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Electrochemical Synthesis and Characterization of Zinc Sulfide Nanoparticles

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Abstract

Electrosynthesis process has been used for preparation of zinc sulfide nanoparticles. Zinc sulfide nanoparticles in different size and shapes were electrodeposited by electrolysis of zinc plate as anode in sodium sulfide solution. Effects of several reaction variables, such as electrolysis voltage, sulfide ion concentration as reactant, stirring rate of electrolyte solution and temperature on particle size of prepared zinc sulfide were investigated. The significance of these parameters in tuning the size of zinc sulfide particles was quantitatively evaluated by analysis of variance (ANOVA). Also, optimum conditions for synthesis of zinc sulfide nanoparticles via electrosynthesis reaction were proposed. The structure and composition of prepared nanoparticles under optimum condition was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and UV-Vis spectrophotometry techniques.

1. Introduction

In recent year's great attraction and interest have been considered for preparation and characterization of inorganic structures with nanosized dimensions and special morphology in material science and nanotechnology [1-3]. Zinc sulfide, is an important inorganic semiconductor with a wide bang gap ranging from 3.5-3.7 eV. This compound has an appropriate potential for application in various fields such as biological labeling, solar cells, photo conductors, field effect transistors, optical sensors, photocatalysts, electroluminescent materials, phosphors, and other light emitting materials [5-8]. Until today, various processes have been proposed for preparation of nano-sized ZnS crystals with different morphologies. All of these methods including thermal chemical vapor deposition [9], microemulsion [10], Microwave-assisted synthesis [11], hydrothermal [4], chemical vapor deposition

[12], precipitation [13] and etc. have their benefits and related limitations. Therefore, more investigations are interested for finding simple, easy to handle and more economical methods in order to prepare ZnS nanoparticles; while the proposed method should have an appropriate potential for scaling-up and large scale production of the product. Therefore, main purpose of the present research was to optimize direct electrodeposition procedure in order to produce ZnS nanoparticles and composition and morphological characterization of the produced nanoparticles

2. Experimental procedure

2.1. Materials and procedure

All reagents were prepared from Merck Company. The electrolyte solutions were prepared using sodium sulfide and deionized water.

Bulk electrosynthesis was performed using a programmable power supply system, by means of potentiostatic electrolysis in a one-compartment cell. The working electrode consisted of a plate of zinc with 2 cm^2 geometric surface area and the cathode was a platinum gauze electrode.

All samples were characterized by scanning electron microscopy (SEM). Scanning electron micrographs were recorded using on a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument. Gold films were prepared by a sputter coater model SCD005 made by BAL-TEC (Switzerland). UV-Vis absorption spectrum of the sample was recorded using a Perkin Elemer Lambda 35 UV-Vis spectrophotometer. X-ray powder diffraction (XRD) was performed using a Philips analytical X-Ray B.V. The sample was prepared by coating on the Cu-carbon coated grid prior to the measurement. The TEM images were obtained by a Ziess- EM900 scanning electron microscope. The sample preparation of ZnS nanoparticles was performed by their coating on the Cu-carbon coated grid prior to the imaging.

For bulk synthesis of zinc sulfide nanoparticles, the electrolyte solution was prepared by dissolving sodium sulfide in de-ionized water at various concentrations shown in Table 1. Electrochemical experiments were carried out by a two electrodes electrolysis system (which zinc electrode acts as anode and platinum as cathode) in a Pyrex cell (V= 400 cm^3) at room temperature (22 ±1 ºC). Prior to the electrolysis, the platinum and zinc electrodes were cleaned with detergent and electrochemically polished. The electrode types and sizes, electrolysis time and temperature were fixed during all experiments. The synthesis was carried out at various applied constant potentials for 30 minutes according Table 1. In order to collect the product, the solution was filtered and the resulted precipitate was washed with ethanol three times, and then dried at 80 ºC for 3h.

3. Results and discussion

3.1. Optimization of electrodeposition variables

Control of particle size and shape is a complex process needing a fundamental understanding of interactions between the reagents and other parameters affecting the particle formation procedure. In this study, an attempt was made to determine how the various parameters of electro-deposition process affect the diameter of ZnS nanoparticles. Therefore, a Taguchi orthogonal array design was used to identify the optimal conditions and to select the parameters having the most principal influence on particle size and particle size distribution of zinc sulfide particles.

