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Temperature Controlled Synthesis of ZnS Nanocrystals by Simple Chemical Precipitation

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Abstract

Nanocrystals of ZnS preparing at 70, 75 and 80 °C have been characterized by X-ray diffraction (XRD), UV-Vis and Fourier transform infrared spectroscopy (FT-IR), atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). The investigation suggests that aggregates of small spherical particles with an average size of 8 nm and well defined morphology were obtained at 80 °C. The particle size appears to increase with a decrease in synthesis temperature.

Keywords: Nanocrystals, synthesis temperature, morphology, aggregates, spherical particles

Introduction

Semiconductor nanocrystals have gained much attention owing to their novel optical and electrical properties, which are different from those of bulk materials, arising from quantum confinement effects [1-3]. As one of the most important II-IV semiconductors, ZnS has found many applications e.g. electroluminescence [4], Light Emitting Diode (LED) [5] and non-linear optical devices [6]. In addition, ZnS crystallites are of great interest for their unique size-dependent optical, electrical and magnetic properties, etc. [3,7]. So a variety of methods have been reported for synthesizing ZnS nanocrystals, such as the solvothermal synthesis [8-10], single source molecular precursor [11], direct elemental reaction [12], the gamma irradiation [13], and rf-magnetron sputtering [14] and so on. In the present study ZnS nanocrystals were synthesized at three different temperatures namely 70, 75 and 80 °C by simple chemical precipitation. Surface morphology and structural properties have been measured by atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The optical properties were studied by UV-Visible spectroscopy.

Experimental procedure

In this synthesis, all chemicals were of analytical grade and were used without further purification. ZnS nanocrystals were prepared by using zinc acetate and sodium sulfide as source materials. 5.5 g of (0.5 M) zinc acetate and 1.95 g (0.6 M) sodium sulfide were dissolved in 50 ml of deionized water and stirred at a constant rate at 70 °C for 45 min. This resulted in a milky white solution, indicating the formation of ZnS. The obtained solution was centrifuged to separate ZnS powder. These nanocrystals of ZnS were repeatedly washed with ethanol, and subsequently dried in an oven at 50 °C. The final product was indexed as S_1. The same procedure was repeated at 75 and 80 °C to get the samples S_2 and S_3. AFM studies were carried out on a Pico scale SPM

(Molecular Imaging, USA). X-Ray Diffraction (XRD) studies were recorded by using a XPer PRO (PANalytical) advanced X-ray diffractometer with CuK α_1 radiation (λ = 1.5406 Å), with 2θ ranging between 20 and 80° at a scanning rate of 0.5 "/S. Absorption spectra were measured by using a Perkin-Elmer lambda 5 UV-Visible Spectrophotometer. FESEM images of the samples were obtained with a Hitachi S-4800 field emission scanning electron microscope.

Results and discussion

Figure 1 showing the XRD patterns of ZnS nanocrystals grown at 70, 75 and 80 °C, respectively. From the patterns three well defined diffraction peaks corresponding to the lattice planes (1 1 1), (2 2 0) and (3 1 1) are observed in all the samples. These peaks are in good agreement with the cubic zinc blended structure (JCPDS No. 05-0566), confirming the purity of the synthesized ZnS nanocrystals. From the XRD patterns it is clear that the peak positions are not changed with a change in the synthesis temperature. However, the peak intensity slightly increases with an increase of synthesis temperature, suggesting a decrease in grain size. The average crystallites sizes were determined according to Scherrer equation D = Kλ/ βcosθ [15], where K is a constant (shape factor about 0.9), λ is the wavelength (0.15418 nm), β is the full width at half maximum (FWHM) of the diffraction line and θ is the diffraction angle. Based on the FWHM of diffraction planes, the average crystalline sizes of ZnS nanocrystals were 10.5, 9.3 and 8 nm for the synthesis temperatures 70, 75 and 80 °C respectively.

