Influence of Polyvinyl Alcohol and Alpha-Methacrylic Acid as Capping Agents on Particle Size of ZnS Nanoparticles

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Abstract

ZnS nanoparticles were synthesized successfully by wet chemical route using two capping agents, polyvinyl alcohol (PVA) and alpha-methacrylic acid (MA) to control particle growth. Optical property and the morphology of the synthesized ZnS nanoparticles revealed the influence of the capping agents in the formation of nanosize ZnS semiconductor. Particle sizes estimated from X-Ray Diffraction (XRD) analysis are 3.75 nm and 2.60 nm for ZnS/PVA and ZnS/MA respectively. The estimated energy band gap of the capped ZnS nanoparticles showed blue shift of 0.60 eV and 1.00 eV for ZnS/PVA and ZnS/MA respectively. The vibrational modes associated with OH-stretching and –COOH from the Fourier transform infrared spectroscopy (FTIR) measurements confirm the presence of the capping agents.

Keywords: ZnS nanoparticles, capping agent, blue shift, chemical route, particle size

1. Introduction

Capping of nanoparticles with functionalized long-chain organic molecule enables the exploitation of novel finite size effects on electronic and optical properties of semiconductor nanoparticles (Kulkarni et al., 2001). These optoelectronic properties include changes in emission colour of semiconductor with size, improved solubility of semiconductor in solvents and improved catalytic properties etc. (Borah & Sharma, 2008a).

Furthermore, capping of semiconductor materials especially during synthesis controls particle agglomeration and passivate the semiconductor surface against surface defect/effect (Borah, Barmam, & Sharma, 2008b; Sharma, Kumar, & Pandey, 2008). This capping agent molecule binds to the surface of the particle by stabilizing the nuclei and larger nanoparticles against aggregation, hence controlling the growth of nanoparticles (Sperling & Parak, 2012).

The choice of a capping agent depends on the material of the nanoparticles core, particle size and the solvent during synthesis. Capping agents with strong binding molecule form dense layer on the particle surface that stabilizes nanoparticles better, while weak binding molecule results to fast particle growth leading to large nanoparticles size and aggregation (Sakura, Takahashi, Kataoka, & Nagasaki, 2005). Therefore, the choice of a suitable capping agent, the dynamic of binding and unbinding, and its concentration becomes the pre-requisite for particle size regime, stabilization against aggregation and high quantum yield during synthesis of nanoparticles.

Zinc Sulfide (ZnS) is a group II-VI semiconductor with a wide direct band gap ranging from 3.5 to 3.7 eV at room temperature (Murali-Krishna, Vijayalakshmi, Venugopal, & Reddy, 2010). It has attracted much research interest due to its excellent properties at nanoscale and low toxicity when compared to other chalcogenides (Borah et al., 2008b; Ashish, Khan, & Kher, 2011a; Ashish, Khan, Kher, & Dhoble, 2011b; Luna-Martinez et al., 2011). These properties make ZnS suitable for several applications in nanoelectronic devices, bioelectronics, biosensor fluorescence, phosphors and light emitting devices (Haresh, Patrzia, Luca, Salvatore, & Gloria, 2011). As a direct band gap material, ZnS nanoparticles exhibit momentum conservation in the process of light emission with regards to electro-photo luminescence phenomena. In addition, ZnS nanoparticles emission efficiency and thermal stability increase upon reduction of the particle size as a result of confinement of electrons and holes (Murugados, Rajamannan, & Ramasamy, 2010). As a semiconductor nanoparticle, the quantum dots atom are aligned periodically in a given crystal lattice structure, hence ZnS nanoparticles usually

have the cubic zinc blende or hexagonal wurtzite structure (Hui, 2008).

A wide variety of synthesis method have been adopted for the preparation of ZnS nanoparticles such as wet chemical (Di Stefano, Cabanillas, Trigub, Rodriguez-Torrez, & Walsoe de Recca, 2010), sol–gel (Arachchige & Brock, 2007; Hebalkar et al., 2001), solid state (Calandra, Longo, & Liveri, 2003), micro emulsion (Rubio, 2010), chemical vapor deposition (Verma, Pandey, & Bhargava, 2009), hydrothermal technique (Gnanam & Rajendran, 2011) etc.