Table 1 shows the structure of Taguchi's orthogonal array design and the average results of particle size measurements.

Table 1. Orthogonal array designed for parameter optimization in zinc sulfide synthesis by electrodeposition reaction

Experiment Number	S^{2-} Concentration (M)	Voltage (V)	rpm	Temperature (°C)	Size of ZnS particles (nm)
1	0.01	16	250	0	74
2	0.01	20	500	25	109
3	0.01	24	1000	50	151
4	0.05	16	500	50	103
5	0.05	20	1000	0	113
6	0.05	24	250	25	124
7	0.1	16	1000	25	184
8	0.1	20	250	50	170
9	0.1	24	500	0	236

The scanning electron microscopic (SEM) was used to characterize the morphology of the prepared zinc sulfide particles. SEM images for four samples of zinc sulfide obtained by this method under various conditions are shown in Fig. 1. These images show that operation conditions affect the particle size of product.

On the other hand, average particle size of zinc sulfide correspond to the effect of each studied parameter under any level was computed [13,16] and the results for all investigated parameters are presented in Table 2. The results presented in this table determine how the size of produced ZnS particles will vary when the level of the parameters varies.

The purpose of the analysis of variance (ANOVA) is to investigate which factors significantly affect the quality characteristic (which in this study was particle size of product, ZnS) [15,16]. The results for analysis of variance (ANOVA) correspond to the effect of various experimental parameters on the particle size of ZnS are shown in Table 3.

Table 2. Results of the main effects for each variable on the diameter of the ZnS nanoparticles.

Factor	Level	Results (nm)[a]
Sulside ion concentration (M)	0.01	111.33
Sulside ion concentration (M)	0.05	113.33
Sulside ion concentration (M)	0.1	196.67
Voltage (V)	16	120.33
Voltage (V)	20	130.67
Voltage (V)	24	170.33
rpm	2.5	122.67
rpm	10	149.33
rpm	40	149.33
Temperature (°C)	0	141.00
Temperature (°C)	25	139.00
Temperature (°C)	50	141.33

[a]These results are diameter of ZnS nanoparticles.

In this study, the effect of sulfide ion concentration on the particle size of synthesized zinc sulfide at three different levels (0.01, 0.05 and 0.1 mol/L) was investigated. The results show that 0.01 M is the best concentration for the production of ZnS particles with smallest diameter. The effect of various electrodeposition voltage (16, 20, 24 V) on the diameter of the ZnS nanoparticles was also investigated and 16 V was found to be the best voltage for the production of ultrafine ZnS particles. We further found that 25 °C and 250 rpm are the optimum temperature and stirring rate for the synthesis.

Table 3. ANOVA results for synthesis ZnS particles via electrsyntheis procedure using OA_9 (3^4) matrix while diameters of synthesized ZnS nanoparticles (nm) are as responses

					Pooled[a]			
Factor	**Code**	**DOF**	**S**	**V**	**DOF**	**S'**	**F'**	**P'**
S^{2-} concentration (mol/L)	S	2	14230	7115	2	14230	1489.9	71.7
Voltage	V	2	4180	2090	2	4180	437.7	21.0
RPM	R	2	1422	711	2	1422	148.9	7.1
Temperature (°C)	T	2	9.6	4.8	-	-	-	-
Error	E	-	-	-	4	9.6	-	0.2

[a]The critical value was at 90% confidence level; pooled error results from pooling insignificant effect.

