

A rapid microwave route for the synthesis of ZnS nanoparticles

Masoud Salavati-Niasari ^{a,*}, Mehdi Ranjbar ^a, Davood Ghanbari ^b

^a *Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317–51167, I. R. Iran*

^b *Young researchers Club, Arak Branch, Islamic Azad University, Arak, Iran*

Article history:

Received 11/11/2011

Accepted 20/2/2012

Published online 1/3/2012

Keywords:

Nanoparticles

Semiconductor

Zinc sulfide

*Corresponding author:

E-mail address:

Salavati@kashanu.ac.ir

Phone: +98 361 591 2383

Fax: +98 361 5552935

Abstract

ZnS nanoparticles were synthesized via a simple surfactant free microwave route. In this synthesis, thioacetamide was used as sulfur source. The effects of different parameters such as type of zinc precursor, time and power of irradiation on the morphology and particle size of the products have been investigated. The nanostructures were characterized by means of X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and photoluminescence (PL) spectroscopy.

2012 JNS All rights reserved

1. Introduction

Nanostructured materials have attracted much attention in the last few years due to their unique properties that are different from the bulk materials [1–3]. Zinc sulfide as an important semiconductor with wide band gap (3.6 eV) has been widely used for the light emitting diodes, flat panel displays, electroluminescent and infrared devices [4]. ZnS is observed in nature in two polymorphs, zinc blend and wurzite, with cubic and hexagonal lattice structures, respectively. Atoms in the bulk of both

polymorphs being four-coordinated and have tetrahedral coordination. The zinc blend phase is more stable than wurzite and it is common to find both in the same sample. Many efforts have been made in the fabrication of one-dimensional, two-dimensional and three-dimensional of ZnS nanostructures. We have been interested in the synthesis of sulfide nanostructures for a few years [5–8]. In this paper, we report a simple and rapid microwave method for preparation of ZnS nanostructures. The nanostructures were synthesized

from reaction between zinc ethylenediamine (Zn(en)_2) and thioacetamide (TAA). The effects of different parameters such as power of oven and time of irradiation were also studied.

2 Experimental

2.1 Materials and characterization

All the chemical reagents were of analytical grade and were used without further purification. X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Fourier transform infrared (FT-IR) spectrum was recorded by a Nicolet Magna-550 spectrometer in KBr pellets. The electronic spectrum of the sample was taken on Perkin-Elmer LS-55 luminescence spectrometer. Scanning electron microscopy (SEM) images were obtained on LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Pt to make the sample surface conductor and prevent charge accumulation.

2.2. Synthesis of Zn(en)_2^{2+} complex

Zinc ethylenediamine was achieved according to our previous work [9]. First $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.01 mol) was dissolved in ethanol. 0.02 mol of ethylenediamine was then added to the solution. The reaction mixture was heated under reflux for 2 h and the solvent was removed under reduced pressure. The resulting yellow precipitate was collected and washed with deionized water and ethanol and finally it was dried at 80°C in a vacuum oven.

2.3. Synthesis of ZnS nanoparticles

In a general procedure, 0.01 mol of Zn(en)_2 was dissolved in 20 mL of propylene glycol under vigorous stirring at 90°C . 10 mL of thioacetamide (1.0 M) was then added drop wise to the solution. Afterward, the solution was exposed to microwave irradiation with different powers and times. The microwave oven followed a working cycle of 30s on and 70s off (30% power). After heating under

microwave irradiation, the samples were cooled to room temperature naturally. Precipitates were flittered, washed with deionized water and ethanol, and then dried at room temperature.

3. Results and discussion

XRD patterns of the synthesized products after annealing at different temperatures 100, 200 and 400°C are shown in Figs. 1a-c respectively. Patterns of the samples were indexed as a cubic phase (space group $F-43m$) which is very close to the values in the literature (JCPDS No. 80-0020 with cell constant $a = 5.3450 \text{ \AA}$). The strong and sharp reflection peaks in the XRD pattern indicated that ZnS products were well-crystallized. No peaks from any other impurities such as ZnO or other compounds are detected.

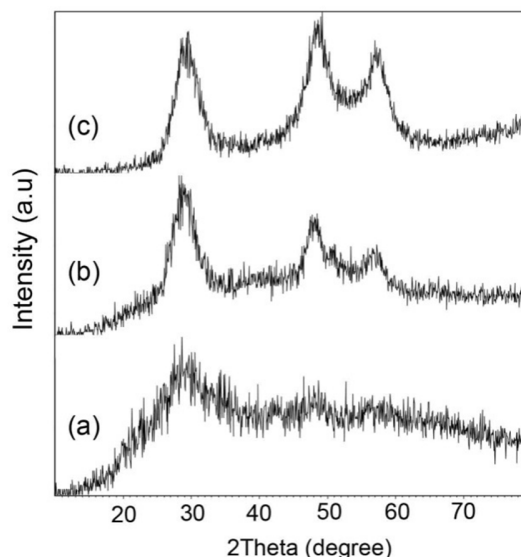


Fig. 1. XRD patterns of the as-synthesized products at different annealing temperature at (a) 100 (b), 200, and (c) 400°C .

