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Original research

Synthesis and characterization of ZnS nanoparticles by chemical precipitation method

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Abstract:

Nanoparticles form a connection between molecular and bulk states of matter, it shows size-dependent physical and chemical properties. In the present work, we aimed to prepare zinc sulfide (ZnS) nanoparticles by chemical precipitation method using Sodium sulfide ($Na_2S.x\ H_2O$) as sulfur source and zinc acetate dihydrate [$(CH_3COO)_2Zn.2H_2O$] as a source of zinc. Characterization was performed by UV–Vis Spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR)، and transmission electron microscopy (TEM). X-ray diffraction revealed that the prepared ZnS nanoparticles comprise a cubic structure and the average grain size of ZnS is 6.41 nm. UV–Vis spectrum shows quantum confinement effect by a sharp peak around 345 nm. The optical bandgap of the ZnS nanoparticles was found to be 4.5 ev, TEM micrograph depicts the spherical particles which are agglomerated with size 7.9 nm.

Keywords: Nanoparticles, ZnS, Chemical precipitation method

1- INTRODUCTION

Nowadays, there has been considerable concern in semiconductors of nanomaterials because of the quantum size effect that they display. Nanocrystalline semiconductors have properties intermediate between those of molecular objects and macrocrystalline solids. Nanocrystalline semiconductors show unusual properties due to the three-dimension confinement of electrons (Abbas et al. 2013**).**

Zinc sulphide (ZnS) is a significant member of the II-VI group inorganic semiconducting material. The interest in ZnS nanoparticles has increased due to their great properties, as direct recombination and large band-gap energy. It is a direct bandgap material and has been used in infrared windows, sensors, photodetectors, and solar cells because of its stability and controllable morphological properties (Lu et al. 2004, Yi et al. 2019).

ZnS is an important semiconductor with a direct, wide bandgap (3.6 eV), high refraction index, and high transmittance in the visible range (La Porta et al. 2017).

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Nanostructured ZnS such as nanocrystals, nanobelts, nanocluster, nanorods, nanoparticle, nanosheet, nanoflower, hollow sphere, nanotube, and nanowires show great optical and electronic performances **(**Yesu et al. 2012, Sabaghi et al. 2018).

The nanoparticle surface is more critical than the surface of the bulk because nanoparticles have a larger surface-to-volume ratio, surface atoms are joined by smaller forces because of missing neighbors, which causes high surface reactivity **(**Yesu et al. 2012**).**

ZnS shows great transparency over the wide spectrum range between 380 nm and 25 μm and the electrical resistivity is in the order of $10^4\Omega$.cm with n-type electrical conductivity. (Slewa. 2014)**,** it exists in two structures, cubic (sphalerite) or hexagonal (wurtzite) (Yesu et al. 2012).

The hexagonal structure is a thermodynamically metastable phase, which is always stable at very high temperatures, and the cubic structure is a thermodynamically stable phase at low temperatures(Slewa . 2014).

There are several methods have been employed for the preparation of ZnS nanoparticles. sol-gel, hydrothermal process, capped precipitation, sonochemical synthesis, solvothermal synthesis, microwave synthesis, thermal decomposition method, chemical vapor deposition, solid-state reaction method, and chemical precipitation method, etc. (Wang and Hong. 2000)**,** Jothibas et al. 2017**,** La Porta et al. 2017).

Among them, the chemical precipitation method is a simple, clean, and inexpensive technique to obtain ZnS nanoparticles.

In this paper, we report the synthesis of ZnS nanoparticles by chemical precipitation method using Sodium sulfide ($Na_2S.x\ H_2O$) as a sulfur source. The obtained ZnS nanoparticles were characterized by X-ray diffraction (XRD), UV–Vis absorption, Transmission electron microscopy, and Fourier transform infrared spectra (FTIR).

2- MATERIALS AND METHODS

2.1 Materials

Zinc acetate dehydrate and Sodium sulfide ($Na_2S.x\ H_2O$) were purchased from Sigma Aldrich**,** distilled water was used to prepare solutions.

2.2 Methods

Zinc sulfide nanoparticles were obtained by chemical precipitation method (Figure 1). First, an amount of (12.331) g of Sodium sulfide ($Na_2S.x\ H_2O$) was dissolved in 100 ml distilled water, then (17.56) g of zinc acetate dihydrate [$(CH_3COO)_2Zn.2H_2O$] were dissolved in 100 ml distilled water (DW), the two solutions were mixed together and stirred for five hours. A cloudy white solution was obtained which indicated the formation of ZnS nanoparticles. Finally, the precipitate ZnS was filtered, washed, and dried.

