

Conditional Optimization of Displacement Synthesis for Pioneered ZnS Nanostructures

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Abstract: The present work describes ZnS nanoparticles are prepared by chemical displacement method using CTAB as a stabilizer or Surfactant. For source of Sulphur ion, we used thiourea as fuel. The structural, morphological, and optical properties of as synthesized nanoparticles are investigated by using x-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy Dispersive Analysis Of X-Ray (EDAX), Fourier transform infrared spectroscopy (FTIR), Thermals analysis (TGA-DSC) and Transmission electron microscopy (TEM). The x-ray diffraction patterns revealed that the particles exhibited a zinc-blended crystal structure and also shows average particle size of ZnS nanoparticles are around 32-48 nm. From SEM and EDAX analysis shows good morphology and percentage of metal ion of synthesized ZnS nanostructures. The Transmission electron microscopy (TEM) shows crystalline size of structures.

Keywords: Nanoparticles, zinc sulfide, XRD, FTIR, SEM, EDAX, TEM, TGA/DSC.

1 Introduction

The ZnS nanoparticles belong to group II–VI semiconductor with wide band gap of around 3.68 eV. ZnS crystallizes in the zinc blende (ZB) or wurtzite (WZ) structures at room condition with a band gap of 3.68 eV or 3.77 eV [1] respectively. As a typical nontoxic wide band gap semiconductor material like ZnS has been used as optical devices, such as ultraviolet light emitting diodes [2,4] flat panel displays,[5,6] solar cells,[6] and optical sensors.[8] ZnS with a band gap of 3.68 eV corresponds to ultraviolet radiation for optical inter band transition. Wide-band gap semiconductors such as ZnS are ideal materials for the study of discrete states in the gap. Visible luminescence can originate only from transitions involving these localized states. The reported luminescence spectrum and absorption in ZnS both show an emission peak at around 420 nm [9,11]. Synthesis of various nanoparticles by Using several methods, like Solution combustion method for Synthesized La2O3 nanoparticles using Propylene glycol and Glutaric acid as fuel and chelating agent [12]. ZnS Nanocrystals have been success-fully synthesized by various methods and their properties have been investigated [13,16] these general preparation techniques include the co-precipitation method, sol–gel, solution combustion method, reverse-micelle method, microwave method, hydrothermal process etc. At the Nanoparticle sizes of a semiconductor, the energy gap (band gap) increases, and the optical spectrum is shifted toward the short-wavelength region [17] and some of their physical properties differ Conspicuous from those of the corresponding bulk material. These properties of Nanocrystals make them an interesting category of material for optoelectronic applications.

In this work, ZnS nanoparticles are prepared by displacement reaction using Zn (NO₃)₂ as metal salt, CTAB as surfactant, thiourea as fuel and Ethanol as solvent to control the particle sizes by a simple chemical route. The crystalline and morphology are studied using x-ray powder diffraction (XRD) and scanning electron microscope (SEM). The Zn-S bond are discussed from Fourier transform infrared (FTIR) (Bruker αT model) and metal detection by using EDAX analysis. Thermals analysis was done by TGA-DSC Analyzer (Metler Toledo).

