

# Effect of Sodium Carboxymethyl Cellulose concentration on the Photophysical Properties of Zinc Sulfide Nanoparticles

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## ABSTRACT

The effect of sodium carboxymethyl cellulose (CMC) as capping agent on the optical (photo) and structural (physical) properties of zinc sulfide (ZnS) nanoparticles was studied. The capped nanoparticles were grown by the precipitation technique. The capping ratio of precursor (ZnS) to surfactant (CMC) (vol/vol) considered were 1:1 (S<sub>1</sub> sample), 1:2 (S<sub>2</sub> sample) and 1:3 (S<sub>3</sub> sample). Analyses carried out include; X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy and photoluminescence studies. SEM analysis revealed particles as agglomerates. The obtained band gap energies of 4.13, 4.20 and 4.27 eV for S<sub>1</sub>, S<sub>3</sub> and S<sub>2</sub> samples, respectively are blue shifted when compared to the energy of bulk ZnS semiconductor indicating quantum effect. The calculated particle sizes from XRD (2.34, 3.35 and 3.54 nm for S<sub>1</sub>, S<sub>3</sub> and S<sub>2</sub> samples, respectively) and effective mass approximation (3.59, 3.77 and 3.96 nm for S<sub>2</sub>, S<sub>3</sub> and S<sub>1</sub> samples, respectively) were found to vary with the capping amount. Capping ZnS with higher amount of CMC provided more stable nanoparticles, although with lower luminescence. The emission peaks were red-shifted S<sub>3</sub> and S<sub>2</sub> samples when compared to S<sub>1</sub> sample. At low CMC capping amount, the luminescence was found to be very high and blue shifted due to a greater participation of surface trap states.

**Keywords:** Zinc Sulfide, sodium carboxymethyl cellulose, nanoparticles, stability, surface.

## 1. INTRODUCTION

The growing interest in the study of semiconductor materials at nanoscale is primarily because of the unique photophysical properties associated with semiconductors in this small size regime. Semiconductor nanocrystallites such as ZnS have their optical properties such as absorption and luminescence changed from their bulk counterpart through quantum confinement effect. As the size of the semiconductor is reduced to a size comparable to its exciton Bohr radius, changes in the electronic structure and physical properties occur [1]. These changes include; stoke shift of energy, discretization of energy spectra, concentration of the oscillator strength, geometrical confinement of phonons and increase in surface effect [1].

Zinc sulfide (ZnS) nanocrystals have also been studied extensively because of their potential application in electronic devices such as flat panel displays, light emitting diodes,

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thin film electroluminescence devices, photocatalysis and as window materials [2, 3]. Some of the properties that make ZnS semiconductor a promising material in optoelectronics devices are its wide band gap (3.6 eV) and the relative stability of the semiconductor under atmospheric conditions when compared to other chalcogenides like CdS [4]. At room temperature ZnS stabilizes as cubic (zinc blende) structure, but transforms into wurzite structure when synthesized at elevated temperatures. Another promising property of ZnS is the ability to engineer the band gap in order to tune its optoelectronic properties. By varying ZnS particle size, blue and white emissions have been obtained [2, 5]. However, because of large-surface-to-volume ratio of these small nanocrystallites, surface related recombination may become dominant and reduce the luminescence (or quantum) efficiency of the nanoparticles significantly [6 - 8]. Also, apart from surface effect, Ostwald ripening and Vander-Waals interactions between particles could lead to agglomeration of small particles into larger particles if the synthesis process does not involve capping agents [8].

One way of reducing surface effects and controlling particles agglomeration is through nanoparticles surface passivation (or capping) with organic or inorganic molecules [9]. The choice of the capping molecule is critical. The bonding between the capping molecule and nanocrystals precursor need to be neither too weak nor too strong [10]. Weak bonding triggers fast particle growth and larger crystallites, while strong bonding may not form nanocrystals [10]. Thus, the nature of capping molecules, temperature of reaction, the dynamics of attaching and de-attaching of nanocrystals and surfactant complexes, and the concentration of the capping molecules are critical to obtaining the desired nanoparticles [10].

Several organic materials have been used to sterically and electrostatically stabilize nanoparticles against agglomeration and formation of surface defect sites or traps. These polymer materials include polyvinyl alcohol [11, 12], hexadecylamine [13], Oleic acid [7], thioglycerol [14], polyethylene glycol [15], polyvinyl pyrrolidone and thioglycolic acid [7, 16], methacrylic acid [17], Styrene butadiene rubber latex – SBR [18] and sodium carboxymethyl cellulose [19, 20].

Sodium carboxymethyl Cellulose (CMC) is obtained by activation of cellulose with aqueous NaOH in a slurry of an aqueous organic solvent followed by reacting the cellulose with monochloroacetic acid. The functional properties of CMC depend on the degree of substitution of cellulose backbone structure and the degree of carboxymethyl substituents [21]. CMC has high transparency [20], is low cost and environmentally friendly [22] and so when used as a capping material will help reduce the potential for toxicity. The presence of both carboxylated and hydroxyl groups makes CMC to readily form complexation with divalent alkaline metals. The higher molecular weight and a net negative surface charge of CMC have been utilized to stabilize nanoparticles against agglomeration through steric hindrance and electrostatic stabilization [19, 20]. CMC-copper complexes have also been prepared as paper additive and were found to enhance durability and strength properties of pulp paper sheet [20]. In this paper, we report the effect of concentration of sodium carboxymethyl cellulose (CMC) on the structural and optoelectronic properties of ZnS nanoparticles.

