

Controlled Synthesis of Cobalt Sulfide Nanocrystalline by Ultrasonic Spray Pyrolysis Process

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Abstract: Cubic Co₉S₈ fracture structure nanoshells and cubic Co₃S₄ nanocrystallines were prepared by an ultrasonic spray pyrolysis process using cobalt chloride (CoCl₂·6H₂O) and thiourea (CH₄N₂S) as the starting materials. The as-prepared Co₉S₈ nanoshells and Co₃S₄ nanocrystallines were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) with energy-disperse X-ray spectroscopy (EDX) attachment and Fourier-transform infrared (FTIR) spectrometer. It is found that the phase transition could be controlled by adjusting the reaction temperature, while morphologies of final products could be influenced by the molar ratio and reaction time of the precursor. And the possible mechanism for the formation of hollow and solid crystalline structures of the product was proposed.

Key words: nanocrystallines; synthesis; cobalt sulfide; ultrasonic spray pyrolysis

In recent years, transition metal sulfide has received considerable attention due to its unique electronic, magnetic, optical and mechanical properties and wide variety of potential applications including solid lubricants, catalysts, lithium battery cathodes, scanning probes, photoconductors and shockwave resistance materials^[1-9]. Among these materials, cobalt sulfide nanocrystalline compounds consisting of CoS, Co_{1-x}S, CoS₂, Co₃S₄, and Co₉S₈ have been devoted to many efforts for their excellent chemical, physical and mechanical properties^[10-17]. For instance, as nonprecious materials, Co₉S₈ shows excellent electrochemical performance^[18] and exhibits great electrocatalytic activities towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), suggesting their potential application as non-noble bifunctional catalysts for regenerative fuel cells and metal-air batteries^[19], and as a counter electrode material, Co₉S₈ could be used as dye-sensitized solar cells^[20,21]; nano-sized Co₃S₄ crystals could be used as high-performance electrochemical supercapacitors^[22,23] etc.

So far, various synthesis methods including hydrothermal/solvothermal routes, electrochemical syntheses, wet-chemical methods, colloidal syntheses and catalytic chemical vapor

deposition have been successfully applied in controlling the morphology of cobalt sulfide nanocrystallines^[24-31]. In the present work, Co₉S₈ fracture hollow nanoshells and Co₃S₄ nanocrystallines were synthesized by an ultrasonic spray method using cobalt chloride and thiourea as the starting materials on glass substrates. The as-prepared samples were characterized by X-ray powder diffraction (XRD) and scanning electron microscope (SEM) equipped with an energy-disperse X-ray spectroscopy (EDX) system, and Fourier-transform infrared (FTIR) spectra using KBr-pellet technique in the range 400~4000 cm⁻¹. Possible formation mechanisms of these nanostructures were proposed.

1 Experiment

All the chemicals with analytic grade were purchased from Shanghai Chemical Reagent Factory (China) and used without further purification. The cobalt sulfide products were fabricated by an ultrasonic spray pyrolysis method keeping a constant flow rate of argon gas in all reaction process.

In a topical procedure, 0.005 mol cobalt chloride hexahydrate (CoCl₂·6H₂O) and 0.02 mol thiourea (CH₄N₂S) were added into a beaker which contained 100 mL distilled

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water and stirred until the starting materials melt completely. After that the as-obtained solvent was put into the ultrasonic spray device which could produce the fog drop, and then the fog drops were carried by the argon gas onto a hot glass substrate (300 °C) which were placed in the center of quartz tube furnace for 20 min, finally the glass substrate was allowed to cool to room temperature and black precipitates were found on the substrate.

