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Morphology-controlling synthesis of ZnS through a hydrothermal/solvthermal method

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Abstract

Different morphologies of ZnS have been synthesized by a solvothermal process, through the reaction of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $SC(NH_2)_2$ in different mixed solvents, changing the density of the surfactant ($C_{12}H_{25}SO_3Na$). The samples were characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX) techniques. The results show that the as-prepared ZnS have different morphologies, such as lamellar ZnS, smooth microspheres, roughen microspheres, plate-like ZnS and so on. So far, to our knowledge, lamellar ZnS have not been synthesized by solvothermal route before.

Keywords: Morphology-controlling; ZnS; Hydrothermal/solvthermal method; Lamellar structure

1. Introduction

ZnS is an important semiconductor compound of the II–VI groups, whose band gap is 3.66 eV at the room temperature [1]. Its excellent photoelectric conversion characteristic and luminescent properties, promise the wide use of ZnS in different fields, such as nonlinear optical device, electroluminescence, flat panel display, cathode-ray luminescence, light emitting diode, field effect transistor, solar cell, dielectric light absorbable, infrared window material, dye and catalytic agent extensively. Additionally, it can be also used in fabrication of sensors and nanomaterial laser. As a result, morphology-controlled synthesis and properties of ZnS attracted many scholars' attentions.

Recently, interest in morphology-controlled synthesis has been greatly increased, as the structures of material decide properties. Materials with different morphologies, sizes and structures have different properties. Many researchers have found that changing morphologies and size of the material may make it express some properties that common materials do not possess [2]. Zinc sulfide [3], as an important semiconductor compound of the II–VI groups, has been successfully synthesized with some particular structures like quantum dots [4], nanorods [5,6], nanowires [7], hollow spheres [8], nanosheets [9], and so on. Some methods [10–12] have been developed to prepare the ZnS with different phases and morphologies, among which the hydrothermal method or solvothermal route [13–16] show many advantages such as mild reaction conditions, less energy consumption, simple equipment required, and the most important one is large number of variable factors to control the sample morphology, because the reaction path is very sensitive to the experimental conditions such as source species, surfactant molecules, reaction temperature, time and solvent.

Herein, a solvothermal approach was developed to prepare different morphologies of ZnS, starting from $Zn(CH_3COO)_2{\cdot}2H_2O$ with $SC(NH_2)_2$ in mixed different solvents, using $C_{12}H_{25}SO_3Na$ as the surfactant or without the surfactant. Simultaneously, the effects of ethylenediamine and surfactant on morphology-controlling of ZnS have been also researched.

2. Experimental procedure

In our work, different morphologies of ZnS have been synthesized by a solvothermal process, though the reactions of $Zn(CH_3COO)_2{\cdot}2H_2O$ with $SC(NH_2)_2$ in mixed different solvents, changing density of the surfactant ($C_{12}H_{25}SO_3Na$).

This approach has very positive significance to improve microstructures of ZnS.

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Table 1
Material of different experimental groups' type and composition.

Number	$Zn(CH_3COO)_2{\cdot}2H_2O$ (mol/L)	$SC(NH_2)_2$	Solvent	$C_{12}H_{25}SO_3Na$ (mol/L)
#1	0.125	0.125	Ethylenediamine	0.07
#2	0.125	0.125	Water	0.07
#3	0.125	0.125	Water	0
#4	0.125	0.125	Ethylenediamine/water (1:1 vol.%)	0
#5	0.125	0.125	Ethylenediamine/water (1:1 vol.%)	0.035
#6	0.125	0.125	Ethylenediamine/water (1:1 vol.%)	0.07
#7	0.125	0.125	Ethylenediamine/water (1:1 vol.%)	0.105

All of the reactants were of analytical grade and were used without any further purification. In this study, seven experimental groups were divided according to the different compositions, while ensuring the time and temperature keep consistent in each experimental procedure like Table 11. Take #6 for example, concrete experimental procedure is introduced. 0.125 mol/L of zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and 0.125 mol/L of thiourea [$SC(NH_2)_2$] were dissolved in the mixed solvent of ethylenediamine/H_2O (1:1 vol.%), then $C_{12}H_{25}SO_3Na$ was added into the solution (concentration of 0.07 mol/L). The mixture were stirred vigorously for 60 min, then transferred into a Teflon-lined autoclave up to 80% of the total volume. The autoclave was sealed, maintained at 160 °C for 12 h, and then cooled to room temperature naturally. At last, the white product was collected by filtration, washed with distilled water and ethanol, and then dried at 60 °C in vacuum (Table 1).