In this paper, chemical co-precipitation method using suitable capping agent have been used to synthesize the ZnS nanoparticles. This synthetic method is simple, economical and also has the advantages of producing size-controlled and un-agglomerated nanoparticles.

2. Materials and Method

2.1 Materials

Zinc sulphate hepta-hydrate ($ZnSO_4 . 7H_2O$), Sodium sulphide nonahydrate ($Na_2S . 9H_2O$), ethanol, polyvinyl alcohol (PVA), alpha-methacrylic acid (MA) and deionized water. All chemical used were of analytical grade and were used as purchased without further purification.

2.2 Preparation of ZnS: PVA and ZnS: MA Nanoparticles

In a typical process, 0.3 M of PVA or 0.3 M of MA was dissolved in deionized water and stirred with a magnetic stirrer at room temperature until a clear solution was formed. 8.78g of zinc sulphate heptahydrate dissolved in 100 ml of deionized water was added to the PVA or MA water solution and kept under stirring for 30 minutes. 9.60 g of sodium sulfide nanohydrate dissolved in 100ml of deionized water was then added drop-wise to the zinc sulphate and PVA-water or MA-water mixtures at room temperature under continuous stirring for 30 minutes until white precipitates were formed. The white precipitate of ZnS-PVA or ZnS-MA was separated from the reaction mixture by centrifugation at 3500 rpm for 20 minutes, and washed several times with the solution of toluene ethanol mixture. The white precipitates were then filtered, dried at about 120°C under air oven for two hours and the dried solid grinded in an agate mortar to achieve fine powder.

Optical absorption spectra of the sample dispersed in ethanol were recorded using a UV-Visible spectrophotometre (Model: Heλios-V4024) to determine the energy band gap of the ZnS/PVA and ZnS/MA nanoparticles. The crystallite phase formation and size of ZnS/PVA and ZnS/MA nanoparticles were analyzed by X-ray diffraction (XRD) measurements at room temperature, using PAN analytical X-Ray Diffraction machine with Cu Kα radiation (λ = 0.154056 nm). Carl-Zeiss MA-10 series Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM with EDXA) was used to obtain the morphology and elemental composition of the prepared capped ZnS nanoparticles. FTIR spectra were recorded in an FTIR spectrometer (FTIR-8400S) to verify the presence and effect of the capping agents.

3. Results and Discussion

3.1 UV-visible Results

Figure 1.0(a) shows the absorption edge shift to the blue for both ZnS/PVA and ZnS/MA nanoparticles, using the Tauc's formular (Tauc, 1974).

$$\alpha(\text{v}) = \frac{A(h\text{v} - E_g)^m}{h\text{v}} \tag{1}$$

where $\alpha(\text{v})$ is the absorption coefficient, $m = \frac{1}{2}$ for allowed direct transition, and $m = 2$ for allowed indirect transition, E_g is the optical band gap, hv is the photon energy and A is a constant related to the extent of the band tailing. Figure 1.0(b) shows a plot of $(\alpha h\text{v})^2$ against photon energy (hv), the energy band gap of the material is estimated by extrapolating the straight-line portion of the spectrum to a zero absorption coefficient value. The optical band gap of ZnS/PVA and ZnS/MA are 4.20 eV and 4.60 eV respectively. These band gap values are 0.60 eV and 1.00 eV blue shifted compared to the average of the bulk ZnS band gap energy of 3.60 eV (Masoud, Fatemeh, & Mehdi, 2009). These results also indicate that at the same molar concentration, MA restricted the agglomeration of particles better than PVA.

