# Structural and Optical Behaviour of ZnS Nanoparticles Using Different Capping Agents

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**Abstract : The ZnS nanoparticles were prepared by co-precipitation method using various capping agents like PVA (polyvinyl alcohol) and PEG-4000 (polyethylene glycol). These were characterized by UV-Visible spectra, X-ray diffraction (XRD) studies, Fourier Transform Infra-red spectra (FTIR) and Scanning electron microscopy (SEM). UV-Visible absorption spectra were used to find the optical band gap and the values obtained have been found to be in the range of 3.0-3.4eV. The particle size of nanoparticles calculated from XRD pattern has been in the range of 10-12 nm. It is also observed that the particle size of nanoparticle is affected by the nature of capping agent.**

**Keywords: Co-precipitation method, Kinetic study, Photocatalytic activity, ZnS nanoparticle.**

## I. INTRODUCTION

The Nanoparticles defined as small particles with 1-100 nm in diameter at least in one dimension has opened an alternative way in the design of materials bringing a great difference in physical and electronic properties as compared to bulk materials. Among the family of semiconductors, II-VI group semiconductor compounds have immense technological importance in various applied fields of science and technology. For instance, ZnS[1,] CdS, ZnO[2] , CdTe[3] etc., are important because of their excellent electronic and optical properties for optoelectronic applications. Among these, ZnS is an important member in II-VI group semiconductors having a larger value of band gap energy[4]. It has two structures: a cubic form and a hexagonal form[5-6] . Transition from bulk to nanoparticles leads to the display of quantum mechanical properties and an increased dominance of surface atoms which increases the chemical reactivity of a material. Notable examples include the tunable band gap [7] and catalytic behaviour of nanoparticles. For nano particles prepared by solution based chemical methods, a capping agent which adsorbs to the nano particles surface, generally is added both to control the size of nano crystals and to prevent agglomeration of synthesized nano material. Polymers are chosen as good host materials because they usually exhibit long-term stability and possess flexible reprocess ability. In addition, the small size and high optical activity of ZnS nanoparticles make them interesting for optoelectronic applications operating in the ultraviolet region [8-10]. In the past decade, semiconductor nanoparticles have been synthesized through various methods including hydrothermal process [11], micro-emulsion method [12], sol-gel method [13], chemical co-precipitation method[14], sonochemical method , microwave irradiation and solvothermal method[15] etc. However, these methods normally consist of two or more steps and rigorous conditions, such as high pressure or high temperature are required [16]. Fabrication of inorganic nanoparticles in solid polymer matrices has attracted considerable interest because, the combination of inorganic particles and polymers provide a simple route for the preparation of stable and processable materials having the promising properties of both components[17].

ZnS nanoparticles could be used as good photo catalysts due to rapid generation of the electron-hole pairs by photo-excitation and highly negative reduction potentials of excited electrons; as conduction band position of ZnS in aqueous solution is higher than that of other semiconductors such as $TiO_2$ and ZnO[18]. Since, a larger ratio of surface to volume of a catalyst would facilitate a better catalytic activity[19-20]. The size controlled synthesis of ZnS nanostructures to produce a larger ratio of surface to volume is of great importance. The enhanced surface to volume ratio causes increase of surface states, which change the activity of electrons and holes[21], affecting the chemical reaction dynamics. The size quantization increases the band gap of photo catalysts. ZnS nanoparticles are prepared by co-precipitation technique using PVA and PEG-4000 as capping and stabilizing agents, which modifies the surface of nanoparticles and prevents the growth of the particle to larger size. The effect of capping agent on optical absorption spectra has been investigated. XRD, FTIR and SEM studies are conducted for these samples.

