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Hydrothermal synthesis of CoSe nanostructures without using surfactant



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ABSTRACT

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1. Introduction

Extensive attention has been paid to the preparation and characterization of metal selenides owing to their interesting properties and potential applications [1-7]. Cobalt selenide semiconductors have extensively been studied. According to the phase diagram of the Co-Se system [8] there are two homogeneous and stable phases at room temperature, CoSe₂ and CoSe, and two other possible compositions: Co₃Se₄ and Co₂Se₃. Lots of methods of synthesizing cobalt selenide nanostructures have been developed, including solvothermal [9,10], hydrothermal [11,12], co-electrodeposition [13], chemical bath deposition technique [14], one-pot reaction between metal salts [15] and so on [16–19]. In this paper, we report a hydrothermal route for the preparation of cobalt selenide nanostructures. In this route, SeCl₄ is used as a new selenium source. To the best of our knowledge, studies on the synthesis of cobalt selenide nanostrucrures by using SeCl₄ have not been reported to date. In this research, we present the results of our perfect experiments on the dependence of the morphology, particle size, and phase of the products on the type of metal salt and reductant, reaction time and temperature.

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, and purchased from Merck and used as received without further purification. A Teflon-lined stainless steel cylindrical closed chamber with 150 ml capacity was used for the synthesis. Powder X-ray diffraction (XRD) patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K α radiation (λ = 1.54 Å). Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope (SEM). Transmission electron microscopy (TEM) images were obtained on a JEM-2100 with an accelerating voltage of 60–200 kV equipped with a high resolution CCD camera. The energy dispersive spectrometry (EDS) analyses were studied by a XL30, Philips microscope. The magnetic properties of the samples were detected at room temperature using a vibrating sample magne-

tometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

2.2. Synthesis of CoSe nanostructures

CoSe nanostructures are synthesized by hydrothermal route in the presence of reductant, without using surfac-

tant. In this work, we use from SeCl₄ as a new selenium source. By varying the type of metal salt and reductant,

reaction time and temperature, the method permits us to synthesize products with different morphologies. SEM

and TEM images show the morphology and size of the as-synthesized samples. Chemical composition of the samples is characterized by XRD and EDS. Magnetization measurement shows paramagnetic behavior for CoSe

In a typical experiment for the synthesis of CoSe nanostructures, cobalt salt (chloride, acetate, sulfate) were dissolved in 40 ml distilled water. After stirring the solution for 15 min, SeCl₄ was dissolved in 20 ml of distilled water and added into the solution under strong magnetic stirring at room temperature. Then reductant (N_2H_4 · H_2O , KBH₄,·Zn) was added drop-wise. The solution was added to a Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 h. The autoclave was cooled to room temperature on its own. The precipitates were separated by centrifugation, then washed with distilled water and anhydrous ethanol several times, and dried under vacuum at 60 °C for 4 h. Table 1 lists the reaction conditions of the synthesized CoSe nanostructures.

3. Results and discussion

Fig. 1 shows SEM images of cobalt selenide nanostructures produced from $CoCl_2 \cdot 6H_2O$ and $SeCl_4$ in the presence of hydrazine at 180 °C for

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Table 1	
The reaction conditions of the	products synthesized in this work.

Sample no.	Co:Se ratio	t (h)	T(°C)	Reductant	Surfactant	Se source	Cobalt salt
1	1:1	6	180	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoCl ₂ ·6H ₂ O
2	1:1	12	180	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoCl ₂ ·6H ₂ O
3	1:1	18	180	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoCl ₂ ·6H ₂ O
4	1:1	12	220	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoCl ₂ ·6H ₂ O
5	1:1	12	150	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoCl ₂ ·6H ₂ O
6	1:1	12	120	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoCl ₂ ·6H ₂ O
7	1:1	12	180	$N_2H_4 \cdot H_2O$	-	SeCl ₄	CoSO ₄ ·7H ₂ O
8	1:1	12	180	$N_2H_4 \cdot H_2O$		SeCl ₄	$Co(CH_3COO)_2 \cdot 4H_2O$
9	1:1	12	180	KBH ₄	-	SeCl ₄	CoCl ₂ ·6H ₂ O
10	1:1	12	180	Zn	-	SeCl ₄	CoCl ₂ ·6H ₂ O



Fig. 1. SEM images of samples prepared from $CoCl_2 \cdot 6H_2O$ and $SeCl_4$ in the presence of hydrazine at 180 °C for: (a) 6 h (sample no. 1), (b) 12 h (sample no. 2) (inset: low-magnification SEM image of sample no. 2), (c) 18 h (sample no. 3).



Fig. 2. SEM images of samples prepared from $CoCl_2 \cdot 6H_2O$ and $SeCl_4$ in the presence of hydrazine after 12 h hydrothermal reaction at: (a) 220 °C (sample no. 4) (inset: low-magnification SEM image of sample no. 4), (b) 150 °C (sample no. 5), (c) 120 °C (sample no. 6).

the different reaction times (6 h, 12 h and 18 h). According to the Fig. 1a, sponge-like structures are prepared after 6 h of hydrothermal reaction (sample no. 1). With increasing of time reaction from 6 h to 12 h (sample no. 2), flower-like structures are formed, as shown in Fig. 1b. The longer time of reaction allows ample time for the sponge-like structures to agglomerate and grow into more regular shapes. The low-magnification SEM image of sample no. 2 inserted in Fig. 1b, clearly reveals the diameter of the flowers is about $5-12 \mu m$. The flower-like structures are broken down and agglomerated nanospheres with an irregular manner are observed (Fig. 1c), with increasing time to 18 h (sample no. 3).

