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# Synthesis and characterization of nanocrystalline zinc sulfide via zinc thiobenzoate-lutidine single-source precursor

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#### ABSTRACT

ZnS nanocrystals were prepared both in the form of mesoporous powder and thin films by one step thermal decomposition technique from a single-source procure (SSP) [Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O]. The final product was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), N<sub>2</sub> adsorption–desorption isotherm, UV–Vis absorption spectroscopy and photoluminescence (PL) study. Structural analyses of the prepared ZnS revealed the formation of cubic crystallites with diameters around 5 and 10 nm for the thin films and powder materials, respectively. On the other hand, the powder form showed mesoporous nature (type IV isotherm) with an average pore diameter of 37.9 Å and BET specific surface area of 51.73 m<sup>2</sup>/g.

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# 1. Introduction

During the past decade, "small-particle" research has become quite popular in various fields of chemistry and physics. The "small-particles", now being called nanostructured materials, are interesting both for scientific reasons and practical applications [1,2]. Nanostructured semiconductor materials of various shapes and sizes (triangles, rods, cubes, arrows and tetrapods) [3,4] have been successfully synthesized and extensively studied due to their unique properties that are different from those observed in their spherical counterparts [5–7]. Moreover, nanoparticles having mesoporous nanostructures have higher surface to volume ratio, higher chemical activity and better stability compared with the same size nanoparticles.

ZnS nanoparticles, an important II–VI compound semiconductor with a large band gap, have been extensively investigated as it has numerous applications to its credit. It is used as a key material for light-emitting diodes, cathode-ray tubes, thin film electroluminescence, reflector, dielectric filter, chemical/biological sensors, photocatalyst and window layers in photovoltaic cells [8–14]. In recent years, ZnS nanocrystals (NCs) have been extensively studied and are reported to have potential as photocatalyst in environmental contaminant elimination, CO<sub>2</sub> reduction, and H<sub>2</sub> evolution [15– 19]. Many synthetic methods have been employed to prepare ZnS nanocrystals like sol–gel process [20], sonochemical preparation [21], microwave heating [22], hydrothermal or solvothermal route [23,24], template method [25], reverse micelle [26], chemical vapor deposition [27,28], chemical bath deposition [29,30], thermolysis of single-source precursor (SSP) [31–34] etc.

The use of SSP can potentially provide several advantages over the other routes. For example, the existence of preformed bonds can lead to a material with fewer defects and/or better stoichiometry. It is possible to carry out the deposition with relatively simple installations. Another advantage is the air stability of the SSP, which renders easier handling and characterization. For this reason, there is an increasing interest for the synthesis of ZnS nanoparticles through the SSP route. Mu et al. deposited cubic ZnS nanocrystals through a self-assembled thin film precursor route at relatively low temperature [32]. It has been found by Lan et al. [33] that when the precursor was heated in NaCl flux, cubic ZnS nanocrystals were transformed to hexagonal morphology. Hampden-Smith and co-workers and Vittal et al. prepared different types of ZnS nanocrystals from SSP using thiocarboxylate complexes of zinc [34-37]. Researchers also used dimethylthiophosphinates [38], [Zn(S<sub>2</sub>P<sup>i</sup>Bu<sub>2</sub>)<sub>2</sub>]<sub>2</sub> [39] and dialkyldithiocarbamato metal complexes with general formula [Zn(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>] (symmetrical) or  $[Zn(S_2CNR'R_2)_2]$  (unsymmetrical) (R = Me, Et or <sup>i</sup>Pr; R' = alkyl) [40–42] for the preparation of ZnS NCs. As a continuation



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of our studies in related system [43], this work describes the preparation and characterization of ZnS nanoparticles both in the form of thin film and mesoporous powder using  $Zn(SOCPh)_2Lut_2 \cdot H_2O$  as the SSP.

## 2. Experimental

## 2.1. Commercial chemicals

All the materials  $[ZnCO_3, Zn(OH)_2 \cdot 2H_2O]$  (Qualigens), 3,5dimethylpyridine/lutidine (C<sub>7</sub>H<sub>9</sub>N, Lut) (Aldrich, 98+%), thiobenzoic acid (C<sub>7</sub>H<sub>6</sub>OS, PhCOSH) (Aldrich, 90%) and toluene (Rankem, 99.0%) were purchased commercially and used as received.

