RESEARCH ARTICLE

The Morphology of Zinc Sulfide Nanocrystals Synthesized by Different Methods

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ABSTRACT

In recent years, nanostructured materials have attracted a great deal of attention due to their special properties as compared to bulk materials. Semiconductor nanoparticles can be synthesized in several methods, including chemical capping, reverse micelles, and hydrothermal. In this research, different methods of ZnS nanoparticle fabrication and the role of the main parameters on the particle size and morphology of the samples were investigated by validated methods such as SEM, TEM, XRD and EDAX. In all mentioned methods, decreasing the concentration of reactants reduces the particle diameter. Also, increasing the rate of addition of the reactants reduces the size of the produced nanoparticles. The results of SEM and TEM imaging show that the hydrothermal method using thioacetamide as a source of sulfide ion, in addition to the uniformly formed nanoparticles, has high reproducibility which is a good criterion for increasing the scaling rate.

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INTRODUCTION

In recent years, nanostructure materials have attracted much attention because of their special properties for bulk materials (1-3). Zinc sulfide semiconductor due to its large band gap (3.6 EV) as an important material in ultraviolet light emitting and injection lasers, flat panel displays, electroluminescence devices and infrared windows (4-10) as applied. In recent years, due to some properties of ZnS Nano crystals that are different from the properties of bulk crystals, the scope of application of this material has expanded (11-13).

Given these applications, the study of ZnS nanostructures is of great importance and much effort has been focused on the fabrication and investigation of its physical properties (14-16).

Semiconductor nanoparticles can be prepared in several ways, including chemical capping, reverse micelles, and hydrothermal (17-19). One of the main advantages of these methods is the low temperature required for the preparation of these compounds and the disadvantages are that to prevent particle aggregation the inactivation of the surface of the particle with appropriate coating or surface-active material is required.

When the particle size is less than the Bohr radius, the particles exhibit effects dependent on quantum constraints, which are related to the accumulation of charge carriers, which is why they are called quantum dot.

Quantum dots are capable of producing light at specific wavelengths, in fact by controlling the dimensions of the quantum dots; the electromagnetic field emits light in different colors and wavelengths. For example, quantum dots of

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3 nm cadmium arsenide emit green light, while particles as large as 5.5 nm emit red light.

Numerous reports are indicating the production of semiconductor nanoparticles by chemical coating method. Here, the surface atoms of the nanoparticles are attached to organic or inorganic molecules in such a way that they provide the necessary protection for the nanoparticles without affecting their core properties. Covering compounds include thiophenol, mercaptoethanol, trioctylphosphine oxide and sodium polyphosphate. The chemical coating method is generally performed in two general ways, one at high temperature and the other at room temperature.

Zinc sulfide Nano crystals were first developed in 1985 as a fully stable colloid in water and methanol using Na_2S and Zn (ClO4) 2 precursors (20). In another attempt, cubic nano crystals of ZnS in various sizes and shapes were fabricated from the thermal reaction of $ZnCl_2$ and S in oleylamine in the presence of trioctylphosphine oxide (TOPO) (21). In addition, ZnS hexagonal Nano crystals were synthesized at a temperature below 150 ° C by using $ZnCl_2$ and S as precursors in the polyol environment (22). also, the use of ZnO or zinc-fatty acid precursor in place of zinc alkyl activator was suggested for the growth of Nano crystals of ZnS using greener chemicals in an environmentally friendly manner (23). Recently, a simple construction method using single-source precursor has been reported (24). In this method, injection of ethyl xanthate solution on $Zn(exan)_2$)) (As supplier of Zn^{2+} + and S^{2-} ions) containing trioctylphosphine (TOP) to hexadecylamine hot solution and TOP or octylamine (OA), zinc sulfide Nano crystals is produced.

Metal nanoparticles, metal oxides and different semiconductors have been fabricated by multiple groups using the reverse micelles technique. The shape, size, and composition of these nanoparticles are well controlled in this method by using surfactants, amphiphilic short- or long-chain hydrocarbon molecules or monomeric molecules (39).

Among the various methods, hydrothermal methods are of particular value for the manufacture of Nano crystals due to their low cost, high efficiency and scaling potential. (25-27).The main point in preparing semiconductor Nano-clusters is precise size control, size distribution and particle retrieval and stabilization.

A gentle hydrothermal method for the fabrication of metal sulfides using thioglycolic acid as an informal template has been proposed (28). Spherical species of ZnS smaller than microns have been produced by hydrothermal conditions (29) in presence of silica and polystyrene spheres or the use of polyethylene glycol surfactant (PEG) (30, 31) and thioglycolic acid (14).

ZnS nanoparticles are also made from the reaction of zinc ions and sulfur-containing organic compounds such as thioacetamide in solution (32). Under these conditions thioacetamide (CH_3CSNH_2) hydrolyzes in water to produce hydrogen sulfide:

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COOH + H_2S + NH_3$$

In a solution containing Zn^{2+} + ions and thioacetamide, zinc sulfide precipitates from the HS^-induced hydrolysis reaction and Zn^{2+} ions at pH<3 and is formed at pH>3 by direct reaction of thioacetamide and Zn^{2+} ions:

$$Zn\ (AC)_2 + CH_3CSNH_2 \rightarrow ZnS + CH3CN + 2\ HAC$$

Therefore, thioacetamide is used as a suitable substitute for hydrogen sulfide in single-phase sulfide nanoparticles (4, 33).

In general, chemical methods of nanoparticle fabrication have a comparative advantage in the ability to design surface properties of particulate matter.

Many efforts have been made to produce a variety of ZnS forms including: ((6, 22), (34).

The purpose of zinc sulfide nanoparticles preparation in this study is to investigate the effect of different manufacturing methods and the role of the main parameters on particle size and morphology of the samples using validated methods such as SEM, TEM, XRD and Energy Dispersive X-Ray Analysis.

EXPERIMENTAL SECTION

Synthesis of zinc sulfide nanoparticles

Chemicals

Different zinc ion salts including zinc nitrate, $Zn\ (NO_3)_2.\ 6H_2O$, zinc acetate, $Zn\ (Ac)_2.\ 2H_2O$, zinc chloride, $ZnCl_2$ and zinc sulfate, $ZnSO_4$ were purchased from Sigma-Aldrich. Sodium sulfide salt was purchased from Aldrich Company with a purity of 60-63%. Thioacetamide was also purchased from Merck, Germany with 99% purity and 2-mercaptoethanol with 98% purity. Other additives such as ethylenediaminetetraacetic acid (EDTA) and surfactants such as sodium bis

Table 1. Investigation of the role of different parameters in the manufacture of zinc sulfide nanoparticles (Method One)

Entry	Sample Number	**Ion source Zn^{2+}**	**Zn^{2+}** ion concentration (mol / l)	**Na_2S** salt concentration (mol / l)	Covering agent	Coating agent concentration (mol / l)	XRD based particle size
1	Z-1	Zn $(NO_3)_2$	0.1	0.1	SDS	0.01	(nm)
2	Z-2	Zn $(NO_3)_2$	0.1	0.1	2-mercaptoethanol	0.03	(4.6 nm)
3	Z-3	Zn$(NO_3)_2$	1	1	-	-	(2.4 nm)
4	Z-4	Zn $(Ac)_2$	0.5	0.5	2-mercaptoethanol	0.5	(3.7 nm)
5	Z-5	Zn $(Ac)_2$	0.1	0.1	2-mercaptoethanol	0.1	
6	Z-6	Zn $(Ac)_2$	0.1	0.1	2-mercaptoethanol	0.5	(2nm)

(2-ethylhexyl) sulfosuccinate (AOT), sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), acetone and other solvents are purchased in pure. In all experiments, deionized water prepared by the Petroleum Industry Research Institute, Iran was used. Sulfide nanoparticles were synthesized on three general methods in this study.

