

A facile synthesis of ZnS nanocrystallites by pyrolysis of single molecule precursors, Zn (cinnamtscz)₂ and ZnCl₂ (cinnamtsczH)₂

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Abstract. ZnS nanocrystallites were synthesised by pyrolysis method using Zn (cinnamtscz)₂ and ZnCl₂ (cinnamtsczH)₂ (cinnamtsczH = cinnamaldehyde thiosemicarbazone) as single source precursors. The prepared ZnS nanocrystallites were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction, UV-Vis and fluorescence spectroscopy. The peak broadening in XRD and emission at shorter wavelength in fluorescence spectra showed the presence of nanocrystallites. The blue shift in UV-Vis absorption spectroscopy also proved the formation of nanocrystallites. TEM images show presence of plate-like and spherical ZnS nanoparticles obtained from Zn(cinnamtscz)₂ and ZnCl₂ (cinnamtsczH)₂ respectively.

Keywords. Nanocrystallites; zinc sulphide; thiosemicarbazones.

1. Introduction

ZnS exists in two phases, i.e. cubic phase (sphalerite) and hexagonal phase (wurtzite). It is an important direct wide-band gap (3.68 eV) semiconductor. Due to wide band gap it is useful in optoelectronics (Johnson *et al* 2002), sensors (Ding *et al* 2004), etc. Zinc sulphide has been extensively studied because of its important physical and chemical properties and applications in thin film electroluminescent devices (Chen and Lockwood 2002), flat-panel displays, infrared windows and lasers (Bredol and Merichi 1998; Wang *et al* 2005). It is used as phosphor (Calandra *et al* 1999) and for storage of solar energy (Baojun *et al* 2000). In recent years nanostructure doped ZnS materials have attracted considerable attention because of their good luminescence characteristics as compared to bulk ZnS (Bhargava and Gallagher 1994; Yu *et al* 2005).

Various forms of ZnS nanostructures have been prepared due to their potential applications. Thus, synthesis of ZnS nanorods (Li and Alivisatos 2003), nanowires (Xiong *et al* 2004), nanotubes (Zhu *et al* 2003) and nanobelts (Pan *et al* 2001) have been reported. Several synthesis methods such as solvothermal decomposition (Ghoshal *et al* 2007; Kedarnath *et al* 2007), microwave synthesis (Panda *et al* 2006), solution route (Zhang *et al* 2004), colloidal synthesis (Lu *et al* 2003), pyrolysis in furnace (Ghoshal *et al* 2007; Kedarnath *et al* 2007), hydrothermal method (Liu *et al* 2005), etc., have been used for preparation of these materials. Usually a high decomposition tempe-

perature is required to get ZnS. For example, Sun *et al* have reported the preparation of ZnS nanocrystallites above 750°C (Sun *et al* 2007). In the present investigation, ZnS nanocrystallites were prepared using Zn(cinnamtscz)₂ and ZnCl₂(cinnamtsczH)₂ (where cinnamtsczH = cinnamaldehydethiosemicarbazone) as single source precursors by pyrolysis method at temperatures as low as 515°C. This single source approach is very convenient. The ZnS nanocrystallites obtained were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), absorption and photoluminescence (PL) spectroscopy.

2. Experimental

2.1 Synthesis of precursors

The precursors were prepared as follows.

2.1a *Preparation of Zn (cinnamtscz)₂ (I)*: 97.1 mg (2.02 mmol) sodium hydride was added to 20 ml isopropanol in a two necked round bottom flask. The reaction mixture was stirred for half an hour to get a clear solution of sodium isopropoxide. To this 83.1 mg (4.04 mmol) of cinnamaldehydethiosemicarbazone dissolved in 10 ml tetrahydrofuran (THF) was added with constant stirring and was refluxed for 2 h. It was then cooled to room temperature and 27.6 mg (2.02 mmol) ZnCl₂ dissolved in 10 ml THF was added to it. The whole mixture was refluxed for 24 h with continuous stirring. The by-product (NaCl) obtained was filtered through G-4 filtration assembly. The solvent was evaporated in vacuo to get a yellow

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coloured solid. It was repeatedly washed with cyclohexane (5 × 5 ml) to remove any impurities present and then dried under vacuum (yield, 72.0 mg, 75.15%) m.p.: 215°C.

