

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

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ABSTRACT

Zinc sulphide (ZnS) is one of the most used semiconductors chalcogenides in electro-optical devices like flat panel displays. At nanoscale, photoluminescence emission is limited by surface traps and hence the need for green capping agents likes sodium carboxymethyl cellulose (CMC). Nanoprticles synthesis was carried out using precipitation method. Analyses carried out include; Fourier Transform Infra-red (FTIR), Scanning Electron Microscopy (SEM), UV-Vis spectroscopy, X-ray diffraction (XRD) and luminescence spectroscopy. Pure ZnS nanoparticles synthesized show some agglomeration. The obtained energy band gap value of $E_n \geq 4.0 \text{ eV}$ indicates quantum confinement effect. Capping ZnS at a ratio of 1:3 (vol/vol) of nanoparticles to CMC amount (1_3CMC) provided the best stability towards oxidation. Photoluminescence emission (PL) shows a greater participation of surface state in the emission of ZnS/CMC at capping ratio of 1:1 (vol/vol). The enhanced PL intensity is attributed to a further surface passivation by $\text{Zn}(\text{OH})_2$ or ZnO obtained from the oxidation process. The mean particle size was found to increase with CMC amount, that is, 3.35 -5.20 eV. Capping ZnS with CMC at higher concentration provided more stable nanoparticles with enhanced surface passivation against traps.

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

1. INTRODUCTION (ARIAL, BOLD, 11 FONT, LEFT ALIGNED, CAPS)

The growing interest in the study of nanostructured materials is primarily because of the unique photophysical properties associated with semiconductors in this small size regime. Nanosized semiconductor crystallites have their optical properties such as absorption and luminescence changed from their bulk 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. 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, 4]. 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 [5 - 7]. 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 [7].

One way of reducing surface effects and controlling particles agglomeration is through nanoparticles surface passivation (or capping) with organic or inorganic molecules [8]. 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 [9]. Weak bonding triggers fast particle growth and larger crystallites, while strong bonding may not form nanocrystals [9]. 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 [9].

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 [10, 11], hexadecylamine [12], Oleic acid [6], thioglycerol [13], polyethylene glycol [14], polyvinyl pyrrolidone and thioglycolic acid [6, 15], methacrylic acid [16], Styrene butadiene rubber latex – SBR [17] and sodium carboxymethyl cellulose [18, 19]. In this paper, we report the effect of concentration of sodium carboxymethyl cellulose (CMC) on the structural and optoelectronic properties of ZnS nanoparticles.

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 [20]. CMC has high transparency [19], is low cost and environmentally friendly [21] 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 [18, 19]. CMC-copper complexes have also been prepared as paper additive and were found to enhance durability and strength properties of pulp paper sheet [19].

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 1_1CMC, 1_2CMC and 1_3CMC, CMC respectively) of CMC. The pH of this mixture was adjusted to the required value. 0.2M of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was drop-wise added to the mixed solution at room temperature. The mixture was kept under

stirring for another 15 min after the last drop of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added for complete mixing of species.

The white precipitate obtained was then centrifuged at 3500 rpm for 20 min and washed several times with a mixture of toluene- ethanol solution. This was followed by filtration to obtain white solid ZnS/CMC nanoparticles. The solid particles was then dried at 90°C for 6 hours in a vacuum oven and then made into fine powder by grinding. The powders of 1_1CMC, 1_2CMC and 1_3CMC samples were then characterized using UV-Visible spectroscopy (JENWAY 6405), Scanning Electron Microscope (Carl-Zeiss), Fourier transform Infrared Spectroscopy (Shimadzu-IR 4800s), X-ray Diffraction (PANalytic X'Pert PRO) and Photoluminescence analysis (using Jobin Yvon monochromator equipped with a pulse laser excitation source and ICCD camera detection).

