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ORIGINAL ARTICLE

Synthesis and characterisation of Gadolinium doped ZnS nanoparticles by chemical precipitation method and its antibacterial activity

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Abstract

Semiconductor nanoparticles have attracted a major role in several new technologies. The synthesis and study of nanostructured materials have become a major interdisciplinary area of research. Gadolinium $(CH_3COO)_2$. $2H_2O$ (Gd) at different concentrations doped ZnS nanoparticles synthesized by chemical precipitation method. The synthesised nanoparticles were investigated by XRD, SEM, EDAX, HRTEM and UV Visible spectral studies. The XRD result shows that Gadolinium doped ZnS nanoparticles exhibit a zinc blende (cubic) structure with uniform size distribution. The optimum concentration of doping Gd was determined as 3.5% from the XRD study. The EDAX spectrum confirmed the composition of the elements (Zn, Gd and S) in the sample. The Gd ion is in-corporated into the cubic Zinc blend phase of ZnS. The surface morphology of Gd doped ZnS nanoparticles was characterised by SEM. The HR TEM confirmed particle size as 20 nm. The optical band-gap energies of Gd doped ZnS nanoparticles increased as the concentration of Gd increased. The result obtained from the agar diffusion method displayed that the Gd doped ZnS nanoparticles have good antibacterial activity than undoped ZnS nanoparticles.

Keywords: *Band Gap Energies; Chemical Precipitation; Optimum Concentrations; Semiconductors; Surface Morphology; ZnS : Gd.*

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INTRODUCTION

Nanoparticle semiconductors have played an important role in the development of a number of new technologies. Over the last two decades, the synthesis and analysis of nanostructured materials have grown into a significant interdisciplinary field of study. Group II-VI semiconductor nanomaterials are very important in the field of optics due to their excellent optical properties. As a result, many electronic and Optoelectrical devices have been developed [1]. Zinc sulphide (ZnS) is used in optical sensors, ultraviolet (UV) light sensors, chemical sensors, biosensors, nano-generators, and other applications [2].

Lanthanide-doped nanoparticles via Intra-4f or 4f-5d transition are received significant attention due to the benefits of high-band emissions, it increases fluorescence life, excellent Photobleaching resistance, and multiple ultraviolet (UV) to infrared (IR) emission bands, through single wavelength stimulation and is enabling a wide range of in-background-less applications. Light-triggered drug delivery, solar energy harvesting, and super-resolution microscopy are all examples of biological sensing [3-9].

The compounds II-VI are well known as Crystal Phosphorus and are commonly used as Cathedral Tube Screen Materials. Along with Si, Ge, and III-V compounds, they are currently well-known semiconductors. The reaction of Group II elements with Group VI elements produces

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compounds with distinct properties. The earth contains natural minerals such as ZnO (Zincite), ZnS (Zinc Blend, Wurtzite), ZnSe (Stillite), and CdS (GreenOCkite, Hawleyite). Natural crystals with stimulating properties, such as ZnS and CdS, are well-known. These compounds are formed when Group II elements react with Group VI elements. ZnO is a natural mineral.

These materials band-gaps typically range from 2 to 4 EV is a direct result of a high optical transition. It was because of this advantage that they were initially used as luminescent materials [9]. There is a wealth of literature available to characterize ZnS materials doped with lanthanide and transition elements, but systematic investigations into the influence of Gd doped ZnS are almost non-existent.

To investigate the structural and characterization of Gadolinium doped Zinc Sulphide (Gd : ZnS) nanoparticles with varying molar concentrations of $Gd(CH_3COOH)_2$. The primary goal of this study is to investigate the effect of Gd doping on the structural and characterization of (Gd : ZnS) nanoparticles synthesised via chemical precipitation method.

MATERIALS AND METHODS

Chemicals used for the synthesis

The Chemicals zinc acetate $Zn(CH_3COOH)_2.2H_2O$, Gadolinium acetate Gd $(CH_3COO)_2.2H_2O$ and Sodium sulphide ($Na_2S.xH_2O$), 99 percent were purchased from Sigma Aldrich. The aqueous solutions were prepared with ultra-pure deionized water.

To synthesize ZnS solution by chemical precipitation method the aqueous medium solutions of (5.48 gm) 0.5M $Zn(CH_3COO)_2.2H_2O$ and (2.75gm) 0.5M Na_2S in 50 ml deionized water were taken. A magnetic stirrer is used to vigorously stir a zinc acetate solution at room temperature for up to 60 minutes. Drop by drop, sodium sulphide solution was added to the above solution the white precipitate appeared then the precipitate were collected and thoroughly washed with distilled water and ethanol before being in vacuum dried at 80° C for 3 hours.

Synthesis of ZnS : Gd nanoparticles

The ZnS nanoparticles doped with different Gd concentrations using deionised water without using capping agent. In a typical experiment [10], Gadolinium acetate in 25 ml aqueous with different concentrations (0.5%, 1.5%, 2.5%, 3.5%, 4.5%, 5.5% and 6%) were added drop by drop in ZnS solution. The concentrations of Gd were adjusted by controlling other quantities of Gadolinium acetates in there above mixture. The mixture was magnetically stirred at room temperature a homogeneous and colourless solution is obtained. The white precipitate is separated from the reaction mixture by filtered and washed several times with de-ionized water and ethanol to remove all sodium particles and impurities and finally vacuum dried at 80 °C for 3 hours.

