A Review on Structural and Optical Performance of ZnS Nanoparticles Synthesized via Chemical Route

D. K. BHOI
Asst. Prof., M.N.College, Visnagar
Hemchandracharya North Gujarat University, Patan

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. Also, the SEM result shows the spherical morphology of the nanoparticles.

Keywords: *ZnS nanoparticles, XRD, TEM, Optical band gap, FTIR, PL*

1. Introduction

Zinc sulphide, a direct wide band gap (3.8 eV) transparent semiconductor, is one of the most important materials used in photonics research.ZnS is a potential candidate for variety of applications such as electroluminescent devices, soalr cells and other optoelectronic devices. The preparation of ZnS particles is of particular interest due to their potential excellent optical and optoelectronics properties, however, only a few numbers of publications related to ZnSnanocrystals can be found in the literature due probably to the difficulty in their preparation since there is no chemical precursor which can give directly ZnSparticles. ZnS is one of the semiconducting materials discovered in ancient times. It is known to be a direct band gap semiconductor and has immense interest among researchers because of its potential applications, such as optical coating, photoconductors, optical sensors, phosphors, window material, dielectric filter, the field emission display and also in LEDs Xiaosheng Fang et al., (2010), Pathak CS et al., (2013). In this review we focus about the developments in ZnS nanoparticle processing techniques, properties and applications.

Semiconductor nanoparticles have attracted a lot of analytical curiosity due to their spectacular properties originating from quantum confinement impact. 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.

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.

2. Methods of Preparations

2.1 Experimental

AR graded zinc acetate dehydrate (Zn(CH3OO)2.2H2O), thiourea (CH4N2S) and triethanol ammine (TEA) (C6H15NO3), ammonia in aqueous solution as starting materials. TEA was used as capping agent in precipitation. Ammonia solution was used as a stabilizer. ZnS nanoparticles have been synthesized using metal precursor, i.e. Zinc acetate [(CH3COO)2 Zn, 2H2O] (A.R. Merck) and Sodium Sulphide [Na2S, H2O] (extra pure Loba Chemie) was used as a supply of sulphur. N-N Dimethyl Formamide (DMF) (CH3)2NC(O)H (Merck) is employed as stabilizing agent.

The solution was obtained by dissolving a weighted amount of zinc acetate and thiourea in distilled water. 3mL of TEA was added to the solution. The pH of the solution was adjusted to 9 by adding ammonia solution. 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 600 for 8 hours. The product are then crushed into fine powder and subsequently collected in a sample bottle for the characterization.

2.2 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-Kα radiation (λ = 0.15406 nm) scanning 2θ in the range 100- 900. 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.

3.Result and Discussion

3.1 X-ray Diffraction Analysis

The XRD pattern of prepared sample were taken by Bruker D8 Advance X-ray diffractometer using the characteristic CuKα (1.5418 Å). The size of ZnS nanocrystals has been calculated using Debye-Scherrer formula using reflection from the XRD pattern. Debye-Scherrer formula for crystallite size determination is given by (t = 0.9 λ/ B Cosθ_B) Where t is the crystallite size, λ is the wavelength of X-ray used (λ =1.54A0) and B is the full width at half maximum (FWHM) after correcting the instrument peak broadening (B expressed in radians) and θ_B is the Bragg's angle.

The average crystallite size is calculated using Debye-Scherrer formula10 D = Kl/bCosq, where D is the crystallite size, K is the geometric factor (0.9), λ is the X-ray wave length (1.54Ao), β is the full with at half maxima (FWHM) of the diffraction peak (in radian) and θ is the diffraction angle. The XRD pattern of synthesized ZnS nanoparticles is displayed in Figure-1. The XRD pattern of ZnS has three strong peaks at the angles 2θ = 28.87^0, 48.03^0, & 56.81^0 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.

