

Photoluminescence Characteristics of Chemically Synthesized Ag Doped ZnS Nanoparticles

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Abstract: *The study of group II-VI semiconductor nanomaterials have shown widespread interest due to their potential application. Amongst this group, Zinc sulfide (ZnS), which has further improved optical or magnetic properties when doped with one or more transition metal, is versatile and promising for diverse applications such as in the field of photocatalysis, imaging and some electronic devices. In the current study silver doped ZnS nanoparticles were synthesized by varying the doping concentration of Ag from 0.05% to 10%. The Ag doped ZnS were synthesized without capping agent by chemical co-precipitation method in de-ionized water. The synthesized nanoparticles have a narrow particle size distribution with improved optical properties. The phase analysis and optical properties of the doped ZnS nanoparticles have been carried by powder X-ray diffraction, UV-vis spectrometer and photoluminescence spectrometer. The result shows doping of Ag ions in ZnS nanocrystals, and improved optical property is the result of the sulfur atom interaction with metal ions on the surface of the nanocrystals. The synthesized ZnS nanoparticles doped with silver can be a promising agent for photocatalytic activity.*

I. INTRODUCTION

In recent years, nanoparticles of binary semiconductors of group II-VI such as ZnS, ZnSe, CdS, and CdSe have been extensively studied. This is because of unusual structural, optical and electronic properties of nanoparticles in comparison with bulk material [1, 2]. These semiconductor materials of group II-VI compound has been studied for wide range of applications, such as photocatalyst, LEDs, field effect transistors, solar cells and optical sensors [3-5]. Among these semiconductors, most interesting and broadly studied semiconducting nanoparticles are of ZnS. These nanoparticles have low toxicity, more chemical stability and technologically better than other semiconductors of II-VI compound. It is semiconductor having bandgap of 3.7 eV, so it could be used for short wavelength optoelectronic applications [6-8].

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Zinc sulfide shows improved optical property when it is doped with transition metal ions. These transition metal ions lead to formation of impurity states, which play significant role in altering the light emitting properties [9]. Doped ZnS shows different optical property in contrast to pure ZnS; because the doping ions act as recombination centers for electron-hole pairs [10, 11]. Thus, transition metal doping leads to alter the emission of ZnS nanoparticles [12, 13]. Many studies have been published on Mn, Fe, Cu, Co, Ni, Cr doped ZnS nanosystems which shows great luminescent characteristics. The results lead to formation of new class of luminescent material with doped semiconductor nanocrystals, which have a variety of application in displays and lighting to lasers and sensors [14]. As silver is a biocompatible material and ZnS exhibits unique photoluminescence property, it will find application in fluorescent contrast agents for bioassays and bioimaging. Thus, the scope of this material ranges from photocatalyst to imaging to nano devices such as sensors and light emitting materials. Still there are very few reports are available on silver doped ZnS nanosystems till now. Therefore, in the current study investigation of photoluminescence of ZnS nanoparticles incorporated with silver is carried out.

II. EXPERIMENTAL

A. Synthesis

The semiconducting nanoparticles of silver doped and undoped Zinc sulfide were synthesized by chemical co-precipitation method. This technique is very simple technique with easy handling and also suitable for large scale production [9]. Analytical grade Zinc sulfate ($ZnSO_4 \cdot H_2O$), silver nitrate ($AgNO_3$) and Sodium sulfide ($Na_2S \cdot 3H_2O$) are used without further purification. $ZnSO_4$ of 1M concentration was dissolved in 10ml deionized water and stirred continually using magnetic stirrer with temperature of 60–70 °C. After 30min of continuous stirring, an equimolar aqueous solution of sodium sulfide (Na_2S) has been poured dropwise to the above solution with vigorous stirring, resulting in colloidal solution. After that, the sample is washed with deionized water for several times to separate sample from solvent. The washed precipitates then dried overnight and were cursed into fine powder. For synthesis of Ag doped ZnS nanoparticles, all the prerequisites are maintained same and $AgNO_3$ of calculated amount is added in beaker along with $ZnSO_4$.

