

# Synthesis and Optical Properties of L-cystine Capped ZnS:Co Nanoparticles

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## ABSTRACT

L-cystine capped  $\text{Co}^{2+}$  doped ZnS nanoparticles have been prepared through a soft chemical route, namely the chemical co-precipitation method. The nanostructures of the prepared samples have been analyzed using energy dispersive analysis of X-rays (EDAX), high resolution transmission electron microscope (HRTEM), Fourier transform infrared spectra (FTIR), UV-visible-NIR and photoluminescence (PL) spectrophotometers. The average sizes of the as prepared undoped and doped nanoparticles are found to be  $\sim 2.4$  nm and 4.5 nm, respectively. Room-temperature PL spectrum of the undoped L-cystine capped sample exhibits emission in the blue region with a sharp spectral band peaked at  $\sim 315$  nm under 250 nm UV excitation. In the L-cystine capped  $\text{Co}^{2+}$  doped ZnS samples quenching ( $\sim 96\%$ ) of 315nm light emission takes place under same excitation wavelength.

**Keywords:** Cystine capped, cobalt doping, zinc sulphide, nanostructures, quenching, photoluminescence

## 1 INTRODUCTION

IV-VI nanocrystalline semiconductors are of great interest for fundamental studies as well as in technical applications, such as in light emitting devices, fluorescence biosensor, and solar cells [1-12]. Amongst other semiconductor materials ZnS is the most important for application as a phosphor for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices. We have previously reported that Mn doping in ZnS leads to yellow-orange light emission under excitation by UV light [2]. Quantum confinement effect in semiconductor nanoparticles (NPs) modifies the electronic structure of the NPs when the sizes of the nanoparticles are comparable to that of Bohr excitonic radius of those materials. There are several methods for preparation ZnS NPs, such as chemical precipitation method [3-10], micro-emulsion method [11]. Recent studies suggest that the NPs may have molecular biological applications, such as in DNA detection studies [12-13]. In most of the methods stabilizers used to inhibit particle growth included reverse micelles [14], organic compounds [15] and DNA [16]. In a recent investigation we have reported an enhancement of visible light emission from uncapped  $\text{Co}^{2+}$  doped ZnS nanoparticles [17]. Various metal ions and biological

samples coming from industrial effluents are threatened to all human beings. So the determination of these toxic elements by organic fluorophore based sensor is of tremendous interest and important for analytical chemists. Photoluminescence (PL) emissions from semiconductor NPs depend on the doping concentration as well as on the capping agent, in case of capped samples. The optical properties of cystine capped nanocrystalline semiconductor have been studied extensively in recent years for their non toxic behavior and are used for the synthesis of water soluble nano fluorescent probe for chemical sensing [18-21]. Previous studies on Cystine capped ZnS shown striking differences in the pH-dependent changes in optical spectra [18]. Koneswaran *et al.* [19] reported the synthesis of the L-cystine-capped ZnS quantum dots as fluorescence sensor for the  $\text{Cu}^{2+}$  ion through both dynamic and static quenching mechanism. Borse *et al.* [20] shows the effect of iron and nickel metal ion doping on quenching of blue light emitted by mercaptoethanol capped ZnS nanoparticles. However, there are only few reports available in the literature on ZnS doped with  $\text{Co}^{2+}$  and capped with cystine. Cystine is water soluble amino acid can be used as a capping agent for ZnS NPs. The surface modification of ZnS NPs with cystine prevents the agglomeration of the NPs [21]. Hence, synthesis and characterization of the optical properties of NPs of ZnS doped with  $\text{Co}^{2+}$  capped with cystine is interesting.

Here we have adopted chemical precipitation method being simpler than all other available methods for preparation of ZnS NPs. The average sizes of the cystine capped ZnS and ZnS:Co NPs have been estimated as 2.4 nm and 4.5 nm from the HRTEM measurements. Photoluminescence (PL) spectra of the prepared ZnS NPs have also been recorded at different excitation wavelengths. However, the peak emission takes place at excitation wavelength of 250 nm and the peak PL emission takes place at 315 nm for cystine capped undoped samples, whereas for the  $\text{Co}^{2+}$  doped sample,  $\sim 96\%$  quenching of the PL emission at 315 nm takes place under the same excitation wavelength.

