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Zinc Sulfide luminescent nanoparticles synthesized by using Zinc metal complexes of S-benzyl dithiocarbazate with microwave irradiation route

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ABSTRACT

In this paper, we have reported highly luminous Zinc sulfide nanoparticles grown by microwave irradiated single molecular precursors. The precursor was obtained by Schiff bases of S-benzyl dithiocarbazate (SBDTC) ligand using 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde; 4NNbiscyno diethylamino benzaldehyde and p-amino acetophenone. The nanoparticles obtained were characterized by X-ray diffraction studies for structural, Transmission electron micrographs (TEM) for morphological analysis, and UV Vis spectra for optical analysis. X-ray diffractograms exhibit mixed structures analysis (wurtzite and cubic) for particles obtained using 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde and 4NNbiscyno diethylamino benzaldehyde. However, the particles obtained by p-amino acetophenone Schiff bases of SBDTC exhibit only wurtzite structure. Variation in optical properties is also observed with the precursors used. The excellent optical properties of ZnS nanoparticles signify the role of microwave irradiation in synthesis. Photoluminescence (PL) study shows the luminescence in visible region and intensity is maximum for ZnS particles obtained by Zinc complex of p-amino acetophenone Schiff base of S-benzyl dithiocarbazate. The microwave-assisted process can be used for large-scale production of nanoparticles for emitting light in the visible region in various detecting and sensing applications

Keywords: Chalcogenides**;** Schiff bases; Single molecule precursor; Zinc Sulfide; nanoparticles.

1. INTRODUCTION

Zinc Sulfide (ZnS) is an environmentally friendly material, chemically more stable, and on the technological front, excellent semiconductor nanomaterials with a broad direct band gap (E_g=3.68eV) [1-3]. High refractive index., excellent transmittance in the visible range [4], and good exciton binding energy (40meV) [5, 6] make Zinc sulfide nanoparticles fit for a variety of optoelectronic uses. It is one of the oldest and probably one of the most important materials in the electronics industry, with a huge range of applications in phosphors electronics devices. At ambient conditions, ZnS exhibit two different crystal structures, a cubic phase and wurtzite. Compared with the cubic phase, wurtzite ZnS have much better optical properties; however, it is less stable than the cubic structure. At ambient conditions, wurtzite of smaller size can easily transform into a cubic structure [7]. Due to its unique properties of ZnS nanocrystals have versatile potential applications [8, 9] in ultraviolet light-emitting diodes[10], solar cells [11,12], field emitters [13], injection lasers [14,15], sensors [16], thin film based electronics devices, electroluminescent devices, IR windows [17-19] etc. Many synthesis routes have been developed for the synthesis of ZnS nanostructures. However, many of them contain toxic chemicals and harmful by-products [20-24]. Production of large-scale ZnS nanoparticles for various applications is also a challenge. In this paper, we have reported rapid and large-scale synthesis of optically important ZnS nanostructures obtained using microwave decomposition of single molecular precursors obtained using Zinc complexes of 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde,4NNbiscyno diethylamino benzaldehyde p-amino acetophenone Schiff base of S-benzyl dithiocarbazate.

2. MATERIAL AND METHODS

2.1 Materials used

All the chemicals used were of Analytical grade. Potassium hydroxide (KOH), Carbon disulfide, Ethanol, Dimethyl Sulfoxide (DMSO), Zinc acetate, Hydrazine hydrate, Para Aminoacetophenone, 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde, 4-NN biscynodiethylamino benzaldehyde were obtained from CDH fine chemical. India /Ranbaxy India and used as such without further purification.