3. RESULTS AND DISCUSSION

3.1 Crystal structure and size determination

In figure 1 is shown the XRD diffractograms for (a) 1_1 CMC, (b) 1_2 CMC and (c) 1_3 CMC nanoparticles (NPs), respectively. Sample 1_1 CMC, which is ZnS capped with sodium carboxymethyl cellulose at 1:1 (vol/vol) of precursor to surfactant, have broader diffraction peaks characteristics of nanoparticles (Fig.1-a). The diffraction peaks can be indexed to the mixed cubic and hexagonal phase of ZnS. The diffraction peaks (2θ) at 28.0632° , 47.5652° and 56.3377° corresponding to d-spacing of 3.1480 nm, 1.8639 nm and 1.5531 nm, respectively are identified to originate from (111), (220) and (311) planes of the cubic (zinc blende) phase of ZnS (ICDD reference number 00-001-0792 or JCPDS No. 05-0566). The other diffraction peaks may be coming from the oxidation/degradation of the components of the sample. In the nanoparticles stabilization process, the presence of carboxylate (- COO-) and hydroxyl (-OH) functional groups in CMC provides a net negative surface charge which ensure nanocrystals (NCs) stability through electrostatic interaction. Therefore, with higher amount of CMC in the ZnS NPs formation, there is higher electrostatic interaction between NPs and CMC leading to a well stabilized NPs. At low amount of CMC the number of carbonyl and hydroxyl groups available for complexation is decreased, allowing more ZnS NPs to interact with each other and the environment. Also, steric hindrances dominate in limiting particles growth at this low CMC concentration; unfortunately, this may not be very effective in the stabilization process. The poor particles stabilization could lead to faster degradation of the NPs as can be observed in Fig.1-(a) with the emergence of peaks at 17.2135° , 19.0794° , 23.2002° , 29.0274° , 32.8787° , 33.8803° , 37.6414° and 42.3012° . These peaks could be coming from the oxidation of ZnS into its constituents like $\text{Zn}(\text{OH})_2$, ZnO , ZnSO_4 and absorbed water. For example the peaks at 32.8787° , 33.8803° and 37.6414° can be indexed to (100), (002) and (101) planes of ZnO [8, 22, 23].

Similarly, the diffraction pattern of the 1_2 CMC (b of Figure 1) sample have (2θ) peaks positioned at 28.7536° , 47.6318° , 56.1381° corresponding to d-spacing of 3.1339 nm, 1.9092 nm and 1.6076 nm respectively. These peaks are also identified to originate from (111), (220) and (311) planes of the zinc blende structure of ZnS (JCPDS No. 05-0566). The extraneous peaks are located at the same position as those found in 1_1CMC sample pattern. The peaks are fewer in number and have lower intensities variations. The reason may be that the increase in amount of CMC in the 1_2 CMC sample provided better coordination and stability of the nanoparticles surface. The XRD diffraction pattern of 1_3 CMC (c in Figure 1) shows that the nanocrystals have their diffraction peaks located at the 2θ angles of 28.5144° , 47.4650° and 56.1883° corresponding to d-spacing of 3.2281 nm, 1.8715 nm and 1.5345 nm respectively. These peaks are also assigned to the (111), (220) and (311) planes of the cubic structure of ZnS (JCPDS No. 05-0566). Most of the extraneous peaks found in the XRD patterns of 1_1CMC sample have almost vanished in the 1_3CMC

sample due to better complexation of all the 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.* [18] 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) [24]. The broadening of the diffraction peaks is an indication that the synthesized ZnS semiconductors have particles with dimension in the nanometer scale [16]. The average crystallite size from the most intense peak (111) was estimated from the XRD data using the Debye-Scherrer formula (equation 1) [25]:

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

where D = average crystallite size perpendicular to crystallographic orientation (hkl); β is the full width at half-maximum (FWHM) of the (hkl) crystal face diffraction peaks; λ is the wavelength of X-ray radiation (0.154060 nm); θ 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.

