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## Original Research Article

# Structural and optical properties of L-alanine passivated ZnS nanoparticles

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### ABSTRACT

We report synthesis and characterization of ZnS nanoparticles (NPs) passivated using L-alanine amino acid by simple co-precipitation method at room temperature. The samples in powder form were characterized by X-ray diffractometry (XRD), Energy dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy (HR-TEM), ultra-violet visible (UV-vis) spectroscopy and fourier transform infrared (FT-IR) spectroscopy. XRD, EDS and HR-TEM confirms the formation of ZnS NPs with desired phase and purity and ZnS NPs with average particle size of 4nm were observed for L-valine capped NPs. UV-vis spectra show strong blue shift in the maximum absorption peaks and the shift upto 295nm was observed for the ZnS sample prepared using highest concentration of L-alanine justifying its role in the efficient surface passivation. FT-IR spectrum confirms the presence of amino-acid group.

## 1. Introduction

Nanotechnology deals with the devices built using the particles having at least one dimension in the nano range. Particles in this dimensions show extra-ordinary properties and today's technologies are driven by these outstanding properties. These novel properties are the results of high surface to volume ratio and quantum size effect of the particles in nano-regime. Particles in this dimensions show potential applications in various areas e.g. sensors, optoelectronics, paints, lasers, display devices, imaging, etc. [1-6]. Metal and metal oxide nanoparticles have already shown outstanding properties [7, 8].

Non-oxide nanoparticles such as metal sulfides took special attention due to their advanced NLO properties. Silver sulfide is the most studied QD sample [9]. Other most frequently studied metal sulfide samples include CdS and ZnS QDs. Zinc sulfide (ZnS) from II-VI group semiconductor, is an interesting material having wide band gap energy of 3.72eV [10, 11] and has a promising applications in the field of optoelectronics industry such as electro luminescent devices, solar cells, light-emitting diodes (LEDs) and other optoelectronic devices. In the nanoparticles synthesis, surface modifying agents (capping agents) are often use. Choice of selecting the capping agent may depend on various parameters. Amino acids have been used as capping agent by many authors due to their easy availability, low cost, biodegradability, non-toxicity and environment friendly properties [12]. Synthesis of ZnS NPs using L-alanine as capping agent has been reported in this paper.

## 2. Materials and methods

### 2.1 Materials

Low cost simple chemical co-precipitation method was utilized for the synthesis of ZnS NPs. All chemicals used were of analytical reagent grade and used without further purification. Zinc chloride ( $ZnCl_2$ ), sodium sulfide flakes ( $Na_2S$ ) and ethanol, all AR grade, were procured from SD-fine Chemicals, Mumbai. L-alanine was purchased from Sigma Aldrich, USA.

### 2.2 Methods

In order to synthesize pure and L-alanine capped ZnS NPs by chemical co-precipitation method, stock solutions of 1M  $ZnCl_2$ , 1M  $Na_2S$  and 1M L-alanine in double distilled water (DDW) have been prepared in separate beakers. For the synthesis of ZnS NPs without using capping agent (sample name ZS-Pure), 5ml  $ZnCl_2$  from stock solution is added into the beaker containing 100 ml DDW. The solution is kept under vigorous constant stirring using magnetic stirrer. Then, 5ml  $Na_2S$  from stock solution is added into the resultant solution drop wise under vigorous stirring. White color precipitate (ppt) is obtained as soon as we add  $Na_2S$  confirming the formation of ZnS NPs. The resultant solution is stirred for another 30mins.

For the synthesis of ZnS NPs using L-alanine as a capping agent (sample name ZS1), 5ml  $ZnCl_2$  from stock solution is added into the beaker containing 100 ml DDW under constant stirring. Then, 1 ml L-alanine was added into the solution drop wise and solution is stirred for 30 mins. 5ml  $Na_2S$  from stock



solution is then added into the resultant solution drop wise under vigorous stirring to get white ppt of ZnS NPs. The resultant solution is stirred for another 30 mins. Two more samples (ZS2 and ZS3) have been prepared adding 2 ml and 3 ml L-alanine into the solution before addition of Na<sub>2</sub>S.

