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STRUCTURAL AND OPTOELECTRONIC PROPERTIES OF ZnS NANOPARTICLES EXPOSED TO ORGANIC AND INORGANIC CAPPING AGENTS

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ABSTRACT

ZnS nanoparticles capped with Sodium Carboxyl-methyl Cellulose (CMC-organic) and Tetraethylorthosilicate (TEOS-inorganic) as capping agentswere synthesized by chemical co-precipitationand sol-geltechnique respectively. Structural, morphological and optical studies of thesynthesizes nanoparticles were carried out using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Vis spectroscopy and Fourier transformsinfrared spectroscopy (FTIR) . Studies of the capped ZnSnanoparticles revealed zinc blende structure. Particle sizes calculated from Williamson-Hall (W-H) analysis of Uniform Deformation Model (UDM) were $2 \cdot 57\mathrm{nm}$ (ZnS:CMC) and $1 \cdot 58\mathrm{nm}$ (ZnS:SiO_2). The average strain values calculated from the model indicated that ZnS:SiO_2has $10 \cdot 3 \times 10^{-3}$ while ZnS:CMC has $5 \cdot 5 \times 10^{-3}$ All samples had smooth surfaces due to passivation of the capping agents. Optical absorption studies shows a blue shift of the absorption edge with band gap values of $5 \cdot 00\mathrm{eV}$ and $3 \cdot 73\mathrm{eV}$ for ZnS:CMC and ZnS:SiO_2 which are higher than the bulk value of $3 \cdot 60\mathrm{eV}$ of ZnS nanoparticles due to quantum confinement effect.The vibrational modes associated with OH-stretching at $3484 \cdot 25\mathrm{cm}^{-1}$ and the carboxylic group –COOH at $1703 \cdot 02\mathrm{cm}^{-1}$ confirms the presence of capping agent from the Fourier transform infrared spectroscopy measurement.

Keywords: *ZnS, Capping agents, Chemical route, Sol-gel, Nanoparticle sizes, Strain and Optoelectronic*

INTRODUCTION

Semiconductor nanoparticles as an advance research material for most dynamic area of scientific research have significant fundamental and commercial interest. ZnS as an important group II–VI semiconductor compound with average wide band gap energy of

has shown excellent properties in luminescence, photochemistry and low toxicity compared to other semiconductors (Amah *et al.*, 2012). This is because of the wide range of its application in areas such as phosphors, optics, electronics, solar cells, catalyst and sensors, hence the need for intensive investigation in order to understand the workability of the device in the above aforementioned applications (Ravi, 2011; Ahemen *et al.*, 2013) .

Nanoparticles generally are zero dimensional structures which are size dependent. As they approach the nanoscale regime, quantization and domination of atoms at the surface becomes significant due to the large surface area of the nanoparticles. Therefore during synthesis or preparation of nanoparticles the choice of capping agent in engineering of size and surface structure is of both theoretical and practical importance due to the inherent mechanical, chemical, electrical, optical, magnetic, electro-optical and magneto-optical properties that are substantially different from those observe for their corresponding bulk (Gnanam and Rajendran, 2011).

These capping agents which is either organic or inorganic during synthesis determines the material to be synthesized, since they are responsible for the stability on the surface of the nanoparticles through covalent or ionic interaction as well as isolation of individual nanoparticles under ambient conditions (Kalu *et al.*, 2013).

Organic capping agent's which are polymeric in nature consist of molecules that bind to the surface of the particles with a network of hydroxyl head group and an alky tail chain. They restrict the growth of the nanometric size of the particles by stabilizing the nuclei and larger nanoparticles against aggregation, as well as accurate control of size and surface structure (Sperling and Parak, 2012).

Inorganic capping agents has been observed to be wide band gap semiconductors, whose primary aim is the elimination of surface related defect states at the particle surface during synthesis and the confinement of charge carriers to the core material. This usually results to increase quantum yield and luminescence efficiency. They also decrease poly-dispersity which enhances colloid stability at control growth rate. The lowering of density of trap states in surface passivated samples has been attributed to the effect capping agent, hence its application in luminescent semiconductors (Reiss *et al.,* 2002).