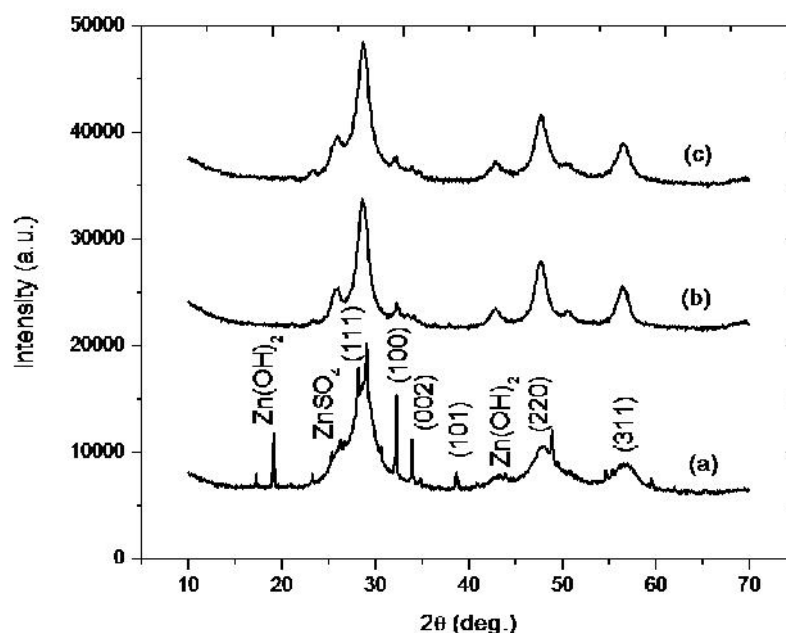


Fig.1 XRD pattern of (a) 1_1 CMC, (b) 1_2 CMC, (c) 1_3 CMC

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 [Ref....]. The results in Fig. 2-(b), Fig.2-(c) and Fig. 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 (Fig. 3-a and 3-b). From the spectrum in Fig. 3-a, CMC can be seen to be composed of carbon, oxygen and sodium. The gold, chlorine and aluminium may be from the sample preparation and instrument. In Fig. 3-b, 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.

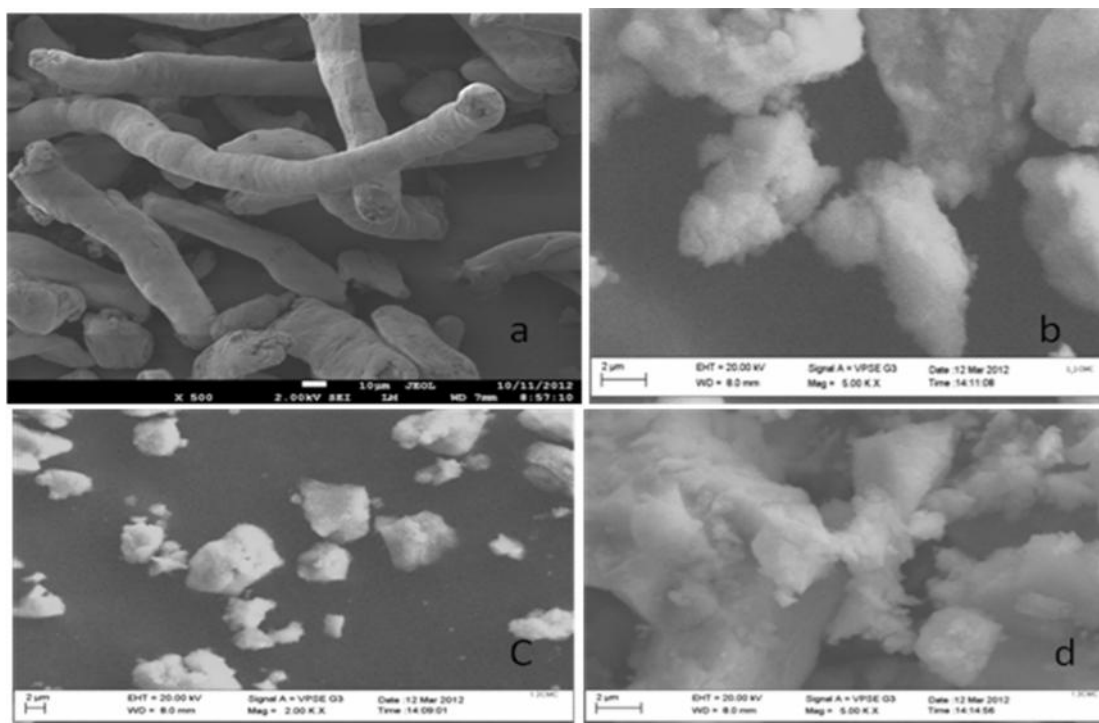


Fig. 2 SEM micrographs of (a) CMC, (b) 1_1CMC, (c) 1_2CMC and (d) 1_3 CMC samples.