Instrumental

The SEM (Philips Netherlands Electron Microscope Model XL30) and ENERGY DISPERSIVE X RAY ANALYSIS mounted on it, TEM (Philips Model CM 120, KeV 120), XRD (Philips Model 1840, KeV 40, 30 mA, with Cu lamp) analysis was used to determine the structure of the nanoparticles.

- Method 1: Synthesis of zinc sulfide nanoparticles using zinc salt and sodium sulfide in the presence of coating agent

First, solutions of a specified concentration (0.01–1.0 mM) are prepared from zinc salt and coating agent (Table 1). Then a solution of sodium sulfide with appropriate concentration is slowly added to Zn^{2+}. After the deposition reaction is complete, the precipitate is filtered or centrifuged and dried.

- Method Two: Manufacture of Zinc Sulfide Nanoparticles Using Zinc and Thioacetamide (TAA) as a Source of Sulfide Ions

The zinc acetate salt is first dissolved in deionized water at a specified concentration (0.01-1.0 mM) then added to the equivalent of the thioacetamide and the reaction temperature is brought to about 70-100 ° C. After the reaction is complete, the precipitate is filtered off by centrifugation and thoroughly rinsed with deionized water. In this method, the parameters of reactant concentration, reaction temperature, type of Zn^{2+} ion source and type of coating as well as reproducibility of the method have been evaluated (Tables 2-4).

- Method Three: Manufacture of Zinc Nano Sulfide under microemulsion conditions

In this series of experiments, a mixture of ethanol / water with ratio of 3 was used. All the reactants in this solvent mixture are dissolved separately then gradually or rapidly added to each other. SDS as a surfactant has also been used to produce microemulsion under these conditions (Tables 5 and 6).

RESULTS AND DISCUSSION

The size of the crystals in ZnS nanoparticles is calculated by the Shearer equation;

$$D=k\lambda/\beta\ COs\Theta$$

Which D is the crystal size, k = 0.9 , λ is the radiation wavelength of Kα Cu and β is the corrected half width of the diffraction peak. In Table 1, the role of different parameters in the fabrication of zinc sulfide nanoparticles has been shown.

In general, all zinc sulfide particles made in the first method do not have a perfectly uniform structure, but the particle size is very small. The XRD specifications showing the diameter of the crystal are all below 10 nm. It can be explained that the mere estimation of the size of the nanoparticles is not sufficient based on the XRD results (In some published articles the measurement of nanoparticle diameter by XRD has been the sole criterion for diagnosis). But with the help of SEM and TEM imaging, we can get more reliable results on product quality. Using the XRD spectra, the type of nanoparticle structure can be obtained. In other words, due to the presence of three known peaks in the regions of 28.56, 47.52 and 56.29 nm, the cubic structure (sphalerite) can be attributed to the produced nanoparticles.

The data in Table 1 are divided into two sections, first a set of reactions using $n(NO3)_2$ as the source of Zn^{2+} ions. Comparison of the XRDs of the products in this group shows particles with identical but small dimensions. A mere consideration of the XRD results may give rise to the notion that the nanoparticles are very desirable (Fig. 1). But more assurance has been obtained

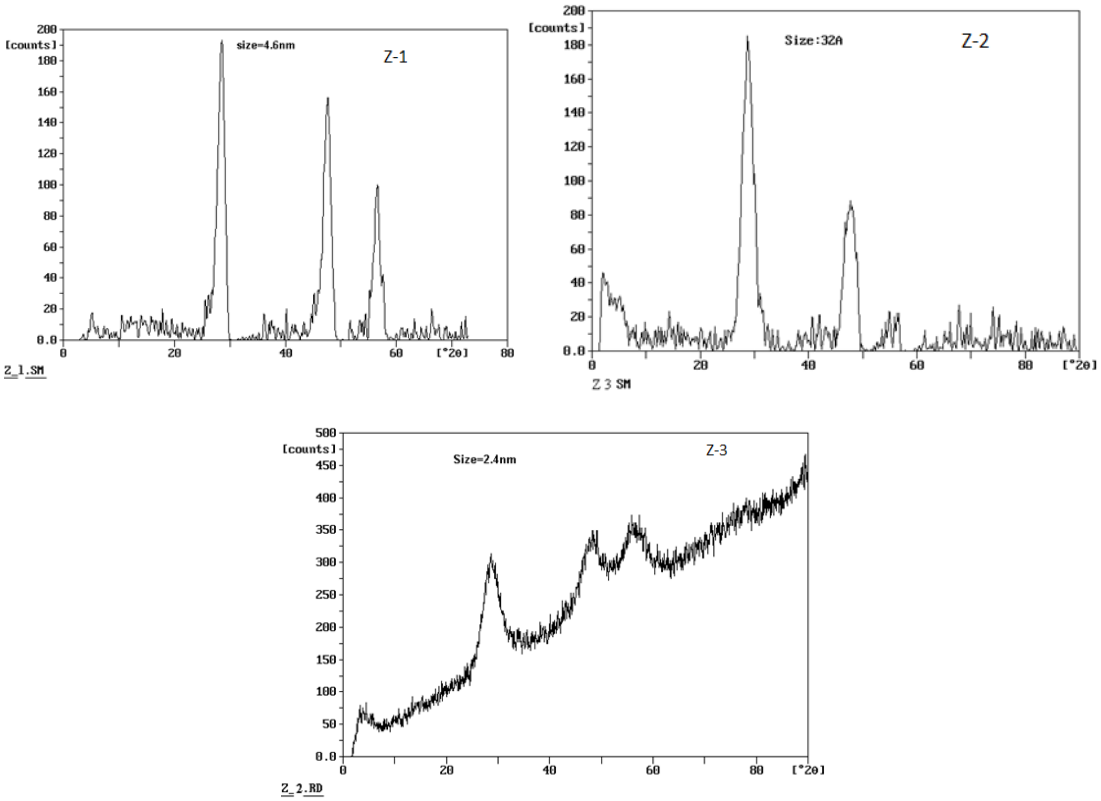

Fig. 1. Comparison of XRDs of three nanoparticles of $Zn(NO_3)_2$ in the presence of SDS coatings(Z-1), 2-mercaptoethanol (Z-2) and uncoated (Z-3)