Elemental analysis (%) for $\text{ZnC}_{20}\text{H}_{20}\text{N}_6\text{S}_2$, found (calcd): Zn: 13.73 (13.80), C: 50.73 (50.70), H: 4.18 (4.25), N: 17.43 (17.73), S: 13.02 (13.51).

IR: 3455 cm^{-1} , 3281 cm^{-1} (ν_{NH_2} assym. and sym.), 1577 cm^{-1} ($\nu_{\text{C=N}}$ shifted to lower wavenumber after complexation), 1042 cm^{-1} , ($\nu_{\text{C=S}}$ shifted to lower wavenumber after complexation).

NMR (δ in ppm) ^1H : 7.09–8.28 (s, NH_2 ; m, $\text{C}_6\text{H}_5\text{-CH=CH-CH=N}$); ^{13}C : 173.79 ($\underline{\text{C=S}}$), 152.08 ($\underline{\text{CH=N}}$), 140.86, 136.14 ($\underline{\text{CH=CH}}$), 129.76, 129.52, 127.56, 124.08 (aromatic carbons).

2.1b Preparation of $\text{ZnCl}_2(\text{cinnamtsczH})_2$ (II): To a round bottom flask containing 72.2 mg (3.66 mmol) of cinnamaldehydethiosemicarbazone dissolved in 20 ml THF, 25 mg (1.83 mmol) ZnCl_2 in 10 ml THF was added with continuous stirring and stirring was continued for 36 h. The solvent was evaporated in vacuo, and a yellow solid obtained. It was repeatedly washed with cyclohexane (5 × 5 ml) to remove any impurities present and then dried under vacuum to get free solid. (yield, 89.21 mg, 89.03%) m.p.: 103°C.

Elemental analysis (%) for $\text{ZnC}_{20}\text{H}_{22}\text{N}_6\text{S}_2\text{Cl}_2$, found (calcd): Zn: 11.80 (11.95), C: 43.50 (43.92), H: 4.35 (4.05), N: 15.47 (15.36), S: 12.02 (11.72), Cl: 12.50 (12.96).

IR: 3406 cm^{-1} , 3277 cm^{-1} (ν_{NH_2} assym and sym), 3171 cm^{-1} (ν_{NH}), 1545 cm^{-1} ($\nu_{\text{C=N}}$ shifted to lower wavenumber after complexation), 1036 cm^{-1} , ($\nu_{\text{C=S}}$ shifted to lower wavenumber after complexation).

NMR (δ in ppm) ^1H : 6.84–8.15 (s, NH_2 ; m, $\text{C}_6\text{H}_5\text{-CH=CH-CH=N}$), 11.38 (s, NH); ^{13}C : 177.99 ($\underline{\text{C=S}}$), 145.21 ($\underline{\text{CH=N}}$), 139.35, 136.30 ($\underline{\text{CH=CH}}$), 129.34, 129.14, 127.37, 125.52 (aromatic carbons).

2.2 Synthesis of ZnS nanocrystallites

ZnS nanocrystallites were synthesized by pyrolysis method. In a typical experiment, 100 mg of precursor was taken in quartz boat which was then inserted to the center of a horizontal wall furnace. The furnace was then heated to 515°C at a heating rate of 25°C/min and then the temperature was held at 515°C for 2 h. The inert (N_2) atmosphere was maintained throughout the experiment. The furnace was then cooled to room temperature. The residue obtained in boat was characterized by XRD, TEM, SAED, UV-Vis and PL spectroscopy.

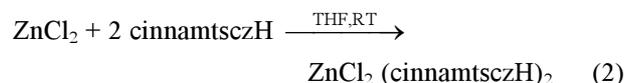
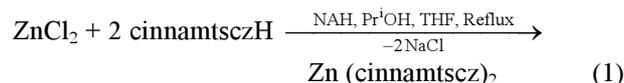
3. Instrumentation

The elemental analysis was carried on Thermo Finnigan, Italy Model FLASH EA 1112 Series elemental analyzer.

