RESEARCH PAPER

Fabrication and Characterization of Zinc Sulfide Nanoparticles and Nanocomposites Prepared via a Simple Chemical Precipitation Method

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ABSTRACT

In this research zinc sulfide (ZnS) nanoparticles and nanocomposites powders were prepared by chemical precipitation method using zinc acetate and various sulfur sources. The ZnS nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, ultraviolet-visible and fourier transform infra-red. The structure of nanoparticles was studied using X-ray diffraction pattern. The crystallite size of ZnS nanoparticles was calculated by Debye–Scherrer formula. Morphology of nano-crystals was observed and investigated using the scanning electron microscopy. The grain size of zinc sulfide nanoparticles were in suitable agreement with the crystalline size calculated by X-ray diffraction results. The optical properties of particles were studied with ultraviolet-visible absorption spectrum.

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INTRODUCTION

Among the family of semiconductors, II-VI group semiconductor compounds have immense technological importance in various applied field of science and technology. For instance ZnS, CdS, ZnO, CdTe etc., are important because of their excellent electronic and optical properties for optoelectronic applications [3].

Zinc sulfide is a very important semiconductor with a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [1]. Therefore, ZnS nanoparticles have many applications in solar cells [2], gas sensor [3], anti-virus agent in coating [4] and electroluminescent devices [5]. The nonlinear properties of ZnS are very interesting for the production of optical devices [6]. ZnS has been synthesized using several methods as like homogeneous precipitation [7] microwave methods [8] thermal evaporation [9], pulsed laser deposition [10], spray pyrolysis [11] and solution–gelation (sol–gel) [12].

So far, extensive efforts have been made on the synthesis of low dimensional ZnS nanostructures, including nanoparticles, nanowires, nanobelts, nanocables, and nanotubes.

For ZnS, the sphalerite (cubic zinc blende) structure is a stable phase at low temperature, whereas the wurtzite (hexagonal) structure is a high-temperature stable phase. Recent studies found that the optical properties of wurtzite ZnS are more excellent than those of sphalerite ZnS. However, it is difficult to synthesize pure wurtzite ZnS nanocrystals at relatively low temperatures; most ZnS nanocrystals synthesized via low- temperature solution- phase methods have the sphalerite structure. Exploring the low- temperature synthesis of highly crystalline

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wurtzite ZnS nanocrystals has been a hot field of current ZnS material research [13].

Nanoparticles (NPs) which are smaller than that of the bulk Bohr excitonic radius exhibit blue shift in the optical transition and yields high photoluminescence (PL) property.

In this regard ZnS is a technologically important II-VI luminescent semiconductor and shows band gap energies of 3.68 eV for cubic and 3.9 eV for wurtzite phase [14].

Color of light emitted by the semiconductor material is determined by the width of band gap[10].

The band gap of ZnS increases with reduction of its size from bulk material to nanomaterial.

Thus, ZnS, nanoparticles are considered to be highly promising material having numerous applications in solar cells, electro-optical, and electronic devices. ZnS can readily absorb moisture and can oxidize in air, which makes ZnS less stable as pure compound in atmosphere [15, 16].

Quantum confinement effect modifies the electronic structure of the nanocrystals when the sizes of the nanoparticles are comparable to that of Bohr excitonic radius of those materials. When the particle radius falls below the excitonic Bohr radius, the band gap energy is widened, leading to a blue shift in the band gap, emission spectra etc. on the other hand, the surface states will play a more important role in the nanoparticles, due to their large surface-to-volume ratio with a decrease in particle size(surface effects) [17, 18].

Nevertheless II-VI semiconductor nanoparticles are themselves highly unstable and in the absence of a trapping medium or some other form of encapsulation they agglomerate or coalesce extremely quickly. If this growth of particles is not controlled, the particles agglomerated and settle due to Ostwald ripening and Van der Waals' interactions between particles. For this reason, the bonding of capping agents to the nanoparticles is necessary to provide surface passivation and also to improve the surface state, which significantly influences the optoelectronic properties of nanoparticles [19, 20].

In this work, the precipitation method was used to prepare ZnS/ZnO nanoparticles. Then the crystallinity, size, morphology, and optical properties of ZnS nano particles were investigated.

MATERIALS AND METHODS

For the synthesis of zinc sulfide nanoparticles, the following procedure was used. The chemical precursors used in reaction zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), thio urea, sodium sulfate, thioglycolic acid and distilled water (all materials from Merck Company were used without further purification). 0.001 mol of zinc acetate and 0.001 mol of sulfur source were dissolved in 100 ml of deionized water. Sodium hydroxide and potassium hydroxide were added as precipitating agents. The obtained solution was heated using a hot plate on 80 °C with a magnetic stirring until forming the white precipitate.

