Passivative Effect of Polyethyleneglycol and Carboxylmethly Cellulose as Capping Agents on Particle Size of ZnS Nanoparticles

Agents on Particle Size of ZnS Nanoparticles.
Ahemen, Iorkyaa: Department of Physics, University of Agriculture, Makurdi. Benue, State, Nigeria.
Amah, Alexander Nwabueze (Corresponding Author): Department of Physics, University of Agriculture, Makurdi. Benue State, Nigeria (e-mail: (odunnze@gmail.com).or (odunzalex@yahoo.com).
Kalu, Onyekachi: Department of Physics, University of Agriculture, Makurdi. Benue, State, Nigeria.

Abstract
ZnS nanoparticles were synthesized using wet chemical co-precipitation method. During synthesis, polyethylene glycol (PEG) and carboxylmethly cellulose (CMC) molecule were used as capping agents. The effect of the capping materials was analyzed for their effectiveness in limiting the growth of ZnS nanoparticles. The prepared ZnS nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-rays (EDX). The estimated crystal sizes from XRD are 3.92 nm and 3.89 nm for ZnS/PEG and ZnS/CMC nanosize semiconductors respectively. The effect of capping agent on the energy band gap of the capped ZnS nanoparticles were blue shifted at 0.16 eV and 0.28 eV for ZnS/PEG and ZnS/CMC respectively. Fourier transform infrared spectroscopy (FTIR) confirms the interaction of the capping agents with ZnS.

Key words: ZnS nanoparticles, capping agent, polyethylene glycol, precipitation and sodium carboxymethyl cellulose

1.0 Introduction

Capping agent with functionalized long-chain which helps to spatially confine electron (hole) on nanoparticles is believed to alter the physical, optical, electronic, catalytic and magnetic properties of semiconductor materials by limiting their particle growth at the beginning of their formation. These optoelectronic properties which include changes in semiconductor emission color with size, improved solubility in solvents and improved catalytic properties are dependent on capping of the nanoparticles (Borah *et al.* 2008; Borah & Sarma 2008 and Park *et al.* 2009).

Several researchers have used different organic materials such as polyethylene glycol (PEG), carboxylmethyl cellulose (CMC) to stop particle agglomeration and to obtain mono-dispersed nanoparticles of sizes less than 5 nm (Gupta *et al.* 2006 and Luna-Martinez *et al.* 2011). Recently, our report on the influence of Polyvinyl alcohol and alpha-methacrylic acid on ZnS nanoparticles revealed particle sizes of 3.75 nm and 2.60 nm respectively (Amah *et al.* 2012).

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 *et al.* 2010). This semiconductor has attracted much research interest due to its excellent properties and low toxicity when compared to other chalcogenides (Luna-Martinez *et al.* 2011; Mamun *et al.* 2011; Ashish *et al.* 2011a and Ashish *et al.* 2011b). These properties make ZnS suitable for several applications in electronic devices, bioelectronics, biosensor fluorescence, phosphors and light emitting devices (Haresh *et al.* 2011). As a direct band gap semiconductor, ZnS exhibits momentum conservation in the process of light emission with regards to electro-photo luminescence phenomena (Mamun *et al.* 2011). In addition, the emission efficiency and thermal stability of ZnS increases upon reduction of the particle size as a result of confinement of electrons and holes (Murugadoss *et al.* 2010).

A number of synthetic methods have been used for the preparation of ZnS nanoparticles. Such methods include; precipitation method (Di-Stefano *et al.* 2010), sol–gel technique (Arachchige & Brock 2007; Hebalkar *et al.* 2001), solid state reaction method (Calandra *et al.* 2003), micro emulsion (Rubio, G. 2010), chemical vapor deposition (Verma *et al.* 2009), hydrothermal technique (Gnanam & Rajendran 2011) etc.

In this paper, chemical co-precipitation method with suitable capping agents is used to synthesize the ZnS nanoparticles in order to control the particle size and enhance stability. This synthetic method is simple, economical and has the advantages of producing size-controlled and un-agglomerated nanoparticles.

2.0 Materials and Method

2.1 Materials

Zinc sulphate heptahydrate ($ZnSO_4{\cdot}7H2O$), sodium sulphide nonahydrate($Na_2S{\cdot}9H_2O$), ethanol, polyethylene glycol (PEG) and sodium carboxylmethyl cellulose (CMC). All chemicals used were of analytical grade and were used as purchased without further purification.