Products were characterized by powder XRD on a Model D8 Advance. EDAX and SEM were performed on a JSM-6700F scanning electron microscopy.

3. Results and discussion

3.1. Preparation of ZnS powder

Using zinc acetate $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.125 mol/L) as zinc source, thiourea $SC(NH_2)_2$ (0.125 mol/L) as sulfur source, hydrothermal reactions occur, in solvents of ethylenediamine/water (1:1 vol.%) with $C_{12}H_{25}SO_3Na$ (as the surfactant (0.07 mol/L)) or pure water (without surfactant), respectively, at 160 °C for 12 h.

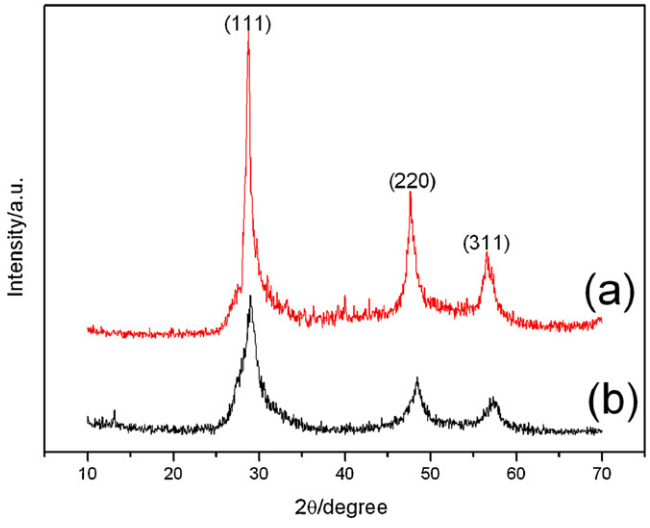

Fig. 1. XRD patterns of #6 (ethylenediamine–water–0.07 mol/L surfactant) system (a) and #3 (water) system (b).

In the case of #6 system (ethylenediamine–water–0.07 mol/L surfactant) and #3 system (water), XRD patterns of the as-prepared products are shown in Fig. 1. All the peaks can be indexed to cubic phase zinc blende crystalline (sphalerite) phase of ZnS (JCPDS No: 01-0792). The three strong peaks with 2θ values of 28.58, 47.56 and 56.40 correspond to the three crystal plane of (1 1 1), (2 2 0) and (3 1 1) of zinc blende ZnS, respectively. No other characteristic peaks of impurities can be observed, which indicates a high purity and well crystallinity of these ZnS. As the XRD patterns show, the diffraction peaks of #6 system are more obvious and sharper than those of #3 system, which indicates the gradual formation of ZnS crystals. From the obtained peak width of XRD pattern, by calculating, we conclude that the size of ZnS crystals of #6 system is bigger than that of #3 system.

The representative EDAX spectrums of #6 system (ethylenediamine–water–0.07 mol/L surfactant) and #3 system (water) are shown in Fig. 2 a and b. The results obtained from EDAX of the two systems are in accord with the results of XRD. It reveals the products are made up of Zn and S, and the average atomic ratio of Zn/S is 1.15:1 and 1.12:1, respectively, which are consistent with ZnS. The signal of C and O is probably from unavoidable surface-adsorption of the sample exposed to air during sample processing.

