

MICROWAVE IRRADIATION EFFECTS ON HYDROTHERMAL AND POLYOL SYNTHESIS OF ZnS NANOPARTICLES

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Cubic structure of spherical ZnS nanoparticles with relatively small size and narrow size distribution were synthesized via microwave-hydrothermal (M-H) and microwave-polyol (M-P) methods from zinc acetate and thioacetamide as starting materials. Distilled water and ethylene glycol were used as solvents for the M-H and M-P method respectively. To monitor the effect of microwave irradiation, the reactions were carried out in different irradiation time from 5 to 40 min. An increase in irradiation time increases the reaction yield and the average particle size, which subsequently decreases the optical band gap. ZnS nanoparticles synthesized by M-H method have narrower size distribution between 3 and 7 nm, while those synthesized by M-P method were between 2 and 9 nm. Moreover, the formation of hierarchical nanoballs ZnS were observed in the M-H method after 25 min irradiation time. Because of lower dielectric constant, higher dielectric loss, and higher boiling point of ethylene glycol compared to water, in the M-P method the heating rate and final temperature are higher than in M-H method, leading to the decomposition of thioacetamide, promoting higher rate of nucleation. ZnS nanocrystals synthesized with the polyol method have a higher degree of crystallinity compare with those synthesized using the hydrothermal method.

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1. Introduction

In recent years, nanoscale II–IV binary compound semiconductor, including zinc sulfide (ZnS) have attracted considerable attention due to their unique physical and chemical properties that are different from their bulk. They exhibit size dependent properties such as tuning of band gap with particle size, a blue shift of absorption onset and an enhancement of photocatalytic activities with decreasing crystallite size. These novel properties are due to the large number of surface atoms and the three dimension confinement of electrons [1-2]. They have outstanding potential applications owing to their nonlinear optical and luminescent properties that governed by quantum size effect, and other important physical and chemical properties [3-5]. They are used in light-emitting diodes, solar cells, optoelectronic devices, photocatalysis, luminescent nanocomposites, environmental sensors and biological sensors, and so on [6-9]. ZnS is a well-

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known wide and direct bandgap II–VI semiconductor with Zincblende and Wurtzite crystal structure, having band gap energies of 3.68 and 3.80 eV at room temperature, respectively [10]. The Zincblende structure of ZnS is stable at room temperature, while Wurtzite is stable above 1020 °C at atmospheric pressure [11].

Currently, a variety of synthesis methods are being used for the preparation of ZnS nanoparticles such as hydrothermal method [6], solvothermal method [12], sonochemical method [13], gamma-irradiation [14], microwave irradiation [10] and micro-emulsion method [15]. Ideally, the methods employed for synthesis are expected to form nanoparticles with narrow size distribution and to easily modify particle properties, such as size and surface during the synthesis. More interestingly, the methods that can produce very fine particles (1–10 nm) are intensively pursued because of the unique properties of these nanoparticles. Among these methods, microwave assisted route is one of the novel methods and is a very rapidly developing area of research. Compared with conventional methods, microwave synthesis requires very short reaction time, and is capable of producing small particles with a narrow particle size distribution and high purity [16]. These advantages could be attributed to fast homogeneous nucleation and ready dissolution of the gel [17]. The microwave quantum energy (1.24×10^{-6} – 1.24×10^{-3} eV) is much lower than the ionization energies of compounds. This energy can act as a non-ionizing radiation that causes molecular motions of ions and rotation of the dipoles, but does not affect molecular structure. Microwave-enhanced chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects. Microwave heating results from the interaction of the electromagnetic wave with the irradiated medium which produce a force on charged particles and cause them to rotate or further polarized. The rotation of the dipoles in an alternating field causes friction, which produces heat up to 10°C/s [18–20]. Heat is dissipated inside the irradiated medium and transfers occur from the treated medium to the outside and much faster temperature increases can be obtained. However, in heterogeneous mixtures that field distribution is not even in the irradiated material, energy is not homogeneously dissipated, and “hot spots” occur if heat generation is faster than heat transfers. These localized hot spots may have temperatures 100–150 °C above the measured bulk temperature. On the other hand under microwave heating the surface of the wall is generally not heated and energy is dissipated inside the bulk liquid and boiling only occurs when the internal energy overcomes the intermolecular attractive forces. This accounts for the observed microwave overheating of liquids. This overheating increases with the increase input power of microwave [21–22].