2.2 Preparation of ZnS:PEG and ZnS:CMC nanoparticles

In a typical process, 0.3M PEG, 0.3M CMC were dissolved in deionized water separately and stirred with magnetic stirrer at room temperature until they formed clear solutions. In a separate container, 8.78g of zincsulphate heptahydrate was dissolved in 100ml of deionized water and then added to the PEG, CMC water solutions. 9.60g of $Na_2S.9H_2O$ dissolved in 100ml of deionized water was then added drop-wise to the precursor-surfactant mixtures (i.e. Zn^{2+}/PEG, Zn^{2+}/CMC mixtures) at room temperature under continuous stirring for 30minutes until white precipitates were formed. The white precipitate was separated by centrifugation at 3500 rpm for 20minutes, and washed several times with ethanol. The white precipitates were then filtered and dried at about 120^{o}C under air oven for two hours. The dried solids were then made into fine powders by grinding.

2.3 Method of Analysis

Optical absorption spectra of the samples dispersed in ethanol were recorded using a UV-Visible spectrophotometer (Heλios-V4024).The structures were analyzed by X-ray diffraction (XRD) measurements using PAN analytical X-ray diffraction machine with Cu Kα radiation (λ = 0.154056 nm). Carl-Zeiss MA-10 series scanning electron microscope (SEM) with energy dispersive x-ray analysis (EDX) was used to obtain the morphology and elemental compositions of the prepared capped ZnS nanoparticles. FTIR spectra were recorded in an FTIR spectrometer (Shimadzu FTIR-8400S) to verify the presence and effect of the capping agents.

3.0. Results and Discussion

3.1. UV-visible results

Fig.1 shows the absorption spectra for ZnS/PEG and ZnS/CMC nanoparticles. The energy band gaps of the synthesized nanoparticles were obtained from Tauc's formula (Pankov 1971):

$$\alpha(\nu) = \frac{A(h\nu - E_g)^m}{h\nu} \qquad (1)$$

where $\alpha(\nu)$ is the absorption coefficient, $m = \frac{1}{2}$ for allowed direct transition, E_g is the optical band gap, hν is the photon energy and A is a constant related to the extent of the band tailing. Fig. 2 shows a plot of $(\alpha h\nu)^2$ against photon energy (hν), the energy band gap of the material was estimated by extrapolating the straight-line portion of the spectrum to the energy axis where $(\alpha h\nu)^2 = 0$. The obtained optical band gap of ZnS/PEG and ZnS/CMC are 3.76 eV and 3.88 eV, respectively. These band gap values are 0.16 eV and 0.28 eV blue shifted from the bulk ZnS value of 3.60 eV (Masoud *et al.* 2009).

Nanoparticles sizes were estimated using the hyperbolic band model (HBM) (Auxier *et al.* 2004) given by equation (2);

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

where E_g is the energy band gap of the nanoparticles, R is the particle's radius and m^* is the electron mass. Particles sizes were also calculated using the effective mass approximation (EMA) proposed by Brus in 1983 (Rajesh & Ryan 2008) given by equation (3);

$$E_g - E_b = \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e{}^*} + \frac{1}{m_h{}^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 R} - \frac{0.124e^4}{\hbar^2(4\pi\varepsilon\varepsilon_0)^2}\left(\frac{1}{m_e{}^*} + \frac{1}{m_h{}^*}\right)^{-1} \qquad (3)$$

where E_b is the energy of bulk ZnS, m_h^* is the effective mass of hole, ε_0 is the permittivity in free space, ε is permittivity of material, e is the electronic charge and all other symbols have their meanings as it was for equation (2).

The estimated particle sizes from both models are presented in the Table 1. The results indicated that zinc sulfide capped with CMC has a larger band gap and smaller average particles size when compared with ZnS capped with PEG. The results revealed better surface passivation of ZnS nanoparticles when capped with CMC. This might be because CMC consist of two functional groups, that is; the carbonyl and the hydroxyl groups. The presence of these functional groups ensures nanoparticle's surface stabilization through electrostatic repulsive forces while the larger molecular weight of CMC prevented particles growth through steric hindrances. In the case of PEG the only functional group is the hydroxyl group, which together with the high molecular weight of PEG restricts particles growth mainly by steric hindrances. From Table 1, the HBM gave smaller average particle sizes for the capped ZnS nanoparticles when compared to the particle sizes estimated from EMA. The reason for this variation in particle sizes have been reported elsewhere (Sharma *et al.* 2009).

Table 1: Calculated particle sizes of capped ZnS nanoparticles from band gap variation using HBM and EMA models.

