



Antimicrobial activity of zinc sulphide nanoparticles and to study their characterization

M.Sathishkumar¹, M. Saroja², M. Venkatachalam² and M.Senthilkumar³

¹ Department of Electronics and Communication System, Nehru Arts and Science College, Coimbatore-641 105.

² Department of Electronics, Erode Arts and Science College (Autonomous), Erode-638 009.

³ Department of Electronics and Communication System, KG college of Arts and Science, Coimbatore-641 035.

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ABSTRACT

In the present study, the objective was the ZnS nanoparticles are prepared by chemical co-precipitation method and analysis Antimicrobial activity against oral pathogens is demonstrated, and the characteristics of synthesized nanoparticles are investigated by using x-ray diffraction (XRD), scanning electron microscopy(SEM), ultraviolet-visible (UV-Vis), Fourier transform infrared spectroscopy(FTIR).

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Introduction

Semiconductor nanocrystals, whose electronic and optical properties are tunable, have aroused considerable interest as technologically important materials. As a typical nontoxic wide band gap semiconductor material of the II–VI group, ZnS has been used as optical devices, such as ultraviolet light emitting diodes,[1–3] flat panel displays,[4,5] solar cells,[6] and optical sensors.[7] ZnS crystallizes in the zinc-blende (ZB) or wurtzite (WZ) structures at room conditions with a band gap of 3.68 eV or 3.77 eV,[8] respectively. ZnS with a band gap of 3.68 eV corresponds to ultraviolet radiation for optical interband transition. Wide-band gap semiconductors such as ZnS are ideal materials for the study of discrete states in the gap. Visible luminescence can originate only from transitions involving these localized states. The reported luminescence spectrum and absorption in ZnS both show an emission peak at around 420 nm.[9–11] Bulk and nano-scale ZnS crystals have been successfully synthesized by various methods and their properties have been investigated.[12–15] These general preparation techniques include the precipitation method, sol–gel, reverse micelle method, microwave method, hydrothermal process, wet-chemical method, spray pyrolysis, etc. At the nanoparticle sizes of a semiconductor, the energy gap (band gap) increases, and the optical spectrum is shifted toward the short-wavelength region[16] and some of their physical properties differ noticeably from those of the corresponding bulk material. These properties of nanocrystals make them an interesting category of material for optoelectronic applications.

ZnS is extensively studied as it has numerous applications to its credit. There are various chemical based methods available for the synthesis of ZnS nanomaterials[17–18].

But there is a growing concern towards use of these chemicals as they are reported to be very toxic for the environment.

Apart from the toxicity, these chemical based methods are also not cost effective, a major disadvantage for synthesis of nanoparticles at the industrial scale. Due to these problems, various eco-friendly approaches for the synthesis of ZnS nanoparticles are being adopted[19–20]. ZnS nanostructures have gained a lot of attention that can be attributed to the properties arising from their size in the nanometer range[21–22]. The antibacterial, antifungal, and antiviral actions of sulfide nanoparticles have been broadly investigated in comparison with other metals[23–25].

In this work, ZnS nanoparticles are prepared using EDTA as precursor to control the particle sizes by a simple chemical route. The crystallinity and morphology are studied using x-ray powder diffraction (XRD) and a KYKY-EM3200 scanning electron microscope (SEM). The vibrational structure and the changes of the optical properties with particle size are discussed from Fourier transform infrared (FTIR) (Thermo Scientifica-NICOLET iS10) and UV-visible spectra. The antimicrobial activity is assessed against oral pathogens and these results confirmed that the zinc sulphide nanoparticles are exhibiting good antimicrobial activity.

Materials and Methods

Antibacterial activity Preparation of inoculums

Stock cultures were maintained at 4°C on slopes of nutrient agar. Active cultures of experiment were prepared by transferring a loopful of cells from the stock cultures to test tube of Muller-Hinton broth (MHB) 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.