For investigating the effect of reaction temperature on the morphology of the products, the reactions carried out in the presence of hydrazine at four different temperatures, including 120, 150, 180 and 220 °C, and other reaction parameters remained unchanged. Fig. 2a and b shows SEM images of cobalt selenide nanostructures obtained at 220 °C and 150 °C, respectively. These images show that products have sponge-like morphology. SEM image of sample obtained at 180 °C (Fig. 1b) showed formation of flower-like structures. Fig. 2c shows formation sphere-like nanostructures at 120 °C. It can be observed that with increasing temperature, regular agglomeration of nanostructures increases and more regular structures (flowers and sponges) are formed. SEM images reveal that morphology of products change with using from different cobalt salts. In case of sample obtained from sulfate salt (sample no. 7), the aggregated nanoparticles with nearly even distribution are obtained, as shown in Fig. 3a. Changing the metal salt to acetate (samples no. 8), we can see aggregated nanospheres (Fig. 3b). The morphology of as-prepared cobalt selenides changes from nanospheres to flower-like structures, when use from chloride salt (Fig. 1b). The different types of particle size and morphology can be due to the different release rates of Co^{2+} and Se^{2-} ions from the cobalt salts and SeCl₄, respectively.

In continuation, the effect of the type of reductant on the morphology of the nano-sized cobalt selenides at 180 °C for 12 h was investigated. Fig. 4 shows that the reductant plays a key role in the morphology and size, and therefore the properties, of cobalt selenides. In the presence of hydrazine in sample no. 2, nanoflowers were formed (Fig. 1b). On changing hydrazine to KBH₄ (sample no. 9), nanospheres with even distribution are formed (Fig. 4a). In the presence of Zn (sample no. 10), the as-prepared products have two morphologies. From Fig. 4b, it is found that the samples are mixture of aggregated nanoparticles and nanospheres. The strong reductant KBH₄ and hydrazine in combination with stirring rapidly create a large number of nuclei and further growth of the nuclei is limited. The nuclei are aggregated regularly and flowerlike nanostructures (in case of hydrazine) and nanospheres with even distribution (in case of KBH₄) are formed. Zn is slower in the reduction rate compared to hydrazine and KBH₄. Our group attributes the slower action of Zn as the reason for the formation of the structures with irregular morphologies.



Fig. 3. SEM images of samples prepared in the presence of hydrazine at 180 °C for 12 h from SeCl₄ and: (a) $CoSO_4 \cdot 7H_2O$ (sample no. 7), (b) $Co(CH_3COO)_2 \cdot 4H_2O$ (sample no. 8).



Fig. 4. SEM images of samples prepared from CoCl₂· $6H_2O$ and SeCl₄ at 180 °C for 12 h in the presence of: (a) KBH₄ (sample no. 9), (b) Zn (sample no. 10).



Fig. 5. (a) TEM image, (b) HRTEM image and (c) SAED pattern of sample no. 8.



Fig. 6. XRD pattern of sample no. 2.

In order to further elucidate the size and the crystal structure of the products, TEM image and SAED spectrum were taken. TEM image in Fig. 5a shows the formation of nanospheres with diameters in the range 10–30 nm. The HRTEM image in Fig. 5b shows the distance between the two adjacent planes is measured to be 0.25 nm. The intensity and ordered diffraction spots, also diffused halo ring in the SAED

spectrum in Fig. 5c indicate that the nanospheres prepared are well crystallized.

The crystal structure and composition of the as-prepared products are determined by XRD. Fig 6 shows XRD pattern of sample synthesized by the reaction between $CoCl_2 \cdot 6H_2O$ and $SeCl_4$ in presence of the hydrazine, without surfactant at 180 °C for 12 h (sample no. 2). The peaks at



Fig. 7. EDS spectrum of the as-synthesized cobalt selenide.



Fig. 8. M-H hysteresis at 300 K for sample no. 2.

2Theta values 51.4, 45.5, 33.9 indicate the formation of hexagonal phase of CoSe.

EDS measurements provide further information for the evaluation of the composition and purity of cobalt selenides. In the EDS spectrum in Fig. 7 the characteristic peaks of Co and Se are observed, which indicate formation pure cobalt selenide.

The magnetic property of cobalt selenide nanostructures has been measured. Fig. 8 shows plot of the variation of magnetization with magnetic field at 300 K for sample no. 2. The plot shows paramagnetic behavior. The magnetic properties of nanomaterials are believed to be highly dependent on the material structure, size and shape of the grain, crystallinity, magnetization and applied field direction, lattice spacing, chemical composition, temperature, defect concentration, atomic order, impurities and so on.

4. Conclusions

In this paper, we develop a novel hydrothermal synthetic route to CoSe semiconductors and study the growth process, structure, morphology and magnetic property of samples. It is shown that the type of metal salt and reductant, reaction time and temperature play important roles in controlling the composition, structure and morphology of products.

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