

丙烯酰胺辅助溶剂热技术调控硫化镍的物相及形貌

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摘要: 以硝酸镍和硫脲为原料、乙二醇为溶剂、丙烯酰胺作为表面活性剂, 采用溶剂热技术制备了立方相 NiS_2 、六方相 $\alpha\text{-NiS}$ 和菱形 $\beta\text{-NiS}$ 空心球, 并用 XRD 及 TEM 对产物进行了表征。结果显示: 丙烯酰胺能够有效调控硫化镍的物相组成和形貌结构。最后利用异相晶化及卷曲机理(rolling-up mechanism)解释了 $\beta\text{-NiS}$ 空心微球的形成过程。

关键词: 丙烯酰胺; 溶剂热; 硫化镍; 空心微球

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Phase and Shape Control for Nickel Sulfides by Acrylamide-Assisted Solvothermal Route

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Abstract: A series of single-phase nickel sulfides, such as cubic NiS_2 , hexagonal $\alpha\text{-NiS}$ and rhombohedral $\beta\text{-NiS}$, were synthesized in ethylene glycol through an acrylamide-assisted solvothermal process by using thiourea and nickel nitrate as the starting materials. The product was characterized by XRD and TEM. The results show that the surfactant acrylamide plays an important role in controlling the phase composition and morphology of nickel sulfides. The formation of $\beta\text{-NiS}$ hollow nanospheres with cross-linked structure could be explained by the heterogeneous crystallization and rolling-up mechanism.

Key words: acrylamide; solvothermal; nickel sulfide; hollow sphere

0 Introduction

In recent years nickel sulfide has attracted considerable attention because of its unique attributes as a metal-insulator, a paramagnetic-antiferromagnetic transition material, a catalyst for hydrodenitrogenation and hydrosulfurization, and a transformation toughener in window glass, as well as its potential application in IR detectors, rechargeable lithium battery and solar storage^[1-5]. Nickel sulfide contains a variety of phases including NiS , NiS_2 , $\beta\text{-Ni}_3\text{S}_2$, $\alpha\text{-Ni}_{3+x}\text{S}_2$,

$\text{Ni}_4\text{S}_{3+x}$, Ni_6S_5 , Ni_7S_6 , Ni_9S_8 and Ni_3S_4 ^[6]. Of the binary nickel sulfides, NiS exhibits a low-temperature rhombohedral $\beta\text{-NiS}$ and a high-temperature hexagonal $\alpha\text{-NiS}$ ^[7]. NiS_2 holds a triclinic phase and a cubic phase^[8]. Here we choose NiS and NiS_2 as the subject of investigation because of their growing importance in industry. As reported, a variety of techniques have been developed to synthesize nickel sulfide nanocrystals with different morphologies including nanoparticles, nanorods, nanoprisms, nanoneedles, hollow spheres, flower-like architectures, urchin-like nanocrystallines,

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layer-rolled structures, etc.^[9-16]. Among them, hydrothermal or solvothermal method is regarded as a very effective and potential soft-chemistry route to tune the architectures of nickel sulfides. Qian et al.^[8] prepared NiS nanobelts and NiS₂ microspheres hydrothermally. Yang et al.^[11] fabricated cubic NiS₂ dodecahedrons and microspheres via solvothermal synthesis. Li et al.^[12] obtained NiS hollow microspheres through a solvothermal process. Huang et al.^[16] obtained β -NiS hollow spheres consisting of nanoflakes hydrothermally. Though great progress has been made in shape and size-controlled growth of nickel sulfides, the precise modulation of the phase and morphology by controlling the reaction process remains a challenge. Herein we demonstrate an acrylamide-assisted solvothermal route to continuously synthesize cubic NiS₂ solid spherical particles, hexagonal α -NiS aggregation and rhombohedral β -NiS hollow sphere. A possible formation mechanism of β -NiS hollow spheres with cross-linked structure is also presented.

