The Nucleus 52, No. 4 (2015) 165-168

www.thenucleuspak.org.pk

The Nucleus

ISSN 0029-5698 (Print)

ISSN 2306-6539 (Online)

Green One Step Microwave Assisted Synthesis of ZnS Nanoparticles

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ARTICLE INFO

Article history :
Received : 31 July, 2015
Revised : 29 October, 2015
Accepted : 12 December, 2015

Keywords :
Zinc sulfide
Nanoparticle
Microwave radiation
Bandgap

ABSTRACT

Microwave radiations are used to synthesize zinc sulphide (ZnS, cubic phase) nanoparticles by using single precursor at different synthesis temperature and irradiation time. Absorption peaks of ZnS nanoparticles of size ~15 nm are found within the range of 250-320 nm by UV-Visible spectroscopy. The band gap energies of prepared ZnS nanoparticles are higher than the bulk value of ZnS. The blue shift of UV absorption peak gives evidence of decrease in particle size. Aggregates of large number of small sized spherical nanoparticles are observed by scanning electron microscope (SEM).

1. Introduction

Semiconductor nanoparticles have played a major role in many practical applications. The demand of semiconductor nanoparticles in industrial area is increasing day by day due to their vast applications in electronic and optoelectronic devices. Zinc sulfide (ZnS) semiconductor belongs to group II-VI of periodic table and has attracted a vast attraction due to its efficient properties. Band gap of ZnS is 3.72eV for cubic zinc blende and 3.77eV for hexagonal wurtzite structures. As band gap of ZnS can be tuned in ultraviolet region so, ZnS semiconductor is most suitable and appropriate for UV-Light based devices like solar cells, transducers, field effect transistors, gas sensors, biosensors, nano-generators, chemical sensors and UV-light sensors [1]. High refractive index and quantum confinement makes the ZnS nanocrystals as a useful emitting source within blue to ultraviolet range. ZnS is highly transmitted material within visible range and widely used as best materials for light emitting diodes (LEDs). These LEDs are used in reflectors [2] and flat panel displays [3] etc. due to their best results in color emission and high resolution.

Among a number of techniques for controllable shape, size and growth of ZnS nanoparticles, radiation assisted approach is one of the emerging method to synthesize nanoparticles in one step. Electromagnetic radiations like ultraviolet, microwaves and laser etc. are widely used to prepare nanoparticles on commercial scale. Radiation based approach is simple, quick, and efficient to synthesize nanostructure within short time period [4]. Synthesized nanoparticles, clusters, powders and wires are nowadays used in commercial areas to make different devices at nanoscale with enhanced mechanical strength, thermal stability and electrical conductivity.

Microwaves (MW) are the electromagnetic waves with long range 1mm-1meter and have frequency of 300MHz-300GHz. Microwaves provide a rapid heating and the nanostructures are prepared within several minutes under Megawatts power. Microwave assisting synthetic technique is also a quick, facile and less hazardous technique to prepare nanoparticles of different crystallized structure.

Many conventional and microwave hydrothermal methods were adopted by researchers for synthesis of zinc sulfide (ZnS), copper sulfide (CuS) and tin sulfide (SnS) nanoparticles of different shapes and size. The best results were reported for sulfides prepared by microwave hydrothermal process at low temperature of 100-200°C within 15 min. [5]. Flake like ZnS nanoparticles of hexagonal phase were synthesized at 110 °C in 5 min. by microwave thermolysis technique successfully [6]. Hexagonal phase of irregular shaped ZnS nano crystallites were displayed as prepared by microwave assisted Solvothermal (MAS) approach [7]. The microwave assisted technique has advantages over other synthetic routes that include synthesis of nanoparticles and phase achievement at low temperature and less time scale by

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controlling different parameters. Many nanostructured materials like nano wires, rods, dendrites, tubes and particles can be synthesized using MW radiation assisted approach [8].

2. Experimental

ZnS nanoparticles were prepared by using (zinc acetate) Zn $(CH_3COO)_2$ (Riedel-deHaen, Sigma-Aldrich), elemental sulfur (S) (ORBIT Laboratories) as precursors and (dimethylsulfoxide DMSO) C_2H_6OS (Fluka Riedel Sigma Aldrich) as a solvent. All the chemicals used were of analytical grade 99.9% pure without further purification. An appropriate amount of Zn $(CH_3COO)_2$, as mentioned in Table 1 was mixed with elemental sulfur S in 50 ml of DMSO accordingly as reported [9-11]. Solution of weighed material was stirred for 10 min using magnetic stirrer to homogenize the solution properly. Initially the ZnS solution was transparent. Series of these prepared samples were annealed under microwave (Domestic microwave oven Haier hpk-2070m/ms having 2.45GHz frequency radiations and power of 700-900W) radiations for 60, 90, 120, 150, 180, 210, 240 seconds, respectively. Table 1 illustrates the number of samples and their synthesis varying parameters.

