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Controlled synthesis and morphology evolution of nickel sulfide micro/nanostructure

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1. Introduction

Chalcogenide nanostructure has attracted considerable attention owing to the unique optical, electrical, and magnetic properties [1–9]. As a family member of the chalcogenide nanomaterial, nickel sulfide has shown excellent application in catalysts [10-13], photoconduction [14], rechargeable lithium ion battery cathode [15–17], and solar storage [18]. Up to now, three main approaches including solid-state reactions, vapor phase reactions and soft chemistry method have been developed successfully to fabricate nickel sulfide nanostructures [19–22], and different morphologies of nickel sulfide nanostructures such as nanoneedles [23], nanorods [24], nanotubes [25] and core-shell structures [26] have been synthesized successfully. In particular, the hydro-/solvothermal method has been used widely, because the high purity, good dispersed, and size-controlled nickel sulfide nanostructures can be easily obtained. For example, Wang et al. have prepared hexagonal phase NiS nanobelts by hydrothermally, which were 50 nm in thickness, 70-200 nm in width and about 10 nm in length [27]; Zhao et al. have

ABSTRACT

A facile hydrothermal method has been developed for synthesis of nickel sulfide micro/nanostructure using Ni(NO₃)₂·6H₂O as nickel source, S=C(NH₂)₂ as sulfur source and 1,2-ethylenediamin/sodium dodecyl sulfate as surfactant. Different morphologies such as petal-, urchin- and sphere-like nickel sulfide structures have been synthesized by tuning the reaction time, reaction temperature, and the surfactant. The as-prepared products were characterized by X-ray diffraction, Field-emission scanning electron microscope, and Photoluminescence spectra. The relationship of the fluorescence properties with their morphology and phase was studied, and the possible growth mechanism of nickel sulfide structure was proposed based on the morphology evolution of nickel sulfide.

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successfully prepared hexagonal structured β -NiS hollow spheres by a dodecanethiol-assisted hydrothermal process [28]. However, a rational method to synthesize the morphology-controlled nickel sulfide still remains as a challenge.

In this paper, different morphologies such as petal-, urchin- and sphere-like nickel sulfide structures have been successfully synthesized by a simple hydrothermal method. The reaction effects, such as reaction time, reaction temperature, and the surfactant on the morphologies of the as-prepared products were systematically investigated. The growth mechanism of the morphology-controlled nickel sulfide has been supposed based on experiment results.

2. Experimental

2.1. Materials and physical measurements

All chemicals were analytical grade purity and used as purchased without further purification. The X-ray diffraction (XRD) pattern of the products was recorded on a Bruker AXS D8 Discover diffraction system with a Cu Kα radiation source ($\lambda = 0.15405$ nm) at a scanning rate of 0.02° /s in the 2θ range of $15-60^{\circ}$. The images of the as-prepared product were obtained on a HITACHI S-4800 field emission scanning electron microscope (FE-SEM) at 1.0 kV. The photoluminescence (PL) spectra were obtained on a Hitachi fluorescence spectrometer (F-7000) with a Xenon laser at room temperature.

2.2. Micro/nanostructure nickel sulfide prepared by hydrothermal method

Experimental details for petal-, urchin- and sphere-like nickel sulfide products were as following: Ni(NO₃)₂·6H₂O (0.5 g), S=C (NH₂)₂ (0.6525 g) and 0.2 ml of 1,2-ethylenediamine (or/and 2.0 g of sodium dodecyl sulfate) were added into 50 ml of

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Table 1

SEM images of the as-prepared products with different surfactant at 160 °C in 24 h.



distilled water with vigorous stirring. Then the mixed solution was transferred into a 100 ml Teflon-lined autoclave with 60% capacity of the total volume. The autoclave was sealed and maintained at 160 °C for 24 h. Finally, the autoclave was cooled to room temperature naturally. The precipitates were collected by centrifugation and washed with distilled water and alcohol for 3 times, respectively. Then the products were dried under vacuum at 60 °C for 10 h.