## 2. MATERIAL AND METHODS

### 2.1 Synthesis of ZnS nanocrystals capped with different amount of CMC

In the present approach, 1g of CMC was dissolved in 99g of deionized water at room temperature until a clear solution was formed. 25 ml of (0.2M)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was mixed with 1:1, 1:2 and 1:3 (vol/vol) ratios (named S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>, CMC respectively) of CMC. The pH of this mixture was adjusted to 4.0. 0.2M of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  was drop-wise added to the mixed

89 solution at room temperature. The mixture was kept under stirring for another 15 min after  
90 the last drop of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  was added for complete mixing of species.

91 The white precipitate obtained was centrifuged at 3500 rpm for 20 min and washed  
92 several times with a mixture of toluene- ethanol solution. This was followed by filtration to  
93 obtain white solid ZnS/CMC nanoparticles. The solid particles was dried at  $90^\circ\text{C}$  for 6 hours  
94 in a vacuum oven and made into fine powder by grinding. The synthesized nanoparticles  
95 were stored for six months before characterization. The powders of  $\text{S}_1$ ,  $\text{S}_2$  and  $\text{S}_3$  samples  
96 were then characterized using UV-Visible spectroscopy (JENWAY 6405), Scanning Electron  
97 Microscope (Carl-Zeiss), Fourier transform Infrared Spectroscopy (Shimadzu-IR 4800s), X-  
98 ray Diffraction (PANalytic X'Pert PRO) and Photoluminescence analysis (using Jobin Yvon  
99 monochromator equipped with a pulse laser excitation source and ICCD camera detection).

### 102 3. RESULTS AND DISCUSSION

#### 104 3.1 Crystal structure and size determination

106 In Figure 1 is shown the XRD diffractograms for (a)  $\text{S}_1$ , (b)  $\text{S}_2$  and (c)  $\text{S}_3$  nanoparticles (NPs),  
107 respectively. Sample  $\text{S}_1$ , which is ZnS capped with sodium carboxymethyl cellulose at 1:1  
108 (vol/vol) of precursor to surfactant, have broader diffraction peaks characteristics of  
109 nanoparticles (Figure 1a). The diffraction peaks can be indexed to the mixed cubic and  
110 hexagonal phase of ZnS. The diffraction peaks ( $2\theta$ ) at  $28.0632^\circ$ ,  $47.5652^\circ$  and  $56.3377^\circ$   
111 corresponding to d-spacing of 3.1480 nm, 1.8639 nm and 1.5531 nm, respectively are  
112 identified to originate from (111), (220) and (311) planes of the cubic (zinc blende) phase of  
113 ZnS (ICDD reference number 00-001-0792 or JCPDS No. 05-0566). The other diffraction  
114 peaks may be coming from the oxidation/degradation of the components of the sample. In  
115 the nanoparticles stabilization process, the presence of carboxylate ( $-\text{COO}^-$ ) and hydroxyl ( $-\text{OH}$ )  
116 functional groups in CMC provides a net negative surface charge which ensure  
117 nanocrystals (NCs) stability through electrostatic interaction. Therefore, with higher amount  
118 of CMC in the ZnS NPs formation, there is higher electrostatic interaction between NPs and  
119 CMC leading to a well stabilized NPs. At low amount of CMC the number of carbonyl and  
120 hydroxyl groups available for complexation is decreased, allowing more ZnS NPs to interact  
121 with each other and the environment. Also, steric hindrances dominate in limiting particles  
122 growth at this low CMC concentration; unfortunately, this may not be very effective in the  
123 stabilization process. The poor particles stabilization could lead to faster degradation of the  
124 NPs as can be observed in Figure 1(a) with the emergence of peaks at  $17.2135^\circ$ ,  $19.0794^\circ$ ,  
125  $23.2002^\circ$ ,  $29.0274^\circ$ ,  $32.8787^\circ$ ,  $33.8803^\circ$ ,  $37.6414^\circ$  and  $42.3012^\circ$ . These peaks could be  
126 coming from the oxidation of ZnS into its constituents like  $\text{Zn}(\text{OH})_2$ ,  $\text{ZnO}$ ,  $\text{ZnSO}_4$  and  
127 absorbed water. For example the peaks at  $32.8787^\circ$ ,  $33.8803^\circ$  and  $37.6414^\circ$  can be indexed  
128 to (100), (002) and (101) planes of  $\text{ZnO}$  [9, 23, 24].

129 Similarly, the diffraction pattern of the  $\text{S}_2$  (Figure 1b) sample have ( $2\theta$ ) peaks  
130 positioned at  $28.7536^\circ$ ,  $47.6318^\circ$ ,  $56.1381^\circ$  corresponding to d-spacing of 3.1339 nm,  
131 1.9092 nm and 1.6076 nm respectively. These peaks are also identified to originate from  
132 (111), (220) and (311) planes of the zinc blende structure of ZnS (JCPDS No. 05-0566). The  
133 extraneous peaks are located at the same position as those found in  $\text{S}_1$  sample pattern. The  
134 peaks are fewer in number and have lower intensities variations. The reason may be that the  
135 increase in amount of CMC in the  $\text{S}_2$  sample provided better coordination and stability of the  
136 nanoparticles surface. The XRD diffraction pattern of  $\text{S}_3$  (Figure 1c) shows that the  
137 nanocrystals have their diffraction peaks located at the  $2\theta$  angles of  $28.5144^\circ$ ,  $47.4650^\circ$  and  
138  $56.1883^\circ$  corresponding to d-spacing of 3.2281 nm, 1.8715 nm and 1.5345 nm respectively.  
139 These peaks are also assigned to the (111), (220) and (311) planes of the cubic structure of  
140 ZnS (JCPDS No. 05-0566). Most of the extraneous peaks found in the XRD patterns of  $\text{S}_1$   
141 sample have almost vanished in the  $\text{S}_3$  sample due to better complexation of all the  $\text{Zn}^{2+}$  by