Antibacterial activity

The Agar diffusion technique was used to test the antibacterial activity. In the agar, a nutrient agar set was prepared, and the plate was allowed to coagulate. Nutrient agar is made by dissolving 1.3 of nutrient broth and agar-agar in 100 mL of water. On an agar plate, *E. coli*, *S. aureus*, and *K. pneumonia* were cleansed. The coagulated plate was fed up to form five 10mm diameter wells. The wells were injected with varying concentrations of pure ZnS and Gd doped ZnS. Ciprofloxacin was used as a standard antimicrobial agent [11].

Characterisation

Bruker D8 Advance was used to record the X-ray diffraction (XRD) patterns of selected samples, and the source is a 2.2 kW Cu anodes, ceramic X-ray tube operating at a voltage of 40 kV and a current of 30 mA. The microphotographs of these samples were taken with a high-resolution FEI Quanta FEG – 200. To determine the atomic percentage of major elements present in the samples was performed alone with the Quanta 200 FEG energy dispersive X-ray analyzer. The Tecnai TF30, a 300 kV field-emission gun energy-filtering high-resolution analytical technique, was used to capture high-resolution transmission microscope images. For UV-Vis spectral studies, a Shimadzu UV-2450 spectrophotometer was used.

RESULTS AND DISCUSSION

X-Ray Diffraction Studies

The powder X-ray diffractometry (XRD) patterns of the samples (pure ZnS and Gd doped ZnS) were displayed in (Fig. 1). Gadolinium dopant mole per cent ratios were 0.5, 1.5, 2.5, 3.5, 4.5, 5.5, and 6d%, respectively. The three diffraction peaks correspond to planes (111), (220), and (311),

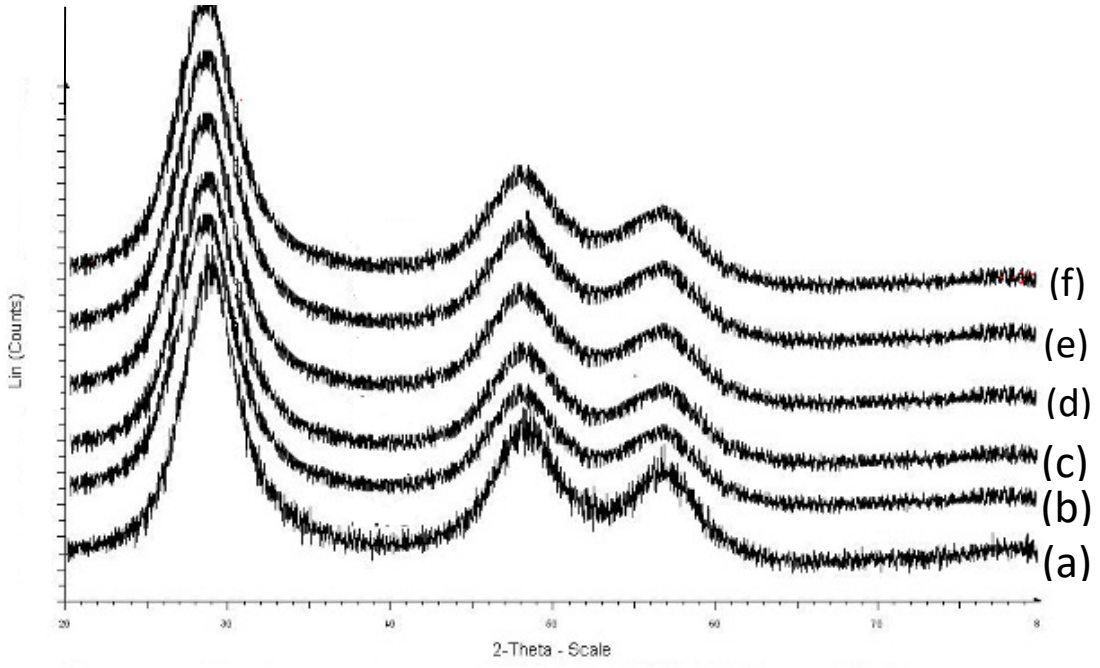

Fig. 1. X-ray diffraction (XRD) pattern of pure ZnS and Gadolinium doped ZnS nanoparticle samples (a) Pure ZnS (b) 0.5% Gd doped ZnS (c) 1.5% Gd doped ZnS (d) 2.5% Gd doped ZnS (e) 3.5% Gd doped ZnS (f) 4.5% Gd doped ZnS.

respectively, of another cubic crystalline ZnS, with reflections observed at 2q=28.70, 48.30, and 56.70, which are in good agreement with JCPDS data (80-0020) [10]. It denotes the corresponding peaks of the Zinc blend. Typical wurtzite peaks (100), (101), (102), and (103) were not found. The size effect causes the XRD to broaden and their widths to increase as the particle size decreases. The determination of phase composition, structure, and particle size is critical for physical property discussions.

These nano crystals have fewer lattice planes than the bulk, which contributes to the nanosecond time required to diffuse to an energetically favourable site. It could also be caused by a lack of peak broadening in the diffraction patterns. This broadening of the peak could also be caused by micro-straining of the crystal structure caused by defects such as dislocation and twinning. These flaws are thought to be associated with chemically synthesised nano crystals, which grow spontaneously during the chemical reaction.