Table 1: Experimental conditions employed for microwave assisted synthesis of ZnS nanoparticles

Sr No	Zinc acetate (g)	S (g)	DMSO (ml)	Microwave irradiation time (sec)
1	0.702	0.082	50	60
2	0.702	0.082	50	90
3	0.702	0.082	50	120
4	0.702	0.082	50	150
5	0.702	0.082	50	180
6	0.702	0.082	50	210
7	0.702	0.082	50	240

3. Mechanism of Reaction

Synthesis of ZnS nanoparticles may follow by the decomposition of precursors by heat and radiations as a result number of chemical reactions took place. Dimethylsulfoxide (C_2H_6OS) solvent decomposed to produce hydrogen sulfide (H_2S) gas. Zinc acetate (Zn $(CH_3COO)_2$ was decomposed and reacted with H_2S gas to produce zinc sulphide (ZnS) along with sulfuric acid and methyl alcohol as bye products.

$$C_2H_6\,OS \xrightarrow{\text{heat }\&\,radiations} \dot{C}H_3SO + \dot{C}H_3 \quad (1)$$

Water molecules of cupric acetate break by assisting microwave radiations

$$2H + elemental\ S \xrightarrow{\text{heat }\&\,radiations} H_2\,S(gas) \quad (2)$$

$$Zn(CH_3COO)_2 \xrightarrow{\text{heat }\&\,radiation} Zn^{2+}2CH_3COO^- \quad (3)$$

$$Zn^{2+} + 2CH_3COO^- + 2H^+ + S^{2-} \xrightarrow{\text{heat }\&\,radiations} ZnS_{(solid\,)} + 2\,CH_3COOH \quad (4)$$

$$^{\cdot}OH + O\dot{H} + CH_3SO + CH_3 \xrightarrow{\text{heat \& radiations}} \mathrm{CH_4O_3S\ (methyl\ sulfonic\ acid\,) + CH_3\,OH\ (methyl\ alcohol)} \quad (5)$$

After a given reaction time, the sample was washed many times with distilled water and centrifuged. The series of prepared solutions were irradiated by microwave radiations for different time and temperature, as controlled parameters. The color of solution changed to milky from transparent, when it was assisted to microwave radiations for 30 sec at temperature greater than 40°C. The increase in time and temperature showed change in color of irradiated solutions from pale yellow to dark yellow.

After irradiating the solution for different time and temperature it was kept for few days to let the particles settle down properly at the bottom of beakers. After that yellowish solution prepared under microwaves assisted nanoparticles were dried at 200°C in an electric oven (The Wiseman, Daihen, Korea conventional drying oven) for an hour.

4. Results and Discussion

Optical properties were analyzed by using UV-VIS spectroscopy. The absorption peaks of the prepared ZnS nanoparticles were found to be in ultraviolet region as compared to bulk in visible region. Optical absorption spectra recorded for ZnS nanoparticles annealed by microwaves for different time as shown in Fig. 1. The absorption peaks were broader than peaks recorded for ZnS nanoparticles synthesized by ultraviolet radiations [12]. This may arise as the nanoparticles synthesized by microwave assisted approach are less mono-dispersive

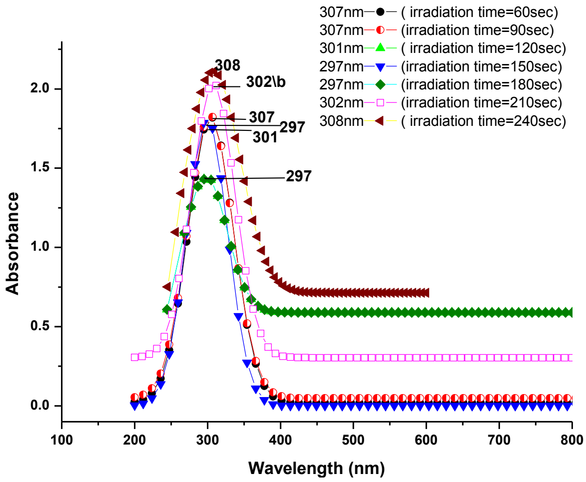

Fig. 1: Comparative graph of UV-VIS absorption spectra for ZnS nanoparticles synthesized by microwaves at different time

because of the fact that this technique is abrupt and rapid and particles agglomerate with each other and couldn't get enough time to settle themselves as mono-depressed particles.