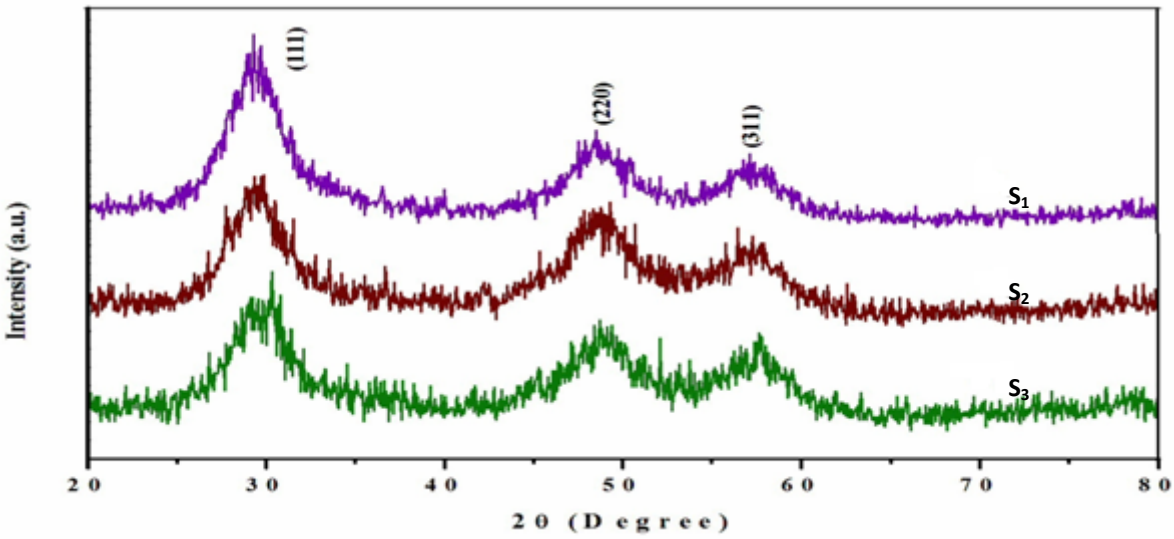


Figure 1 XRD patterns of ZnS nanoparticles preparing at different temperatures (S_1 at 70 °C, S_2 at 75 °C and S_3 at 80 °C).

The UV-Visible spectrum usually depends on the size of the nanocrystals and the absorption maximum wavelength decreases with the particle size [16]. UV-Visible spectra of ZnS nanocrystals are shown in **Figure 2**. Absorption edges of ZnS nanocrystals are 302, 300.3 and 299 nm at 70, 75 and 80 °C, respectively. These peaks are desirably blue shifted compared to that of bulk phase ZnS (340 nm) [17]. This shift in absorption is mainly due to quantum confinement effects, revealing a change in band gap along with excitation features, which can be considered as a measure of particle size and size distribution [18]. The calculated band gaps of the ZnS nanocrystals were 4.11, 4.13 and 4.15 eV at 70, 75 and 80 °C, respectively, whereas the band gap of bulk ZnS is 3.64 eV. The band

gaps of nanocrystals synthesizing at 75 and 80 °C were blue shifted when compared to ZnS synthesizing at 70 °C as a result of a reduction in particle size. These results indicate that the size of the particles is associated with the band gap and a size increases on lowering the synthesis temperature. A fact is confirmed by AFM, XRD and FESEM studies.

FT-IR spectra of the synthesized ZnS nanoparticles were recorded in the range of 4000 - 400 cm^{-1} and are shown in **Figure 3**. The peaks at 1116 and 643 are due to Zn-S vibration and 2360 and 1636 cm^{-1} are due to microstructure formation of the sample. The broad absorption peak in the range of 3435 - 3445 cm^{-1} corresponds to the –OH group and indicates the existence of water absorbed onto the surface of the nanocrystals. No major shift in the peak positions was at different synthesis temperatures.