We also estimated the particle sizes of the nanoparticles with different capping agents using the hyperbolic band model (HBM) in the equation (Auxier et al., 2004).

$$(\hbar\omega)^2 = E_g^2 + \left(\frac{2\hbar^2 E_g^2}{m^*}\right)\left(\frac{\pi}{R}\right)^2 \tag{2}$$

From the HBM equation R can be evaluated as,

$$R = \sqrt{\frac{2\pi^2 \hbar^2 E_{gb}}{m^*(E_{gn}^2 - E_{gb}^2)}}$$

where R is the particle radius, E_{gb} is the bulk energy band gap of the semiconductor , E_{gn} is the energy band gap of the nanoparticles and m* is the effective mass of electron.

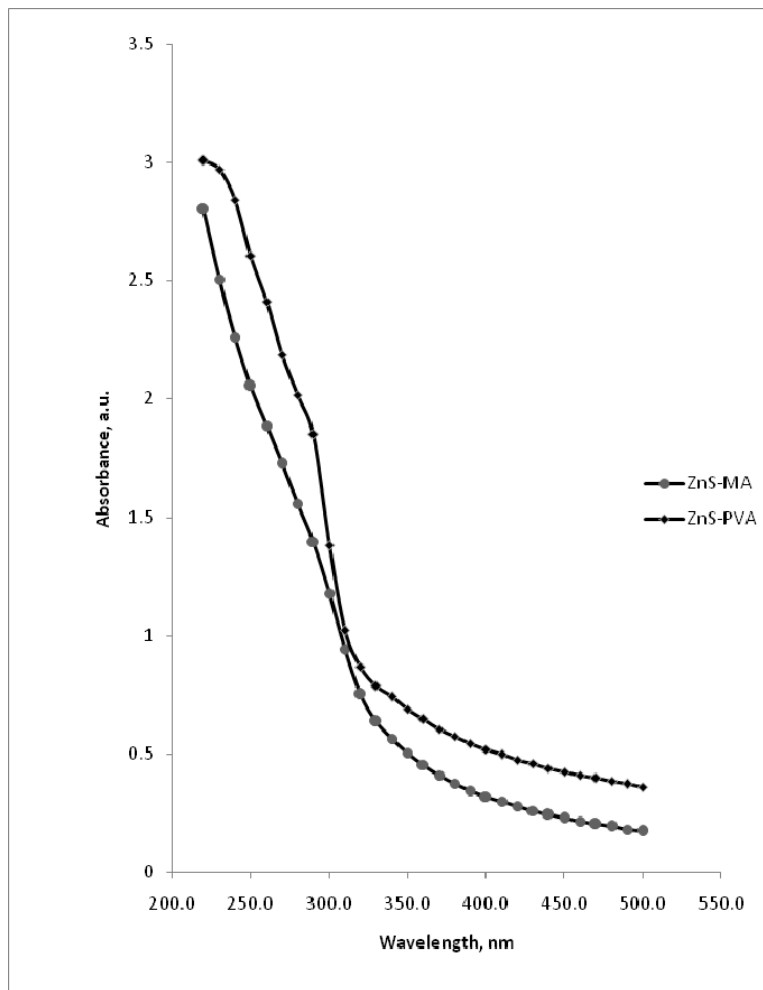The estimated average particle sizes are 3.4 nm and 2.9 nm.
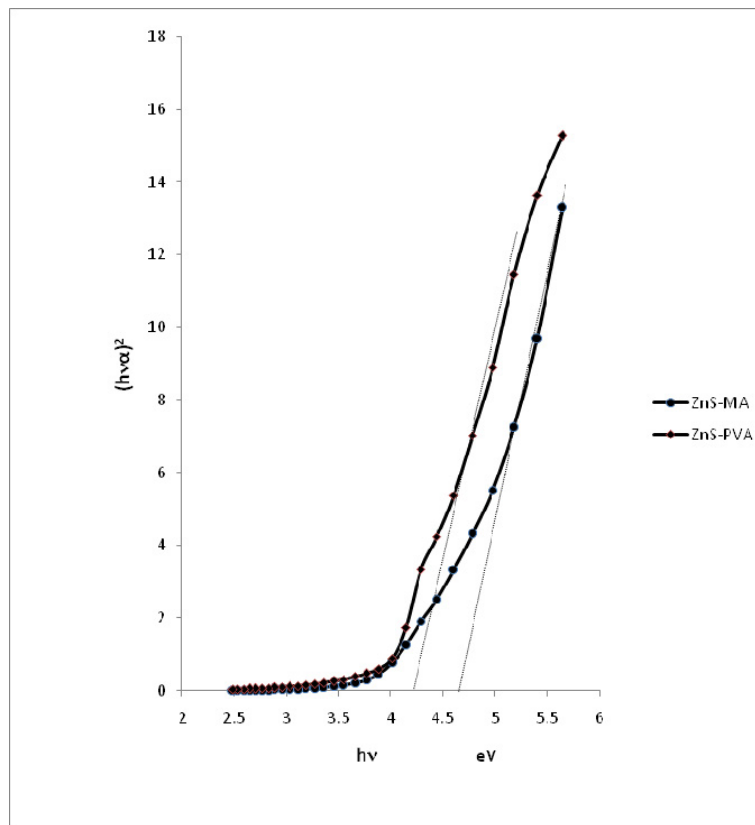