3. CHARACTERIZATION

The samples were characterized using TEM and X-ray diffraction to confirm their sizes, crystallinity, and purity. The optical property of the sample was studied using UV-Visible absorption spectroscopy, the composition, and quality of the sample analyzed by Fourier transform infrared spectra (FTIR).

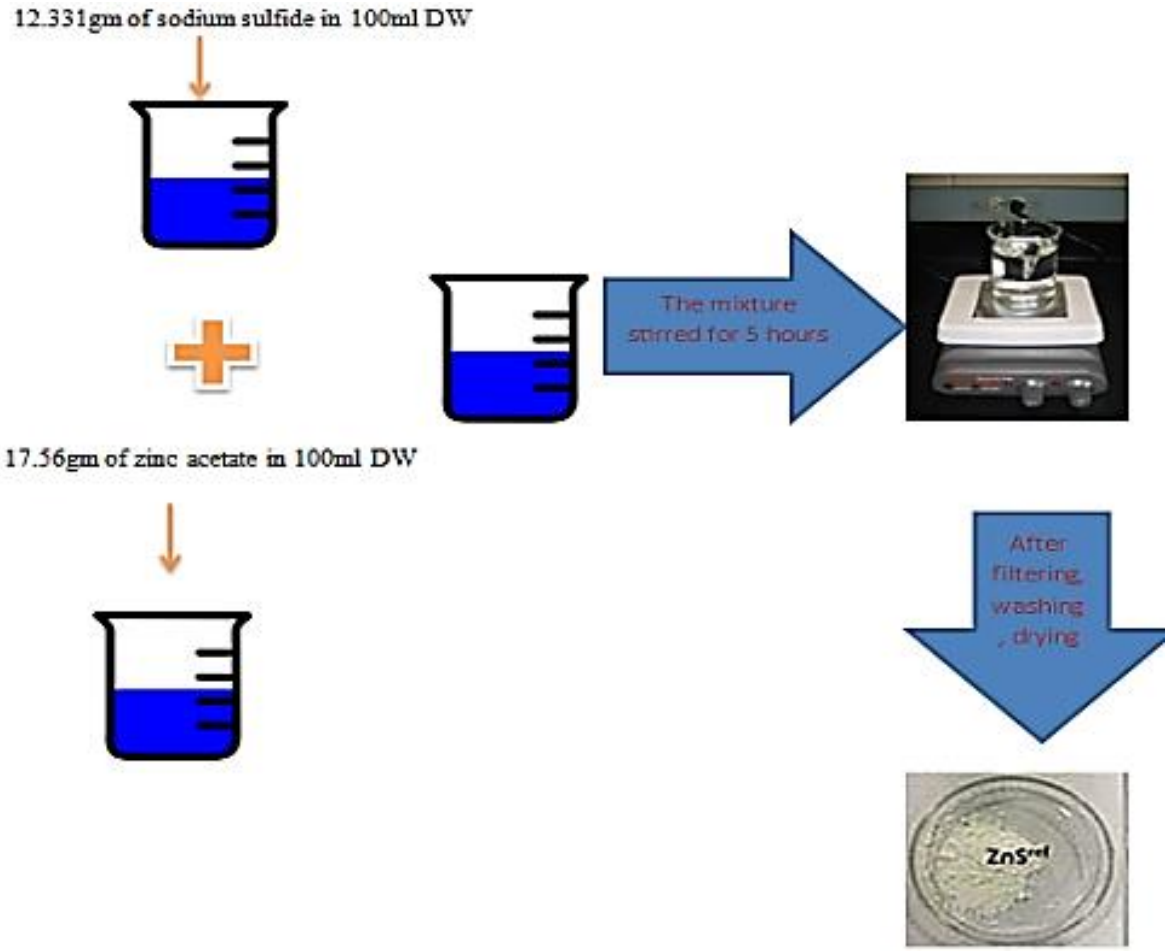


Fig 1. Schematic representation of the chemical precipitation procedure of ZnS nanoparticles

4. RESULTS AND DISCUSSION

4.1. X-ray diffraction analysis of ZnS

X-ray diffraction (XRD) pattern is the effective method for determining the phase and crystallite size of the Prepared ZnS.

