PREPARATION AND CHARACTERIZATION OF ZINC SULPHIDE NANOPARTICLES USING HONEY AS CAPPING AND STABILIZATION AGENTS

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Abstract

Zinc sulphide (ZnS) nanoparticles were successfully prepared by using Zn $(NO_3)_2.6H_2O$ and Na_2S as precursors and different volumes of honey as capping and stabilizing agents. The structural, morphological, thermal and optical properties of as synthesized nanoparticles were investigated using x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy- energy dispersive x-rays spectroscopy (SEM-EDX), Fourier transform infrared spectroscopy (FT IR), thermogravimetric differential thermal analysis (TG-DTA) and UV-visible spectroscopy. ZnS nanoparticles were indexed as hexagonal crystal structure with particles size ranging from 12.9 to 17.2 nm. The average particle size was also measured by TEM using image J software. EDX analysis revealed the high purity of synthesized zinc sulphide nanoparticles. From TG-DTA analysis and FT IR, biomolecules were involved in synthesis of ZnS nanoparticles because of the presence of organic compounds. *The ultraviolet absorption spectra showed the blue shift in absorption maxima due to the quantum effect.* The results revealed the direct relationship between volume of honey while the reverse relation were observed for absorption wavelength, crystallite size and refractive index of ZnS nanoparticles.

Keywords: zinc sulphide nanoparticles, honey, capping and stabilizing agents, hexagonal

Introduction

Honey mediated synthesis is a relatively novel concept used during the past few years to synthesize metal nanoparticles (Balasooriya *et al.*, 2017). It provides a simple, cost effective, biocompatible, reproducible, rapid, and safe method and also offers several advantages over the microorganism mediated synthesis. Honey acts as both a stabilizing and a reducing agent in nanoparticle synthesis. Honey can be produced by bees using nectar from flowers and hence, is a natural sweetener. It contains several biomolecules responsible for the reduction and stabilization of nanoparticles from metal salts precursors and has been exploited by several groups for the synthesis of metal nanoparticles and semiconductor nanoparticles (Buba *et al.*, 2013). Nanoparticles refers to objects that are sized on a nanometer scale where at least one of the dimensions of a particle must be less than 100 nm. Nanomaterials as promising in many fields including cosmetics, healthcare, biomedical, food and feed, environment, health, mechanics, optics, chemical industries, electronics, industries, energy science, catalysis, light emitters, single electron, transistors, nonlinear optical devices and photoelectron chemical application (Thangam *et al*., 2012). ZnS crystallizes as two allotropic forms; zinc blende which can exist in cubic form and wurtzite which can exist in hexagonal close packing form (Hedayati *et al*.,2016). Zinc sulphide is a semiconductor material of the II–VI group and it can be widely utilized in photonics, optical devices, such as ultraviolet light emitting diodes, flat panel displays, optical coatings, field effect transistors, sensors, solar cells and optical sensors (Chaliha *et. al*., 2019).

The main aim of this study is to prepare zinc sulphide by using honey as capping and stabilization agent and to characterize the prepared zinc sulphide.

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Materials and Methods

Samples Collection

In the present work, honey samples were collected from Mrauk-Oo Township in Rakhine State. Honey samples were stored in clean air-tight bottles at an ambient temperature to avoid moisture absorption. Honey samples were later taken to the Laboratory of the Department of Chemistry, Yangon University. The chemicals used in this research work were the products from British Drug House (BDH), London and Kanto Chemical Co., Japan.

Preparation of Zinc Sulphide Nanoparticles

ZnS nanoparticles were prepared by homogeneous chemical co-precipitation method using $Zn(NO_3)_2.6H_2O$ and Na_2S precursors and honey was applied as stabilizer and capping agent. Aqueous solution of zinc nitrate hexahydrate (3g in 25 mL of distilled water) and sodium sulphide (1.3 g in 25 mL of distilled water) were freshly prepared. Into the mixture aqueous solution of zinc nitrate hexahydrate and 25 mL of honey, sodium sulphide solution was added drop-wise with continuous magnetic stirring at 2000 rpm. After the formation of white precipitate, stirring was continued for 30 min for the completion of the reaction. The product obtained in the form of white precipitate was centrifuged and washed with distilled water and dried at room temperature (Dilpazir *et al*., 2015).