The size and shape of the products were identified by SEM. SEM images of the products with a low and high magnification are shown in Fig. 3 a and b for #6 system (ethylenediamine–water–0.07 mol/L surfactant), Fig. 3 c and d for #3 system (water), respectively. To #6 system, the low magnification SEM image (Fig. 3 a) presents that the as-prepared products show sheet morphologies with surface acreage ranging from about 1 μm × 1 μm–5 μm × 5 μm. In the high magnification SEM image (Fig. 3 b) which offer a clearer view of the surface morphology, the products exhibit a typical laminate structure, which is composed of several sheets. The thickness of each sheet is about 50–200 nm and the distance of them is about 10–50 nm. The SEM images of Fig. 3 c and d show that the products of #3 system exhibit spherical morphology with about 0.5–3 μm in diameters which are smaller than the laminate structure of ZnS, and the surface is smooth. It is in accord with the widening of the peaks of X-ray diffraction in Fig. 1. The SEM images

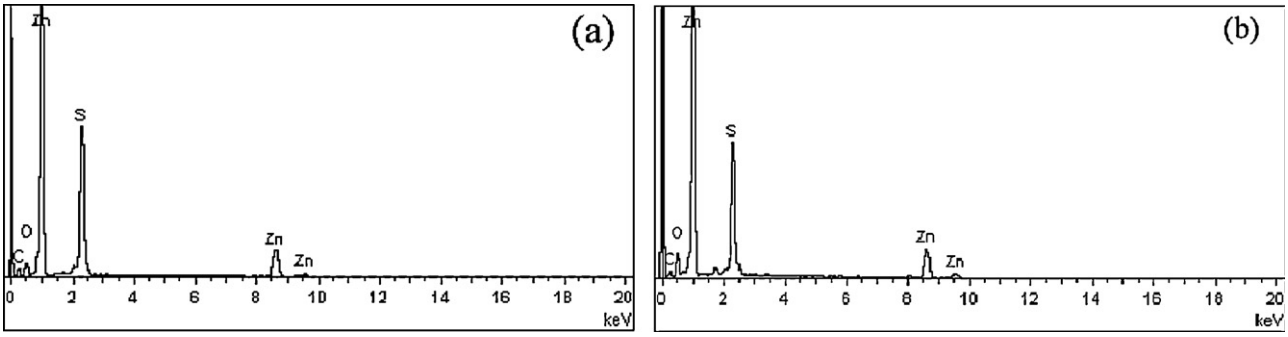

Fig. 2. EDAX spectrums of #6 (ethylenediamine–water–0.07 mol/L surfactant) system (a) and #3 system (water) (b).

indicate that ethylenediamine and $C_{12}H_{25}SO_3Na$ play an important role in the morphology of the products.

The results show that the synthesis condition we use to obtain ZnS powders is feasible. Solvent and surfactant have obvious effects on morphology of ZnS powders. In #3 system (water), spherical morphology with smooth surface of ZnS powders was obtained, while in #6 system (ethylenediamine–water–0.07 mol/L surfactant), laminate structure of the ZnS powders was obtained.

3.2. Effects of solvent on the morphology of ZnS

As we known, morphology is sensitive to the solvent. So we will discuss the effects on the morphology of ZnS with changing solvent. Experimental procedure is as follows: using #2 system (water–0.07 mol/L surfactant), #6 system (ethylenediamine–water–0.07 mol/L surfactant), #1 system (ethylenediamine–0.07 mol/L surfactant) as solvent, respectively, different products are obtained through the reactions of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $SC(NH_2)_2$ (0.125 mol/L) at 160 °C, for 12 h.

The XRD patterns of the as-prepared products are shown in Fig. 4. The peaks of different solvents are in accord with characteristic peaks of ZnS, which indicates that changing the content of solvents has no effect on crystalline of the as-prepared products. Therefore, we focus our investigations on the effects of ZnS's morphology.