3. Results and discussion

3.1. Morphologies and structures of the as-prepared nickel sulfide products

The FE-SEM images of as-prepared products using 0.5 g of Ni(NO₃)₂·6H₂O, 0.6525 g of S=C(NH₂)₂, and 0.2 ml of 1,2-ethylenediamine (or/and 2.0 g of sodium dodecyl sulfate) were shown in Table 1. The micrometer-sized self-assembled structures products were synthesized successfully on a large scale (Table 1(a)). The petal-like nickel sulfide structures were uniform, and most of them were around 5 µm in diameter (as shown in Table 1(b)). The petals with a zigzag surface were around 2 µm in length. Table 1(c) and (d) show the nanorod urchin-like nickel sulfide structure, and the nanorods around 500 nm in diameter radiated from the center of urchin-like crystals. Table 1(e) shows the sphere-like nickel sulfide pattern with 10 µm in diameter. The detail information of the surface shows that the surface of the sphere is composed by dendrite-like nanostructures (Table 1(f)).

3.2. Morphology evolution of the petal-like nickel sulfide structure

The petal-like nickel sulfide structures were prepared when 1,2-ethylenediamine was used as surfactant. The influence factors including reaction temperature, reaction time and the concentration of 1,2-ethylenediamine effect on the morphology evolution of the petal-like structure were systematically investigated.

The effect of reaction temperature on the morphology was shown in Fig. 1. When the reaction temperature was in the range of 120-140 °C, about 2 µm nanosheet nickel sulfide spheres were obtained, and the nanosheet is 50 nm in thickness (Fig. 1(a)). When the temperature was 160 °C, perfect petal-like structures were obtained (Fig. 1(b)) and the petal shows a zigzag surface. When reaction temperature was 180 °C, the petal surface became smooth (Fig. 1(c)). XRD patterns of petal-like structures prepared at different temperature show that the morphology of nickel sulfide has close relationship to the phase (Fig. 1(d)). When the temperature was in the range of 120–140 °C, the sphere structure was pure Ni₃S₄ phase. When the temperature increased to 160 °C, the petal-like structure with zigzag surface was NiS phase. Higher reaction temperature such as 180 °C can convert all Ni₃S₄ phase to NiS phase, and then the zigzag surfaces were developed into smooth ones.

The reaction time effect on the morphology of the petal-like structure was likewise studied at $160 \degree C$ (as shown in Table 2). After 2 h reaction, the nanosheets microspheres were prepared, and the nanosheet is about 200 nm in thickness. When the reaction time extended to 8 h, petals structures were formed. It seems that the petals grow up on the surfaces of spheres. When the reaction time increased to 24 h, zigzag structured petals were formed, and scarce bumps appeared on the surface of the petals. When the reaction time was 48 h, the bumps were disappeared and the zigzag surfaces were developed into smooth.

To substantially understand the effect of 1,2-ethylenediamine on the morphology of the nickel sulfide structures, different amounts of 1,2-ethylenediamine was used in the experiments (as shown in Table 2). Only NiS nanotubes were obtained in the



Fig. 1. SEM images of the as-prepared nickel sulfide products at different temperatures (a) 120-140 °C; (b) 160 °C; (c) 180 °C; and (d) XRD pattern of the as-prepared petal-like pattern nickel sulfide at different temperature (\bigcirc indicates α -NiS peaks; \oplus indicates Ni₃S₄ peaks; Δ indicates β -NiS peaks).

 $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 g) and S=C (NH₂)₂ (0.6525 g) solution were used without surfactant. The protrudent corners were grown on the surface of the spheres when 0.05 ml of 1,2-ethylenediamine was used, which is similar with the tendency of orientation growth mechanism [29,30]. When the 1,2-ethylenediamine increased to 0.15 ml, the protrudent corners grow to petal structures obviously. When 0.2 ml of 1,2-ethylenediamine was used, petal-like structures with zigzag surface were generated, and scarce bumps were grown on the zigzag surfaces. Under similar conditions, when 1,2-ethylenediamine increased from 0.05 ml to 0.2 ml, an obvi-

Table 2

FE-SEM images of the as-prepared samples under different reaction conditions.