the available carboxylic groups in the CMC. The three major diffraction peaks are less broadened with lower intensity variations, which may account for better stability. The fact that particles capped with larger amount of CMC provided more stability while those capped with smaller amount of CMC have smaller size distribution agrees with the report by Sakulchaicharoen *et al.* [19] that more stable nanocomposites are formed through electrostatic stabilization while particles growth is controlled by steric hindrance (density or molecular weight of CMC).

The calculated lattice constants using the values of d-spacing for the (111) plane are in good agreement with the standard lattice constant of bulk ZnS with d-spacing of 3.1230 nm ( $a = 0.540$  nm) [25]. The broadening of the diffraction peaks is an indication that the synthesized ZnS semiconductors have particles with dimension in the nanometer scale [17]. The average crystallite size from the most intense peak (111) was estimated from the XRD data using the Debye-Scherrer formula (equation 1) [26]:

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $D$  = average crystallite size perpendicular to crystallographic orientation ( $hkl$ );  $\beta$  is the full width at half-maximum (FWHM) of the ( $hkl$ ) crystal face diffraction peaks;  $\lambda$  is the wavelength of X-ray radiation (0.154060 nm);  $\theta$  is the Bragg diffraction angle of ( $hkl$ ) crystal face;  $K$  is a constant with values between 0.89 to 1 depending on the crystal symmetry; 0.94 for FWHM of integral breadth of spherical crystals with wurzite or cubic symmetry. The calculated average particle sizes are shown in Table 1.

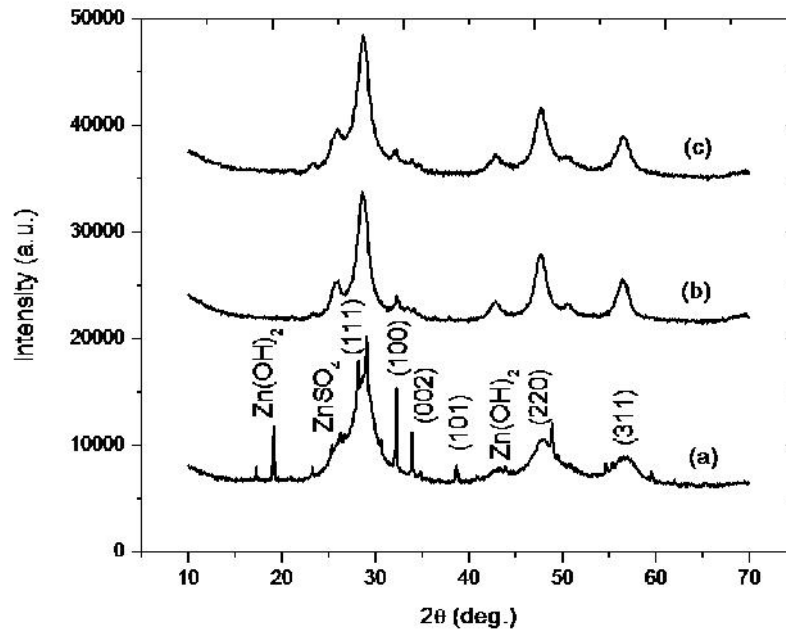


Figure 1 XRD pattern of (a) S<sub>1</sub>, (b) S<sub>2</sub>, (c) S<sub>3</sub>

### 3.2 Morphological and elemental characterization

Figure 2(a) is the SEM image of the CMC used in this work. The CMC molecules are rod-like which is similar to other reported images for a typical CMC molecule. The results in Figure 2(b), Figure 2(c) and Figure 2(d) show agglomerates of ZnS nanoparticles embedded in the CMC matrix. The smooth surface observed in the respective micrographs suggests that CMC act as a good passivating agent during ZnS synthesis.

The elemental composition of both raw CMC and CMC-capped ZnS nanoparticles are shown in the EDX spectra (Figure 3a and 3b). From the spectrum in Figure 3(b), CMC can be seen to be composed of carbon, oxygen, sodium, gold, chlorine and aluminium. The gold is most likely coming from the sample holder. In Figure 3(a), the peaks at 1.0 KeV, and 8.6 KeV correspond to the transition of zinc (Zn) while the peak at 2.4 KeV correspond to the transition of the sulfide (S) indicating ZnS embedded in the CMC matrix. The  $\text{Na}^+$  found in Figure 3(a) shows that  $\text{Na}^+$  ions were not completely displaced by the  $\text{Zn}^{2+}$  ions in the reaction.