SEM images of the products with a high magnification are shown in Fig. 5a for #2 system (water–0.07 mol/L surfactant), Fig. 5b for #1 system (ethylenediamine–0.07 mol/L surfactant). And those of #6 system (ethylenediamine–water–0.07 mol/L surfactant) are shown in Fig. 3a and b. When using water as solvent (#2 system), the as-prepared products are irregular microspheres. Compared with using water as solvent but

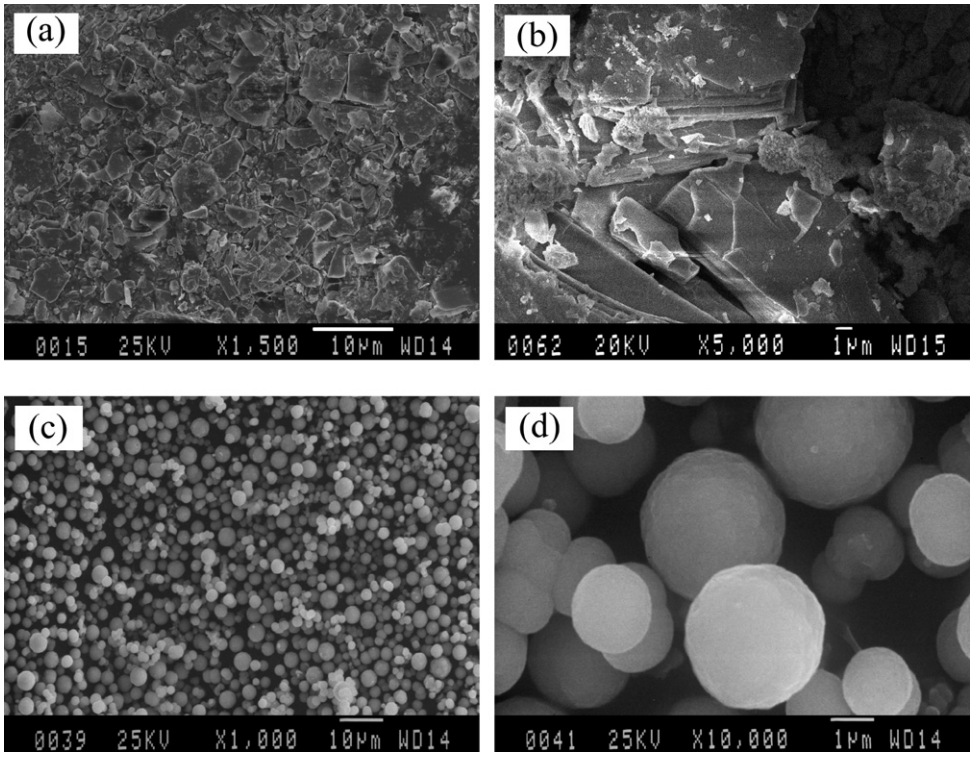

Fig. 3. SEM images of #6 system (ethylenediamine–water–0.07 mol/L surfactant) (a) and (b) and #3 system (water) (c) and (d).

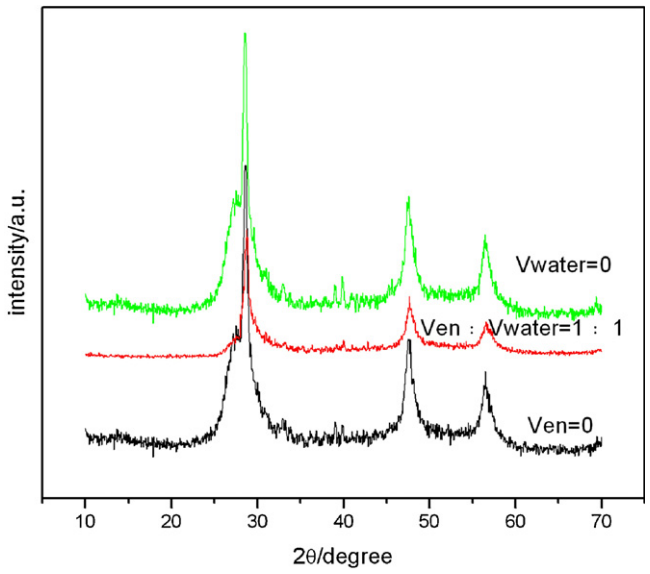

Fig. 4. XRD patterns of #2 system (water–0.07 mol/L surfactant), #6 system (ethylenediamine–water–0.07 mol/L surfactant), #1 system (ethylenediamine–0.07 mol/L surfactant).