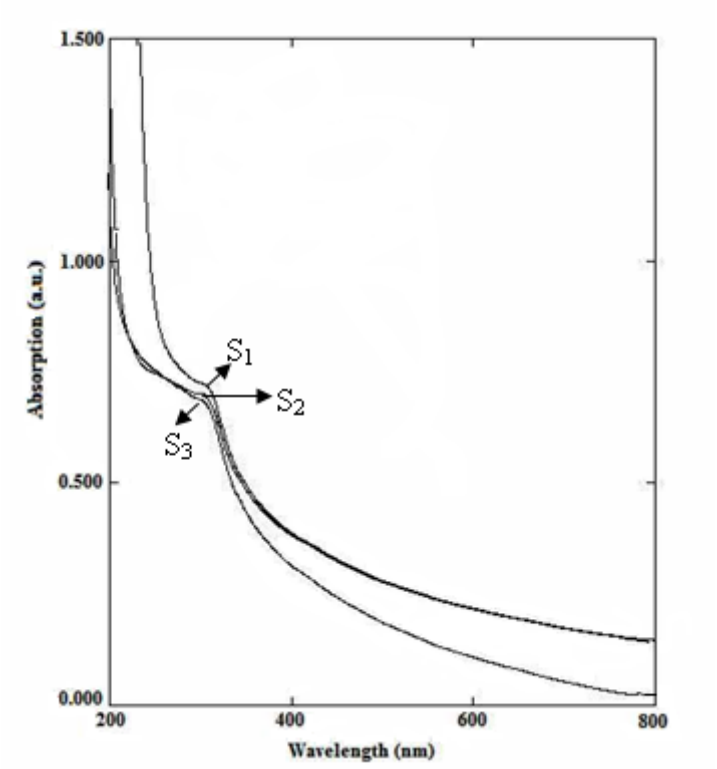


Figure 2 UV-Vis absorption spectra of ZnS nanoparticles preparing at different temperatures (S_1 at 70 °C, S_2 at 75 °C and S_3 at 80 °C).

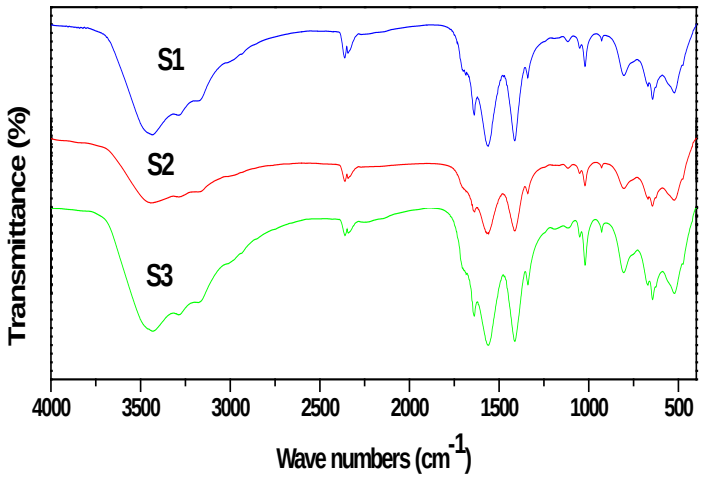


Figure 3 FT-IR spectra of ZnS nanoparticles preparing at different temperatures (S_1 at 70 °C, S_2 at 75 °C and S_3 at 80 °C).

Figure 4A shows the AFM image of ZnS synthesizing at 70 °C. The AFM image reveals that the size of the particles is increased due to self aggregation of nanocrystals as a result of the low temperature. Further the Oswald ripening may cause the random oriented self-aggregation in the nanocrystals because the free energy is reduced by decreasing the number of small particles. **Figure 4D** shows the 3D projection of the nanocrystals. The domains of the nanocrystals are clearly seen in this image. The size of an individual nanoparticle was found to be 75 nm as shown in **Figure 4B**. The FESEM image (**Figure 4C**) shows a porous structure formed by a network of interlinked or agglomerated ZnS crystals with particle sizes in the range of 26.7 - 73.6 nm.

