

Effect of pH Variation on the Structural and Optoelectronic Properties of Zinc Sulfide Nanoparticles Capped with Sodium Carboxymethyl Cellulose

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This work presents the required pH value for the synthesis of ZnS semiconductor nanocrystals capped with sodium carboxymethyl cellulose (CMC). The nanoparticles were synthesized using the precipitation technique. Structural, morphological and optical properties of nanoparticles synthesized at different pH values were investigated using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy and photoluminescence studies (PL). The structure of the nanoparticles is predominantly cubic zinc blende except for nanoparticles synthesized at pH 10 which is oxidized. All samples show agglomeration of particles with smooth surfaces. FTIR spectrum confirms the interaction of ZnS with CMC. The energy band gap shows stoke shift of 0.53-0.60 eV indicating quantum confinement effect. The obtained results show that nanoparticles stability is obtained at pH value of 4.0, 7.0 and 8.0 of precursor-surfactant mixture. These pH values maintain the viscosity of sodium carboxymethyl cellulose and hence the stability of nanoparticles over time. PL shows enhanced emission intensity for samples at these three pH values.

Keywords: pH value, Zinc sulfide, Nanoparticles, Sodium carboxymethyl cellulose, Stability, Precipitation.

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1. INTRODUCTION

Zinc sulfide (ZnS) is one of the most important II-VI semiconductor material with wide range of applications such as phosphor in flat panel display and thin film electroluminescence, solar cells and IR window [1, 2]. ZnS has a wide band gap (3.60 eV) and is the most stable and a much less toxic chalcogenide compound [2]. Recently, many research works have been devoted to the preparation and characterization of nano-sized ZnS materials [3]. This is because at this low particle dimension, ZnS like other semiconductor materials exhibits fascinating behaviour with unique optical properties, which originate from quantum confinement effect.

However, a large surface-to-volume ratio at this small size regime means a large portion of atoms are located at or near the surface of the nanoparticles [4]. These surface atoms act as surface trap sites for non-radiative relaxation. A large population of surface trap sites caused by reduced structure dimension can lead to a drastic reduction of quantum yield and stability of nanoparticles [5]. Therefore, the control of nanoparticles surface is critical if highly luminescent and stable nanocrystals are required.

Stable nanoparticles can be obtained by increasing repulsive forces between particles such that agglomeration is suppressed or is kinetically slow through electrostatic or steric stabilization of organic molecules [6]. Another form of particle stabilization is to inorganically cap nanocrystals. Here, an inorganic – shell is grown onto the core nanocrystals to eliminate dangling bonds. However, proper passivation of nanomaterial depends on the synthetic conditions such as temperature, pH, organic matter content and concentration [7]. For example, Zhang and Clapp reported that small molecules carrying a net surface charge in organically capped nanoparticles exhibit variable stability with changes in pH.

In this work, ZnS nanocrystals are prepared with sodium carboxymethyl cellulose (CMC) as capping agent. The effect of pH variation on the physical and optoelectronic properties of ZnS capped with CMC is investigated.

2. EXPERIMENTAL

The synthesis was carried out as follows; 25 ml (0.2M) ZnSO₄·7H₂O was mixed with equal volume of CMC solution (1 % wt/wt in deionized water) and the pH adjusted to 4 (ZSC1) using acetic acid. This was followed by adding (drop-wise) 25 ml of (0.2M) Na₂S·9H₂O using a pipette to the Zn²⁺/CMC precursor solution under continuous stirring. The stirring continued after the last drop of the S²⁻ precursor solution was added for another 15 min to allow for complete mixing of reactants and precipitation. The product was then centrifuged at 3500 revolution per minute (rpm) for 20 min and the obtained white solid was washed several times with deionize / toulene mixed solution, followed by washing with deionized water. The white solid was then dried at 90 °C in a vacuum oven for 6 hours. The dried sample was made into fine Powders by grinding with pestle and mortar and then characterized. Note that before drying part of the washed precipitate was taken out and re-dispersed in deionized water for optical measurements. The above procedure was repeated for pH values 6 (ZSC2), pH 7 (ZSC3), pH 8 (ZSC4), pH 10 (ZSC5), respectively.