2.2 Instruments used

Microwave, Ultrasonicator, Bath with magnetic stirrer

2.3 Experimental

Synthesis of CdS nanoparticles single molecular complex and obtaining CdS nanoparticles consists of several steps. Firstly, the S-Benzyl dithiocarbazate (SBDTC) ligand was synthesized. Synthesis of Ligand obtained by S-Benzyl dithiocarbazate and their Schiff base have already been reported by the group [25-27]. This SBDTC ligand was used to obtain Schiff bases of 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde (Schiff base 1); 4NNbiscyno diethylamino benzaldehyde (Schiff base 2), *and* p-amino acetophenone (Schiff base 3). In the third step, these Schiff bases were used to make complexes with Zinc salt. Zinc complex 1, was obtained using schiff base 1 of 5-Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde; Zinc Complex 2 was obtained using Schiff base 2 of 4NNbiscyno diethylamino benzaldehyde *and* Zinc Complex 3 obtained using Schiff base of p-amino acetophenone precursors. These Complexes were used to synthesize ZnS nanoparticles by irradiated microwave decomposition.

The potassium salt of dithiocarbazic acid was used to obtain a ligand based on S-benzyl dithiocarbazate. Ethanol and distilled water were mixed in a ratio of 9:1. Finally, the potassium salt of dithiocarbazic acid was added to about 140 ml solution and stirred thoroughly using a magnetic stirrer.

This mixture was then kept at a low temperature with the help of ice water. 22.8g of Potassium hydroxide and 20g of Hydrazine hydrate were added slowly to the cooled mixture. The solution was stirred well for a few hours. Now the solution of Carbon disulfide (CS_2) was prepared by adding 30.4g CS_2 in 25ml ethanol. The CS_2 solution was added dropwise into a cooled solution of hydrazine hydrate and KOH using a dropping funnel. The mixture was kept idle after continuous stirring for another 1 hour. The oily layer, yellow in colour, was separated using a separating funnel and kept in the ice bath. 25 ml Benzyl chloride was added and stirred for 10min until the white product was separated. In order to get the final product, it was washed with water several times and, filtered, finally treated with air to dry.

Synthesis of Schiff base of SBDTC ligand

0.02M S-benzyl dithiocarbazate (3.96g) was added in ethanol (120ml) at a temperature 40°C and then mixed thoroughly to obtain the solution. The solution was divided equally into three parts. The solutions of 0.2M of Schiff base 1, Schiff base 2, and Schiff base 3 were obtained using ethanol in separate flasks.

Finally, one part solution of S-benzyl dithiocarbazate ligand was added to the solution of Schiff base 1, Schiff base 2, and Schiff base 3**,** respectively. The obtained mixture was kept at 60°C for 5h and stirred magnetically. Finally, the solution was kept at room temperature to cool. After sufficiently cooling the solution, it was washed several times with water and filtered.

Synthesis of Zinc ion complexes

For Zinc complex preparation, Zinc acetate was used as the starting material. 0.5mM of salt solution was prepared in 25ml of ethanol. Constant stirring was done to get the fine solution. Another solution of Schiff base is prepared by dissolving 1M Schiff base 1, Schiff base 2, and Schiff base 3 in ethanol (30ml). Both solutions were added with uninterrupted stirring. After 3 hours, the White precipitate was obtained. The White precipitate was washed thoroughly with ethanol and filtered. Three Zinc complexes were obtained namely Zinc complex of Bromo-4-hydroxy-3-methoxy-2-nitro Benzaldehyde (Zinc Complex 1); 4NNbiscyno diethylamino benzaldehyde (Zinc complex 2, *and* p-amino acetophenone (Zinc complex 3).