Fig. 2 shows SEM image of ZnS powder obtained with $\text{Zn}(\text{CH}_3\text{COO})_2$ for 5 min at 750 W, which consist of particles with diameters about 100–200 nm. Figures 3-5 show SEM images of obtained products with $[\text{Zn(en)}_2]^{2+}$ precursor. The effect of power of oven on the morphology and particle size of the products was investigated. SEM images of the obtained products at 4 minute at different powers at

600, 750 and 900 W are shown in Figs. 3a-3c respectively. As shown in Fig. 3, when the power of the oven was raised from 600 to 900, nanoparticles with smaller sizes (30–40nm) were obtained.

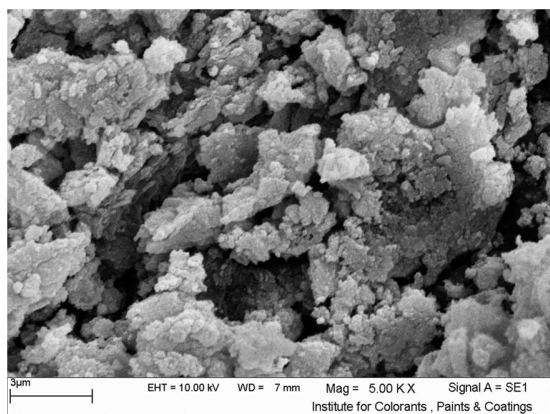


Fig. 2. SEM image of ZnS achieved with $\text{Zn}(\text{CH}_3\text{COO})_2$ at 750 W in 5 min.

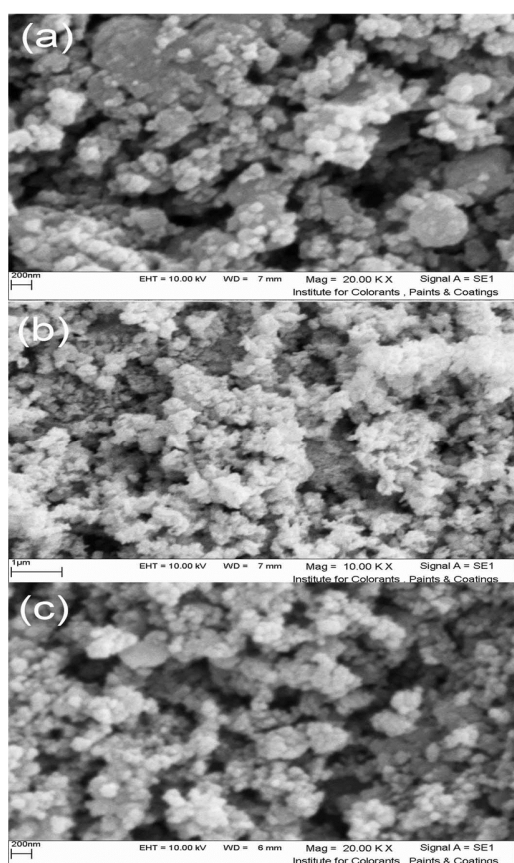


Fig. 3. SEM images of the obtained ZnS at 4 min at different powers (a) 600 W, (b) 750 W, (c) 900 W.

Results show in higher powers nucleation stage overcome to growth stage and smaller particles were achieved. The effect of time on the morphology of the products was also investigated. SEM images of obtained products at 8 minute at different powers at 600, 750 and 900 W are shown in Figs. 4a-c respectively.