Time	1, 2-Ethylenediamine			
	0 ml	0.05 ml	0.15 ml	0.2 ml
2 h	_	-	_	
8 h	_	_	_	
24 h	Zjur	comm	600nm	STORE Im
48 h	_	-	_	700nm



Fig. 2. FE-SEM images of the as-prepared urchin-like nickel sulfide products at different reaction times (a) 4 h; (b) 12 h; (c) 24 h.



Fig. 3. FE-SEM images of the as-prepared sphere-like pattern nickel sulfide products at different temperatures (a) 120 °C; (b) 140 °C; (c) 160 °C.

ous morphology evolution from sphere to petal-like structure was observed.

3.3. Morphology evolution of the urchin- and sphere-like nickel sulfide structures

The urchin- and sphere-like nickel sulfide structures were prepared with different surfactant at 160 °C for 24 h. The urchin-like nickel sulfide was prepared with sodium dodecyl sulfate, and the sphere-like nickel sulfide was prepared with the co-existence of 1,2-ethylenediamin and sodium dodecyl sulfate.

As to the morphology of urchin-like nickel sulfide, the reaction time shows more profound effect than that of the reaction temperature. When the reaction time was 4 h, nanorods clusters were formed (Fig. 2(a)). When reaction time was 12 h, imperfect urchinlike structures were formed, and the nanorods radiated from the center of crystals (Fig. 2(b)). When the hydrothermal treatment time was prolonged to 24 h, entire urchin-like nickel sulfide structures were generated. The nanorods around 500 nm in diameter radiated from the center developed into the complex urchin-like structures (Fig. 2(c)).

In addition, the reaction temperature shows profound effect on the morphology of the sphere-like nickel sulfide. When the reaction temperature was 120 °C, scarce nanoparticles around 200 nm in diameter were appeared (Fig. 3(a)). When the temperature increased to 140 °C, particles around 200 nm in diameter were formed (Fig. 3(b)). Perfect sphere-like structures about 5 μ m in diameter constructed by nanorods were obtained in the range of 160–180 °C. High resolution SEM image shows that the surface of the sphere is pinaster-like structure (Fig. 3(c)).

3.4. Phase control of the microcrystal

XRD patterns of as-prepared products were shown in Fig. 4. When 1, 2-ethylenediamin was added into the solution, NiS (α and β -) and Ni₃S₄ were obtained. When sodium dodecyl sulfate was used, the products were composed of NiS₂, β -NiS and Ni₃S₄. It confirmed that Ni₃S₄ is always presented in the samples [31]. When 1,2-ethylenediamine was used as the surfactant, pure NiS phase was easily obtained. When sodium dodecyl sulfate was used as the surfactant, the NiS_2 phase was easily obtained. Therefore, the surfactants showed that which significantly effected on the phase composition. Interestingly, the broad diffraction lines existed in all samples indicated that the assembled microstructures were composed by very small particles [32] (Fig. 4). The particle size was evaluated by Scherrer formula [33]:

$$D = \frac{K\lambda}{\beta\,\cos\theta}$$

where *D* is the averaged dimension of crystallites; *K* is the Scherrer constant, (*K* = 0.89); λ is the wavelength of the CuK α_1 radiation (0.15405 nm), θ is the Bragg angle of the peak and β is the corrected half-width of the diffraction peak. The average crystalline size of petal-, urchin- and sphere-like product is about 46.0 nm, 23.9 nm, and 54.6 nm, respectively, and these small particles were assembled into the microstructures.



Fig. 4. XRD patterns of the as-prepared products (a) petal-like; (b) sphere-like; (c) urchin-like. (Δ indicates α -NiS peaks; \bullet indicates NiS₂ peaks; \bigcirc indicates Ni₃S₄ peaks; the β -NiS was not marked).



Fig. 5. Growth mechanism of the as-prepared nickel sulfide products (EN: 1,2-ethylenediamin; SDS: sodium dodecyl sulfate).