The above procedure was repeated with 50 mL and 75 mL of honey. The ZnS precipitate obtained were designated as S1, S2 and S3, respectively, for using 25 mL, 50 mL and 75 mL of honey. The chemical equation for the formation of ZnS is given as below:

$$Zn(NO_3)_2 + Na_2S \xrightarrow{\text{honey}} ZnS + 2NaNO_3$$

Characterization of Zinc Sulphide Nanoparticles

Prepared zinc sulphide nanoparticles were characterized by XRD technique using as X-rays diffractometer (D-max 2200, Rigaku Co., Tokyo, Japan) of the wavelength 0.154 nm. The morphology of the ZnS sample was studied using a scanning electron microscope (SEM) and the purity and elemental analysis was carried out using energy dispersive X-ray spectrscopy (EDX) by Shimadzu Super Scan SSX-550. The crystal structure and size of ZnS were obtained by TEM image using TEM (JEOL TEM-3010) with an accelerating voltage of 100 kV at State Key Laboratory, College of Science, Beijing University of Chemical Technology, China. The crystallite sizes of ZnS NPs were calculated by using Image J software. TG-DTA analysis was carried out by (DTG-60H) Thermal Analyzer, Shimadzu, Japan. FT IR spectra were recorded by FT IR spectrophotometer, Perkin Elmer. UV-Visible spectra were recorded in a Thermo Scientific Evolution 201 Spectrometer.

Results and Discussion

XRD Analysis

Figure 1 shows the x-ray diffractograms of ZnS nanoparticles obtained by using 25 mL, 50 mL and 75 mL honey, respectively. All the peaks in the XRD patterns are well matched with the standard diffraction pattern of zinc sulphide. No other impurity peaks were observed. Three dominant peaks were observed in the diffractogram of S1 at 2θ values of 28.6°, 47.5° and 56.7° corresponding to the Miller indices of (006), (108) and (116) planes, respectively. For S2 and S3 these dominant peaks appeared around the above mentioned 2θ values. ZnS nanoparticles were

indexed as hexagonal packed wurtzite structure. Phase identification by XRD results showed that only single phase of zinc sulphide with no other phase was found in each XRD pattern (Table 1).

The average crystallite size (t) of the ZnS sample was calculated using the Scherrer formula:

$$t = 0.9\lambda / \beta \cos \theta$$

Where, t is thickness of the crystallites (nm), λ= 1.54056 Å is wavelength of X –ray, θ is diffraction angle of the Bragg peak and β is the full width at half maximum (FWHM) of that peak in radian. Table 2 shows the crystallite sizes of ZnS nanoparticles obtained by using three different volumes of honey. The calculated average crystallite size of zinc sulphide nanoparticles was estimated to be 17.2 nm, 15.6 nm and 12.9 nm by using 25mL, 50 mL and 75 mL of honey, respectively. The calculated values were not much different from the data obtained by XRD. The average crystallite size was found to vary in the range of 12 nm -18 nm for the samples with decreasing trend as the amount of honey was increased. It was observed that by using higher volume of honey smaller crystallite sizes of ZnS nanoparticles were obtained.