Antimicrobial susceptibility test

The disc diffusion method (Bauer *et al.*, 1966) was used to screen the antimicrobial activity. *In vitro* antimicrobial activity was screened by using Muller Hinton Agar (MHA) obtained from Hi-media (Mumbai).

The MHA plates were prepared by pouring 15 ml of molten media into sterile petri plates. The plates were allowed to solidify for 5 minutes and 0.1% inoculums suspension was swabbed uniformly and the inoculums were allowed to dry for 5 minutes. The concentration of extracts is 40 mg/disc was loaded on 6 mm sterile disc. The loaded disc was placed on the surface of medium and the extract was allowed to diffuse for 5 minutes and the plates were kept for incubation at 37°C for 24 hrs. At the end of incubation, inhibition zones formed around the disc were measured with transparent ruler in millimeter

Method of preparation of ZnS nanoparticles

Synthesis of ZnS nanoparticles was carried out by aqueous co-precipitation method using zinc chloride (ZnCl₂) and sodium sulphide (Na₂S) as source materials. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at 40°C temperature and ambient conditions. In a typical preparation solution of 1M Na₂S was added drop by drop to 1M ZnCl₂ solution which was kept on stirring using a magnetic stirrer at 70°C for 2 hours; this resulted in formation of ZnS nanocolloid. The nanoparticles were collected by centrifugation at 2000 rpm for 15 minutes and further purification was made in ultrasonic bath. The resultant product was finally dried at 200°C for 2 hours.

Preparation of zinc sulphide nanoparticle solution

To prepare ZnS nanoparticle solution 0.01g of the synthesized ZnS nanoparticles were dissolved in 10 ml of sterile distilled water with the help of a magnetic stirrer. The final concentration of ZnS nanoparticles in the solution was 1µg/ml. This solution was applied in the wells bored in the agar plates for the study of antimicrobial activity.

Ultra- Violet Spectroscopy

The UV spectrum provides a useful means of detecting conjugated unsaturated chromophores within a molecule such as polyenes, α, β-unsaturated ketones and aromatic compounds. This can be particularly helpful in the identification of chromophores and flavones. The UV spectrum may be caused by the summation of chromophores from different parts of a polyfunctional molecule, and this should be considered in the light of deduction drawn from other spectroscopic methods and chemical degradation.

FTIR Spectroscopy

Infrared light from suitable source passes through a scanning Michelson interferometer and Fourier Transformation gives a plot of intensity versus frequency. When a powdered plant sample is placed in the beam, it absorbs particular frequencies, so that their intensities are reduced in the interferogram and the ensuing Fourier transform is the infrared absorption spectrum of the sample.

Scanning Electron Microscope

Scanning electron microscopic (SEM) analysis was performed using the Hitachi S-4500 SEM machine. Thin films of the sample were prepared on a carbon coated copper grid by simply dropping a very small amount of the sample on the grid, with excess solution being removed using blotting paper. The film on the SEM grid was then allowed to dry by putting the grids under a mercury lamp for 5 min.

X-Ray Diffraction

Zns nanoparticles were examined by X-ray diffractometer. The powdered metal was stucked in the cubes of XRD and then the result was taken in the XRD equipment.

Result and Discussion

X-ray Diffraction Analysis

The analysis of x-ray pattern (Fig.1) shows that ZnS sample crystallize in cubic symmetry (F-43M space group) with lattice parameter $a = 5.368(4) \text{ \AA}$ and unit cell volume $V = 154.7157(8) \text{ \AA}^3$. The three different peaks of the sample correspond to the lattice planes of (111), (220), and (311), which match very well with the cubic zinc blende structure (JCPDS No. 05-0566).