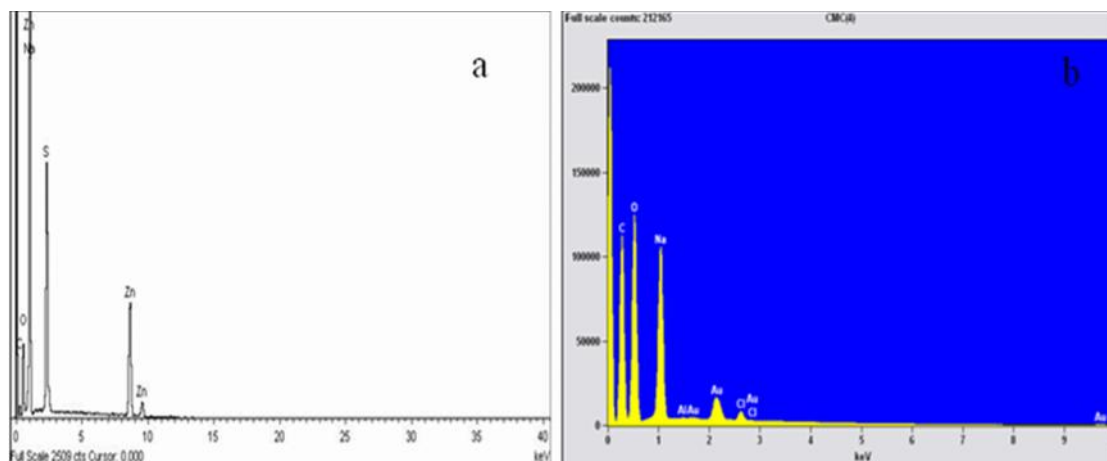


Figure 3 EDX spectra of (a) ZnS capped with CMC and (b) typical raw CMC used in this work.

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

Fig. 4(I) shows the room temperature UV-Vis spectra of samples 1_1 CMC, 1_2 CMC and 1_3 CMC respectively. The absorption peaks are located at 285 nm, 290 nm and 300 nm respectively. The spectra are similar to those obtained by [26] for ZnS: Mn²⁺ using similar spectrophotometer (JENWAY 6405 UV-Vis spectrophotometer).

Fig. 4(II) is the plots of the square of the absorption coefficient, $\alpha(h\nu)^2$ versus $h\nu$ 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 [27]:

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

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

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 [27]:

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

The plot of $\alpha(h\nu)^2$ verses $h\nu$ 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) [28]. It is clear from the blue shift in energy that quantum confinement of the electrons and holes has taken place [29].

Using the values of the band gap energies in Table 1, the average particle size of each sample was determined using the EMA [30]:

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

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, ϵ and ϵ_0 is the dielectric constant of the material and free space respectively.

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 [31 - 33]. The particle sizes determined using EMA is a good agreement the crystallite sizes obtained from XRD. Again, contrary to the observation made by [19], it is observed that the 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.

Table 1 Calculated band gap energy, 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
1_3 CMC	4.20	0.60	4.47	43	4.46
1_2 CMC	4.27	0.67	4.72	85	4.32
1_1 CMC	4.13	0.53	3.24	163	4.62