The samples characterization was carried out using UV-Visible spectroscopy (JENWAY 6405 at Engineering Materials Development Institute Akure, Nigeria), Scanning electron microscope (Carl-Zeiss and JEOL, JSM-6301F at Sheda Science and Technology Complex Abuja, Nigeria), Fourier Transform Infrared spectroscopy (Shimadzu-IR 4800s at the Redeemer University,

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Osun State, Nigeria), Fluorescent Spectroscop (Jobin Yvon monochromator with ESKPLA pulse laser source at of Laboratoire de Chimie de la Matière Condensée de Paris, France) and X-ray Diffraction (PANalytic X'Pert PRO at Engineering Materials Development Institute Akure, Nigeria).

3. RESULT AND DISCUSSION

3.1 Effect of pH on Crystal Structure of ZnS / CMC Nanoparticles

The XRD patterns shown in Fig. 1a-e indicates the presence of three prominent broad peaks in all the samples (ZSC1, ZSC2, ZSC3, ZSC4, ZSC5) synthesized. The three peaks positioned around 2θ values of 28° , 47° and 58° can be indexed to (111), (220) and (311) diffraction planes (JCPDS card, No. 5-0566), respectively indicating cubic structure for the synthesized nanocrystals. In addition to these peaks, the patterns shown Fig. 1b and e have 2θ peaks positioned at 31.35° , 33.29° and 36.99° , 61.52° , 69.47° , 76.02° for ZSC5 sample (Fig. 1e). These peaks correspond to (100), (002), (101) (103), (201) and (202), diffraction planes respectively, of hexagonal wurzite structure of polycrystalline ZnO (JCPDS Card, No. 891397) [8, 9]. This result closely suggests partial oxidation of ZnS / CMC sample synthesized in low acidic medium (pH 6.0) and a complete oxidation of ZnS / CMC in a strongly basic medium (pH 10.0).

In Hercules [10] report, CMC has the best stability and maintains its maximum viscosity at pH range of 7.0 to 9.0. The viscosity of the CMC increases at pH value less than 4.0, but decreases at $\text{pH} \geq 10.0$. Therefore, it is evident from Fig. 1a-e that if smaller particles size distribution as well as the stability of ZnS / CMC nanocrystals is required, the appropriate pH values of the reactant Mixture should be 4.0 and 7.0. If larger particles with good stability of the nanocomposite are needed, then the reaction mixture should be maintained at pH 8.0.

The average crystallite sizes calculated using the Scherrer formula (equation 1) shows that ZSC1 sample has the least average crystallite size of 2.73 nm, while ZSC4 sample has the largest average crystallite size of 3.41 nm. Table 1 shows the calculated average crystallite sizes (D) of all samples. The Scherrer equation is given by [7]:

$$L = 0.89\lambda / \beta \cos \theta \quad (1a)$$

$$D = 4L/3 \quad (1b)$$

where L is the coherence length related to the particle diameter, D , λ is wavelength of $\text{CuK}\alpha$ irradiation, β is the full width at half maximum intensity of the diffraction peak and θ is the diffraction angle.

This observation agrees fairly well with the relationship between viscosity of a medium (molecular weight) and nanoparticles size distribution as defined by the Brownian equation [11]:

$$d = \frac{2KT}{\pi\mu\Delta x} \cdot \frac{\Delta t}{\Delta x}, \quad (2)$$

where $\Delta x = \sqrt{6D_B\Delta t}$ is the three dimensional mean transfer distance, D_B and Δt are the Brownian coefficient and time respectively, μ is the medium viscosity,