Also capped zinc sulfide nanoparticles with varying emission spectra and decay times have been reported due to passivation of the nanocrystal's surface which plays important role in the optical properties and the controlling of dispersed particle sizes (Kalu *et al.*, 2013).

Widening of a semiconductor band gap stemming from quantum size effect can be obtained when the semiconductor particle size reaches or become less than the Bohr radius. Therefore to prepare such nanoparticles at engineered size and surface structure requires limiting their growth at the beginning of their formation when capped (Kalu *et al.*, 2013; Pawar *et al.*, 2010,).

The variation of particle size is a crystal distortion due to the confinement caused by capping. The strain-induced broadening stemming from such distortions depends largely on the lattice parameters and the diffraction angle which can be evaluated. Lattice strain is therefore a measure of the distribution of the lattice constants arising from crystal imperfections (Mote *et al*, 2012). Crystallite size and lattice strain affect the Bragg peak in different ways. Such as increase in width of the peak, the intensity of the peak and shift peak 2? to a position accordingly.
(Kumar and Rao, 2013).

This research investigated the effect of organic and inorganic capping agents on the particle sizes of ZnS nanoparticles and analyzed the associated strain induced due to peak broadening using Williamson-Hall Model.

MATERIALS AND METHOD

The ZnS nanoparticles were prepared from analytical grade of zinc sulphatehepta-hydrate $(ZnSO_4 \cdot 7H_2O)$, sodium sulphidenona-hydrate $(Na_2S \cdot 9H_2O)$, toluene, ethanol, deionized water, Sodium carboxyl-methyl cellulose (CMC) and tetraethylorthosilicate (TEOS) .

The synthesis process was carried out by mixing 0.2M of CMC solution (1 % wt / wt in deionized water) with 50 ml of (4.39g) of $ZnSO_4.7H_2O$ under stirring for 25min. This was followed by adding (drop-wise)50 ml of (4.80g)of $Na_2S.9H_2O$ using a pipette to the Zn^{2+}/ CMC precursor solution at room temperatureunder continuous stirring. Continuous stirring was uninterrupted until the last drop of the S^{2-}precursor solution was added for another 25min to allow for complete mixing of the reactants and formation of a white precipitate. The precipitate was then centrifuged at 3500 revolution per minute (rpm) for 20min to obtain a white precipitate which was washed several times with toluene / ethanol mixed solution. The white precipitate was filtered andthen dried at 100^0C in a vacuum oven for 4 hours. The dried sample (ZnS:CMC) was grinded in an agate mortar and pestle to obtain a fine powder for characterization. Note that before drying, part of the washed precipitate was taken out and re-dispersed into ethanol for optical measurements. The above procedure was repeated using tetraethylorthosilicate (TEOS) as an inorganic capping agent with little modification during synthesis for the sample (ZnS:SiO_2).

Characterization of the synthesized nanoparticles (ZnS, $ZnS:CMC$ and $ZnS:SiO_2$)was carried out using X-ray Diffraction (PANalytic X-ray Diffraction machineat Engineering Materials Development Institute Akure, Nigeria) with Cu Kα radiation (λ = 0.154056 nm), Scanning electron microscope (Carl-Zeiss MA 10 series machine at Sheda Science and Technology Complex Abuja, Nigeria) for the morphologies of the synthesized samples deposited on a carbon-coated grid for examination. Optical absorption spectra of the nanoparticles samples dispersed in ethanol were recorded at room temperature using a UV-Visible spectroscopy (JENWAY 6405 at Federal University Lafia, Nasarawa State Nigeria) and Fourier Transform Infrared spectroscopy between the range of $400 - 4000cm^{-1}$ were recorded (Shimadzu-IR 8400s at the National Research Institute of Chemical Technology, Zaria, Kaduna State, Nigeria)to verify the presence of capping agents.