The XRD planes (220) and (311) could not be followed in the case of the mole percent of 3.5 % and 4.5 % Gadolinium doped ZnS samples. After 3.5 % Gadolinium doped ZnS samples, the XRD peaks become wider with increasing Gd dopant concentration, which is primarily due to alloy fluctuation, amorphous state, and increased lattice stress in samples. The size of the crystallite was calculated using the full width at half maximum (FWHM) of the major XRD peak using the Debye Scherrer equation.

$$D=0.9\,\lambda / \beta \cos q$$

D represents the crystallite size, the λ -ray wavelength, the full peak width at half maximum (FWHM), and the Brag's angle. The average size (grain size) of the undoped and Gd doped ZnS samples, calculated from the most intense peak using the Debye Scherer formula, is summarised in (Table1). It shows the average particle size obtained from the Scherrer formula for ZnS and Gd doped ZnS nanoparticles, which ranges from 28 to 42 nm.

Scanning Electron microscope

Images from a scanning electron microscope (SEM) of a Gd doped ZnS samples were shown in (Figs. 2a-2f). Individual crystallites can be imaged using SEM, and a statistical description of the size and shape of the particles in a sample can be developed. However, the actual size of the

Table 1. Crystallite size as calculated by using the Debye – Scherrer's Formula from XRD.

Samples	Peak position (111) plane	FWHM (deg)	Particle size(nm
Pure ZnS	28.705	2.25	38.11
0.5% Gd:ZnS nanoparticles	28.843	2.76	31.07
1.5% Gd:ZnS nanoparticles	28.788	3.10	26.08
2.5% Gd:ZnS nanoparticles	28.960	2.75	31.19
3.5% Gd:ZnS nanoparticles	28.961	3.05	28.13
4.5% Gd:ZnS nanoparticles	28.600	2.25	38.10
5.5% Gd:ZnS nanoparticles	28.799	3.04	42.88
6.5% Gd:ZnS nanoparticles	28.898	3.02	38.12

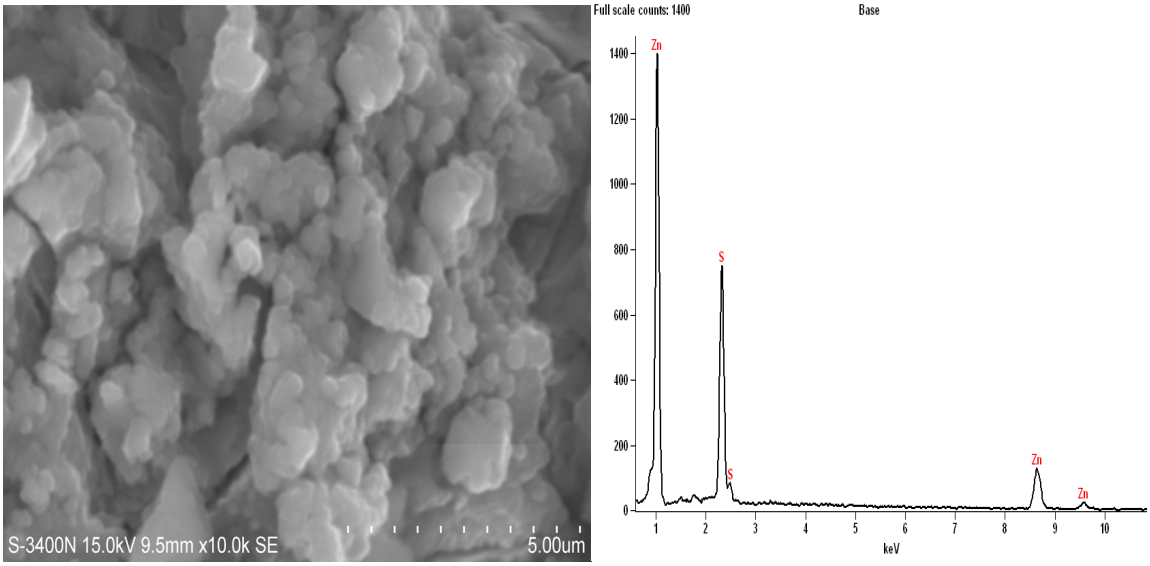

Fig. 2a. The SEM and EDA X spectrum of pure ZnS compound.

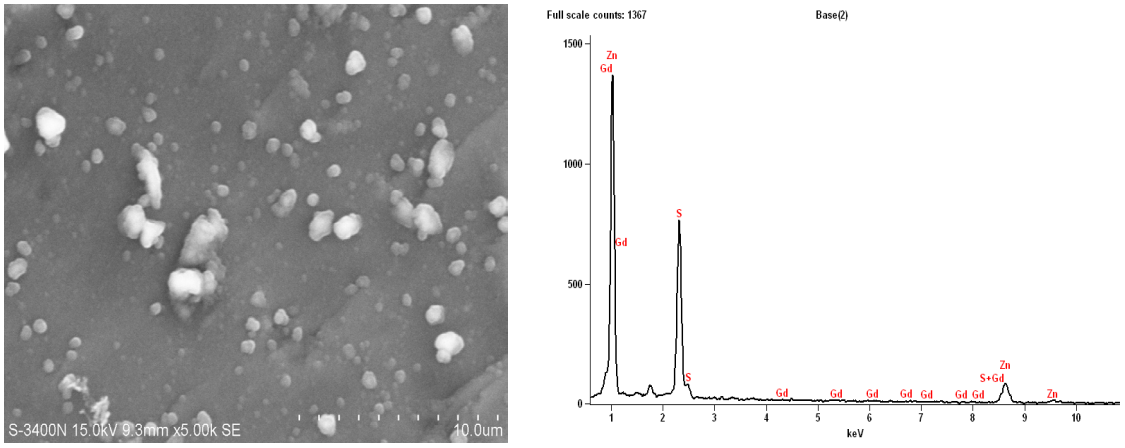

Fig. 2. b. The SEM and EDAX spectrum of 2.5% Gd doped ZnS compound.