ZnS NPs doped with 0.5, 1, 2, 5 and 10 wt% of Ag ($Zn_{1-x}Ag_xS$; $x = 0.005, 0.01, 0.02, 0.05$ and 0.1) are coded as A1, A2, A3, A4 and A5 respectively. Undoped ZnS is coded as A0 for simplification.

B. Characterization

The size of pure and doped Zinc sulfide nanoparticles are determined by X-ray diffractometer(Rigaku, MiniFlex) with CuK α radiation ($\lambda=1.5406\text{\AA}$). XRD data is collected with diffraction angle $2\theta = 20-80^\circ$. EDS (Energy Dispersive Spectrometer) is performed to confirm the formation and purity of the nanoparticles. For this purpose Bruker XFlash 6I30 is used. Scanning electron microscopy (FEI Nova Nano SEM 450) is used to determine morphology of nanoparticles. UV-visible spectrometer (U-3010 Spectrophotometer LABINDIA Model: UV-3000) is used to record the absorption spectra of the sample in the range of 200 to 800nm. The PL spectrum of the pure and doped Zinc sulfide nanoparticles were measured at room temperature with Cary Eclipse Spectrophotometer.

III. RESULTS AND DISCUSSION

A. Structural and morphological studies

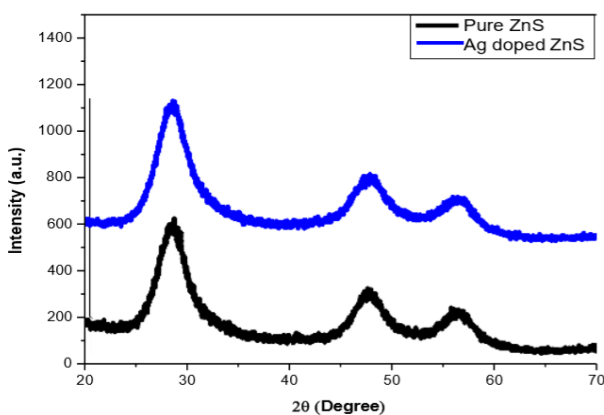


Figure 1. XRD of pure and doped Zinc sulfide nanoparticles

Fig. 1 shows the XRD spectra of pure and Ag-doped Zinc sulfide nanocrystals prepared by colloidal method. The XRD pattern of samples exhibit three well marked peaks centered at $2\theta = 28.50^\circ, 47.72^\circ$ and 56.56° which correspond to (111), (220) and (311) miller planes respectively [15]. The broader peaks of XRD spectra indicate formation of nanoparticles [16]. The obtained peaks in the XRD spectra indicate that the pure and Ag-doped Zinc sulfide nanoparticles possess a cubic zinc blende crystal structure. Only three peaks, without any additional peaks indicate the high purity ZnS nanoparticles. The Ag impurity ions does not introduce additional peaks, confirms that the impurity ions inserted into the cubic structure.

Debye-Scherrer formula is used to calculate the average crystalline size of nanoparticles

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where D is the mean grain size, k is the constant (around 0.9),

λ is the wavelength of X-ray(1.54056\AA), β is full width of half-maxima of the diffraction peak(FWHM), and θ is the Bragg's angle [17]. The average crystal size was calculated to range from 3 nm to 5 nm.