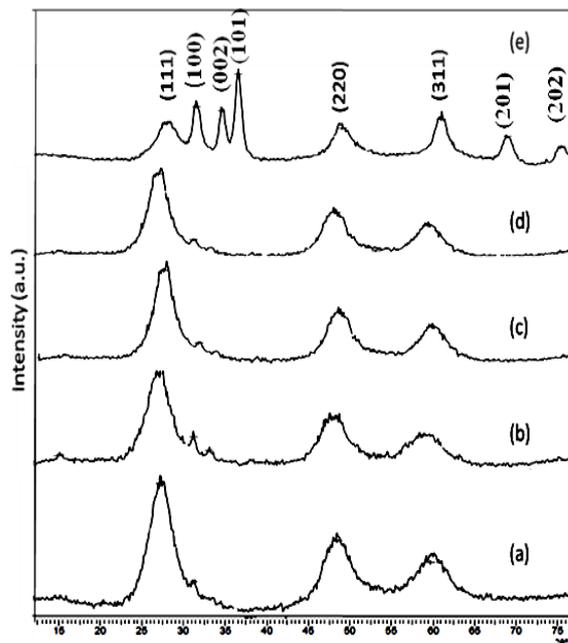


Fig. 1 – XRD patterns of (a) ZSC1 (pH 4), (b) ZSC2 (pH 6), (c) ZSC3 (pH 7), (d) ZSC4 (pH 8) and (e) ZSC5 (pH10) samples

T is absolute temperature, K is the Boltzmann constant and d is the nanoparticles size.

It is clear from this relationship that the average particle size distribution depend on the pH of the reactant (viscosity depend on pH), as well as the solid fraction of the suspension in the CMC matrix.

3.2 Morphology and Elemental Composition

The SEM micrograph of ZSC1, ZSC2, ZSC3, ZSC4 and ZSC5 samples shown in Fig. 2a-e did not reveal any distinct features among all the samples. The samples are agglomerates of smaller crystallites with surfaces well passivated by the CMC matrix as can be seen from the smoothness of their surfaces. The EDX spectrum (Fig. 2-f indicates that ZnS / CMC nanoparticles are of high purity with no other impurities present. It also shows a non stoichiometry in the amount of sulfur and Zinc in the material, with Zn^{2+} having twice the percentage by weight composition in the nanocrystals as the S^{2-} .

3.3 Effect of pH on Optoelectronic Properties of ZnS / CMC

The result of UV-Vis spectroscopy presented in the spectra of Fig. 3(I) shows a well resolved absorption edge for all samples. The absorption wavelengths range from 295-300 nm for ZSC1-ZSC5. Fig. 3(II) is the plots of the square of the absorption coefficient, $\alpha(h\nu)^2$ versus energy ($h\nu$) was used to determine the energy band gaps for all the samples. The absorbance measurement data (A) were converted to transmittance using equations (1a) and (1b) as follows [12, 13]:

$$\alpha = \frac{2.303A}{t}, \quad (3)$$

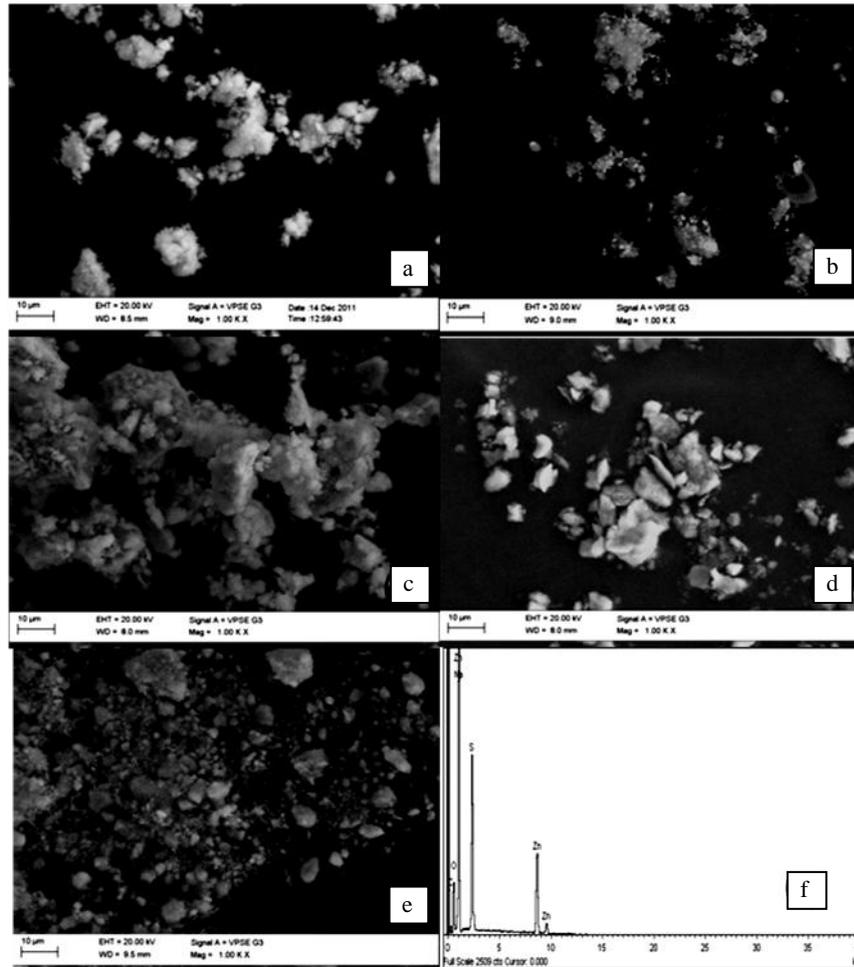


Fig. 2 – SEM micrograph for (a) ZSC1, (b) ZSC2, (c) ZSC3, (d) ZSC4, (e) ZSC5 and (f) EDX of ZSC5.

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right). \quad (4)$$

Equating (3) and (4) gives equation (5);

$$T = e^{-(2.303A)}. \quad (5)$$

Secondly, the transmittance in equation (5) was normalized and the coefficient of absorption in equation (4) when squared $\alpha(h\nu)^2$ becomes:

$$\alpha(h\nu)^2 = \left[\frac{1}{t} \ln \left(\frac{1}{T_N} \right) \right]^2, \quad (6)$$

where t is the thickness of the film and T_N is the normalized transmittance.

Equation (6) was then substituted into the Tauc's formula (equation 7) for direct band gap semiconductor [13, 14]:

$$\alpha(h\nu)^2 = (h\nu - E_g) \quad (7)$$

The plot of $\alpha(h\nu)^2$ verses $h\nu$ gave discontinuities at the transition energy of the sample in the plot (Fig. 3II). 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.

Table 1 – Energy band gap and average crystals of ZSC samples

Sample Type	Bandgap Energy (eV)	Crystallite size from XRD (nm)
ZSC1	4.20	2.73
ZSC2	4.20	3.13
ZSC3	4.13	3.17
ZSC4	4.13	3.41
ZSC5	4.13	3.40

The obtained band gap energy gave small average particle sizes with band gap energies greater than 4.0 eV (Table 1). The values of the energy band gaps are blue shifted (0.53-0.60 eV) when compared to the energy of bulk ZnS $E_g = 3.60$ eV indicating quantum confinement effect [15, 16].

3.4 Fourier Transform Infrared Spectroscopy

The FTIR spectrum of ZSC5 samples in Fig. 4 show bands at 617 and 669 cm^{-1} are likely due to the vibrational mode of ZnS host [17, 18]. The vibration bands at frequencies of 418, 518 and 584 cm^{-1} shows the presence of small amount of ZnO in the ZnS/ CMC or sulfur – oxygen interaction [19]. The peak vibrating at 898 and 1055 cm^{-1} frequencies are associated with ZnO-H and C = O Vibrations [20, 21]. The appearance of the