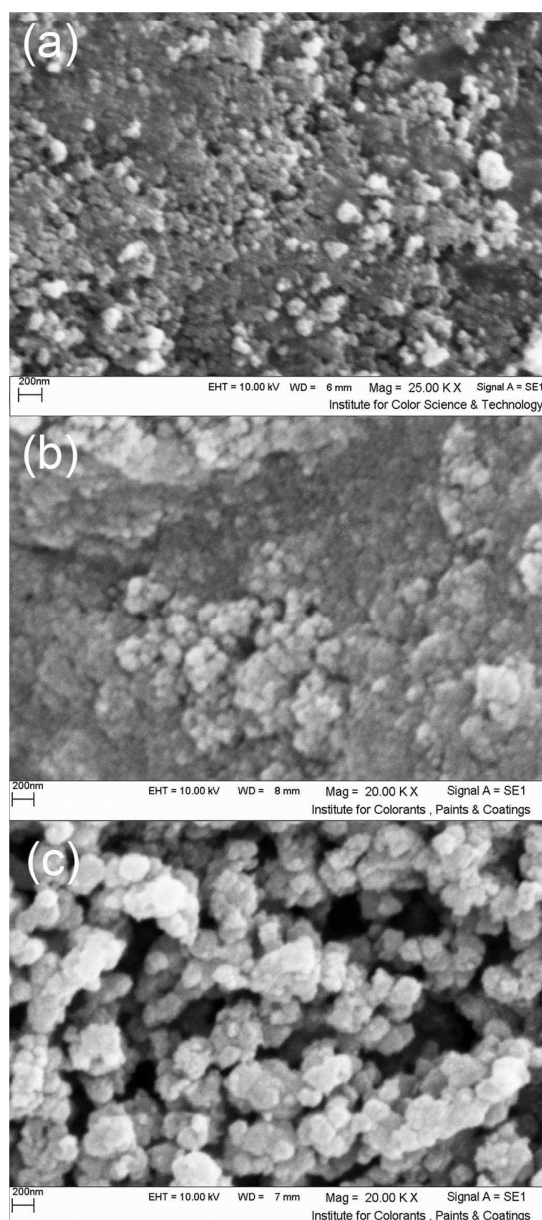


Fig. 4. SEM images of the ZnS at 8 min at different powers (a) 600 W, (b) 750 W, (c) 900 W.

SEM images of the as-synthesized products at 12 minute at different powers at 600, 750 and 900 W are exhibited in Figs. 5a-c respectively. When the reaction time was prolonged, from 4 to 12 minute, nanoparticles with smaller particle size were obtained.

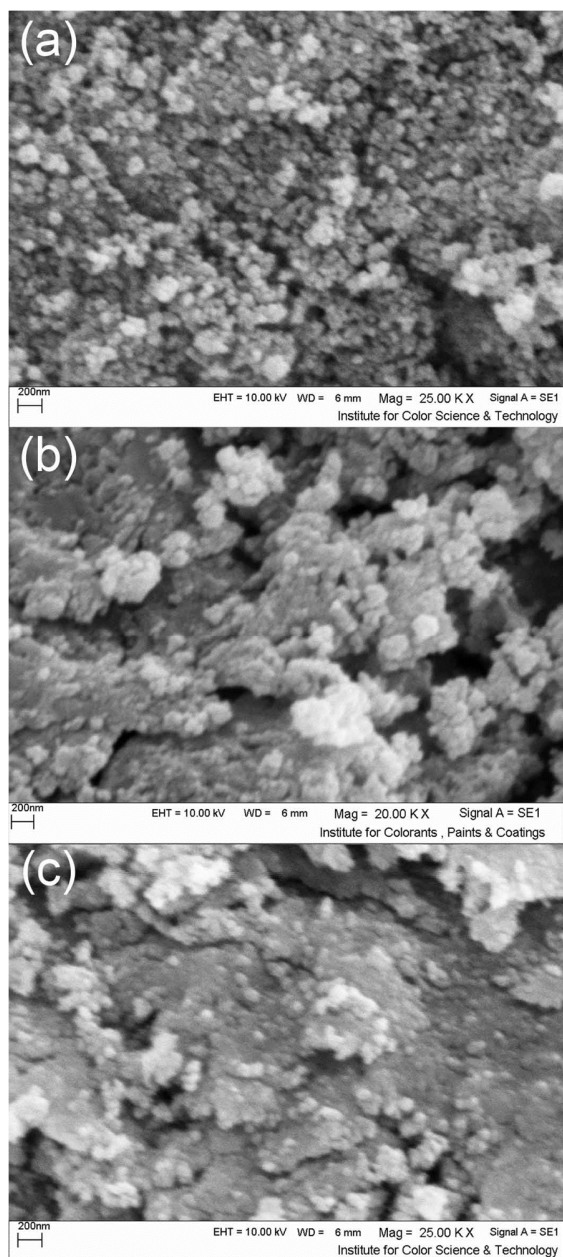


Fig. 5. SEM images of the obtained ZnS at 12min at different powers (a) 600 W, (b) 750 W, (c) 900 W.

The purity of ZnS nanoparticles was also confirmed by energy-dispersive X-ray (EDX) analysis (Fig. 6), where the L_a and K_a lines of Zn and K_a of S are obviously observed.

