

Structural and Optical Performance of ZnS Nanoparticles Synthesized via Chemical Route.

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Abstract:--- In this analysis, ZnS nanoparticles have been synthesized employing an easy chemical co-precipitation route using metal precursors and DMF (CH₃)₂NC(O)H as a stabilizing agent. The obtained ZnS nanoparticles have been characterized through XRD, TEM, UV-Vis, FTIR and PL measurements. The foremost intense broad peaks in the diffraction outline reveal the crystalline character of the prepared material with the particle length is approximately 4.7 nm. The optical band gap has been evaluated from the UV-Vis. absorption spectrum which is found to be about 3.95 eV. The blue swing in absorption spectra validates the formation of nanoparticles. Further, the TEM micrograph revealing the ZnS particles are in nano dimension. FTIR study has been carried out for the bond evaluation. The PL measurement shows the emission of colour in the blue area.

Keywords--- ZnS nanoparticles, XRD, TEM, optical band gap, FTIR, PL

I. INTRODUCTION

Semiconductor nanoparticles have attracted a lot of analytical curiosity due to their spectacular properties originating from quantum confinement impact [1-3]. Among the range of semiconductor nanoparticles, zinc sulphide (ZnS) is a crucial II-VI category inorganic semiconductor due to its huge scope of applications which includes in solar cells, cathode-ray tubes (CRT), field emission display (FED), phosphors for a long time, flat panel display. The ZnS has additionally been used for electroluminescent devices and photodiodes in addition to catalysts. Further, the ZnS nanomaterials exhibit exceptional physical and chemical features compared with their bulk material [4-7]. Within the past decade, ZnS nanoparticles have been synthesized through numerous ways which might be divided into two categories: physical technique and chemical technique which encompass hydrothermal method, micro-emulsion technique, a sol-gel technique, chemical co-precipitation technique, sonochemical technique, microwave irradiation, wet chemical technique and solvothermal technique. The physical way needs high reaction temperature, extensive use of organic solvents, high expenditure of kit operation and sophisticated method management, whereas the chemical technique is easy, low priced and handy to

perform. Therefore, the chemical co-precipitation technique is typically accustomed synthesizing the zinc sulphide (ZnS) nanoparticles [8-12]. ZnS may be commercially vital II-VI semiconductor having good optical band gap, rendering it awfully engaging material for optical application particularly in nanocrystalline type. The ZnS has two completely different crystal structures (zinc blend and wurtzite) each of those have same band gap energy and also the direct band structure.

In the present study, the straightforward and cheap method, chemical co-precipitation technique has been utilized to prepare ZnS nanoparticles. The optical properties of ready ZnS nanoparticles have been investigated. The XRD, TEM, UV-Vis, FTIR and PL techniques have been adapted to characterize the synthesized ZnS nanoparticles.

Organization of this research paper is done into five sections: Introduction, Related work, Materials and Methods, Results with Discussion and Conclusions. Introduction section provides the brief review of literature related to our present study. Related work section elaborates on some work done by various researchers on optical characterization of ZnS nanoparticles. Materials and methods section contains precursors and chemicals utilised for the synthesis of ZnS nanoparticles, details of

experimental route and the characterizations techniques employed for the analysis of prepared ZnS nanoparticles by chemical co-precipitation technique. Results and Discussion section provides a brief details on the characterization of ZnS nanoparticles and the analysis. Conclusion section provides the major conclusions drawn from the results.

II. RELATED WORK

There are some reports on the structural and optical characterization of ZnS nanoparticles. Some of the related works done by various researchers are, S. K. Kulkarni et. al. 2001 [13] reported optical properties of chemically capped CdS, ZnS, ZnCdS nanoparticles. Qihua Xiong, et. al. 2004 [14] investigated optical properties of rectangular cross-sectional ZnS nanowires. Gopa Ghosh et. al. 2006 [15] reported synthesis and characterization of PVP-encapsulated ZnS nanoparticles. J. P. Borah et. al. 2008 [16] studied optical and optoelectronic properties of ZnS nanostructured thin films. S. Farjami Shayesteh et. al. 2013 [17] have described about the effect of pH on the structural and optical properties of ZnS nanoparticles embedded in PVA matrix.