Fig. (2) shows the corresponding results of XRD for the prepared ZnS sample. The XRD peaks are found at 2θ values of 28.6°, 47.6°, 56.3°, 69.6°, 76.9°, and 88.6° referring to diffraction from (111), (220), (311), (400), (331) and (422), respevtively. No peaks from any impurities are detected this suggests high crystallinity and the pure phase feature of ZnS material. The figure indicates that particle sizes are in the nanometer range. The peaks indicating a cubic structure for the synthesized nanocrystals because of the low-temperature process, the hexagonal ZnS is relatively difficult to prepare. The cubic ZnS is stable at room temperature, while the hexagonal ZnS is formed at high temperatures. (Kole and Kumbhakar. 2012) The most intense diffraction peak centered at 2θ=28.5°, this set of peaks is characteristic of ZnS in cubic phase which all are in good agreement with, primary reference Calculated from NIST using POWD-12++, Space group: F-43m, The broadening peaks in the XRD patterns indicates the formation of ZnS nanocrystals of small size. The broadening peaks are significant in producing nanoparticles.

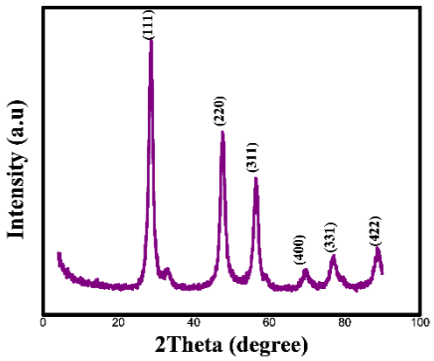


Fig 2.X-ray diffraction patterns of ZnS

The crystallite size was calculated using the Debye Scherrer formula (Ebnalwaled et al. 2017) :

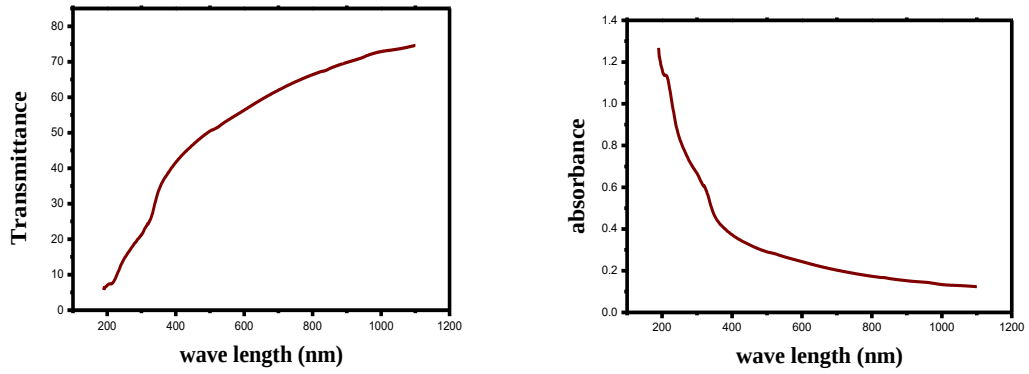
$$D=0.9\lambda/\beta\cos\theta \quad (1)$$

Where D is the crystallite size, λ is the wavelength of X-rays, β is the full-width at half-maxima (FWHM) in radians and θ is the diffraction angle. The average crystallite size was calculated to be 6.41 nm.

The average calculated crystallite size of the ZnS nanoparticles displays that the synthesized nanoparticles are in the quantum confinement regime these nanoparticles also be known as quantum dots.

4.2. UV–visible spectrum

In this part, we study the interaction between ZnS nanoparticles and the incident light using UV-visible spectroscopy. UV-Visible spectroscopy is one of the most significant techniques for calculation the energy bandgap (Eg) of crystalline structures. This study was performed by measuring the absorbance of dispersed ZnS nanoparticles in the region 190–1200 nm. A very small amount of the sample is dispersed into the water and the solution is sonicated in an ultrasonic bath for 10—15 min to obtain the uniform dispersion. Fig.3 shows the absorption and the transmission spectrum of the obtained ZnS nanoparticles.



(a) (b)

Fig. 3. (a) The transmission spectrum (b) The absorption spectrum of the synthesized ZnS nanoparticles

The spectra of ZnS nanoparticles show high absorbance in the ultraviolet; however, the absorbance at the visible region is low (Nazerdeylami et al. 2012). ZnS nanoparticles have an absorption edge that has a blue shift as compare with bulk ZnS for which the peak is at 345 nm **(**Abbas et al. 2013**).**

The optical transmission and absorption spectra of ZnS nanoparticles are shown in Figure 3 (a, b).