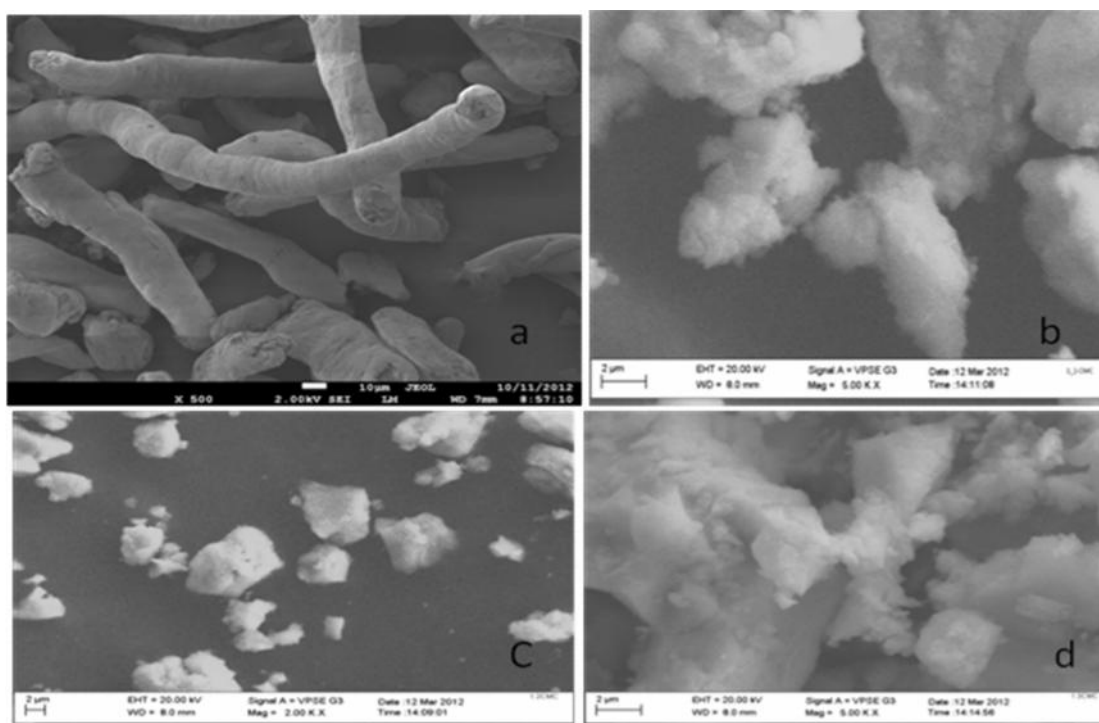


Figure 2 SEM micrographs of (a) CMC, (b) S<sub>1</sub>, (c) S<sub>2</sub> and (d) S<sub>3</sub> samples.

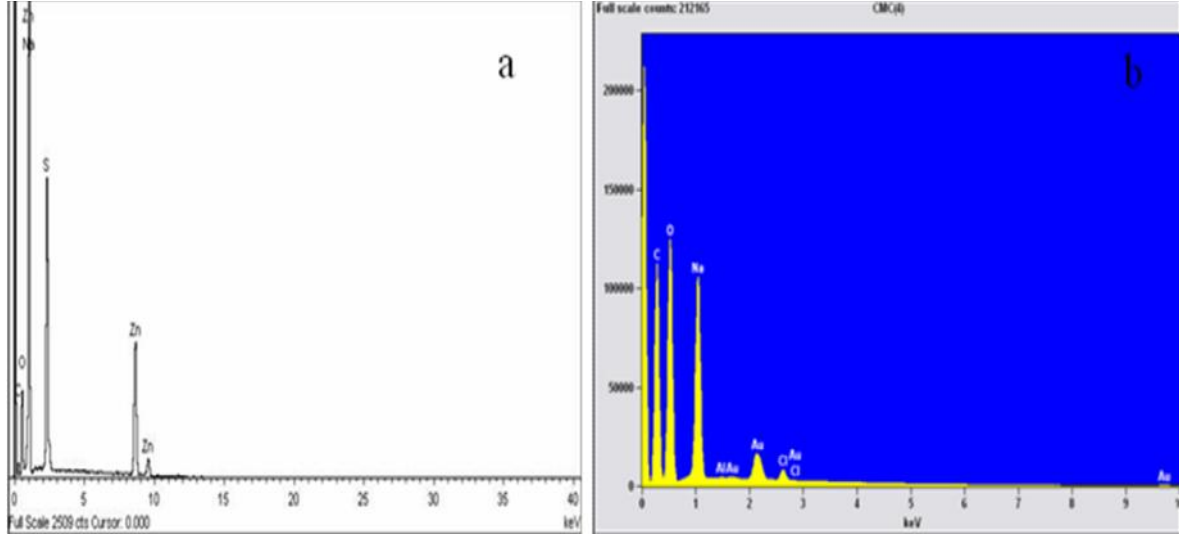


Figure 3 EDX spectra of (a) ZnS capped with CMC and (b) typical raw CMC used in this work.

### 3.3 Determination of ZnS/CMC energy band-gap and particle size using effective mass approximation (EMA)

Figure 4(I) shows the room temperature UV-Vis spectra of samples  $S_1$ ,  $S_2$  and  $S_3$  respectively. The absorption peaks are located at 285 nm, 290 nm and 300 nm respectively. The spectra are similar to those obtained by [27] for ZnS:Mn<sup>2+</sup> using similar spectrophotometer (JENWAY 6405 UV-Vis spectrophotometer).