3.5. Growth mechanism of the as-prepared products

Based on the SEM and XRD results, the growth mechanisms of the nickel sulfide structures were proposed (Fig. 5). Amine molecules could serve as coordinate ligand, architecture template, and the S^{2-} attaching reagent [34]. When 1,2-ethylenediamine was used, the nanosheet spheres were prepared in the initial stage, and then petals grown on the nanosheet sphere. The SDS microspherical capsules were generated and the hydrophilic sulfonic group would absorb on the surface of the capsules when high concentration sodium dodecyl sulfate (SDS) was added in the solution. Due to the electrostatic interaction of sulfonic group with Ni²⁺, the outer surface of the capsules would be occupied by lots of Ni²⁺. The absorbed Ni²⁺ ions were converted into nickel sulfide nanorods, and then the nanorods grownradiately from the center of the urchin-like crystals [35]. Moreover, the influence of the mixed 1,2-ethylenediamine and sodium dodecyl sulfate solution was studied. The "cooperative effect" of mixed solutions of surfactants could induce the growth of pinaster-like dendrite structure [36]. Moreover, the mixed surfactant solution assisted the formation of small nanoparticles in the initial stage, and then developed into the sphere-like nickel sulfide structure.

3.6. Photoluminescence property

Previous research reported that the fluorescence spectrum was influenced by the different phases, shapes, structural complexity, and the surface/volume ratio [37]. The fluorescence property of as-prepare nickel sulfide was shown in Fig. 6. Each PL spectra of the three samples showed a sharp emission peaks at 316 nm and a broad emission peak at 386 nm (excited at $\lambda_{ex} = 277$ nm), and both of them were ultraviolet emission. The fluorescence emission of petal- and sphere-like microcrystal had a maximum at about 316 nm, and the fluorescence emission of the urchin-like microcrystal had a maximum at about 386 nm (Fig. 6). It may be attributed to NiS phase in the petal-like and sphere-like structure, and the NiS₂ phase in the urchin-like structure. So different kinds of surfactant could induce different phases, shapes, and defects density



Fig. 6. Fluorescence spectra of the as-prepared products (a) petal-like pattern structure; (b) urchin-like pattern microstructure; (c) sphere-like pattern microstructure.

etc., which might be responsible for the differences in the PL spectra [38,39].

4. Conclusions

In summary, petal-, urchin- and sphere-like nickel sulfide microstructures were prepared successfully via a facile hydrothermal method. The reaction parameters such as reaction temperature, reaction time and the surfactants played critical roles in determining the morphology of nickel sulfide nanostructures. Based on the experiment results, a possible growth mechanism of nanostructures had been proposed. Moreover, the relationships of the fluorescence properties of microcrystal with their morphologies and phase were studied.

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References

- M. Salavati-Niasari, M. Bazarganipour, F. Davar, J. Alloys Compd. 499 (2010) 121–125.
- [2] X.H. Kong, T.J. Lou, Y.D. Li, J. Alloys Compd. 390 (2009) 236-239.
- [3] M. Salavati-Niasari, D. Ghanbari, F. Davar, J. Alloys Compd. 488 (2009) 442–447.
 [4] M. Salavati-Niasari, F. Davar, M. Reza Loghman-Estarki, J. Alloys Compd. 481 (2009) 776–780.
- [5] M. Salavati-Niasari, F. Davar, M. Mazaheri, J. Alloys Compd. 470 (2009) 502–506.
- [6] M.Y.C. Teo, S.A. Kulinich, O.A. Plaksin, A.L. Zhu, J. Phys. Chem. A 12 (2010) 4173-4180.
- [7] B.Y. Wan, C.G. Hu, Y. Xi, J. Xu, X.S. He, Solid State Sci. 12 (2010) 123-127.
- [8] S.A. Khan, F.A. Al-Agel, A.S. Faidah, S.J. Yaghmour, A.A. Al-Ghamdi, Mater. Lett. 64 (2010) 1391–1393.
- [9] P.A. Chate, P.P. Hankare, D.J. Sathe, J. Alloys Compd. 505 (2009) 140-143.
- [10] K.M. Abraham, J.E. Ellion, J. Electrochem. Soc. 131 (1984) 2207–2211.
- [11] H. Vandenborre, Ph. Vermeiren, R. Leysen, Electrochem. Acta 29 (1984) 297-301.
- [12] W.M. Kriven, J. Am. Ceram. Soc. 71 (1988) 1021-1030.
- [13] A. Olivas, J. Cruz-Reyes, V. Petranovskii, M. Avalos, S. Fuentes, J. Vac. Sci. Technol. A 16 (1998) 3515–3520.
- [14] S.D. Sartale, C.D. Lokhande, Mater. Chem. Phys. 72 (2001) 101.