During the formation of the nanoparticles under microwave irradiation, solvents can have an important influence on the size and morphology of the final products. In different solvents, the collision rate between reactant molecules, the heating rate, and the temperature of the reaction are different. Water has a very high dipole moment, which makes it one of the best solvents for microwave assisted reactions [16]. Method which involves water at pressures from 1 atm to several kilobars and temperatures from 100–10,000°C are called hydrothermal method [23]. The combination of microwave field with the hydrothermal method which is named the “microwave-hydrothermal” (M-H) process accelerates the kinetics of the reaction [24].

Polyol solvents like ethylene glycol are also suitable for microwave assisted reactions due to their relatively high dipole moment and loss factor. Another advantage of using ethylene glycol as a solvent is its reducing power, which can be enhanced with the inducement of microwave irradiation [25–28]. Reduction method based on ethylene glycol is known as the polyol method [25]. The combination of microwave field with polyol method is named “microwave-polyol” (M-P) process. Since the polyols are normally low-weight molecules, they may act as weak stabilizers, which can be removed from the particle surface under certain experimental conditions.

In this paper, we reported two simple M-H and M-P methods for the synthesis of ZnS nanoparticles through the reaction of zinc acetate with thioacetamide in distilled water and ethylene glycol as solvents, respectively. The reactions carried out in 5 to 40 min irradiation time without using any surfactant or polymer as a capping agent. The obtained ZnS nanoparticles were characterized by XRD, TEM and UV-Vis spectroscopy. For both methods, the mechanism of formation and the effect of irradiation time on the size and size distribution, degree of crystallinity and optical absorption of nanocrystalline ZnS and yield of reaction were investigated and compared with each other.

2. Experimental

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and thioacetamide (CH_3CSNH_2) were used as zinc and sulfur sources respectively. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and distilled water were used as solvents. Zinc acetate was purchased from R & M Chemical, thioacetamide from Sigma–Aldrich and ethylene glycol from ALFA Chemical Co. All chemicals are analytical grade products and used without further purification.

In a typical synthesis, 0.005 M of Zinc acetate and 0.006 M of thioacetamide were added into glass beakers of 100 ml containing 20 ml of solvent (distilled water for M-H method and ethylene glycol for M-P method) and stirred with 500 rpm for 30 min. The beakers were placed in a high power microwave oven (1100W) operated using a pulse regime with 20% power. The reactions were carried out by changing irradiation time at 5, 10, 15, 20, 25, 30 and 40 min. The precipitates were centrifuged (3500 rpm, 10 min) and washed several times with distilled water and absolute ethanol. The white products were dried in air at 60°C for 24 h under control environment. The products were characterized by X-ray diffraction (XRD) at a scanning rate of 5°/min in the 2θ range 20–70° using a Philips X-ray diffractometer (7602 EA Almelo) with Cu K α radiation ($\lambda = 0.1542$ nm). The particle size and size distribution were determined from the transmission electron microscopy (TEM) micrographs (HTACHI H-7100 TEM). The TEM characterization was carried out at 100 keV. The optical properties of ZnS nanoparticles were characterized using UV–visible absorption spectroscopy (UV-1650PC SHIMADZU).

3. Result and discussion

It is understood that microwave heating behavior of reaction system can be affected by some factors such as the microwave power, material composition, physical state, dielectric constant and dielectric loss [29]. In our experiments, all materials and conditions are considered the same for both methods except the solvents which induce different reaction mechanisms and heating processes. In M-H method, the reaction of H_2O with thioacetamide causes the formation of H_2S which is responsible for the reaction with zinc acetate to yield ZnS nanoparticles [30]. In M-P method due to high dielectric loss of ethylene glycol (Table 1), the temperature of the reaction system goes up quickly and reaches to the ethylene glycol boiling point. In this high temperature thioacetamide will be decomposed and provides the sulfur ions which promoting high rate of nucleation and growth of ZnS nanoparticles.