III. MATERIALS AND METHODS

A. Experimental:

ZnS nanoparticles have been synthesized using metal precursor, i.e. Zinc acetate $[(\text{CH}_3\text{COO})_2\text{Zn}, 2\text{H}_2\text{O}]$ (A.R. Merck) and Sodium Sulphide $[\text{Na}_2\text{S}, \text{H}_2\text{O}]$ (extra pure Loba Chemie) was used as a supply of sulphur. N-N Dimethyl Formamide (DMF) $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ (Merck) is employed as stabilizing agent. All the chemicals employed in this examination are of analytical chemical reagent (AR) grade and used with no further refining. The deionised water has been used as the solvent for all the solutions referred in this analysis.

0.1 M Zinc acetate solution was prepared by dissolving appropriate weight of zinc acetate in 100 ml double distilled water and 0.1 M sodium sulphide is likewise made in 100 ml double distilled water. The ready zinc acetate solution was mixed with certain quantity of DMF and stir for 10 minutes. Then 100 ml sodium sulphide solution was introduced in the aggregate drop with the aid of drop with constant stirring for 3 hours. This ends up in milky white solution. This solution is stored overnight. Later on that was washed with double distilled water many times in centrifugal machine and at last with acetone to remove the un-reacted molecules. The obtained product has been filtered and dried in vacuum oven at 60° for 8 hours. The product are then crushed into fine powder and

subsequently collected in a sample bottle for the characterization.

B. Characterization of ZnS nanoparticles:

The structural analysis of ZnS nanoparticles was carried out with the aid of the use of X-ray powder diffractometer (Model: D-8 Advance) with Cu-K α radiation ($\lambda = 0.15406$ nm) scanning 2θ in the range $10^\circ - 90^\circ$. The morphology of the prepared sample was examined through transmission electron microscopy (TEM) with Tecnai 20 G² (FEI) version make under 200 KV. A UV-Vis absorption spectrum was recorded using Jasco spectrometer, (Model V-770, Serial No. A013161801) for the wavelength range 200-1100 nm. FTIR spectra has been recorded the use of Bruker, Germany. Model: Vertex 70 with resolution 0.5 cm^{-1} . PL spectra has been recorded the use of model: F-7000 FL Spectrophotometer, Serial number: 2702-001.

IV. RESULTS AND DISCUSSION

A. X-ray Diffraction Analysis

The XRD pattern of synthesized ZnS nanoparticles is displayed in Figure-1. The XRD pattern of ZnS has three strong peaks at the angles $2\theta = 28.87^\circ$, 48.03° , & 56.81° which may be well indexed to nanocrystallite with (111), (220) and (311) planes respectively of cubic ZnS crystal lattice that is well matched with JCPDS card file no. (80-0020). The broad diffraction peaks as seen within the XRD spectra is the direct consequence of the decreased particle length and attributed to the fine size of the grains of the sample. The broadness of the diffraction peaks suggests the formation of the nanoparticles and also the sharp peaks designates the crystalline character of the material [2].