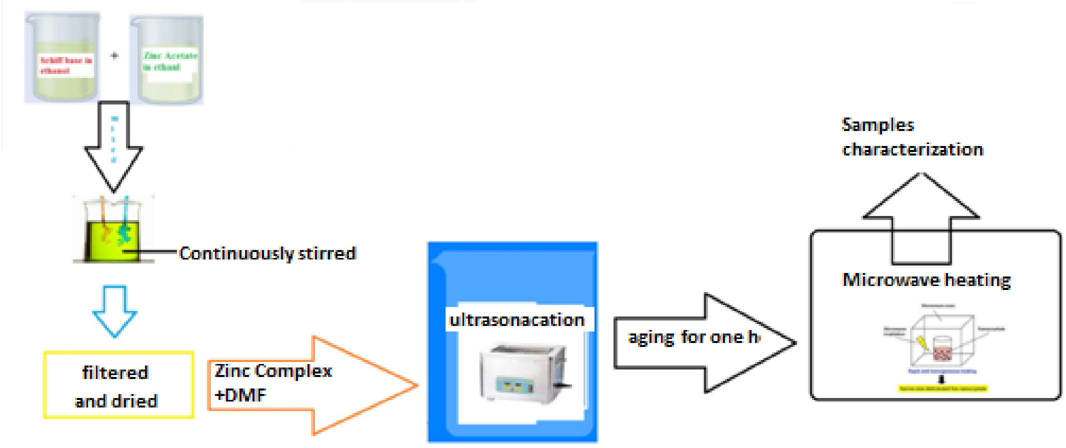

Fig. 1. Block representation of process of synthesis of ZnS nano structures

Microwave heating is used for the decomposition of precursors. In microwave heating, 1g of Zinc Complex was dissolved in 20ml dimethyl sulfoxide in a 100ml beaker. The solution was thoroughly mixed using ultrasonication for 30 minutes at 75°C and then kept idle for another 30minutes. Finally, the ultrasonically treated solution was kept in the microwave oven to irradiate with 720W microwaves for 10minutes. Methanol and Chloroform were used several times for washing. Steps are shown through the block diagram in Fig.1.

The samples were collected and analyzed for structural studies by X-ay diffractograms, morphological studies by TEM, and optical studies by UV Visible & PL spectroscopy. X-ray diffractograms were obtained using an analytical X-ray diffractometer, X PertPro PAN in the 2θ range 20^0C to 80^0C with Cu Kα radiation of wavelength 1.546Å. Transmission electron microscopy and high-resolution TEM were used to obtain micrographs using TECHAI G2 F20 operated at 300kV. Perkin Elmer PL-55 fluorescence spectrophotometer at excitation wavelength 300nm was used for obtaining emission spectra in the range 200nm to 800nm.

3. RESULTS AND DISCUSSION

Microwave heating is used for synthesizing ZnS nanoparticles. Microwave heating plays a vital role in encouraging the breaking of chemical bonds in the complex. Dimethyl sulfoxide (DMSO) solvent has a high boiling point and permanent dipole moment, hence beneficial as a polar solvent. Dimethyl sulfoxide (DMSO) is a brilliant absorber of microwave irradiation deviate it from the surface of monodispersed ZnS nanoparticles. This results in direct heat up of polar solution [25-29]. The polar solvent Dimethyl sulfoxide acts as both dispersion media and reaction media. . Adding Dimethyl sulfoxide to the reaction medium results in the axial growth of ZnS. Thus, it is clear from this reaction that the addition of a catalytic amount of polar solvents could generate the heating, which in turn helps in the decomposition of the metal complexes [29-31]. The yield of the product was calculated at about 40%, and the melting point at about 123°.

3.1 Structural studies

X-ray diffraction patterns of ZnS nanoparticles, synthesized by using Zinc complex 1, Zinc complex 2, and Zinc complex 3, respectively, are shown in Fig 2(a-c). Sharp peaks are observed in Fig 2(a). The (100), (002), (101), (102), (110) (103) and (112) peaks are identified for wurtzite structure. Along with this, cubic peaks are also observed at (200) , (220), (311), and (400). This shows mixed-phase formation for ZnS nanoparticles [25, 28-33]. Rapid decomposition of the precursor may cause the mixed phase ZnS structures. Figure 2(c) shows the X-ray diffractogram of ZnS nanoparticles obtained from complex 3. The peaks are broad and have small intensities. Three peaks of wurtzite structure, namely(002), (110), and (103) are observed. Broadness indicated the formation of small size particles. The formation of rock salt cubic structure is possible under modest external pressure or the pressure generated by the precursor. The precursor has the advantage of generating excess pressure that leads to the conversion of the wurtzite structure into a cubic structure. Wurtzite zinc oxide transforms into the rock salt structure at relatively modest external hydrostatic pressures. The transformation occurred due to the reduction of the lattice dimensions, resulting in interionic Coulomb interaction that favors the ionic behavior more than the covalent nature. The size of particles is calculated using Debye Scherrer equation 1 for (002) peak. The obtained particle size is estimated about 5-8 nm.