RESULTS AND DISCUSSION

The result presented in Fig.1 shows that the XRD pattern of the samples ZnS, ZnS:CMC and $ZnS:SiO_2$ nanoparticle has a zinc blende (cubic) crystal structure respectively.

The spectrum as deployed in Fig.1 shows that the diffraction peaks at about 2θ values were

$$32.07^0, 51.96^0, 60.54^0(ZnS), 27.0^0, 51.72^0, 59.86^0(ZnS:CMC) and 26.25^0, 49.08^0 58.54^0(ZnS:SiO_2)$$

whose corresponding diffraction planes are (111), (220) and (311). It is clear from Fig.1 that there are three major diffraction peaks. The highest intensity reflection peak is at about 27.0○ for capped samples (ZnS:CMC , $ZnS:SiO_2$)with two other small intensity peaks at $51.72^0, 59.86^0$ and $49.08^0 58.54^0$ respectively indicating that [111] is the preferred direction and at 32.07^0 for the uncapped sample (ZnS).The broadening of the XRD peak confirms the formation of the ZnS nanocrystals at particle sizes regime of 7.61nm, 2.57nm and 1.58nm for ZnS, ZnS-CMC and $ZnS-SiO_2$ respectively as calculated from the full-width half-maximum(FWHMs) for specific diffraction peaks using the Williamson-Hall (W-H) analysis of Uniform Deformation Model (UDM) (Mote *et al.*, 2012) . However the nature of XRD pattern for the $ZnS-SiO_2$ sample may be associated with Ostwald ripening and phase transformations occurring concurrently during the poly-condensation reactions followed by gel transforms into a solid mass.

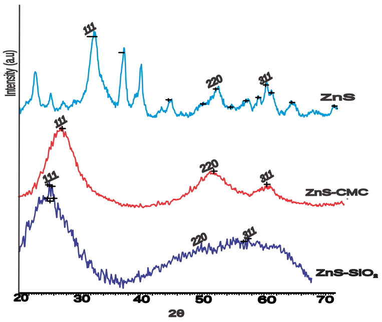

Fig.1. XRDpattern for (a)ZnS (b)ZnS:CMC and (c) $Zn:SiO_2$ nanoparticles

The information concerning the strain and the particle size were obtained from the full width at half maximum (FWHMs) of the three diffraction peaks. The FWHMs (*β*) can be expressed as a linear combination of the contributions from the strain (*ε*) and particle size (*D*)nm of the Scherrer's equation which are components for the formation of Williams Hall analysis for particle size and lattice strain with the following relation shown below

$$\beta_{hkl} = \frac{k\lambda}{D\cos\theta} + 4\varepsilon\tan\theta \qquad \text{..........................} (1)$$

$$\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + 4\varepsilon\sin\theta \qquad \text{..........................} (2)$$

Equation (1) represents the Uniform Deformation Model (UDM) of Williamson-Hall equation for strain analysis whose plot separates the contribution due to strain (ε) and crystallite size (D) towards the line broadening.

The result in Fig.2 below represent the plot of $\beta_{hkl}\cos\theta$ verse $4\sin\theta$ whose amount of strain is the slope of the linear fit and calculated cry(ε)llite size from the intercept on $\beta_{hkl}\cos\theta$ axis.

(ε)

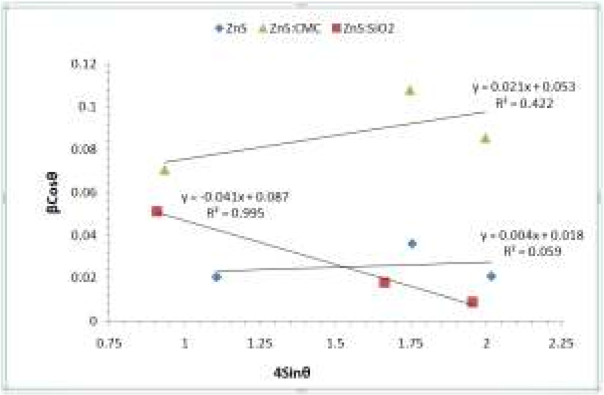

Fig.2. Williamson-Hall plots of powdered XRD data of ZnS,ZnS:CMC andZnS:SiO_2

Table 1. Lattice parameter, structure, energy band gap, particle sizes and the strain values