without surfactant of #3 system, the surface of #2 system is not smooth but with some ditches, and diameters of the microspheres are not homogeneous. It may be due to the existence of surfactant. Without lamellar structure observed in Fig. 5a indicates that ethylenediamine plays an important role on the formation of lamellar structure. From the SEM images of #1 system (ethylenediamine–0.07 mol/L surfactant) in Fig. 5b, it can be noticed that most of the as-prepared products are microspheres, and the remaining ones are lamellar. Compared with #2 system, we concluded that surfactant also has an impact on the formation of lamellar structure. In Fig. 3a and b, there are many lamellar structures, and the reason is as the presence of water makes the surfactant combined better with solvent to form lamellar templates.

The results show that when changing the kinds of solvent, the morphologies of #2 system, #6 system, #1 system are irregular and rough microspheres, lamellar structure, microspheres with a small amount of lamellar structures, respectively. Specific formation mechanism will be discussed below.

3.3. Effects of concentration of surfactant on the morphology of ZnS

From the previous experiment, we know surfactant plays an important role on the morphology formation of ZnS. So we will discuss the effects of different surfactant concentrations on the morphology of ZnS. The experimental procedure is as follows: 0.125 mol/L of zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and 0.125 mol/L of thiourea [$SC(NH_2)_2$] were dissolved in the mixed solvent of ethylenediamine/H_2O (1:1 vol.%), then $C_{12}H_{25}SO_3Na$ was added into the solution (concentrations of 0 mol/L, 0.035 mol/L, 0.07 mol/L, 0.105 mol/L). The mixture were stirred vigorously for 60 min, then transferred into a Teflon-lined autoclave up to 80% of the total volume. The autoclave was sealed, maintained at 160 °C for 12 h, and then cooled to room temperature naturally.

XRD patterns of each system's products are shown in Fig. 6. It can be well observed that products of different surfactant concentrations have the same crystal structure of ZnS, which indicates that different surfactant concentrations have no effects on crystalline of ZnS. As the surfactant concentration increased, the size of crystal grain increased gradually.

SEM images of different surfactant concentrations (0 mol/L, 0.035 mol/L, 0.105 mol/L) are shown in Fig. 7. In Fig. 7 a, without surfactant, small lamellar structures are observed. Comparing with the smooth microspheres of Fig. 3c and d (water), it can be drawn that ethylenediamine plays an important role on forming lamellar structures. Therefore, combining the lamellar structures of Fig. 3a and b (ethylenediamine–water–0.07 mol/L surfactant) with the irregular microspheres of Fig. 5a (water–0.07 mol/L surfactant), it can be drawn that lamellar templates of the lamellar ZnS are generated from the interaction of ethylenediamine and surfactant in template. The microspheres which are made by shaped of rod and tube are obtained. This also proves that surfactant template plays the guiding role of the morphology of ZnS. It bas been reported that [16] when the surfactant concentration exceeds 0.07–0.105 mol/L, the lamellar morphology disappeared, then the bulk morphology with a certain thickness are formed. The bulk morphology is obtained because of the formed bulk template when the surfactant concentration reaches a certain value.