Band gap energies for all the ZnS nanoparticles irradiated by microwaves were plotted using Tauc's equation. The band gap energies calculated for all the ZnS nanoparticles and are found to be 3.79, 3.85, 3.89eV, 3.92, 4.0 and 4.1 eV, respectively. These values are greater than bulk ZnS value of 3.71eV. This arises due to manifestation of quantum confinement in particles as the reduction in particle size increased the energy level spacing and hence wider band gap energies were recorded for particles. The energy level varied as a function of size, hence wider band gap showed decrease in particle size as a result of quantum confinement.

Comparative Tauc's plots of all the samples are shown in Figs. 2 and 3. From these plots band gap energies were calculated by extrapolating linear region to the X-axes.

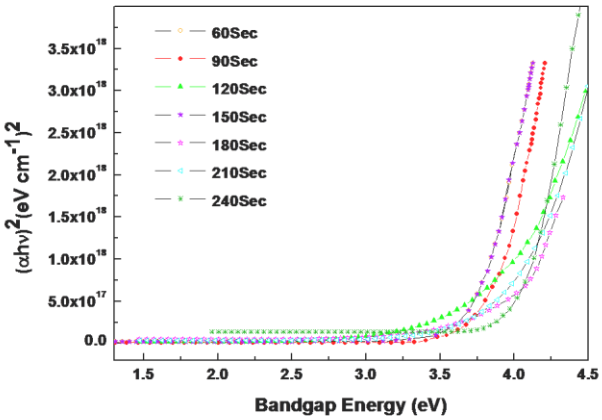

Fig. 2: Comparative illustration of Tauc's plot to determine bandgap energies for all the prepared ZnS

The calculated band gap energies are shown in Table 2 and are plotted in Fig. 4. This showed that as the radiation time increased the band gap energies of ZnS particles also increased.

4.2. *Morphological Studies*

Micrographs of ZnS nanoparticles were taken by S-3400 Hitachi, Japan, Pitman, PCSIR Lab. to observe role of synthesis time and temperature on surface morphology.

The Fig. 4 showed SEM images of the prepared ZnS nanoparticles. The images were taken at high and low resolution that showed the irregular collective large number of small nanoparticles. The samples prepared by microwaves were irregular aggregates of large number of small nanoparticles. The average size of spherical nanoparticles calculated from Image J software was found to be 15 nm to 20 nm [13].

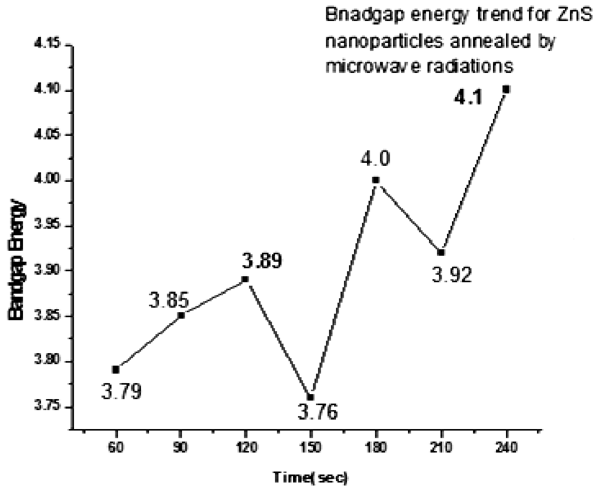

Fig. 3: Band gap energy trend for ZnS nanoparticles annealed by microwave radiations

Table 2: Absorption peaks and band gap energies of ZnS nanoparticles

No. of Samples	Microwave Irradiation time (sec)	Band gap Energy (eV)	Absorption peaks (nm)
1	60	3.79	307
2	90	3.85	307
3	120	3.89	301
4	150	3.76	297
5	180	4	297
6	210	3.92	302
7	240	4.1	308

In literature the role of specific assisted radiations and different parameters like time and temperature for the synthesis of ZnS nanoparticles and their affect on size, shape and morphology of prepared particles was investigated and the solvent used DMSO (dimethylsulfoxide) was also helpful to develop nanoparticles of spherical shape [13].

5. Conclusions

The microwave method provide quick rise in temperature and this makes the technique as a quick way to produce small nanosized particles. But on the other hand parameters of microwave synthesis technique were difficult to control as compare to other radiation based synthesis technique.

Radiation based synthesis of ZnS nanoparticles was found to be easy to use and environment friendly as ZnS nanoparticles were prepared by less hazardous single source precursor. Non-ionizing character of microwaves radiations made this technique quite suitable for practical point of view.