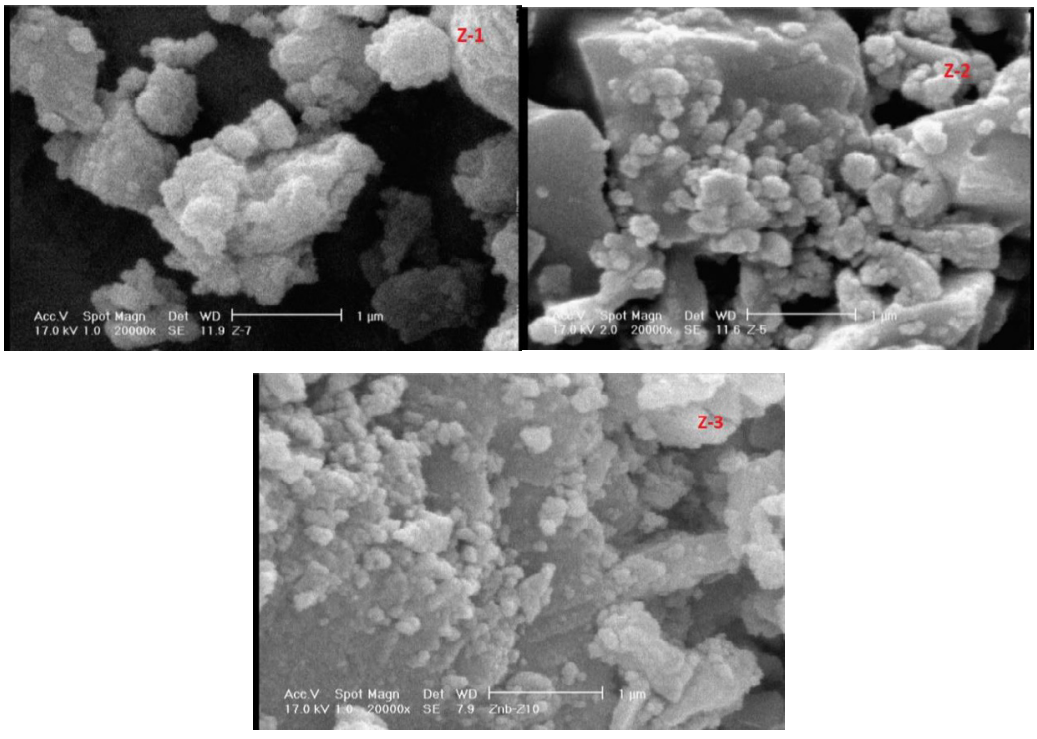

Fig. 2. SEM for samples Z-2, Z-1, Z-3

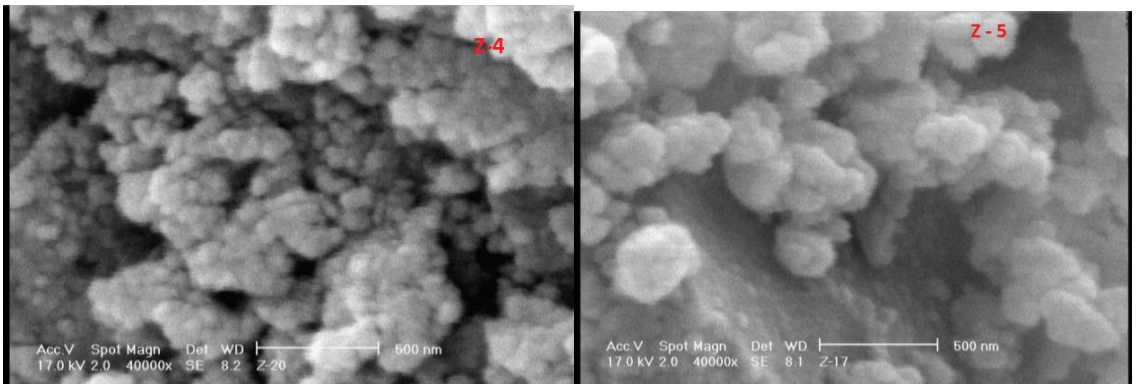

Fig. 3. SEM for samples Z-4, Z-5.

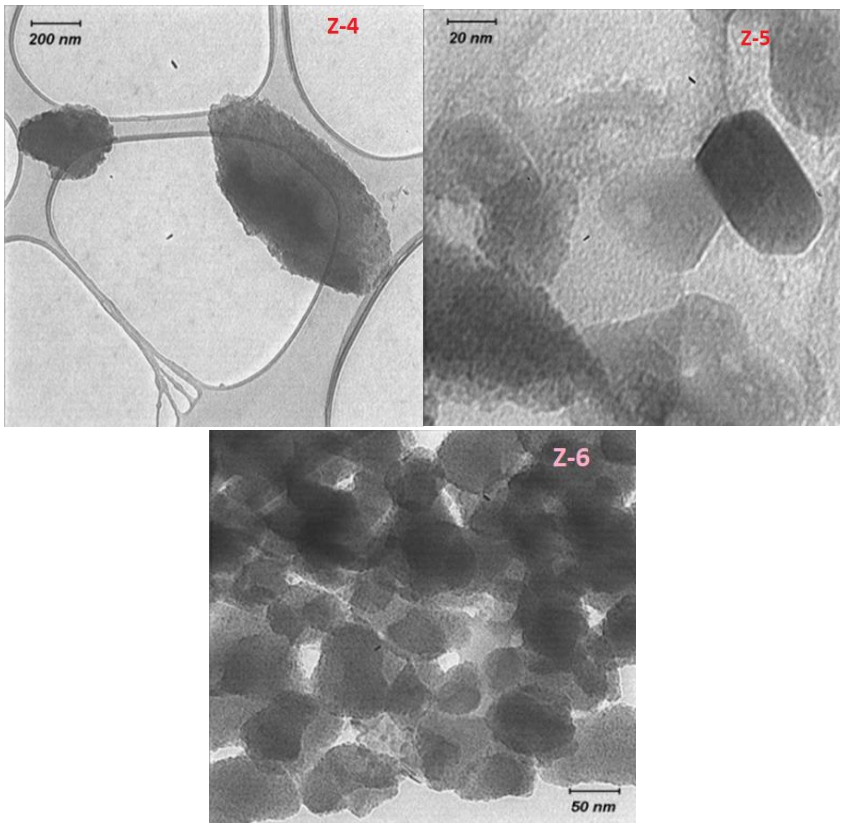

Fig. 4. TEM images of samples Z-4, Z-5 and Z-6

from electron scanning electron microscopy (SEM) images showing nanoparticle aggregation. SEM comparison of samples Z-1, Z-2, Z-3 indicates that at similar concentrations of reactants, the change in the type of surfactant in this method is partially influenced by the crystallite size and the amount of nanoparticle accumulation. And the presence of anionic coating SDS causes more adhesion of the nanoparticles (Fig. 2, SEM Z-1).

In most cases, an increase in concentration causes the particles to stick together and produce larger particles. The second part of Table 1 deals with the manufacture of Nano ZnS samples using $Zn(Ac)_2$ as the source of Zn^{2+} ions. SEM (Figs. 3), TEM images of Z-4, Z-5 and Z-6 samples (Figs. 4) show the effect of species and coating concentration on the nanoparticle's diameter.