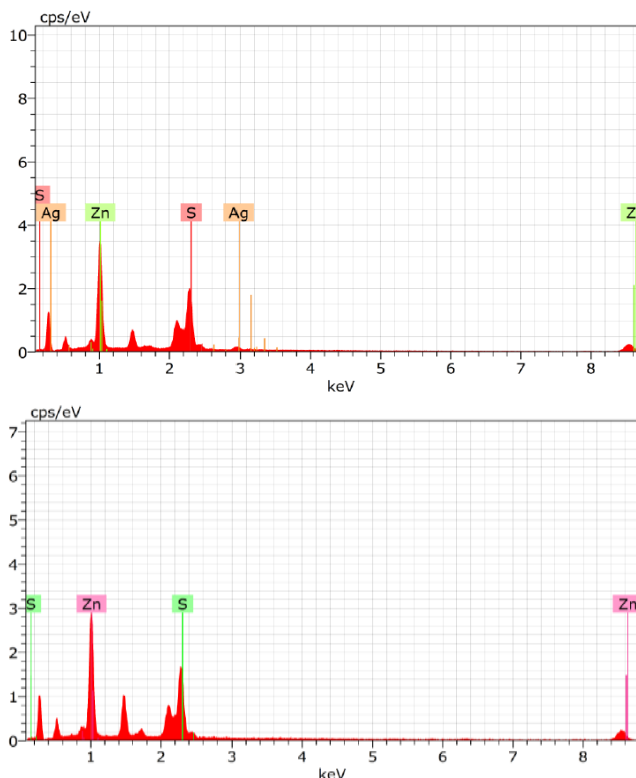
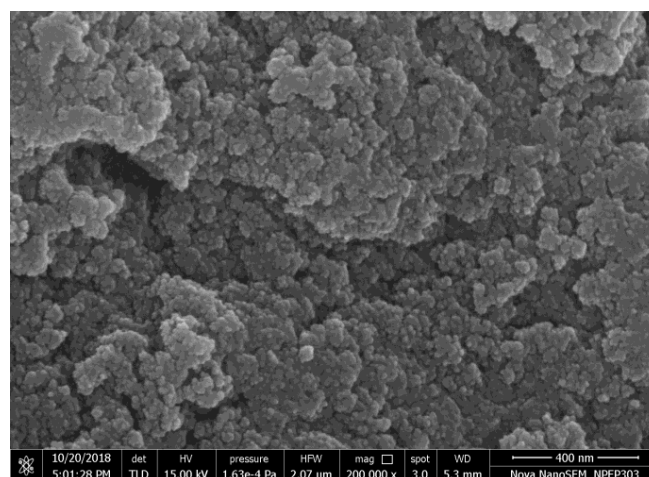
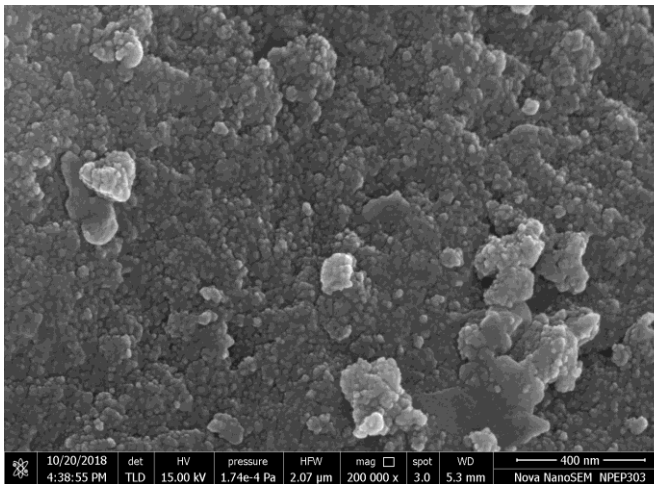


Figure 2. EDS Spectrum of undoped and doped zinc sulfide

Fig.2 shows energy dispersive spectroscopy (EDS) spectrum of undoped and Ag doped zinc sulfide nanoparticles. The EDS spectra of pure ZnS confirm the presence of zinc and sulfur, indicating purity of the sample. Also, Ag doped ZnS show Zn,S and Ag which indicates the doping of the Ag [18].



3(a)



3(b)

Figure 3. SEM images of (a) pure zinc sulfide and (b)doped zinc sulfide

Fig.3 shows the SEM image of undoped and silver doped zinc sulfide nanoparticles. The spherical shape of zinc sulfide nanoparticles are observed in SEM images [19]. It also shows narrow size distribution of pure and doped ZnS.