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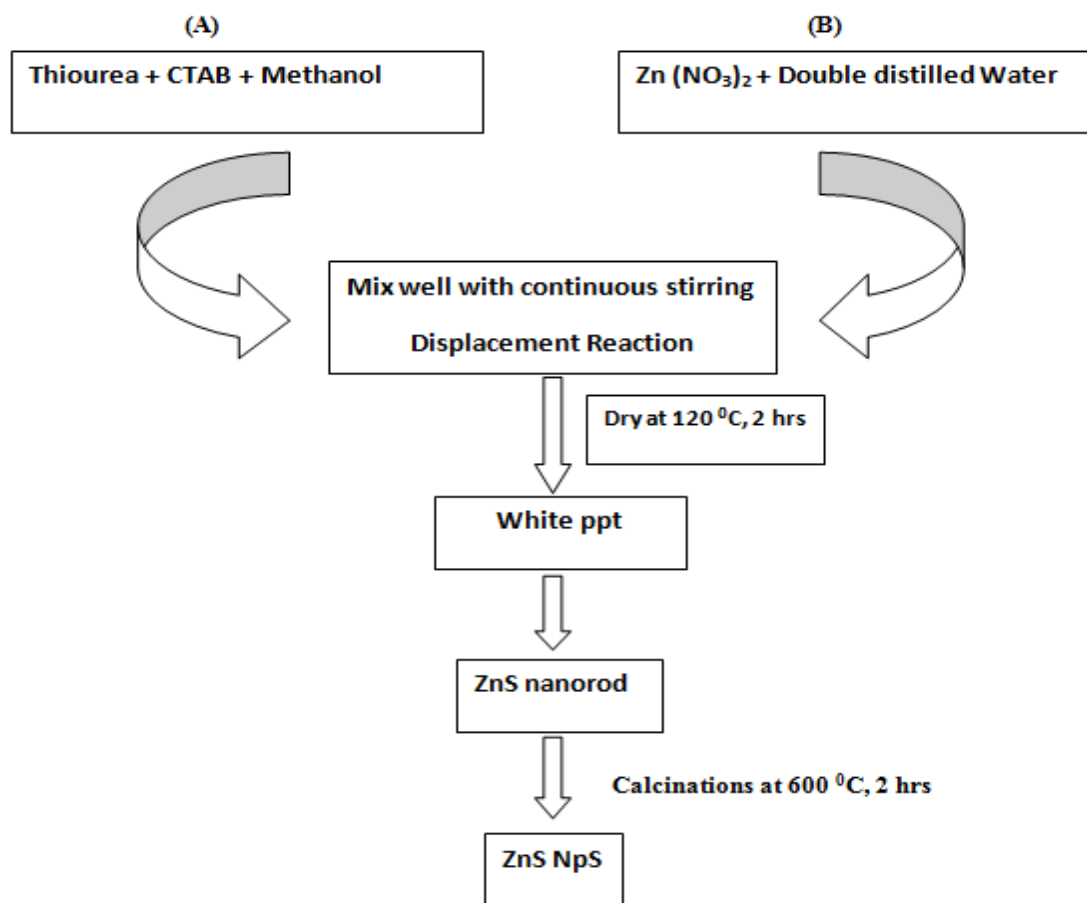
2 Materials and Method

2.1 Materials

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), and thiourea (NH_2CSNH_2) purchased from Hi-Media chemicals and CTAB was collected from S. D. Fine Chemicals were used without further purification. All chemicals were analytical grade. Distilled water was used in all experiments.

2.2 Synthesis of ZnS Nanoparticles by Displacement Method

Nanosized particles of ZnS crystals were prepared by displacement reaction using zinc Sulphate ($\text{Zn}(\text{NO}_3)_2$), thiourea (NH_2CSNH_2), and CTAB as source materials. CTAB acted as the surfactant. All of the reagents were analytical grade in purity and used without further purification, and the deionized water was used as a solvent. The ZnS nanoparticles were prepared in the following sequence 1mol $\text{Zn}(\text{NO}_3)_2$ was dissolved in 50 ml of deionized water under continuous stirring and another beaker taking 2 mol thiourea (NH_2CSNH_2) and 1mol CTAB were added in 50 ml of Ethanol. The thiourea and CTAB solution was then poured into $\text{Zn}(\text{NO}_3)_2$ solutions. After the reaction was completed, a white precipitate formed. Then ppts were filtered and washes with double distilled water for three times and then heated up to 600°C for 2 h in muffle furnace for purpose of calcinations. After the calcinations we get fine ZnS Nanoparticles.



3 Results and discussion

3.1 X-Ray Diffractometer Analysis

The analysis of x-ray pattern (Fig.1) shows that ZnS sample crystallize in cubic symmetry (F-43M space group) with lattice parameter $a = 5.368(4) \text{ \AA}$ and unit cell volume $V = 154.7157(8) \text{ \AA}^3$. The three different peaks of the sample correspond to the lattice planes of (111), (220), and (311), which match very well with the cubic zinc blende structure (JCPDS No. 05-0566).