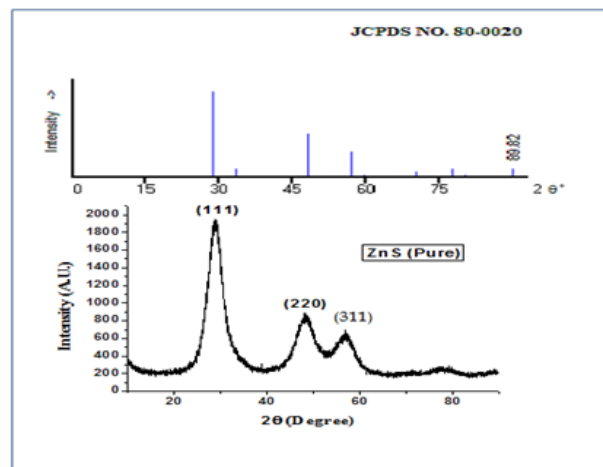


Figure. 1: XRD Pattern of ZnS nanoparticles

From Full Width at Half Maximum (FWHM) of the foremost intense peak, the particle length has been estimated the usage of Debye-Scherer's rule [18]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Wherein $\lambda = 0.1541$ nm is the wavelength of X-ray diffraction, β is the FWHM in radian of the most intense XRD peak and θ is the angle of diffraction. The particle size for ZnS nanoparticles as calculated is determined to be 4.7 nm. The lattice parameter 'a' for ZnS nanoparticles is calculated via equation

$$a = \left[\frac{\lambda}{2 \sin\theta} \sqrt{h^2 + k^2 + l^2} \right] \text{ \AA} \quad \text{and is found to be } 5.3664 \text{ \AA}.$$

The d-spacing for cubic system for $2\theta_{(111)}$ is calculated by using equation

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \text{ \AA} \quad \text{and is found to be } 3.0982 \text{ \AA}.$$

B. TEM Analysis

The surface morphology of the sample is studied employing Transmission Electron Microscope (TEM). TEM photograph with SAED pattern is given in Figure 2(a). The TEM photograph reveals that the surface morphology of the prepared sample are assembled to form nanoparticles which forms crystalline aggregates consistently scattered above the whole surface. Further, the image shows particles are terribly slim and spherical in form.

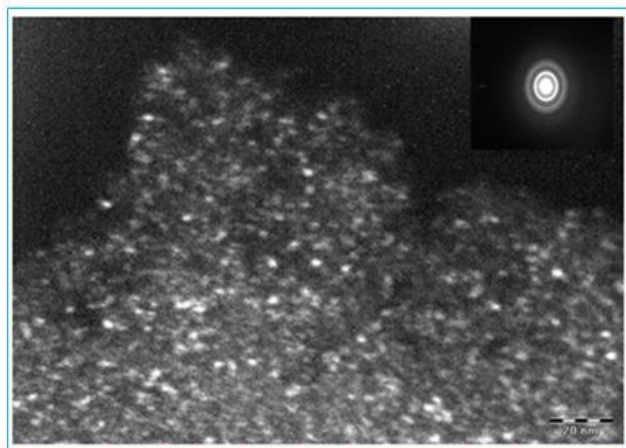


Figure 2(a): TEM image of ZnS with SAED pattern

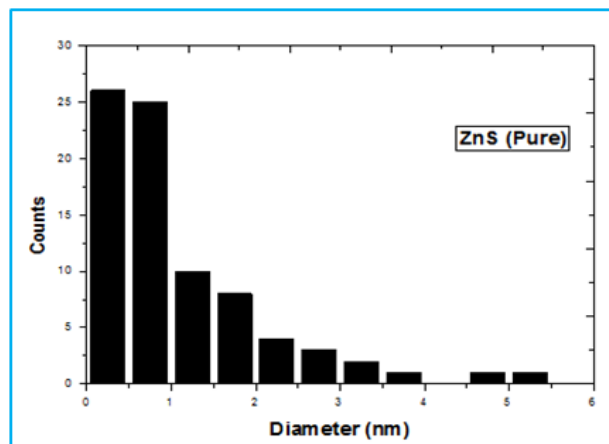


Figure 2(b): Size distribution histogram of ZnS

The particle size distribution histogram is demonstrated by Figure-2(b). Approximately 81 numbers of particles were selected for calculating the particle size distribution. The typical particle size of the ZnS nanoparticles is determined to be about 4.2 nm. This result is in sensible concurrence with the dimension estimated by XRD pattern and validates the formation ZnS nanoparticles.