- [15] S.C. Hana, H.S. Kima, M.S. Songa, J.H. Kima, H.J. Ahnb, J.Y. Lee, J. Alloys Compd. 351 (2003) 273–278.
- [16] J. Cui, Z. Gao, Acta Chim. Sin. 54 (1996) 838-845 (in Chinese).
- [17] S.C. Han, K.W. Kim, H.J. Ahn, J.H. Ahn, J.Y. Lee, J. Alloys Compd. 361 (2003) 247–251.
- [18] A.M. Fernandez, M.T.S. Nair, P.K. Nair, Mater. Manuf. Process. 8 (1993) 535.
- [19] R. Coustal, J. Chem. Phys. 38 (1958) 277.
- [20] D. Delafosse, P. Barret, C. R. Acad. Sci. 252 (1961) 888.
- [21] L.Z. Zhang, J.C. Yu, M. Mo, L. Wu, Q. Li, K.W. Kwong, J. Am. Chem. Soc. 126 (2004) 8116–8117.
- [22] B. Zhang, X.C. Ye, W. Dai, W.Y. Hou, Y. Xie, Chem. Eur. J. 12 (2006) 2337.
- [23] D.L. Chen, L. Gao, J. Cryst. Growth 262 (2004) 554–560.
- [24] ShenF G.Z., D. Chen, K.B. Tang, C.H. An, Q. Yang, Y.T. Qian, J. Solid State Chem. 173 (2003) 227–231.
- [25] W. Wang, S.Y. Wang, Y.L. Gao, K.Y. Wang, M. Liu, Mater. Sci. Eng. B 133 (2006) 167–171.
- [26] S. Huang, K.D.M. Harris, E. Lopez-Capel, D.A.C. Manning, D. Rickard, Inorg. Chem. 48 (2009) 11486–11488.
- [27] L.L. Wang, Y.C. Zhu, H.B. Li, Q.W. Li, Y.T. Qian, J. Solid State Chem. 183 (2010) 223-227.
- [28] P.T. Zhao, Q.M. Zeng, K.X. Huang, Mater. Lett. 63 (2009) 313-315.
- [29] Y. He, W.B. Sang, J. Nanopart. Res. 7 (2005) 307-311.
- [30] X.W. Wang, G.T. Fei, X.J. Xu, J. Phys. Chem. B 109 (2005) 24326-24330.
- [31] A. Ghezelbash, M.B. Sigman Jr., B.A. Korgel, Nano Lett. 4 (2004) 537-542.
- [32] Rashi Mathur, D.R. Sharma, S.R. Vadera, GuptaF S.R., Nanostruct. Mater. 11 (1999) 677–686.
- [33] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Material, John Wiley & Sons, 1974.
- [34] G. Beobide, O. Castillo, A. Luque, Inorg. Chem. 45 (2006) 5367-5382.
- [35] X.C. Song, Y. Zhao, Y.F. Zheng, Cryst. Growth Des. 7 (2007) 159-162.
- [36] L.M. Qi, J. Li, J.M. Ma, Adv. Mater. 14 (2002) 300-303.
- [37] L.L. Wang, Y.C. Zhu, J. Solid State Chem. 183 (2010) 223-227.
- [38] B.Y. Jung, N.Y. Kim, C. Lee, C.K. Hwangbo, Appl. Opt. 41 (2002) 3312-3318.
- [39] B.X. Li, Y. Xie, Y. Xu, C.Z. Wu, Z.Q. Li, J. Solid State Chem. 179 (2006) 56-61.