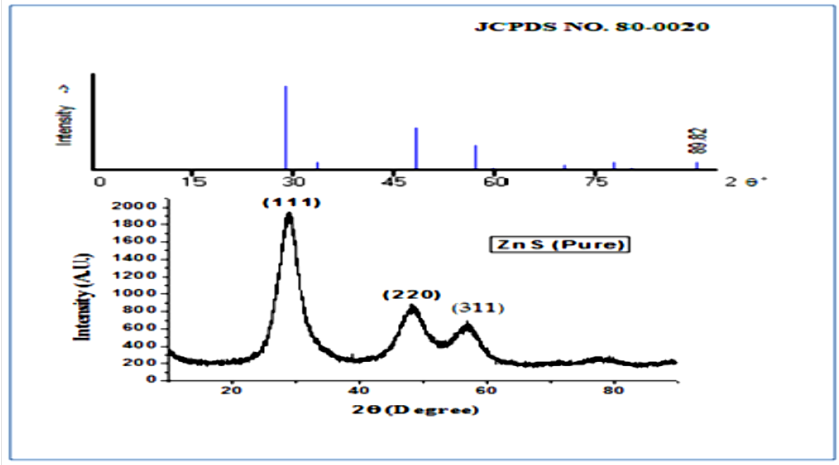


Figure. 1: XRD Pattern of ZnS nanoparticles

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 λ = 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

$$a = \left[\frac{\square}{\square\,\square\square\square}\sqrt{\square^{\square} + \square^{\square} + \square^{\square}}\right]$$ **Å** and is found to be **5.3664 Å.**

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

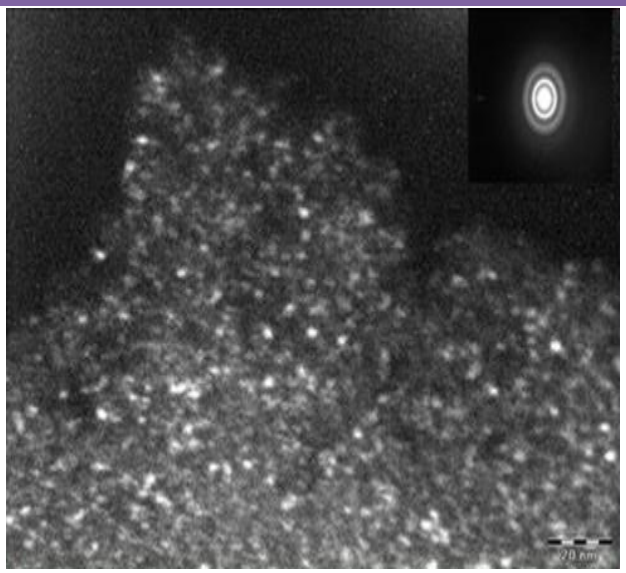
$$d = \frac{\square}{\sqrt{h^2+\square^2+\square^2}}$$ **Å** and is found to be **3.0982 Å.**

Table-1: Structural Parameters of ZnS nanoparticles

2 θ (degree)	Plane (hkl)	Interplaner Spacing 'd'(A^0)	Lattice Constant 'a'(A^0)	FWHM (rad)	Average Crystallite Size D(nm)	Dislocation density □(lines/m)	Average Strain (□□□□)
28.32	(111)	3.14	5.37	0.044	5.26	$8.1x10^{16}$	$43x10^{-3}$
47.73	(220)	1.91	5.37	0.023	5.26	$8.1x10^{16}$	$43x10^{-3}$
56.50	(311)	1.63	5.37	0.031	5.26	$8.1x10^{16}$	$43x10^{-3}$

3.2 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. The rings have been indexed to (111), (220) and (311) planes of the cubic ZnS phase which correspond to d(111) = $3.1114A^0$, d(220)=$1.904A^0$ and d(311)=$1.6277A^0$ respectively, confirming the presence of cubic phase of ZnS crystal[16].