S/N	Sample name	Band-gaps (eV)	Hyperbolic band model(HBM) particle size(nm)	Electron-mass approximation model(EMA) Particle size(nm)
1.	ZnS-PEG	3.76	6.78	9.00 nm
2.	ZnS-CMC	3.88	5.09	5.24 nm

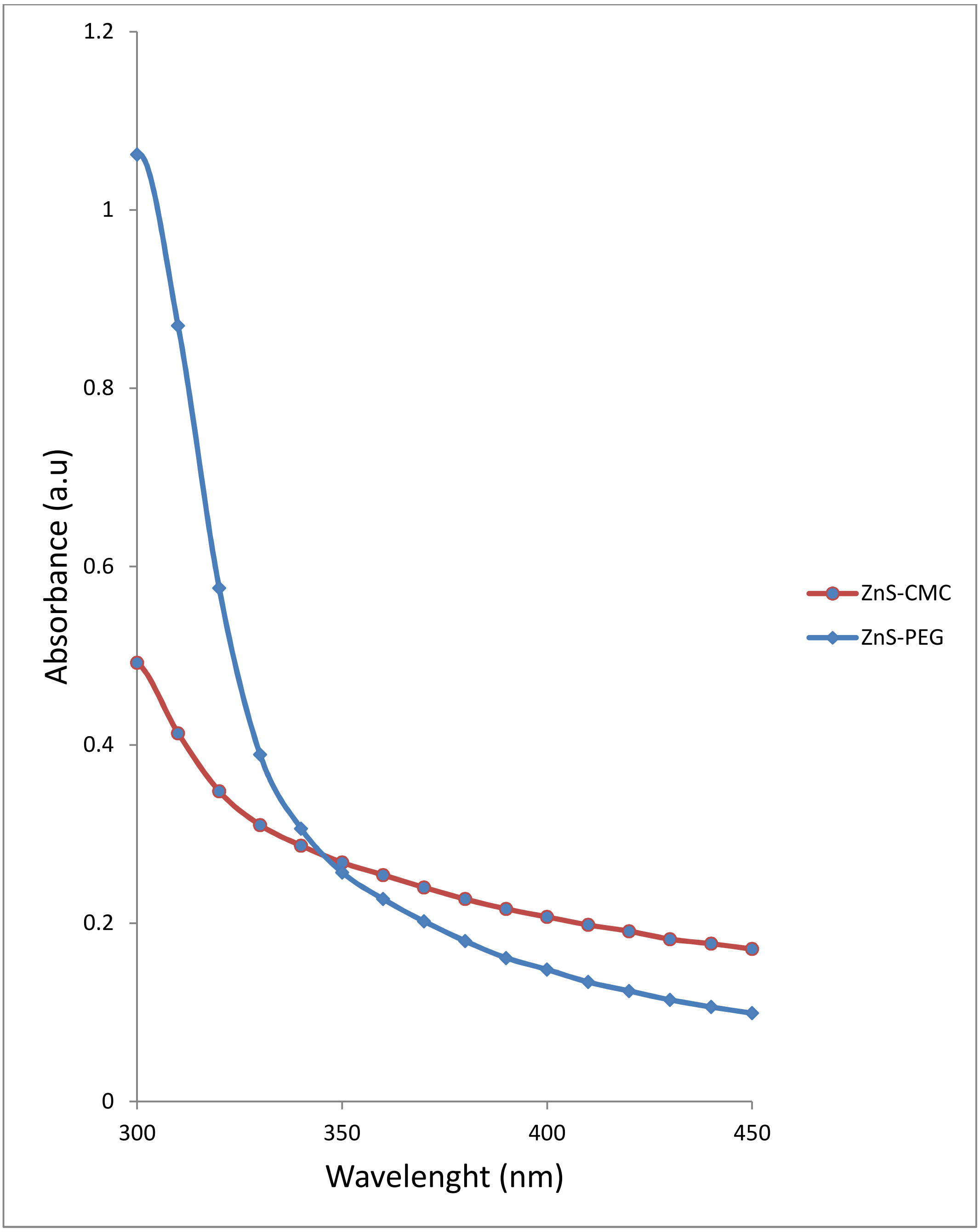

Figure 1: Absorption spectrum of ZnS/PEG and ZnS/CMC

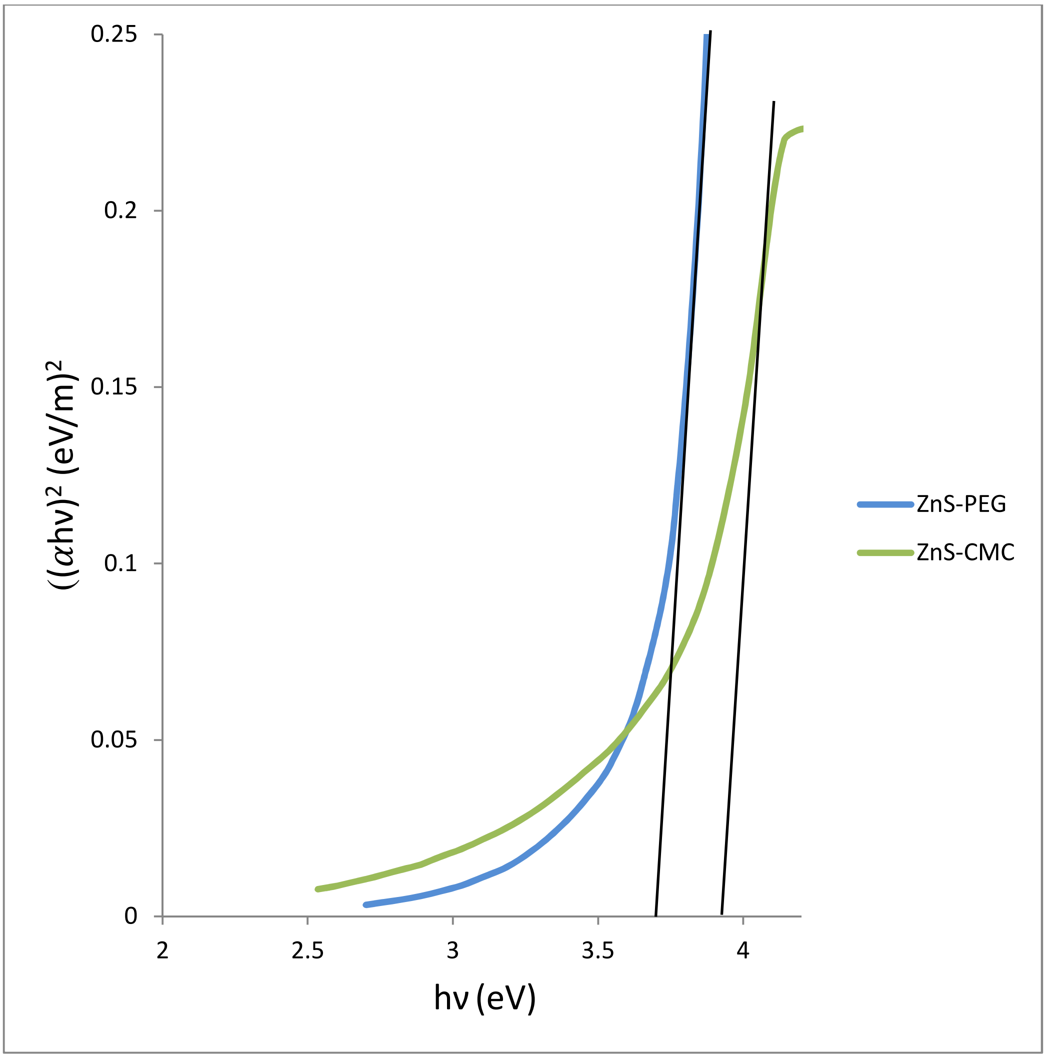

Figure 2: Graph of $(\alpha h\nu)^{1/2}$ against photon energy(hν) for ZnS/PEG and ZnS/CMC

3.2 Structural and mophological results

The powder X-ray diffraction pattern of ZnS/PEG and ZnS/CMC semiconductor nanoparticles are shown in Fig. 3(a and b), respectively. All the three peaks can be assigned to a zinc blende crystal structure without extra phases. The broadening of the peaks indicates the formation of ZnS nanoparticles (Murugadoss *et al.* 2010).

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

$$D = \frac{k\lambda}{\beta cos\theta} \tag{5}$$

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

The calculated average crystallite sizes of the nanoparticles are 3.92 nm and 3.89 nm for ZnS/PEG and ZnS/CMC, respectively. These values agree fairly well with the particle sizes calculated from EMA and HBM using band gap values from the optical absorbance spectrum.