Sample	2θ	hkl	d_{hkl} Å	Lattice Constant Å	Structure	Energy band gap (eV)	Williamson-Hall method (UDM) Particle Size (nm)	Strain (ε)
ZnS	32.07	111	2.7886	4.8299	cubic			
	51.96	220	1.7584	4.9735		3.60	7.61	0.0011
	60.54	311	1.5281	5.0681				
ZnS:CMC	27.00	111	3.3002	5.7161	cubic			
	51.72	220	1.7662	4.9955		3.73	2.57	0.0055
	59.66	311	1.5439	5.1205				
$ZnS:SiO_2$	26.25	111	3.3925	5.8759	cubic			
	49.08	220	1.8547	5.2458		5.00	1.58	0.0105
	58.54	311	1.5755	5.2253				

The results presented in Table 1, show that the particles sizes obtained using Williamson-Hall Uniform Deformation Model (UDM) confirmed changes in particle sizes due to capping effect. Also the calculated values of the strain induced on the nanoparticles were directly proportional to the energy band gap and inversely proportional to the nanoparticle sizes. In comparison, it is observed that $ZnS:SiO_2$ has the smallest particle size, high induced strain and the largest energy band gap which indicates an excellent combination for tuning optoelectronic properties.

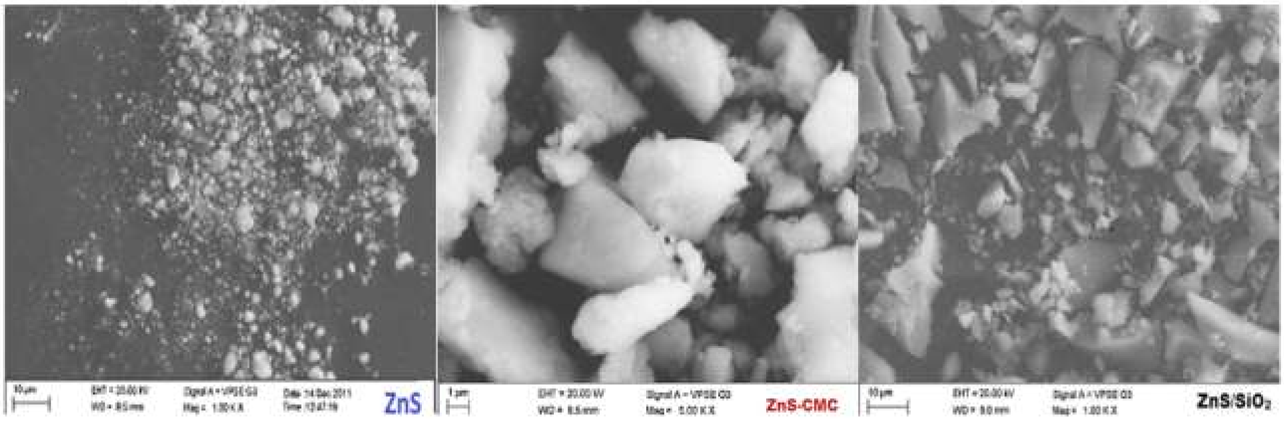

Fig.3. SEM micrograph of ZnS, ZnS:CMC and ZnS:SiO$_2$

The results in Fig.3 shows the SEM micrographs of the organic and inorganic capped ZnS nanoparticles synthesized in this work. The morphology of the nanoparticles depends on the capping agent used such that the ZnS sample has a rough surface texture while that of ZnS:CMC and ZnS:SiO$_2$revealed smooth surfaces confirming the presence of capping agent.