The formation of ZnS nanoparticles can be observed by the color change of the solution from colorless to white and confirmed by XRD studies. Fig. 1 shows the XRD patterns of ZnS nanoparticles prepared with M-H method in different irradiation times. The XRD peaks were observed at 2θ values of 28.9, 48.1 and 57.1, which matching perfectly with the (111), (220) and (311) crystalline planes respectively for the cubic structure of ZnS (ICDD PDF 80-0020) with lattice parameter 5.3 Å. It was also shown in Fig. 2 that XRD pattern of the obtained ZnS nanoparticles with M-P method in different irradiation times at 2θ values of 28.6, 47.5, and 56.3, respectively matched with the (111), (220) and (311) crystalline planes of the cubic structure of ZnS (ICDD PDF 65-1691) with lattice parameter 5.4 Å. No peaks corresponding to impurities were detected, indicating high purity of the products. It is to be noted that preparation method and irradiation time do not have any significant effect in the crystal structure of the nanoparticles.

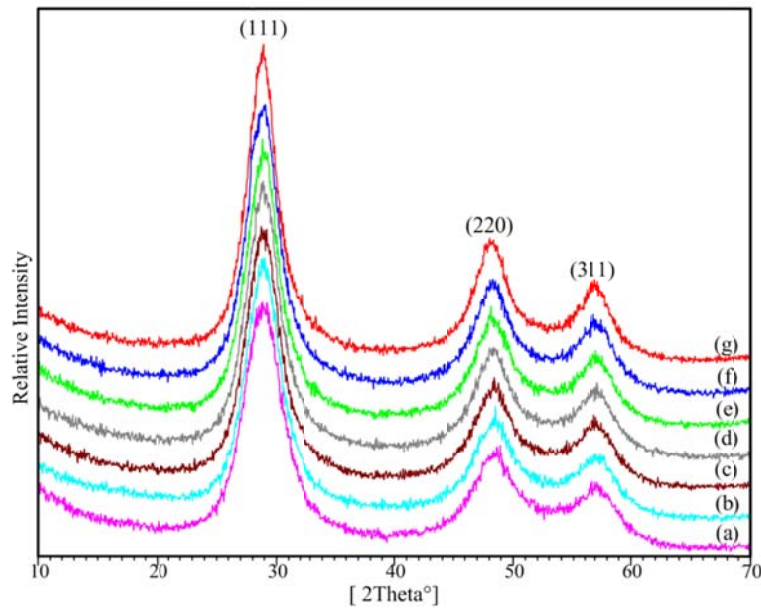


Fig. 1. XRD patterns of the ZnS nanoparticles synthesized with M-H method in (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30 and (g) 40 min irradiation time.