0.005 mol cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and 0.01 mol thiourea ($\text{CH}_4\text{N}_2\text{S}$) were added into a beaker which contained 100 mL distilled water and stirred until the starting materials melt completely. Then the as-prepared precursor underwent a similar processing while the temperature of the glass substrate rose up to 350 °C

X-ray diffraction (XRD) patterns of the samples were carried out on a Switzerland X'TRA X-ray diffractometer with $\text{CuK}\alpha$ radiation at scanning rate of 0.02° in 2θ range of $10^\circ \sim 70^\circ$ to determine crystalline phase and the purity of the products. The morphologies of the products were characterized by scanning electron microscopy (SEM, JSM-5610LV-VANTAGE, Accelerating voltage of 15 kV) with energy-disperse X-ray spectroscopy (EDX) attachment. The Fourier -transform infrared (FTIR) spectra were measured with Perkin-Elmer Spectrum One FTIR Spectrometer using KBr-pellet technique in the range $400 \sim 4000 \text{ cm}^{-1}$.

2 Results and Discussion

For the formation of Co_9S_8 and Co_3S_4 products using cobalt chloride hexahydrate and thiourea as precursor, a possible reaction mechanism has been proposed to explain the growth as follows:

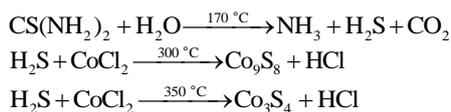


Fig.1a shows the typical XRD pattern of the as-synthesized product by the ultrasonic spray pyrolysis technique at 300 °C for 20 min using cobalt chloride and thiourea as precursor with molar ratio of 1:4. All peaks can be indexed to a cubic phase of cobalt pentlandite (Co_9S_8), partly matching well with its standard XRD pattern (JCPDF No. 73-1442) as shown at the bottom of Fig.1a. No other impure diffraction peaks are detected, indicating the high purity of as-synthesized Co_9S_8 product. Wide peaks in Fig.1a suggesting the nanostructure property of synthesized Co_9S_8 products and size of the obtained crystalline were calculated using Scherrer's equation:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite dimension, λ is the wavelength of incident X-rays, θ is the diffraction angle, and β is the full width at half maximum, and size of synthesized Co_9S_8 crystallines is about 7.43 nm. Meanwhile, the cell constant is calculated to be about 1.0112 nm which is close to

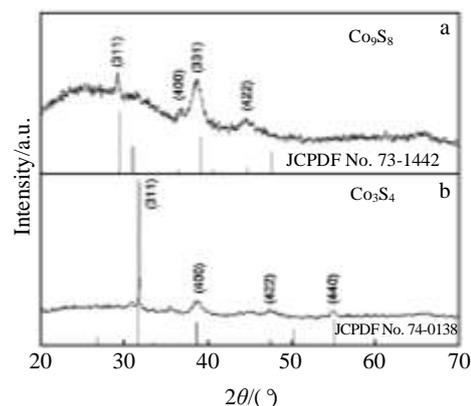


Fig.1 XRD patterns of as-synthesized products: (a) Co_9S_8 nanoshells and (b) Co_3S_4 nanocrystallines

the data (0.9928 nm) reported in the JCPDS cards.

Fig.1b displays the corresponding XRD pattern of the product by the ultrasonic spray pyrolysis technique at 350 °C for 20 min using cobalt chloride and thiourea as precursor with molar ratio of 1:2. It can be seen that the diffraction peak is different from that of the obtained Co_9S_8 product as shown in Fig.1a. All the peaks are indexed to those of cubic Co_3S_4 phase; partly agree well with the standard XRD pattern (JCPDF No. 74-0138). No other impure diffraction peaks are detected suggesting the purity of as-synthesized product, and the sharp peaks along the (311) plane indicate good crystallinity of the as-synthesized product. Meanwhile, crystal size of the Co_3S_4 product was calculated by Scherrer's equation (40.84 nm), and the cell constant (0.9328 nm) is close to the reported result in the JCPDS cards (0.9382 nm). Furthermore, different phases may mainly attribute to the reaction temperature, a higher symmetric linnæite Co_3S_4 can be obtained at the temperature of 350 °C; however, cobalt pentlandite Co_9S_8 are observed at the temperature of 300 °C. It indicates that lesser symmetric Co_9S_8 transforms into higher symmetric Co_3S_4 gradually with increasing of the reaction temperature^[32].