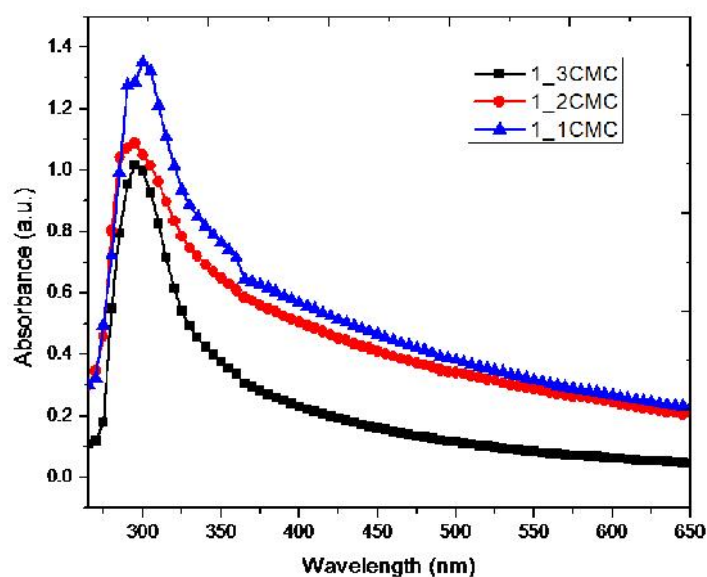


Fig. 4 (I) Absorption spectra for 1_1 CMC, 1_2 CMC and 1_3 CMC samples

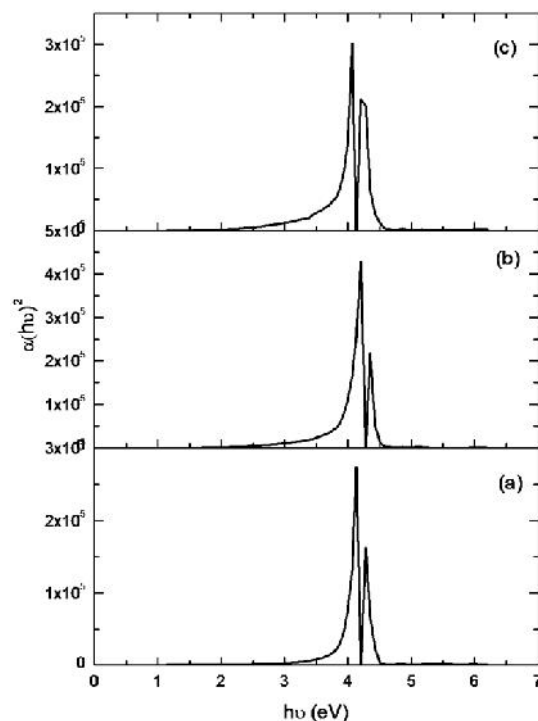


Fig. 4(II) Energy band gap for (a) 1_1 CMC, (b) 1_2 CMC and (c) 1_3 CMC samples

3.4 Fourier transform infra-red (FTIR) analysis

Fourier Transform Infrared spectrum (FTIR) of 1_3CMC sample shown Fig. 5 was used to confirm the presence of the capping agent even after rigorous washing. The peak at 381 and 480 cm^{-1} are assigned to the metal – oxygen bonds [34] while the peak position at 619 and 669 cm^{-1} originate from ZnS band, possibly due to Zn-S stretching [35]. The band at 1001 cm^{-1} can be assigned to $-\text{CH}-\text{O}-\text{CH}_2$ vibration of ether groups [36]. Vibrational mode peak at 1126 can be assigned to the C – O stretching band vibration. The absorption bands at 1770 cm^{-1} , and 3202 cm^{-1} are due to C=O and $-\text{OH}$ stretching bands respectively of the carboxylic acid [35, 37]. Also, the broad absorption band at 3416 is due to the stretching frequency of $-\text{OH}$ group [38]. The symmetric and asymmetric modes of stretching vibration of carbonyl (COO^-) group at 1614 and 1446 cm^{-1} , respectively are observed [19, 39, 40]. Thus, the existence of the carboxymethyl substituent (COO^- , $-\text{CH}_2$ and $-\text{O}-$) group confirms the presence of capping agent (sodium carboxymethyl cellulose, CMC) on ZnS nanoparticles [39]. 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.