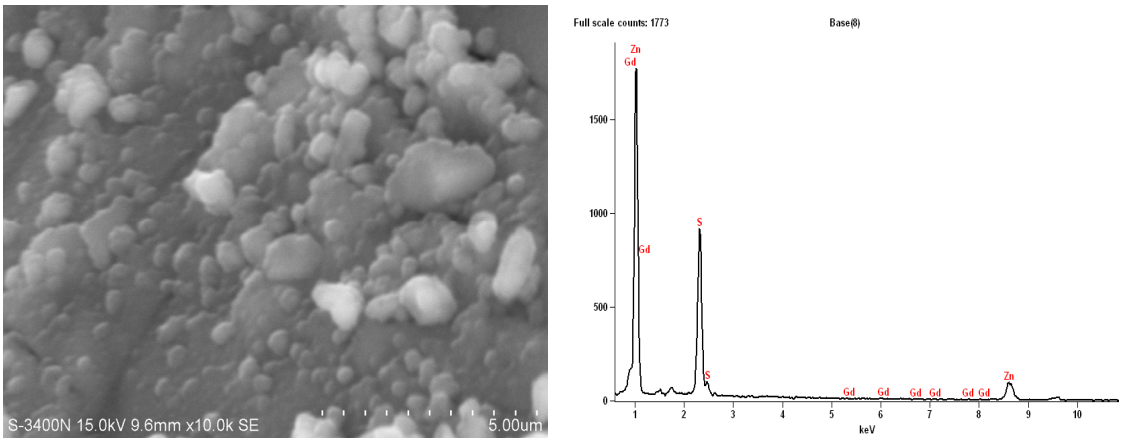

Fig. 2c. The SEM and spectrum of 3.5% Gd doped ZnS compound.

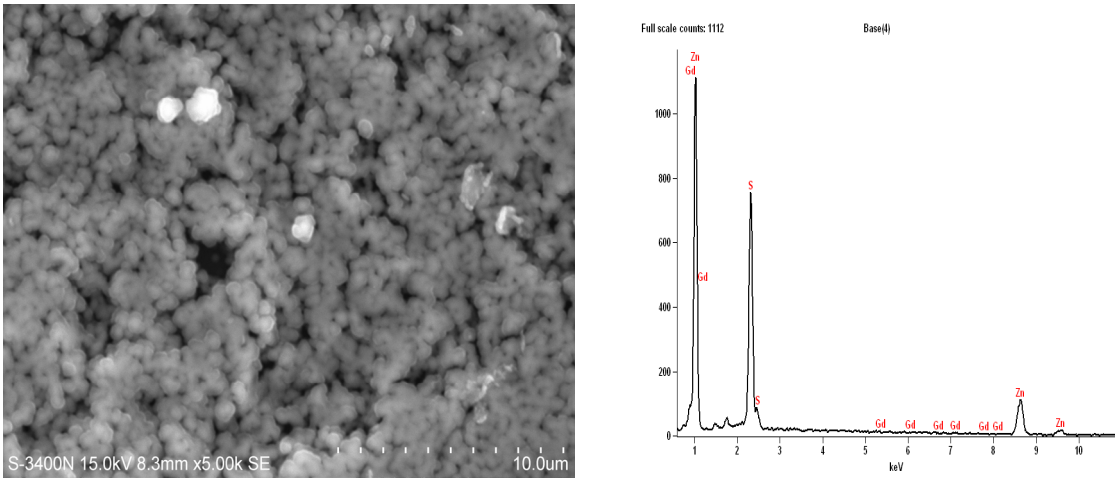

Fig. 2d. The SEM and EDAX spectrum of 4.5% Gd doped ZnS compound.

