conventional drug regime is the reason why research into nanoparticles for antimicrobial applications is gaining more attention [9].

II. EXPERIMENTAL DETAILS

2.1 Synthesis of ZnS Thin Films

Zinc sulfidethin films on glass slides are deposited using the chemical bath deposition method. The materials used are $Zn(CH_3COO)_2$, $CS(NH_2)_2$, Triethnolammine (TEA), NH_4OH and double distilled water.

The substrate used for thin films deposition is glass slides. The glass slides before deposition were degreased with chromic acid, ethanol, etched with HCl for 30 min and ultrasonically cleaned by de-ionized water, acetone and finally dried in air[10]. Zinc Acetate used as source of Zinc cation, thiourea as source of Sulphur anion, TEA as capping agent and ammonia as a complexing agent as well as to adjust the pH. All the chemicals were of AR grade (Loba Chemicals Ltd). They are extremely pure and don't require further purification [5]. In double distilled water, solutions of 0.1 M Zinc acetate, 1 M thiourea are prepared. To create a homogeneous solution, 15 ml of zinc acetate and 5 ml of TEA were mixed and stirred for 30 minutes on a magnetic stirrer. This was followed by the appropriate amount of 1 M Thiourea being added drop by drop while being vigorously stirred for an hour. The pH of solution is adjusted to 12 using ammonia. The thoroughly cleaned glass slides were dipped in the beaker containing precursor solution. The resulting solution is kept in water bath at 80℃for one hour [5].The solution having dipped glass slides is aged for 36 hours at room temperature to get uniform and well adhered films on glass slides. White colored well deposited films are used for further characterization and antimicrobial, antifungal activity.

2.2 Characterization Techniques

UV-vis Spectrophotometric study was done by using Shimadzu UV-2600i, Japan. UV visible analysis is done to study absorption spectrum of prepared thin films. Understanding optical absorption is crucial to understanding how semiconductor nanoparticles behave. The band gap or the energy difference between the filled valence band and the empty conduction band is a fundamental characteristic of semiconductors.Powder XRD and TEM were used for determination of crystal structure, shape and size of prepared ZnS thin films nanoparticles. XRD data is collected by using Ultima IV, Rigaku corporation, Japan instrument. TEM images are recorded using JEOL JEM 2100 plus, Japan instrument. SEM images are recorded using JEOL JSM-6360 instrument to study the morphology. The surface roughness is determined by AFM analysis by using INNOVA 1B3Be instrument.

III. RESULTS AND DISCUSSION

3.1 Structural and Optical Property Analyses

1. UV-Visible Measurements

Spectra in the UV-Visible range are very useful for locating the nanomaterials. Strongly permitted optical excitation of electrons across the band gap results in an abrupt increase in absorption at the wavelength associated with the band gap energy. The optical absorption edge is the term for this aspect of the optical spectrum[5]. A UV-Visible spectrophotometer was used to investigate the ZnS nanoparticle's optical absorption properties.The UV-Visible absorption spectra of prepared ZnS thin films is recorded in the range of 300 nm to 600 nm. A typical absorption peak at 312 nm is observed as shown in Figure 1. The observed peak corresponds to band gap of 3.57nm.

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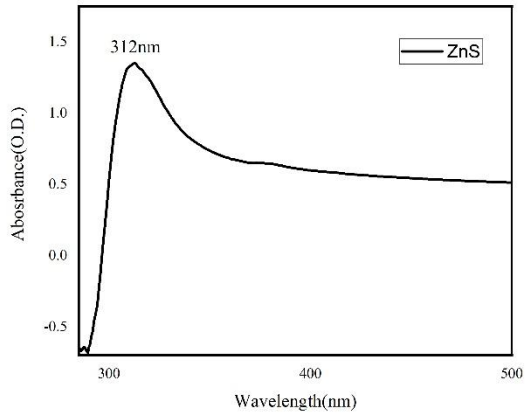

