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Cobalt selenide nanostructures: Hydrothermal synthesis, considering the magnetic property and effect of the different synthesis conditions

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ABSTRACT

Cobalt selenide (CoSe) nanostructures are produced via hydrothermal route from the reaction of cobalt salt and SeCl₄ as precursors, in the presence of surfactant (CTAB, PVA, SDS) and reductant (N_2H_4 , H_2O). It is found that the temperature reaction, type of cobalt salt and surfactant play important roles in controlling the composition, structure, morphology and particle size of products. The experimental techniques of XRD, SEM, TEM, EDX and VSM are used to characterize the products and study their magnetic properties.

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1. Introduction

Transition metal chalcogenides, as important semiconductors materials, have attracted widely attentions because of their wonderful physical and chemical properties, quantum size effect, luminescence and non-linear optical properties [1–7]. Also, much attention has been focused on lithium intercalation in metal chalcogenides due to their potential application as rechargeable battery electrodes and electrochromic displays [8,9]. The properties (including physical and chemical properties) and applications of materials are usually determined by their compositions, phase structures and morphologies. The control of chemical composition, crystal structure, size and shape of materials allows people to observe the unique properties of nanocrystals and to tune their chemical and physical properties [10,11].

CoSe as a typical example has been selected for synthesis in this work. According to the phase diagram of the Co–Se system [12] there are two homogeneous and stable phases at room temperature, CoSe₂ and CoSe, and two other possible compositions: Co₃Se₄ and Co₂Se₃. Traditionally, cobalt selenides were synthesized by using a variety of methods, such as solvothermal [13,14], hydrothermal [15,16], co-electrodeposition [17], chemical bath deposition technique [18], one-pot reaction between metal salts [19], etc. [20–23].

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In this paper, we report the synthesis of CoSe nanostructures by hydrothermal method. This method is simple, convenient and effective controlled synthetic procedure and provided an effective way to the synthesis of chalcogenide materials. The physical properties as well as the magnetic properties of the new materials are reported. This study also describes a comparison of features observed from the products obtained from various conditions. Over the past years, great interest has been focused on controlling the shape, structure and size of nanostructured materials because of the strong correlation between these parameters and their physical/chemical properties [24]. SeCl₄ was selected in our experiments to provide a highly reactive selenium source in aqueous solution and has given good results. To the best of our knowledge, it is the first time that SeCl₄ was used as Se source for the synthesis of cobalt selenides. Following this method, we herein report a convenient and controllable synthetic method for obtaining a series of cobalt selenides. By simply adjusting the temperature reaction, type of surfactant and cobalt salt, we could obtain CoSe samples with the best size and morphology.

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

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Fig. 1. SEM images of samples prepared at 180 °C for 18 h: (a) in the absence of surfactant (sample no. 1) and in the presence of: (b) CTAB (sample no. 2), (c) PVA (sample no. 3) and (d) SDS (sample no. 4).

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 ($\lambda = 1.54$ 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. X-ray energy dispersive spectroscopy (EDS) analysis with 20 kV accelerated voltage was done. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

2.2. Synthesis of CoSe nanostructures

In a typical experiment for the synthesis of CoSe nanostructures, $CoCl_2 \cdot 6H_2O$ and surfactant were dissolved in 40 ml distilled water. After stirring the solution for 15 min, $SeCl_4$ was dissolved in 20 ml of distilled water and added into the solution under strong magnetic stirring at room temperature. Then hydrazine was added drop-wise. The solution was added to a Teflon-lined stainless steel autoclave and maintained at 180 °C for 18 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.

3. Results and discussion

Fig. 1a–d illustrates SEM images of the products synthesized in the presence of different surfactants at 180 °C after 18 h of hydrothermal reaction. Fig. 1a shows the SEM image of the product obtained in the absent of surfactant (sample no. 1). The formation of nanoparticles with high agglomeration is seen in this figure. When the CTAB is used as surfactant (sample no. 2), nanoplates with a diameter of 70–150 nm are formed (Fig. 1b). Fig. 1c shows that the nanoplates are also obtained in the presence of PVA (sample no. 3), but with bigger area. The SEM image in Fig. 1d shows formation of nanoparticles with spherical morphology in the presence of SDS (sample no. 4).

The effects of reaction temperature on the morphology and shape of the as-synthesized products in the presence of CTAB and PVA are shown in Fig. 2. According to Fig. 2a, aggregated nanoparticles are formed in the presence of CTAB at 120 °C (sample no. 5). With increasing of the temperature to 150 °C (sample no. 6), the asprepared samples have two morphologies: nanoparticles and nanoplates (Fig. 2b). The nanoparticles disappear at 180 °C, while there are still nanoplates as was shown in Fig. 1b. Fig. 1c showed formation of nanoplates in the presence of PVA at 180 °C. Fig. 2c shows formation of flower like structures with increasing temperature to 200 °C in the presence of PVA. As a result, the high temperatures increase regular agglomeration of nanoparticles and formation of nanoplates or nanoflowers.



Fig. 2. SEM images of samples prepared in the presence of: (a, b) CTAB at 120 °C (sample no. 5) and 150 °C (sample no. 6), respectively and (c) PVA at 200 °C (sample no. 7).

Fig. 3 shows the effect of the reaction temperature on the morphology of the products in the presence of CTAB and acetate salt. With increasing of the temperature, regular aggregated structures are formed. With change at the cobalt salt from chloride to acetate, the morphology of the as-prepared products is changed from nanoplates (Fig. 1b) to aggregated nanoparticles (Fig. 3a). We consider that this phenomenon results from the different interactions between anions and Co^{2+} cations. The different anions have different coordinations with metal cations, which might favor the preferential crystal growth [25].