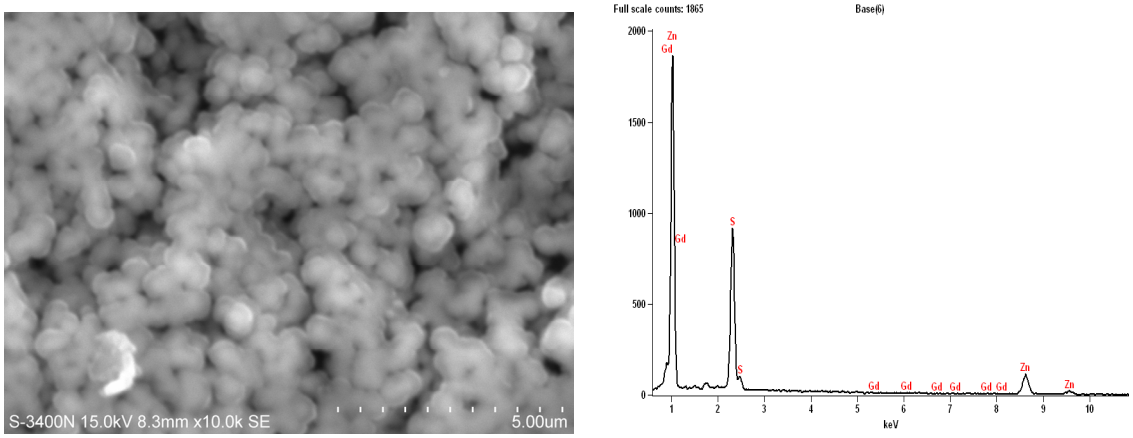

Fig. 2e. The SEM and EDAX spectrum of 5.5% Gd doped ZnS compound.

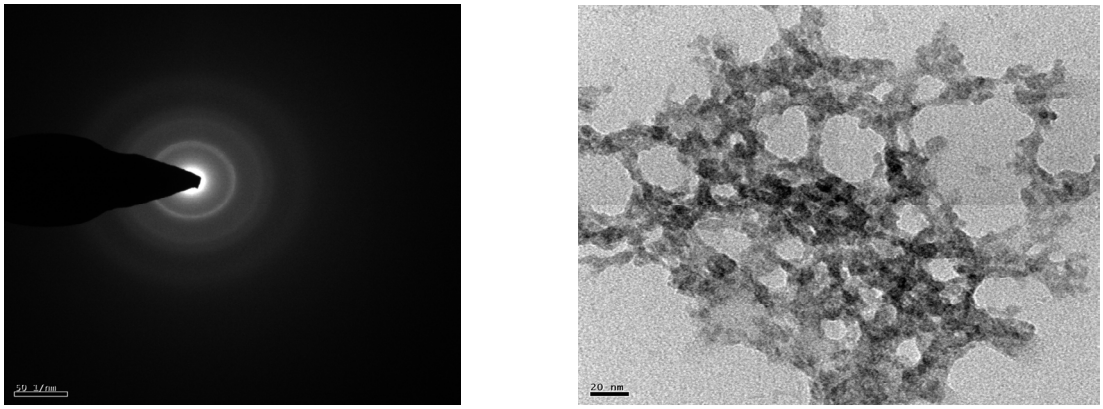

Fig. 3. HRTEM image Gd doped ZnS nanoparticles.

nanoparticles cannot be determined from the SEM image because the resolution of the used SEM image, as an instrument, is limited. Simultaneously, when Gd interacts with host ZnS, it generates a number of aggregates on the surface due to the increasing nucleation rate. This is the identification of the film's cluster-by-cluster formation, which corresponds to the previous report [12].

EDAX

The chemical composition of synthesis of pure ZnS and Gd : ZnS nanoparticles was in characterized by energy dispersive analysis of X- rays (EDAX) were shown in Fig. (2a-e). The EDAX spectrums confirmed the composition of ZnS and Gd: ZnS samples. This reveals that the Gd ion is incorporated in the Zn^{2+} lattice sites. The images show that Gd doped on the surface of the ZnS : Gd (3%) nanoparticles as the optimum concentration [13, 14].

TRANSMISON ELECTRON MICROSCOPE

Fig. 3 depicts typical TEM micrographs of Gd doped ZnS nanoparticles. It demonstrates hexagon-shaped well-formed nano-crystallites of Gd doped ZnS. It corresponds to the Zinc blend structure with Gd inclusion. However, moderate agglomeration with a calculated size of 20 nm has been observed [15].

UV-Visible spectra

The UV-Vis absorption spectra of the synthesised Gd doped ZnS nanoparticles were measured to determine their bandgap, as shown in (Fig. 4). The spectra show the nanoparticles absorption edge in the range of 350 to 370 nm, indicating that the nanoparticles are blue-shifted compared to bulk ZnS, which is at 366 nm. The absorption edge of a nanoparticle suspension is much broader. The bandgap values obtained for both samples are greater than the bulk values of ZnS. (3.43 eV). The blue shift in the absorption edge is caused by quantum confinement to the excitonic in the sample, resulting in a more discrete energy spectrum of the individual nanoparticles.

The blue shift in the absorption spectrum edges indicates that dopant has been incorporated into the ZnS lattice. Table 2 displays the bandgap energy values. Furthermore, the improvement in conductivity and transporter focus for the prepared films can be attributed to the upgrade of free electrons caused by the presence of trivalent Gd^{3+} particles in the divalent host cross-section. Furthermore, the lack of Sulphur, which acts as an acceptor, would have played a role in improving free electrons for the doped nanoparticles [16]. The formula is used to calculate bandgap energy.