Figure 1. UV-visible absorption spectrum of ZnS thin films

2. X-ray Diffraction Measurements

X-ray diffraction pattern of the as-deposited ZnS thin films by chemical bath deposition was shown in Figure 2.The three main diffraction peaks at 28.7, 48 and 56.9° corresponds to (111), (220) and (311) lattice planes confirms ZnS cubic sphalerite structure (JCPDS 01-077-2100). The cubic phase is stable at room temperature, while the hexagon alone is stable above1020°C [16]. Minor peaks observed at 32.9, 70.3 and 77.6 ° corresponding to planes (200), (400) and (331). The distinctive small particle effect is thought to be the cause of the broad diffraction peaks [5].

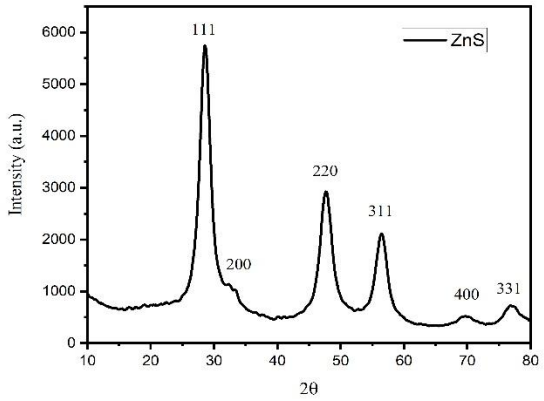

Figure 2. XRD patterns of prepared ZnS thin films.

More consideration should be given to the peak broadening at lower angles when determining particle size. As a result, the Debye-Scherrer formula was used to determine the size of the nanoparticles using the (111) reflection from the XRD pattern. The Debye-Scherrer formula for determining particle size is provided by[5],

$$D = \frac{0.94\lambda}{\beta cos\theta}$$

Where λ=1.5405Å wavelength of incident beam CuKa1, θ is Bragg's angle in radian, β is (FWHM) full width half maximum of peak.

Table 1. Band gap and particle size of nanoparticles

Optical band gap(eV)	Particle Size from XRD (nm)
3.57	23

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3. SEM Analysis

Scanning electron microscopy (SEM), a flexible method for examining microstructure, was used to observe the surface morphology of ZnS thin films. SEM images are used to investigate the structural and morphological formation of pure and ZnS thin films. The SEM Image of the ZnS thin films as shown in Figure 3, clearly shows the size of particles as expected, were found to be in cluster form. The surface morphology of the ZnS in some place various sizes of the particles are observed, that is particle size randomly distributed[11].