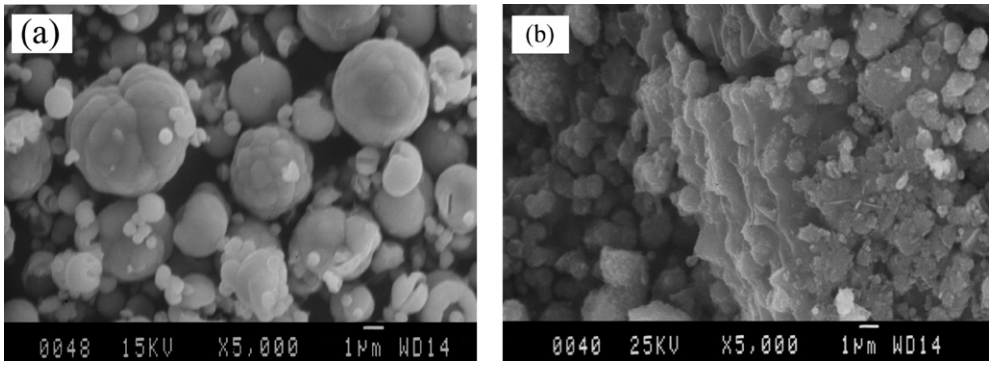

Fig. 5. SEM images of #2 system (water–0.07 mol/L surfactant) (a) and #1 system (ethylenediamine–0.07 mol/L surfactant).

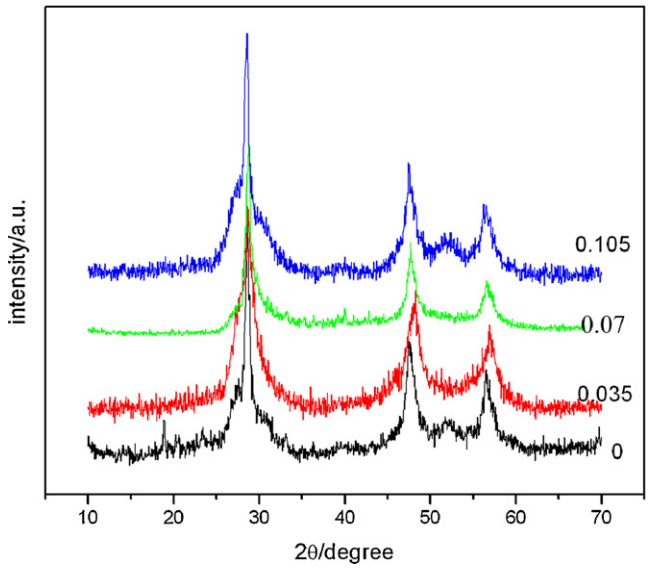

Fig. 6. XRD patterns of different surfactant's concentrations (0 mol/L, 0.035 mol/L, 0.07 mol/L, 0.105 mol/L).

The results show that different surfactant concentrations have no effect on crystalline of ZnS, but impact the morphologies. When the surfactant concentrations are 0 mol/L, 0.035 mol/L, 0.07 mol/L, 0.105 mol/L, the morphologies are small lamellar, flower-shaped microspheres, lamellar, bulk, respectively.

3.4. Lamellar ZnS

From the above we can see that using $C_{12}H_{25}SO_3Na$ as the surfactant, the lamellar zinc sulfide was obtained by a solvothermal method, through the reaction of $Zn(CH_3COO)_2{\cdot}2H_2O$ with $SC(NH_2)_2$ in mixed solvents of ethylenediamine (en) and water. In Fig. 3a and b for #6 system (ethylenediamine–water–0.07 mol/L surfactant), it offers a clearer view of the surface morphology. When using the mixture of water and ethylenediamine as the reaction solvent, ethylenediamine will guide the growth of the crystal structure by flake to form the lamellar structure. As is reported, this is because ethylenediamine and Zn^{2+} have a very strong binding capacity and Lewis base [17]. Therefore, the mechanism of lamellar ZnS is as follows:

When mixing the reaction solution together, $C_{12}H_{25}SO_3^-$ and Zn^{2+} will form a group because of the combined electrostatic force, then putting the solution into the reactor for heating. As the temperature rising, Zn^{2+} and S^{2-} are reacting to form ZnS particles, which are gathered on $C_{12}H_{25}SO_3^-$. If there is no ethylenediamine, template formed by surface active agents will curl to form a kind of smooth surface microspheres. But when using water and ethylenediamine as reaction solvent, the structure of ZnS crystal is sheet because of the guiding of ethylenediamine. With the effect of surface active agent, lamellar ZnS are obtained.