Figure 4(II) is the plots of the square of the absorption coefficient,  $\alpha(h\nu)^2$  verses  $h\nu$  used to determine the energy band gaps for the three samples. The absorbance measurement data (A) were converted to transmittance using equations (2) and (3) as follows [28]:

$$\alpha = \frac{2.303A}{t} \quad (2)$$

$$\alpha = \frac{1}{t} \ln \left( \frac{1}{T} \right) \quad (3)$$

Equating (2) and (3) gives equation (4);

$$T = e^{-(2.303A)} \quad (4)$$

Secondly, the transmittance in equation (4) was normalized and the coefficient of absorption,  $\alpha(h\nu)$  in equation (3) becomes:

$$\alpha(h\nu) = \left[ \frac{1}{t} \ln \left( \frac{1}{T_N} \right) \right]^2 \quad (5)$$

where  $t$  is the thickness of the film and  $T_N$  is the normalized transmittance. Equation (5) was then substituted into the Tauc's formula (equation 6) for direct band gap semiconductor [28]:

$$\alpha(h\nu) = (h\nu - E_g) \quad (6)$$

The plot of  $\alpha(h\nu)^2$  versus  $h\nu$  gave discontinuities at the transition energy of the sample in the plot. The minimum point in the discontinuity region where the value of  $\alpha(h\nu)^2 = 0$  corresponds to the absorption energy  $h\nu$  of the material. The obtained band gap energy gave small average particle sizes with band gap energies greater than 4.0 eV (Table 1). The energy band gaps are blue shifted from bulk ZnS (3.60 eV) [29]. It is clear from the blue shift in energy that quantum confinement of the electrons and holes has taken place [30].

Using the values of the band gap energies in Table 1, the average particle size of each sample was determined using the EMA [31]:

$$E_n = E_b + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 r} - \frac{0.124e^4}{\hbar^2 (4\pi\epsilon\epsilon_0)^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)^{-1} \quad (3)$$

where  $E_n$  is the energy of nanoparticle,  $E_b$  is the energy of bulk ZnS (3.6 eV),  $m_e^*$  and  $m_h^*$  are the effective masses of electron and hole respectively,  $r$  is the radius of nanoparticle,  $e$  is electronic charge,  $\epsilon$  and  $\epsilon_0$  is the dielectric constant of the material and free space respectively. The effective masses used for calculation in this work are;  $m_e^* = 0.23m_0$  and  $m_h^* = 0.34m_0$  for electron and hole, respectively, while  $m_0$  is the electron rest mass [32].

The calculated results for particles size using EMA are shown in Table 1. The values of the average particle sizes calculated from XRD and EMA are both comparable to the exciton Bohr radius ( $a_B \sim 5.0$  nm) for ZnS, supporting the confinement effect [28]. The particle sizes calculated using EMA are comparable to the obtained crystal sizes from XRD patterns. It has been reported that EMA overestimates the size of particles smaller than 5.0 nm, but gives the true average particle size for larger particles size distribution [33 - 35]. Nevertheless, particle sizes determined using EMA are in good agreement with the crystallite sizes obtained from XRD pattern. Again, contrary to the observation made by [19], it is observed that particle size increased for higher CMC concentrations; it therefore seems the concentration of CMC does not effectively restrict particle growth during synthesis, but provided better particles stabilization in the long term. The pH of the solution could also have acted towards enhancing particles growth.

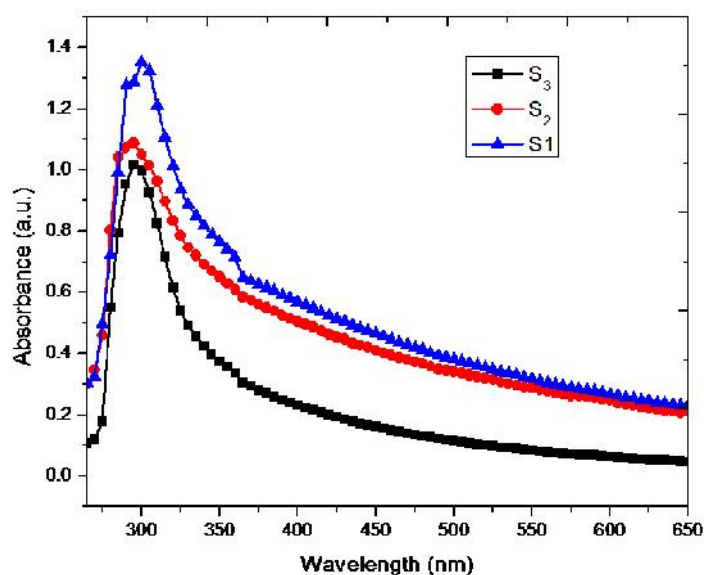
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**Table 1** Calculated band gap energies, stoke shift, crystallite size (Scherrer formula) and particle size (EMA) of ZnS/CMC samples.

| Sample               | Band-gap Energy , eV | Energy Stoke Shift, eV | Crystal size (XRD), nm | Particles size (SEM), nm | Particle size (EMA), nm |
|----------------------|----------------------|------------------------|------------------------|--------------------------|-------------------------|
| <b>S<sub>1</sub></b> | 4.13                 | 0.53                   | <b>2.43</b>            | 163                      | <b>3.98</b>             |
| <b>S<sub>2</sub></b> | 4.27                 | 0.67                   | <b>3.54</b>            | 85                       | <b>3.59</b>             |
| <b>S<sub>3</sub></b> | 4.20                 | 0.60                   | <b>3.35</b>            | 43                       | <b>3.77</b>             |

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Figure 4 (I) Absorption spectra for **S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>** samples