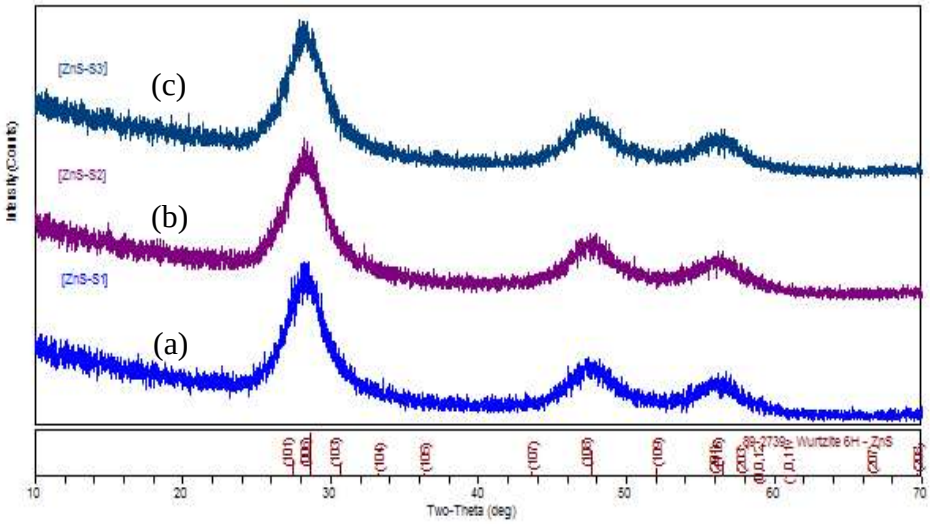


Figure 1 XRD pattern of zinc sulphide nanoparticles using (a) 25 mL of honey (S1) (b) 50 mL of honey (S2) and (c) 75 mL honey (S3)

Table 1 Phase Identification of Zinc Sulphide Nanoparticles Using Different Volumes of Honey

Samples	Diffraction Angle '2θ'(°)	Interplanar Spacing d(Å)	Miller Indices (h k l)	Remark
S1	28.6	3.11	006	ZnS
	47.5	1.91	108	
	56.4	1.62	116	
S2	28.6	3.11	006	ZnS
	47.7	1.91	108	
	56.6	1.63	116	
S3	28.6	3.12	006	ZnS
	47.8	1.90	108	
	56.9	1.63	116	

Table 2 Crystallite Sizes of Zinc Sulphide Nanoparticles using Different Volumes of Honey

No.	Diffraction Angle '2θ'(°)	FWHM 'β' (°)	FWHM 'β' (radian)	Calculated Crystallite Size (nm)	Crystallite Size from XRD (nm)
S1	28.6	0.94	0.016	17.2	18.5
	47.5	0.54	0.009		
	56.4	0.23	0.004		
S2	28.6	0.64	0.011	15.6	17.4
	47.7	0.58	0.010		
	56.6	0.38	0.017		
S3	28.6	0.54	0.019	12.9	14.8
	47.8	0.66	0.012		
	56.9	0.67	0.011		

TEM Analysis

Crystallite size of ZnS nanoparticles (S1) obtained by using 25 mL honey was also studied by transmission electron microscopy. Figure 2 shows the TEM image of ZnS nanoparticles. TEM image of sample indicated the evident morphology and regular (spherical) shape. The average particle size measured by using image J software which was nearly the same as that measured by XRD of 17.2 nm.

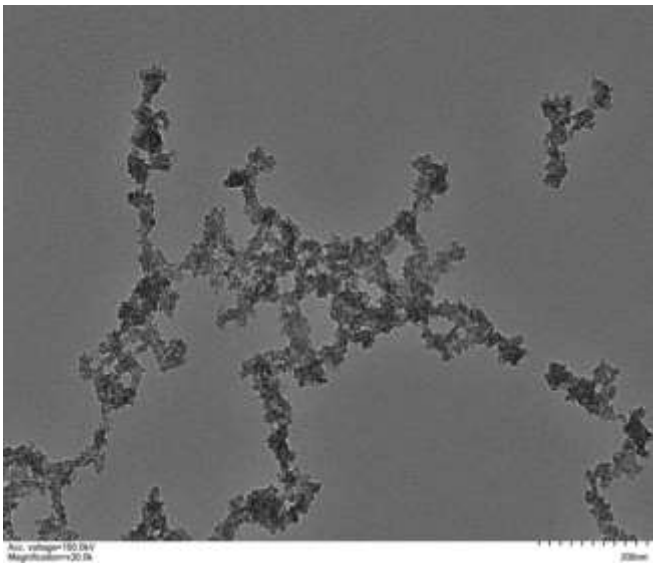


Figure 2 TEM image of zinc sulphide nanoparticles using 25 mL of honey (S1)

SEM –EDX

The morphology as well as the composition of the prepared ZnS nanoparticles were investigated by SEM-EDX.