The solution containing ZnS NPs is centrifuged at 4000 rpm using REMI centrifuge machine model 4R-C and washed with DDW several times. The obtained ppt was then dried in hot air oven at 80°C for 4h. The dried powder then crushed into fine powder using agate mortar pestle. As synthesized samples of ZnS NPs are shown in Table 1.

**Table 1:** ZnS NPs synthesized using L-alanine as a capping agent

Sample	ZnCl <sub>2</sub> (1 M)	Na <sub>2</sub> S (1 M)	L-alanine (1 M)
ZS-Pure	5 ml	5 ml	--
ZS1	5 ml	5 ml	1 ml
ZS2	5 ml	5 ml	2 ml
ZS3	5 ml	5 ml	3 ml

### 2.3 Characterizations

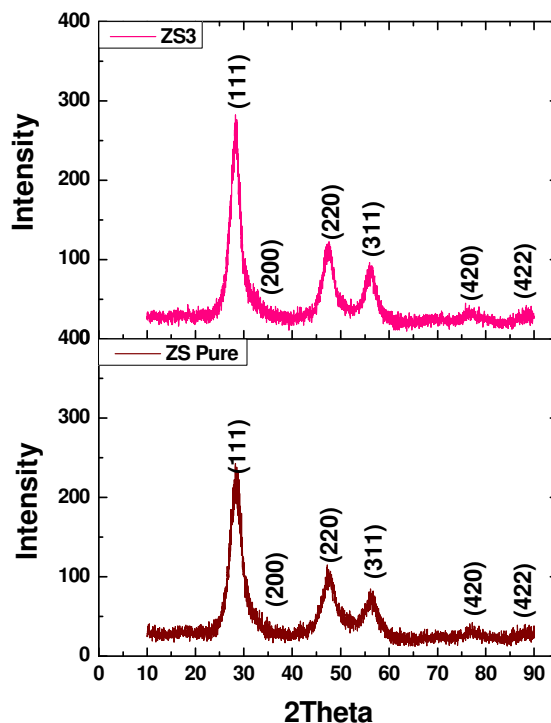
Prepared ZnS NPs were subjected to structural characterization by X-ray diffraction (XRD) using Rigaku diffractometer Miniflex II with nickel filtered CuK<sub>α</sub> radiation ( $\lambda = 1.54059 \text{ \AA}$ ). Energy dispersive X-ray spectroscopy (EDS) was performed by Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) Model JSM-7600F. Ultraviolet visible (UV-vis) spectroscopy was performed using UV-visible spectrophotometer (BLK-C-SR, Stellarnet, USA). Fourier transform infra-red (FT-IR) spectra were recorded using IR double beam spectrophotometer, Shimadzu, Japan. High resolution transmission electron microscopy (HR-TEM) has been performed using FEG-TEM 300KV Model FEI Tecnai G2, F30.

## 3. Results and discussion

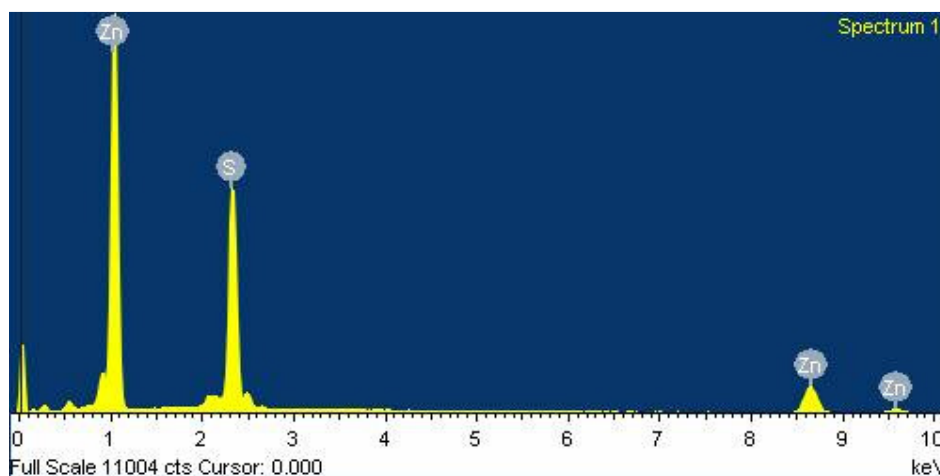
### 3.1 Structural study using XRD, EDS and HR-TEM

