

Structural, Morphological and Antimicrobial Activity of pure and Aluminum doped Zinc Sulfide Nanoparticles

M. Sathishkumar ^{a,*}, M. Saroja ^b, V. Venkatachalam ^b

^a PG and Research Department of Electronics, Nehru Arts and Science College, Coimbatore, Tamil Nadu, India

^b Department of Electronics, Nehru Arts and Science College, Coimbatore, Tamil Nadu, India

***Corresponding Author**
mskeasc@gmail.com
 (M. Sathishkumar)
 Tel.: +91 98658 61230

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ABSTRACT: Undoped and Aluminum (Al) doped Zinc Sulphide (ZnS) Nanoparticles (NPs) has been prepared by chemical co-precipitation method using plant zinc sulphate, Aluminum sulphate and Thiourea . The X-Ray Powder Diffraction (XRD) studies reveals Cubic structure for undoped and Aluminum doped ZnS NPs. Scanning Electron Microscopy (SEM) images shows formation of smooth surfaced ZnS NPs and average particles size was found in the range of 17 nm from the result the Aluminum doped ZnS were influenced to increase ZnS NPs particle size. The disk diffusion method was used to screen the antimicrobial activity of Aluminum doped ZnS NPs against different gram positive, gram negative bacterial and fungus culture from this investigation Aluminum doped ZnS NPs have potential antimicrobial agent which was show excellent zone of inhibition (ZoI) at different concentration against all tested microorganisms.

Keywords: Zinc Sulphide, Aluminum doped, XRD, SEM zone of inhibition, Antimicrobial Activity.



M. Sathishkumar received his UG, PG and M. Phil degree in Electronics from Erode Arts and Science College affiliate to Bharathiar University, Tamil Nadu, India in 2012. Now he is working as Assistant Professor of Electronics in Nehru Arts and Science College, Coimbatore and he pursuing part time Ph.D in

Electronics at Erode Arts and Science College, Erode, Tamil Nadu, India. His research interest mainly focused on the bio-fabrication of semiconductor nanoparticles for antimicrobial applications.

semiconductor for solar cell application and she guided 10 Ph.D and 35 M.Phil scholars from various state universities and he published more than 100 articles in well reputed international/national and SCI journals.



Dr. M. Venkatachalam received his Ph. D degree in physics from Bharathiar University in 2008. Currently he works a Head and Associate Professor of Electronics, Erode Arts and Science College, Erode, Tamil Nadu, India. His research interest is fabrication of

nanomaterial's for photo catalysis and solar cell application and he guided 7 Ph.D and 30 M.Phil scholars from various state universities and he published more than 120 articles in well reputed international/national and SCI journals



Dr. M. Saroja received her degree B. Sc degree in Physics in 1985, M. Sc degree in Material Science in 1988, M. Phil and Ph. D in Physics specialization in Electronics from Bharathiar University in 2004. Currently she works an Associate Professor of Electronics, Erode Arts and Science College, Erode, Tamil

Nadu, India. Her research interest in fabrication

1. Introduction

Zinc Sulphide (ZnS) is important semiconductor component in II-VI group with direct and large value of band gap energy, High refractive index and dielectric constant it appears two type of crystal structure: hexagonal wurtzite (WZ) and cubic zinc blended (ZB) ZnS structure, These two structures have different band gap energy WZ structures has high band gap 3.77 eV and ZB structures 3.72 eV due to the minute atomic arrangement of ZnS structures, Both structures have different properties such as large ionization transition and phase stable in normal atmosphere conditions [1-2], There are different method use to synthesis ZnS NPs such as hydrothermal method, chemical vapor deposition, chemical bath deposition, chemical precipitation, chemical co-precipitation, microwave irradiation sol-gel technique [3-6]. ZnS semiconductor NPs are extensively investigated in various fields in nanoelectronics because of its excellent properties in optical, electrical, luminescence and photochemistry, ZnS NPs have versatile potential applications in optoelectronics, ultraviolet light-emitting diodes, Sensors, field emitters, injection lasers, infrared windows, flat-panel displays, thin film electroluminescent devices, photocatalytic Activities and Antimicrobial activity [7-8] In this present work first time reported antimicrobial activity of undoped and aluminum doped ZnS NPs.