## II. EXPERIMENTAL

### 2.1. Preparation of ZnS nanoparticles

All the chemicals were purchased from Merck Specialities Private Ltd and these are of analytical grade and used without any further purification. ZnS nano

particles were synthesized using PVA and PEG-4000 as capping agents by simple co-precipitation technique. The starting materials for the synthesis of ZnS nanoparticles were ZnO (as Zinc source) and Sodium sulphide (as sulphur source). First, 5 gm of Zinc oxide is mixed with 100 ml distilled water and to which dilute HCl is added till complete dissolution takes place to get a transparent solution. This solution is stirred vigorously for 1 hour along with the drop wise addition of Sodium sulphide through a burette and appropriately mixed with various capping agents like PVA and PEG-4000 until a white precipitate is obtained. The precipitate is washed several times with double distilled water and dried in an oven at 90˚C for 4 hours; it is then crushed to fine powder to obtain Zinc sulphide nanoparticles.

$ZnO + 2HCl \text{ -----> } ZnCl_2 + H_2O$

$ZnCl_2 + Na_2S \text{ ---} \rightarrow ZnS + 2NaCl$

### 2.2. Characterization of ZnS nanoparticles :

The absorption spectra of ZnS nanoparticles were recorded with an UV-Visible spectrophotometer (UV-3600 series, Shimadzu) in the range of 200-800nm. X-ray diffraction (XRD) measurement of ZnS nanoparticles was carried out on X'pert Pro X-ray diffractometer (Panalytical B.V., Netherlands) operating at 40 kV and a current of 30 mA at a scan rate of 0.388 $min^{-1}$ to determine the nano crystalline phase and structure. The FTIR spectra of the samples were recorded with Shimadzu spectrophotometer in the range of 4000-400 $cm^{-1}$ using KBr pellet technique. The size and morphology of the nanoparticles were determined by SEM .

## III. RESULTS AND DISCUSSION

### 3.1. Structural Studies

Fig. 1(a)and Fig. 1(b) show the XRD patterns of the ZnS nanoparticles prepared by using PVA and PEG as capping agents respectively. These patterns show three prominent peaks that can be attributed to characteristics peaks of ZnS and it reveals the cubic zinc blend structure for the as – prepared nanoparticles. The broad diffraction peaks are attributed to small particle size and its broadening at lower angle is used for the calculation of particle size which show obvious size broadening effects, indicating the finite size of the nanoparticles [22].

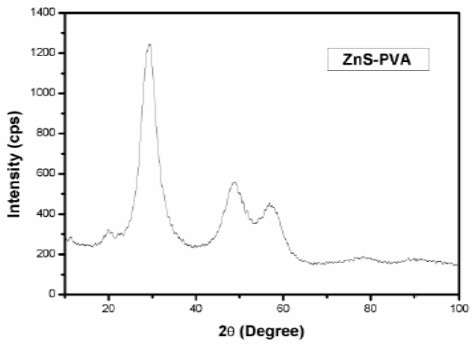



**Fig. 1(a) XRD pattern of ZnS-PVA nanoparticles**

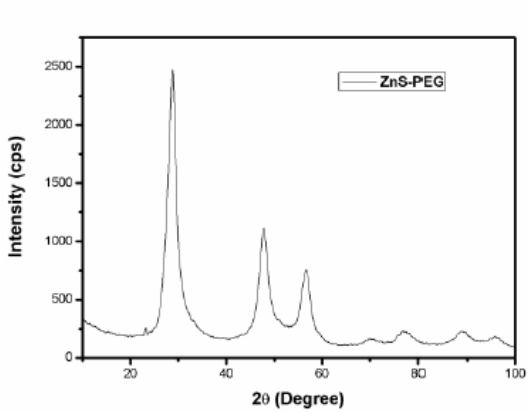



**Fig. 1(b) XRD pattern of ZnS-PEG nanoparticles**

The average particle size from the most intense peak was estimated calculated using Debye- Scherrer formula [23] .

$$D = k\lambda/\beta\cos\theta$$

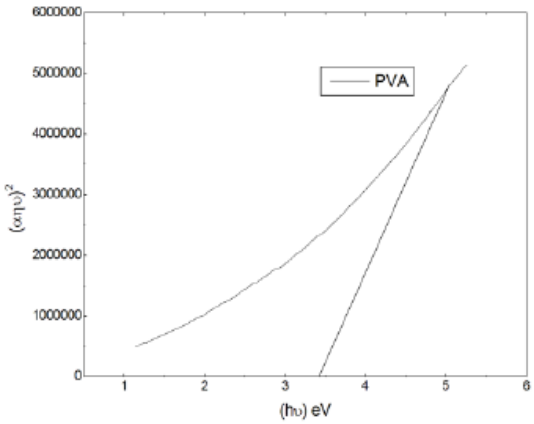
where D is the mean grain size, k is a geometric factor, λ is the X-ray wavelength, β is the FWHM of diffraction peak and θ is the diffraction angle. The FWHM of the XRD peaks may also contain contributions from lattice strain.