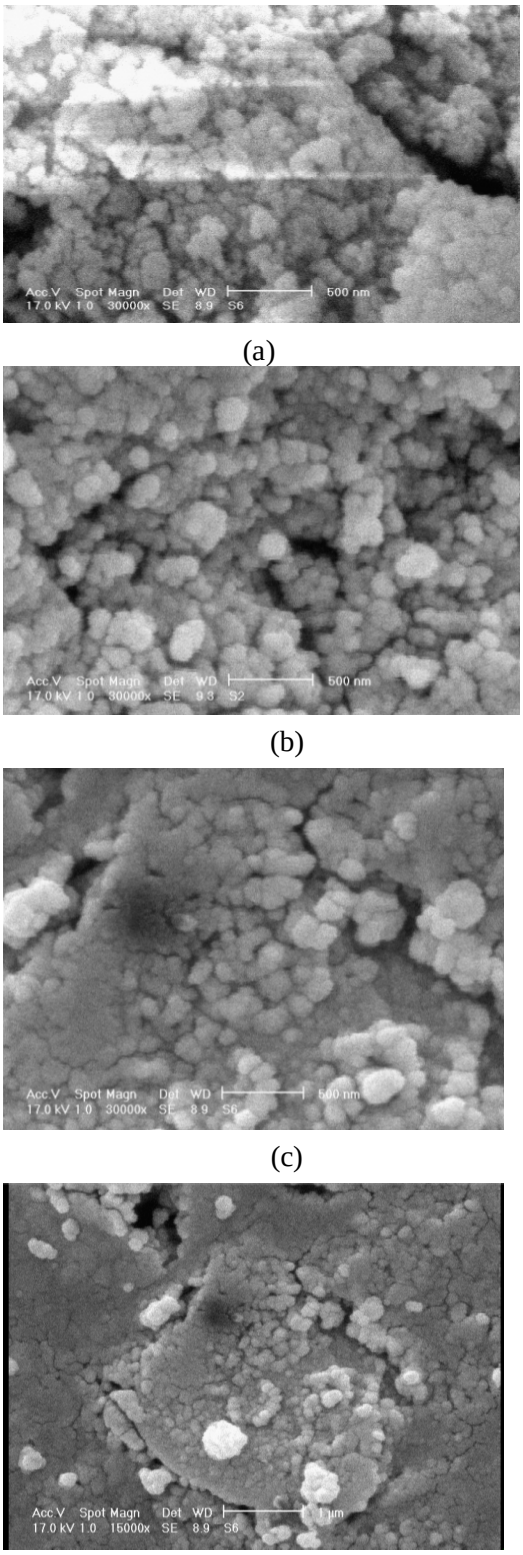

Fig. 1. SEM images of ZnS particles obtained under d runs of Table 1 by electrodeposition method: (a) run 1, 2, (c) run 4, and (d) run 6.

In the next step of this study, analysis of variance (ANOVA) was carried out on the average particle sizes of the produced particles obtained under different conditions mentioned in Table 1, the results of which are shown in Table 3, where *S* represents the sum of square for each variable or error term and *V* represents the variance of results corresponding to each factor. The purpose of the analysis of variance (ANOVA) was to investigate the most effective factors influencing the quality characteristic – particle size of the produced ZnS. It was found that at a 90% confidence interval, all studied parameters, except for temperature of reactor -i.e. concentration of the S^{2-} solution, electrolysis voltage and stirring rate- have significant effects on the size of product. It should be noted that the interactions between the parameters were neglected.

Under the optimized levels of significant factors, obtained from performing the analysis of variance on the experimental results of OA_9 (3^4) matrix (Table 3), the particle size of zinc sulfide produce by electrodeposition procedure and value of confidence interval for this estimated particle size could be predicted according to the appropriate expression [15,16].

Considering the average particle size of ZnS for controlling the factors at various levels presented in Table 2 and gaining the results of ANOVA shown in Table 3, the optimum conditions for synthesis ZnS nanoparticles via electrodeposition reaction could be pointed out as: 0.01 M as concentration of sulfide ion, 16 V as electrolysis voltage and 250 rpm as stirring rate of electrolyte solution.

Calculations for prediction of the particle size of zinc sulfide as product under optimum

condition of electrodeposition and value of confidence interval for this estimated particle size showed that at 90% confidence level under optimum conditions, the size of ZnS particles will be 73.4 ± 5.6 nm.

As could be seen in Table 1, the first run in this table contains the proposed optimum condition by ANOVA (0.01 M as concentration of sulfide ion, 16 V as electrolysis voltage and 250 rpm as stirring rate of electrolyte solution) for preparation of ZnS nanoplates via electrodeposition reaction. SEM image revealed that the synthesized ZnS via this experiment (run 1) have about 74 nm average diameter (Fig.1a); which is in agreement with the estimated range for diameter of ZnS particles under the optimum condition of precipitation reaction. Furthermore, the transmission electron microscopy (TEM) image of ZnS nanoparticles presents a cross-sectional view of the synthesised nanoparticles (Fig. 2).

Thus, ZnS nanoparticles prepared under this experimental condition (run 1) were used for composition and structure characterization studies such as TEM, XRD and UV-Vis.