2. Experimental procedure

2.1 Preparation of pure and Al doped ZnS nanoparticles

ZnS NPs were synthesized by using zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), Thiourea (NH_2CSNH_2), all materials good analytical grade (99% Purity) were purchased from Sigma-Aldrich India. Typical synthesis process of undoped ZnS solution was obtained by mixing, 0.1 M of ZnSO_4 , 0.1 M of Thiourea and 1% Ammonia solution. 0.1 M of ZnSO_4 were dissolved in 50 ml of deionized water and the mixture was stirred for 30 min, while continuous stirring 0.1 M of Thiourea solution (which was kept continuous stirred for 30 min with 50 ml of deionized water and Thiourea) is added drop by drop on ZnSO_4 solution and mixture were kept 60 min stirring at room temperature and it was centrifugation at 2000 rpm for 20 Min then the solution was further treated air heated furnace at 100°C

for 5 hours then collected final crushed fine powder. For comparative study 2% of aluminum doped ZnS NPs was prepared above mentioned process but before centrifugation Al solution was added in the final solution drop wise and abbreviated as following namely Undoped ZnS is ZnS, 2% of aluminum doped ZnS is Al:ZnS

2.2 Characterization and Antimicrobial susceptibility preparation method

ZnS and Al:ZnS NPs were successfully characterized by the following techniques, powder X-ray diffraction techniques used to determine the crystal structure of the NPs by (X'per PRO model) using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), at 40 keV in the 2θ range of 10° – 80° with the step size of 0.1° . The Hitachi S-4500 scanning electron microscope (SEM) help to found surface morphology and formation of nanoparticles with 5 kV acceleration voltage. Muller Hinton Agar (MHA) plates. MHA are obtained from Hi-Media Mumbai used to screening In vitro antimicrobial activity all the stock culture (staphylococcus aureus, Basicillus subtilis, Escherichia coli, Psedomonas aeruginosa, Candida albicans, Aspergillus niger) was maintained 4°C on slopes of nutrient agar, the loopful of cells process to treat transfer stock culture into test tube of Muller Hinton broth for bacteria that were incubated without agitation for 24 hrs at 37°C and 25°C respectively. The cultures were diluted with fresh Muller-Hinton broth to achieve optical densities corresponding to 2.0×10^6 colony forming units (CFU/ml) for bacteria and fungus strains were inoculated separately in Sabourad's dextrose broth for 6 hour and suspensions were approximately 10^5 CFU/ml. Before transfer the cultures the MHA plates are treated different process for purification, 15 ml pouring of molten media in to sterile plates, use to prepare MHA plates and allow 5 min for solidify then the minimum amount 0.1% of stock cultures inoculums were swapped in MHA plate surface and allowed 5 min to dry, The 60 mg/disc concentration of disc are placed MHA plate surface each disc have 6 mm width.

3. Result and Discussion

3.1 Crystalline Structure

Figure 1 shows the X-ray diffraction pattern of ZnS and Al:ZnS NPs were analyzed samples and all the diffraction peaks exhibits cubic phase structures with

lattice constant of $a = b = 5.345 \text{ \AA}$ (JCPDS card no 80-0020), any other extra impurities diffraction peaks not detected from that so it is indicated well formation of ZnS NPs are obtained. Fig. 1(a) shows the diffraction peak pattern of pure ZnS in which 2θ at $28.9^\circ, 48.1^\circ$ and 57.7° corresponding plane to the (111), (220), and (311) reflection. The XRD spectrum of ZnS NPs. In addition fig.1(b) shows the four major diffraction peak pattern of Al:ZnS in which 2θ at $28.9^\circ, 48.1^\circ, 57.7^\circ$, and 69.5° corresponding plane to the (111), (220), (311), and (400) reflection, in the presence XRD spectrum Al:ZnS NPs was increase the peak broadening, from this the plant extract are good bonding with ZnS NPs. The average crystallite size (D) is estimated by Debye-Scherers formula based on the diffraction peak corresponding to the plane, In Table 1. The 2θ , FWHM, D spacing, Crystalline size and band gap energy of synthesized ZnS NPs is given.