$E = hc / \lambda$

Application

Antibacterial Activity

Antibacterial activity was tested against three pathogenic bacteria, including gram-positive (*Staphylococcus aureus)* and gram-negative (*Klebsiella pneumonia*, *Escherichia coli*). DMSO serves as a control (negative). (Tables 3 and 4) show the results of the quantifiable antibacterial assessment by agar diffusion method. Both gram-positive *(Staphylococcus aureus*) and gram-negative (*Klebsiella pneumonia, Escherichia coli*) bacteria were tested for antibacterial activity. The Zone of Inhibition was found to be smaller at low

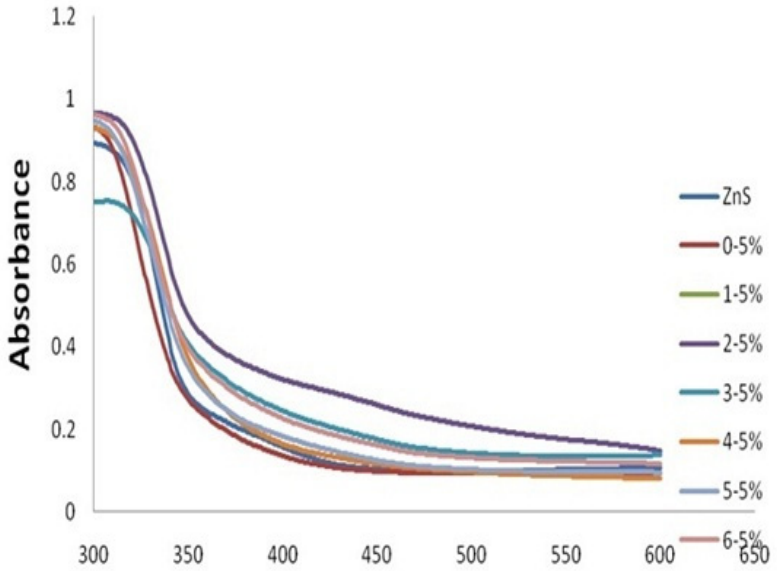

Fig. 4. The UV-visible spectrum of pure ZnS and Gd doped ZnS compounds with various concentrations.

Table 2. Band gap of pure and Gd doped ZnS compounds calculated from optical absorption spectrum.

Samples	Wavelength (nm)	Energy (eV)
Pure ZnS	362	3.43
0.5% Gd:ZnS nanoparticles	360	3.45
1.5% Gd:ZnS nanoparticles	358	3.47
2.5% Gd:ZnS nanoparticles	356	3.48
3.5% Gd:ZnS nanoparticles	341	3.64
4.5% Gd:ZnS nanoparticles	375	5.30
5.5% Gd:ZnS nanoparticles	370	5.37
6.5% Gd:ZnS nanoparticles	351	5.66

Table 3. Zone of Inhibition of nanoparticles against bacteria.

S.No	Micro organisms	Control	ZnS	1.5%	2.5%	Ciproflaxacin
1.	*Klebsiella pneumoniae*	-	9 mm	10 mm	13 mm	23 mm
2.	*Staphylococcus aureus*	-	5 mm	6 mm	7 mm	24 mm
3.	*Escherichia coli*	-	7 mm	6 mm	6 mm	26 mm

Table 4. Zone of Inhibition of Gd doped ZnS nanoparticles.

S.No	Micro organisms	Control	3.5%	4.5%	5.5%	Ciproflaxacin
1.	*Klebsiella pneumoniae*	-	13 mm	11 mm	5 mm	25 mm
2.	*Staphylococcus aureus*	-	9 mm	10 mm	12 mm	24 mm
3.	*Escherichia coli*	-	8 mm	6 mm	9 mm	25 mm

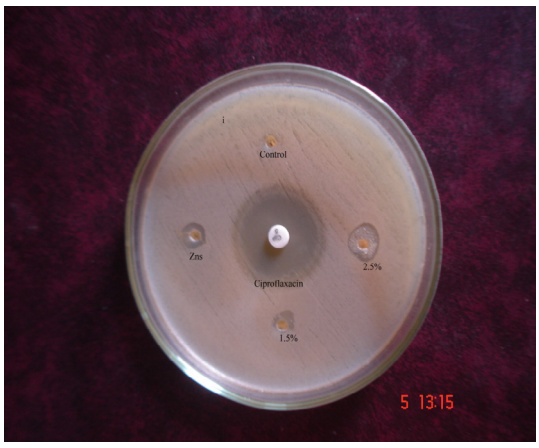

Fig. 5a. Agar diffusion test of undoped a) ZnS b) ZnS : Gd 1.5% c) ZnS : Gd 2.5% against *Klebsiella pneumonia.*

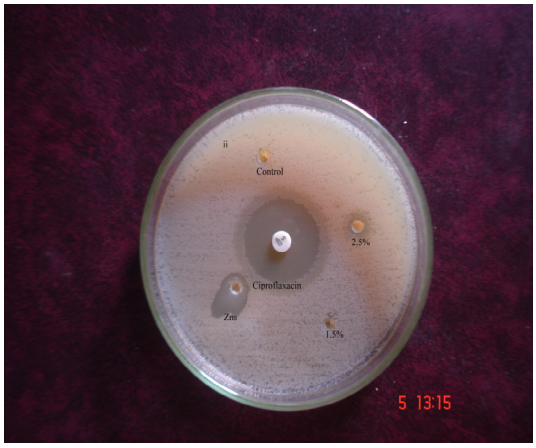

Fig. 5b. Agar diffusion test of a) undoped ZnS b) ZnS : Gd 1.5% c) ZnS : Gd 2.5% against *Staphylococcus aureus.*

