



Synthesis and Antimicrobial Activity of Zinc Sulphide Nanoparticles

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Abstract

Semiconductor nanocrystals have got considerable interest due to their distinctive structural, electronic and optical properties resulting from their large surface/volume (S/V) ratio and quantum confinement effect. Cubic ZnS, a semiconductor with a broad band gap, has fascinated much consideration because of its electroluminescent applications due to its stability, low cost and low toxicity. In the present study, the synthesis and antimicrobial activity of zinc sulphide nanoparticles against oral pathogens is demonstrated. The nanoparticles of ZnS are prepared by chemical co-precipitation method at room temperature. The process for the synthesis of zinc sulphide (ZnS) nanoparticles is fast, novel, and ecofriendly. The sample was characterized by XRD and UV-visible spectroscopy. The average particle size was determined from the X-ray line broadening and by using Debye-Scherrer equation. The antimicrobial activity was studied against oral pathogens such as *Streptococcus* sp. *Staphylococcus* sp. and *Candida albicans* and these results confirmed that the sulphide nanoparticles exhibit good bactericidal activity.

Keywords: Nanoparticles, zinc sulphide, XRD, UV-visible, antimicrobial activity.

Introduction

Nanotechnology is the tool for design, production, characterization and applications of nanostructure materials. It generally deals with the structures sized between 1-100 nanometers in at least one dimension. It has been emerged as a growing and rapidly changing field and presents potential opportunities to create better materials and products.

Nanostructured materials are a technically considerable object that possesses optical and electrical properties that depend impressively on the dimension and shape of the nanoparticles. This is due to confinement of the charge carriers in the constricted space of the nanocrystal^{1,2}. The properties of nanoparticles powerfully depend on their size. Their high specific surface area results in high chemical reactivity. The decrease of their size also leads to an increase of the band-gap energy that is known as quantum size effect.

Recently, II-VI semiconductor nanoparticles are playing consideration in enormous fields due to their exceptional and distinctive optical and electrical properties which present a major benefit over their mass counterparts^{3,4}. Amongst those ZnS is an important member in II-VI group semiconductors having a better value of band gap energy⁵. Polymers are also excellent host materials as capping agents and stabilizers as they check agglomeration and precipitation of the particles. Sulfide is a semiconductor nanomaterial processing a lot of remarkable physical properties and potentially used in mesoscopic electronic⁶ biolabeling⁷ and photocatalysis⁸. Metals have been used for centuries as bactericidal agents; silver, copper, gold,

titanium, and zinc have fascinated particular consideration, each having different properties and spectra of activity⁹.

The antibacterial, antifungal, and antiviral actions of sulfide nanoparticles have been broadly investigated in comparison with other metals¹⁰⁻¹². In the present work, we report the synthesis of zinc sulphide nanoparticles by the chemical co-precipitation method. UV-Vis spectrophotometer and X-ray diffraction techniques are used to characterize the synthesized sulphide nanoparticles.

Oral pathogens can cause severe break which may show the way to serious issues in human disease like blood circulation and coronary disease. Various oral foods, including toothpaste, now integrate powdered zinc salts to control the development of dental plaque.

The antimicrobial activity is assessed against oral pathogens such as *Streptococcus* sp. *Staphylococcus* sp. and *Candida albicans* and these results confirmed that the sulphide nanoparticles are exhibiting good bactericidal activity.

Material and Methods

Synthesis of ZnS Nanoparticles: The nanoparticles of zinc sulphide are prepared by chemical co-precipitation method. The principle involved in this technique is the precipitation of metal ions with sulfide ions in the solution in presence of capping agent. ZnSO₄ and Na₂S are used as Zinc source and Sulphur source respectively. ZnSO₄ and Na₂S are obtained from Merck Specialties Private Ltd. These are of high purity and used without any future purification.

First, solutions of 0.1 M Zinc sulphate, 0.1M sodium sulfide and 1% by weight of EDTA as capping agents were prepared in double distilled water. 0.1 M aqueous solution of zinc sulphate and 0.1 M aqueous solution of sodium sulfide were mixed in the presence of EDTA. 15 ml of zinc sulphate and 15 ml of 1% of EDTA were mixed together and stirred for 30 minutes on a magnetic stirrer to get a homogeneous solution.

This was followed by drop wise addition of appropriate amount of 0.1 M Sodium sulfide under vigorous stirring for 1 hour. A white colour precipitate was obtained which was separated by centrifugation and washed several times with double distilled water. The precipitate was dried in oven at 80°C for 4 hours to get powder sample.

Antimicrobial activity of Nanoparticles: The disc diffusion method was used to study the antibacterial activity of the synthesized ZnS nanoparticles.