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta} \tag{1}$$

With Complex 1 and Complex 2, mixed wurtzite and cubic structures peaks are obtained, However with complex 3 only wurtzite structure peaks are observed. This indicates the strong structural dependence of ZnS particles with the complex used.

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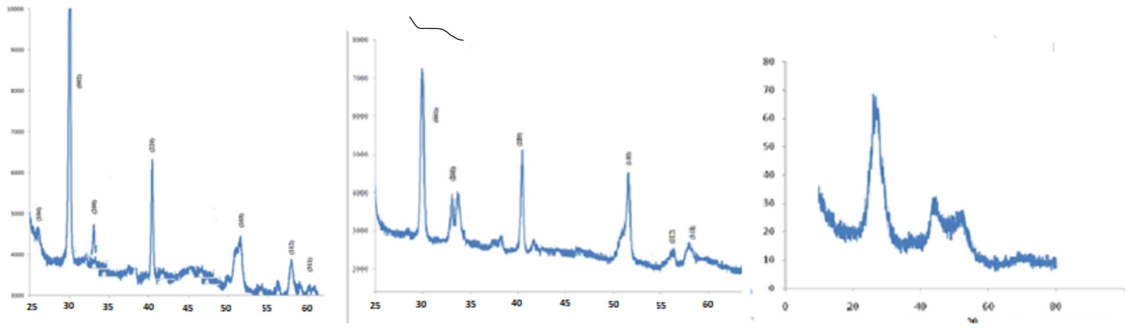

(a) (b) (c)

Fig.2 X ray diffractograms of ZnS nano particles synthesized (using (a) Zinc complexes1, (b) Zinc complexes 2and Zinc complexes 3).

3.2 Morphological Studies (TEM)

Transmission electron microscopy and High-resolution Transmission electron microscopy provide a micrograph for ZnS nanoparticles obtained by metal complex 1 are shown in Figure 3. Spherical particles are observed with uniform size distribution as shown by histogram. SAED pattern and HRTEM show crystalline behavior of particles. The size of the particles is about 25-35nm, as per the TEM micrograph.