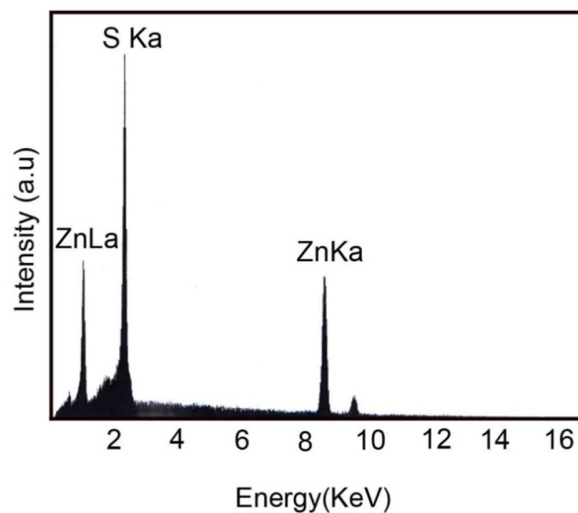


Fig. 6. EDX analysis of ZnS nanoparticles.

Photoluminescence study of ZnS was carried out at room temperature with excitation wavelength 352 nm which are laid out in Fig. 7. The PL spectrum was consisted of a strong peak at 397 nm that can be ascribed to a high level transition in ZnS semiconductor crystallites. It has been reported that this kind of bandedge luminescence arises from the recombination of excitons and/or shallowly trapped electron-hole pairs [7].

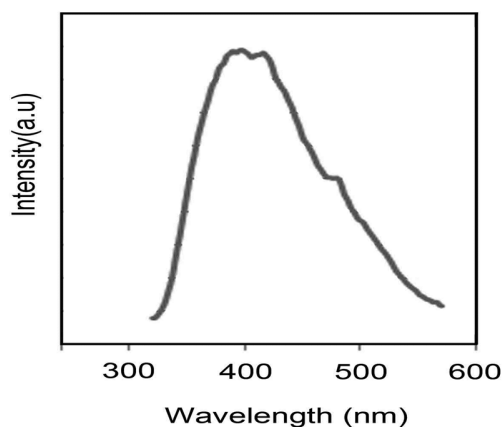


Fig. 7. Room temperature photoluminescence spectrum of ZnS nanoparticles.

Fig. 8 shows the FT-IR spectrum of the achieved ZnS at 750 W at 5 min. Absorptions at 561 cm^{-1} and 671 cm^{-1} are attributed to stretching vibrations of Zn-S bonds. Also absorptions at 3441 cm^{-1} (attributed to stretching vibrations O-H bond), proved the presence of moisture on the surface of ZnS nanostructures.

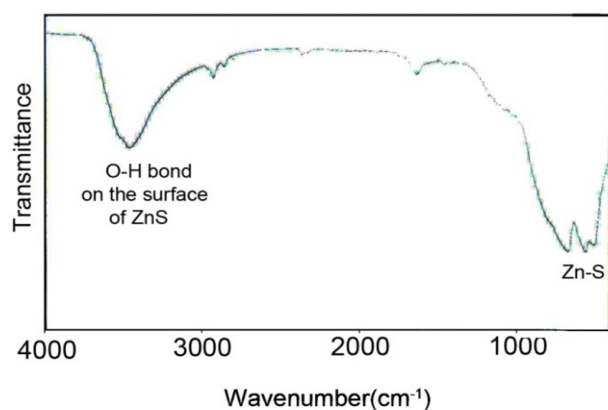


Fig. 8. FT-IR spectrum of ZnS nanoparticles.

4. Conclusion

ZnS nanostructures were synthesized via microwave method employing thioacetamide as a sulfur source. This method is rapid, simple and can be easily controlled. Effects of different parameters such as type of zinc precursor, time and power on the morphology and particle size of the products were also investigated. The nanostructures were characterized by XRD, EDX, SEM, FT-IR and PL spectroscopy.

References

- [1] M. Salavati-Niasari, F. Davar, M. Mazaheri, J. Alloy. Compd, 470 (2009) 502–506.
- [2] M. Salavati-Niasari, D. Ghanbari, F. Davar, J. Alloys Compd, 492 (2010) 570-575.
- [3] D. Ghanbari, M. Salavati-Niasari, High Temp. Mater. Proc, doi:10.1515/htmp-2012-0158.
- [4] T. Yamamoto, S. Kishimoto, S. Iida, Physics. B, 308 (2001) 916.
- [5] M. Yousefi, F. Gholamian, D. Ghanbari, M. Salavati-Niasari, Polyhedron, 30 (2011) 1055–1060.
- [6] M. Salavati-Niasari, D. Ghanbari, F. Davar, J. Alloy. Compd, 488 (2009) 442-447.
- [7] M. Salavati-Niasari, D. Ghanbari, M. R. Loghman-Estarki, Polyhedron, 35 (2012) 149-153.
- [8] M. Yousefi, M. Salavati-Niasari, F. Gholamian, D. Ghanbari, A. Aminifazl, Inorg. ChimActa, 371 (2011) 1-5.
- [9] F. Davar, M. Salavati-Niasari, J. Alloy. Compd, 509 (2011) 2487-2492.