Morphological analysis

Figure 3 shows the SEM images of ZnS nanoparticles. The image for the samples depicts the homogeneous plate-like form. The SEM also produces images of high resolution, which means

that closely features can be examined at a high magnification. However, the actual size cannot be determined by SEM due to the limitation of the resolution of the instrument

Element analysis

The EDX spectra of as synthesized zinc sulphide samples are shown in Figure 4. The clear peaks of Zn and S confirmed the presence of zinc and sulphur. Other element oxygen was also recorded possibly due to the elements from honey. The average atomic percentages of zinc and sulphur were found to be 65.08: 33.02 in S1, 63.81: 31.32 in S2 and 62.08: 31.02 in S3. These ratios of Zn and S atoms are very close to the theoretical expectation of 1:1 for the atom ratio in ZnS nanoparticles. Similarly, the weight ratios of Zn and S in all sample particles were also found to be nearly 2:1 of zinc sulphide nanoparticles.

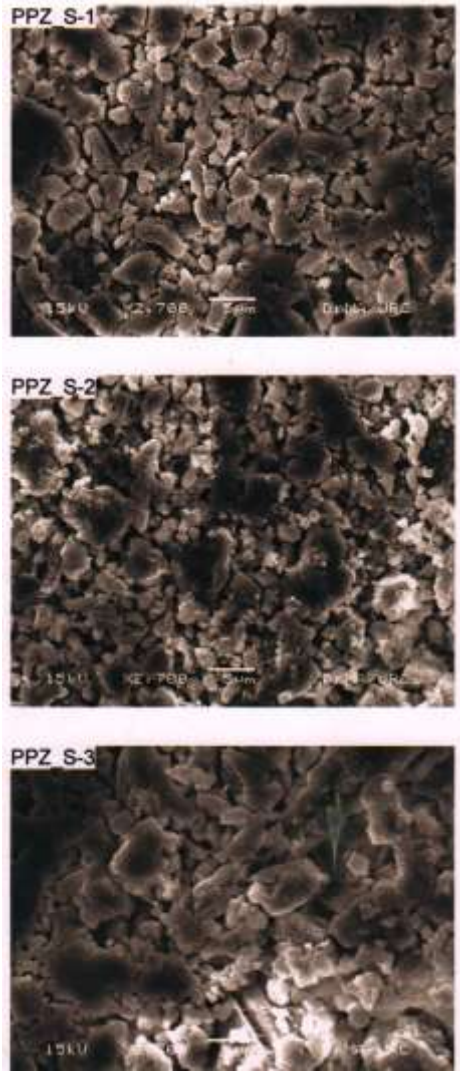


Figure 3 SEM images of zinc sulphide nanoparticles using (a) 25 mL of honey (S1), (b) 50 mL of honey (S2) and (c) 75 mL of honey (S3)