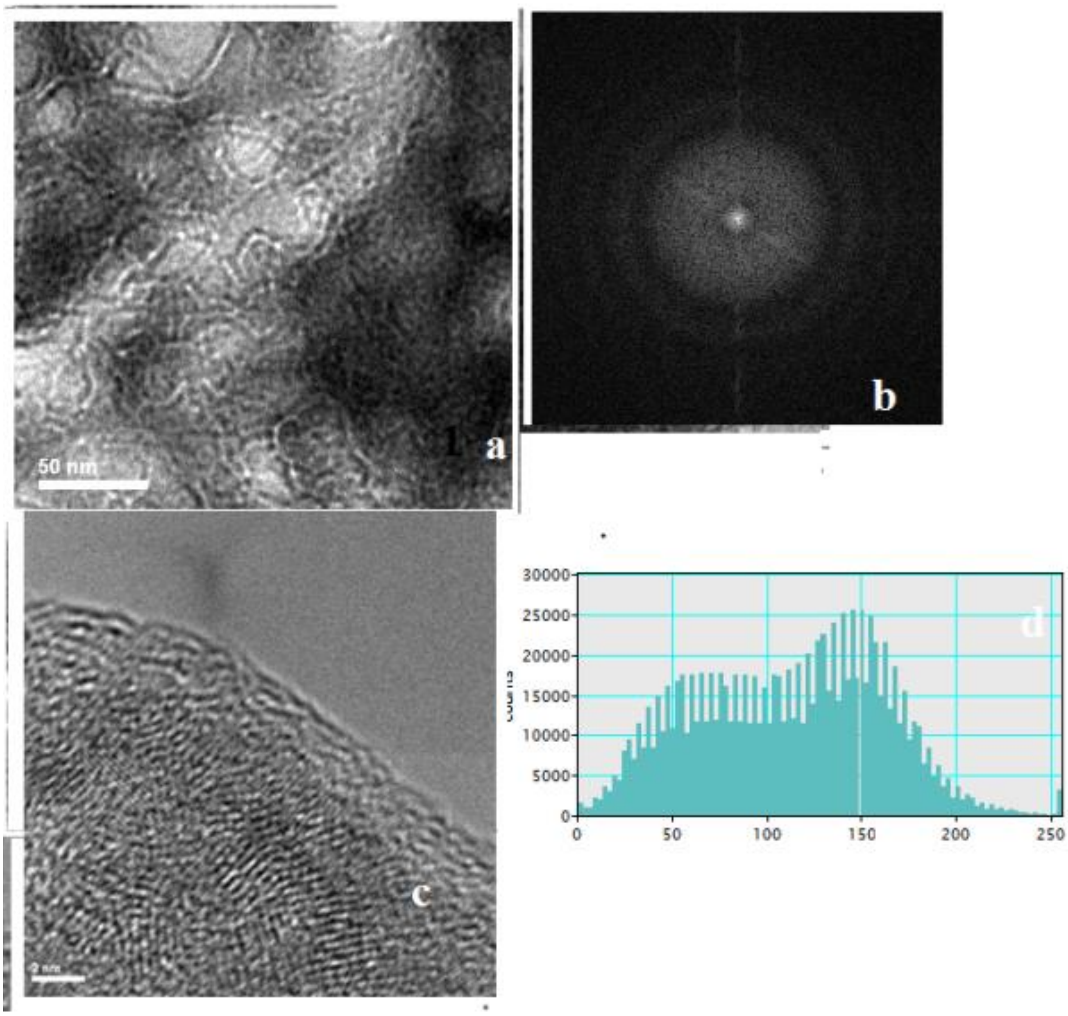

Fig 3 TEM of ZnS particles synthesized using Zinc complexe1 (a) TEM (b) SAED pattern (c) HRTEM micrograph (d) histogram

HRTEM of ZnS nanostructures obtained using metal complex 2 along with selected area (electron) diffraction (SAED) and Histogram patterns are shown in Fig.4. High-resolution lattice images show the formation of suitable quality particles. Bright points are observed in SAED, indicating good crystallinity of the particles. A histogram indicates uniform size distribution of particles [31]. HRTEM micrographs of the ZnS structures, obtained using metal complex 3 shown in Fig 5 with bright and dark fringes, indicate the presence of crystallinity.

The TEM/HRTEM results indicates the good crystallinity in ZnS nanoparticles obtained with complex 3. π conjugation in acetophenone helps in obtaining good quality nanoparticles as compare to other Benzaldehyde complexes.

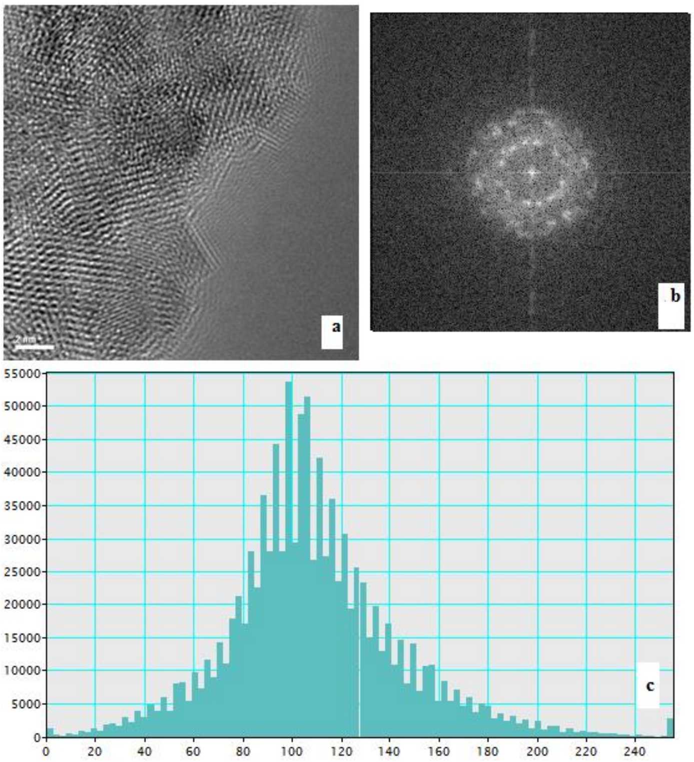

Fig.4. HRTEM image Histogram of ZnS particle obtained using Zinc complex 2.