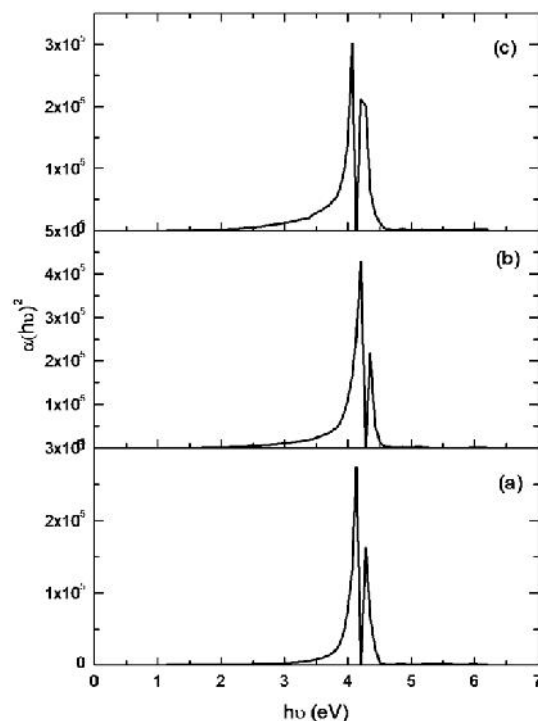


Fig. 4(II) Energy band gap for (a)  $S_3$  (b)  $S_2$  and (c)  $S_1$  samples

### 3.4 Fourier transform infra-red (FTIR) analysis

Fourier Transform Infrared spectrum (FTIR) of the CMC used for capping ZnS nanoparticles and  $S_3$  sample are shown Figure 5(a) and Figure 5(b), respectively. The FTIR spectrum of CMC (Fig. 5a) was used as standard to confirm the presence of the capping agent on the  $S_3$  sample even after rigorous washing. From Figure 5(b), the peaks at 381 and 480  $\text{cm}^{-1}$  are assigned to the metal – oxygen bonds [36] while the peak positioned at 619  $\text{cm}^{-1}$  originate from ZnS band, possibly due to Zn-S stretching [37]. The band at 1001  $\text{cm}^{-1}$  can be assigned to  $-\text{CH}-\text{O}-\text{CH}_2$  vibration of ether groups [38]. Vibrational mode peak at 1126 can be assigned to the C – O stretching band vibration. The absorption bands at 1770  $\text{cm}^{-1}$ , and 3202  $\text{cm}^{-1}$  are due to C=O and  $-\text{OH}$  stretching bands respectively of the carboxylic acid [37, 39]. Also, the broad absorption band at 3416 is due to the stretching frequency of  $-\text{OH}$  group [40]. The symmetric and asymmetric modes of stretching vibration of carbonyl ( $\text{COO}^-$ ) group at 1614 and 1446  $\text{cm}^{-1}$ , respectively are observed [20, 41, 42]. Some of these peaks observed in Figure 5(b) are also found in Figure 5(a), though with a shift in energy toward higher vibrations. The existence of the carboxymethyl substituent ( $\text{COO}^-$ ,  $-\text{CH}_2$  and  $-\text{O}-$ ) group in Fig. 5(a) and Fig. 5(b) confirm the presence of the capping agent (sodium carboxymethyl cellulose, CMC) on ZnS nanoparticles [41]. The presence of CMC after rigorous washing of the colloidal nanoparticles suggests that CMC inhibit the growth of particle by electrostatic stabilization and/or steric hindrances.