The pathogenic bacteria, *Streptococcus* sp., *Staphylococcus aureus* and *Candida albicans*, were used as model test strains.

The method involves the inoculation of small filter paper disks with the synthesized nanoparticle specimen and placing the disks on an agar plate that has been inoculated with an indicator organism. The plate is then incubated, typically overnight at 35°C–37°C. The specimen created a zone of bacterial inhibition as it diffuses through the agar. This indicates the presence of antimicrobial activity in the prepared ZnS specimen.

The process was followed by the evaluation of antimicrobial activity by measuring the zone of growth inhibition surrounding the discs. Larger the diameter of zone of inhibition, greater is the antimicrobial activity.

Results and Discussion

UV-Visible measurements: UV-Visible spectra are very much helpful in identifying the nanomaterials. The optical absorption spectrum of ZnS Nanoparticles is shown in figure-1. The study of optical absorption is important to recognize the actions of semiconductor nanoparticles.

An elementary property of semiconductors is the band gap i.e. the energy separation between the filled valence band and the empty conduction band.

Optical excitation of electrons across the band gap is strongly allowed, producing a sudden increase in absorption at the wavelength corresponding to the band gap energy (E_g). This feature in the optical spectrum is known as the optical absorption edge¹³.

The band gap energy is calculated by extrapolating the linear portions of the $(\alpha h\nu)^2$ vs $h\nu$ graph on the $h\nu$ axis to a =0. The obtained band gap energy value is given in table.

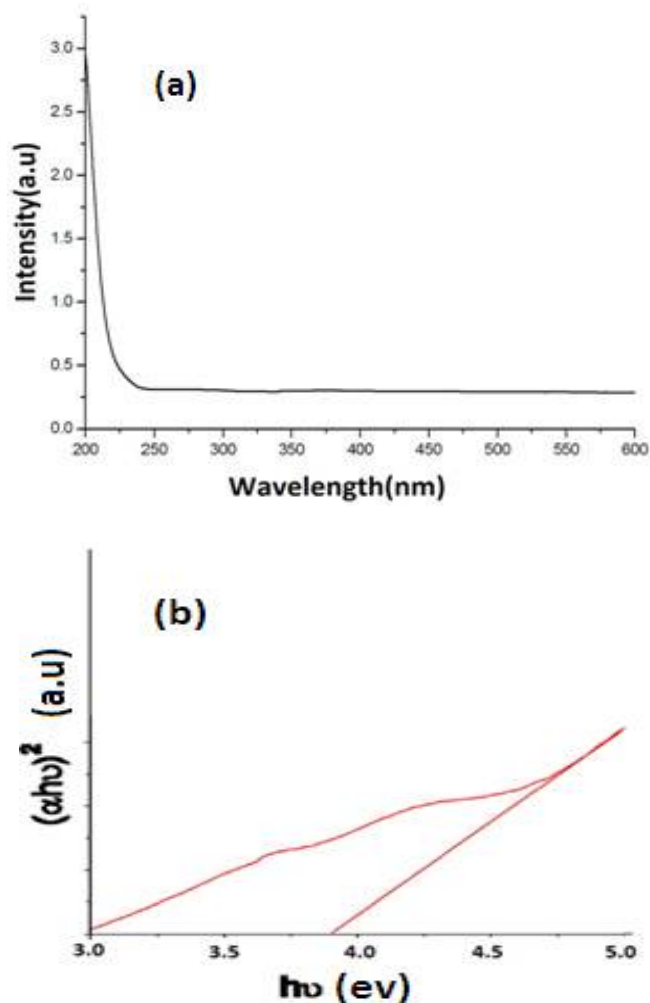


Figure-1
(a) UV-Vis spectra and (b) Tauc plot of ZnS nanoparticles

X-ray diffraction measurements: The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The x-rays were produced using a sealed tube and the wavelength of x-ray was 0.154nm (Cu K-alpha).

Figure-2 shows the typical powder XRD patterns of prepared ZnS nanoparticles using EDTA as capping agent by co precipitation technique. In the pattern three reflections from (111), (220) and (311) planes are observed indicating the cubic zinc blende structure (cubic, β -ZnS)¹⁴⁻¹⁵. The typical broadening of the three diffraction peaks is also observed, implying that the size of ZnS nanoparticles is very small. The broad diffraction peaks are attributed to the characteristic small particle effect¹⁶. The peak broadening at lower angle is more consequential for the calculation of particle size. Therefore size of nanoparticles has been calculated using Debye-Scherrer formula using (111) reflection from the XRD pattern. Debye-Scherrer formula for particle size determination is given by¹⁷:

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

Where, D is the particle size, λ is the wavelength of X-rays (1.54056\AA), β is the full width at half maximum after correcting the instrument peak broadening (β expressed in radians) and Θ is the Bragg's angle.