Figure 1a. Absorption spectrum of ZnS/PVA and ZnS/MA

Figure 1b. Graph of $(\alpha h\nu)^2$ against photon energy (hν) for ZnS/PVA and ZnS/MA

3.2 Structural and Mophological Results

The powder x-ray diffraction of ZnS/PVA and ZnS/MA semiconductor nanoparticles are shown in Figure 2(a) and Figure 2(b) respectively. All peaks can be assigned to a zinc blende crystal structure without extra phases. The peaks are significantly broadened, which is characteristic of the nanoparticles (Murugadoss et al., 2010). The average particle sizes

(D in nm) were calculated from XRD patterns using the Scherrer's equation;

$$D = \frac{k\lambda}{\beta cos\theta} \tag{3}$$

where k is a constant which equals to 0.89, λ is the X-ray wavelength which equals to 0.154056 nm, β, the full width at half maximum intensity (FWHM) and θ, the half diffraction angle.

The calculated average crystallite sizes of the nanoparticles are 3.75 nm and 2.60 nm for ZnS/PVA and ZnS/MA respectively. These values agree fairly well with the result of the optical absorbance spectrum.
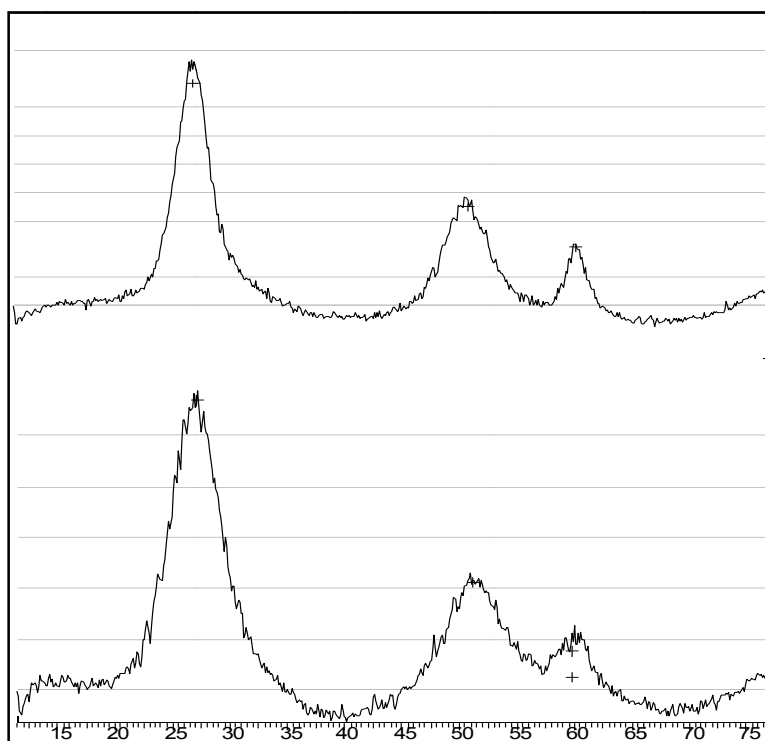
Figure 2. XRD pattern of capped (a) ZnS/PVA and (b) ZnS/MA