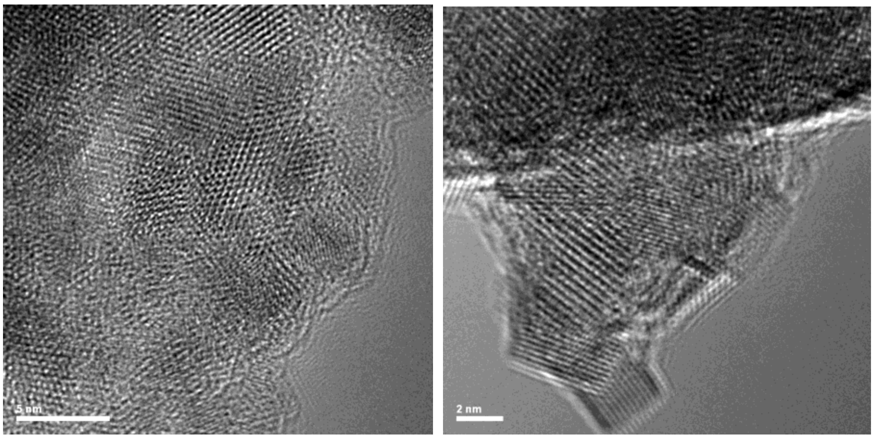

Fig5. TEM and HRTEM of ZnS nano particles synthesis using zinc complex 3

3.3 Optical Studies

Optical spectra of ZnS particles synthesized using Zinc complex 1, 2 and 3 are shown in fig. 6.

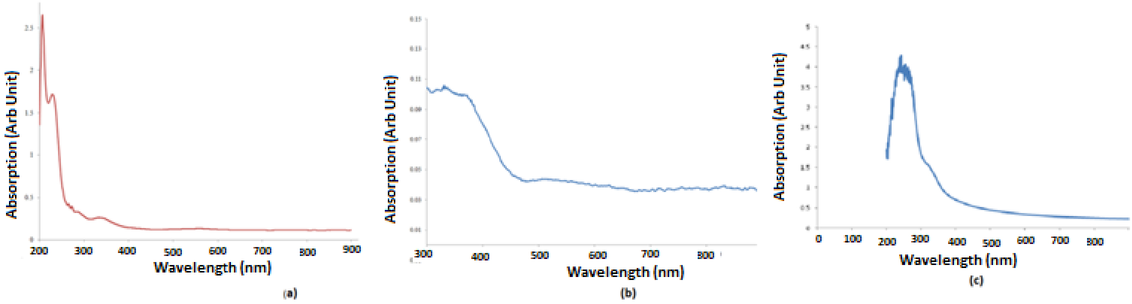

Fig6. Optical absorption spectra of ZnS nanoparticles (a) Zn Complex 1 (b) Zn Complex 2 and (c) Zn Complex 3.

In Fig 6, absorption starts at 225nm, and another peak is observed at about 245nm, again sharp absorption for higher wavelengths and even well before visible region absorption reduces to a minimum. The particles are transparent to visible light [32-35]. The absorption spectrum for ZnS structures obtained using Zinc complex2 is shown in fig. 6. (b) Absorption is not very sharp. However, the particles are almost transmission in the visible region. The absorption spectrum for ZnS structures obtained using Zinc complex3 is shown in fig. 6(c). Sharp absorption occurs at about 300nm due to small size of the particles. Nanoparticle size using absorption spectra, estimated using empirical model [47]. The particle size using the first excitonic absorption peak in the UV–Vis spectra according to Equation (2) can be calculated.