Comparison of the two samples Z-4 and Z-5 shows that increasing the concentration of the reactants increases the concentration of

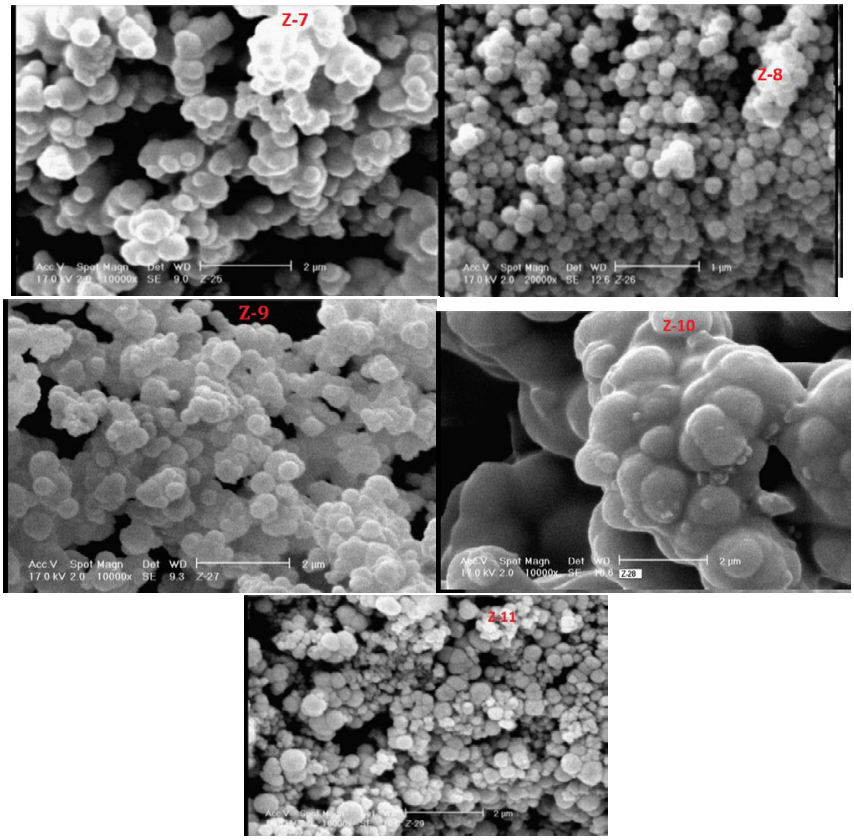

Fig. 5. SEM images of Z-7 to Z-11 samples

the particles and the higher the concentration of the reactants increases the particle diameter due to the accumulation of particles. This is particularly evident in the TEM images of the Z-4 and Z-5 samples. Comparison of the TEM images of the Z-5 and Z-6 samples shows that under similar conditions the concentration of the reactants (Zn^{2+} and S^{2-} ions) can be increased by increasing the concentration of the coating agent (2-mercaptoethanol) and reducing the particle size.

Investigation of the effect of reactant concentration using Zinc and Thioacetamide (TAA) as a source of sulfide ions

As mentioned, in this method, the ZnS nanoparticles are made from the reaction of zinc ions and sulfur-containing organic compounds such as thioacetamide in solution. The results of SEM imaging show that there is a significant difference in the particle shape of this method (using thioacetamide as S^{2-} ion source) compared to the first method (using Na_2S salt). In such a way that the particles obtained by the latter method are evenly spherical and almost uniform, even in the absence of coating agent. Whereas the particles from Na_2S salt application have a more irregular structure. Table 2 investigates the effect of the reactant concentration on the size of zinc sulfide nanoparticles at 90 ° C without coating agent.

As can be seen from the SEM images of the Z-7 to Z-11 samples, increasing the concentration of the reactants increases the particle accumulation and eventually increases the particle size (Fig. 5). For example, in this category, samples of Z-8 and Z-11, which have the lowest concentration of reactants, have the best particle quality. Likewise, Z-10 has the highest concentration According to SEM images; the highest aggregation and interconnection of particles are observed. Fig. 6 is an example of a TEM image of a Z-7 nanoparticle.

The validated Energy Dispersive X-Ray Analysis technique can be used to evaluate the purity of nanoparticles. The basis of this system is that the electron beam is radiated to the sample surface, the elements present at the sample surface are excited, and each element produces a mild

Table 2. Investigation of the effect of reactant concentration on the size of zinc sulfide nanoparticles at 90 ° C without coating agent

Entry	Number	Concentration of thioacetamide (Mole/liter)	Zinc acetate concentration (Mole/liter)	Product Analysis Method
1	Z-7	0.05	0.05	SEM TEM
2	Z-8	0.01	0.01	SEM
3	Z-9	0.1	0.1	SEM XRD=3.1nm
4	Z-10	1	1	SEM
5	Z-11	0.02	0.02	SEM

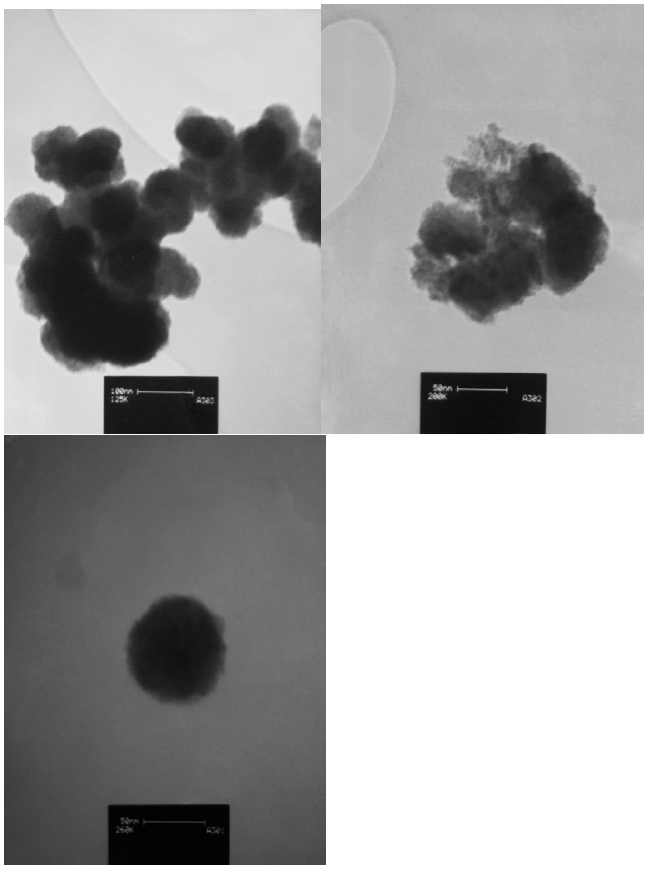

Fig. 6. TEM image of the Z-7 nanoparticle.

x-ray with its own energy. The software detects the element of that peak based on the energy of each peak and calculates its percentage based on the area under the curve. Comparing Energy Dispersive X-Ray Analysis with samples of Z-10 (1 M concentration) and Z-7 (0.05 M concentration), it can be concluded that sample Z-7 (percentage of Zn: S atoms equals (35.24: 64.74) has a higher purity than the sample Z-10 (the ratio of Zn: S atoms is 23: 77) (Fig. 7).

The temperature effect

In Table 3, the effect of temperature in the manufacture of Zinc Nano Sulfide in the second method (using thioacetamide as a sulfide ion source) on particle size and adhesion is investigated. According to SEM imaging, it is quite evident that at the same concentration conditions the decrease in temperature leads to more particle accumulation (comparing Z-8 with Z-12 and Z-7 with Z-13) (Fig. 8).