B. Optical absorption studies

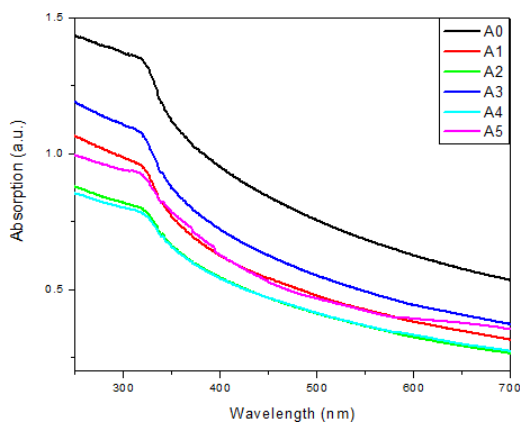
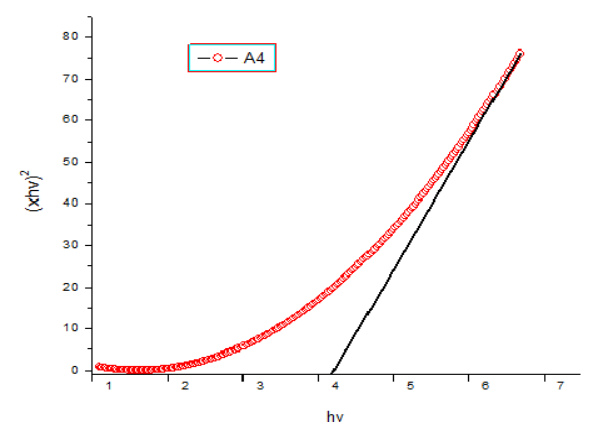
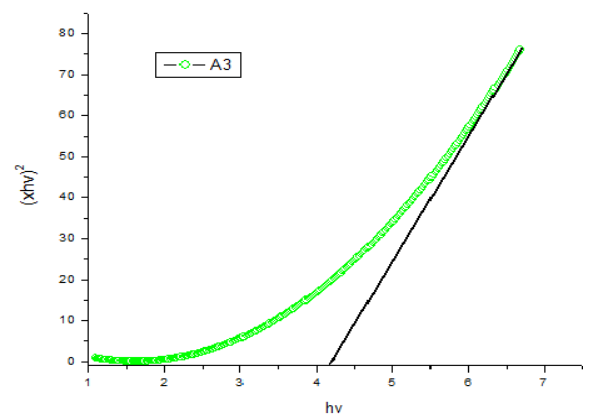
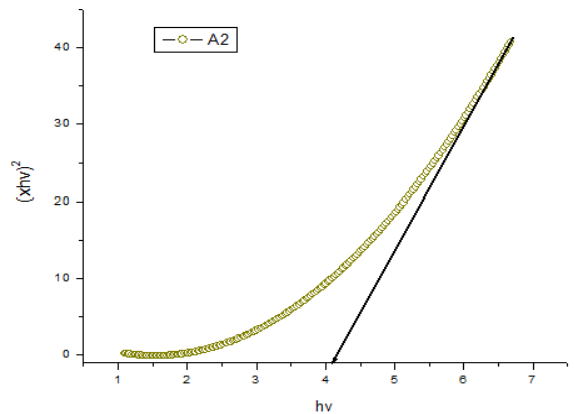
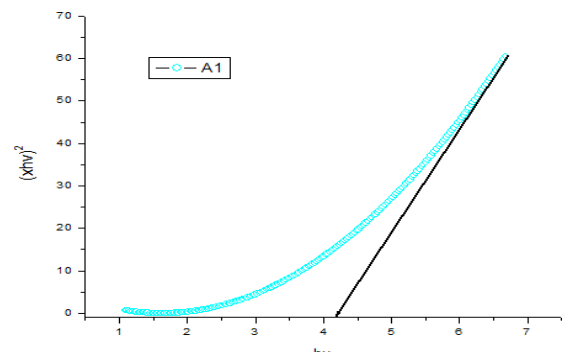
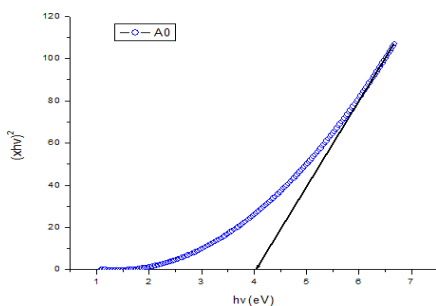


Figure 4. UV-visible spectra of undoped and silver doped zinc sulfide nanoparticles

Fig.4 shows the UV–visible absorption spectra of pure and silver doped zinc sulfide nanoparticles. The absorption edge with shoulder about at 320nm was observed. The position of the absorption shoulder shows minor blue shift with doping of silver [20]. The concentration of doping ion is very low thus it does not change crystalline size and there is no noticeable shift.