The infrared spectra were recorded as KBr pellets on a Perkin Elmer FT-IR spectrometer in 4000–400 cm^{-1} range. ^1H and ^{13}C NMR were recorded in 5 mm NMR tube in $\text{DMSO-}d_6$ on a Bruker Avance II 300 MHz NMR spectrometer. The ^1H and ^{13}C chemical shifts are relative to internal standard TMS. The absorption spectra were recorded on a UV-2401 PC Shimadzu UV-Vis spectrophotometer. The fluorescence spectra were recorded on a RF-5301 PC Shimadzu spectrofluorophotometer. XRD studies were carried out on a X'pert PRO PANalytical X-ray diffractometer (Philips) using $\text{CuK}\alpha$ radiation (1.54180 Å). TEM and SAED were performed on a PHILIPS, Model no-CM 200 with operating voltages 20–200 kV.

4. Results and discussion

The precursors were prepared by reacting ZnCl_2 with cinnamaldehyde thiosemicarbazone ligand (figure 1). A reaction between sodium salt of ligand and ZnCl_2 gave $\text{Zn}(\text{cinnamtscz})_2$ (I) with elimination of sodium chloride (1). Whereas simple addition reaction resulted in $\text{ZnCl}_2(\text{cinnamtsczH})_2$ complex (II) (2).



These complexes were characterized by elemental analysis, IR and NMR (^1H and ^{13}C) spectroscopy. In the IR spectra, the bands observed at 3455 cm^{-1} (I) and 3406 cm^{-1} (II) are assigned to ν_{NH_2} asymmetric stretching mode. Whereas bands observed at 3281 cm^{-1} (I) and 3277 cm^{-1} (II) are due to ν_{NH_2} symmetric stretching mode. The N–H stretching mode is observed at 3171 cm^{-1} in the IR spectrum of (II). This mode is absent in the spectrum of precursor (I) indicating deprotonation of the ligand in this complex. The bands due to $\nu_{\text{C=N}}$ and $\nu_{\text{C=S}}$ are observed at 1577 cm^{-1} and 1042 cm^{-1} for precursor (I) and 1545 cm^{-1} and 1036 cm^{-1} for precursor (II) respectively. These values are shifted to lower wavenumbers compared to those in the spectrum of free ligand.

In the ^1H NMR spectrum of precursor (II) signal due to proton of –NH group is observed at 11.38 ppm. This peak is absent in the spectrum of precursor (I) showing depro-

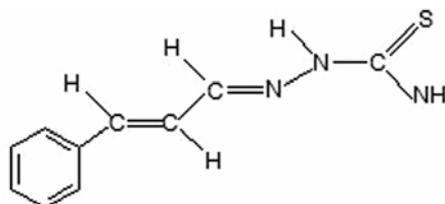


Figure 1. Structure of cinnamaldehyde thiosemicarbazone ligand.

tonation of –NH group during the reaction. These observations are consistent with ligand coordination through azomethine nitrogen and sulphur atoms (Samus *et al* 2006).

Thermal decomposition of these complexes was carried out at 515°C in furnace under nitrogen atmosphere. The black powders obtained were further characterized by powder XRD, TEM, SAED, absorption and PL spectra.

Figure 2 shows a typical XRD pattern of the ZnS nanoparticles obtained by pyrolysis of Zn (cinnamtszcz)₂ complex. All the diffraction peaks could be indexed to cubic phase (sphalerite) of ZnS (JCPDS: 77-2100). The presence of broad peaks in XRD implies presence of smaller particles. The average grain size (D) was calculated from Scherrer's formula (Sapra and Sarma 2005). The calculated average grain size using (111) diffraction

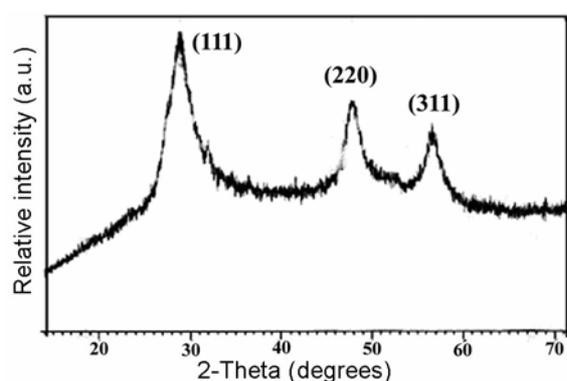


Figure 2. XRD pattern of cubic ZnS nanocrystallites (JCPDS: 77-2100) obtained from Zn(cinnamtszcz)₂.