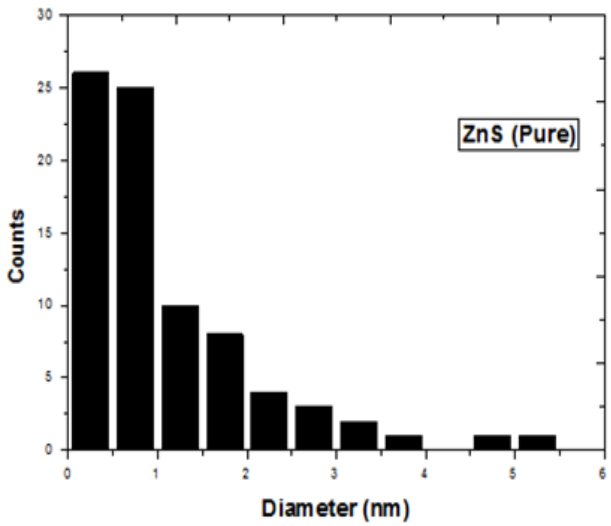


Figure 2(a):TEM image of ZnS with SAED pattern **Figure 2(b): Size distribution histogram of ZnS**

3.3 UV-Visible Absorption Spectra

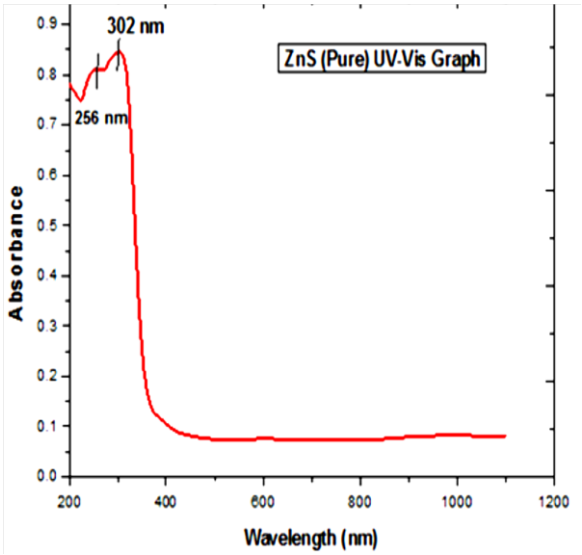
The optical absorption performance of ZnS nanoparticles is displayed in Figure 3(a). The semiconductor nanoparticles show the amazing change in size quantization of the optical absorption spectra. As a result, the UV-Visible absorption analysis has been employed to look at the optical performance of 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 equlation is express as:

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

The direct band gap value of ZnS sample have been acquired from (αhν)2 Vs hν 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.

$$E_{g(nano)} = E_{g(bulk)} + \frac{h^2}{8\square^2}\left(\frac{1}{\square^*_{\square}} + \frac{1}{\square^*_h}\right) - \frac{1.8\square^2}{4\square\square_0\square_{\square}}$$

where Eg (nano) = 3.95 eV, Eg (bulk) = 3.72 eV, $\square^*_{\square}$ = 0.25 m_e is the effective mass of electron, $\square^*_h$ = 0.59 m_e is the effective mass of hole, me is the free electron mass and R is the particle radius, $\square_{\square}$ is the dielectric constant and $\square_0$ is the permittivity of free space.



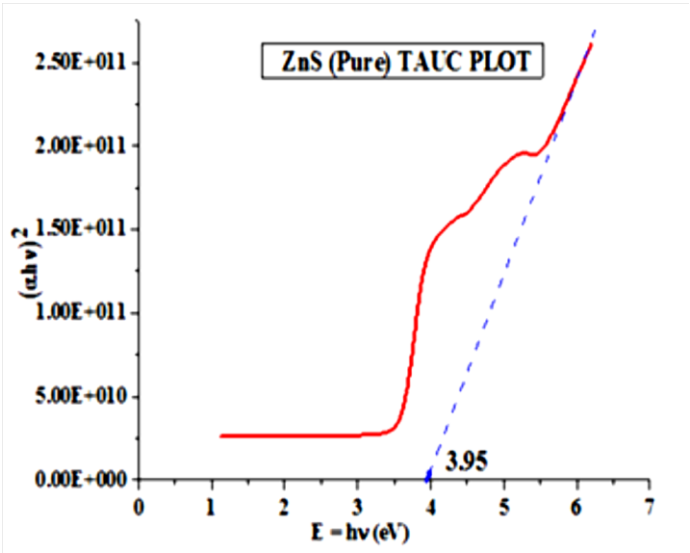


Figure 3(a): UV-Vis absorption spectra of ZnS **Figure 3(b): Tauc plot of ZnS nanoparticles**