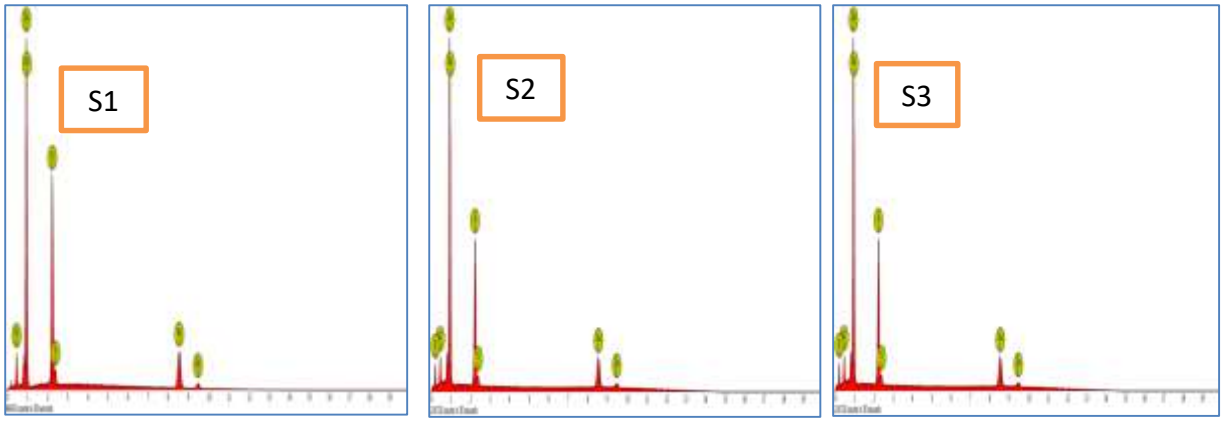


Figure 4 EDX spectra of zinc sulphide (S1, S2 and S3) nanoparticles

Table 3 EDX Spectral Data of Zinc Sulphide Nanoparticles Using Honey

Samples	Element Number	Element Symbol	Element Name	Atomic (%)	Weight (%)
S1	30	Zn	Zinc	65.08	62.74
	16	S	Sulphur	33.02	34.95
	8	O	Oxygen	1.90	1.31
S2	30	Zn	Zinc	63.81	62.87
	16	S	Sulphur	33.32	30.50
	8	O	Oxygen	2.87	5.63
S3	30	Zn	Zinc	62.08	60.73
	16	S	Sulphur	34.68	34.85
	8	O	Oxygen	2.24	3.42

Thermogravimetric -Differential Thermal Analysis

Figure 5 shows the thermograms of ZnS nanoparticles **(**samples S1, S2 and S3). In each thermogram, one endothermic peak and one exothermic peak were observed. The endothermic peak was due to the evaporation of residual moisture on the surface of the samples and the exothermic peak was attributed to the combustion of residual organic compounds from honey. The TGA showed significant weight losses arising from desorption of water below 200 ºC and the decomposition of organic components occurred between 250–320 ºC. The weight losses were 23.3 % for sample (S1), 24.4 % for sample (S2) and 31.3 % for sample (S3), and the results were described in Table 4.

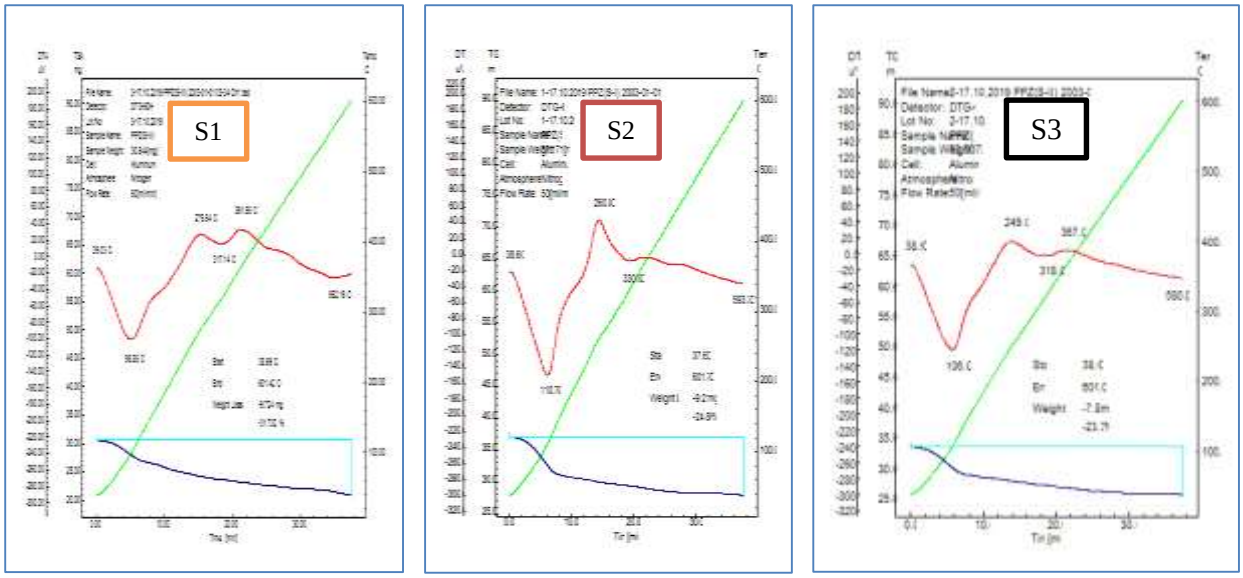


Figure 5 TG-DTA thermogram of zinc sulphide nanoparticles (S1, S2 and S3)