## 2 EXPERIMENTAL DETAILS

Nanoparticles of ZnS have been prepared by chemical co-precipitation method using AR grade (Mark & SD) chemical. The synthesis is carried out at room temperature of  $20^\circ\text{C}$ . At first, 10ml saturated solution of both zinc

nitrate and sodium sulfide in methanol are prepared. Zinc nitrate solution is vigorously stirred using a magnetic stirrer upto 1h, then calculated amount of L-cystine solution and cobalt salt are mixed with solution of Zinc nitrate. The white precipitate is separated from the reaction mixture by centrifugation for 5min at 10,000 rpm and washed several times with methanol to remove all sodium particles. The wet precipitate is then dried for characterization of optical, and nanostructural properties.

The optical transmission/absorption spectra of the sample dispersed in methanol were recorded using a UV-VIS spectrophotometer (Hitachi, U-3010). The formation of ZnS or ZnS:Co nanoparticle was confirmed using transmission electron microscope (HRTEM, JEOL JEM 2100) using carbon coated copper grid. Scanning electron microscope (SEM with EDXA, Hitachi S-3000N), has been used for compositional analysis of the prepared ZnS nanoparticles. FTIR spectra were recorded in an FTIR spectrometer (Nicolet iS 10) after preparing palette with the KBr. The photoluminescence (PL) spectrum of the ZnS

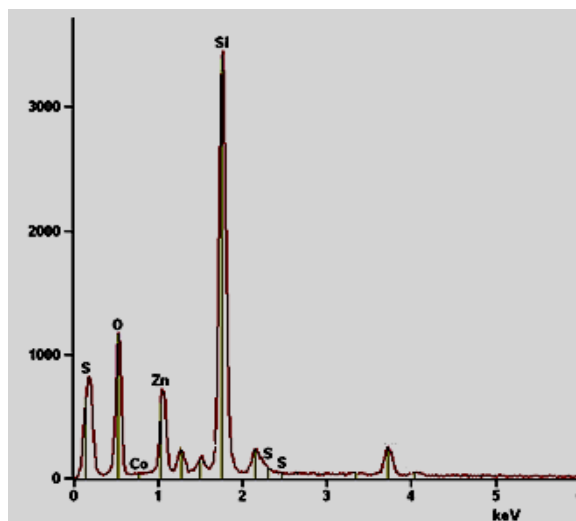


Figure 1: EDAX spectrum of ZnS:Co sample.

nanoparticles dispersed in methanol has been recorded using a spectrofluorimeter (Perkin Elmer, LS 55)

### 3 RESULTS AND DISCUSSIONS

Figure 1 shows the typical representative EDAX spectrum of a cystine capped ZnS:Co sample, which confirmed the compositions of the sample. To obtain the particle size and information about the nanostructure

HRTEM measurement was performed using copper grid. Figure 2 show the HRTEM micrograph of the prepared cystine capped ZnS sample for examples, the

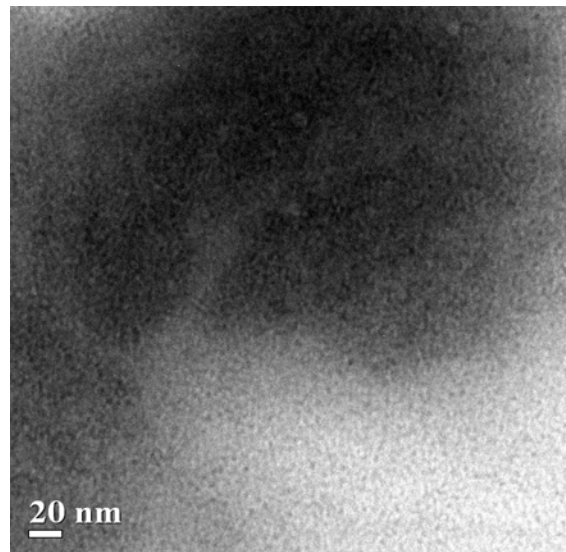


Figure 2: HRTEM micrograph of the cystine capped ZnS sample.

mean particle size of the ZnS:Co and undoped ZnS samples are of 4.5 nm and 2.4 nm respectively. The particle size distributions of undoped cystine capped sample have been shown in Figure 3.