Structure of nanoparticles was studied using X-ray diffraction with CuKα (λ=1.54 Å) radiation. The shape and size of nanoparticles were investigated by scanning electron microscope images. Analyze for elemental was obtained using EDX. The optical properties of ZnS nanoparticles were analyzed using UV–Vis spectroscopy. The FTIR analysis performed in order to determine the materials existed in ZnS sample. FTIR studies are conducted on compressed pills prepared by mixing ZnS powder with potassium bromide.

All the chemical materials were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered CuK_α radiation. Scanning electron microscopy (SEM) images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation.

RESULTS AND DISCUSSION

The XRD pattern of ZnS nanoparticles is shown in Fig. 1. XRD analyses were performed to determine the crystalline structure and phase formation of zinc sulphide nanoparticles.

The XRD pattern of ZnS/ZnO nanoparticles is shown in Fig. 2. The nanoparticles crystallite size was calculated from X-ray line broadening using Debye–Scherrer equation [13]:

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

where λ is the X-ray wavelength (CuKα radiation equals to 1.54Å), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The crystalline size of ZnS nanoparticles calculated about 4 nm by Debye–Scherrer equation.

SEM images of ZnS nanoparticles by KOH are

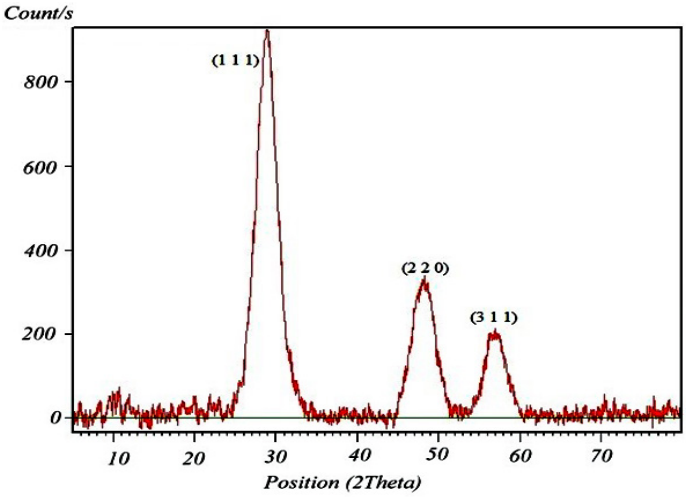

Fig. 1. XRD patterns of ZnS nanoparticles

shown in Fig. 3. Microscopic images confirm star-like nanostructures were synthesized.

SEM image of ZnS nanoparticles by NaOH are illustrated in Fig. 4. Images also approve star-like nanostructures with average diameter less than 100 nm were obtained.

Fig. 5 show SEM images of ZnS nanoparticles obtained at presence of thioglycolic acid (TGA). Results confirm that agglomeration was observed in images and bigger particles with average diameter around 150 nm were synthesized.

SEM image of ZnS nanoparticles synthesized by thio-urea are shown Fig. 6. Outcomes show trigonal nanostructures with mediocre sized less than 100 nm were achieved.

Fig. 7 illustrates SEM images of ZnS nanoparticles synthesized by both thio-urea (TU) and sodium sulfide. Results approve agglomerated nanoparticles with average diameter less than 100 nm were obtained.

It seems by using thioglycolic acid growth stage is preferential compare to nucleation stage.