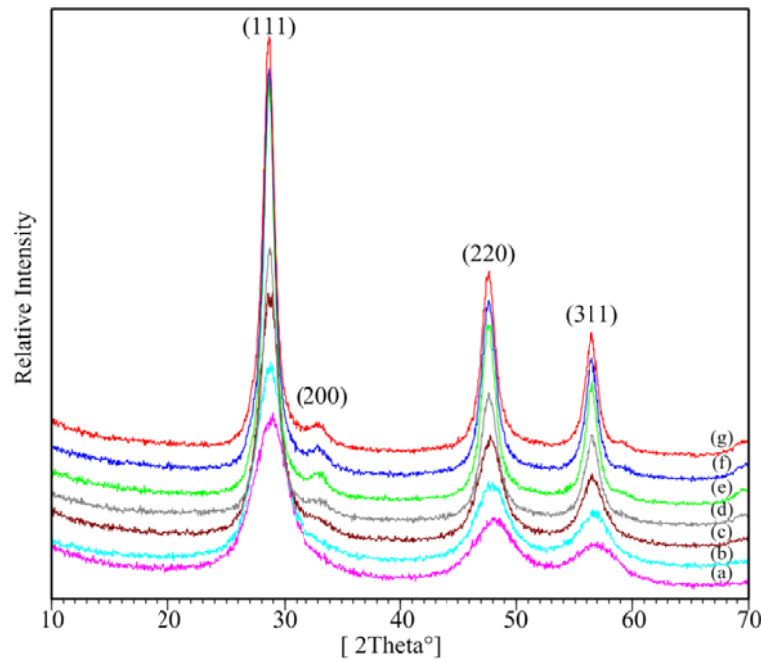


Fig. 2. XRD pattern of the ZnS nanoparticles synthesized with M-P method in (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30 and (g) 40 min irradiation time.

From the width of the XRD peak, the mean crystalline size can be calculated using Scherrer's equation [17, 31-32]:

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

where D is the average crystallite size, k is particle shape factor that varies with the method of taking the breadth and shape of crystallites ($0.89 < k < 1$) [33], λ is the X-ray wavelength used (0.1542 nm), β is the angular line width of half-maximum intensity, θ is the Bragg's angle in degrees. The crystalline size of the ZnS was calculated using (111) reflection of the XRD patterns and estimated sizes synthesized by M-H and M-P methods are listed in Table 1 and Table 2, respectively. The powder XRD patterns of the products all exhibit very broad peaks, which

correspond to a particle size of less than 5 nm (for M-H) and 7 nm (for M-P) for irradiation times between 5 and 40 min.

Table 1. Optical band gap, blue shift and particle size of ZnS particles synthesized using M-H method

sample	Irradiation time (min)	Degree of crystallinity %	Yield of reaction %	Optical band gap (eV)	Blue shift ΔE (eV)	Particle size from (nm)		
						UV	XRD	TEM
1	5	40.1	16.3	4.22	0.54	4.2	3.0	3.3
2	10	42.4	21.1	4.18	0.50	4.4	3.3	3.9
3	15	42.6	24.6	4.16	0.48	4.5	4.2	4.5
4	20	44.6	29.7	4.14	0.46	4.6	4.5	4.6
5	25	46.3	39.9	4.13	0.45	4.6	4.7	4.6
6	30	46.4	43.8	4.12	0.44	4.7	4.7	4.5
7	40	50.8	56.0	4.08	0.40	4.9	4.8	4.8

Table 2. Optical band gap, blue shift and particle size of ZnS particles synthesized using M-P method

sample	Irradiation time (min)	Degree of crystallinity %	Yield of reaction %	Optical band gap (eV)	Blue shift ΔE (eV)	Particle size from (nm)		
						UV	XRD	TEM
8	5	54.5	39.6	4.42	0.74	3.6	3.0	3.2
9	10	61.6	53.4	4.40	0.72	3.7	3.7	3.8
10	15	69.7	57.3	4.37	0.69	3.8	4.7	4.1
11	20	73.6	58.9	4.34	0.66	3.8	5.5	4.2
12	25	100	65.8	4.24	0.56	4.2	6.6	4.2
13	30	89.6	72.2	4.07	0.39	4.9	6.6	4.8
14	40	87.1	76.5	3.98	0.30	5.6	6.0	4.9

Further information that can be obtained from XRD patterns is that the degree of crystallinity which is often preliminary to several material properties such as color, electrical conductivity, and luminescence, especially if an electron transport (e.g., excitation, energy transfer, emission) is involved [34]. The degree of crystallinity increases with increasing intensity of reflection peak. The crystallinity of ZnS samples was estimated by comparing the intensity of the XRD peak of (111) plane with the intensity of a sample synthesized using M-P method at 25 min irradiation time (maximum intensity) that was assumed to be wholly crystalline. The results for M-H method (Table 1) revealed an enhancement in the degree of crystallinity as a function of irradiation time. In the M-P method (Table 2), the degree of crystallinity increases with increasing irradiation time and reaches the maximum at 25 min and then decreases by rising the irradiation time. However, in the same irradiation time, the ZnS nanocrystals synthesized with M-P method have higher crystallinity than those synthesized using M-H method. It is due to the fact that during the usage of polar solvent, the nucleation and growth of particles can be performed at temperature up to (or even slightly higher than) the boiling point of solvent [21-22]. Therefore in M-P method where higher temperature is applied (Table 3); nanoparticles with higher degree of crystallinity were obtained.