1 Experimental

In a typical procedure, different molar ratios of acrylamide to Ni(NO₃)₂·4H₂O (acrylamide: Ni²⁺) (the amount of Ni(NO₃)₂·4H₂O was always 1 mmol) were dissolved into 25 mL ethylene glycol. After 8 mmol of thiourea (Tu) was added and completely dissolved into the above solution, the mixture was transferred into a 45 mL Teflon-lined autoclave, and reacted solvothermally at 220 °C for 24 h. Then the system was cooled to room temperature naturally. The resultant black precipitate was collected by centrifugation, washed with distilled water and absolute ethanol for several times. Finally the black product was dried at 80 °C for 5 h before use.

X-ray diffraction analysis was carried out on a Bruker D8 Advance diffractometer (German, 40 kV, 40 mA) with graphite monochromatized Cu K α radiation ($\lambda=0.154\ 06\ \text{nm}$) at a step size of 0.02° and a scanning speed of 3°min⁻¹ in the range of $2\theta=20^\circ\sim 70^\circ$. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1200 transmission electron microscope working at an accelerating voltage

of 100 kV.

2 Results and discussion

Fig.1 shows the XRD patterns for samples prepared with a typical synthesis procedure with fixed molar ratio of Tu to Ni²⁺(8:1) and varied molar ratio of acrylamide to Ni²⁺. When acrylamide was absent, almost all of the peaks are identified as cubic NiS₂ with the lattice constant (a) of 0.570 8 nm, in agreement with the data in PDF No. 65-3325. Only some negligible peaks belong to the diffraction of hexagonal α -NiS. Keeping n (acrylamide): n Ni²⁺ ratio below 1:1, cubic NiS₂ is still the major phase. Increasing acrylamide: Ni²⁺ molar ratio up to 3:1 or 5:1, hexagonal α -NiS occurs as the dominant phase. When acrylamide: Ni²⁺ ratio is raised to 25:1, all peaks can be readily indexed to (100), (101), (102) and (110) diffraction of hexagonal α -NiS with cell parameters a of 0.342 3 nm and c of 0.533 2 nm, in consistent with the data in PDF No. 02-1280. Upon increasing acrylamide: Ni²⁺ molar ratio up to 50:1, the characteristic peaks of rhombohedral β -NiS occur. With a further increase in acrylamide: Ni²⁺ molar ratio, the diffraction peaks of β -NiS gradually become stronger while those of α -NiS are weakened. When acrylamide: Ni²⁺ molar ratio is elevated beyond 200:1, the characteristic peaks of α -NiS completely disappear and the diffraction peaks obtained are well matched to the rhombohedral structure of β -NiS (PDF No.12-0041) with cell constants a of 0.962 8 nm and c of 0.315 2 nm. The above results imply that a suitable

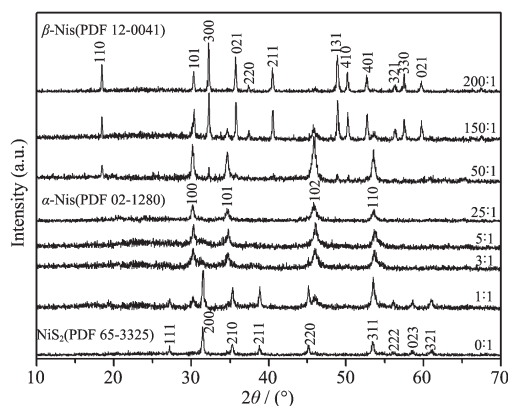


Fig.1 XRD patterns for the samples synthesized in a typical procedure with different molar ratios of acrylamide to nickel nitrate

amount of acrylamide plays a critical role in the formation of nickel sulfides with different crystalline structure and compositions.