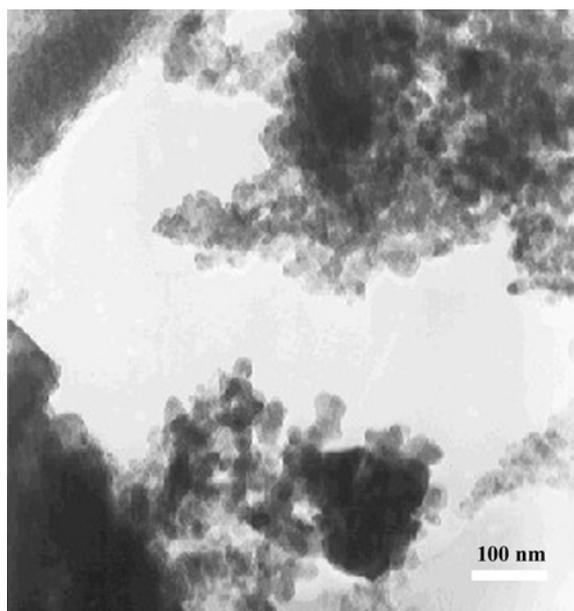


Figure 3. TEM image of ZnS nanocrystallites obtained by pyrolysis of Zn (cinnamtszcz)₂.

peak was 7.72 nm. Figures 3 and 4 show a TEM image and SAED pattern of the ZnS nanocrystals. Aggregated plate-like morphology can be seen in the TEM image. The particle size observed varies from 9 to 30 nm range. These values are slightly higher than the values calculated from XRD. The presence of rings in SAED pattern suggests formation of crystalline cubic ZnS.

Unlike Zn(cinnamtszcz)₂ which gave cubic phase of ZnS, ZnCl₂ (cinnamtszczH)₂ resulted in hexagonal phase (wurtzite) of ZnS on pyrolysis (JCPDS: 05-0492) (Figure 5). The preferred orientation is along (002) direction. The particle size calculated using Scherrer's formula is 23.45 nm. Figure 6 shows TEM image of the ZnS particles obtained from precursor (II). It shows presence of spherical particles with size ranging from 20–48 nm.

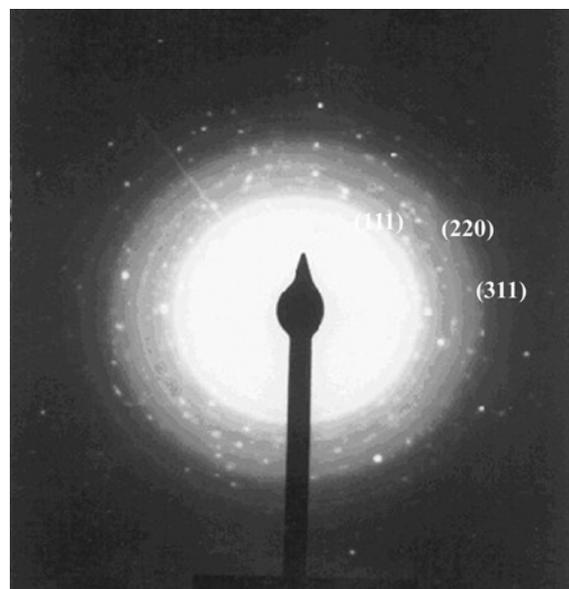


Figure 4. SAED pattern of ZnS nanocrystallites obtained by pyrolysis of Zn (cinnamtszcz)₂.

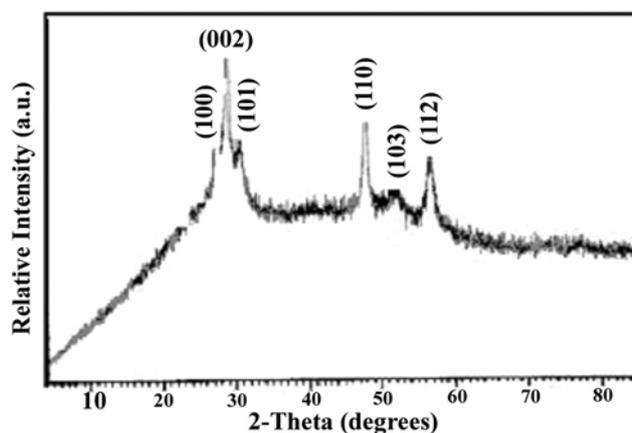


Figure 5. XRD pattern of hexagonal ZnS nanocrystallites (JCPDS:05-0492) obtained by pyrolysis of ZnCl₂ (cinnamtszczH)₂.