$$D = \left(9.8127X10^{-7}\right)X\lambda_{exc}^{3} - (1.7147X10^{-3}X\lambda_{exc}^{2} + 1.0064XX\lambda_{exc} - 194.84\_\text{-----} (\qquad (2)$$

Where λexc (nm) is the wavelength of the first excitonic absorption peak of ZnS Quantum dot, D (nm) is the size of a given nanocrystal sample. Data reveal that the size of nanoparticles is about 26.2nm. The results are also confirmed from Heinlein's empirical model [48] using Equation (3).

$$D = {}^{0.1}/_{(0.1338 - 0.0002345X\lambda_{exc}} \text{------}(\qquad (3)$$

Where D (nm) is the size of a sample, and λexc is the wavelength of the first excitonic absorption peak of Zinc sulfide QDs.

3.4 Luminescence studies for Optoelectronic applications

Based on the results discussed above, it has been found that the ZnS nanoparticle structures and optical studies strongly depend on the precursor used. The structures are almost spherical or hazy, so not much information can be obtained from TEM; however, a Good High-resolution micrograph and observance of dark and bright fingers favor the crystalline nature. ZNS structures are mixed (wurtzite and cubic) in almost all places. Optical absorptions are sharper for some samples than others, where absorptions are gradual. Results are compiled in the Table 1.

Table 1 ZnS nanoparticles grown by different precursors

Precursor used	**Samples**	**Structure**	**Shape**	**Optical Absorption**
[Zn^{II} *(Br Hy Me Ni PhMeSbdtcz)*$_2$ *] Complex 1*	Zinc Complex 1	Mixed Wurtzite and cubic	Almost Spherical shape	Sharp at about 280 nm

[Zn^{II}(NNBiCDEAmPhMeSbdtcz)$_2$] Complex 2	Zinc complex 2	Mixed Wurtzite and cubic	Almost Spherical shape, nice SARD pattern	At 380 nm
[Zn^{II} (AmPhMeSbdtcz)$_2$] Complex 3	Zinc complex 3	Wurtzite	hazy	Sharp at 390 nm

Based on results photoluminescence studies performed for ZNS nanostructures obtained using *[ZnII (Br Hy Me Ni PhMeSbdtcz)2](* Zinc Complex 1*), [ZnII(NNBiCDEAmPhMeSbdtcz)2](* Zinc complex 2*) and* [ZnII (AmPhMeSbdtcz)2] *(*Zinc complex 3*).* Photoluminescence spectra for various samples were obtained and are shown in fig 7. Luminescence is occurred at 467nm and 545nm, respectively, for these ZnS nanostructures and shift towards a higher wavelength, making them suitable for optoelectronic applications. The intensity is almost the same for both samples. The luminescent from the ZnS prepared by Zinc Complex 3 gives a maximum PL intensity that increases multiple times and is also observed at about 470nm. However, the peak is broad and comparatively small. It was reported that emission properties of the complexes can be influence by the π conjugation, which contain lone pair of electron causes, bathochromic shift which causes bathochromic shift towards longer wavelength. Due to π conjugation complex 3 exhibits excellent conjugation. lone pair of electrons caused

Such particles can also be used for various optoelectronic applications.