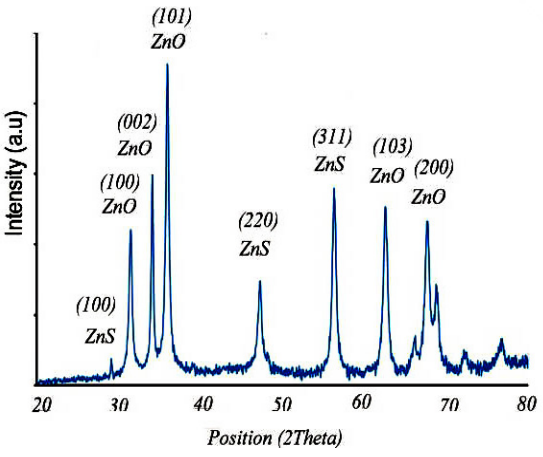

Fig. 2. XRD patterns of ZnS/ZnO nanoparticles

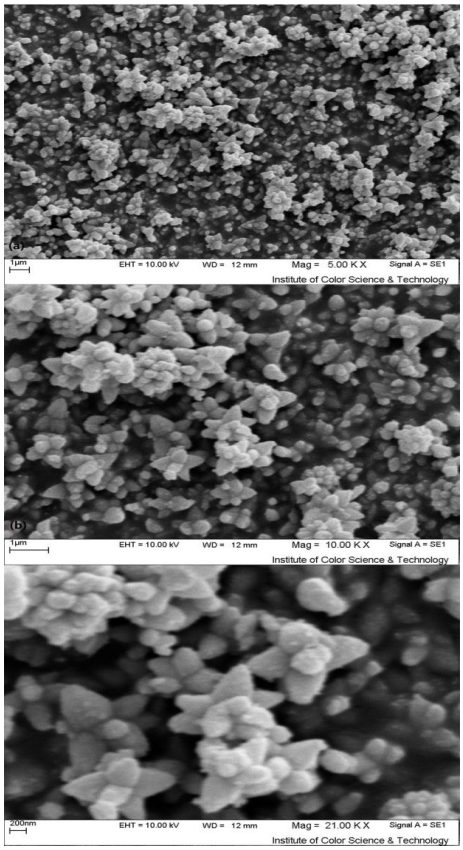

Fig. 3. SEM images of ZnS nanoparticles by KOH

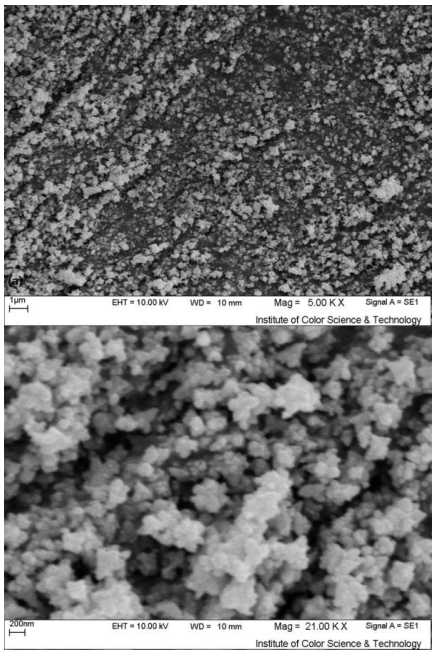

Fig. 4. SEM image of ZnS nanoparticles by NaOH.

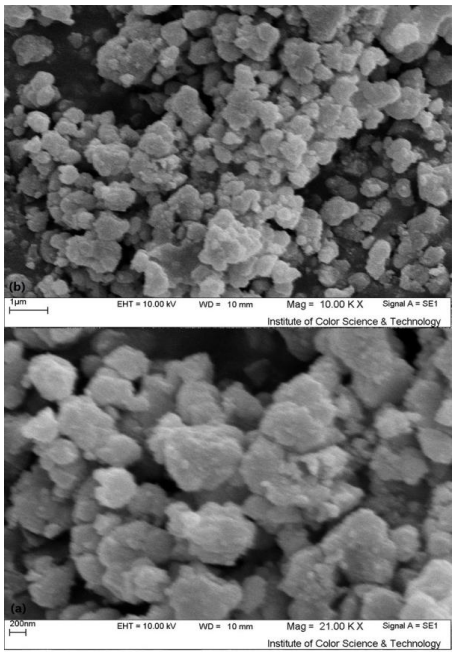

Fig. 5. SEM image of ZnS nanoparticles by TGA

Optical absorption spectra of samples using UV-Vis are indicated in Fig. 8. The absorption spectra indicate the excitonic shoulder peaks of ZnS nanoparticles.

Fig. 9 shows the FTIR spectrum of the ZnS nanoparticles. The peak at 405 cm^{-1} is the characteristic absorption of Zn–S bond. Other weak absorption peaks which corresponding to the sodium sulfate and thio-urea impurities in the materials. This result show suitable agreement with previous works.