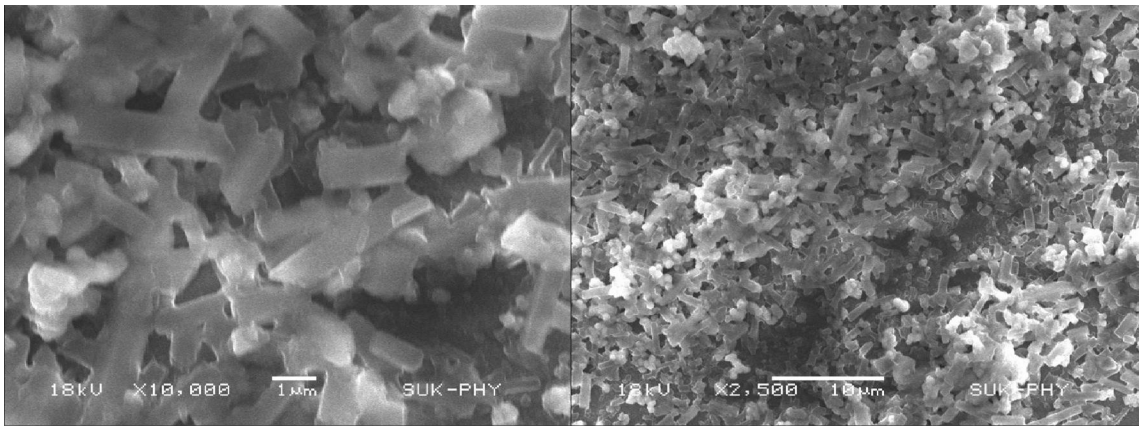

Figure 3. SEM images of ZnS thin films

4. TEM Analysis

By using transmission electron microscopy, the polycrystalline nature of ZnS was examined. X-ray diffraction is simply reflected in the TEM image[12]. Although TEM analysis determines whether thin films are mono-crystalline or polycrystalline, XRD provides information about the crystalline nature of the thin films. The zinc sulfide nanoparticles are in form of nanorods, in a variable sizes and their size, shape are visualized using the TEM techniqueas shown in Figure 4[13].The nanoparticle size is calculated to be □ 25 nm.

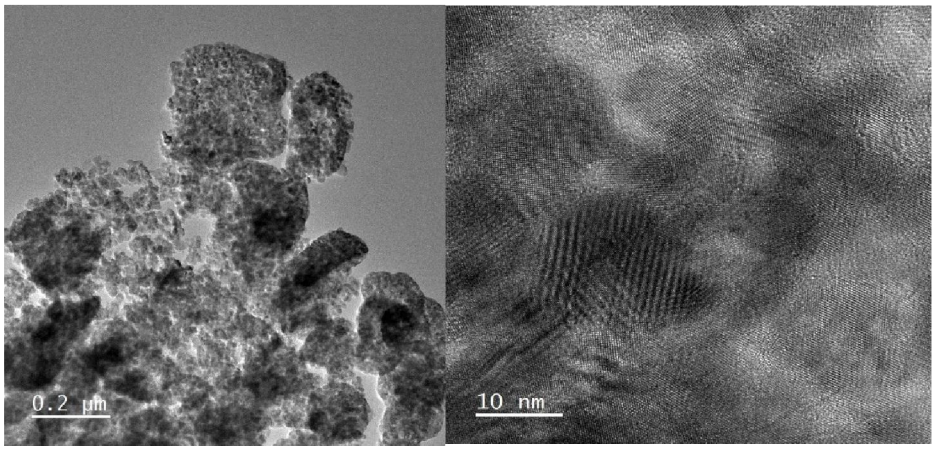

Figure 4. TEM images of ZnS thin films

5. AFM Analysis

High resolution images of a surface are taken using the surface analysis method known as atomic force microscopy (AFM), which also allows for the plotting of topographies that represent the surface relief. ZnS thin films grain size and surface roughness were assessed using AFM studies. The Figure 5 symbolizes atomic force microscopy images for ZnS[10].The average roughness of thin films surface is 5nm.

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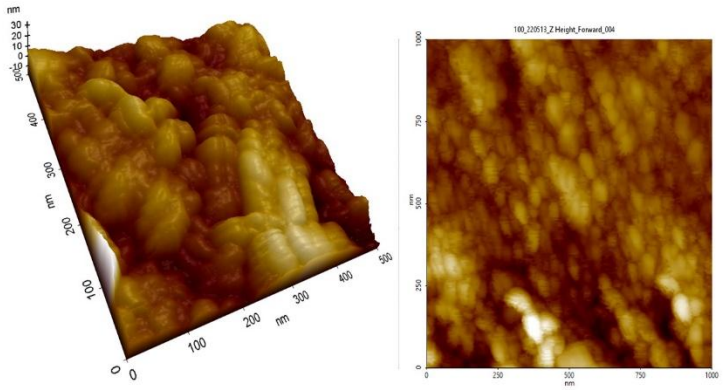