C. UV-Visible Absorption Spectra:

The optical absorption performance of ZnS nanoparticles is displayed in Figure 3(a). The semiconductor nanoparticles show the amazing change in size quantization of the optical absorption spectra. As a result, the UV-Visible absorption analysis has been employed to look at the optical performance of nano regime particles. The synthesized material is of direct band gap temperament. In this analysis optical band gap has been calculated using Tauc equation. The Tauc's equation is express as:

$$(\alpha h\nu)^{1/n} = A (h\nu - E_g)$$

Here α is absorption coefficient, A is constant and E_g is band gap of material and the exponent n depends on the nature of the transition. For direct allowed transition $n = 1/2$, indirect allowed transition $n = 2$, direct forbidden transition $n = 3/2$, indirect forbidden transition $n = 3$. To determine the viable transitions, a graph of $(\alpha h\nu)^2$ against $h\nu$ is drawn and corresponding band gap is estimated from extending the straight part of the curve on $h\nu$ axis. The direct band gap value of ZnS sample have been acquired from $(\alpha h\nu)^2$ Vs $h\nu$ graph as represented in Figure 3(b) and is determined to be 3.95 eV. The bulk band gap of ZnS is 3.72 eV as reported by earlier researchers [19-20]. The calculated band gap is more than the bulk band gap of ZnS (3.72 eV) that is due to quantum confinement impact. The grain size of ZnS nanoparticles may be calculated using following Brus equation [21]

$$E_{g(\text{nano})} = E_{g(\text{bulk})} + \frac{\hbar^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r}$$

where $E_{g(\text{nano})} = 3.95$ eV, $E_{g(\text{bulk})} = 3.72$ eV, $m_e^* = 0.25 m_e$ is the effective mass of electron, $m_h^* = 0.59 m_e$ [22] is the effective mass of hole, m_e is the free electron mass and R is the particle radius, ϵ_r is the dielectric constant and ϵ_0 is the permittivity of free space. The first factor in above equation suggests the confinement effect and the second term is the Coulomb term. The second term is small due to strong confinement and might be ignored [21], so that the particle length estimated to be 4.4 nm.

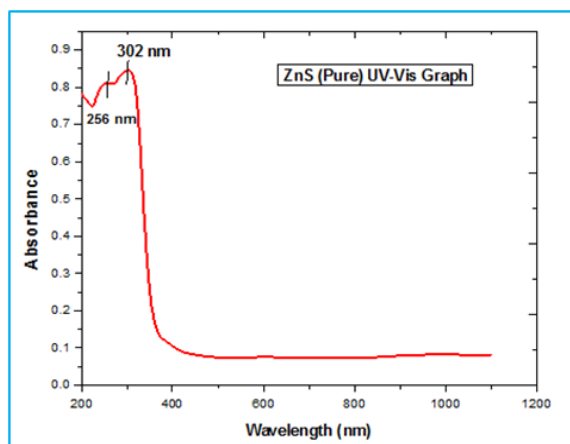


Figure 3(a): UV-Vis absorption spectra of ZnS

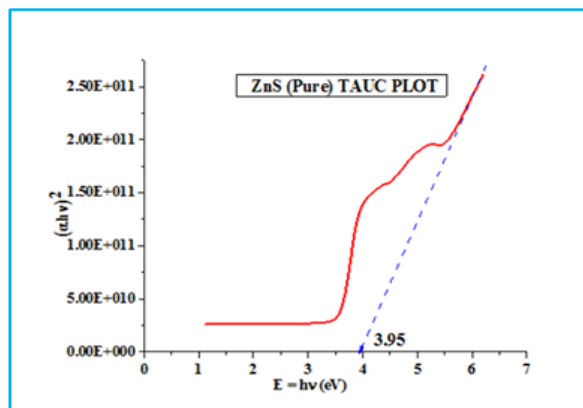


Figure 3(b): Tauc plot of ZnS nanoparticles

D. FTIR Analysis

The FTIR spectrum of pure ZnS sample recorded in the range of 400-4000 cm^{-1} for identification of the functional groups present in the prepared sample is shown in Figure 4. The sample has been prepared in the form of pellet with KBr medium.

