Polyhedron 31 (2012) 438–442

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of cobalt sulfide nanocrystals in the presence of thioglycolic acid via a simple hydrothermal method

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A R T I C L E I N F O

Article history:
Received 13 June 2011
Accepted 28 September 2011
Available online 14 October 2011

Keywords:
Co_3S_4 nanocrystals
Thioglycolic acid
Hydrothermal

A B S T R A C T

Co_3S_4 nanocrystals were synthesized via a hydrothermal technique by adding thioglycolic acid and $Co(CH_3COO)_2{\cdot}4H_2O$ as the precursors. The effect of some parameters, such as the reaction time and temperature and concentration of reactants, on the growth and morphology of the nano-structures has been studied. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) spectroscopy and Fourier transform infrared (FT-IR) spectra.

1. Introduction

Nanometer-scale materials have attracted considerable interest in recent years due to their unique physical and chemical properties, and their potential applications in nanoscale devices [1–6]. Due to these applications, various types of nanomaterials have been synthesized by our group, such as metallic nanomaterials [7,8], metal oxides [9–11] and metal sulfides [12–14]. Among these nanometer-scale materials, metal sulfide nanomaterials have been the focus of considerable interest due to their unique optical and electrical properties and their wide variety of potential applications in nanoscale devices such as electroluminescence and non-linear optical devices [15–18]. One of these metal sulfides is cobalt sulfide. Cobalt usually forms a variety of binary sulfides with the general formula CoS_x, such as Co_9S_8, CoS, Co_3S_4, $Co_{1-x}S$, Co_2S_3 and CoS_2, which have attracted great attention in virtue of their excellent properties and potential application for hydrodesulfurization and hydrodearomatization in many industrial fields [19]. CoS nanoparticles are used in electrochemical capacitors (ECs) or rechargeable lithium batteries [20,21].

Traditionally, cobalt sulfide powders were prepared by solid state methods. For example, cobalt sulfide can be obtained by the reaction of cobalt and sulfur [22,23] or hydrogen sulfide [24], or by the reaction of cobalt monoxide with hydrogen sulfide [25]. Co_9S_8 and CoS_2 were selectively fabricated by the reaction of cobalt chlorides and sodium polysulfide via a toluene thermal process [26]; CoS was obtained from amorphous cobalt sulfide in hydrazine solution at 120 °C [27].

In 2001, the hydrothermal method was also reported to prepare metal sulfide nanostructural materials, which has the potential advantages of relatively low cost, high purity and controlled morphology [28]. Also a mild hydrothermal route has been developed to synthesize metal sulfides with the use of thioglycolic acids as a non-toxic template and sulfide precursor [29,30]. In the current study, cobalt sulfide has been synthesized by the hydrothermal method with the use of $Co(CH_3COO)_2{\cdot}4H_2O$ as a precursor for Co and thioglycolic acids for S.

2. Experimental

2.1. Materials and physical measurements

All chemical reagents in this experiment were of analytical grade and used without further purification. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectrum of the sample was taken on a Perkin-Elmer LS-55 luminescence spectrometer. Scanning electron microscopy (SEM) images were obtained on a LEO-1455VP equipped with an energy dispersive X-ray spectroscope. (FE-SEM) images were obtained on a HITACHI S-4160.

2.2. Preparation of Co_3S_4 nanocrystals

In a typical synthesis, different molar ratios of $Co(CH_3COO)_2{\cdot}4H_2O$ and thioglycolic acid were mixed in 200 mL distilled water under

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0277-5387/$ - see front matter
doi:10.1016/j.poly.2011.09.047

Table 1
The optimizing synthetic parameters of Co_3S_4.

Sample No.	Ratio (Co^{2+}:TGA)	Time (h)	Temperature (°C)
1	1:3	24	120
2	1:3	24	150
3	1:3	24	180
4	1:1	24	150
5	1:2	24	150
6	1:3	48	150
7	1:2	48	150
8	1:1	48	150

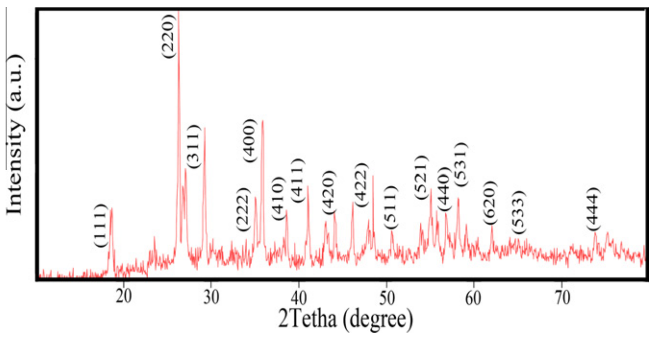

Fig. 1. XRD pattern of the as-prepared sample No. 2.

stirring. After 30 min stirring the final mixed solution was sealed in a 250 mL Teflon-lined stainless steel autoclave and heated at 120–180 °C for 24–48 h in an electric oven. The autoclave was cooled to room temperature naturally, after the required reaction time (Table 1 shows a summary of the reaction conditions). The product was washed with distilled water and absolute ethanol several times to remove excessive reactants and by-products, followed by drying in an electric oven at 70 °C for 10 h.