Figure 1 shows XRD spectrum of as synthesized powder samples of ZS-Pure and ZS3 in the range of 10° - 90°. The spectrum clearly indicates the formation nanoparticles as the

diffraction peaks show broadening [13]. The peak broadening is more in sample ZS3 which is synthesized using L-alanine as capping agent than that of the sample ZS-Pure synthesized without capping agent. This also proves the role of L-alanine as capping agent. All the peaks are perfectly matched with ZnS phase with PCPDF card no. 1100043. No peaks corresponding to impurities were seen validating the purity of our prepared samples. Debye-Scherrer formula was used to calculate particle size of prepared NPs. The average particle size was found to be 4nm for sample ZS3 and 7 nm for sample ZS-Pure. Figure 2 depicts the EDS spectrum of ZnS NPs for the sample ZS3 indicating the peaks corresponding to Zn and S only confirming the purity of the prepared sample. Figure 3 illustrates micrographs of ZnS NPs which shows the formation nanostructures with spherical morphology.



**Figure 1:** XRD spectra of ZnS NPs



**Figure 2:** EDS spectrum of ZnS NPs

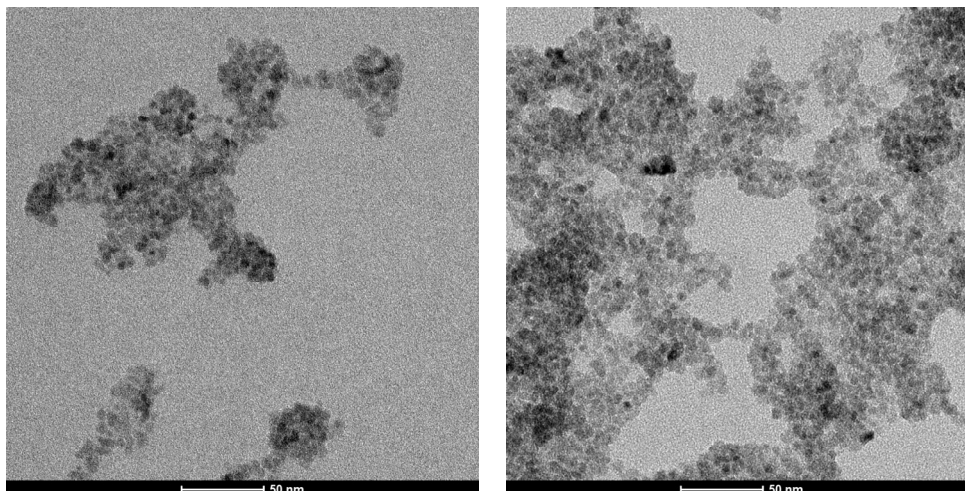


Figure 3: HR-TEM micrographs of ZnS NPs

### 3.2 UV-Vis spectroscopy

Figure 4 illustrates the UV-Vis spectra of pure and L-alanine capped ZnS NPs recorded in the wavelength range of 200-500 nm. Absorption spectra exhibit the absorption edge at 320, 315, 307 and 295 nm for samples ZS-Pure, ZS1, ZS2 and ZS3 respectively, which shows huge blue shift from the bulk ZnS absorption peak at 340 nm ( $E_g = 3.7$  eV) [14]. The blue shift in the absorption peak is a measure of increasing band gap attributed to the presence of nanocrystalline ZnS NPs due to quantum confinement of excitons and result of the formation of new discrete energy levels of individual NPs.