Figure 5A shows the AFM image of ZnS synthesizing at 75 °C. It is clear that there is only a small decrease in aggregation of particles as a result of the slight increase in temperature. The 3D view of the ZnS nanocrystals is shown in **Figure 5D**; here the growth direction of all the particles is not the same. The size of an individual particle was 54 nm as shown in **Figure 5B**. **Figure 5C** shows the FESEM image which indicates the cluster form of nanoaggregates with no uniformity in the particle distribution. The observed particle size in the FESEM study is in the range of 17.5 - 70 nm.

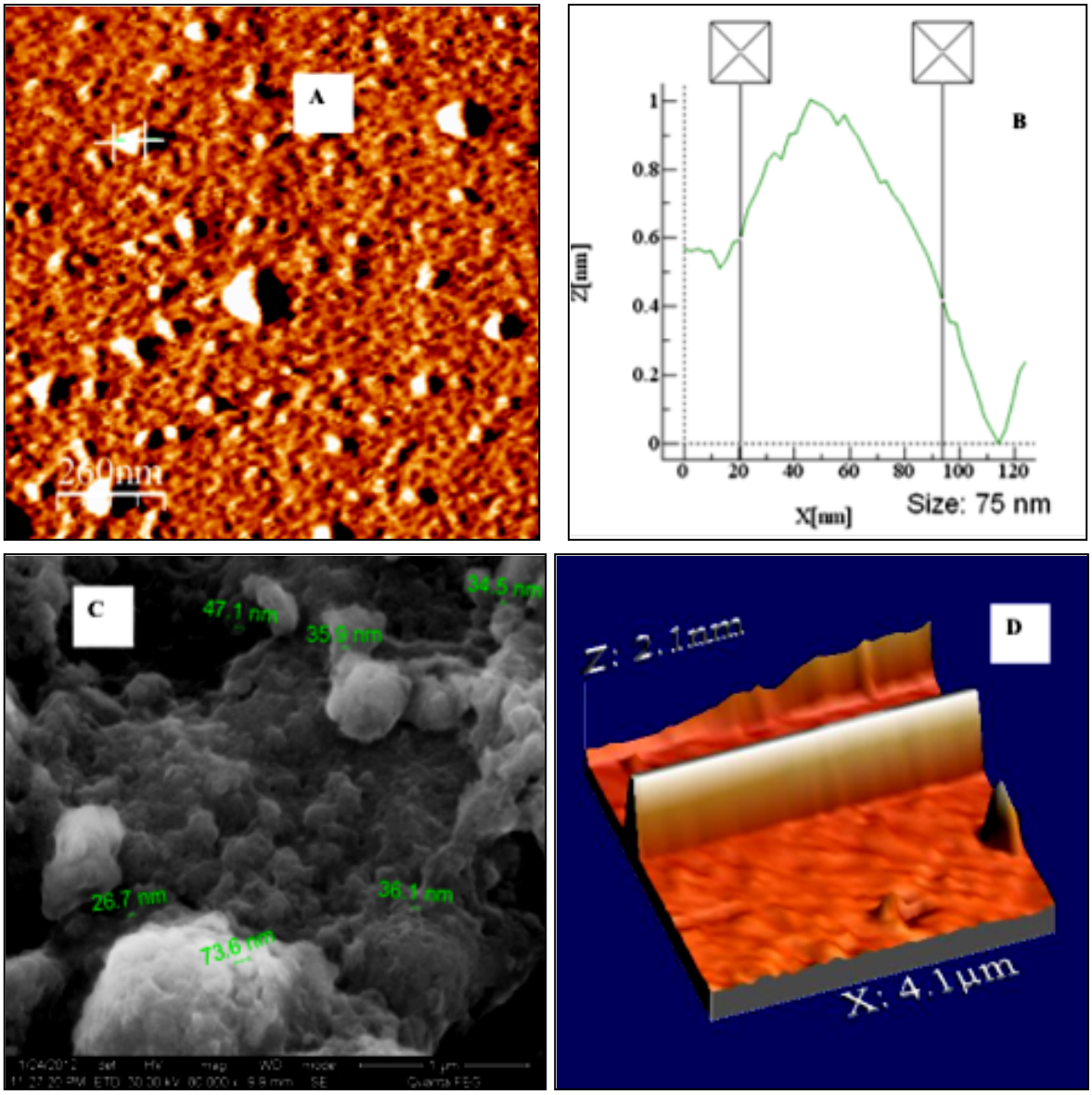


Figure 4 (A) AFM image of ZnS nanoparticles preparing at 70 °C (S_1), (B) Size profile of an individual ZnS nanoparticle, (C) FESEM image of ZnS nanoparticles and (D) 3D view of ZnS nanoparticles.