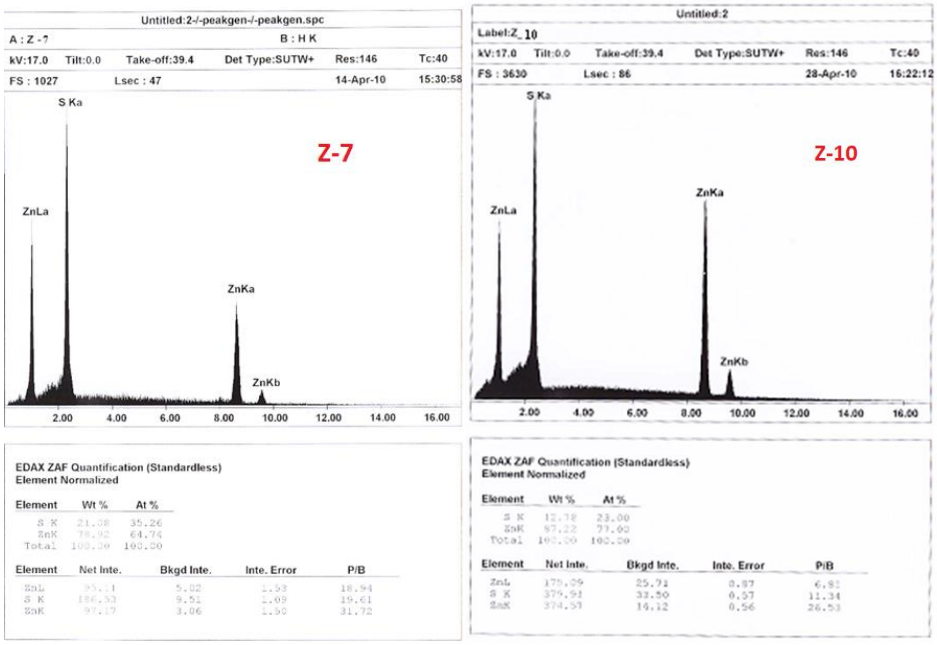

Fig. 7. Energy Dispersive X-Ray Analysis for samples of Z-10 (1 M concentration) and Z-7 (0.05 M concentration).

Table 3. Investigation of the role of temperature on zinc sulfide nanoparticles

Reaction temperature conditions	Concentration of thioacetamide (Mole/Litre)	Zinc acetate concentration (Mole/Litre)	Number
90 °C - Rapid addition of TAA at this temperature	0.05	0.05	Z-7
90 °C - Rapid addition of TAA at this temperature	0.01	0.01	Z-8
70 °C	0.01	0.01	Z-12
70 °C	0.05	0.05	Z-13
70 °C – addition of TAA and gradual increase in temperature	0.05	0.05	Z-14

As the temperature increases slowly and after the reactants addition, the phenomenon of particle adhesion is more likely to occur (Z-13, Z-14 comparison). As can be seen from the SEM image of sample Z-14, at higher concentrations, if the temperature is low, the overall shape of the particles becomes nonspherical and the particles become more irregular.

The effect of coating agent type on nanoparticles using Zinc and Thioacetamide (TAA) as a source of sulfide ions

Due to the effect of coating agents on nanoparticles and their stability in the literature, this study investigates the effect of various coating agents with anionic, cationic and neutral character (Table 4).

According to the structure of each coating agents used (Fig. 9), using the cationic surfactant cetyltrimethylammonium bromide, the particle structure is obtained in a non-perfectly spherical, nearly adherent, particle structure (Fig. 10, SEM Z-15). The use of SODIUM DODECYL SULFATE surfactant creates spherical particles with a perfectly regular surface (Fig. 10, SEM Z-16). By changing the surface-active substance and using sodium bis (2-ethylhexyl) sulfosuccinate a completely different form of nanoparticles is created which appears as a cauliflower with a very regular structure. The sample was re-photographed to confirm the non-

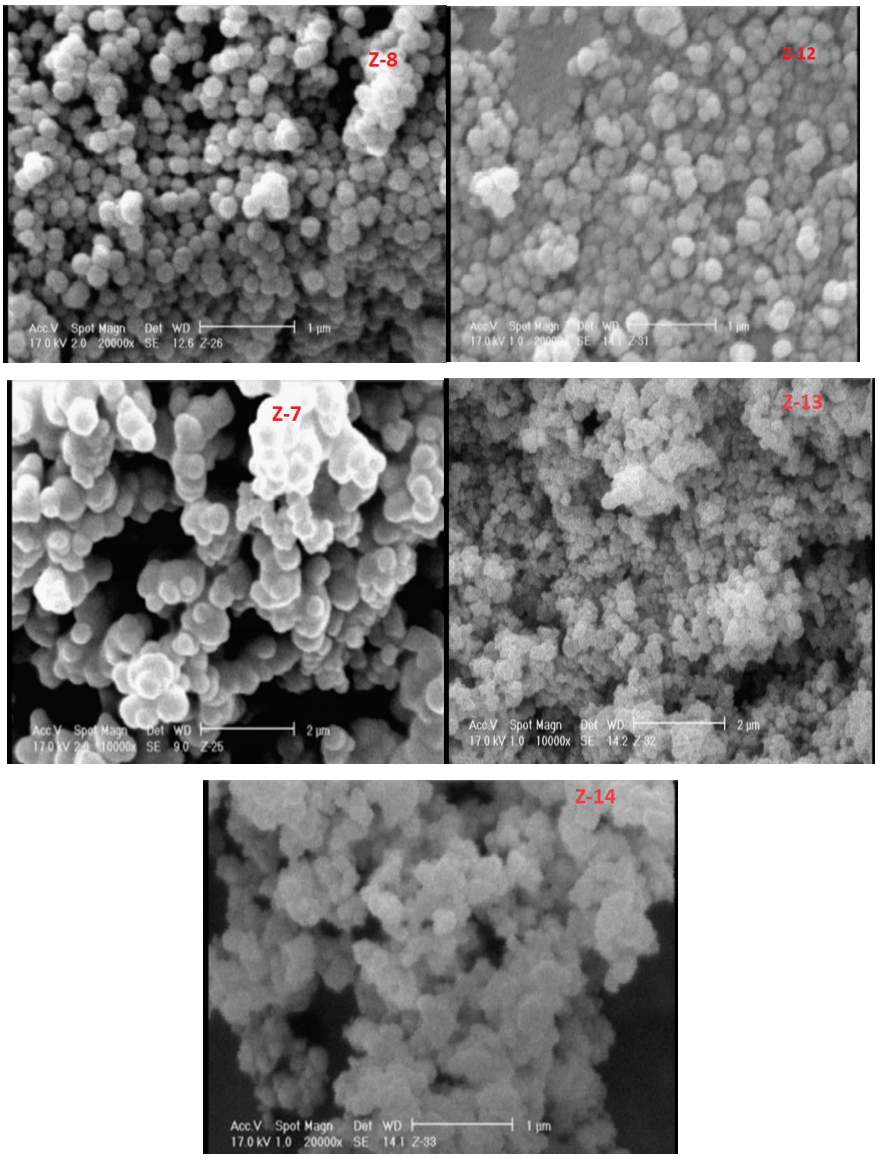

Fig. 8. The effect of temperature in the quality of nanoparticles.