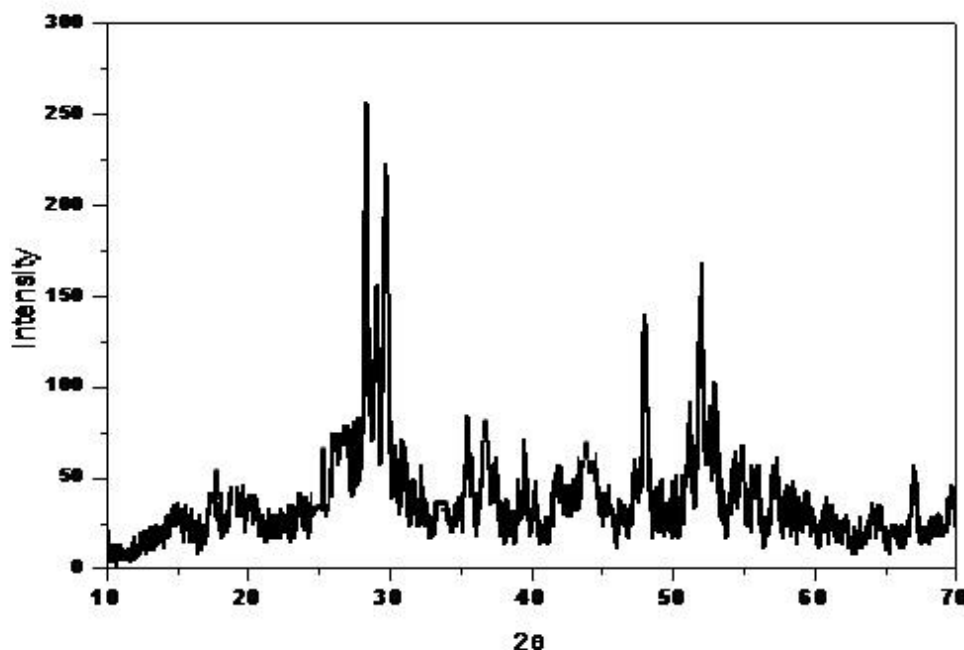


Figure. 1. XRD spectra of ZnS Nanoparticles

The significant broadening of the XRD pattern peaks reveals the small particle (crystallite) size and indicates the nanometric particle size.[18] The average particle size is approximately Calculate by Debye Scherrer formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where, D is the average crystallite size of the particle, λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) of that peak in radian and θ is the diffraction angle of the Bragg peak. The average crystallite sizes of sample are 32-44 nm.

A dislocation is a crystallographic defect that strongly affects many properties of zinc sulfide, so the dislocation density is also calculated from the following relation: [19, 20]

$$\delta = \frac{15e}{aD} \quad (2)$$

The effective strain and also the dislocation density are estimated to be 6.71×10^{-3} and 3.41×10^{15} , respectively.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of ZnS nanoparticles at room temperature is shown in Fig. 3. This spectrum shows the IR absorption due to the various vibration modes. The characteristic major peaks of ZnS can be observed at around 1113, 605, and 538 cm^{-1} . The observed peaks at 1640 cm^{-1} are assigned to the C=O stretching modes, and also shown the broad absorption peaks in a range of 3100 cm^{-1} – 3600 cm^{-1} correspond to O–H stretching modes arising from the absorption of moisture on the surface of nanoparticles.

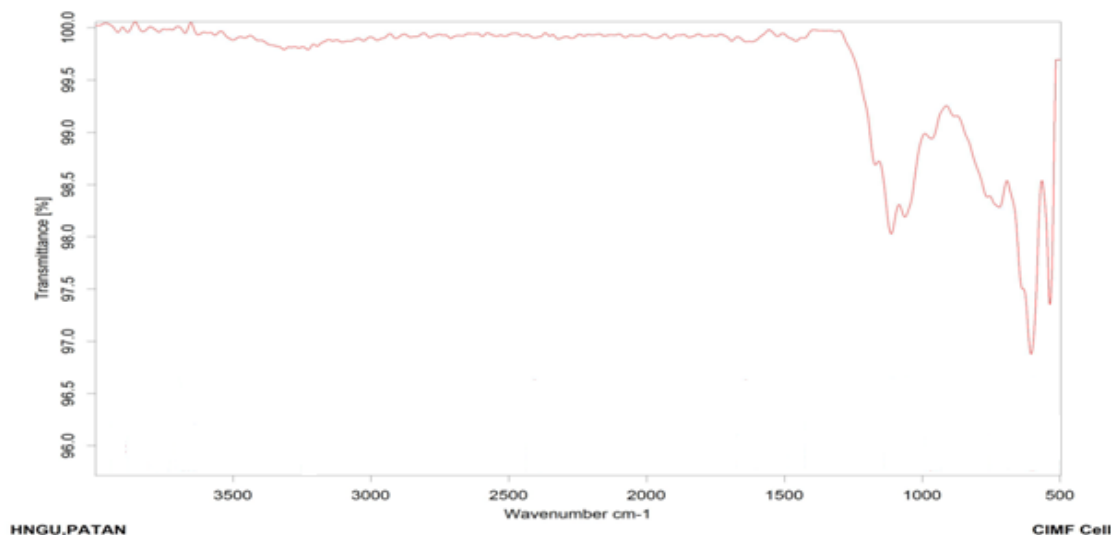


Figure.2 FTIR spectra of ZnS Nanoparticles

3.3 Thermo Gravimetric and Differential Thermal Analysis

The TGA analysis of ZnS Nano particles synthesized using this Method was representing in fig. 3 respectively. The temperature range is 50 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$. The initial weight loss observed at 350 $^{\circ}\text{C}$ to 550 $^{\circ}\text{C}$ corresponds to that of loss of carbonaceous compounds. The peak observed after 400 $^{\circ}\text{C}$ to 550 $^{\circ}\text{C}$ corresponds to decomposition of covalently bond organic material, mainly carbon which was converted into CO_2 at the time of synthesis. From DSC Curves of ZnS Nano particles the exothermic peak present in between 600 $^{\circ}\text{C}$ to 850 $^{\circ}\text{C}$ can be observed due to desorption and decomposition of carbonaceous materials.