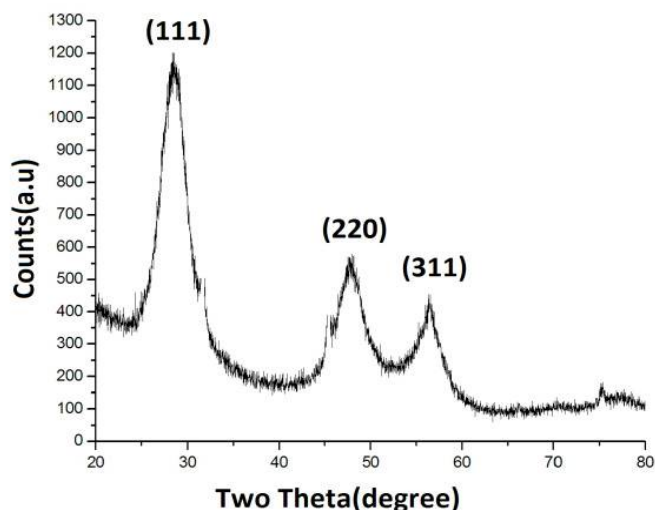


Figure-2
XRD patterns of prepared ZnS nanoparticles

Optical band gap and particle Size of the ZnS nanoparticles

Optical band gap(eV)	Particle Size from XRD (nm)
3.8	4.67

Antimicrobial Activity of Sulphide Nanoparticles: The antimicrobial activity of ZnS nanoparticles was investigated against pathogenic bacteria, such as *Staphylococcus aureus*, *Streptococcus* sp., and *Candida albicans*. The diameter of zone of inhibition (ZOI) was measured around the well with nanoparticles against the test strains. The various concentrations of sulphide nanoparticle were $100\ \mu\text{L}$, $150\ \mu\text{L}$, and $200\ \mu\text{L}$.

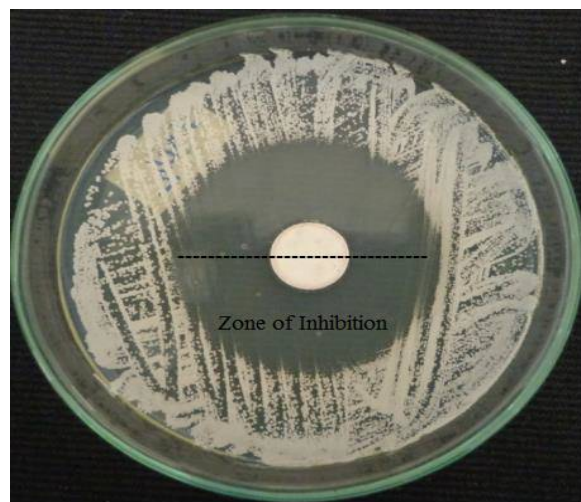


Table-1

Antimicrobial activity of ZnS nanoparticles against oral pathogens

Concentration of ZnS nanoparticles	Zone of inhibition (mm in diameter)		
	<i>Streptococcus</i> sp.	<i>S. aureus</i>	<i>C. albicans</i>
$100\ \mu\text{L}$	16.33 ± 0.43	16.23 ± 0.32	14.33 ± 0.43
$150\ \mu\text{L}$	17.36 ± 0.44	18.23 ± 0.47	16.24 ± 0.22
$200\ \mu\text{L}$	23.53 ± 0.18	24.566 ± 0.60	19.36 ± 0.55

The formation of zone around the ZnS nanoparticles integrated well clearly motivated the antibacterial property of ZnS nanoparticles.

Conclusion

The simple synthesis of the ZnS nanoparticles by co precipitation method using EDTA as capping agent is reported. UV-Vis spectra supported the formation of ZnS nanoparticles. In XRD spectra the particle size was calculated from the Debye-Scherrer formula.

This green chemistry approaches is used to alter biocompatibility of nanoparticles and more beneficial for budding technology researcher to manufacture the nanoparticles using surface coatings and dental devices. Moreover, this process is eco-friendly and nontoxic, and handlings of oral pathogens are also biocompatible.

The present study demonstrates that ZnS nanoparticles have bactericidal activity against the entire test organism. Since this is easily available in the nation and also is used in hospital for biomedical agent, the energetic nanocompound from this can be prepared and used effectively for preventing the growth of the oral pathogens.

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