The morphology of the samples synthesized in a typical procedure is illustrated by TEM images (Fig.2). When acrylamide is absent (Fig.2a), the product consists of uniform spherical particles with a diameter of about 50 nm. Upon increasing acrylamide: Ni^{2+} molar ratio to above 25:1 (Fig.2b), the product is

spherical and uneven. The large particles are composed of the aggregation of nanoparticles with 10~30 nm in diameter. When acrylamide: Ni^{2+} ratio is further increased beyond 200:1, the product is hollow sphere with a diameter of 100~150 nm (Fig.2c). The strong contrast between the dark edge and pale center is evident for the hollow nature of the spheres^[17]. More interestingly, the TEM photographs also reveal that the hollow sphere is cross-linked with each other.

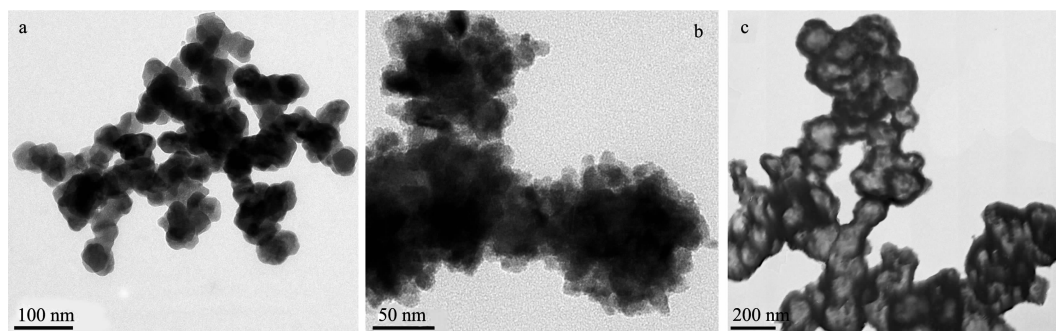


Fig.2 TEM images for samples synthesized in a typical procedure with different molar ratios of acrylamide to Ni^{2+}

The above results show that the phase and morphology of nickel sulfides can be tuned from cubic NiS_2 solid ball to hexagonal α - NiS aggregation, and eventually into rhombohedral β - NiS hollow sphere by modulating acrylamide: Ni^{2+} molar ratio.

Fig.3 displays a series of XRD patterns for intermediates collected after 1.5, 2, 4, 14, 20 and 24 h, keeping the quantity of acrylamide constant (200 mmol). When the reaction time is 1.5 h, all of the peaks can be identified as the hexagonal α - NiS phase. After reacting for 2 h, the sample obtained is a mixture of α - NiS and β - NiS with α - NiS as the major phase. As the

reaction time is extended from 2 to 20 h, the peaks of β - NiS become stronger while the peaks of α - NiS are weakened. When the reaction time is extended to 24 h, the characteristic peaks of α - NiS are further weakened and the orthorhombic β - NiS hexahedral phase is predominant. The strong and sharp diffraction peaks indicate that the orthorhombic β - NiS obtained is highly crystalline. The investigations reveal that the reaction time has a significant effect on the formation and phase transformation of nickel sulfides.

Fig.4 shows TEM images of intermediates collected after 1.5, 2, 4, 14, 20 and 24 h, respectively. The images clearly reveal the transformation process from solid spherical nanoparticles into hollow nanospheres. When the reaction time is reduced to 1.5 h, only a large irregular product is obtained (Fig.4a). Fig.4b displays the image for the sample reacting after 2 h, revealing that the intermediate is aggregation of solid spherical particles with a diameter of about 100 nm. The sphere-like aggregation slowly melts from inside until it melts completely to spread up into nanoflakes after reacting for 4 h (Fig.4c). The nanoflakes have small thickness and large areas. When the reaction time is extended to 14 h, the edge of some nanoflakes partly

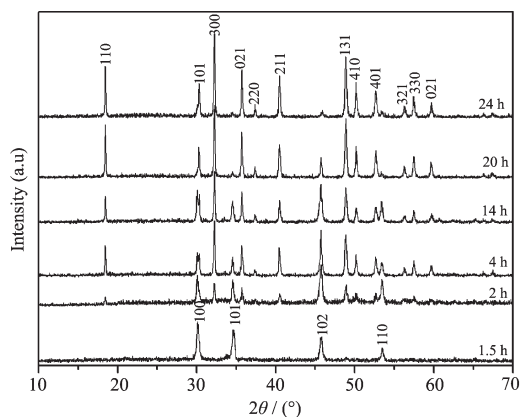


Fig.3 XRD patterns for samples synthesized in a typical procedure with different reaction times