**Table:1 Calculated Particle size of ZnS - PVA and ZnS-PEG**

| S. No. | Sample | Particle size (nm) |
|---|---|---|
| 1 | ZcS-PVA | 12 |
| 2 | ZnS-PEG | 10 |

### 3.1.UV-Visible measurements:

The Tauc plot and the optical absorption spectra of ZnS Nanoparticles with different capping agents like PVA and PEG-4000 are shown in Fig.2(a) and 2(b). The study of optical absorption is important to understand the behaviour of semiconductor nanoparticles..



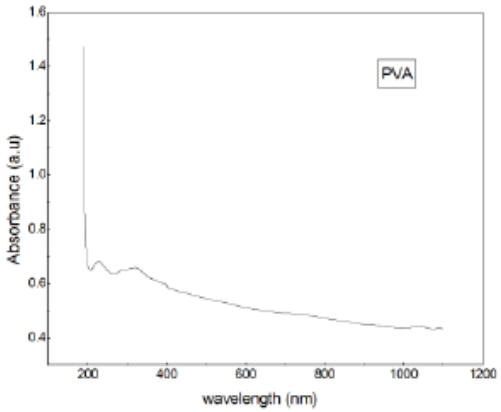



**Fig. 2a.Tauc plot and UV-Visible absorption spectra obtained for ZnS-PVA**

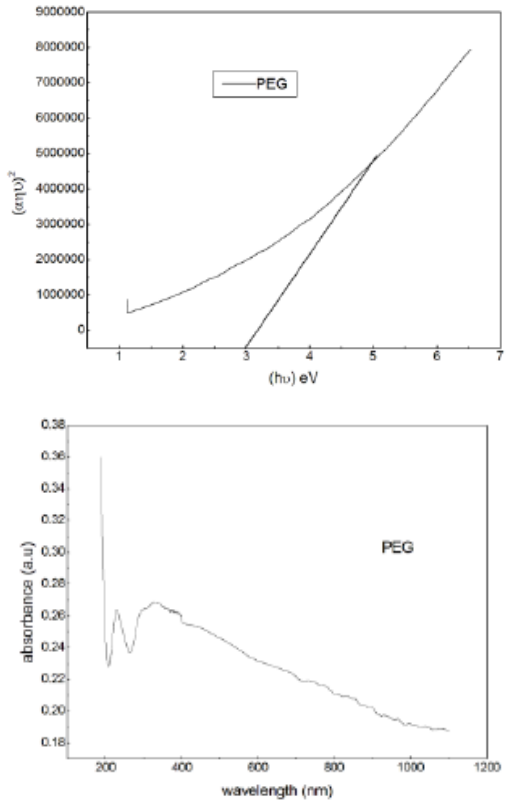



**Fig. 2b. Tauc plot and UV-Visible absorption spectra obtained for ZnS-PEG**

A fundamental property of semiconductors is the band gap – the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt feature in the optical spectrum is known as the optical absorption edge. It is evident that, the samples exhibit a strong absorption wavelength at 318 nm for PVA capped ZnS and 325 nm for PEG capped ZnS nanoparticles suggesting blue shift with respect to the bulk arising from quantum confinement effect of the nanoparticles. The band gap energy of the samples corresponding to the absorption edge is found to be 3.0 eV and 3.4 eV respectively. The band gap of bulk ZnS is 3.68 eV at 300 K. The quantum confinement effect allows one to tune the emission and excitation wavelengths of nanoparticles [24]. The obtained band gap values for different samples are shown in Table 2. From the table, it is clear that the values of optical band gap increase with the increase in the wave length.