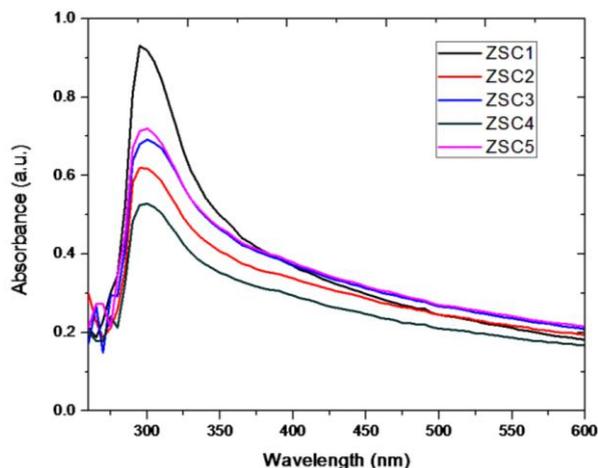


Fig. 3(I) – Optical absorbance of ZnS / CMC at different pH value

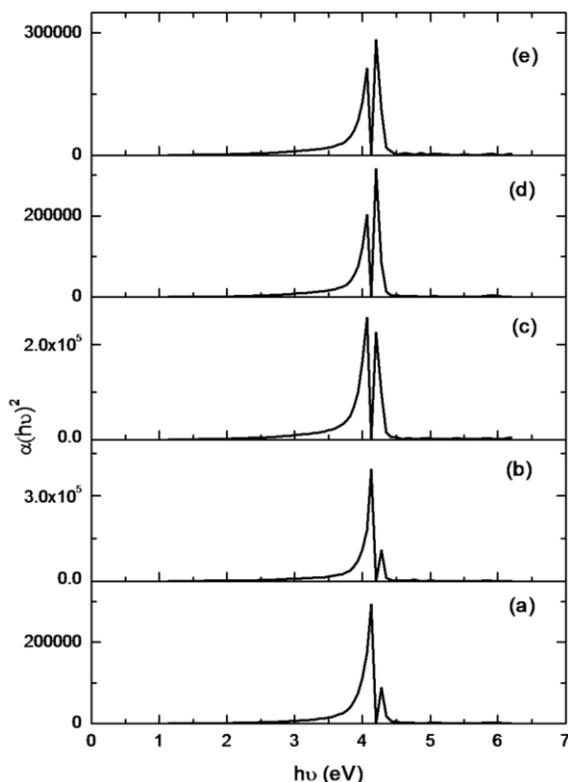


Fig. 3(II) – Energy band gap for (a) ZSC1, (b) ZSC2, (c) ZSC3, (d) ZSC4 and (e) ZSC5 samples

ZnO-H band is an indication of the likely presence of $\text{Zn}(\text{OH})_2$ supporting the XRD results that indeed the ZnS / CMC was been partially oxidized. Also present in the spectrum is the asymmetric bridge stretching vibration band ($-\text{CH}-\text{O}-\text{CH}_2$) positioned at 1112 cm^{-1} . The peaks at 1321 and 1415 cm^{-1} are assigned to $-\text{OH}$ in plane bending and $-\text{CH}_2$ scissoring vibrations, respectively [21-24]. The $-\text{OH}$ groups also cause the appearance of stretching frequencies in the 2360 to 3383 cm^{-1} region [19]. The absorption bands at 1770 cm^{-1} is due to $\text{C}=\text{O}$ stretching band of the carboxylic acid [25, 26].

Therefore, the presence of the carbonyl (COO^-), hydroxyl ($-\text{OH}$) and $-\text{CH}_2$ groups which are carboxyl-methyl substituent is a confirmation that the synthesized ZnS nanocrystals are capped with CMC matrix [27].

3.5 Effects of pH on Photoluminescence of ZnS / CMC Nanoparticles

The average particle sizes calculated from the nanocrystals XRD (Table1) indicate small nanocrystallite suggesting large surface - to - volume ratio. At this size regime, electronic relaxation in semiconductor nanoparticles is often dominated by surface properties. This is because the large surface - to volume ratio possess high density of surface and defect traps states which lies within the band gap and acts to trap photogenerated charge carriers (electrons and holes) [28].

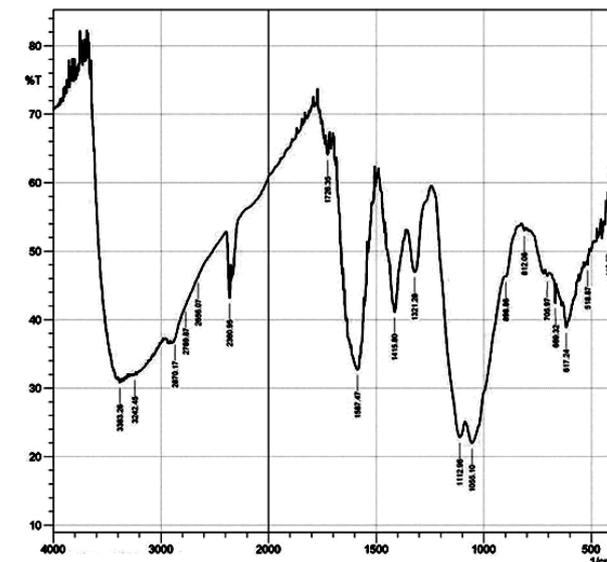


Fig. 4 – The result of FTIR transmittance measurements carried out on sample ZSC5.