3.3 Electron Microscopy and EDX Result

The surface morphology of the samples were studied using a scanning electron microscope (SEM). Figure 3(a) and Figure 3(b) show the SEM micrographs of ZnS nanoparticles capped with PVA and MA respectively. The micrographs show that the particles had smooth surfaces as a result of the passivation by both PVA and MA. The EDX spectrum shown in Figures 3(c) and 3(d) revealed that the samples were pure ZnS nanoparticles. The carbon and aluminum peaks shown in the spectrum may be as a result of the carbon coated aluminum grid used.
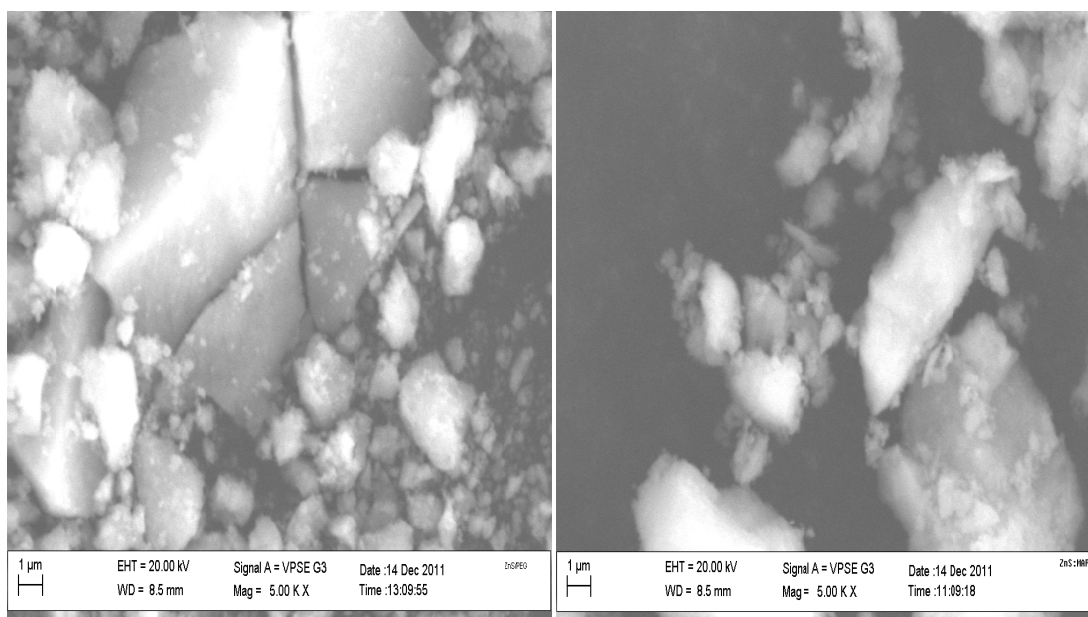