Figure 5. AFM images of ZnS thin films

3.2 Antimicrobial Activity

Antibacterial activity of the thin films was checked by using Muller and Hinton agar plates. For the antifungal activity, sterile potato dextrose agar plates were used. For antimicrobial activity Gram positive pathogens: Staphylococcus aureus, and Bacillus subtilis, Gram negative pathogens, E. coli, and Pseudomonas aeruginosa were used. Antifungal activity was determined against Aspergillus niger and Candida albicans. The stock culture of the bacterial pathogens were first inoculated separately in the sterile nutrient broth and incubated at 37^{o}C at 24 hrs. This broth was diluted with sterile saline and turbidity was adjusted to 0.5 McFarland standards. The sterile Muller and Hinton agar plates were then inoculated with the 200µl of cell suspension of each pathogen separately [8]. The sterile potato dextrose agar plates were inoculated with spore suspension of Aspergillus Niger. Thin films coated glass slides were placed on this plate, making contact of thin films with pathogens. The plates were incubated at 37^{o}C for 24 hrs. The results were recorded as zone of growth inhibition in contact with thin films. In order to compare pure ZnS thin films, ZnS thin films was high inhibition zone against Gram positive, Gram negative bacteria and fungus culture in various concentrations. According to the comparison results, gramnegative bacteria have higher levels of antimicrobial activity than gram positive bacteria because of their cell structure [6]. Grampositive bacteria have a single thick layer of peptidoglycan in their cell wall, which reduces their toxicity. Gram negative bacteria do not have this thick layer. The cell wall of gram negative bacteria is composed of two thin layers: a lipopolysaccharide layer followed by a peptidoglycan layer. The peptidoglycan layer in gramnegative bacteria is much thinner than that in grampositive bacteria, and it also contains repeated units of amino acids and carbohydrates [6].

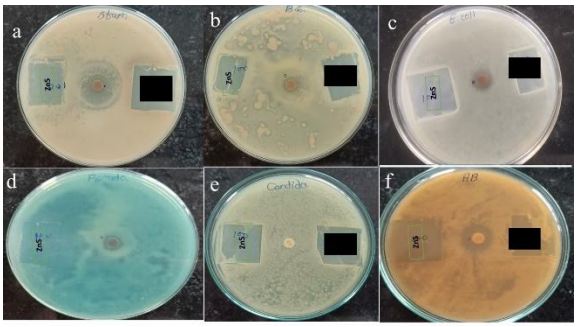

Figure 6. antimicrobial and antifungal acvitiy aginst a) S. aureus b) B. subtilis c) E. coli d) P. aeruginosa e) C. albicans f) A. niger

The zone of growth inhibition was observed against both Gram positive and Gram negative pathogens and also against fungal pathogens[14][15]as shown in Figure 6. The results are depicted in Table 2.

Table 2 Antimicrobial and Antifungal activity of ZnS thin films.

Sr. No.	Pathogen	ZnS thin films
1	*Staphylococcus aureus*	Active

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2	*Bacillus subtilis*	Active
3	*E. coli,*	Active
4	*Pseudomonas aeruginosa*	Active
5	*Aspergillus niger*	Active
6	*Candida albicans*	Active

IV. CONCLUSION

The produced nanoparticles of zinc sulfide thin films were successfully synthesized using a chemical bath deposition method. XRD analysis confirms the ZnS nanoparticles are of the cubic crystal system with an average particle size of 25 nm, which is also confirmed by TEM.SEM images exhibit Nanorods while AFM analysis show that an average roughness of 5nm.Our findings indicate that ZnS nanoparticles are useful not only as an effective antibacterial and fungicide in agricultural and food packaging applications, but also for the topical pathogenic bacterial cultures, fungal cultures.

REFERENCES

[1]. Pachaiappan, R., Rajendran, S., Show, P. L., Manavalan, K., & Naushad, M. (2021). Metal/metal oxide nanocomposites for bactericidal effect: A review. *Chemosphere*, *272*, 128607.

[2]. Mania, S., Cieślik, M., Konzorski, M., Święcikowski, P., Nelson, A., Banach, A., & Tylingo, R. (2020). The synergistic microbiological effects of industrial produced packaging polyethylene films incorporated with zinc nanoparticles. *Polymers*, *12*(5), 1198.