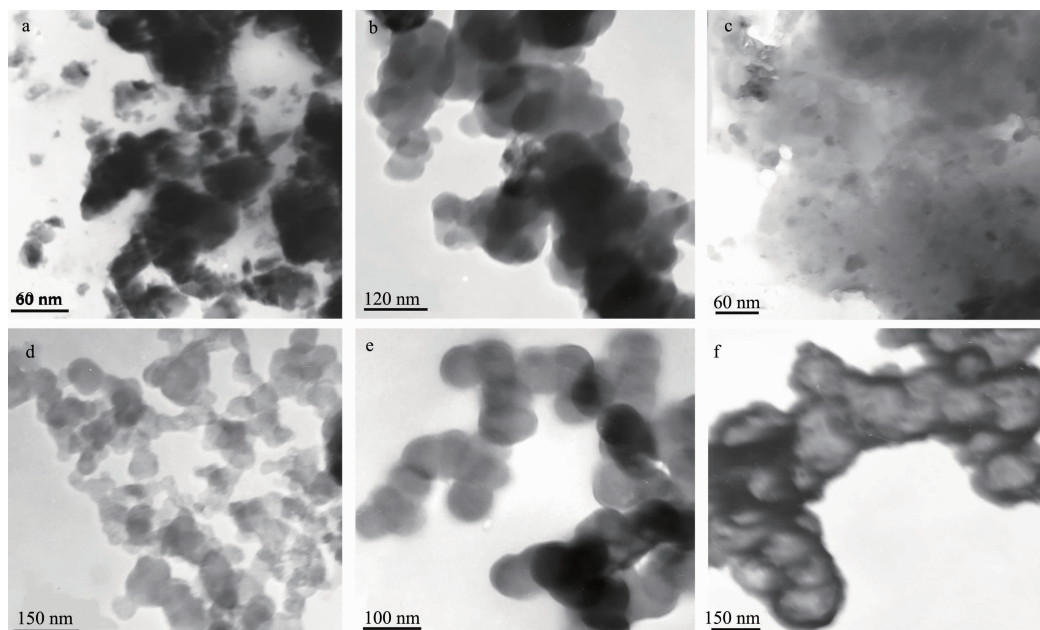


Fig.4 TEM images for samples synthesized in a typical procedure with different reaction times

is rolled and some completely rolled nanoflakes take on spherical particles with an average size of 100 nm (Fig. 4d). With the reaction time up to 20 h, the spherical particles become more regular and uniform with a diameter of 100~150 nm (Fig.4e). The obvious contrast of the light-colored center and the deep-colored sides of the sphere indicates that the nanosphere is a center-hollow one. Moreover, the shell is loose and porous with a thickness of about 20 nm. After the reaction time is extended beyond 24 h, the hollow spheres become cross-linked with each other, as shown in Fig.2c and Fig.4f. On the basis of the above results, we reasonably assume that the formation process of β -NiS with a hollow sphere involves a heterogeneous crystallization and rolling-up mechanism. The irregular hexagonal α -NiS particles are first formed, and then transformed into the mixture of α -NiS and β -NiS with solid spherical particles. Subsequently the solid spherical particles melt and then spread up into thin nanoflakes. The thin nanoflakes gradually roll up and eventually turn into β -NiS hollow nanospheres. Of course, more systematic work should be done to obtain a further knowledge on the formation mechanism.

3 Conclusion

In summary, cubic NiS₂ solid spherical particles,

hexagonal α -NiS aggregation and rhombohedral β -NiS hollow sphere were continuously fabricated via an acrylamide-assisted solvothermal process. The phase and morphology of nickel sulfides can be controlled by modulating acrylamide: Ni²⁺ molar ratio.

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