Table 4 TG-DTA Data of the Prepared Zinc Sulphide Nanoparticles using Honey

Samples	Temperature Range (°C)	Break Temperature (°C)	Weight Loss (%)	Nature of Peak	Remarks
S1	38 -135	98.8	11.3	Endothermic	Removal of water
	135-380	361.5	9.5	Exothermic	Combustion of organic compound
	380- 601		2.5	---	Thermally stable
S2	37 -180	110.8	11.5	Endothermic	Removal of water
	180-290	260.9	9.5	Exothermic	Combustion of organic compound
	290- 601		3.4	---	Thermally stable
S3	38 - 200	106.2	14.2	Endothermic	Removal of water
	200-300	249.3	12.5	Exothermic	Combustion of organic compound
	300-601		4.5	---	Thermally stable

FT IR Study

The FT IR spectra of zinc sulphide nanoparticles were recorded between 400-4000 cm^{-1} as shown in Figure 6. The peaks were observed at 459 cm^{-1} for the sample (S1), 435cm^{-1} for the sample (S2) and 552cm^{-1} for the sample (S3) due to Zn-S stretching vibration. The characteristic major peak of ZnS was reported to be 464 cm^{-1} (Ummartyotin *et al.*,2012). The broad bands between 3200cm^{-1}- 3400cm^{-1} are assigned to the O-H stretching vibration. The absorption peaks of 1617cm^{-1}, 1629 cm^{-1} and 1625 cm^{-1} are assigned to the O-H bending of water molecules. The

vibration bands in the range of 1332cm^{-1} - 1350 cm^{-1} are assigned to the -O-H bending in C-O-H vibration and the bands between 1009 and 1119 cm^{-1} are stretching of C-O in C-O-C group.

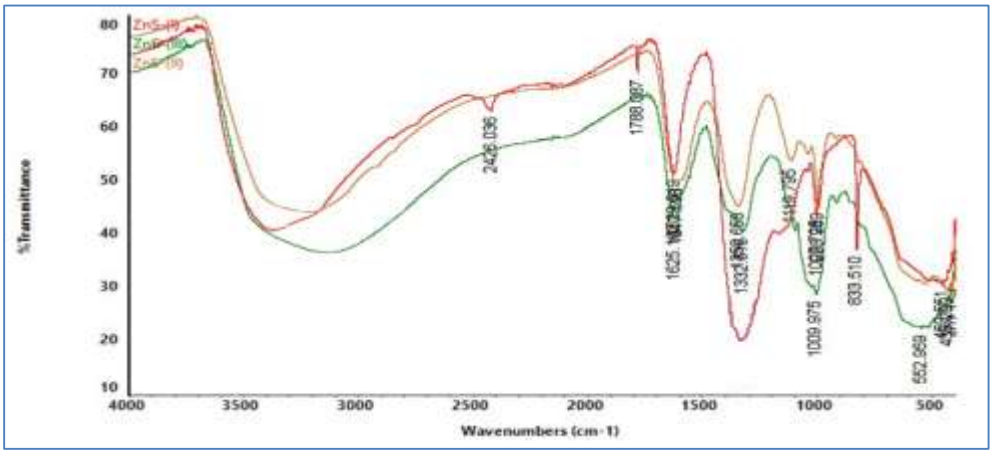


Figure 6 FT IR spectra of zinc sulphide nanoparticles (S1, S2 and S3)

Table 5 FT IR Spectral Data of Zinc Sulphide Nanoparticles using Honey

Wavelength (cm^{-1})				Assignment
S1	**S2**	**S3**	**Reported values**	
3200-3400	3200-3400	3200-3400	3200-3400*	-O-H stretching vibration
1629	1617	1625	1640-1646*	O-H bending of H_2O
1332	1350	1339	1342-1347*	O-H bending in -C-OH
1119	1007	1009	1101-1105*	(C-O) in C-O-C group
459	435	552	464**	Zn-S Stretching