The optical absorption spectra of the synthesized nanoparticles samples (ZnS, ZnS:CMC and ZnS:SiO$_2$) using the measurement from UV-vis spectroscopy are shown in Fig. 4a, withthe absorption wavelengths ranging from 220-308nm. It was observed that at the same concentration of the capping agents the sample peak of (ZnS:SiO$_2$) shifted towards a low value 220nm wavelength(nm) compared to other sample.

The plot of the square of the absorption coefficient $(\alpha hv)^2$ verses energy (hv) for determining the energy band gap for all samples are presented in Fig.b4. The energy band gaps of the samples were estimated by extrapolating the straight-line portion of the spectrum to a zero absorption coefficient using the Tauc's relation of (equation 3)for direct band gap semiconductor (Ahemen *et al*, 2013).

$$(\alpha hv)^2 = (hv - E_g) \quad \text{.......................................} (3)$$

The observed blue shift in the absorption edge is a reflection of the band gap increase owing to quantum confinement effect which can be associated to decrease in particle sizes at nanosize regime. The obtained optical band gap corresponding to the absorption edge for ZnS,ZnS:CMC and ZnS:SiO$_2$ samples were 3.60eV, 3.73eV and 5.00eV respectively as shown in Fig. 4(b). The band gap values of0.13eV and 1.40eV were suggested to be as a result of blue shifted for ZnS:CMC and ZnS:SiO$_2$ samples as compared to the uncapped ZnS sample of energy band gap blue shifted at of 0.00eV (Murali-Krishna *et al.*, 2010). These results also indicate that at the same molar concentration, the capping ligands determine the actual value of electronic and optical properties of the nanoparticles.

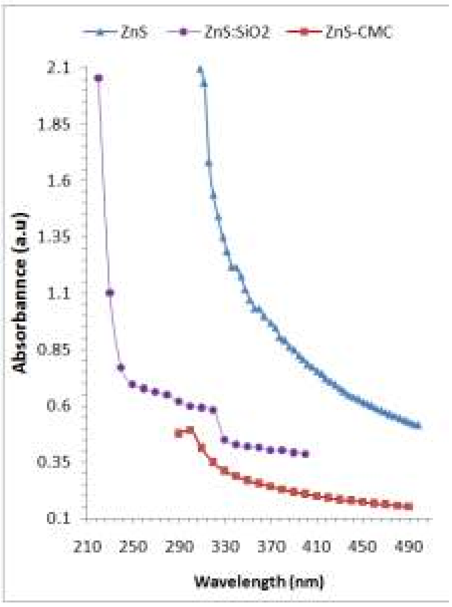

Fig. 4a: Optical Absorbance of ZnS, ZnS:CMC, ZnS:SiO$_2$ nanoparticles

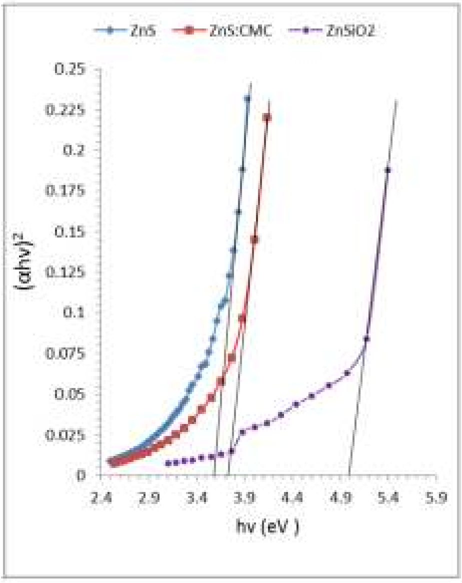

Fig.4b: Energy band-gap for ZnS, ZnS:CMC and ZnS:SiO$_2$

The characteristic absorption peak of the capping agent from FTIR confirmed the effective surface passivation of the nanoparticle in figures 5(a-b) for the capped samples only.