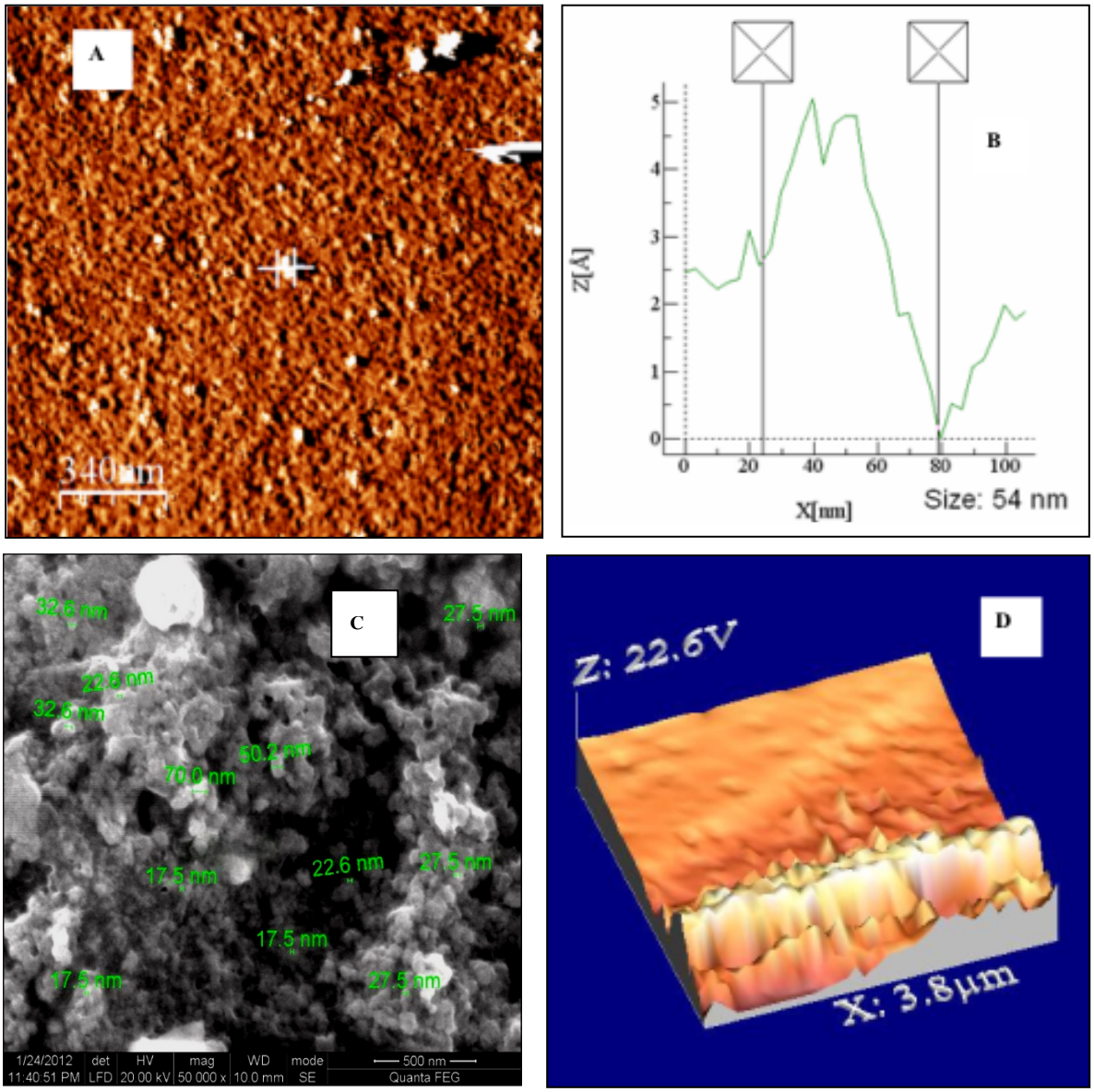


Figure 5 (A) AFM image of ZnS nanoparticles preparing at 75 °C (S_2), (B) Size profile of an individual ZnS nanoparticle, (C) FESEM image of ZnS nanoparticles and (D) 3D view of ZnS nanoparticles.

Figure 6A shows the AFM image of ZnS synthesizing at 80 °C and it reveals the formation of nanocrystals. In this image, most of the particles have a uniform size and are spherical in shape without agglomeration. All the particles were easily distinguishable, with uniform distribution. The 3D view of the ZnS is shown in **Figure 6D**; the growth direction of all the particles is the same. It is clear that the size of the individual nanocrystals was 36 nm as shown in **Figure 6B**. **Figure 6C** shows the FESEM image of ZnS nanocrystals. It shows that the particles spread across the matrix have a spherical shape with the size in the range of 13.7 - 25 nm.

Figure 7 shows the graph of average particle size versus temperature. From this we may conclude that an increase in reaction temperature results in a decrease in particle size, thus a decrease in reaction temperature leads to an increase in particle size. The decrease in particle size and narrow size distribution with an increase in temperature is a well known phenomenon which is normally due to increased reaction rate at higher temperature. As the reaction rate is increased the reactants are consumed more rapidly, hence reactant depletion takes place, leading to the formation of smaller nanoparticles and narrow size distribution at higher temperature [19].