The optical band gap with direct transition can be calculated from the following relation (Jothibas et al. 2017):

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

Where hν is the photon energy, A is a constant that depends on the transition probability, α is the absorption coefficient, E_g is the optical band gap and n is a number that characterizes the transition process, where n =1/2 and 3/2 for direct allowed and forbidden transitions, respectively, and n =2 and 3 for indirect allowed and forbidden transitions, respectively.

In our case for the direct allowed transition we use n = 1/2 to determine the optical bandgap from the following relationship:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (3)$$

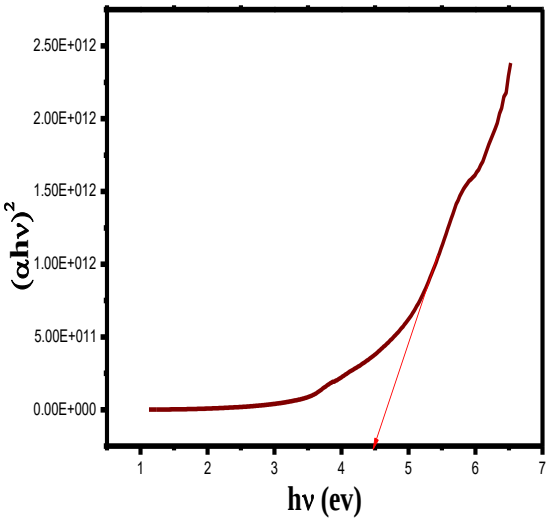


Fig. 4. The relation between $(\alpha h\nu)^2$ and hν for the obtained ZnS Nanoparticles.

The value of the optical band gap Eg of ZnS nanoparticles sample was determined from the curve in Figure 4. The value of Eg is 4.5ev (Fig.4), this value of the band gap is a good indication of blue-shifted of ZnS nanoparticles from that of bulk (340 nm, Eg = 3.7 eV). Increasing bandgap energies of ZnS nanostructures could be evidence of the quantum confinement effect due to decreasing size of structures.

For more understanding of the reasons for increasing the optical band gap for the prepared ZnS nanoparticles, the effective mass model was used to calculate the particle radius according to**:**

$$E_g(\text{nano}) = E_g(\text{bulk}) + h^2/8R^2(1/m_e^* + 1/m_h^*) - 1.8e^2/4\pi\varepsilon\varepsilon_0 R \qquad (4)$$

Where Eg (nano) is the energy band of nanoparticles, Eg (bulk) is the energy band of the bulk sample, R is the average radius of particles**,** h is the Planck's constant**,** m_e^* and m_h^* are the

effective mass of an electron and a hole, respectively**,** and ε stands for the relative dielectric constant (e = 8.76). For ZnS crystal, $m_e^* = 0.23\ m_o$ and $m_h^* = 0.34\ m_o$ (m_o is the free electron mass) (Jothibas et al. 2017**).**

The particle size obtained from this sample is 4.6 nm which is a good agreement determined by XRD.

4.3. Transmission electron microscope (TEM) observation

4.3.1. Transmission electron microscopy

The TEM image of ZnS is shown in Figure (5) which shows spherical particles agglomerated with size 7.9 nm, The size of particles observed in the TEM micrograph is larger than that of the crystallites estimated from the Debye–Sherrer formula. We think that each particle is consists of fine crystallites whose sizes were determined by the XRD technique. Thus, each particle observed in the TEM micrograph was polycrystalline.