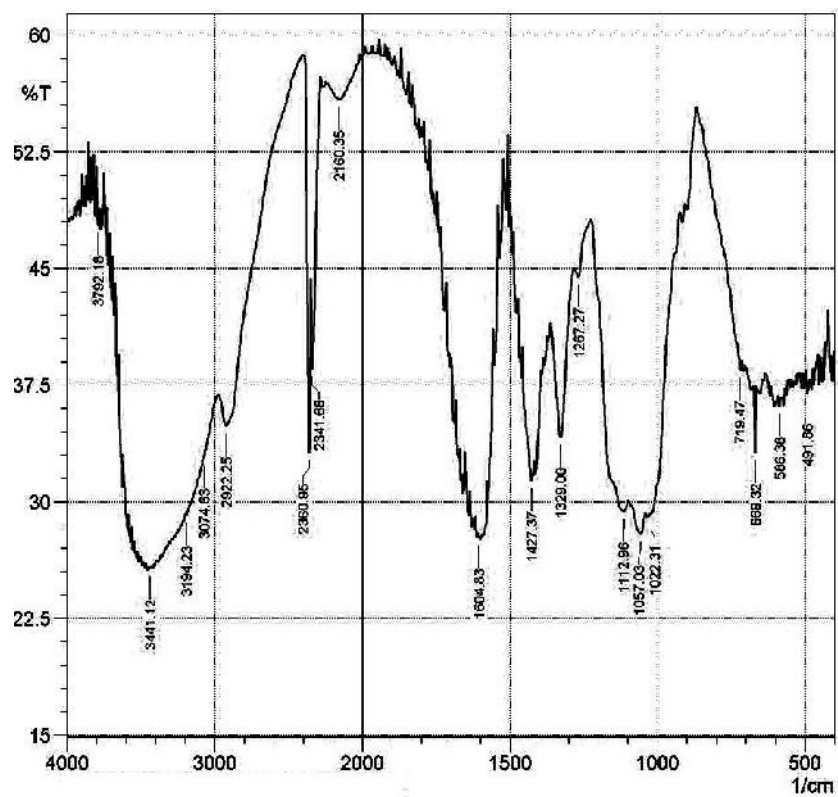


Figure 5(a) FTIR spectrum of the CMC sample

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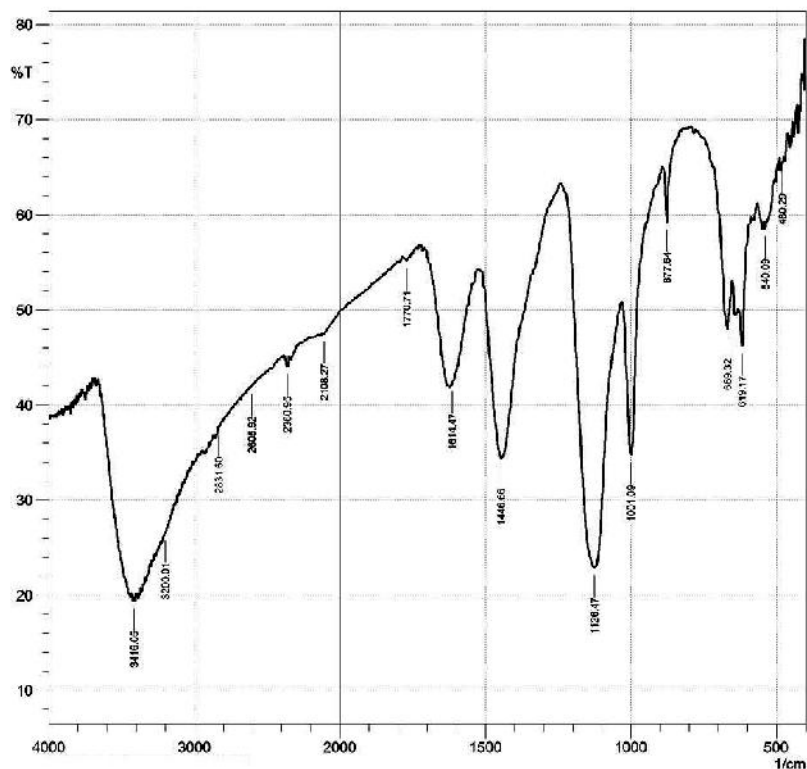


Figure 5(b) FTIR spectrum of  $S_3$  sample

### 3.5 Photoluminescence emission and excitation

Photoluminescence excitation spectra presented in Figure 5 shows the most prominent excitation bands at 285 nm and 330 nm and a broad excitation band at 360 – 450 nm. These bands correspond to the excitonic (or band-to-band) and impurity related excitation wavelengths of ZnS nanocrystals. Figure 6, (I), (II) and (III), show the emission spectra of  $S_1$ ,  $S_2$  and  $S_3$  samples, respectively. All the spectra display single peaks centered at 442, 520 and 521 nm, respectively when the samples were excited with UV light at 320 nm wavelengths. The red shift of emission peaks position for  $S_2$  and  $S_3$  samples can be attributed to changes in the shape and dimension of the nanocrystals [26]. The emission spectrum of  $S_1$  sample shows stronger PL intensity than the other samples. Luna-Martinez *et al.* [20] attributed similar observation to the relative larger amount of ZnS nanoparticles in CMC molecules. We attribute the enhanced photoluminescence emission intensity for the  $S_1$  sample to the oxidation of ZnS and the subsequent formation of thin layers of these oxidants (i.e. ZnO and Zn(OH)<sub>2</sub>) on the nanoparticles surface as can be seen from the XRD pattern. These layers further passivate the nanoparticles surface against dangling bonds or surface trap sites, thereby enhancing their luminescence. Similar observation was reported by [43] and [44]. The broadness of emission peaks of all samples synthesized in this work suggests smaller particles size distribution. This finding is supported by the average particles sizes calculated from XRD and EMA.

The observed blue and green PL emissions centered at 442 nm and 520 nm have been reported by [20] and others [9, 5] to be due to structural defects such as sulfur

vacancies ( $V_s$ ) and zinc interstitial ( $V_z$ ). Specifically Luna-Martinez and co-workers assigned the blue emission peak to surface  $V_s$  in a non-stoichiometry ZnS. Huang *et al*, [5] assigned the blue peak to surface  $V_s$  and the green peak to the transition between internal  $V_s$  and internal  $V_z$ . Surface sulfur vacancies have weak binding energies compared to the internal sulfur defects in nanocrystals [5]. Therefore, with increased CMC amount, the number of surface vacancies can be restrained; as a result the recombination between  $V_s$  donor levels with holes at the valence band becomes dominant. The observed peaks in the PL spectra of  $S_2$  and  $S_3$  samples are red shifted compared to other reports, this is likely due to the structural and particles size increase found for these samples.