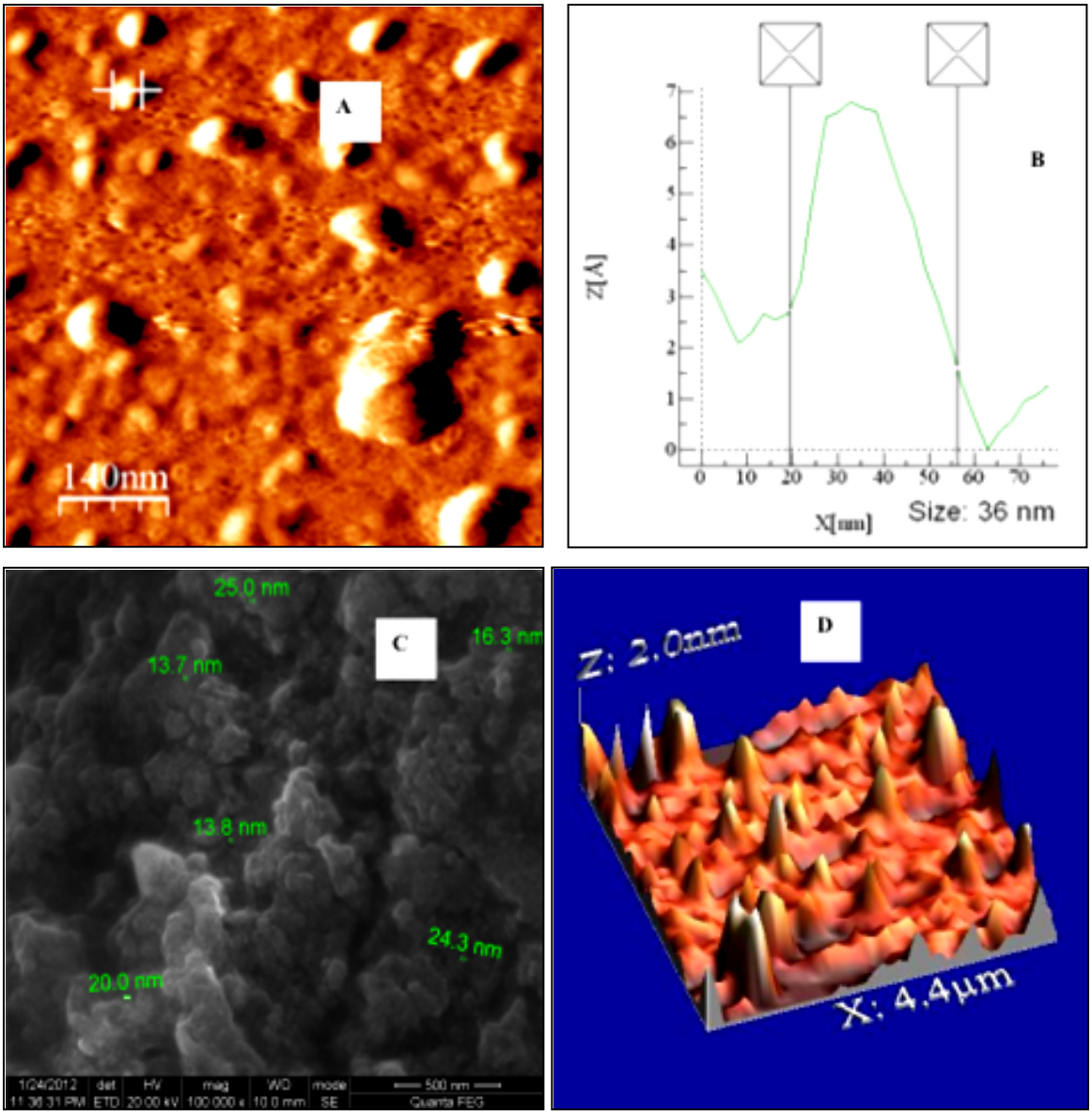


Figure 6 (A) AFM image of ZnS nanoparticles preparing at 80 °C (S_3), (B) Size profile of an individual ZnS nanoparticle, (C) FESEM image of ZnS nanoparticles and (D) 3D view of ZnS nanoparticles.

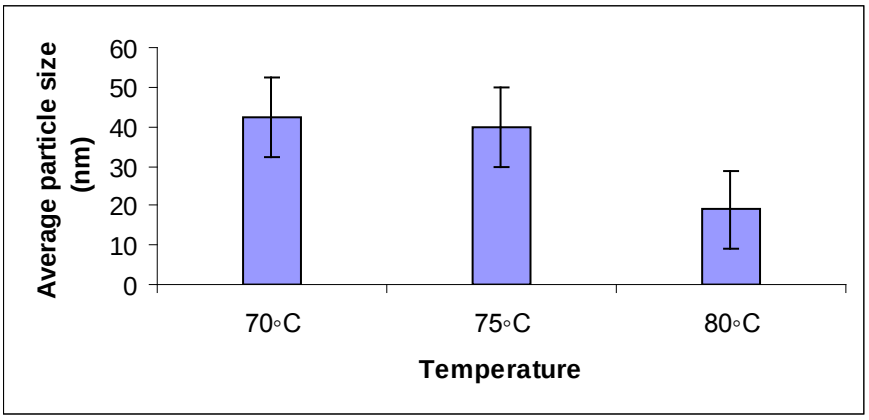


Figure 7 Average particle sizes at different temperature condition.

Conclusions

In this study we have attempted to synthesize ZnS nanocrystals by varying the synthesis temperature. The XRD analysis revealed the formation of a single phase with a cubic zinc blended ZnS structure. Scherrer's formula showed that the particle sizes are in the range of 10.5, 9.3 and 8 nm at 70, 75 and 80 °C, respectively. The FT-IR analysis confirmed the formation of ZnS nanoparticles. The FESEM and AFM studies have shown the morphology of the synthesized particles. The optical absorption showed that UV absorption peaks were blue shifted with higher temperatures. Among the synthesized particles, the particles synthesizing at 80 °C were smaller in size and monodispersed when compared with the other two samples synthesizing at 70 and 75 °C. This leads to the conclusion that an increase in reaction temperature leads to a decrease in the size of the ZnS nanocrystals and an increase in monodispersion.

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