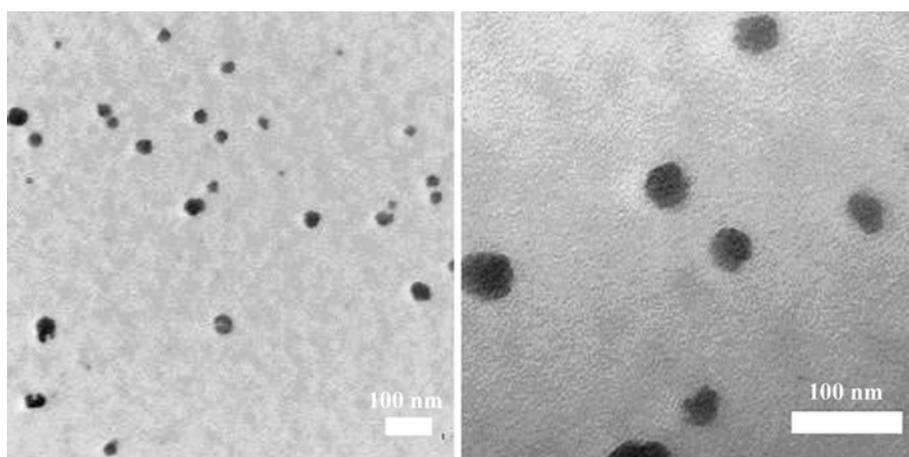


Figure 6. TEM images of ZnS nanocrystallites obtained by pyrolysis of ZnCl_2 (cinnamtsczH)₂.

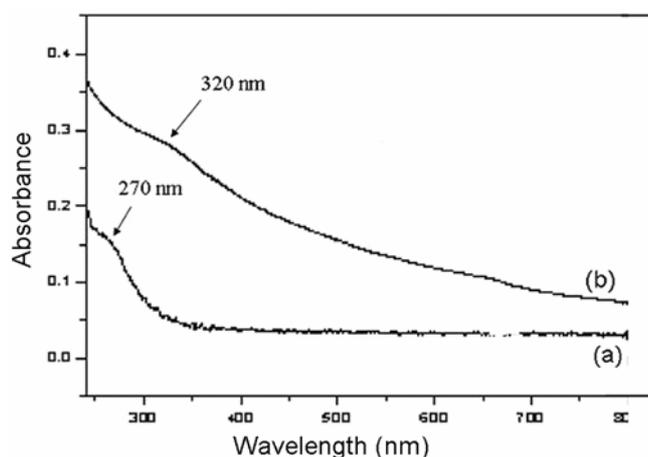


Figure 7. Absorption spectra of ZnS nanocrystallites dispersed in chloroform obtained by pyrolysis of (a) $\text{Zn}(\text{cinnamtscz})_2$ and (b) ZnCl_2 (cinnamtsczH)₂.

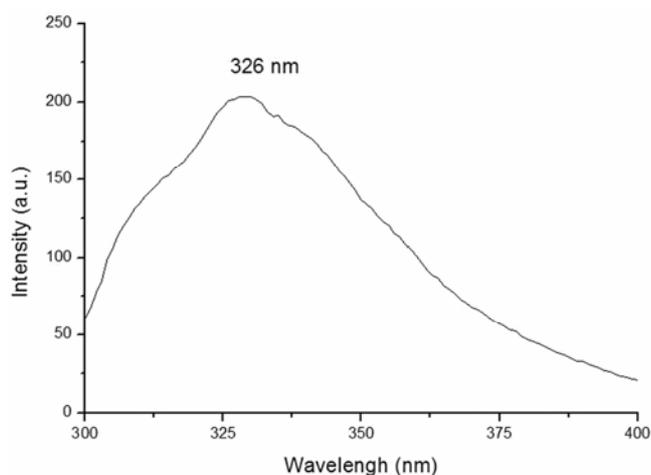


Figure 8. PL spectrum of ZnS nanocrystallites obtained by pyrolysis of $\text{Zn}(\text{cinnamtscz})_2$ dispersed in chloroform (excitation wavelength = 280 nm).