Fig.2a is the SEM image of the Co_9S_8 nanocrystallines, revealing that the product consists of a large amount of fractured nanoshells with average diameter of about 500 nm. The corresponding EDX spectrum (Fig.2b) indicates the atomic ratio of Co and S elements is close to 9:8 by integrating the XRD and EDX results, and the Co_9S_8 formation of the product can be determined. Fig.2c shows the SEM image of the Co_3S_4 sample which displays quasi spherical-like morphology. These microspheres with diameter of about 2 μm consist of a large amount of nanocrystallines with size of about 100 nm, which can be further confirmed by enlarged SEM observation shown in Fig.3b. The corresponding EDX spectrum (Fig.2d) indicates that the microspheres are mainly composed of Co and S elements. Ratio of Co and S elements is close to 3:4, further confirming the formation of Co_3S_4 phase as revealed by the XRD result.

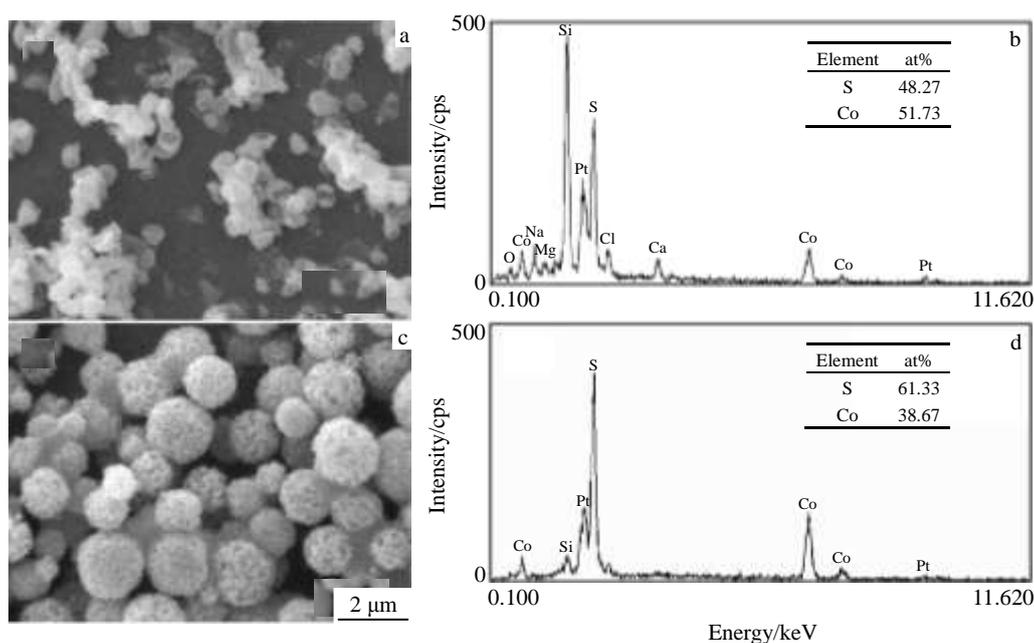


Fig.2 SEM images (a, c) and EDX spectra (b, d) of the fractured Co_9S_8 nanoshells (a, b) and Co_3S_4 nanoparticles (c, d)

Given the molar ratio of precursors and reaction temperature may influence the morphology of the final product; effects of the quantity of thiourea and reaction temperature on the morphology of the as-synthesized products were further investigated. As for the quantity of thiourea influencing the phase of product, Yin et al. have reported Co_9S_8 was the only sulfide phase observed when the molar ratio was lower than 9:8, whereas Co_3S_4 also appeared when the molar ratio exceeded this value^[33]. Here, the molar ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and thiourea is fixed at 1:1, 1:2 and 1:4, and the corresponding morphologies are shown in Fig.3a~3c respectively. As shown in Fig.3a, film with irregular particles is observed at 300 °C for 20 min. If the quantity of thiourea is double to that of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and reaction temperature rise up to 350 °C for 20 min, aggregated quasi spherical-like particles with regular shape are obtained (Fig.3b). If the quantity of thiourea is further increased to fourfold to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ for 20 min, a large amount of fracture nanoshells with average diameter of about 500 nm instead of aggregated spherical-shaped particles can be obtained (Fig.3c).