$$D = 0.9\lambda / \beta \cos \theta \text{ ----- (1)}$$

Where D is crystallite size, 0,9 is the constant shape factor, $\lambda = 1.5405 \text{ \AA}$ represent the wave length of incident beam CuK α 1, β is full width half maximum of the peak, θ is diffraction angle in radian

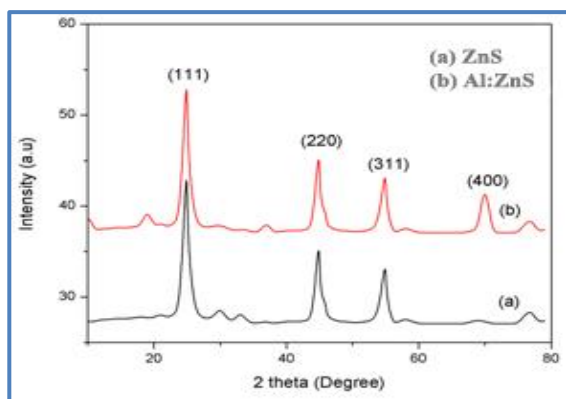


Figure 1. XRD patterns of (a) ZnS (b) Al:ZnS.

Table 1 show the 2θ , (hkl), FWHM, D spacing, crystalline size and Band gap energy of pure and synthesized ZnS NPs

Sample	2θ (hkl)	FWHM (Radian)	D Spacing	Average Crystalline size (nm)	Band gap energy (eV)
ZnS	28.9 (111)	0.5056	3.28	16.94	3.97
Al:ZnS	28.9 (111)	0.5102	3.45	16.71	4.12

3.2 Morphological Studies

The structural and morphological formation of pure and Al ZnS NPs are investigated by SEM image and result are presented the NPs are spherical morphology with narrow particle size distribution and the NPs formation was varied depends on ZnS, and Al:ZnS its shown in figure 2.

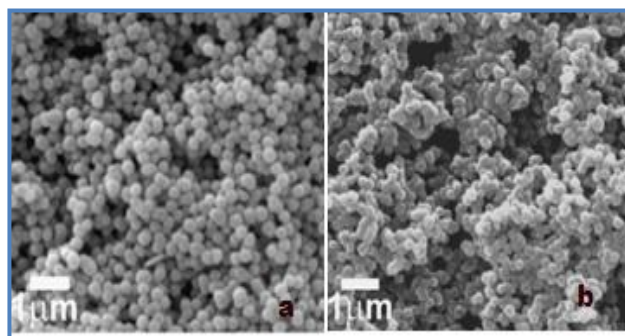


Figure 2. SEM Image of (a) ZnS (b) Al:ZnS.

The Al:ZnS nanoparticles are much smaller than ZnS NPs, this indicates that Aluminum may affect the size of the ZnS NPs and the size of NPs can be controlled by Aluminum. The diameters of the ZnS and Al:ZnS NPs are 203.1 and 218.4 nm respectively.