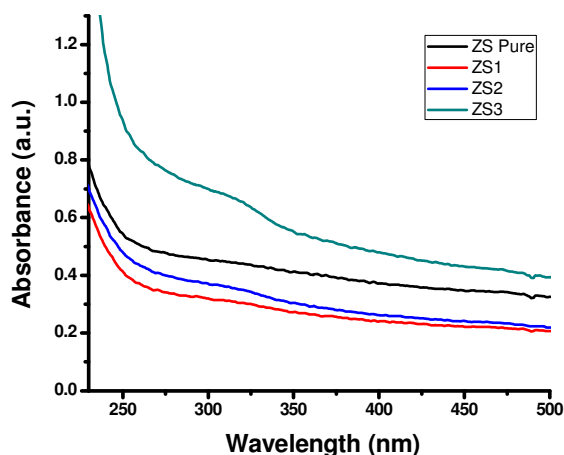


Figure 4: UV-Vis absorption spectra of ZnS NPs

Table 2: Absorption wavelengths for ZnS NPs

Sample	Maximum absorption wavelength (nm)
ZS-Pure	320
ZS1	315
ZS2	307
ZS3	295

### 3.3 FT-IR spectroscopy

The FT-IR spectrum of L-alanine capped ZnS NPs (Sample ZS3) was recorded and shown in Figure 5. The peaks

appearing at 490, 615 and 1110  $\text{cm}^{-1}$  belong to Zn-S vibrations [15-18]. Symmetric and asymmetric stretching of O-H, N-H, and C-H bonding may have caused the broad absorption band from 2331 to 3860  $\text{cm}^{-1}$ . Peak at 1685  $\text{cm}^{-1}$  is due to C=O stretching. Vibrations of COO-group may generate peaks at 1404 and 1327  $\text{cm}^{-1}$ . Peak at 1045  $\text{cm}^{-1}$  is due to C-O bonding and C-H bonding gives peak at 829  $\text{cm}^{-1}$ . COO- bonding again gives peak at 669  $\text{cm}^{-1}$  and torsional modes of  $\text{CNH}_2$  generates peak around 500  $\text{cm}^{-1}$ . All these peaks confirmed the presence of L-alanine and ZnS.

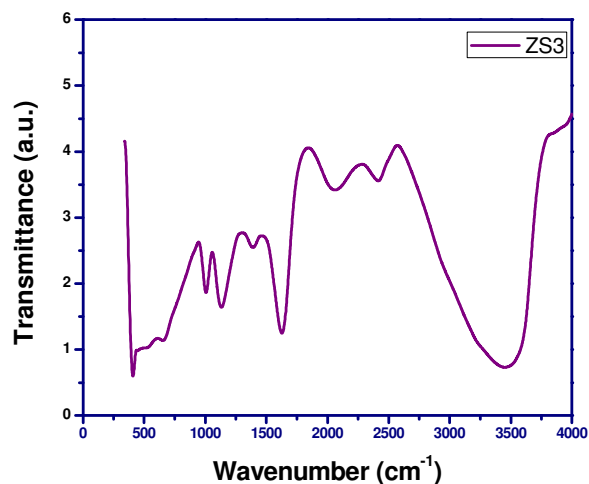


Figure 5: FT-IR spectrum of ZnS NPs

## 4. Conclusions

L-alanine capped and uncapped ZnS NPs have been successfully synthesized by room temperature co-precipitation method. Strong blue shift in the UV-vis absorption spectra is seen for the sample capped with L-alanine confirming the role of the capping agent. UV-vis absorption spectra show maximum absorption peak from 320 nm to 295 nm. XRD, EDS and HR-TEM images show the formation of ZnS pure phase with no impurity content. Peak broadening also confirms the formation of narrow crystallite size. The average particle size from XRD data is found to be 5nm. FT-IR spectrum confirms

the vibration of ZnS and L-alanine components. Obtained NPs may be potentially used in various opto-electronics devices.

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