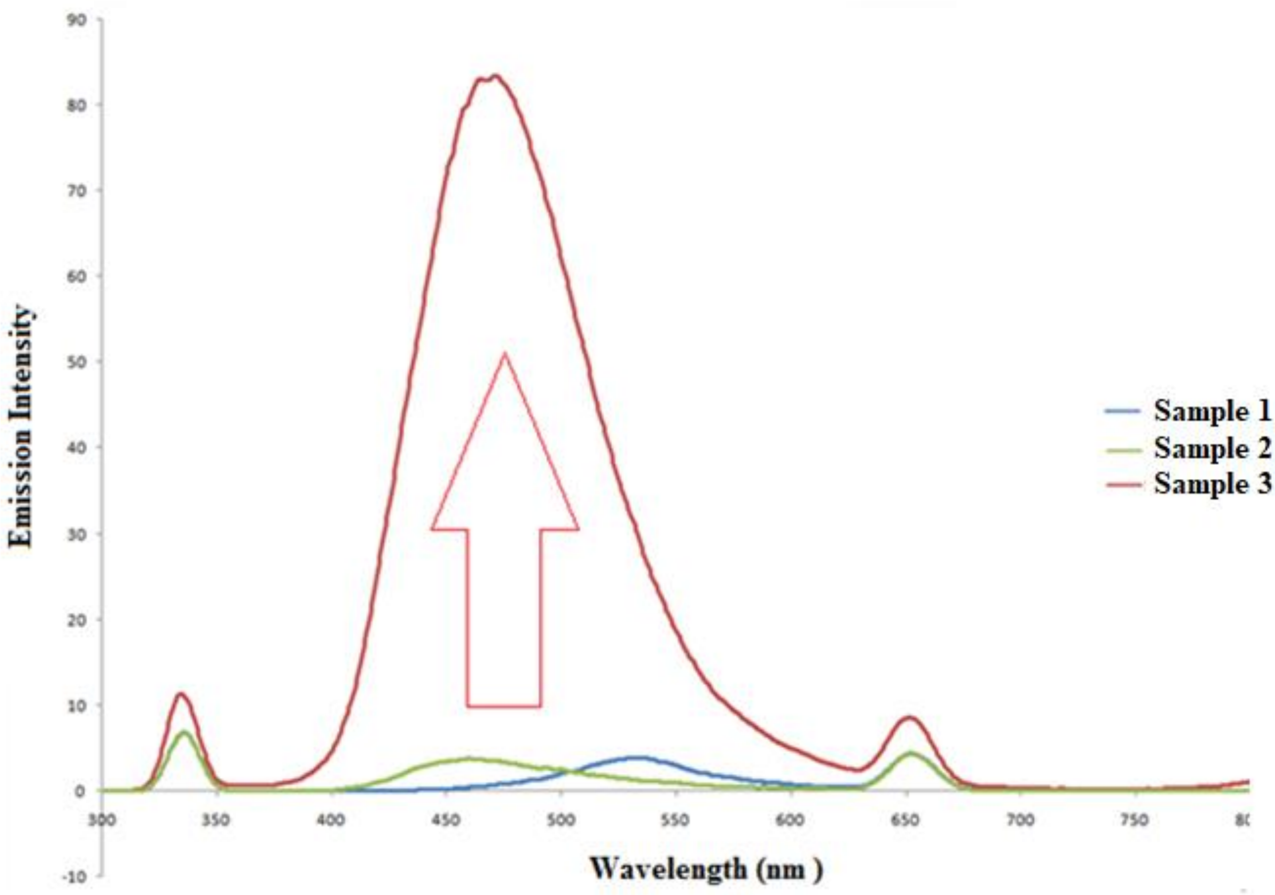

Fig. 7 Luminescence spectra for ZnS samples synthesized using

(a) Zn Complex 1 (b) Zn Complex 2 and (c) Zn Complex 3.

Conclusions

ZnS nanostructures were synthesized using microwave irradiation of Dithiocarbazate ligand as single source precursor. It has been reported that, keeping synthesis conditions almost identical the shape, luminescence strongly depends on complex used as precursor. Use of DMSO for microwave irradiation helps to decompose precursors very fast in the nanoparticles. Dominantly spherical nanostructures of excellent crystallinity were observed. Particles show mixed structures (wurtzite and cubic).. Optical properties also vary with precursors used and based on good sharp absorption transition. It can be said that good quality ZnS nanoparticles can be obtained using microwave irradiation for various optoelectronic applications. PL study was performed for some of the samples. Samples give luminescence in the visible region, and intensity is maximum for ZnS particles obtained using [Zinc complex 3] precursor. The method can be utilized for large scale production of ZnS nanoparticles at relatively low temperature. These particles emit light in visible regions in various detecting and sensing applications.

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