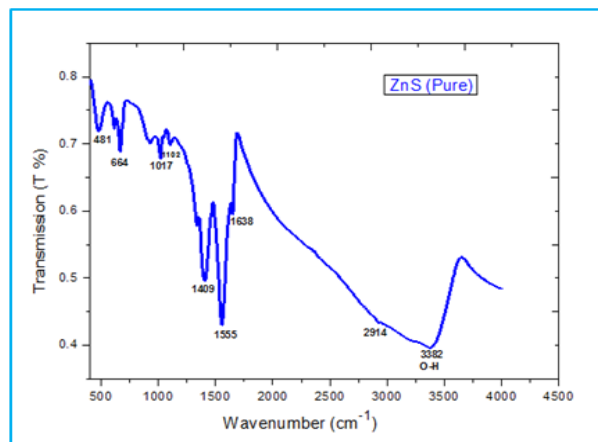


Figure 4: FTIR spectrum of ZnS nanoparticle

In the higher energy area the peak at 3389 cm^{-1} is quite broad and strong which might be assigned to O-H stretching of absorbed water on the floor of ZnS. The peak at 1555 cm^{-1} is assigned to N-H deformation (Amide II band). The peak at 1409 cm^{-1} is assigned to C-N stretching (Amide III band). The peak at 1017 cm^{-1} is assigned to C-O stretching [23]. The peak at 481 and 664 cm^{-1} which have been attributed to vibrations of Zn-S bond [24].

E. PL Study

Photoluminescence (PL) spectrum of pure ZnS sample measured at room temperature, excited at wavelength 405 nm is represented by Figure 5. This spectrum shows broad emission peak centred at around wavelength 492 nm signifying the emission of colour in blue area [25, 26]; it is due to recombination of electrons at the sulphur vacancy donor level. Another peak of smaller intensity is observed at higher wavelength around 611 nm within the region of orange colour.

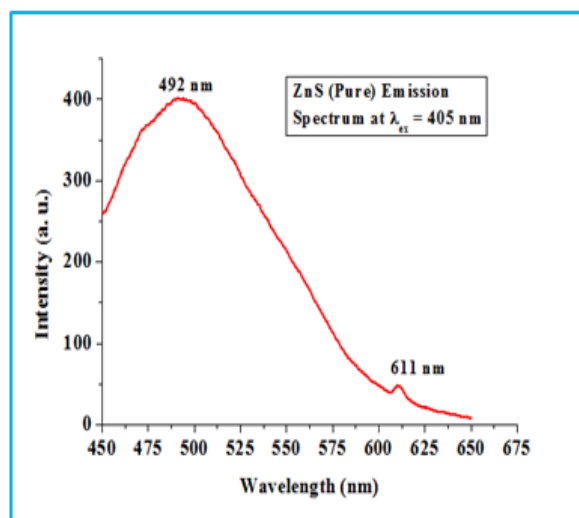


Figure 5: Emission spectrum of ZnS at $\lambda_{\text{ex}}=405$ nm

V. CONCLUSIONS

ZnS nanoparticles are successfully synthesized by simple co-precipitation method. The crystal structure and the grain size of the particles are determined using XRD which is also confirmed by TEM micrograph. Broad peaks in XRD pattern and blue shift in absorption maxima clearly indicates the formation of nanoparticles. TEM micrograph reveals the uniformly distributed fine particles, which form crystalline aggregates. UV-Vis absorption spectrum shows a blue shift indicating quantum confinement of charged particles. The presence of template on nanoparticles is confirmed by FTIR study. PL measurements show the emission of colour in blue region. Increased energy band gap due to nanoparticles size is competent in emitting light of wavelength in the blue range. Hence, prepared ZnS nanoparticles can be used in optical devices like LED, flat panel displays [27]. In future, we plan to study the effect of doping by some metal ions on the structural and optical behaviour of ZnS nanoparticles.

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