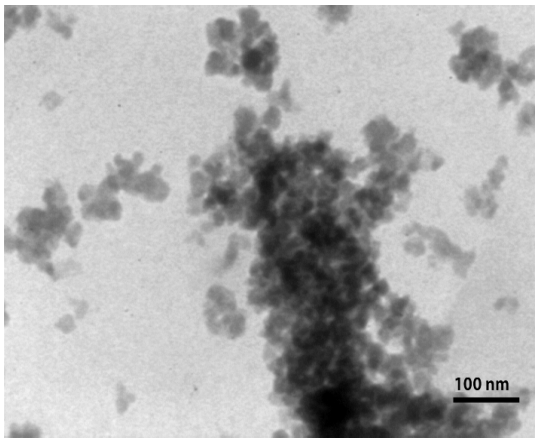

Fig. 2. TEM images of ZnS nanoparticles obtained under optimum conditions.

2.1. Characterization of zinc sulfide nanoparticles

ZnS nanoparticles prepared under optimum condition were investigated by X-ray powder diffraction (XRD) analysis for evaluating the composition and purity. Fig. 3 shows the XRD pattern for precipitated zinc sulfide nanoparticles under optimum conditions. The three peaks (1 1 1), (2 2 0), and (3 1 1) clearly indicate the formation of the cubic sphalerite structure. Relatively strong intensity and a wide and low diffraction spectrum for the produced zinc sulfide were observed. The diffraction peaks indexed in the XRD pattern of sample were in agreement with the structure of zinc sulfide from PC-APD, No: 00-001-0792.

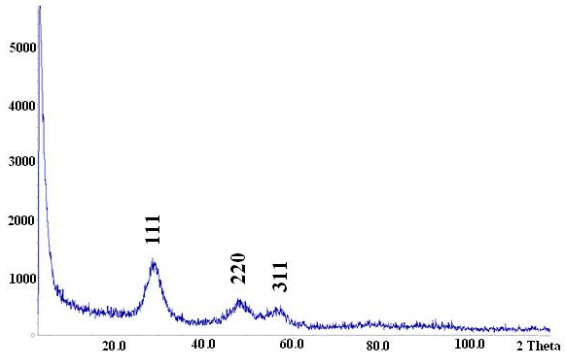

Fig. 3. XRD pattern of ZnS nanoparticles prepared by electrodeposition method under optimum condition.

UV–Vis spectrophotometry was used to characterize the absorption properties of synthesized zinc sulfide sample by electrodeposition while dispersed in solvent. Fig. 4 shows UV–Vis absorption spectrum of the products obtained under optimum condition while dispersed in ethanol. An absorption peak centered at 320nm, which is considerably blue-shifted relative to the absorption onset of bulk ZnS (340 nm) because of the quantum size effects, was found. This UV absorption peak confirms the formation of nanosized zinc sulfide particles [4].

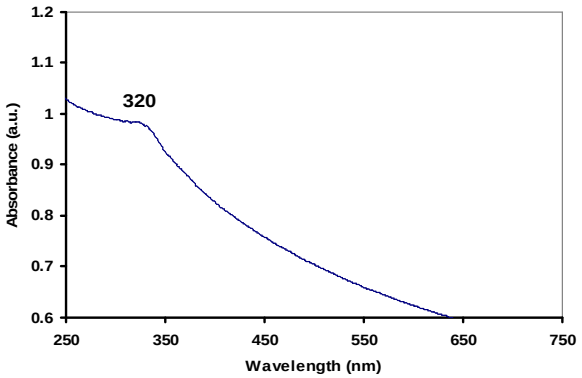

Fig. 3. UV–Vis spectrum for ZnS nanoparticles prepared under optimum condition of synthesis

4. Conclusion

A rapid, clean and simple method for preparation of zinc sulfide nanoparticles via electrodeposition without using any catalyst, surfactant, and template with possibility to control the size and shapes of the nanoparticles has been demonstrated. It was found that electrolysis voltage and sulfide ion concentration in the electrolyte solution are critical parameters for controlling morphology of the electrodeposited nanoparticles. Finally, the results of this investigation showed that electrodeposition is a simple, clean, green and relatively rapid for preparation of zinc sulfide nanoparticles. Furthermore, electrodeposition gives a better selectivity for controlling of the product morphology by changing electrolysis variables which is less tedious.

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