The result in Fig.5a reveals the spectra of capped ZnS:CMC with an associated band belonging to carboxylic groups shifted to a higher wavenumber of 1615.44cm^{-1} for C=O stretching and 1474.63cm^{-1}for C-O stretching. This may linked to their strong interaction with the Zn^{2+} ions forming a Zn–CMC complex during the in situ precipitation process.Fig.5b depicts the spectra of ZnS:SiO$_2$ nanoparticles with bending vibration mode at 1678.13cm^{-1} indicating C=O stretching and C-H out of plane bending at 942.26.cm^{-1} .The peak at 1383.01cm^{-1}may be due to -Si-C_6H_5 stretching.

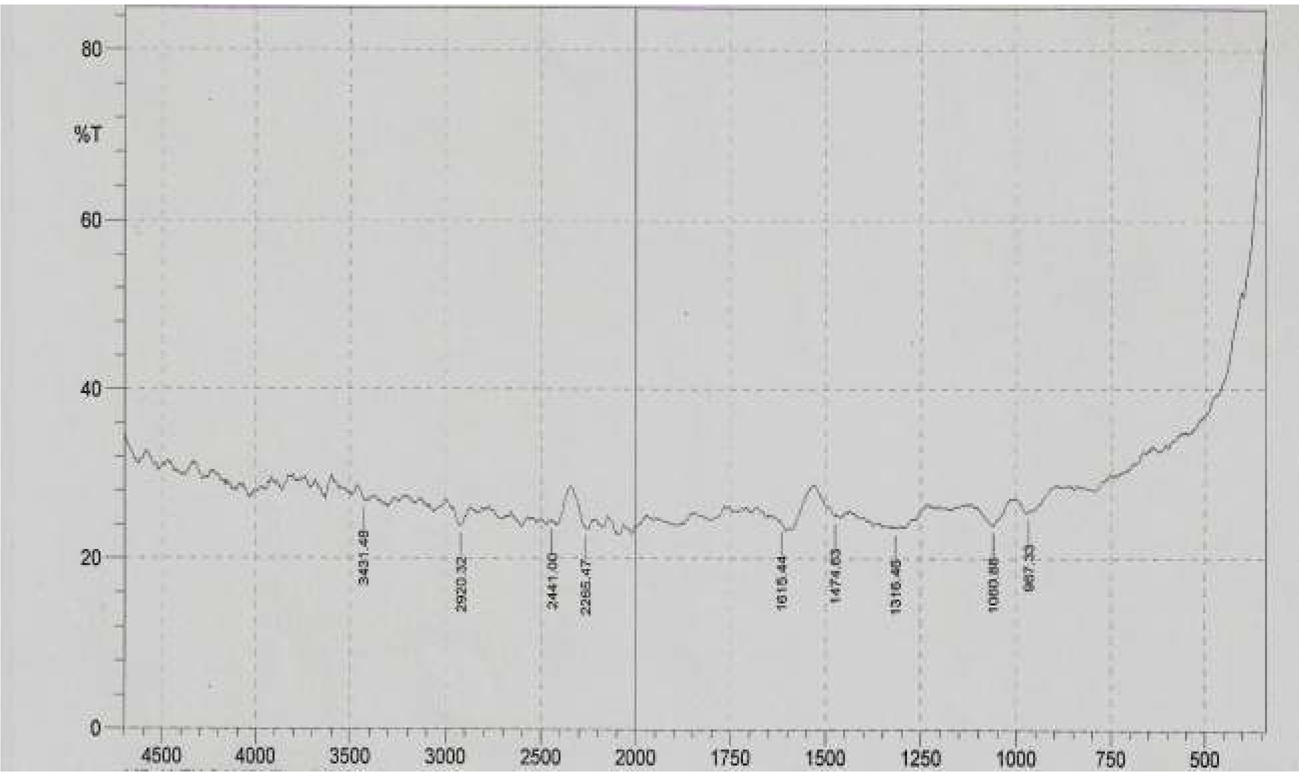

Fig. 5a: FTIR spectrum of ZnS/CMC

Wave number (cm^{-1})