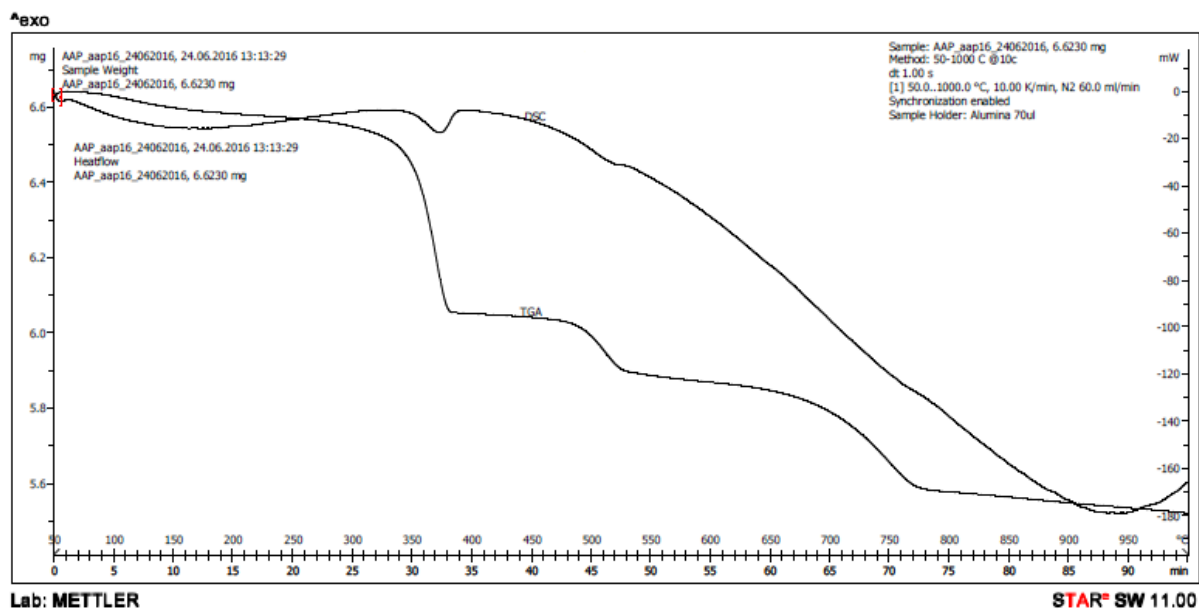


Fig.3 TGA/DSC Curves of ZnS Nanoparticles

The weight loss of the ZnS Nano Particles are Shown in above fig. 3 Shows the Weight Loss for the Sample Synthesized this Method is 14.52%.

3.4 Scanning Electron Microscopy (SEM) and EDAX

The grain size, shape and surface properties like morphology were observed using SEM with different magnifications. The SEM images of ZnS nanoparticles which were prepared using displacement Method was shown in fig. 4 respectively.