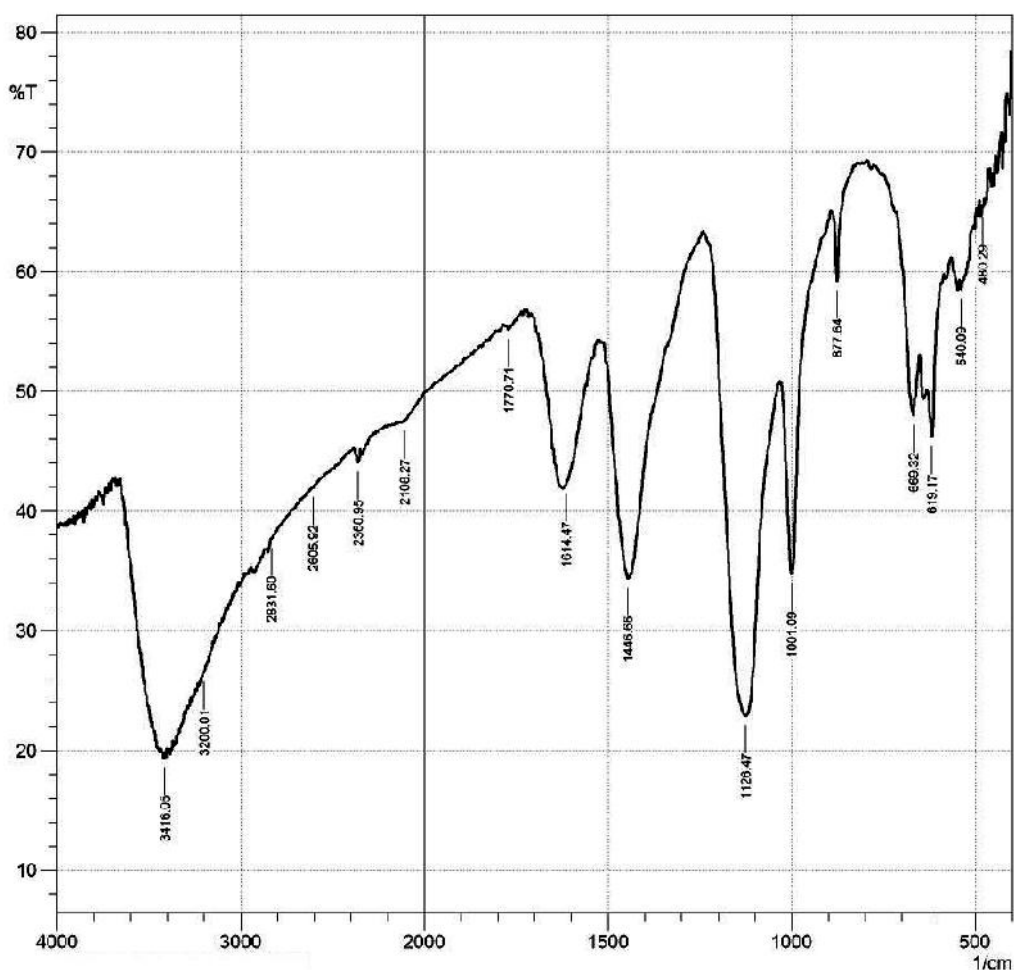


Fig. 5 FTIR spectrum of 1_3CMC sample

3.5 Photoluminescence emission and excitation

Photoluminescence excitation spectra presented in Figure 6, (IV) shows the most prominent excitation bands at 285 nm and 330 nm. These bands correspond to the excitonic or band-to-band excitation wavelength of ZnS nanocrystals. Figure 6, (I), (II) and (III), show the emission spectra of 1_1CMC, 1_2CMC and 1_3CMC 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 1_2CMC and 1_3CMC samples can be attributed to changes in the shape and dimension of the nanocrystals [25]. The emission spectrum of 1_1CMC sample shows stronger PL intensity than the other samples. Luna-Martinez *et al.* [19] attributed similar observation to the relative larger amount of ZnS nanoparticles in CMC molecules. We attribute the enhanced photoluminescence emission intensity for the 1_1CMC sample to the oxidation of ZnS and the subsequent formation of thin layers of these oxidants (i.e. ZnO and Zn(OH)₂) 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 [41] and [42]. 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 around 520 nm have been reported by [19] and others [8, 4] to be caused by 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*, [4] 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 [4]. 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 for the 1_2CMC and 1_3CMC samples are red shifted compared to other reports, this is likely due to the structural and particles size increase found for these samples.

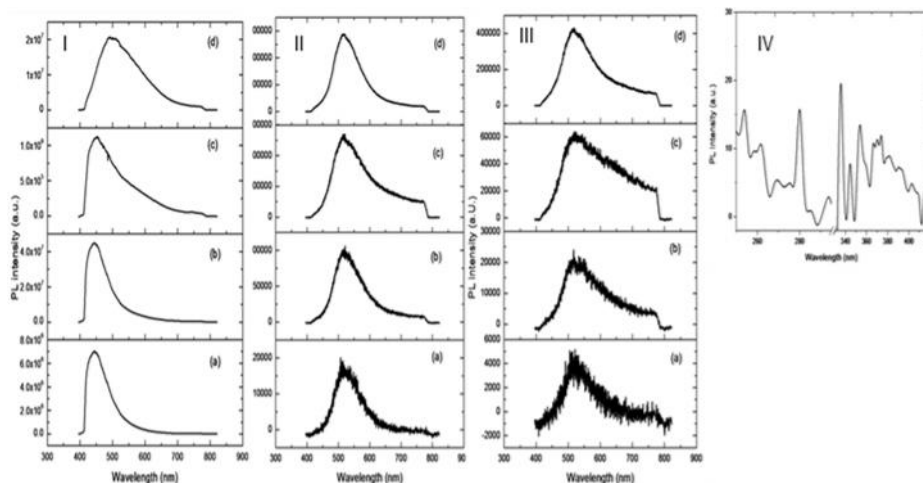


Fig. 6 Photoluminescence emission of (I) 1_1CMC, (II) 1_2CMC and (III) 1_3CMC at (a) 320 nm, (b) 345 nm, (c) 365 nm and (d) 394 nm excitations, and (IV) Photoluminescence excitation spectra.

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 (1_1CMC), show higher degradation, a high emission intensity (with blue shift which is characteristic of surface state emission) and smaller mean crystallite size distribution. The 1_3CMC 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.

ACKNOWLEDGEMENTS

The authors wish to thank Dr Viana Bruno of Laboratoire de Chimie de la Matière Condensée de Paris, France for the photoluminescence analysis. Also, our gratitude goes to National Agency for Science and Engineering Infrastructure Abuja, Nigeria (NASENI) for funding part of this work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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