Table 4. The effect of increasing coating agent on particles at 90 ° C

Type of cover	Thiostamide concentration (mole/litre)	Zinc acetate concentration (mole/litre)	Number
CETYLTRIMETHYLAMMONIUM BROMIDE	0.05	0.05	Z-15
SODIUM DODECYL SULFATE	0.02	0.02	Z-16
SODIUM BIS(2-ETHYLHEXYL) SULFOSUCCINATE	0.02	0.02	Z-17
2-Mercaptoethanol	0.02	0.02	Z-18

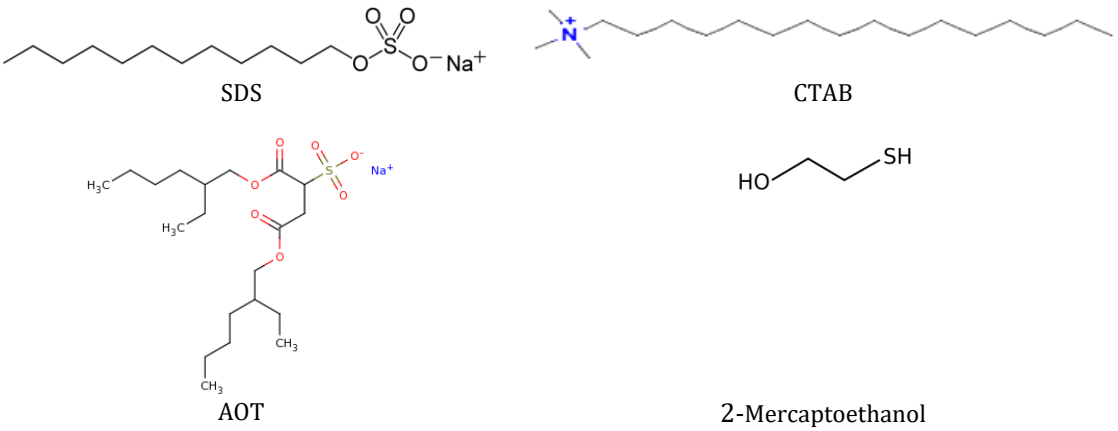

Fig. 9. Structure of the surface active materials used in the manufacture of Zinc Nano Sulfide.

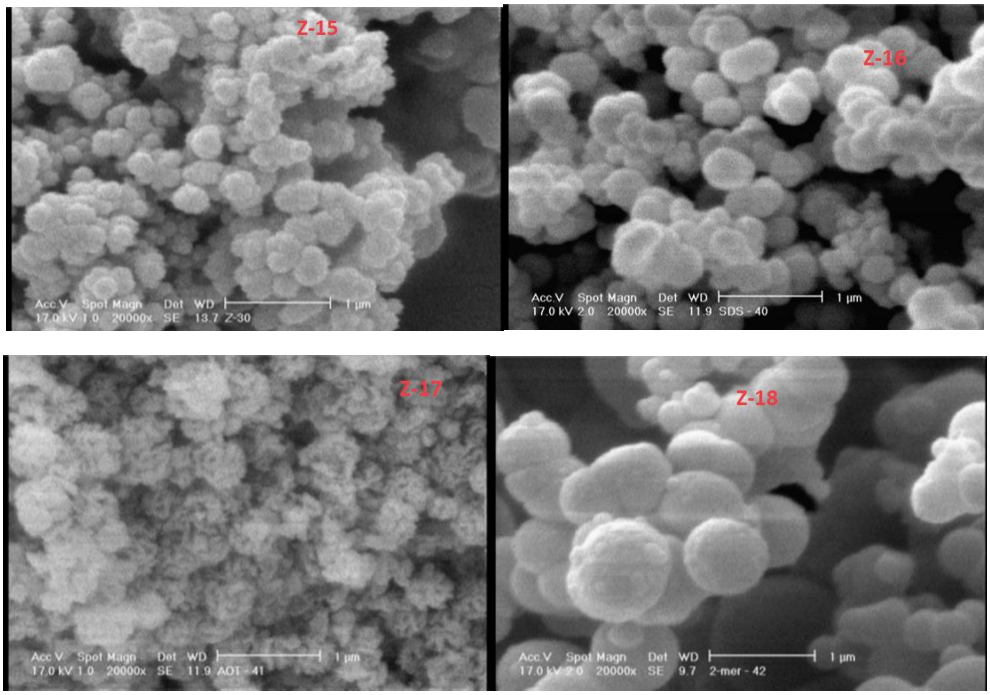

Fig. 10. Influence of coating type on the shape of nanoparticles.

error of the SEM imaging, and the results remained unchanged (Fig. 10, SEM of Z-17).

Probably the difference in the shape of the nanoparticles in the case of sodium bis (2-ethylhexyl) sulfosuccinate relative to other coating agents is due to the bulk structure of this surface-active agent with SO3 anionic group which has placed between the two massive arms of the ester group. This situation prevents the formation of spherical particles.

As it can be seen, in the surface-active substances sodium dodecyl sulfate (SDS), cetyltrimethylammoniumbromide(CTAB) the ionic section of the molecule is located at the beginning of the alkyl chain, which allows the spherical structure to be formed. Molecule 2-mercaptoethanol also provides the above conditions due to its small volume. This phenomenon shows that zinc sulfide nanoparticles are made up of much smaller particles by adhesion (Fig. 10, Z-18).