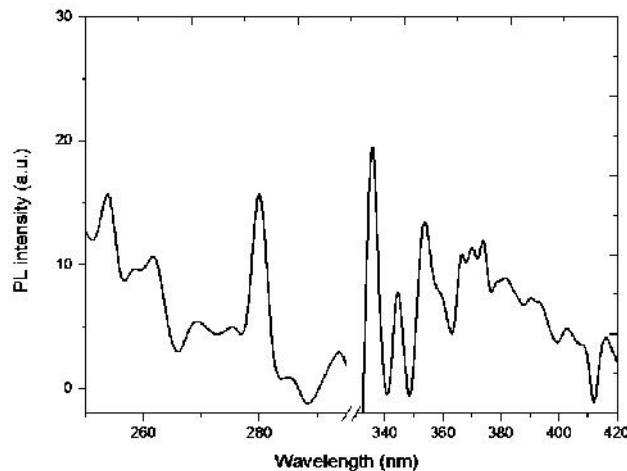


Figure 6 Photoluminescence excitation spectra

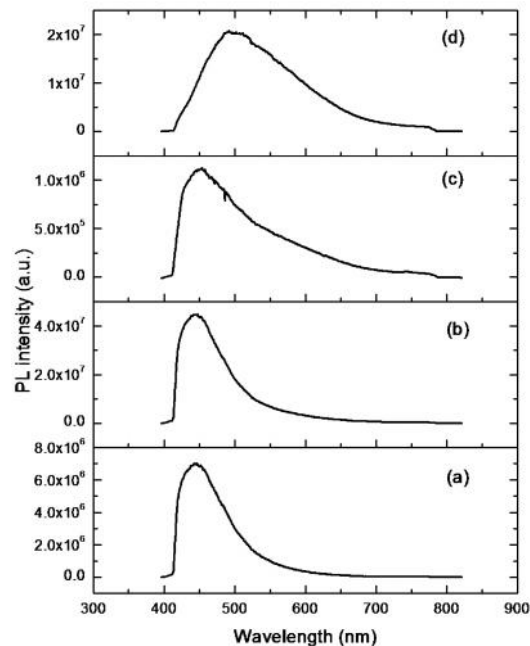


Figure 6(l) Photoluminescence emission of  $S_1$  sample at

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(a) 320 nm, (b) 345 nm, (c) 365 nm and (d) 394 nm excitations

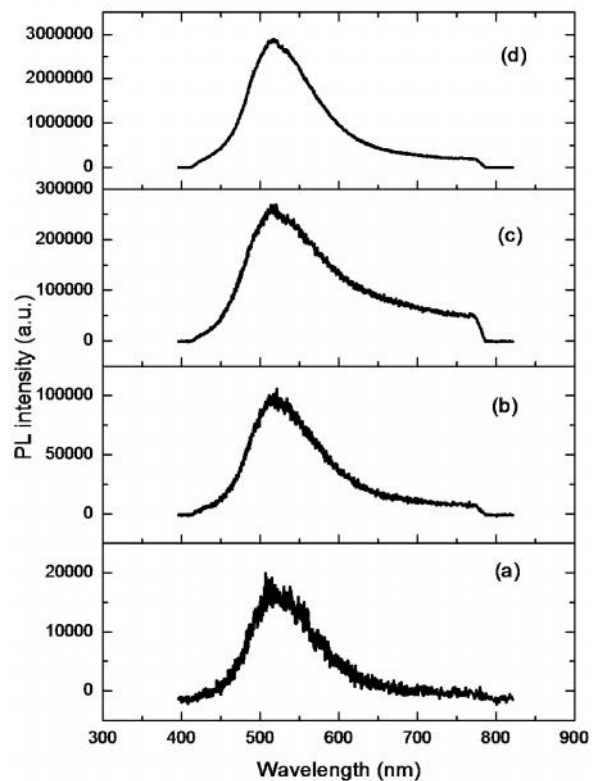


Figure 6(II) Photoluminescence emission of  $S_2$  sample at  
(a) 320 nm, (b) 345 nm, (c) 365 nm and (d) 394 nm excitations

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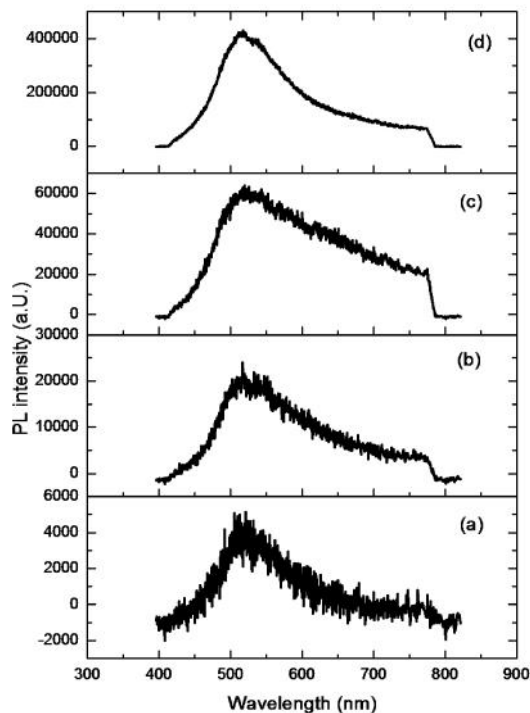


Figure 6(III) Photoluminescence emission of  $S_2$  sample at (a) 320 nm, (b) 345 nm, (c) 365 nm and (d) 394 nm excitations

#### 4. CONCLUSION

ZnS nanoparticles capped with CMC at different amount by volume was synthesized using precipitation method. The nanoparticles show structural degradation when they were kept for six months before characterization. ZnS sulfide capped with CMC at 1:1 (vol/vol) of nanoparticles-to-CMC ratio ( $S_1$ ), show higher degradation, a high emission intensity (with blue shift which is characteristic of surface state emission) and smaller mean crystallite size distribution. The  $S_3$  sample show better stability, a red shift in emission spectra and larger mean crystal size distribution. The obtained mean particle size for all the samples was less than 6.0 nm indicating nanoparticles with weak quantum effect.

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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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