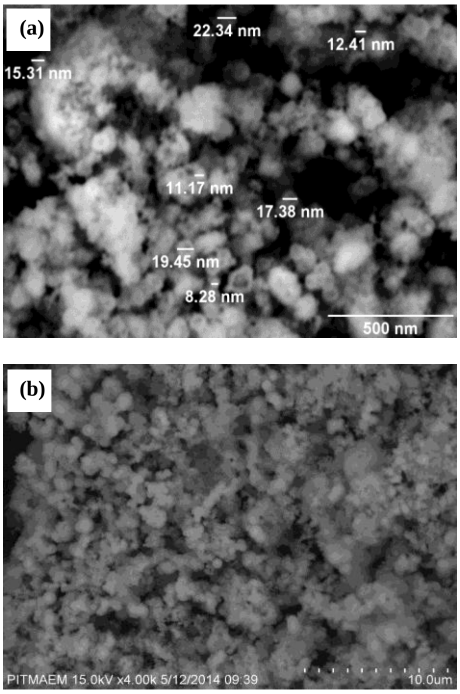

Fig. 4: SEM image of ZnS nanoparticles (a) at high magnification (b) at low magnification

The UV-VIS spectroscopic analysis shows that absorption peak is in ultraviolet region. All the absorption peaks appeared in 250-320 nm. The band gap energies of all the prepared ZnS nanoparticles are higher than the bulk value. The band gap energies display blue shift with increasing irradiation time that gives evidence of reduction in size of particles. Microwave produced smaller nanoparticles because of abrupt microwave heating and as a result reduction in size. Scanning electron microscopy SEM showed the aggregates of large number of small spherical nanoparticles.

Acknowledgement

The authors acknowledge the support of Central Lab Lahore College for Women University Lahore (LCWU) and COMSATS Institute of Information and Technology Lahore for sample analysis and research collaboration.

References

[1] A. Chandran, N. Francis, T. Jose and K.C.George, “Synthesis, structural, characterization and optical bandgap determination of ZnS nanoparticles”, SB Acad. Rev., vol. 17, pp. 17-21, 2010.

[2] A. Rahdar, V. Arbabi and H. Ghanbari, “Study of electro-optical properties of ZnS nanoparticles prepared by colloidal particle method”, Int. J. Mech. Aero. Ind. Mech. Man. Eng., vol 6, pp. 214-216, 2012.

[3] A.L. Rogach, N. Gaponik, J.M. Lupton, C. Bertoni, D.E. Gallardo, S. Dunn, N. Li Pira, M. Paderi, P. Repetto, S.G. Romanov, C. O'Dwyer, C.M. Sotomayor Torres and A. Eychmuller, “Light-emitting diodes with semiconductor nanocrystals”, J. Angew Chem. Int. Ed., vol. 47, pp. 6538–6549, 2008.

[4] R. Xu, W. Pang and Q. Huo, “Modern inorganic synthetic chemistry”, Amsterdam, The Netherland, Elsevier, 2011.

[5] X. Yan, E. Michael, S. Komarnenic, J. R. Brownsond and Z. F. Yana, “Microwave and conventional-hydrothermal synthesis of CuS, SnS and ZnS: Optical properties”, J. Ceram. Int., vol 39, pp. 4757-4763, September 2013.

[6] J. Sun, X.P. Shen, K.M. Chen; Q. Liu and W. Liu, “Low temperature synthesis of hexagonal ZnS nanoparticles by a facile microwave-assisted single source method”, J. Solid State Commun., vol. 147, pp. 501-504, 2008.

[7] F. La Porta, F.A. La Porta, M.M Ferrer, Y. VB de Santana and C. W Raubach, V.M Longo, J.R Sambrano, E. Longo, J. Andres, M.S. Li and J. A Varela, “Synthesis of wurtzite ZnS nanoparticles using microwave assisted solvothermal method”, J. Alloys Compd., vol. 556, pp. 153-159, 2013.

[8] P. Cintas, C. Badea, G. Prodan, I. Popovici and V. Ciupina, “Activated metals in organic synthesis”, Florida, USA, CRC Press, 1993.

[9] A. Dumbrava, C. Badea, G. Prodan, I. Popovici and V. Ciupina, “Zinc sulfide fine particles obtained at low temperature”, Chalcogen. Lett., vol. 6, pp. 437-443, September 2009.

[10] K.P. Tiwari, S. Kumar Choubey and K. Sharma, “Structural and optical properties of ZnS nanoparticles synthesized by microwave irradiation method”, Chalcogen. Lett., vol. 10, pp. 319-323, September 2013.

[11] I. Yu, T. Isobe and M. Senna, “Optical properties and characteristic of ZnS nano-particles with homogeneous Mn distribution”, J. Phys. Chem. Sol., vol. 57, pp. 373-379, 1996.

[12] X. Lu, G. Wang, T .Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong, Y. Li, T. Zhai, S. Xie, Y. Zhao, X. Sun, X. Lu, M. Yu, M. Xu, F. Xiao and Yexiang Tong, “Controllable synthesis of hierarchical ZnO nanodisks for highly photo catalytic activity”, Cryst. Eng. Comm., vol. 14, pp. 1850-1855, 2012.