3.3 Antimicrobial Activity Analysis

The antimicrobial activity of undoped and Al: ZnS NPs was evaluated by measuring the zone of inhibition with various concentrations (40, 50 and 60 $\mu\text{g/mL}$) against all tested microorganisms. The antimicrobial activity of ZnS and Al : ZnS NPs was compared with two gram +ve and gram -ve bacterial cultures such as Staphylococcus aureus (S.aureus), Bacillus subtilis (B.subtilis) and Escherichia coli (E.coli), Pseudomonas aeruginosa (P.aeruginosa), also investigated against two fungus cultures such as Candida albicans (C.albicans), and Aspergillus niger (A.niger) in a different concentration. It was clearly shown in Table 2. The ZnS NPs highest inhibition zone was observed against C.albicans ($29 \pm 0.1 \text{ mm}$) followed by E.coli ($25 \pm 0.1 \text{ mm}$), S.aureus ($23 \pm 1.2 \text{ mm}$), B.subtilis ($22 \pm 0.3 \text{ mm}$), P.aeruginosa ($22 \pm 0.2 \text{ mm}$) and A. niger ($20 \pm 0.3 \text{ mm}$) at a concentration of 60 $\mu\text{g/mL}$. From this result C.albicans inhibition zone was well formed from the beginning concentration. The Al:ZnS NPs exhibit excellent antimicrobial activity against all tested microorganisms compared to other ZnS NPs, at a concentration of 60 $\mu\text{g/mL}$ highest inhibition zones were observed against C.albicans ($29 \pm 0.3 \text{ mm}$) followed by E.coli ($24 \pm 0.1 \text{ mm}$), S.aureus

(23± 1.2 mm), P.aeruginosa (23± 0.1 mm) B.subtilis (22± 0.2 mm)and A. niger (21± 0.2 mm).

Table 2: show the Antimicrobial screening data of pure and Al:ZnS NPs ZoI value* in (mm) concentration at (µg/mL)

Samples / Concentrations (µg/mL)	Gram (+ve) Inhibition zone (mm)						Gram (-ve) Inhibition zone (mm)						Fungi Inhibition zone (mm)					
	S.aureus			B.subtilis			E.coli			P.aeruginosa			C.albicans			A. niger		
	40	50	60	40	50	60	40	50	60	40	50	60	40	50	60	40	50	60
ZnS	16	19	23	14	19	22	18	23	25	14	18	22	24	27	29	16	18	20
Al:ZnS	14	20	23	16	20	22	15	19	24	16	19	23	18	25	29	18	20	21

From this results plant extract ZnS NPs was high inhibition zone against gram +ve, gram -ve bacteria and fungus culture in various concentrations to compare ZnS NPs. From the comparison result maximum antimicrobial activity was observed by gram negative bacterial than the gram positive bacterial due to their cell structure. Here ZnS, and Al: ZnS NPs was discharge irons and react with amide phosphate, carboxyl in the protein of cell membrane and continuously disrupting the cell process and finally broke the cell wall and stop cell growth and formed inhibition zone around cell wall The inhibition zone of C.albicans and A. niger fungus culture also investigated from the result C.albicans has formed maximum inhibition zone to compare A.niger because all ZnS NPs easily affect and penetrate the fungus cell membrane . The Al: ZnS has high antimicrobial activity to compare ZnS because plant extracts functional group bimolecules was controlled or killed the cell membrane of microorganisms. The small particle size and large surface area NPs exhibits high antimicrobial activity in which Al:ZnS NPs have an excellent antimicrobial activity.

spherical shape of the particles and different diameter respectively The antimicrobial activity of Aluminum doped ZnS NPs was investigated against gram positive, gram negative bacterial and fungus cultures, the excellent inhibition zone was formed against gram negative bacterial and fungus, Aluminum doped ZnS NPs has been reported high inhibition zone to compare undoped ZnS NPs due to particle size and biomolecules present, the concentration of ZnS NPs was increase inhibition zone also increase, from the result plant extract ZnS NPs are used various biomedical applications.

4. Conclusion

The ZnS NPs was successfully synthesized by simple chemical co- precipitation method using plant extracts of All the ZnS NPs were confirm the cubic crystalline structure and average particle was 17 nm, to compare pure ZnS NPs the Aluminum doped crystallite size was decrease and morphology of the ZnS NPs reveals

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Competing Interests:

The authors declare that they have no competing interests.

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