CONCLUSION

In this research zinc sulfide (ZnS) nanoparticles and nanocomposites powders were prepared by chemical precipitation method using zinc acetate. The ZnS nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible (UV-Vis) and Fourier

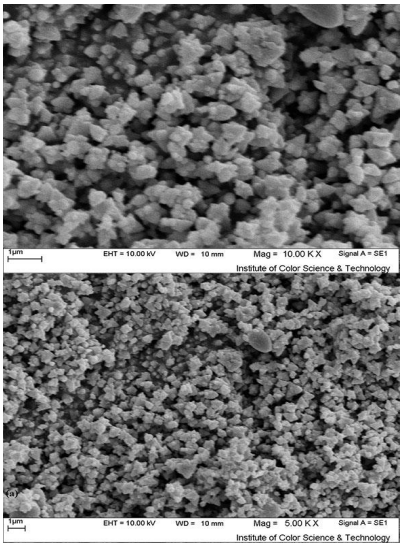

Fig. 6. SEM image of ZnS/ZnO nanoparticles by TU

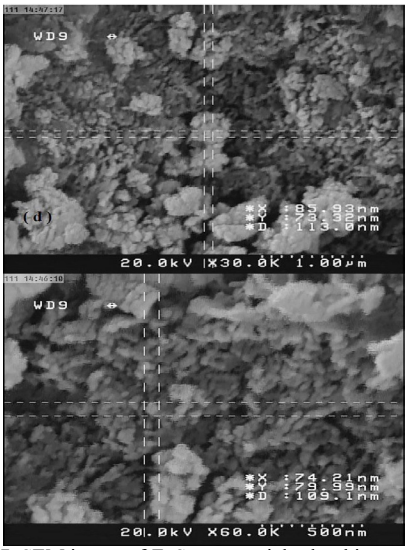

Fig. 7. SEM image of ZnS nanoparticles by thiourea and Na_2S

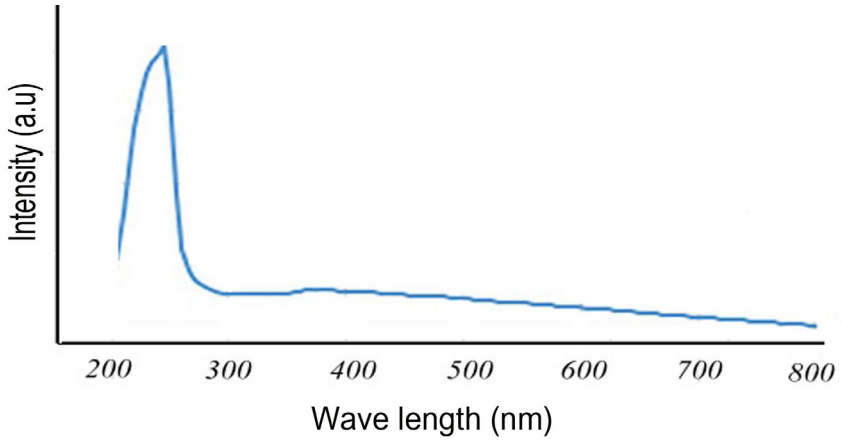

Fig. 8. UV-Vis absorption spectra of ZnS nanoparticles by KOH

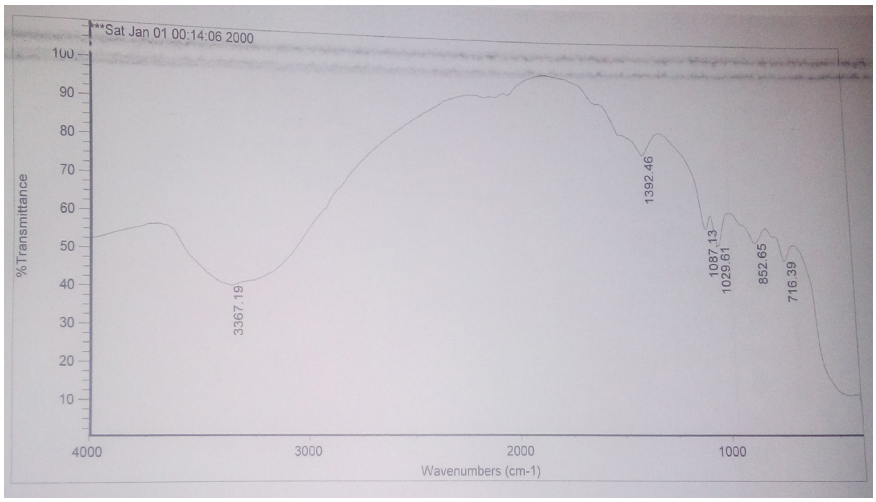

Fig. 9. FT-IR spectra of ZnS nanoparticles by KOH

transform infra-red (FT-IR). The structure of nanoparticles was studied using XRD pattern. The crystallite size of ZnS nanoparticles was calculated by Debye–Scherrer formula. Morphology of nano-crystals was observed and investigated using the SEM. The grain size of zinc sulfide nanoparticles were in suitable agreement with the crystalline size calculated by XRD results. The optical properties of particles were studied with UV-Vis an FTIR absorption spectrum.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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