#### 2.2. Synthesis of $Zn(SOCPh)_2Lut_2 \cdot H_2O$ complex

Zinc carbonate basic  $[ZnCO_3, Zn(OH)_2 \cdot 2H_2O]$  (1.0 g, 3.8 mmol), 3,5-lutidine (0.814 g, 7.6 mmol), and 20 ml of toluene were combined in a round-bottomed flask. Thiobenzoic acid (1.05 g, 7.6 mmol) was dropped into the mixture while stirring rapidly, and the stirring was continued for 2 h at room temperature. As the reaction proceeded,  $CO_2$  bubble formation was observed, and the resulting pale yellow solution became canary yellow. The insoluble part was removed by filtration and the solvent was removed under reduced pressure. The resulting light yellow material was re-dissolved in toluene and filtered to remove any insoluble materials and then kept for slow evaporation. A crystalline solid was collected by filtration. Yield: ~1. 55 gm (70.5% yield based on zinc carbonate).

## 2.3. Experimental data

Anal. Calc. for  $C_{28}H_{30}N_2O_3S_2Zn$ : C, 58.79; H, 5.29; N, 4.90. Found: C, 58.70; H, 5.20; N, 4.89%. FT-IR (cm<sup>-1</sup>): 3452 (br), 3055 (w), 2921 (w), 1602 (s), 1569 (s), 1444 (m), 1382 (w), 1305 (w), 1199 (s), 1170 (s), 1151 (m), 1041 (w), 919 (s), 867 (w), 769 (m), 692 (s), 651 (m), 541 (w), UV-Vis [Toluene,  $\lambda_{max}/nm (\epsilon/M^{-1} cm^{-1})]$ : 288 (12,090), 300 (10,400). Thermogravimetric analysis: the sample of Zn(SOC-Ph)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O complex decomposed between 100 and 550 °C with 16.8 wt.% remaining, (MW(ZnS)/MW(Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O) × 100 = 17.03%. The inorganic residue in the TGA pan was identified as sphalerite ZnS by powder X-ray diffraction. Crystal data: triclinic, space group  $P\bar{1}$ ; a = 10.273(5)Å, b = 11.733(5)Å, c = 12.130(5)Å;  $\alpha = 11.037(5)^\circ$ ,  $\beta = 98.584(5)^\circ$ ,  $\gamma = 92.566(5)^\circ$ ; V = 1341.6(10)Å<sup>3</sup>;  $\rho = 1.411$  g/cm<sup>3</sup>;  $R_1^a = 0.0327$ ;  $wR_2^b = 0.0915$  [ $I > 2\sigma(I)$ ] for 329 parameters and 5574 data.

#### 2.4. Preparation of ZnS nanoparticles from metal precursor

To prepare mesoporous ZnS, the metal precursor complex  $Zn(SOCPh)_2Lut_2 \cdot H_2O$  (880 mg, 1.59 mmol) was taken in a molybdenum boat and heated at 600 °C for 15 min in an argon atmosphere, using a quartz tube furnace. After annealing, the precursor yielded about 131 mg of the metal sulfide.

In order to prepare the thin films of ZnS, a saturated solution of the metal precursor complex in toluene (99%) was made and about five drops of the solution were taken over a properly cleaned transparent conducting oxide (TCO) coated glass substrate of area 2.5 cm  $\times$  1 cm. This was then dried in air for about 15–20 min to obtain a uniform coating of the precursor on the TCO substrate. On annealing in argon atmosphere at 600 °C for 15 min, this coating gets converted into a thin film of ZnS with an average thickness of about 0.5  $\mu$ m (as obtained from cross-sectional SEM, inset of Fig. 5b).

#### 2.5. Physical measurements

Metal thiobenzoate complex we have prepared was typically characterized by carbon, hydrogen, and nitrogen (CHN) elemental analyses (Perkin-Elmer 2400II), Fourier transform infra red (FTIR) spectroscopy (JASCO FTIR-460 Plus), UV-Vis transmission spectroscopy (JASCO V-530), single-crystal X-ray diffraction for structural analysis (Bruker-AXS SMART APEX II) and thermogravimetric analysis (TGA, Perkin-Elmer USA Diamond-200). The TGA experiment was carried out by heating the sample from 25 to 600 °C at a rate of 10 °C/min under dinitrogen purge. The crystalline structure of the metal sulfide species, obtained after annealing (in Argon atmosphere at 600 °C for 15 min), were characterized by X-ray diffraction (XRD) technique (X'pert Pro MPD diffractometer, PANalytical, Almelo, The Netherlands); operating at 40 kV and 30 mA using Ni-filtered Cu K $\alpha$  X-radiation ( $\lambda$  = 1.540598 Å) with X'celerator step size  $2\theta = 0.05^\circ$ , step time 0.5 s, from  $10^\circ$  to  $80^\circ$ . The UV-Vis absorption and transmittance spectra of the ZnS thin film were measured using a JASCO V-530 spectrophotometer and the photoluminescence (PL) measurements were carried out using a PerkinElmer LS-55 fluoremeter, with an excitation wavelength of 325 nm. The surface morphology of the deposited films and the powder material was obtained by field emission scanning electron microscopy (FESEM) (Gemini Zeiss Supra<sup>™</sup> 35VP model; Carl Zeiss Microimaging GmbH, Berlin, Germany) using an accelerating voltage of 4.9 kV. N<sub>2</sub> adsorption-desorption isotherms were collected on a Quantachrome Instruments adsorption analyzer at 77 K. The degassing was done under vacuum and He was used to maintain the inert atmosphere at 300 °C.