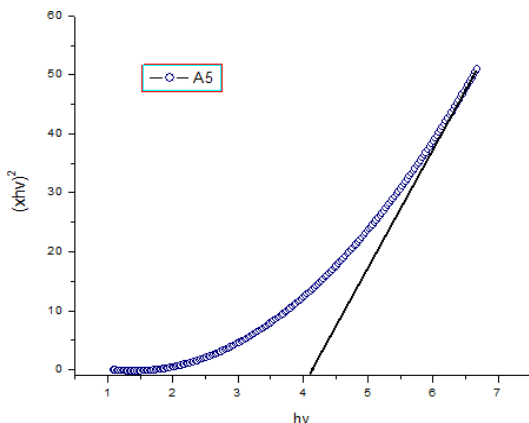


Figure 5. Tauc's plot

Fig.5 shows tauc's plot of pure and Ag doped ZnS nanoparticles. Tauc's plot is used to calculate the bandgap of the nanoparticles [21]. It is found that the bandgap of pure ZnS is 4.09eV and 4.25eV for doped nanoparticles. The higher bandgap value is result of small size of particles.

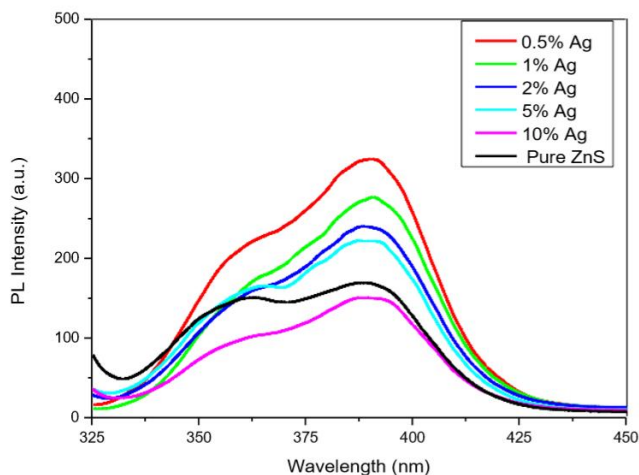


Figure 6. PL of undoped and doped zinc sulfide nanoparticles

Fig.6 shows photoluminescence (PL) spectra of pure and silver doped zinc sulfide (0.5%, 1%, 2%, 5% and 10 %) at room temperature. The measurements have been carried out at an excitation wavelength of 300nm. The spectra has a peak at 390nm, observed from pure ZnS and doped ZnS nanoparticles. This is because of defect related emission of ZnS. ZnS related luminescence of zinc vacancies has peak at 480nm which is not observed in the spectra [22, 23]. This indicates that the emission is totally quenched by energy transfer to the Ag⁺. Here, doping ions works as sensitizing agent. We observed more photoluminescence at less doping concentration. Initially, luminescence improves then the luminescence quenching is observed. This is because the higher doping percentage has non-radiative internal combinations.

IV. CONCLUSION

All nanoparticles, pure and silver doped zinc sulfide nanoparticles were synthesized by colloidal method. The synthesized ZnS nanoparticles have average particles size 3-5nm. The XRD results indicate the cubic zinc blend structure of zinc sulfide and EDS confirms the formation of zinc sulfide nanoparticles and doped zinc sulfide nanoparticles. The SEM images show narrow size distribution of nanoparticles. The room temperature photoluminescence spectra of all the samples peak positions at 390nm and the photoluminescence quenching is observed with high doping concentrations.

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