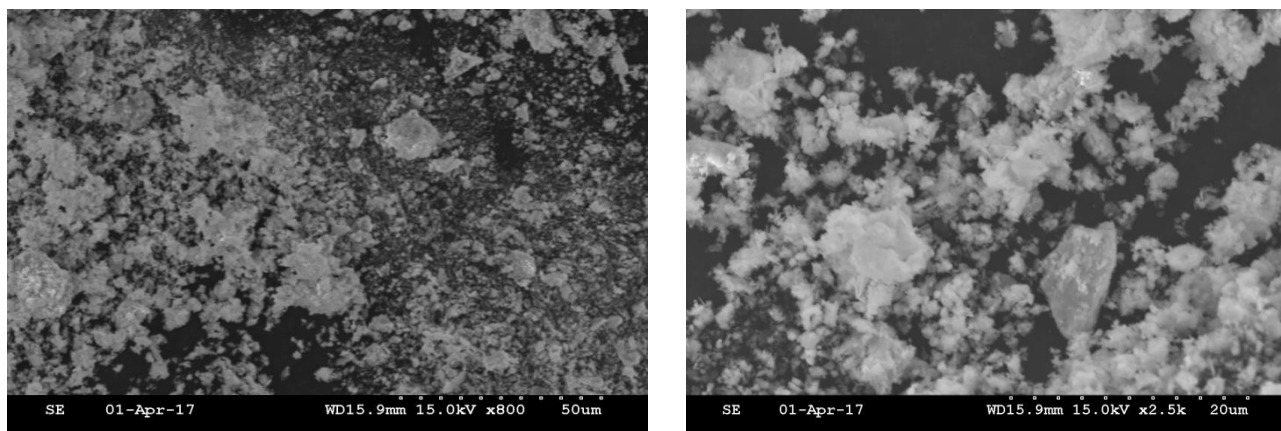


Fig. 4 SEM Images of ZnS Nanoparticles Synthesized by displacement Method.

It shows that, the particles are agglomerated and porous properties. It show that the size of the porous or porosity shows to be increased as the fuel to oxidizer ratio increased. EDAX spectrum of ZnS shows the peaks for Zinc and Sulfur elements indicating the formation of ZnS nanoparticles. Peak indexing of the elements are Sulfur 2.2 keV and Zinc 0.5 keV. The compositions in mass percentage of the elements are Sulfur 35.12% and Zinc 61.21 %. The observed composition matches with the theoretically calculated composition. Below Fig 5 shows the presence of Zinc and sulphur. Other signals including C and O are recorded possibly due to the elements present in thiourea and moistures.

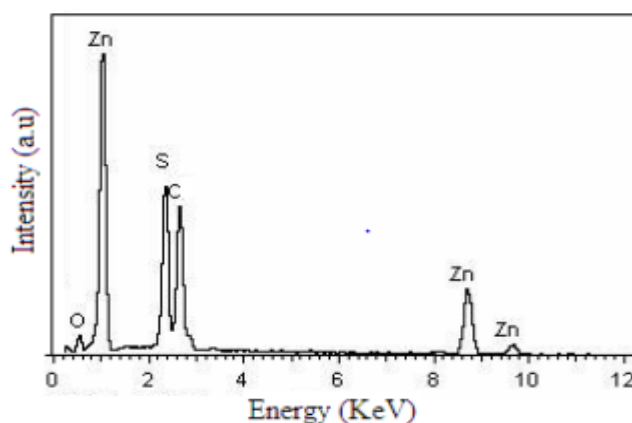


Fig. 5 EDAX Image of ZnS Nanoparticles Synthesized displacement Method.

3.5 Transmission Electron Microscopy (TEM) Analysis

The TEM analysis show the agglomerated sample in Nano range. The below figure shows the TEM micrograph of the sample synthesized using this Method.

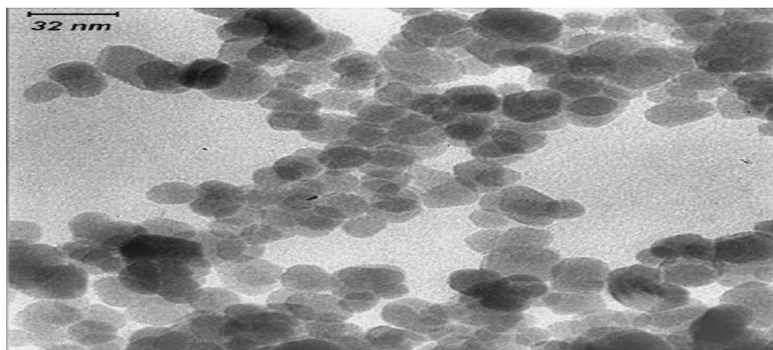


Fig. 6 TEM Images of ZnS Nanoparticles Synthesized by displacement Method

From TEM analysis, it has been found that the samples particles not good in crystal due to severe agglomeration. But the particles are well below Nanometer range to conclude that the obtained particles are Nano particles.

4 Conclusions

ZnS nanoparticles are successfully synthesized via displacement method. The chemical bonding (Zn-S bond) and structural properties of sample are characterized by FTIR and x-ray diffraction to identify the chemical and crystal structure. TGA/DSC reveals the effective weight loss of materials around 350⁰C-550⁰C and exothermic peak shows around at 700⁰C. The x-ray diffraction pattern indicates the very good cubic zinc-blended structure of ZnS Nanocrystals with an average size of 32-48 nm. Structural properties were examined by SEM reveals porous and Porosity was good in network of Nano crystalline ZnS. From the above TEM characterizations we inferred that the sample obtained good phase pure and more crystalline in nature.

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