#### 2.6. Single crystal X-ray diffraction data

Crystallographic data for the Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O complex is summarized in Table 1. Crystals suitable for structure determinations of the molecule were obtained from crystal tube by layering hexane over the compound solution in toluene. The crystals were mounted on glass fibers using perfluoropolyether oil. Intensity data were collected on a Bruker-AXS SMART APEX II diffractometer at 100(2) K using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å). The data were processed with SAINT, and absorption corrections were made with SADABS [44]. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares methods based on  $F^2$  using SHELX-97 [45]. For the structure solutions and refinements, the SHELX-7L software package [46] was used. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at geometrically calculated positions with fixed thermal parameters.

#### 3. Results and discussion

#### 3.1. Synthesis

The complex  $Zn(SOCPh)_2Lut_2 \cdot H_2O$  was prepared by reacting zinc carbonate basic with, 3,5-lutidine and thiobenzoic acid in a ratio 1:2:2, where toluene was used as the solvent. The unreacted  $Zn(OH)_2$  and any insoluble materials were removed by filtration. The  $Zn(SOCPh)_2Lut_2 \cdot H_2O$  complex undergoes thiobenzilic anhydride elimination to form ZnS nanoparticles. The reaction scheme that may be involved in this process can be described as:

$$\begin{split} &ZnCO_3, Zn(OH)_2 \cdot 2H_2O + 3, 5\text{-Lut} + PhCOSH \rightarrow Zn(SOCPh)_2Lut_2 \\ &\rightarrow H_2OZn(SOCPh)_2Lut_2 \cdot H_2O\overrightarrow{\Delta}ZnS \end{split}$$

Similar precursor was also synthesized by us using 2,6dimethylpyridine instead of 3,5-dimethylpyridine, which give very

Table 1		
Summary	of crystallographic	data.

Empirical formula	C <sub>28</sub> H <sub>30</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> Zn
Formula weight	572.03
T (K)	100(2)
Crystal system, space group	triclinic, P1
a (Å)	10.273(5)
b (Å)	11.733(5)
c (Å)	12.130(5)
α (°)	111.037(5)
β (°)	98.584(5)
γ (°)	92.566(5)
V (Å <sup>3</sup> )	1341.6(10)
Z value, $D_{\text{calc}}$ (Mg m <sup>-3</sup> )	2, 1.416
$\mu (\mathrm{mm}^{-1})$	1.103
F (000)	596
Crystal size (mm <sup>3</sup> )	$0.16 \times 0.20 \times 0.32$
Number of data/restraints/parameters	5970, 0, 329
Number of reflections $[I > 2\sigma(I)]$	5574
Goodness-of-fit (GOF) on F <sup>2</sup>	1.045
Final R indices $[I > 2\sigma(I)]$	$R_1^a = 0.0327, wR_2^b = 0.0915$
R indices (all data)	$R_1^a = 0.0350, wR_2^b = 0.0939$

$$\begin{split} R_1(F) &= \sum |F_{\rm o}| - |F_{\rm c}| | / \sum |F_{\rm o}|, \\ w R_2(F^2) &= [w (F_{\rm o}^2 - F_{\rm c}^2)^2 / \sum w (F_{\rm o}^2)^2]^{1/2}. \end{split}$$

low yield (2-5% based on zinc carbonate) and hence the results are not reported.