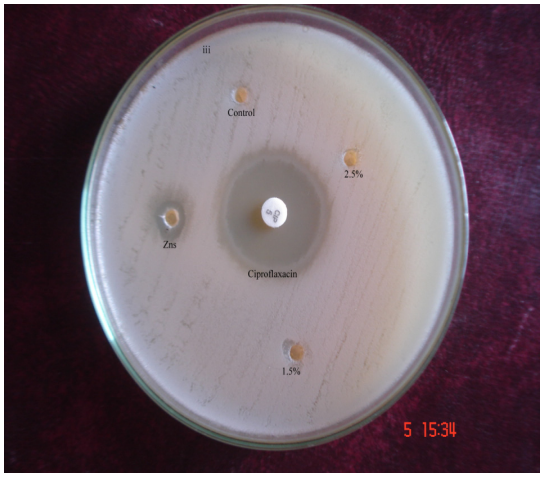

Fig. 5c. Agar diffusion test of a) undoped ZnS b) ZnS:Gd 1.5% c) ZnS : Gd 2.5% against *Escherichia coli.*

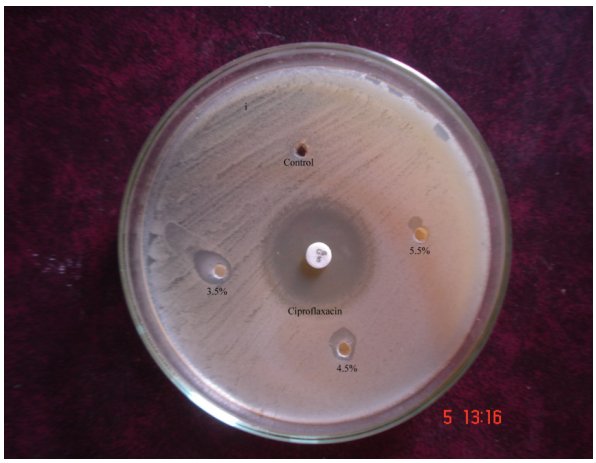

Fig. 5d. Agar diffusion test of doped ZnS : Gd a) 3.5% b) 4.5% c) 5.5% against *Klebsiella pneumonia.*

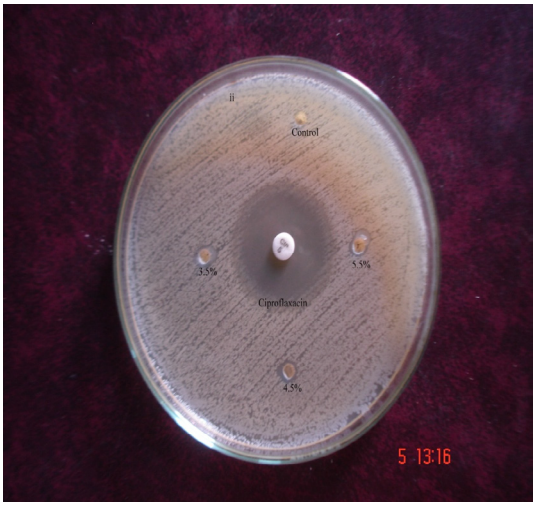

Fig. 5e. Agar diffusion test of doped ZnS : Gd a) 3.5% b) 4.5% c) 5.5% against *Staphylococcus aureus.*

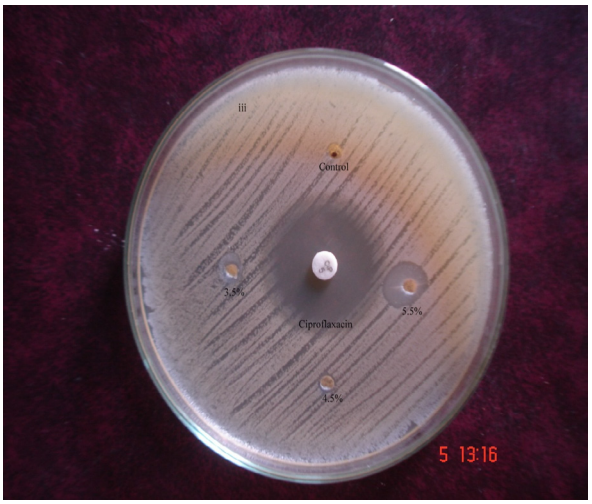

Fig. 5f. Agar diffusion test of doped ZnS : Gd a) 3.5% b) 4.5% c) 5.5% against *Escherichia.*