**Table: 2 Band gap energy of ZnS-PVA and ZnS-PEG**

| S. No. | Capping agents | Band gap (eV) |
|---|---|---|
| 1 | PVA | 3.0 |
| 2 | PEG | 3.4 |

### 3.3. FE- SEM and EDAX Study:

A first sight of the produced structures was obtained with the help of SEM which allowed the synthesis of ZnS: PVA and ZnS: PEG nanopartilces . The Fig.3a and Fig.3c show the SEM images of as-prepared ZnS : PVA and ZnS: PEG deposited on the thin film and it is observed that the particle size varied from 10nm to 50 nm or more. This growth of nanoparticles agglomerated in different shapes and orientation may be attributed to the uncontrolled nucleation growth during the deposition of nanoparticles on the silica glass substrates. The EDAX pattern shown in Fig.3b and Fig.3d confirm the presence of Zinc and Sulphur .

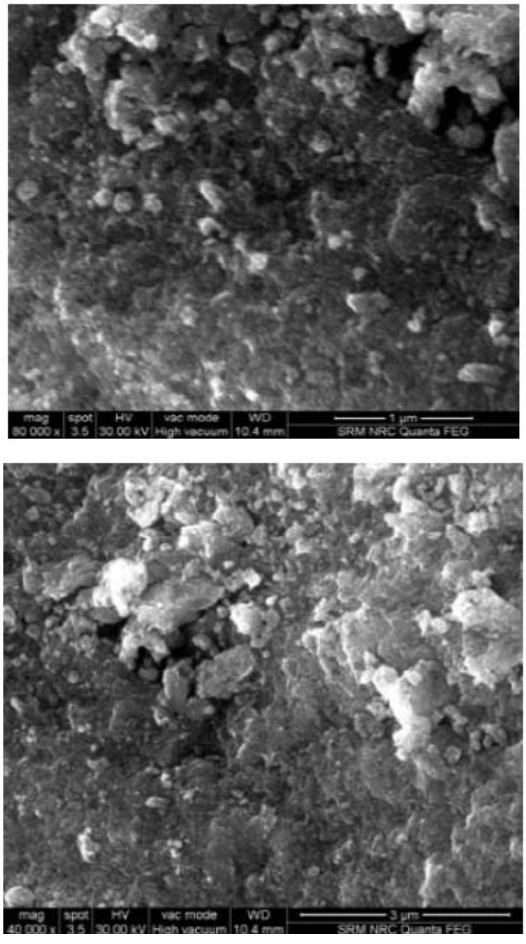


**Fig.3a. SEM images of ZnS-PVA**

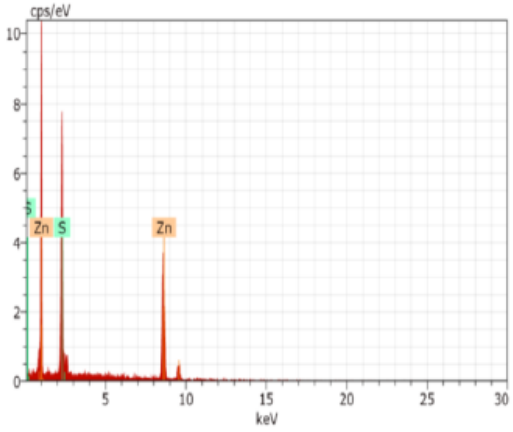
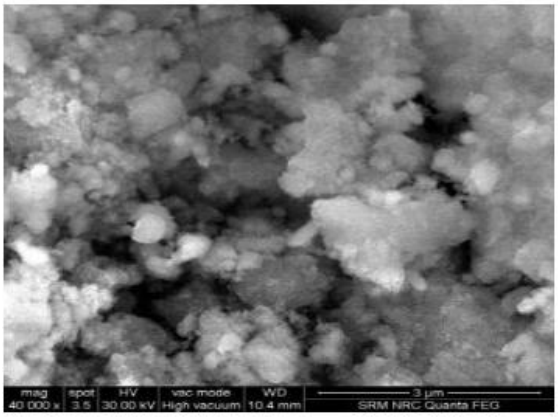