The whole process can be summarized as (*Note*: EDTA was strongly alkaline) [16]:

$$SC(NH_2)_2 + 2OH^- \rightarrow CH_2N_2 + H_2O + S^{2-} \quad (3\text{-}1)$$

$$C_{12}H_{25}SO_3^- + Zn(en)_2^{2+} \rightarrow [C_{12}H_{25}SO_3Zn(en)_2]^+ \quad (3\text{-}2)$$

$$[C_{12}H_{25}SO_3Zn(en)_2]^+ + S^{2-} \rightarrow ZnS + 2en + C_{12}H_{25}SO_3^- \quad (3\text{-}3)$$

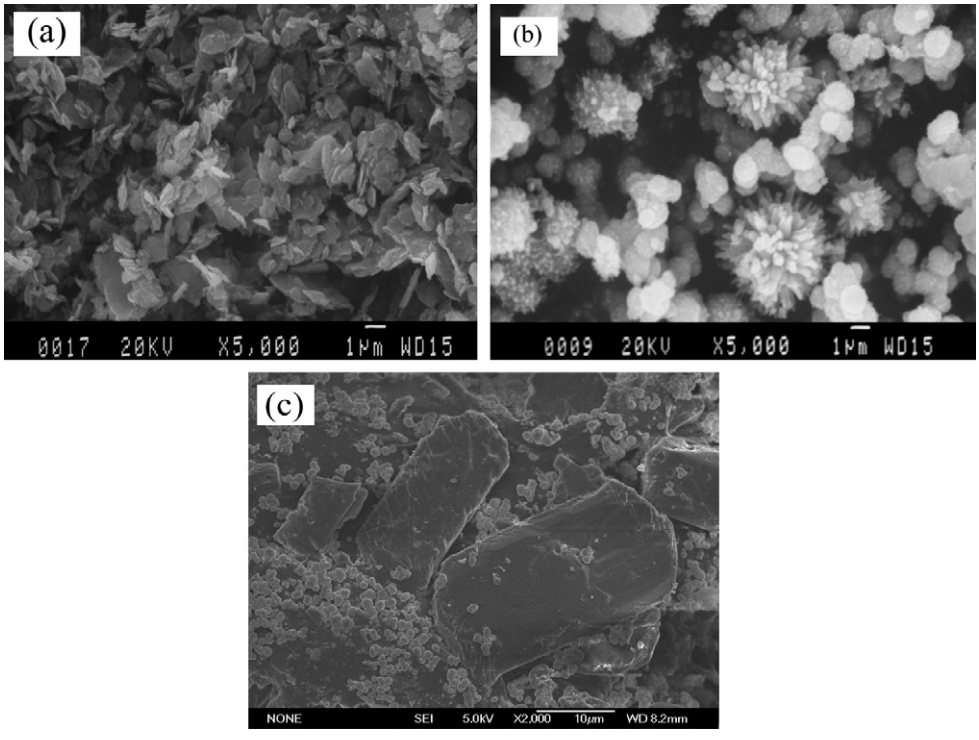

Fig. 7. SEM patterns of different surfactant's concentrations (0 mol/L, 0.035 mol/L, 0.105 mol/L).

4. Conclusions

Different morphologies of ZnS have been synthesized by a solvothermal process, through the reactions of $Zn(CH_3COO)_2{\cdot}2H_2O$ with $SC(NH_2)_2$ in mixed different solvents, changing the concentration of the surfactant ($C_{12}H_{25}SO_3Na$), at 160 °C for 12 h. In #3 system (water) and #6 system (ethylenediamine–water–0.07 mol/L surfactant), the ZnS crystals are spherical morphology with smooth surface and laminate structure, respectively. When changing the kinds of solvent, the morphologies of #2 system (water–0.07 mol/L surfactant) and #1 system (ethylenediamine–0.07 mol/L surfactant) are irregular and roughen microspheres, microspheres with a small amount of lamellar structures, respectively. When the surfactant concentrations are 0 mol/L, 0.035 mol/L, 0.07 mol/L, 0.105 mol/L, the morphologies are small lamellar, flower-shaped microspheres, lamellar, bulk, respectively. Lamellar ZnS are obtained by the effect of both surface active agents and ethylenediamine. Template formed by surface active agents is the basic reason to get lamellar material. Ethylenediamine, as solvent with the effect of surface active agents template, guides ZnS to form sheet grains and prevents template to curl.