UV absorption spectra of ZnS nanocrystallites dispersed in chloroform are shown in figures 7a and b for materials obtained from (I) and (II) respectively. In the spectrum of ZnS obtained from $\text{Zn}(\text{cinnamtscz})_2$, an absorption band at 270 nm is observed which is blue shifted as compared to bulk ZnS which shows absorption band at 340 nm (Yu *et al* 2005). This indicates formation of smaller particles. In the spectrum of ZnS obtained from ZnCl_2 (cinnamtsczH)₂ an absorption band is observed at 320 nm. The blue shift in this case is less compared to ZnS obtained from (I). This suggests larger particle size of ZnS obtained from (II) compared to ZnS obtained from (I). These observations are consistent with the particle sizes obtained from XRD and TEM.

Figures 8 and 9 show PL spectra of ZnS nanocrystals obtained from precursor (I) and (II) respectively. In the former spectrum, fluorescence emission peak is observed at 326 nm, whereas in latter spectrum it is observed at 368 nm. In the above cases excitation wavelengths of 280 nm and 270 nm respectively were used.

Thus, using single-molecule approach we were successful to get phase pure ZnS nanocrystallites at much lower decomposition temperature. The preparations of ZnS reported in the literature utilize either drastic reaction conditions or high temperatures. For example, $\text{Zn}(\text{Cup})_2$ i.e. Zn (II) cupferron complex in presence of H_2S atmosphere gave ZnS nanocrystals (Saravanan *et al* 2004). Use of H_2S can be avoided using single source precursors. However, drastic reaction conditions are required. Thus, ZnS nanocrystallites using single source precursors such as $\text{Zn}(\text{S}_2\text{CNMe}(\text{C}_6\text{H}_{13})_2)_2$ i.e. *bis*[methyl (*n*-hexyl)di-thiocarbamato] (Ludolph *et al* 1998) and $\text{Zn}(\text{DDTC})_2$ i.e. (zinc diethyldithiocarbamate) in Teflon-lined stainless steel autoclave in solvent mixture ethanol and water (Zhang *et al* 2005) have been reported. Further preparation at temperature as high as 1200°C have been reported using thermal evaporation process (Fang *et al*

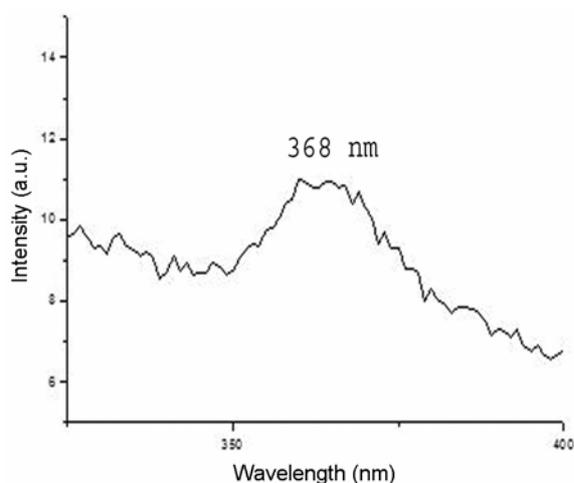


Figure 9. PL spectrum of ZnS nanocrystallites obtained by pyrolysis of $\text{ZnCl}_2(\text{cinnamtsczH})_2$ dispersed in chloroform (excitation wavelength = 270 nm).

2007). In the present method ZnS nanocrystallites were obtained at a comparatively low temperature (515°C). Thus it has advantage over other methods.

5. Conclusions

ZnS nanocrystallites were synthesized by pyrolysis method using single source precursors, Zn (cinnamtscz)₂ and $\text{ZnCl}_2(\text{cinnamtsczH})_2$. Zn (cinnamtscz)₂ gave cubic ZnS whereas $\text{ZnCl}_2(\text{cinnamtsczH})_2$ gave hexagonal ZnS. It implies that specific phase of ZnS can be obtained by using appropriate precursor. The presence of nanocrystallites was confirmed from XRD, TEM, SAED and absorption and PL spectral data.

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