The infrared spectra for the crystalline Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>:H<sub>2</sub>O sample showed the presence of band at 1602  $\text{cm}^{-1}$  which was assigned to uncoordinated v(C=O) in thiobenzoate carbonyls, the v(C=N) band was found at 1569 cm<sup>-1</sup> and the v(C-S) band was observed at 919 cm<sup>-1</sup>, consistent with coordinated v(C–S). All C, H and N elemental analyses agreed with the calculated values for the proposed empirical formulae within the experimental error.

## 3.2. Solid-state structures of the precursor $[Zn(SOCPh)_2Lut_2 H_2O]$

The molecular structures of the Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O molecule determined by single-crystal X-ray diffraction technique are shown in Figs. 1 and 2. The molecule crystallizes in a triclinic crys-



Fig. 2. An ellipsoid diagram of the unit cell, in which two Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O molecules are bonded through hydrogen bond.

tal system with P-1 space group. In a unit cell two water molecules are present as water of crystallization as shown in Fig. 2. The two complex units [Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>] are attached through H-bonds between one of the carbonyl O atom of thiobenzoate group with two water molecules. The O-H bond distances are different, i.e., 3.024 and 2.688 Å, respectively. Two nitrogen atoms from lutidine and two sulfur atoms from thiobenzoate ligands are bonded to the central metal ion to provide a distorted tetrahedron ZnN<sub>2</sub>S<sub>2</sub> coordination environment around the central metal ion. The relevant bond lengths (Å) and angles (°) are shown in Table 2. The geometry around the metal is somewhat similar to the monomers, Zn(SOC-CH<sub>3</sub>)<sub>2</sub>Lut<sub>2</sub> and Zn(SOC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>Lut<sub>2</sub> reported by Hampden-Smith and co-workers [34]. Two Zn-N bond lengths are 2.070 and 2.042 Å, where as two Zn-S bond lengths are 2.329 and 2.297 Å, respectively. The difference in the two Zn-S (0.032 Å) and two Zn-N (0.028 Å) bond lengths are more than that obtained by Hampden-Smith and co-workers, who have used thioacetic acid (Zn-S, 0.003 Å, and Zn-N, 0.004 Å), and thiopivalic acid (Zn-S,



Fig. 1. An ORTEP diagram of Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O complex with 50% probability thermal ellipsoid and the numbering scheme. The hydrogen atoms are omitted for clarity.

Table 2 Relevant bond lengths (Å) and angles (°) of  $Zn(SOCPh)_2Lut_2 \cdot H_2O$  complex.

Bond lengths		Bond angles	
Zn-S(1)	2.329(12)	S(1)-Zn-S(2)	113.74(2)
Zn-S(2) Zn-N(1)	2.297(12) 2.070(18)	S(2)-Zn-N(1)	1102.11(5)
Zn-N(2)	2.042(2)	S(1)-Zn-N(2)	110.87(5)
S(1) - C(21) S(2) - C(28)	1.761(2)	S(2) - 2n - N(2) N(1) - 2n - N(2)	112.19(5) 106.58(6)
O(1)-C(21) O(2)-C(28)	1.220(2) 1.233(2)	$I(1) \Sigma II = I(2)$	100.56(0)

0.019 Å, and Zn–N, 0.012 Å) as complexing agents. This is probably due to the presence of two phenyl rings which influence the geometrical distortion in Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O compared to thioacetate and thiopivalate complexes. The steric hindrance of bulky thiocarboxylates, thiobenzoate and thiopivalte is also reflected in the bond angles of their complexes. The difference between maximum and minimum bond angles of thiobenzoate, thiopivalate and thioacetate are 11.63°, 19.0° and 6.1°, respectively. The minimum difference of bond angles (6.1°) of thioacetate complex indicates more regular geometry due to presence of methyl group.

#### 3.3. TGA-DTG studies of Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O complex

The curves obtained from the thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis for Zn(SOC-Ph)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O complex are shown in Fig. 3. The compound was found to decompose between 100 and 550 °C following several steps, resulting in the formation of metal sulfide (calc. wt.% = 17.03, Found wt.% = 16.8). This fact was also supported by the powder X-ray diffraction pattern of the residue obtained from the TGA pan, where the peaks correspond to only ZnS were obtained and no peaks for the metal oxide (ZnO) were present. The curve showed four pronounced weight loss steps, which was also supported by the DTG maxima. The first weight loss (9.27%) between 70 and 160 °C corresponds to the loss of one lutidine group (calc. wt.% = 9.37). The major weight loss in the second step is observed in the temperature range of 160-250 °C, which matched with the elimination of two S(OCPh)<sub>2</sub> groups and one lutidine group, having calculated and measured weight losses of 51.7% and 52.43 %, respectively. The decomposition in the temperature range between 250 and 330 °C in the third step has been found to be 18.1%, which is very close to the loss of two remaining luti-