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References

[1] X. Wu, K.W. Li, H. Wang, Facile synthesis of ZnS nanostructured spheres and their photocatalytic properties, J. Alloys Compd. 487 (2009) 537–544.
[2] A.P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, Science 271 (1996) 933.
[3] T. Trindate, P.O. Brien, N.L. Pickett, Nanocrystalline semiconductors: synthesis, properties, and perspectives, Chem. Mater. 13 (2001) 3843.
[4] Y.D. Li, Y. Ding, Y. Zhang, Y.T. Qian, Photophysical properties of ZnS quantum dots, J. Phys. Chem. Solids 60 (1999) 13.
[5] M. S-Niasari, M.R. L-Estarki, F. Davar, Controllable synthesis of wurtzite ZnS nanorods through simple hydrothermal method in the presence of thioglycolic acid, J. Alloys Compd. 475 (2009) 782.
[6] H.M. Wang, Z. Chen, Q. Cheng, L.X. Yuan, Solvothermal synthesis and optical properties of single-crystal ZnS nanorods, J. Alloys Compd. 478 (2009) 872.
[7] L.H. Dong, Y. Chu, Y.P. Zhang, Microemulsion-mediated solvothermal synthesis of ZnS nanowires, Mater. Lett. 61 (2007) 4651.
[8] X.Z. Liu, J.H. Cui, L.P. Zhang, W.C. Yu, F. Guo, Y.T. Qian, A solvothermal route to semiconductor ZnS micrometer hollow spheres with strong photoluminescence properties, Mater. Lett. 60 (2006) 2465.
[9] X.Y. Wang, Y.C. Zhu, H. Fang, M.F. Zhang, B.J. Xi, H.Z. Wang, Y.T. Qian, Growth of ZnS microfans and nanosheets: controllable morphology and phase, J. Cryst. Growth 310 (2008) 2525.
[10] C. Kaito, Y. Saito, K. Fujita, A new preparation method of ultrafine particles of metallic sulfides, Jpn. J. Appl. Phys. 26 (1987) 1973.
[11] M. Abboudi, A. Mosset, Synthesis of d transition metal sulfides from amorphous dithiooxamide complexes, J. Solid State Chem. 109 (1994) 70.
[12] V. Stanic, T.H. Etsell, A.C. Pierre, R.J. Mikula, Sol–gel processing of ZnS, Mater. Lett. 31 (1997) 35.
[13] L.C. Wang, L.Y. Chen, T. Luo, Y.T. Qian, A hydrothermal method to prepare the spherical ZnS and flower-like CdS microcrystallites, Mater. Lett. 60 (2006) 3627.
[14] H. Deng, C. Chen, Q. Peng, Y.D. Li, Formation of transition-metal sulfide microspheres or microtubes, Mater. Chem. Phys. 100 (2006) 224.
[15] S.H. Yu, M. Yoshimura, J.M.C. Moreno, T. Fujiwara, T. Fujino, R. Teranishi, In situ fabrication and optical properties of a novel polystyrene/semiconductor nanocomposite embedded with CdS nanowires by a soft solution processing route, Langmuir 17 (2001) 1700.
[16] X. Wang, Y.D. Li, Selected control hydrothermal synthesis of alpha and beta MnO_2 nanowires, J. Am. Chem. Soc. 124 (2002) 2880–2881.
[17] G.H. Yue, P.X. Yan, D. Yan, J.Z. Liu, D.M. Qu, Q. Yang, X.Y. Fan, Synthesis of two-dimensional micron-sized single-crystalline ZnS thin nanosheets and their photoluminescence properties, J. Cryst. Growth 293 (2006) 428–432.