Figure 3a. SEM surface micrograph of capped (a) ZnS/ PVA and (b) ZnS/MA
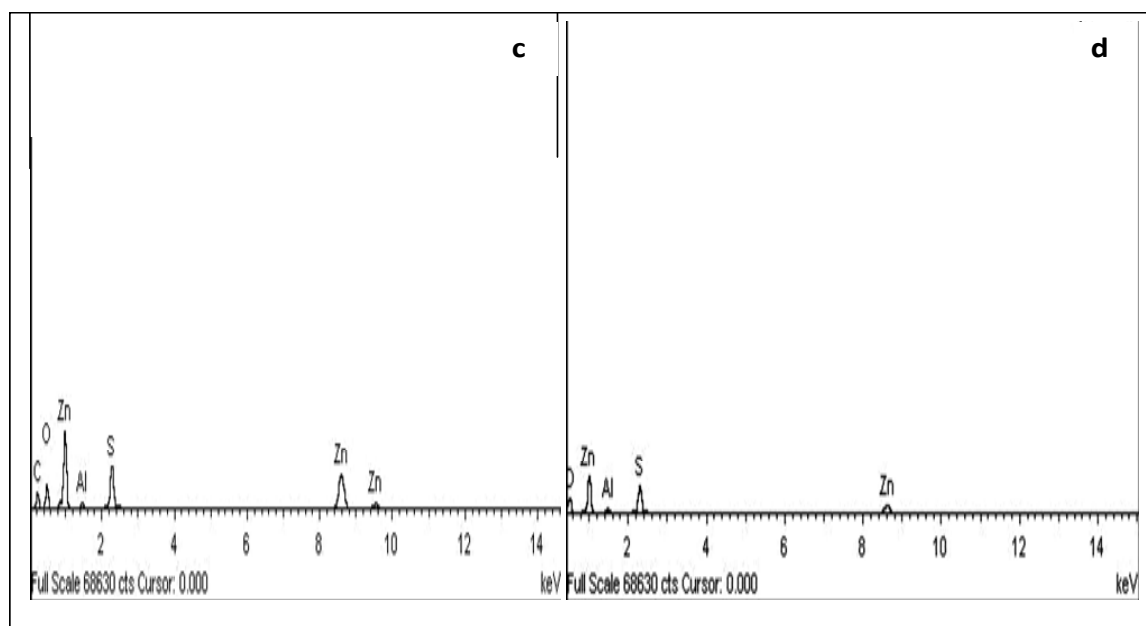
Figure 3b. Elemental composition of capped: (c) ZnS/PVA and (d) ZnS/MA

The presence of the capping agent in the synthesized ZnS nanoparticles was examined by recording their FTIR spectra in the range of 500-4500 cm^{-1}. Figure 4(a) depicts the spectra of ZnS/PVA nanoparticles with absorption peaks at 1567.21 cm^{-1} assigned to the bending vibration mode of water molecule and 3333.10 cm^{-1} indicating -OH stretching of the hydroxyl group (Shehap, 2008). The peak noted at 2893.32 cm^{-1} indicates the presence of -CH$_2$- symmetric stretch bond. In addition, the peaks at 1407.12 cm^{-1} and 1106.21 cm^{-1} are due to C-H stretching and bending bonds respectively which result to co-ordinate bonding between PVA and Zn^{2+} indicating capping on ZnS.

Figure 4b reveals the spectra of MA capped ZnS with bending vibration mode of carboxylic group -COOH at 1703.20 cm^{-1} indicating C=O stretching and stretching vibration of –OH group at 3202.91 cm^{-1}. Other peaks such as 1400.37 cm^{-1} and 1172.76 cm^{-1} are due to -CH stretching.