Meanwhile, the reaction time may influence the morphologies of the final product. When the reaction time maintains 20 min as shown in Fig.3b, microspheres composed of nanocrystallines are obtained; when the reaction time goes up to 1 h, microspheres and nanorods are obtained (Fig.3d), when the reaction time is prolonged to 4 h, nanorods with diameter of about 200 nm and microspheres composed of not nanoparticles but nanorods with diameter of about 200 nm are obtained as shown in Fig.3e and 3f. So we can conclude that both the reaction time and molar ratio of precursor are important in controlling the morphologies of cobalt sulfide

products in the experiment.

For the morphology formation of Co_9S_8 and Co_3S_4 products, possible mechanisms of these micro/nanostructures were proposed as shown in Fig.4. As mentioned above, thiourea can be decomposed at temperature of 170 °C, and releases excessive gas such as H_2S , NH_3 and CO_2 . Among of them, H_2S can react with Co^{2+} , and NH_3 can be dissolved in the water; however, CO_2 will be left in the fog drops. If there are enough excessive gas and the hollow structure can be easily formed (Fig.4b), therefore, excessive gas are limited in the fog drop, and as the rising of reaction temperature as pressure inside of the fog drop growing up, the nanoshells can be easily broken (Fig.4c). However, if the quantity of thiourea is proper, there are not enough excessive gases to support the formation of the hollow structures, and then the aggregated nanoparticles with regular shape will be obtained (Fig.4d), and as prolonging of reaction time, the nanocrystals could grow up to the rod-like structure (Fig.4e).

FTIR was employed to study the infrared absorption properties of cobalt sulfide nanocrystals. Fig.5a shows FTIR spectrum of Co_9S_8 nanocrystals prepared at 300 °C for 20 min in the range of 400~4000 cm^{-1} . As shown in the FTIR spectrum, the sample displays the absorption at about 3400, 1631, 1105 and 630 cm^{-1} . The absorption peaks at 3400 and 1631 cm^{-1} can be assigned to the stretching vibration and bending vibration of OH groups of H_2O . The peak observed at 1105 cm^{-1} are assigned to the C-O stretching vibration originating from the adsorption of CO_2 which may come from atmosphere or the reaction product. The bands at 630 cm^{-1} can be attributed to the Co-S stretching vibration modes in Co_9S_8 . Fig.5b displays the FTIR spectrum of the as-prepared Co_3S_4