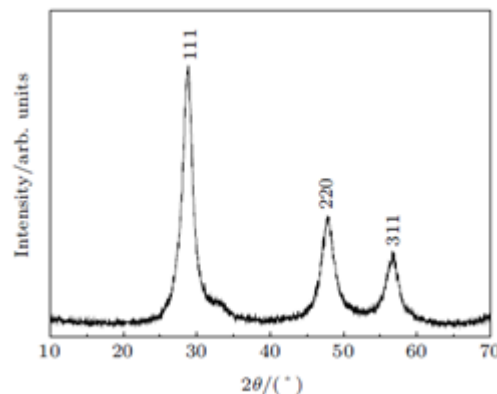


Fig 1: XRD Pattern of ZNS Nanoparticles

The significant broadening of the XRD pattern peaks reveals the small particle (crystallite) size and indicates the nanometric particle size. The average particle size is approximately estimated by Hall's method

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{2\epsilon \sin \theta}{\lambda}, \quad (1)$$

where β is the full width at half maximum (FWHM) of that peak in radian, θ is the diffraction angle of the Bragg peak $\lambda = 1.54056 \text{ \AA}$ is the wavelength of the used x-ray, D is the particle size, and ϵ is the effective residual strain. In this way, D and ϵ can be estimated from the intercept on the $\beta \cos \theta / \lambda$ axis and the slope of the curve by plotting the $\beta \cos \theta / \lambda$ versus $\sin \theta / \lambda$, respectively. An average particle size of about 5.5 nm is obtained. A dislocation is a crystallographic defect that strongly affects many properties of zinc sulphide.

SEM Analysis

The SEM image of ZnS nanoparticles is shown in Fig. 2. The SEM microstructural analysis shows that the synthesized ZnS contains mainly the grains of ZnS particles (crystallite) with cubic regular shape. One can see that nearly spherical nanoparticles have an almost homogenous size distribution with a mean size of 50 nm. The maximum particle size does not exceed 70 nm.

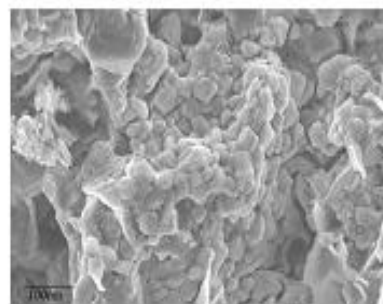


Fig 2. SEM Analysis of ZNS Nanoparticles

FTIR Analysis

ZnS nanoparticles FTIR spectrum was shown in Fig.3. This spectrum shows the IR absorption due to the various vibration modes. The characteristic major peaks of ZnS can be observed at about 1124, 998, and 624 cm⁻¹, which are in good

agreement with the reported results. The observed peaks at 1550 cm⁻¹–1750 cm⁻¹ are assigned to the C=O stretching modes, and also the broad absorption peaks in a range of 3100 cm⁻¹–3600 cm⁻¹ correspond to O–H stretching modes arising from the absorption of water on the surface of nanoparticles

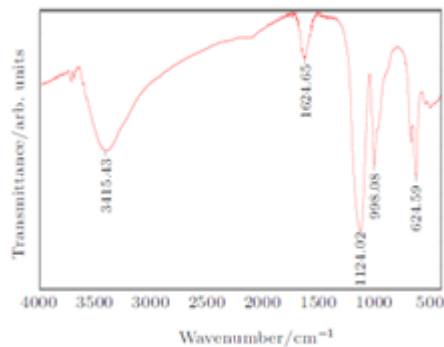


Fig 3. FTIR Analysis of ZNS nanoparticles

UV-Visible Analysis

The optical properties of ZnS nanoparticles are determined from absorbance measurements in the range of 200-300 nm. UV-Visible spectra are very much helpful in identifying the nanomaterials. The optical absorption spectrum of ZnS Nanoparticles is shown in figure-4. The UV-Vis transmission spectra analysis of ZNS NPs powder are highly transparent in the visible region and a sharp fall in transmission is observed below 286nm region. It is found that the absorption edge shifts toward longer wavelength with doping of ZNS.