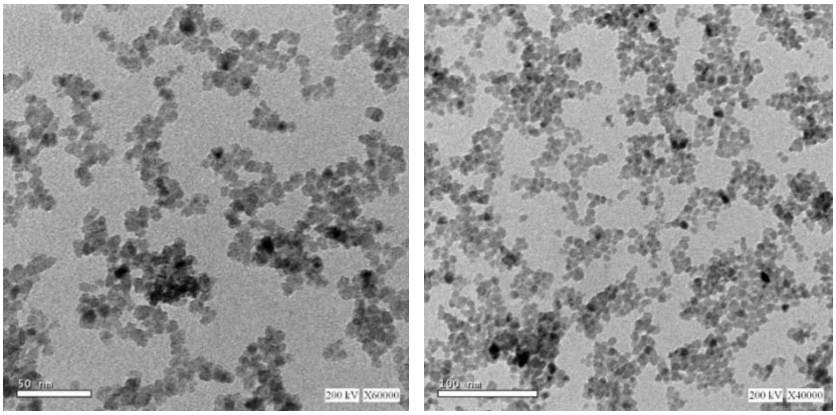


Fig. 5. TEM images of ZnS nanoparticles

4.4. Fourier Transform Infrared measurement

The FTIR spectra are carried out to investigate the composition and quality of the compound, the FTIR spectra could be explained by several peaks (Figure 6) obtained by the sample. The FTIR results showed several absorption bands in the region 4000 - 400 cm^{-1}, the spectrum shows peaks at 415.585, 661.464, 1004.73, 1138.76,1629.55, and 3441.35 cm^{-1}. The peak at 3441.35 cm^{-1} and 1629.55 cm^{-1} related to OH groups that were surrounding around the nanoparticle, the peak at 3441.35 cm^{-1} related to OH stretching vibration, and the peak at 1629.55 cm^{-1} related to H-O-H bending (Sabaghi et al. 2018), the peak at 1138.76 related to S-O impurities (Sabaghi et al. 2018), the peak at 1004.73 may be corresponding to the organic compounds (Wu et al. 2017), the peaks at 405 cm^{-1} and 661.464 cm^{-1} are the characteristic absorption of Zn–S bond (Shaikh and Sonawane. 2016), (Kumar and Upadhyay. 2015).

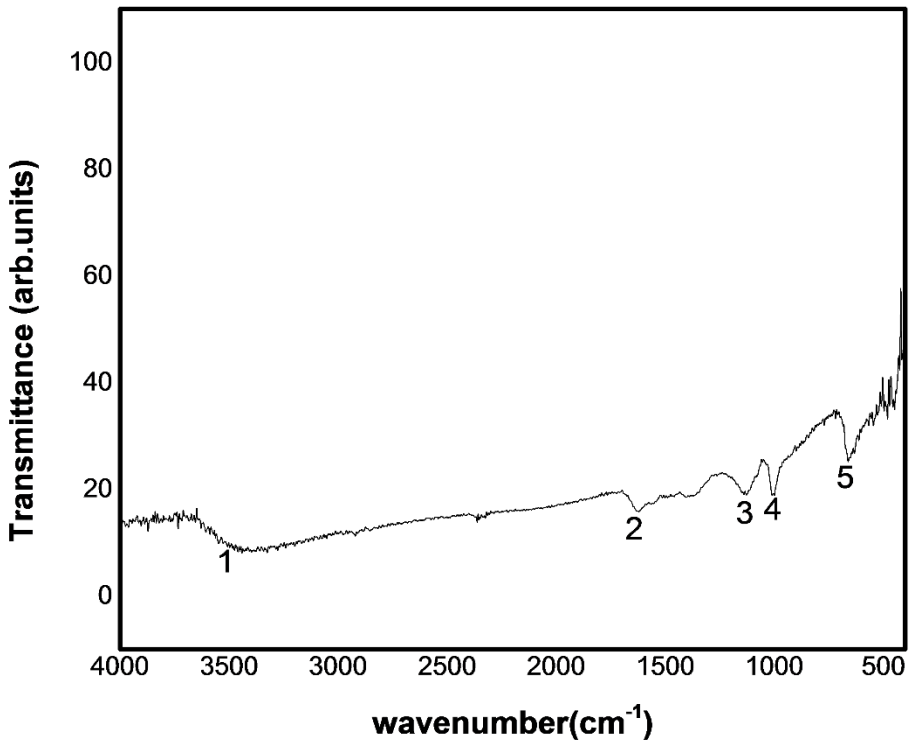


Fig. 6**.** FTIR spectrum of ZnS nanocrystals

5. Conclusions

ZnS nanoparticles were successfully synthesized by chemical precipitation method using sodium sulfide ($Na_2S.x\ H_2O$) as a sulfur source. The XRD results reveal that the particles are polycrystalline with a strong preferred grain orientation along (111) plane and show cubic type crystal structure with grain size equal to 6.41 nm, the optical band gap of the ZnS nanoparticles were obtained from the UV-VIS absorption spectrum which was calculated to be 4.5. TEM images revealed the spherical shape of ZnS nanoparticles with an average particle size is 7.9 nm.

Acknowledgments

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