Table 3. Dielectric properties and boiling point of solvents

solvent	Dielectric constant	Loss factor	Boiling point (°C)
Ethylene glycol	37	1.35	197
Distilled water	70	0.12	100

Besides the temperature, the dielectric properties of solvents are also important factors in nucleation and growth. The dielectric constant represents the ability of a material to be polarized by an external electric field [35] and as is known ions are more stable in a solvent with a high dielectric constant [36]. Therefore, in M-H method that solvent has a higher dielectric constant the stability of ions restricts nucleation and growth of nanoparticles. By contrast, in M-P method the ions saturation easily provides higher rate of nucleation and growth. Moreover, higher loss factor of solvent in M-P method causes rapid heating under microwave [22, 37] which also accelerates the nucleation of ZnS nanoparticles. Therefore, in a given irradiation time the yield of reaction in M-P method is expected to be more than in M-H method. The yield of reaction was estimated by determining weight of products and comparing the molarities of products and precursors. In spite of using the same molarity of precursors in both methods, the results (Table 1 and Table 2) show that in a given irradiation time the yield of reaction in M-P is more than M-H method.

The TEM images of ZnS obtained with M-H methods in different irradiation times were shown in Fig. 3 and Fig 4. It can be seen from the figures that the ZnS nanoparticles are small spherical particles with sizes less than 5 nm which look aggregated. After 25 min irradiation the ZnS particles held together and assembled into nanoball structure by a porous irregular network. In the 30 min irradiation time monodisperse nanoballs with the diameters of 10–70 nm were produced, as shown in Fig 4(b). During microwave irradiation, zinc acetate in the solution act as the seed for precipitation of ZnS nanoparticles. Simultaneously, the CH_3COO^- anions bond on the surface of the ZnS particles prevents the growth of the particles, and on the other hand the hydrogen bond between the CH_3COO^- anions made the particles aggregated [29, 38]. The formation of the spherical morphology of the hierarchical nanostructures might be related to the microwave mode. The electric and magnetic fields associated with dominant microwave mode form closed loops which have a cage-like shape and might take the effect of a template to assembly nanoballs [29].

Fig. 5 shows TEM images and particle size distribution histogram of ZnS obtained with M-P method for 20 and 40 min irradiation time. It can be seen from the figures that the ZnS nanoparticles are spherical in shape with relatively narrow homogeneous distribution which look aggregated in some parts. In this method ethylene glycol acts as a weak stabilizer which may prevent the formation of self assembly nanoballs. Ethylene glycol can be removed from the particle surface after washing the samples.