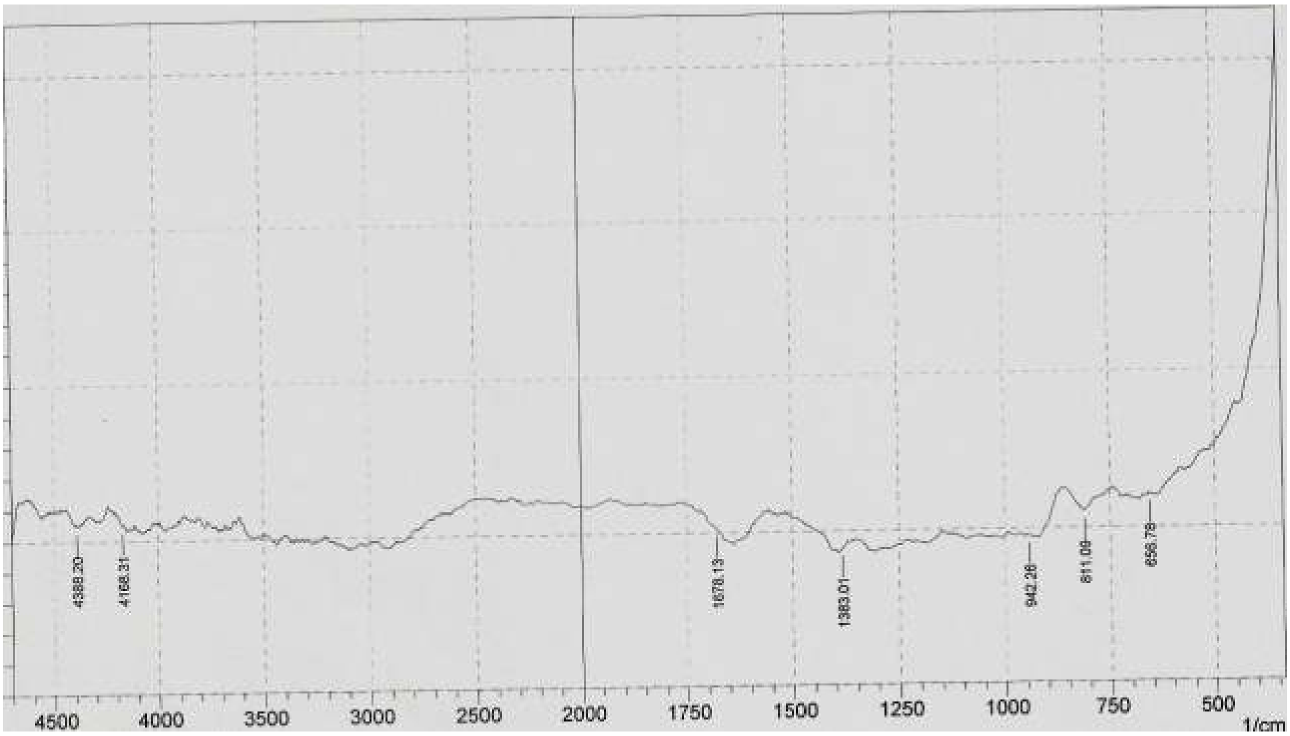

Fig.5b FTIR spectrum of ZnS:SiO$_2$

Wave number (cm^{-1})

CONCLUSION

The studies have revealed that organic and inorganic capping agents prevented particle agglomeration through its adsorption on the surface of nanoparticles. The particle sizes calculated from Uniform Deformation Model (UDM) are in range of 1.58nm to 2.57nm for the capped samples to that of 7.61nm for uncapped ZnS.The obtain energy band gaps shows a blue shift of 0.13eV to 1.40eV as compared to the absorption energy of the bulk ZnS. This suggests the importance of capping agents in determining the actual value of electronic and optical properties of nanoparticlesduring nucleation and limiting the growth of the ZnS particles. In addition the values of crystallite sizes obtained are in good agreement with the values obtained for the energy band gap indicating the presence quantum confinement. In comparison it can be noted that the high strain value caused decrease in particle sizes evaluated which confirms the presence and good effect of capping agents.

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