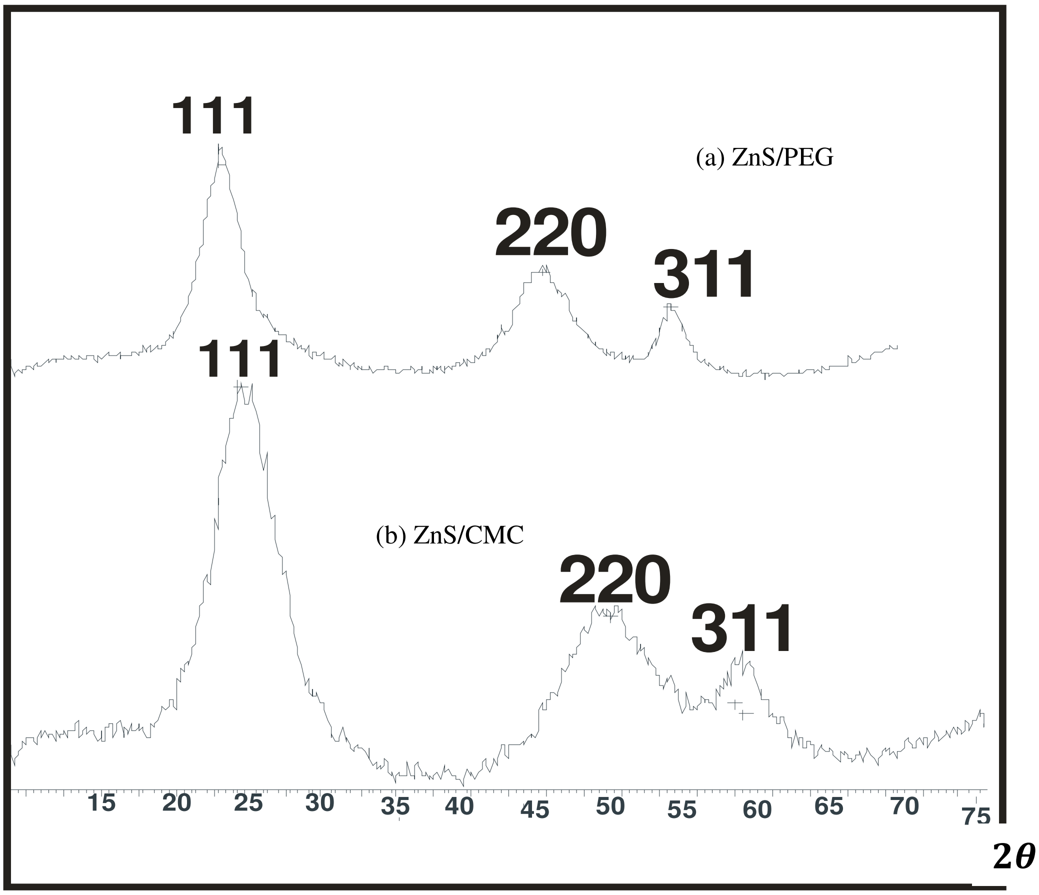

Figure 3: XRD patterns of capped (a) ZnS/PEG and (b) ZnS/CMC

3.3 Electron microscopy and EDX result.

The surface morphology of the samples was studied using a scanning electron microscope (SEM). Figures 4 (a and b) show the SEM micrographs of ZnS nanoparticles capped with PEG and CMC, respectively. The micrographs show that the particles had smooth surfaces as a result of their passivation by both PEG and CMC. The EDX spectra shown in figures 5 (a and b) revealed that the samples were pure ZnS nanoparticles. The carbon and aluminum peaks shown in the spectrum may be coming from the carbon coated aluminum grid used.