These defects are usually not observed in optical absorption but in photoluminescence and dynamics measurements which are sensitive to charge carriers in trap states. Fig. 5 show the photoluminescence emission (PL) spectra of samples (ZSC1-5) prepared at different pH values. Due to quantum confinement effect as observed in the large values of the energy band gaps in Table 1, the ZnS / CMC nanocrystals were expected to emit light in the UV range. However, from the spectra in Fig. 5, the synthesized ZnS / CMC nanocrystals exhibited blue to green photoluminescence within the wavelength range of 435 to 551 nm . This can be attributed to the trap-state emission, which has smaller energy (large wavelength) than the band-edge emission of ZnS / CMC nanocrystals [29]. Bulk defects such as vacancies and interstitials could be the main source of trap states in the ZnS / CMC nanocrystals. The electron transitions could occur between the trap states and the conduction band (or the valence band), giving rise to the observed blue - green emissions. The broad band emission observed for all the samples could be a result of superposition of emission spectra from different trap-states, each emitting in their respective energy states [30].

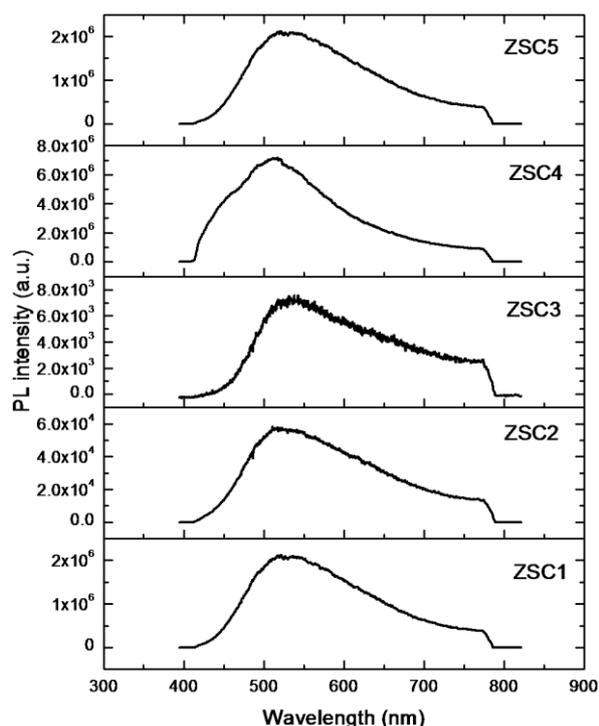


Fig. 5 – Photoluminescence emission of ZnS / CMC at various pH values

The weaker fluorescence observed from ZSC2 and ZSC3 could be an indication of a higher density of trap-states and a higher threshold of trap state saturation

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[28]. Fig. 5 shows the PL clearly depend on pH with noticeable increase in PL for samples synthesized at pH values that keeps the viscosity of CMC stable or high such as pH 4.0, 7.0 and 8.0.

4. CONCLUSION

Zinc sulfide semiconductor nanocrystals capped with sodium carboxymethyl cellulose was synthesized at varying pH values using the precipitation technique. The average crystal sizes calculated from the diffraction peaks using the Scherer formula are in the range of 2.37 to 3.41 nm. These crystal sizes which are comparable to the average particle sizes calculated from the effective mass approximation, shows quantum confined structure. The obtained energy band gaps show a blue shift of 0.53-0.60 eV when compared to the absorption energy of bulk ZnS. Nanoparticles stability was observed at pH values of 4.0, 7.0 and 8.0, that is, pH at which the viscosity of the CMC molecules are maintained in the reaction mixture.

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