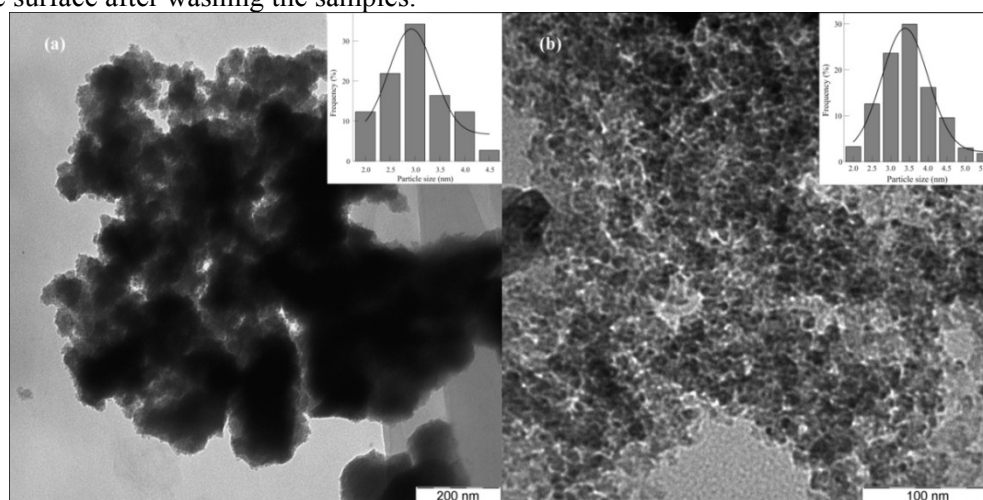


Fig. 3. TEM images of the ZnS nanoparticles synthesized with M-H method for (a) 5 and (b) 15 min irradiation time.

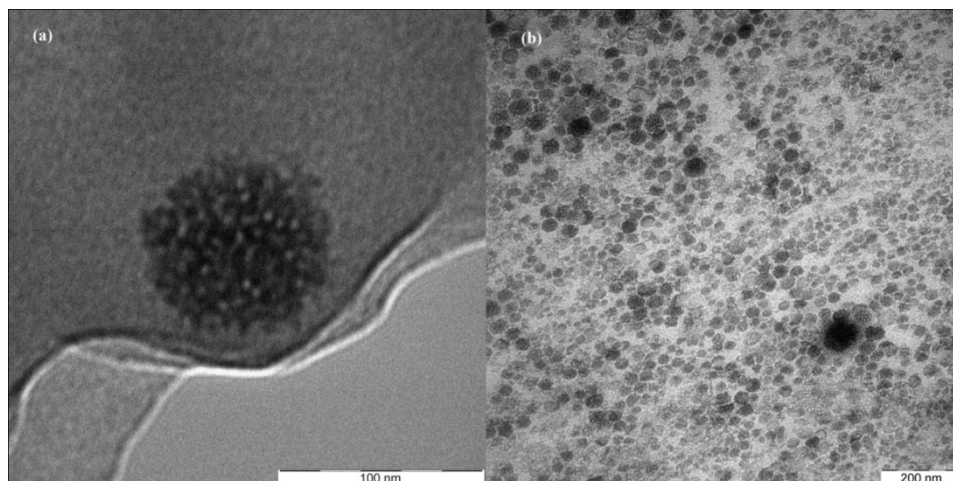


Fig. 4. TEM images of the ZnS nanoparticles synthesized with M-H method for (a) 25 and (b) 30 min irradiation time.

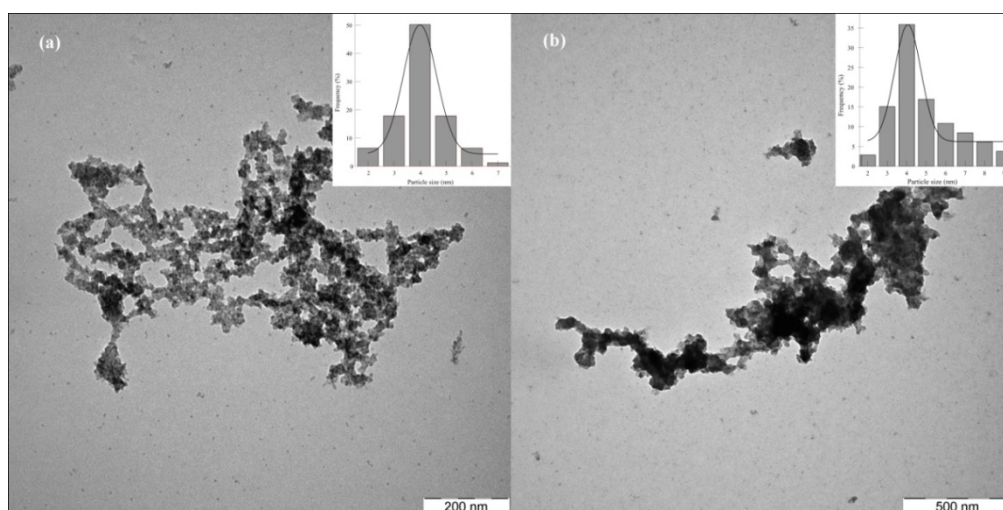


Fig. 5. TEM images and Particle size distribution of the ZnS nanoparticles synthesized with M-P method for (a) 20 and (b) 40 min irradiation time.