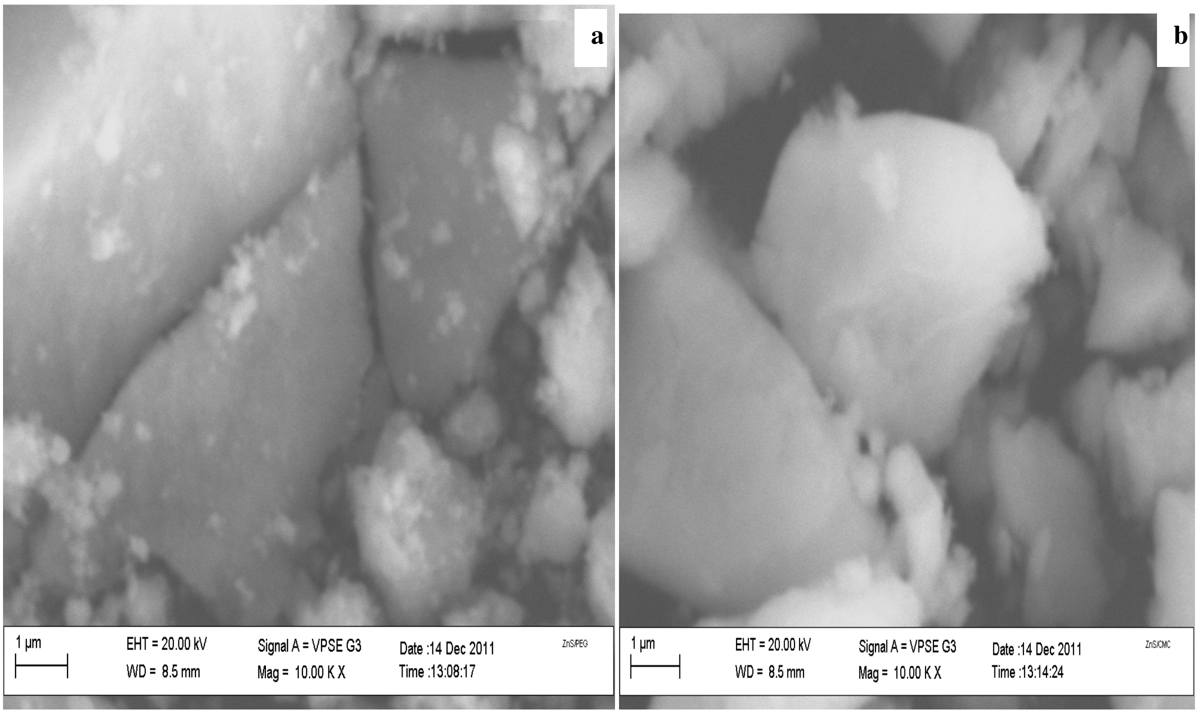

Figure 4: SEM surface micrograph of capped (a) ZnS/ PEG and (b) ZnS/C

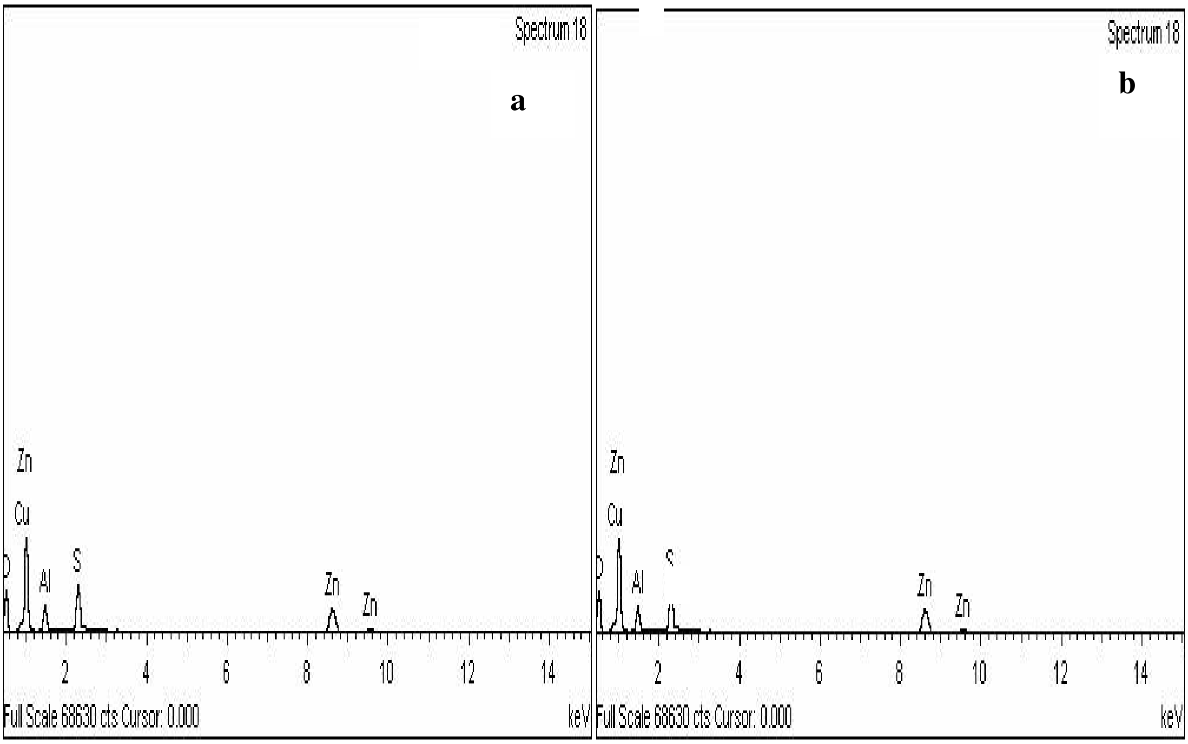

Figure 5: Elemental composition of capped: (a) ZnS/PEG and (b) ZnS/CMC

The presence of the capping agent in the synthesized ZnS nanoparticles was examined by recording their FTIR spectra in the range of 500 - 4500cm^{-1}. Figure 6 depicts the spectra of ZnS/PEG nanoparticles with absorption peaks at 1561.43cm^{-1} assigned to the bending vibration mode of water molecule and 3484.52cm^{-1} indicating –OH stretching of the hydroxyl group. The peak noted at 2932.83 cm^{-1} indicates the presence of -CH$_2$ symmetric stretch bond. In addition, the peaks at 1691.63cm^{-1}and 1428.34cm^{-1} are due to C=O and C-H stretching and bending bonds respectively which may result to co-ordinate bonding between PEG and Zn^{2+} .This indicates capping of ZnS nanoparticles as a result steric repulsive effect from PEG.