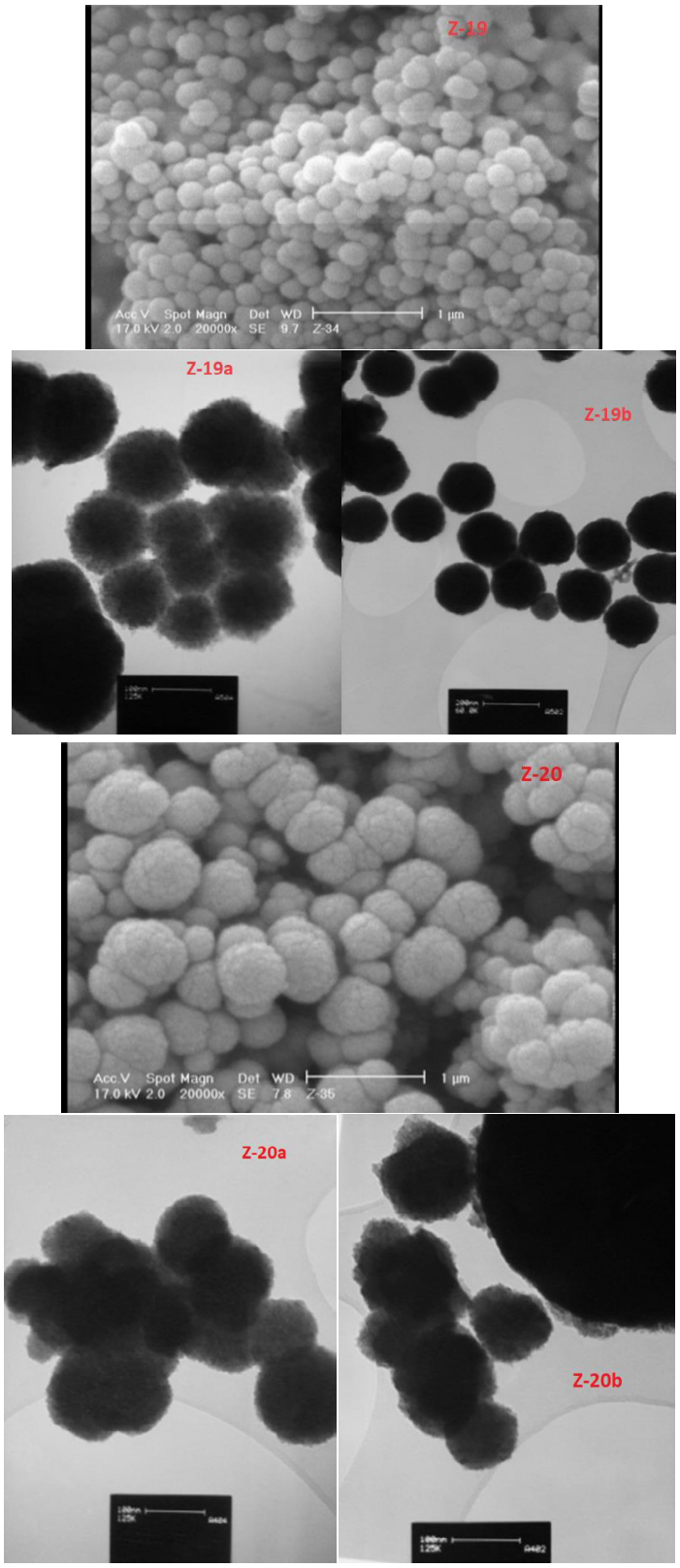

Fig. 11. TEM and SEM images of Z-19 and Z-20 samples (The scale is 100nm).

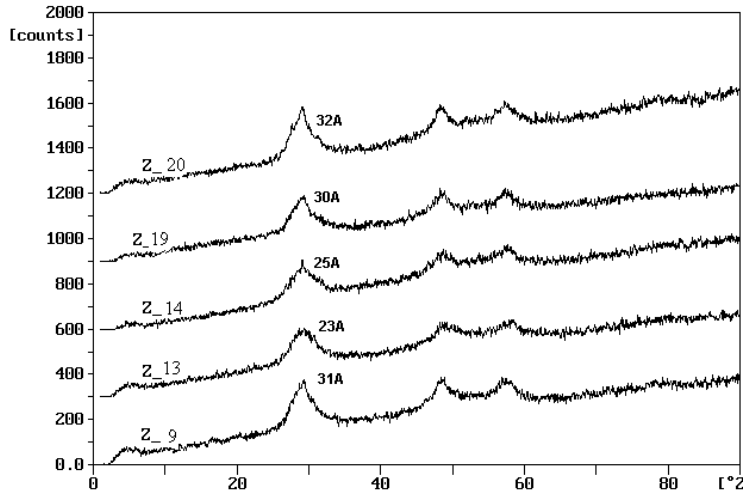

Fig. 12. Comparison of the size of Nano zinc sulfide crystals *using Zinc and Thioacetamide (TAA) as a source of sulfide ions* by XRD.

Table 5. Manufacture of zinc sulfide nanoparticles under micro emulsion conditions

Number	Source and concentration of S^{2-} ions (mole/liter)	Zinc acetate concentration (mole/liter)	Temperature	Method of analysis	Conditions for increasing the S^{2-} ion in zinc acetate solution
Z-21	Na_2S (0.52)	0.26	25 °C	SEM,ENERGY DISPERSIVE X RAY ANALYSIS	Rapid addition of Na_2S solution to zinc acetate
Z-22	Na_2S (0.52)	0.26	25 °C	SEM,ENERGY DISPERSIVE X RAY ANALYSIS	Slow addition of Na_2S solution to zinc acetate
Z-23	Na_2S (0.1)	0.26	25 °C	TEM,SEM	Rapid addition
Z-24	Thioacetamide (0.52)	0.26	70 °C	SEM	Simultaneous addition of the two reactants then a gradual increase in temperature
Z-25	Thioacetamide (0.1)	0.26	90 °C	TEM, SEM	Rapid addition

Reproducibility study

Z-19 (0.01 M concentration) and Z-20 (0.02 M concentration) samples were prepared under conditions similar to those of Z-8 and Z-11 by increasing the scale up to twice. It is observed that the method of fabrication is highly reproducible (Fig. 11). Interestingly, the TEM images of the Z-19 sample represent the mechanism of spherical particle formation due to the adhesion of finer particles that become spherical in a particular order. This trend is well apparent in the SEM images of sample Z-20 as it appears to have formed on the surface of the spheres due to the intercalation of smaller particles into a larger spherical particle.

In sum, the XRD spectra of the samples made by the second method indicate the appropriate size of zinc sulfide nanoparticles (Fig. 12).

Manufacture of Zinc Nano Sulfide under micro emulsion conditions

As mentioned, one of the methods of making nanoparticles is to use micellar media. Most of the sources mentioned in the Zinc Nano Sulfide synthesis have been exploited by the deposition method in the aquatic environment. But since the micro emulsion conditions in some cases produce smaller particles, so a limited number of experiments were performed in this medium. This study is done solely to compare the size, appearance, and amount of particle accumulation. Table 5 shows some experiments on the synthesis of zinc sulfide nanoparticles under micro emulsion

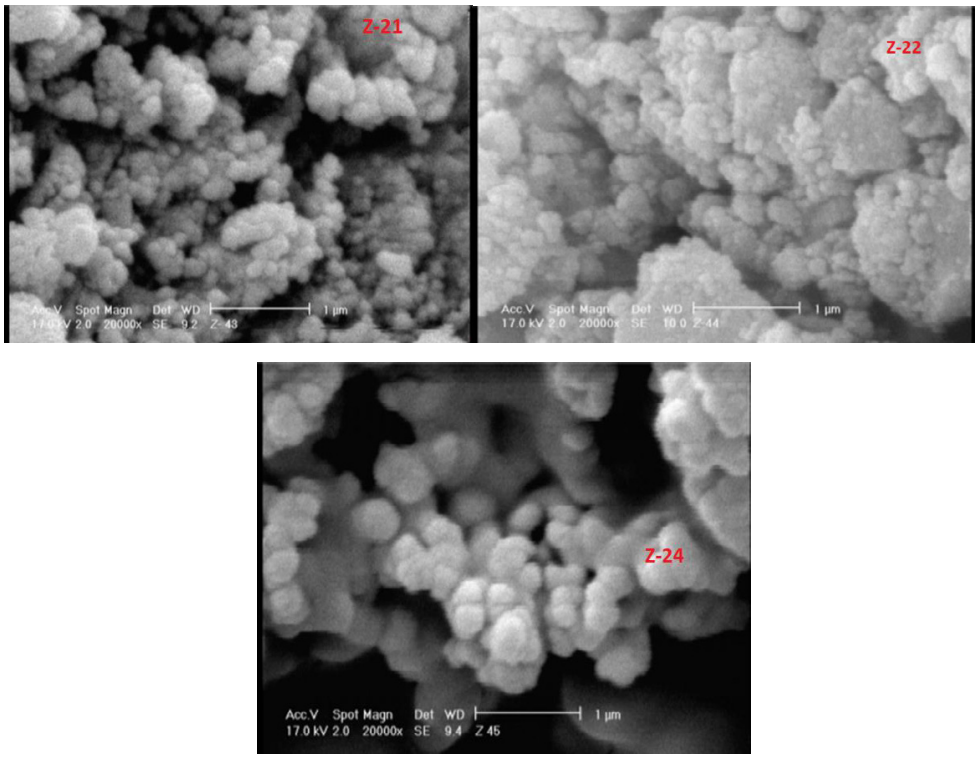

Fig. 13. SEM images of samples Z-24, Z-22, Z-21.