FTIR spectra are recorded for all the samples by preparing palettes of the powder samples with the KBr in the range of  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  (not shown here). Some characteristic peak appeared at  $3469$ ,  $2543$ ,  $1394$ ,  $1130$ ,  $1002$ , and  $612\text{ cm}^{-1}$  with some other associated peaks in all the samples and the presence of cystine was confirmed in all the samples [22]. The broad band at  $3469\text{ cm}^{-1}$  appeared due to valence vibration of the occluded water but it also corresponds to the region where the asymmetric and symmetric stretching modes for a coordinated  $\text{NH}_2$  group appear. Bands appeared around  $900\text{-}1500\text{ cm}^{-1}$  may be due to oxygen stretching frequency (OH stretching) and binding frequency. The additional weak peaks and shoulders are appeared may be due to the nanostructural formation in the samples. The measured absorption characteristics are shown in Figure 4. The prepared nanopowders are first dispersed in methanol and then the UV-visible optical absorption characteristics of the cystine capped ZnS and ZnS: Co NPs are collected. The synthesis of ZnS NPs is clearly evident from the Figure 4.

The small excitonic absorption peaks due to the ZnS nanoparticles appeared at  $280\text{ nm}$ , which reflects the band gap of the particle. For obtaining the absorption characteristics of all the samples, at first the transmittance

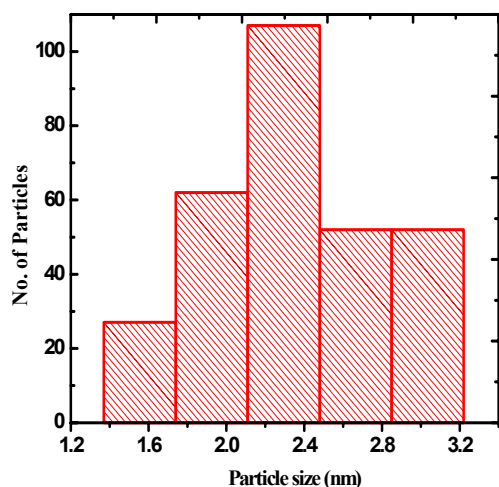


Figure 3. The particle size distribution corresponding to HRTEM image of Figure 2.

( $T$ ) at different wavelength ( $\lambda$ ) are measured and then absorbance ( $\alpha$ ) at the corresponding wavelengths  $\lambda$  are calculated using the Beer-Lambert's relation;

$$\alpha = \ln(T^{-1})/d, \quad (1)$$

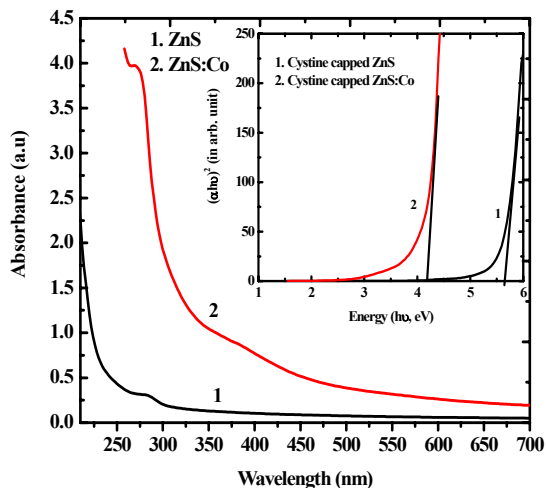


Figure 4: UV-visible absorption characteristics of the prepared samples. Inset shows the calculation of band gap of the samples.

where,  $d$  is the path length. The absorption edge for single crystal ZnS is very sharp and is determined by the nature of the electronic transition between the valence band and conduction band.

From the above Figure 4, it can be observed that the cystine capped  $\text{Co}^{2+}$  doped ZnS exhibits a shift of

absorption peak to longer wavelength and the peak becomes sharper. The relation between the incident photon energy ( $h\nu$ ) and the absorption coefficients ( $\alpha$ ) is given by the following relation.