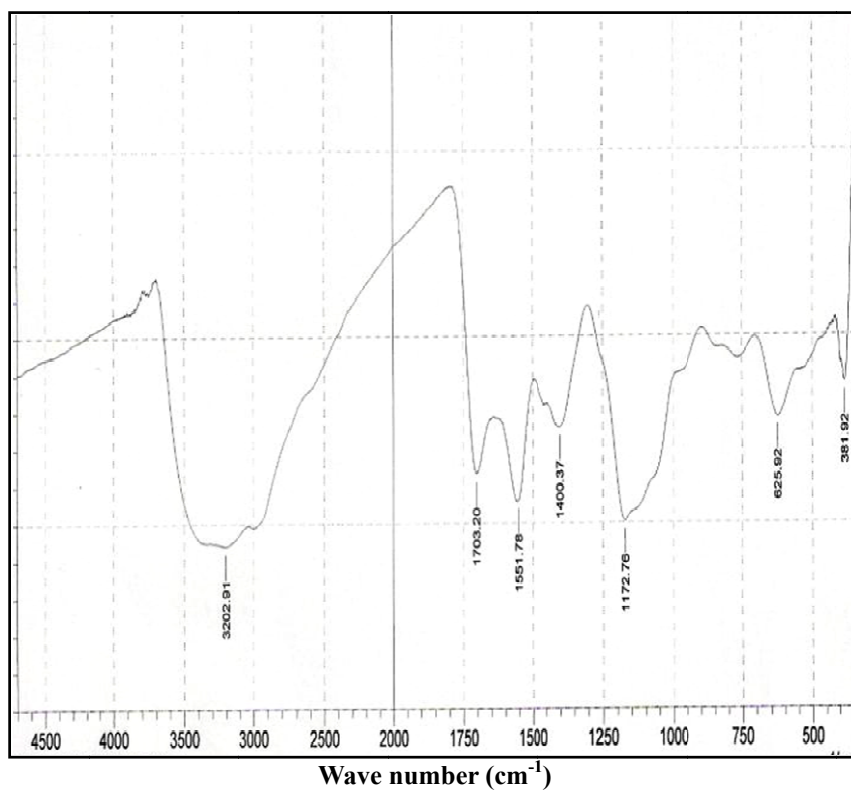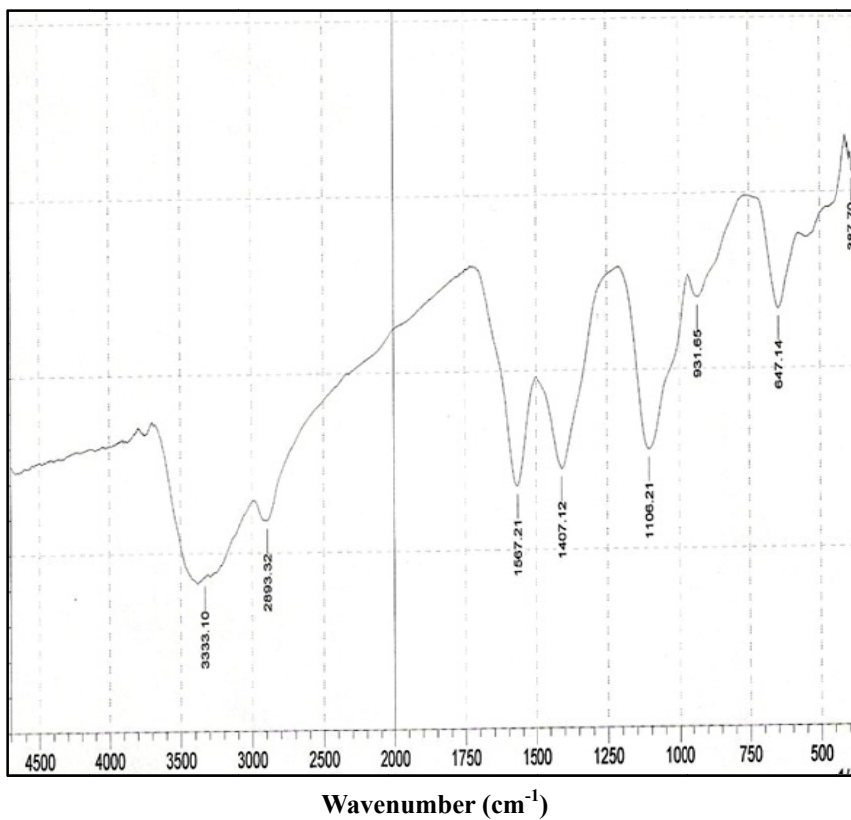Figure 4a. FTIR spectrum of ZnS/PVA

Figure 4b. FTIR spectrum of ZnS/MA

4. Conclusion

The synthesized ZnS nanoparticles via simple chemical method revealed that absorption band was blue shifted from that of the bulk. The decrease in particle size from 3.75 nm - 2.60 nm shows the influence of the various capping agent on particle size of ZnS nanoparticles. FTIR revealed the presence of PVA and MA capping agents and their influence in controlling particle size growth and preventing agglomeration.

Acknowledgements

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