The average size (Table 1 and Table 2) and size distribution of nanoparticles were evaluated in TEM images using UTHSCA Image Tool considering at least 200 nanoparticles for each sample. In both methods with an increase in irradiation time, the average particle sizes slightly increases. Although average particle sizes in a given irradiation time are relatively same for both methods but the size distributions are somewhat different. The particle size histograms show that the ZnS prepared with M-H method have narrower size distribution (from 3 to 7 nm) compared with those prepared with M-P method (from 2 to 9 nm). The formation of uniform nanosized particles demands a uniform growth environment, and microwave heating provides it [16, 39]. Moreover microwave could greatly accelerate the nucleation [16] and decrease the growth of the newborn ZnS nuclei due to induce polarity and the intense frictions and collisions of the created molecules which are more pronounce in solvent with higher dielectric constant.

Fig. 6(a) and Fig. 7(a) show the UV-Vis absorption spectra of ZnS nanoparticles prepared with M-H and M-P methods at different irradiation time, respectively. The samples show a strong absorption below 300 nm. The absorption edges are below 321 and 330 nm for ZnS nanoparticles prepared with M-H and M-P methods, respectively. The blue shift of absorption edge compared to bulk ZnS (onset is at 340 nm [40]) clearly explained the quantum confinement effect of ZnS nanoparticles. In both methods, with increasing the irradiation time the absorption edge moves to

larger wavelength due to the increase of the nanoparticle size, subsequently the optical band gap decreases.

The energy of band gap (E_g) of ZnS nanoparticles can be evaluated from the UV-Vis spectra by Tauc plot of $(h\nu\alpha)^2$ versus $(h\nu)$ and extrapolating of the linear portions of the curves to the energy axis according to [41]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap energy, and B is a constant. The absorption coefficient (α) was determined from the relation $A=I/I_0=e^{(-\alpha d)}$, or it can be calculated using the well-known relation deduced from Beer-Lambert's relation $\alpha = 2.303A/d$, where d is the path length of the quartz cuvette and A is the absorbance determined from UV-Visible spectrum [7]. The Tauc plot of ZnS nanoparticles prepared with M-H and M-P methods in different irradiation times are shown in Fig. 6(b) and Fig. 7(b), respectively and the estimated optical band gaps are listed in Table 1 and Table 2. The energy of band gap decreases with increasing irradiation time which is corresponding to increase in particle sizes.

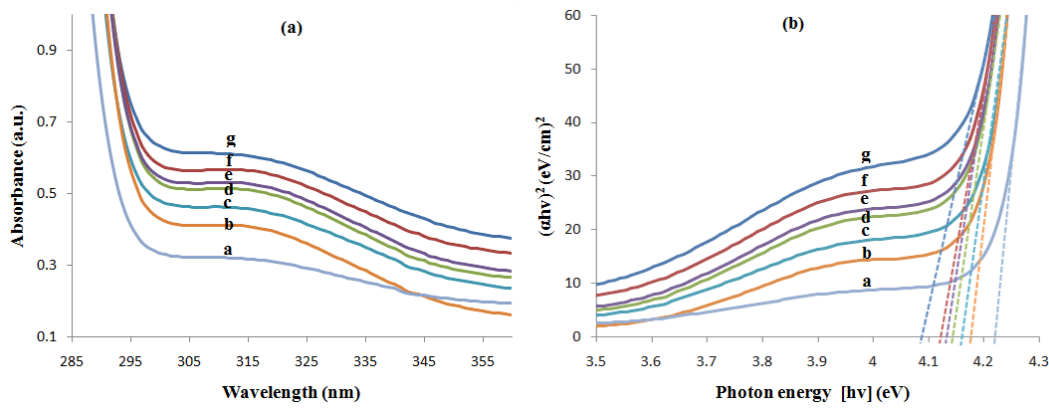


Fig. 6. (a) UV-Vis spectra and (b) Tauc plot of the ZnS nanoparticles synthesized using M-H method in (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30 and (g) 40 min irradiation time.