$$(\alpha h\nu)^{1/s} = C(h\nu - E_g), \quad (2)$$

where,  $C$  is a constant and  $E_g$  is the bandgap of the material and the exponent  $s$  depends on the type of the transition. For direct and allowed transition  $s = 1/2$ , indirect transition,  $s = 2$ , and for direct forbidden,  $s = 3/2$ . For calculating the direct bandgap value  $(\alpha h\nu)^2$  versus  $h\nu$  is plotted and it is shown in inset of Figure 4. By extrapolating the straight portion of the graph on  $h\nu$  axis at  $\alpha = 0$ , the bandgap value is calculated and it is 5.60 eV and 4.20 eV for ZnS and ZnS:Co samples, which is higher than that of bulk ZnS [2]. This blue shift of the bandgap takes place because of the quantum confinement effect [1]. By using the method described in [23], the calculated average size of the undoped sample is 2.5 nm, which agrees quite well with its value obtained from TEM. The sizes of ZnS:Co doped samples are slightly larger; e.g., the average size of the doped sample is 4.5 nm.

Figure 5 show the PL spectra at 250 nm excitation of cystine capped ZnS, and ZnS:Co NPs measured at room temperature. The intense PL emission from cystine capped

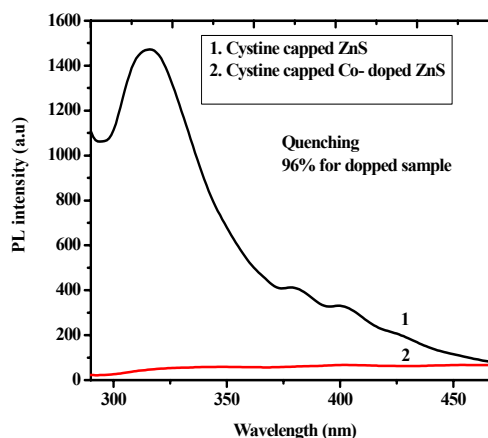


Figure 5: The PL spectra at 250 nm excitation of cystine capped ZnS and cystine capped ZnS:Co samples.

undoped ZnS nanoparticles with a peak at 315 nm along-with two other weak peaks at 380nm and 400nm are observed. The PL intensity of 315 nm peaks quenches by ~96% in the  $\text{Co}^{2+}$  doped ZnS samples. The origin of the blue-luminescence from undoped ZnS NPs has been studied by different groups [1, 2, 9, 24-30]. Becker and Bard [28] have attributed the blue emission band at 428 nm to  $\text{S}^{-2}$  vacancies. Koneswaran *et al.* [19] reported the synthesis of the L-cystine-capped ZnS quantum dots as fluorescence sensor for the  $\text{Cu}^{2+}$  ion through both dynamic and static quenching mechanism. Borse *et al.* [20] suggested that the

PL emission can be quenched by the iron and nickel doping. Wang *et al.* [25] explained the quenching of the PL intensity of conjugated macromolecules by bipyridinium derivatives in aqueous media due to charge dependence. Quenching of PL intensity in ZnS colloidal particles by Cd<sup>2+</sup> ions was investigated by Weller *et al.* [26]. They have attributed this behavior to the formation of co-colloids. In the cystine capped co-doped ZnS nanoparticles, luminescent mechanism and the processes are very complex. Cobalt act as electron trapping centers which results into non radiative recombination and so the quenching of the PL intensity in the cystine capped ZnS:Co NPs have been observed in the present work.

#### 4 CONCLUSION

The synthesis of cystine capped undoped and Co<sup>2+</sup> doped ZnS nanoparticles of sizes 2.4 nm and 4.5 nm respectively, are reported by chemical precipitation method. This method being simpler and with low cost chemical components is suitable for the industrial large scale production. Photoluminescence (PL) emissions measured at room temperature from the prepared nanoparticles are reported. It is found that the cystine capped undoped sample exhibits the PL emission in the blue region. It is also observed that the PL intensity of the cystine capped ZnS:Co nanoparticles quenches by 96% than that of the cystine capped undoped ZnS nanoparticles, under the same excitation wavelength of 250 nm. In the Co<sup>2+</sup>-doped ZnS nanocrystallites, luminescent mechanism and processes are very complex. However, cobalt act as electron trapping centers which results into non radiative recombination and thus the PL intensity of cystine capped ZnS:Co nanoparticles quenches. The prospects of the luminescent materials are directly decided by their fluorescence efficiency. The synthesis of L-cystine capped and Co<sup>2+</sup> doped ZnS nanoparticles can easily be carried out at low cost and also can be used in analytical sensor applications.

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