Figure 7 shows the FTIR spectrum of ZnS/CMC sample. The IR band characteristics of the spectrum shows that the band associated to carboxylic groups has a wave-number of 1615.44cm^{-1} for C=O stretching and 1474.63cm^{-1} for C-O stretching . This can be linked to their strong interaction with the Zn^{2+} ions forming a Zn–CMC complex during the in - situ precipitation process. In addition, the peak at 2914.54cm^{-1} indicated the presence of O-H group of the capped ZnS/CMC. The presence of the carbonyl and hydroxyl group is confirmation that there was a strong interaction between zinc precursor and CMC molecules. The presence of these functional groups is also a confirmation that electrostatic stabilization occurred during precipitation of ZnS/CMC nanoparticles. The adsorption of CMC on ZnS nanocrystal surface ensured the stability of the nanoparticles.

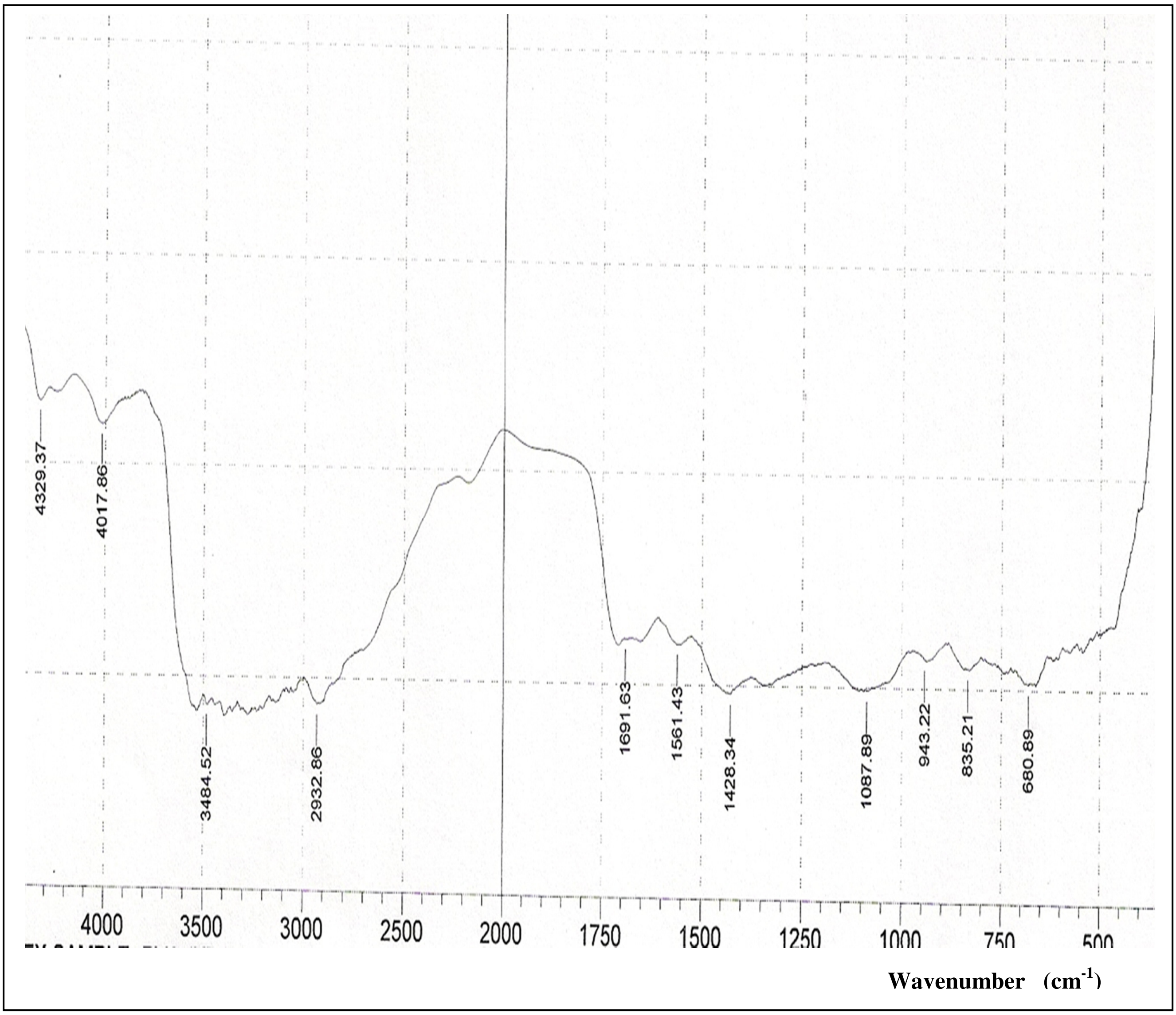

Figure 6: FTIR spectrum of ZnS/PEG

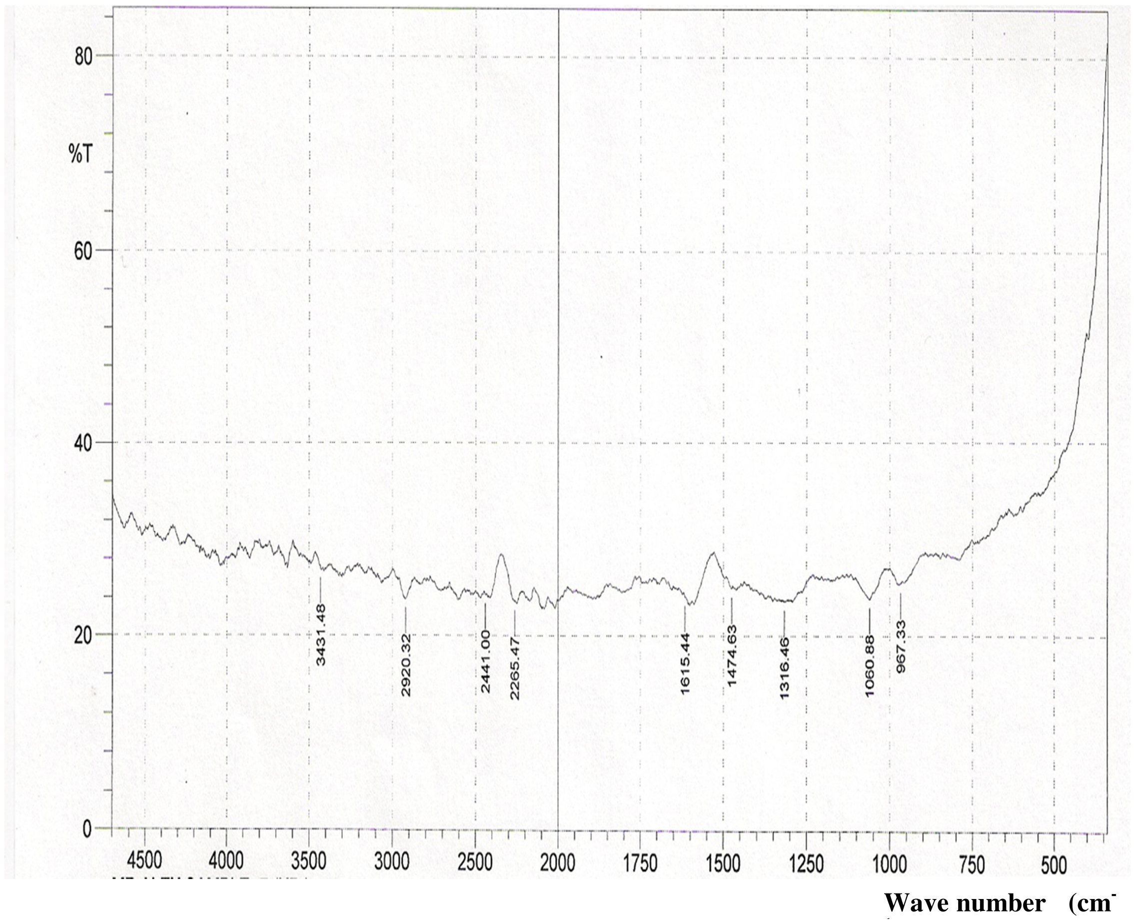

Figure 7: FTIR spectrum of ZnS/CMC

4.0 Conclusion

The synthesized ZnS nanoparticles by simple chemical method revealed that CMC is a better nanoparticles stabilizer than PEG because of the presence of a strong electrostatic stabilization of both the carbonyl and hydroxyl groups. Absorption band of both ZnS/PEG and ZnS/CMC were slightly blue shifted from that of the bulk indicating weak confinement. The particle sizes calculated show that smaller particle size of 3.89 nm was obtained for the ZnS/CMC than the ZnS/PEG nanocrystals with size of 3.92 nm. The variation in particle size due to the presence of the hydroxyl and carbonyl functional groups in the ZnS/CMC confirmed the assertion above.

5.0 Acknowledgement

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