***** Kędzierska-Matysek *et al*.,2018
** Ummartyotin *et al*., 2012

Optical study

The absorption spectra of ZnS nanoparticles are shown in Figure 7. The strongest absorption peak of zinc sulphide nanoparticles appear at λ_{max} of 329 nm for the sample (S1), 315 nm for the sample (S2) and 308 nm for the sample (S3) using different volumes of honey. The ultraviolet absorption spectra showed the blue shift *in absorption maximum, i.e., moved to shorter wavelength* due to the quantum effect.

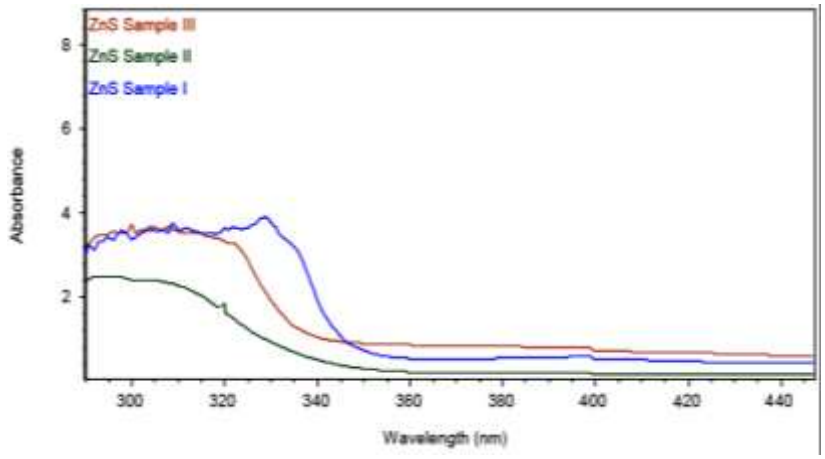
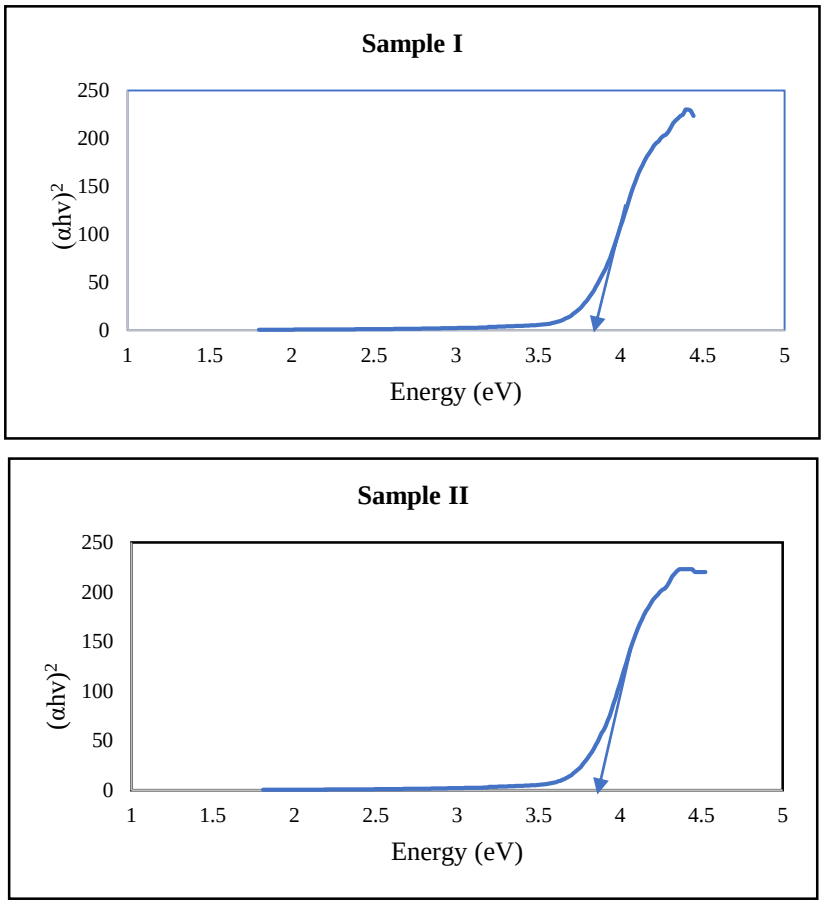