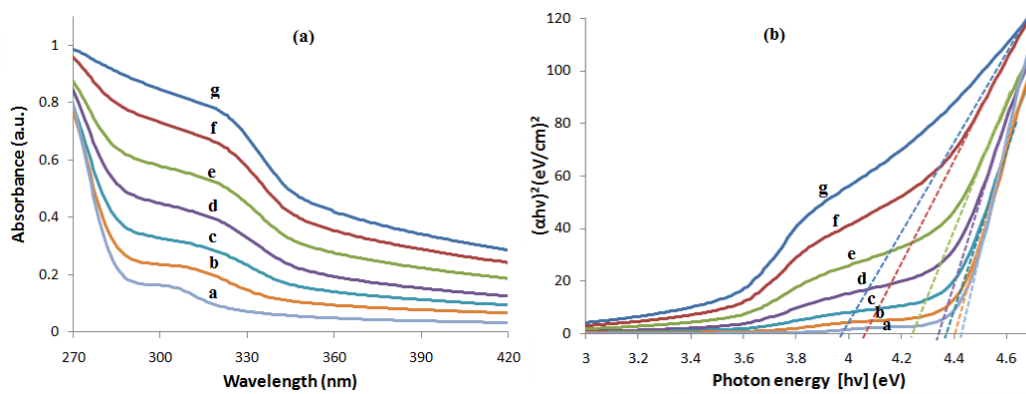


Fig. 7. (a) UV-Vis spectra and (b) Tauc plot of the ZnS nanoparticles synthesized using M-P method in (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30 and (g) 40 min irradiation time.

From the band gap values of nanoparticle and bulk, the particle sizes could be calculated using Brus equation [42]:

$$\Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r} \quad (3)$$

where ΔE is the blue shift of the band gap, m_e^* is the effective mass of electron, m_h^* is the effective mass of hole, r is the radius of the particle, ϵ_r is the dielectric constant and ϵ_0 is the permittivity of free space. The first term indicates the confinement effect and the second term being the Coulomb term. In a strong confinement, as in the present case, the second term is small and can be neglected. The computed particle sizes for M-H and M-P methods are listed in Table 1 and Table 2, respectively. It can be seen from the table that the particle sizes agree fairly well with those determined from X-ray line width broadening and the average sizes measured from TEM, although in some cases minor deviations exist.

4. Conclusions

This paper presented the effects of microwave irradiation time on physical properties of ZnS nanoparticles synthesized using hydrothermal and polyol methods through the reaction between zinc acetate and thioacetamide as zinc and sulfur sources respectively. In both methods ZnS nanoparticles have cubic structure and spherical shape with relatively small average size (less than 5 nm) and narrow size distribution and high purity. Moreover, it was found that in both methods an increase in the irradiation time from 5 to 40 min results an increase in the yield of reaction and the average size of nanoparticles, subsequently the optical band gap of nanoparticles decreases. However in M-H method, due to high dielectric constant and low boiling point and dielectric loss of solvent, the rate of nucleation and growth was lower than M-P method and nanoparticles with narrow size distribution were obtained. While in M-P method, in a given irradiation time the yield of reaction was more than M-H method and nanoparticles with higher degree of crystallinity were obtained. More interestingly, at 25 min irradiation time the degree of crystallinity of nanoparticles synthesized using M-P method reaches its maximum and in M-H method the formation of hierarchical nanoballs ZnS which assembled with the smaller nanoparticles were observed.

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