**Fig.3b. EDAX images ZnS-PEG**



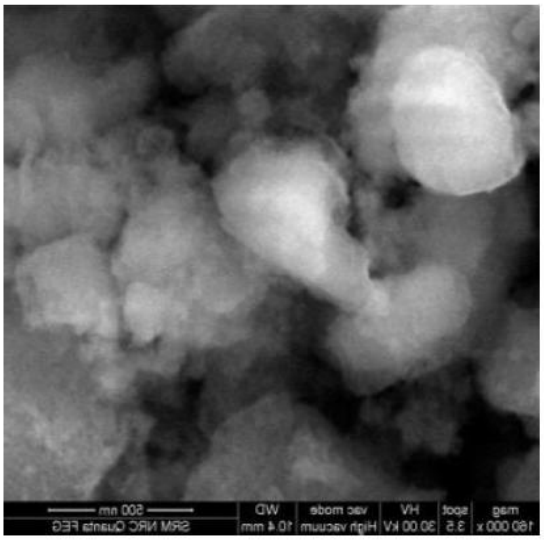


**Fig.3c. SEM images of ZnS-PEG**

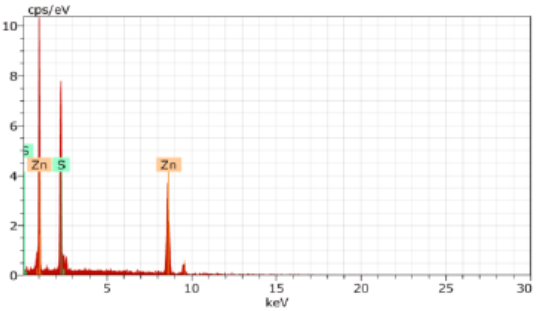



**Fig.3d EDAX images of ZnS-PEG**

### 3.4. FTIR analysis

The FTIR spectra for ZnS-PVA and ZnS-PEG used as capping agents are obtained between 3250-3500 $cm^{-1}$ are presented in Fig.4a and Fig.4b.

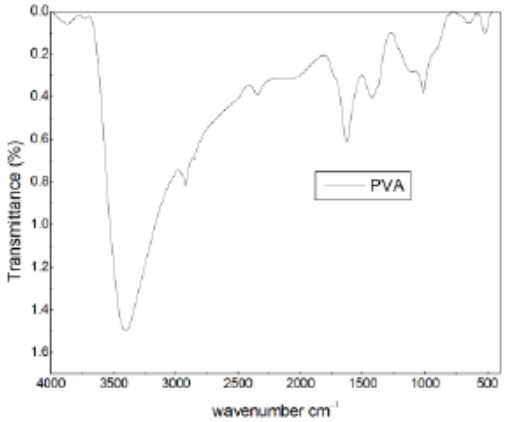



**Fig. 4a FTIR spectra for ZnS- PVA**

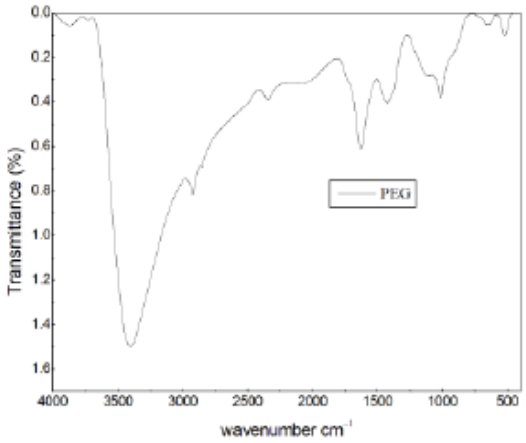



**Fig. 4b FTIR spectra for ZnS- PEG**

## IV. CONCLUSION

The simple synthesis of the ZnS nanoparticles by co precipitation method using various capping agents like PVA and PEG is reported. The UV-Visible spectra revealed that there is a blue shift of absorption band from the bulk. FTIR spectra supported the formation of ZnS nanoparticles .In XRD spectra the particle size (10-12 nm) was calculated from the Debye-Scherrer formula. SEM analysis indicates that the ZnS nanoparticles are small in size.

## V. ACKNOWLEDGEMENTS

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