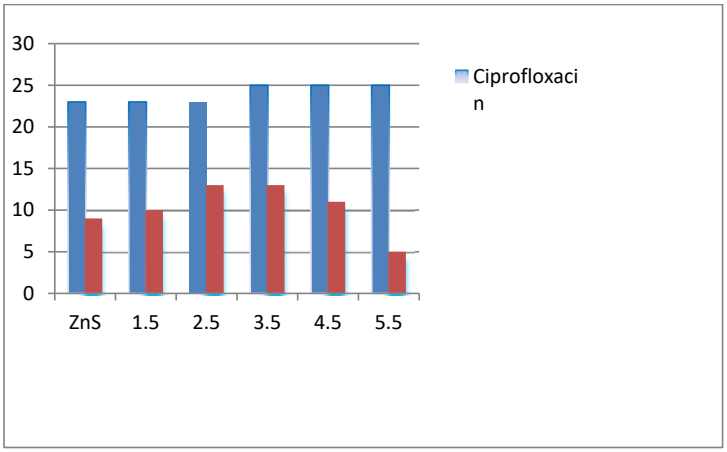

Fig. 6a. Variation of antibacterial activity against *Klebsiella pneumonia.*

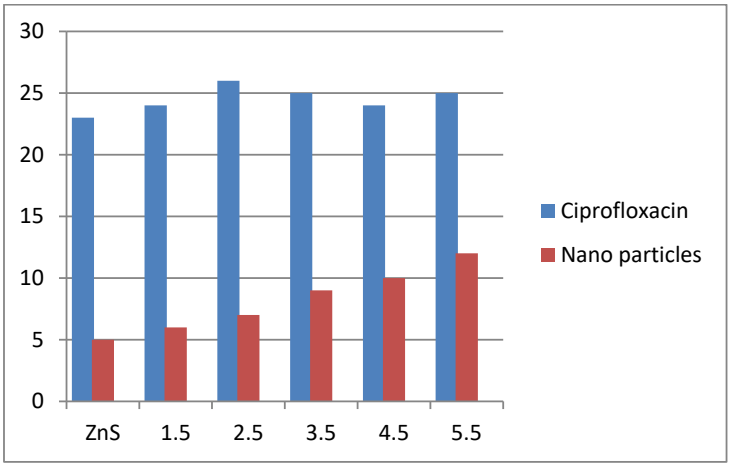

Fig. 6b. Variation of antibacterial activity against *Staphylococcus aureus.*

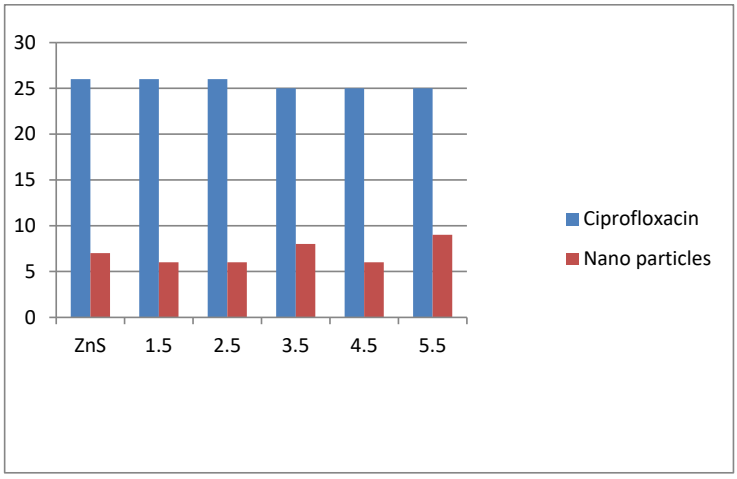

Fig. 6c. Variation of antibacterial activity against *Escherichia coli.*

concentrations compared to the control, and the diameter (mm) of the inhibition zone increased for all three bacteria studied. The antibacterial effect was described as a dose-dependent. Surface area and concentration determine the antibacterial activity, while crystalline structure and particle shape have little effect (Figs. 5a-5f) [17].

Klebsiella pneumonia

The antimicrobial activity of Gd doped ZnS nanoparticles was increased and then decreased against *Klebsiella pneumonia* has higher antibacterial activity at 3.5 %. At 13 mm, the strong inhibition zone is visible. (Fig. 6a)

Staphylococcus aureus

The antibacterial activity of Gd doped ZnS nanoparticles against *Staphylococcus aurous* bacteria increased with increasing concentration. Their inhibition zone is depicted in the table. It performed better at 5.5 % of the zone of inhibition as shown in 12 mm (Fig. 6b).

Escherichia coli (E. coli)

The antibacterial activity of Gd doped ZnS nanoparticles against *E. coli* increases with increasing concentration. At 9 mm, Gd doped ZnS at 5.5 percent showed a good zone of inhibition against *E. coli* (Fig. 6c) [18, 19].

CONCLUSION

The undoped ZnS and Gd doped ZnS nanoparticles were successfully formed by precipitation technique without the use of any additional agents from a homogeneous mixture of zinc, Gadolinium salt mixtures with S2-as accelerating anion shaped. By using these instruments XRD, SEM, EDAX, HRTEM, and UV absorption spectral studies were performed on undoped ZnS and Gd doped ZnS nanoparticles. The XRD results shows that Gadolinium doped ZnS nanoparticles have a zinc blende (cubic) structure with uniform size. The cubic nature of the ZnS nanoparticles has no change and has no influence on the crystalline size. The EDAX range confirmed the components (Zn, Gd, and S) present in the ZnS : Gd. The Gd particle is combined with the cubic Zinc blende structure of ZnS. The calculated value from HR TEM was in good agreement with XRD-determined size. The optical band-gap energies of Gd doped ZnS nanoparticles showed well optical studies. In this paper, we investigated the antibacterial activity of pure and Gd-doped ZnS nanoparticles at various concentrations (1.5%, 2.5%, 3.5%, 4.5%, 5.5%). The antibacterial activity of Gd doped ZnS nanoparticles was found to be greater than that of pure or undoped ZnS nanoparticles.

FUTURE DIRECTIONS

The major trend in the future development of nanomaterials is to make them multifunctional and controllable by external signals or the local environment, effectively transforming them into nanodevices. In the future, Gd doped ZnS nanoparticles will be synthesised for various applications.

CONFLICTS OF INTEREST

The authors do not have any conflicts of interest.

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