Fig. 3. TGA-DTG curve of the Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O complex.

dine groups (calc. wt.% = 18.74). In the final step, weight loss is observed in the temperature range between 330 and 550 °C, which matched well with the elimination of two water molecules by the formation of 2ZnS, with calculated and measured weight losses of 3.15% and 3.4%, respectively. The possible chemical transformation schemes for the thermal decomposition of Zn(SOC-Ph)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O are presented below:

$2[Zn(SOCPh)_2Lut_2 \cdot H_2O] \rightarrow 2[Zn(SOCPh)_2Lut_{1.5} \cdot H_2O] + Lut$	(1)
$2[Zn(SOCPh)_2Lut_{1.5} \cdot H_2O] \rightarrow 2[ZnSLut \cdot H_2O] + 2[S(OCPh)_2] + 1$	Lut(2)
$2[ZnSLut \cdot H_2O] \rightarrow 2[ZnS \cdot H_2O] + 2Lut$	(3)
$2[ZnS\cdot H_2O] \to 2ZnS + 2H_2O$	(4)

The formation of pure crystalline ZnS (as observed from the XRD analyses) in the solid-state thermal decomposition products of the  $Zn(SOCPh)_2Lut_2$ ·H<sub>2</sub>O, suggests that this is the logical precursor to the metal sulfide.

## 3.4. X-ray diffraction analysis

Fig. 4a and b represents the X-ray diffraction (XRD) pattern of the powder material and thin film, obtained after annealing the precursor complex, respectively. The patterns indicate the formation of sphalerite or cubic ZnS (JCPDS ID: 05-0566) with three major diffractions from the  $(1\ 1\ 1)$ ,  $(2\ 2\ 0)$  and  $(3\ 1\ 1)$  planes for both the powder and thin film. Some small diffractions from  $(2\ 0\ 0)$ ,  $(4\ 0\ 0)$  and  $(3\ 3\ 1)$  planes were also obtained, but the  $(4\ 0\ 0)$  peak was absent for the thin film. The high intensity of the peaks indicates high crystallinity of the formed material; however, the relative intensity of the diffraction peaks for thin film was lesser,



**Fig. 4.** X-ray diffraction pattern of the sphalerite ZnS (a) powder material and (b) thin film (the'\*'marked peaks are for the  $SnO_2$  of the TCO substrate).

since the thickness of the deposited film was very low (0.5 µm). On the other hand, the broadness of the diffraction peaks for both the systems indicates the formation of particles with very small dimension. Since, the produced ZnS particles were of regular shape/size, it is possible to calculate the crystallite size using the Debye–Scherrer equation ( $D = 0.9\lambda/(\beta \cos \theta)$ ), where, D is the crystallite size (diameter),  $\lambda$  is the wave length of X-ray, i.e., 1.540598 Å,  $\beta$  is the value of full width at half maximum of the most intense peak (after correcting the instrumental broadening), which is expressed in radians and  $\theta$  is the Bragg's angle. The calculated value of crystallite size was found to be around 5 and 10 nm for the thin film and powder systems, respectively.

## 3.5. FESEM image analyses

Fig. 5a and b shows the surface morphology obtained by FESEM for the powder and the thin film of ZnS, respectively. The powder material shows porous structure formed by the network of the interlinked or agglomerated ZnS crystals. Whereas, highly compact surface morphology composed of uniformly distributed spherical grains, is evident from the FESEM image of the ZnS thin film. The compactness of the film surface indicates that they could be used successfully in various optical and electrical devices. The average grain sizes, as obtained from the FESEM images were 10 and 20 nm for the thin film and the powder, respectively. It can be recalled that the crystallite sizes as derived from the XRD data analysis were 5 and 10 nm, respectively for the thin film and powder. It is evident that, for both the systems, the cubic crystallites coalesced together to form spherical grains with comparatively larger sizes, in order to lower the Gibb's free energy. The inset of Fig. 5b



Fig. 5. FESEM images of (a) powder ZnS nanoparticles and (b) thin film (inset: cross-sectional FESEM image).

represents the cross sectional view of the thin film deposited on TCO taking five drops of the saturated precursor solution. From this cross sectional image, the thickness of the film was determined, which was found to be about 0.5  $\mu$ m.