3.4 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. The IR study confirms the presence of –C-O and –OH groups of glucose have a strong ability to bind metal .So we can infer that ZnS nanoparticles are encapsulated by glucose. It has been earlier reported that gluconic acid derived from glucose can cap the nanoparticles[20]. 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. The peak at 481 and 664 cm^{-1} which have been attributed to vibrations of Zn-S bond. 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.

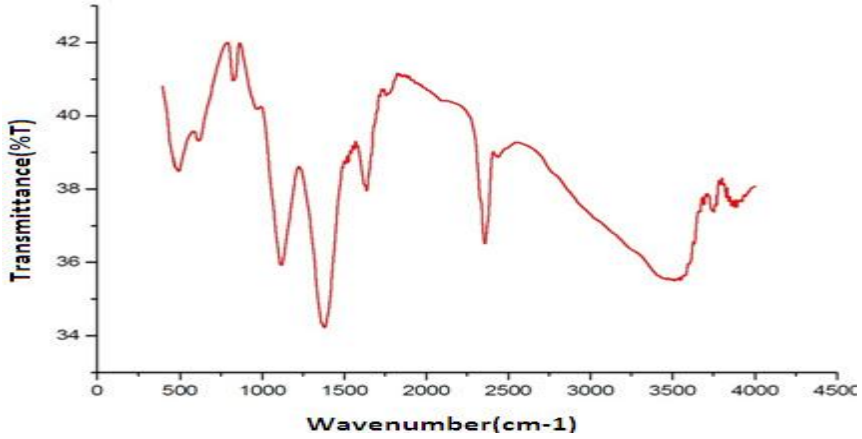


Figure 4: FTIR spectrum of ZnS nanoparticle

3.5 Photoluminescence (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 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. The room temperature photoluminescence spectrum of ZnS sample for excitation wavelength of 280nm . This shows peak centred at 437nm. Appearance of the broad peak centred at 437nm is due to the zinc vacancies present near the valance band[19].

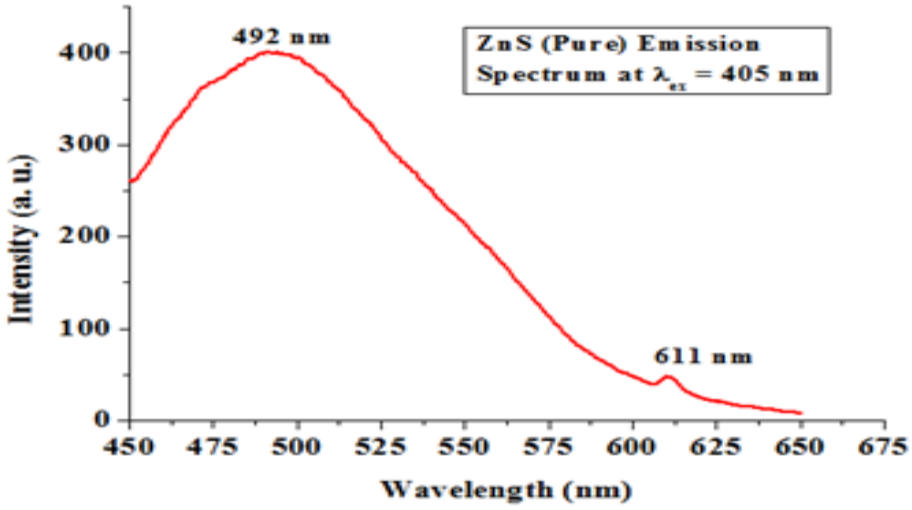


Figure 5: Emission spectrum of ZnS at λex=405 nm

4. Conclusion

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. 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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