[3]. Emerich, D. F., & Thanos, C. G. (2003). Nanotechnology and medicine. *Expert opinion on biological therapy*, *3*(4), 655-663.

[4]. Bao, L., Zhong, C., Jie, P., & Hou, Y. (2019). The effect of nanoparticle size and nanoparticle aggregation on the flow characteristics of nanofluids by molecular dynamics simulation. *Advances in Mechanical Engineering*, *11*(11), 1687814019889486.

[5]. Wadhwani, M., & Jain, S. (2015). Synthesis and antimicrobial activity of zinc sulfide nanoparticles. *Research Journal of Recent Sciences ISSN*, *2277*, 2502.

[6]. Mani, S. K., Saroja, M., Venkatachalam, M., & Rajamanickam, T. (2018). Antimicrobial activity and photocatalytic degradation properties of zinc sulfide nanoparticles synthesized by using plant extracts. *Journal of Nanostructures*, *8*(2), 107-118.

[7]. Kaur, N., Kaur, S., Singh, J., & Rawat, M. (2016). A review on zinc sulfide nanoparticles: from synthesis, properties to applications. *J Bioelectron Nanotechnol*, *1*(1), 1-5.

[8]. Ghosh, P., Chowdhury, A. R., Saha, S. K., Ghosh, M., Pal, M., Murmu, N. C., & Banerjee, P. (2015). Synthesis and characterization of redox non-innocent cobalt (III) complexes of a O, N, O donor ligand: Radical generation, semi-conductivity, antibacterial and anticancer activities. *Inorganica Chimica Acta*, *429*, 99-108.

[9]. Zaidi, R., & Azam, A. (2021, September). Investigation of structural, optical and antibacterial properties of zinc sulfide quantum dots prepared by sol-gel method. In *AIP Conference Proceedings* (Vol. 2369, No. 1, p. 020177). AIP Publishing LLC.

[10]. Oladeji, I. O., & Chow, L. (1997). Optimization of chemical bath deposited cadmium sulfide thin films. *Journal of the Electrochemical Society*, *144*(7), 2342.

[11]. Sathishkumar, M., Saroja, M., Venkatachalam, M., & Rajamanickam, A. (2017). Biosynthesis of zinc sulfide nanoparticles using Phyllanthus emblica and their antimicrobial activities. *Elixir Elec. Eng*, *102*, 44411-44415.

[12]. Kumar, P., Dev, S., Kumar, A., Thakur, R., & Dhar, R. (2021). Impact of indium doping on the anti-biofilm activity of ZnO thin films against Escherichia coli and Staphylococcus aureus. *Superlattices and Microstructures*, *150*, 106741.

[13]. Malarkodi, C., & Annadurai, G. (2013). A novel biological approach on extracellular synthesis and characterization of semiconductor zinc sulfide nanoparticles. *Applied Nanoscience*, *3*, 389-395.

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[14]. Sathishkumar, M., Saroja, M., & Venkatachalam, M. (2017). Characterization and antimicrobial activity of green synthesized zinc sulfide nanoparticles using plant extracts of phyllanthus niruri. *Int. J. Chem. Sci*, *15*(2), 123-130.

[15]. Aouf, D., Henni, A., Selloum, D., Khane, Y., Fenniche, F., Zerrouki, D., ... & Dizge, N. (2023). Facile preparation and characterization of nanostructured ZnS/PbS heterojunction thin films for enhanced microbial inhibition and photocatalytic degradation. *Materials Chemistry and Physics*, *295*, 127059.

[16]. Long, F., Wang, W. M., Cui, Z. K., Fan, L. Z., Zou, Z. G., & Jia, T. K. (2008). An improved method for chemical bath deposition of ZnS thin films. *Chemical Physics Letters*, *462*(1-3), 84-87.