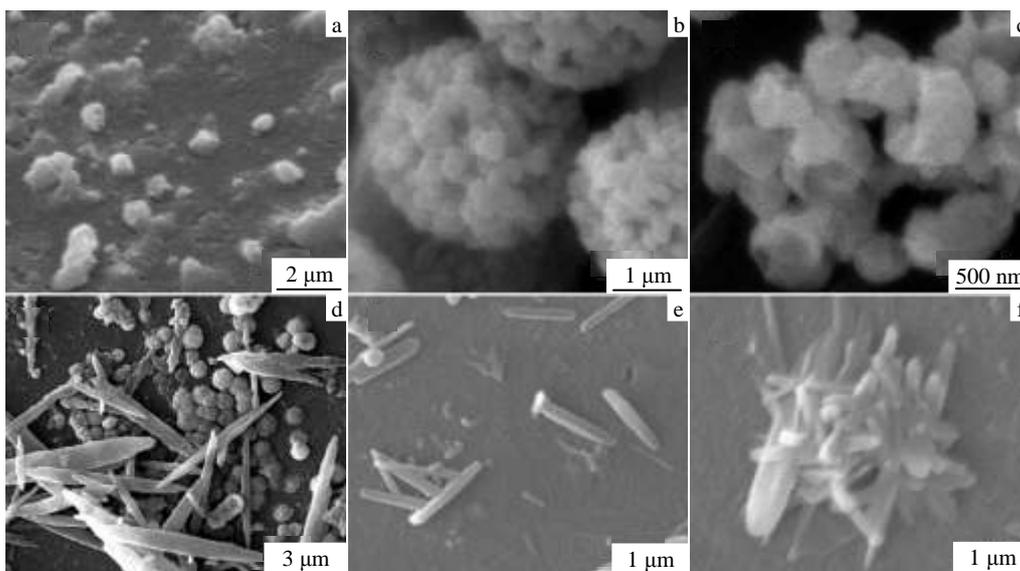


Fig.3 SEM images of the products at different molar ratios between cobalt chloride hexahydrate and thiourea with reaction time of 20 min: (a) 1:1 at 300 °C, (b) 1:2 at 350 °C and (c) 1:4 at 300 °C; SEM images of products at different reaction time at 350 °C: (d) 1 h and (e, f) 4 h

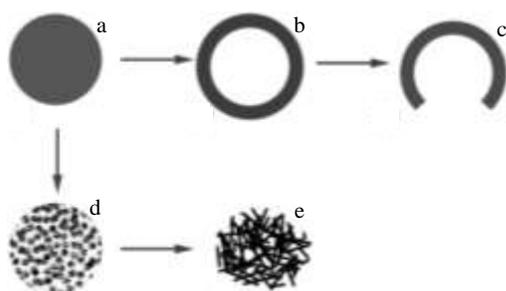


Fig.4 Schematic description of the formation of Co_9S_8 nanoshells and Co_3S_4 nanocrystallines

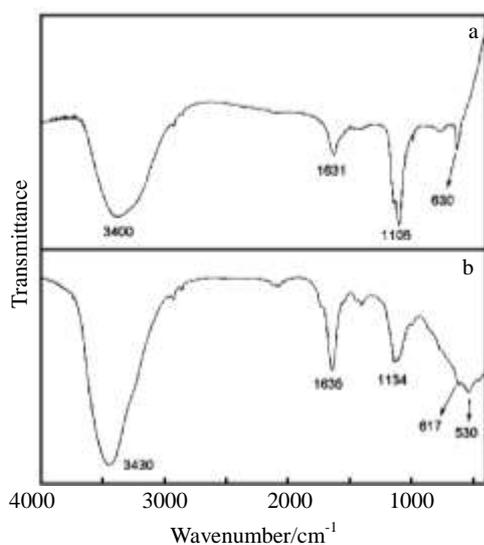


Fig.5 FTIR spectra of the cobalt sulfide nanocrystals: (a) Co_9S_8 at 300 °C and (b) Co_3S_4 at 350 °C for 20 min

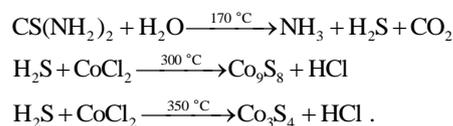
crystals and peaks of the Co-S stretching vibration modes in Co_3S_4 crystals appear at 617 and 530 cm^{-1} which shows a slight absorption difference on the Co-S stretching vibration modes from Co_9S_8 nanocrystals.

3 Conclusions

1) Cubic fractured Co_9S_8 nanoshells and Co_3S_4 nanocrystallines are prepared using cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) as the starting materials by the ultrasonic spray pyrolysis process.

2) The excessive sulfur source provided by thiourea and the reaction time influence the morphologies of the as-synthesized products. Higher reaction temperature leads to higher symmetry of the cobalt sulfide.

3) A possible formation mechanism on the difference morphology of the cobalt sulfide nanocrystals was given as follows:



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硫化钴纳米晶超声喷雾控制生长

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摘要: 以 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 和 $\text{CH}_4\text{N}_2\text{S}$ 为前驱物, 通过超声喷雾热解法, 制备了立方相 Co_9S_8 纳米碎壳和 Co_3S_4 纳米晶。所制备的样品用 XRD, SEM, EDX 和 FTIR 进行了表征, 结果发现过量的硫脲和反应时间对产物的形貌有明显影响。通过控制反应温度可以控制样品的物相, 并且对空心 and 实心晶体结构的产生提出了相应的机理。

关键词: 纳米晶; 合成; 硫化钴; 超声喷雾

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