Table 6. Purification of nanoparticles made by micro emulsion by Energy Dispersive X Ray Analysis.

Atomic Percentage	Element	Sample
34.16	S	Z-17
65.84	Zn	
24.31	S	Z-21
75.69	Zn	
28.62	S	Z-22
71.38	Zn	

conditions (water and ethanol as solvents).

It is noteworthy that the same number of moles of two reactants is used and only the concentrations are different. According to the SEM images of the samples Z-24, Z-22, Z-21 as expected under the micro emulsion conditions the particle size is reduced but irregularity of the spherical state is observed and accumulation is also observed in the sample (Fig. 13). In this regard, it is observed that the rapid addition of the S^{2-} ion solution to zinc acetate at the same concentration reduces the accumulation (comparing SEM images of samples Z-22 and Z-21).

As with the previous method, changing the sulfide ion source from Na_2S to thioacetamide increases the possibility of spherical clusters. In this case, the particle size is slightly smaller than the non-emulsion conditions, but due to the higher concentration of reactants under micro emulsion conditions, the particle adhesion is more pronounced. Comparison of ENERGY DISPERSIVE X RAY ANALYSIS spectra of Z-22 and Z-21 samples (Micro emulsion conditions, Na_2S salt and Surface-active ingredient (sodium dodecyl sulfate with Z-17 (aqueous, thioacetamide, sodium bis (2-ethylhexyl) sulfosuccinate)) indicates higher purity under non-micro emulsion conditions (Table 6).

In order to complete the information in this section, by reducing the concentration, it was tried

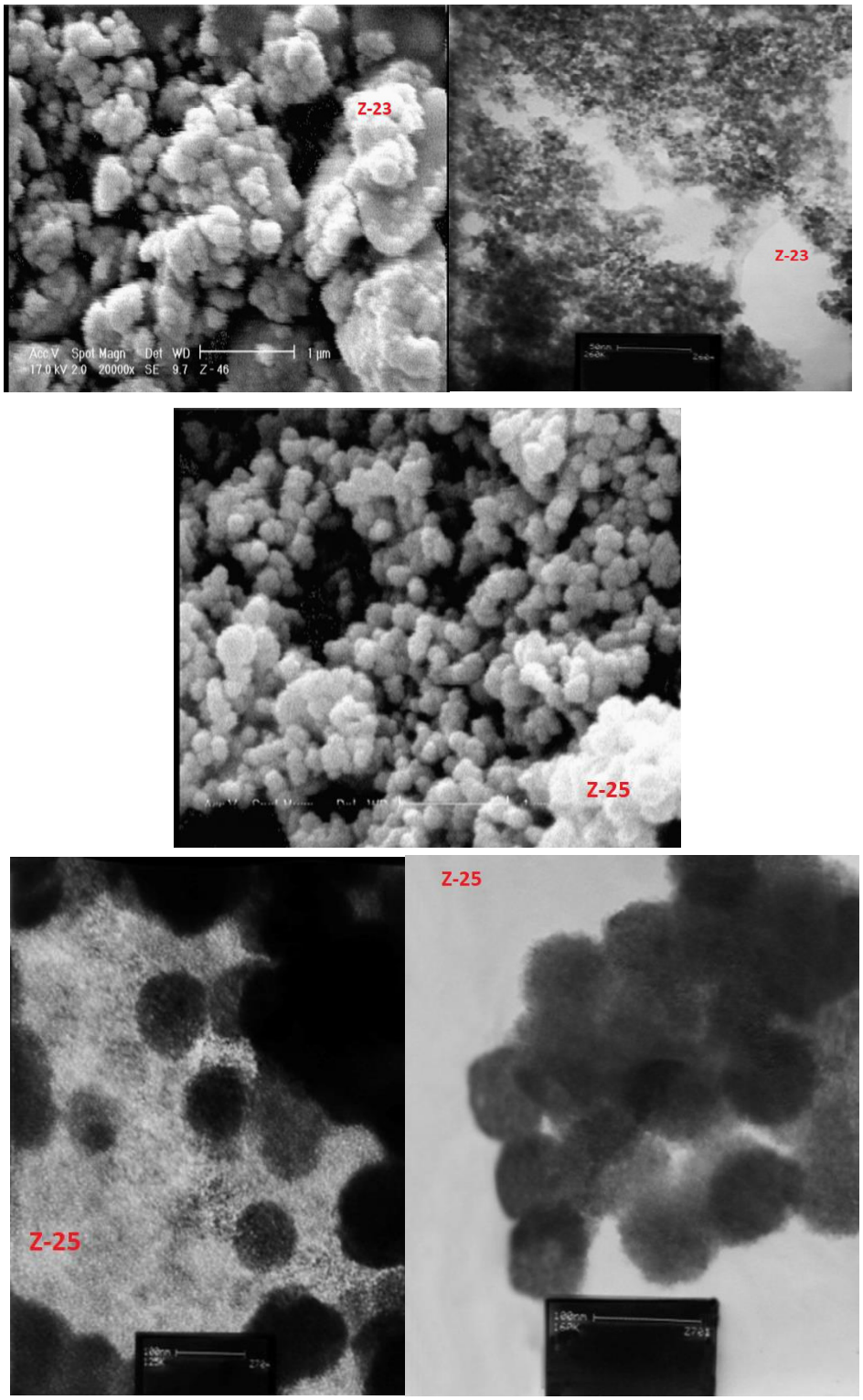

Fig. 14. SEM and TEM images of samples Z-25, Z-23.

to improve the particle size and adhesion. For this reason, the Z-23 sample was prepared using Na_2S salt as the source of the sulfide ion and the addition of reagents has been done quickly.

In addition to the decrease in the concentration of thioacetamide, the thioacetamide was rapidly added (Z-25) at high temperature (Fig. 14). As can be seen from the TEM images of these two samples, the decrease in concentration reduces the particle size to below 5 nm (Z-23).

SUMMARY AND CONCLUSION

Zinc sulfide nanoparticles were prepared by three main methods according to the literature and were investigated in the following order in this project.

1- Chemical Capping
2- Hydrothermal method
3- Reverse Micelles

Each of these three methods has its own advantages and disadvantages, in which the use of the aquatic environment and the use of coating agents are paramount. The second option is the gradual release of sulfide ions by thioacetamide without any coatings. Small particle size is one of the major indices in the third method.

Due to the fact that it is not possible to measure the particle diameter at all stages due to high cost, it is possible to obtain acceptable results by comparing SEM images and in some cases by XRD spectra.

Considering that the purpose of zinc sulfide nanoparticles in this research is to give an overview of different fabrication methods and the role of main parameters on particle size and purity of the samples. Overall, it can be concluded that in all three mentioned methods, decreasing the concentration of reactants decreases the particle diameter. Also, increasing the rate of addition of the reactants reduces the size of the produced nanoparticles. The results of SEM and TEM imaging show that the use of thioacetamide as a sulfide ion source has high reproducibility, which is a good criterion for increasing the scaling rate.

Also, the energy dispersive X RAY ANALYSIS spectra show more purity of samples made by thioacetamide in an aqueous medium than micro emulsion methods. And shows the percentage of atoms at different points on the sample surface with little error than the ZnS formula (65:32 atomic mass).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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