3. Results and discussion

The crystal structures of the as-prepared products have been identified. As a typically example, the XRD pattern of sample No. 2 is shown in Fig. 1, which reveals the nanocrystalline nature of the as-prepared sample due to the broadening of the diffraction peaks. All of the diffraction peaks can be indexed to face-centered

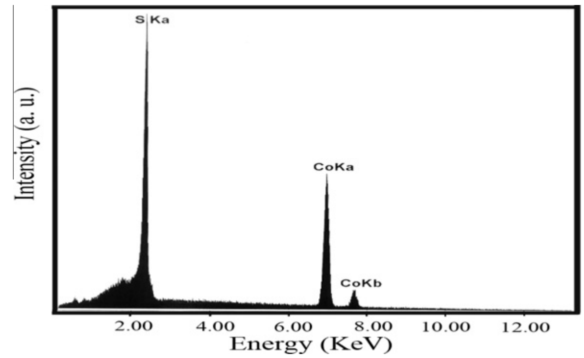

Fig. 2. EDX spectrum of sample No. 2.

cubic Co_3S_4, being very close to the values in the literature (JCPDS Nos. 73–1703 with lattice parameters), and no characteristic peaks of impurities were detected. Acceptable matches are observed for the compound, indicating the presence of only one crystalline phase in the samples. From the broaden peaks in the XRD it can be concluded that the particle size of the product is small.

The average crystallite diameter of the obtained product was estimated from the Debeys–Scherrer equation:

$$Dc = \frac{k\lambda}{\beta \cos \theta}$$

where β is the breadth of the observed diffraction line at its half-intensity maximum, k is the so-called shape factor, and λ is the wavelength of the X-ray source used in the XRD. By using the (220) peak, the average crystallite diameter of the obtained products was about 35 nm.

A typical EDX spectrum (sample No. 2) is shown in Fig. 2, which indicates the presence of Co and S in the product. Based on the calculation of the peak areas, the ratio of cobalt to sulfide is found to be approximately 3:4, as expected. Therefore, both XRD and EDX analyses show that pure Co_3S_4 nanocrystals are successfully produced via the present synthetic route.

The SEM and FE-SEM images of the as-synthesized Co_3S_4 have been used to investigate the effect of different conditions on the product morphologies. FE-SEM images (Fig. 3) of samples which were obtained at different temperatures while other conditions were constant revealed that the best temperature is 150 °C. Below this temperature, the products were composed of bulk particles

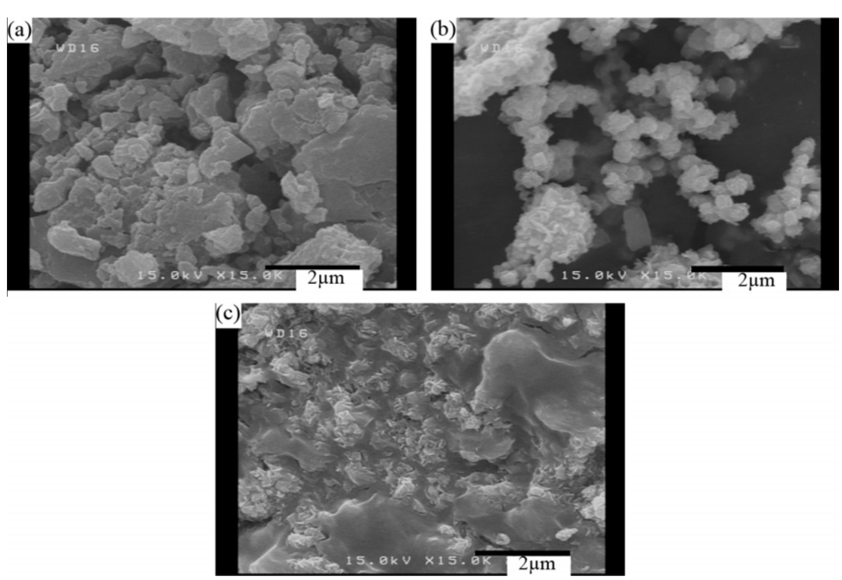

Fig. 3. FE-SEM images of the samples obtained at different temperatures: (a) sample No. 1, (b) sample No. 2, and (c) sample No. 3.