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ARTICLE

Controlled Synthesis of Cobalt Sulfide Nanocrystalline by Ultrasonic Spray Pyrolysis Process

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Abstract: Cubic Co_9S_8 fracture structure nanoshells and cubic Co_3S_4 nanocrystallines were prepared by an ultrasonic spray pyrolysis process using cobalt chloride ($CoCl_2·6H_2O$) and thiourea (CH_4N_2S) as the starting materials. The as-prepared Co_9S_8 nanoshells and Co_3S_4 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, $Co_{1-x}S$, CoS_2, Co_3S_4, and Co_9S_8 have been devoted to many efforts for their excellent chemical, physical and mechanical properties[10-17]. For instance, as nonprecious materials, Co_9S_8 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, Co_9S_8 could be used as dye-sensitized solar cells[20,21]; nano-sized Co_3S_4 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, Co_9S_8 fracture hollow nanoshells and Co_3S_4 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 ($CoCl_2·6H_2O$) and 0.02 mol thiourea (CH_4N_2S) 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 ($CoCl_2 \cdot 6H_2O$) and 0.01 mol thiourea (CH_4N_2S) 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 CuKα radiation at scanning rate of 0.02° in 2θ range of 10°~70° 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 400~4000 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:

$$CS(NH_2)_2 + H_2O \xrightarrow{170\ ^\circ C} NH_3 + H_2S + CO_2$$
$$H_2S + CoCl_2 \xrightarrow{300\ ^\circ C} Co_9S_8 + HCl$$
$$H_2S + CoCl_2 \xrightarrow{350\ ^\circ C} Co_3S_4 + HCl$$

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

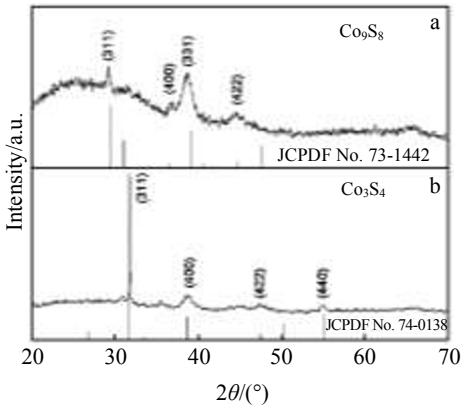

Fig.1 XRD patterns of as-synthesized products: (a) Co_9S_8 nano-shells and (b) Co_3S_4 nanocrystallines

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 linnaeite 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.