#### 3.6. N<sub>2</sub>-sorption studies

Typical nitrogen adsorption-desorption isotherms at 77 K for the powder ZnS material and the corresponding pore size distribution are shown in Fig. 6. The resulting isotherm could be identified as a Type IV isotherm, characteristic of the mesoporous materials (Fig 6a). The small hysteresis loop in the isotherm was generated due to the capillary condensation of the absorbate in the mesopores of the solid. This loop also indicates that the pores are accessible by the gas molecules without much hindrance. Similar isotherm for mesoporous ZnS nanoparticles was also observed by Rana et al. [47]. As calculated using the Barrett–Joyner–Halenda (BJH) method from the adsorption isotherm, the average pore diameter was found to be around 37.9 Å (Fig. 6b), whereas, the specific surface area for the sample was found to be 51.73 m<sup>2</sup>/g from the Brunauer–Emmett–Teller (BET) analysis.

# 3.7. Optical analyses

## 3.7.1. UV-Vis studies

Optical study (i.e., UV–Vis absorption spectroscopy and PL) is one of the most important methods to reveal the energy structures



Fig. 6. (a)  $N_2$  adsorption-desorption isotherms for powder ZnS and (b) the corresponding pore size distribution curve.



**Fig. 7.** UV-Vis absorption (plot a), transmittance (plot b) specrua and in inset  $(\alpha hv)^2$  vs. *hv* plot for ZnS thin film.

of semiconducting materials. Fig. 7 is the UV-Vis absorption and transmittance spectra and in inset the Tauc plot  $[(\alpha hv)^2$  versus hv] for the ZnS thin film is given. The UV–Vis absorption spectrum (Fig. 7a) showed an onset of absorption at  $\sim$ 350 nm and the transmittance spectrum (Fig. 7b) showed 80-90% transmittance in the wavelength range of 370-550 nm. The band gap energy was calculated using the Tauc's relation  $[(\alpha hv)^{1/n} = A(hv - E_g)]$  [48], where, hv is the incident photon energy, 'A' is a constant and 'n' is the exponent the value of which is determined by the type of electronic transition causing the absorption and can take the values 1/2 or 2 depending upon whether the transition is direct or indirect, respectively. Since, ZnS is well established as a direct band gap semiconductor [48], we can evaluate the value of  $E_{g}$ , from the intercept of the straight line at  $\alpha = 0$  from the plot of  $(\alpha h v)^2$  versus hv. From the Tauc plot (inset of Fig. 7) the value of  $E_g$  for the deposited ZnS films was found to be about 3.58 eV. Bandgap energy in the similar range was also observed by Rana et al. [47] for their mesoporous ZnS.

## 3.7.2. Photoluminescence (PL) studies

ZnS is well known for its photoluminescence properties. The room temperature PL spectrum of the ZnS thin film on TCO substrate was measured with an excitation wavelength ( $\lambda_{exc}$ ) of 325 nm, which is shown in Fig. 8. In general, both Schottky and Frenkel defects exist in all solids, but one type should be dominant



Fig. 8. Room temperature PL spectrum for ZnS thin film.

since their formation energies are normally unequal [49]. It is also established previously that, Schottky defects are dominant in cubic ZnS system [50]. Therefore, deep traps in cubic ZnS mainly involved internal  $Zn^{2+}$  and  $S^{2-}$  vacancies. From the PL spectrum, a strong and broad emission peak centered at 358 nm along with two weak emissions at ~450 and ~493 nm were observed. The peak centered at 358 nm is assigned to the band-to-band transition of ZnS and the emission at 450 nm may be attributed to the presence of sulfur vacancies in the lattice, which was also reported earlier by Manam et al. [48], Zhang et al. [51] and other researchers [52,53]. The very weak green emission at 493 nm might be due to the presence of trapped surface states in the ZnS lattice [54,55].

#### 4. Conclusion

A new approach has been introduced to synthesize ZnS nanoparticles both in the form of powder and thin films, from a single-source precursor complex [Zn(SOCPh)<sub>2</sub>Lut<sub>2</sub>·H<sub>2</sub>O]. Both powder material and thin film were found to have cubic crystallites (5 and 10 nm crystal diameter, respectively) which coalesced to form spherical grains (10 and 20 nm grain diameter, respectively). The homogeneity in the surface morphology for the deposited films was also evident from its FESEM images. For the powdered material, BET analysis showed that the specific surface area was 51.73 m<sup>2</sup>/g, whereas, from the pore size distribution curve, mesoporous nature of the material was established. The percentage transmittance (80–90%) of ZnS thin film was high, indicating their probable potential applications as solar cell window material.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.093.

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