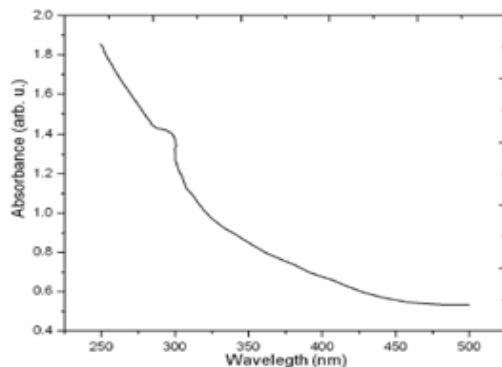


Fig 4. UV-Visible Analysis of ZNS nanoparticles.

Antimicrobial activity of ZNS Nanoparticles

The antimicrobial activity of ZNS nanoparticles was studied at concentrations of 10, 20, 30 and 40µl against the oral pathogens organisms, *E.coli*, *B.subtilis*, *S.aureus*, *M.smegmatis*, *c.albicans* and *f.oxysporum*. There was no activity against *E.coli*, *B.subtilis*, and *M.smegmatis* at concentration of 10µl. Only *S.aureus*, *c.albicans*, *f.oxysporum* were inhibited at concentration 10µl. At concentration 20 µl, only *M.smegmatis*, *c.albicans* have inhibited, 30 µl and 40 µl, highest inhibition was found against *E.coli*, *M.smegmatis*, *B.subtilis* followed by, *f.oxysporum*, *c.albicans*. and very smallest inhibition against *S.aureus* in all concentrations.

Table 1. Analysis of Antimicrobial Activity of ZNS Nanoparticles.

S.No.	Name of Organism	Concentration of Samples			
		10 µl	20 µl	30 µl	40 µl
1.	<i>E.coli</i>	00	04±0.5	11±0.5	18±0.5
2.	<i>B.subtilis</i>	00	05±0.5	09±1	16±0
3.	<i>S.aureus</i>	02±0.5	02±0.5	05±1	12±1
4.	<i>M.smegmatis</i>	00	12±0.5	15±0.5	18±0.5
5.	<i>c.albicans</i>	03±0.5	08±0.5	10±0.5	14±1
6.	<i>f.oxysporum</i>	01±0.5	01±0.5	10±0.5	15±0

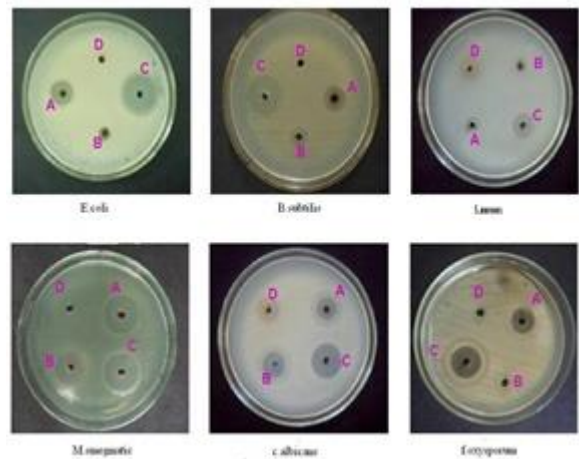


Fig 5 . Antimicrobial activity of ZNS Nanoparticles

Note: (A) 30 µl, (B) 20 µl, (C) 40 µl, (D) 10 µl concentrations of ZNS.

Conclusion

The present study clearly indicates that ZnS nanoparticles could be synthesized by a simple aqueous chemical coprecipitation method resulting in primary particle sizes of 55 nm and cubic zinc blende structure. This particle size was calculated by Hall's method. SEM image was used to study the morphology of the synthesized nanoparticles. FTIR spectra showed functional group of the ZnS nanoparticles. The UV-Visible spectra analysis of ZNS NPs powder are highly transparent in the visible region and a sharp fall in transmission is observed below 286nm region. From These study have maximum Anti bacterial activity against pathogens organisms *E.coli*, *B.subtilis*. However in case of *M.smegmatis* *f.oxysporum* have maximum Antifungal activity, So in this study was reported ZnS nanoparticles have Antimicrobial activity against the entire test organism and these nanoparticles using for various applications.

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