Figure 7 Absorption spectra of zinc sulphide nanoparticles (S1, S2 and S3)



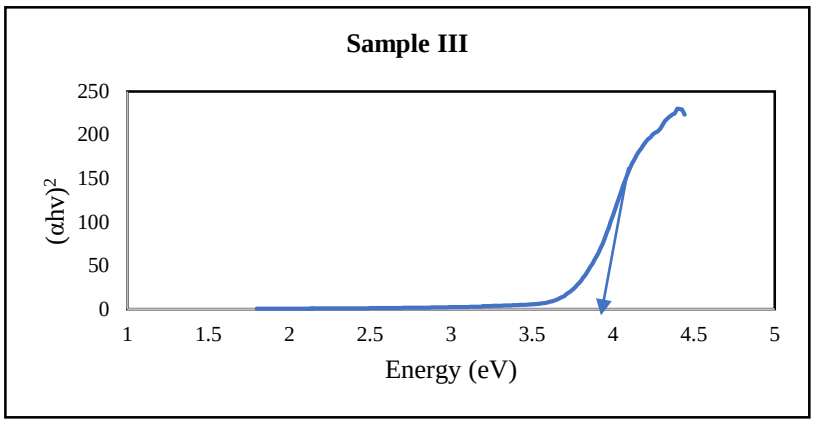


Figure 8 Tauc plots for calculation of band gap energy values of zinc sulphide nanoparticles (S1, S2 and S3)

The optical band gap energy of the ZnS nanoparticles was calculated from the UV absorption study using the following equation;

$$\alpha\, h\nu = A(h\nu - E_g)^n$$

where, α is the absorption coefficient,

$h\nu$ is the incident photon energy,

A is a constant, and

E_g is the optical band gap energy of the material.

Figure 8 shows the Tauc plots of ZnS nanoparticles to calculate the band gap energy. The optical band gap energy data of the all samples are found to lie in the range of 3.7 – 3.9.eV (Table 6). The band gap was found to increase from 3.7 eV to 3.9 eV as the λ_{max} of ZnS nanoparticles decreased . The obtained band gap values were higher than that of the bulk value (3.7 eV) owing to the quantum confinement effect. The refractive index of the ZnS nanoparticles S1, S2 and S3 were calculated using the relation:

$$n^4\, E_g = 59\ eV$$

where, n is the refractive index

E_g is the band gap of the sample.

The refractive indices were in the range of 1.9 to 1.7 for ZnS nanoparticles (S1, S2 and S3). It was found that as the λ_{max} decreased, the band gap increased and the refractive index decreased.

Table 6 Wavelength of Maximum Absorption, Band Gap and Refractive Index of ZnS Nanoparticles Using Honey

Sample	Wavelength of maximum absorption (nm)	Band gap (eV)	Refractive Index
S1	329	3.7	1.9
S2	315	3.8	1.8
S3	308	3.9	1.7

Conclusion

ZnS nanoparticles were successfully synthesized using three different volumes of honey as capping and stabilizing agents. ZnS nanoparticles in this study were indexed as hexagonal structure with the average crystallite size between 12.9 to 17.2 nm. TEM image of sample indicated the evident morphology and regular shape. SEM images for the samples showed homogeneous plate-like form. EDX analysis confirmed the presence of Zn and S with correct atomic and weight ratios. TG-DTA analysis showed endothermic and exothermic peaks due to loss of moisture and combustion of organic compounds from honey. The FT IR study showed the characteristic peak of zinc sulphide. ZnS nanoparticles exhibited the absorption maximum in the range of 329 nm and 308 nm. From this study it was found that when the volume of honey was increased, the band gap energy of ZnS nanoparticles increased but particle size and refractive index decreased.

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