In order to further elucidate the size and the crystal structure of the products, TEM image was taken. For preparation of the TEM image, the powder was dispersed in high-purity ethanol via ultrasonic equipment for 10 min. Fig. 4a shows the formation of nanoplates in the presence of PVA at 180 °C for 18 h (sample no. 3) and confirms SEM results (Fig. 1c). The HRTEM image of sample no. 3 in Fig. 4b shows the nanoplates are highly crystalline and distance between the two adjacent planes is measured to be 0.15 nm. The intensity and highly ordered diffraction spots, also diffused halo ring in the SAED spectrum in Fig. 4c indicate that the nanoplates prepared in the presence of PVA are well crystallized.

The crystal structure and composition of the as-prepared products were determined by XRD. Figs. 5 and 6 show XRD patterns of samples synthesized by the reaction between cobalt salt and SeCl₄ in presence of the different surfactants. In XRD pattern of sample obtained in the presence of SDS at 180 °C for 18 h (sample no. 4, Fig. 5a), the peaks at 2Theta values 51.4, 45.5, 33.9 indicate the formation of hexagonal phase of CoSe. The type of product changes from hexagonal CoSe to mixture of hexagonal Se and orthorhombic CoSeO₃, when use from PVA at 180 °C for 18 h (sample no. 3, Fig. 5b), indicating that these reaction temperature and time are not quite enough for reduction of SeCl₄ and formation of pure CoSe in the reaction system. In the presence of PVA, with increasing the reaction time and temperature to 36 h and 200 °C, respectively (sample no. 7), the samples are found to be the pure hexagonal CoSe, as shown in Fig. 5c.

In the presence of CTAB and cobalt chloride salt, after hydrothermal reaction at 120 °C for 18 h (sample no. 5), impure CoSe is formed, as shown in Fig. 6a. XRD patterns in Fig. 6b and c show the formation of the pure CoSe in the presence of CTAB and cobalt acetate salt. No remarkable diffractions of other phases such as Se, CoSeO₃ or their other compounds can be found in this figure. With increasing the reaction time and temperature, intensity and width of the peaks, crystallinity, are unchanged. The XRD results show that at high reaction temperatures and times the purer products will produce.

Plot of magnetization versus applied field (M-H) at 300 K for samples no. 4 and 7 are shown in Fig. 7. The plots show paramagnetic behavior in both samples. Paramagnetism is a form of magnetism whereby the paramagnetic material is only attracted when in

 Table 1

 The reaction conditions of the products synthesized in this work.

Sample	Ratio of Co:Se	Time (h)	Temperature (°C)	Reductant	Surfactant	Selenium source	Cobalt salt	Effect
1	1:1	18	180	$N_2H_4 \cdot H_2O$	_	SeCl ₄	CoCl ₂ ·6H ₂ O	Surfactant
2	1:1	18	180	$N_2H_4 \cdot H_2O$	CTAB	SeCl ₄	$CoCl_2 \cdot 6H_2O$	
3	1:1	18	180	$N_2H_4 \cdot H_2O$	PVA	SeCl ₄	$CoCl_2 \cdot 6H_2O$	
4	1:1	18	180	$N_2H_4 \cdot H_2O$	SDS	SeCl ₄	$CoCl_2 \cdot 6H_2O$	
5	1:1	18	120	$N_2H_4 \cdot H_2O$	CTAB	SeCl ₄	$CoCl_2 \cdot 6H_2O$	Temperature
6	1:1	18	150	$N_2H_4 \cdot H_2O$	CTAB	SeCl ₄	CoCl ₂ ·6H ₂ O	
7	1:1	36	200	$N_2H_4 \cdot H_2O$	PVA	SeCl ₄	CoCl ₂ ·6H ₂ O	Temperature
8	1:1	18	180	$N_2H_4 \cdot H_2O$	CTAB	SeCl ₄	$Co(CH_3COO)_2 \cdot 4H_2O$	
9	1:1	24	200	$N_2H_4 \cdot H_2O$	CTAB	SeCl ₄	$Co(CH_3COO)_2 \cdot 4H_2O$	



Fig. 3. SEM images of samples prepared from Co(CH₃COO)₂·4H₂O in the presence of CTAB at (a) 180 °C (sample no. 8) and (b) 200 °C (sample no. 9).



Fig. 4. (a) TEM image, (b) HRTEM image and (c) SAED pattern of sample no. 3.

the presence of an externally applied magnetic field. Paramagnetic materials have a relative magnetic permeability greater or equal to unity (i.e., a positive magnetic susceptibility) and hence are attracted to magnetic fields. The magnetic moment induced by the applied field is linear in the field strength; it is also rather weak. Paramagnetic materials have a small, positive susceptibility to magnetic fields. These materials are slightly attracted by a magnetic field and the material does not retain the magnetic properties when the external field is removed. Paramagnetic properties are due to the presence of some unpaired electrons, and from the realignment of the electron paths caused by the external magnetic field. 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.

EDS analysis measurement was employed to investigate the chemical composition and purity of as-synthesized products. The EDS pattern in Fig. 8 shows that there exist only elements Co and Se, and shows the formation of a purity cobalt selenide phase.

4. Conclusions

In this paper, we report a convenient method based on reaction in aqueous system for the synthesis of CoSe nanostructures. The effects of preparation parameters such as: the temperature reaction, type of cobalt salt and surfactant on morphology, particle size, phase and purity of the products are investigated. In comparison to other similar works, our method is facile, low cost and employs nontoxic materials and solvent. This method provides an effective way to the synthesis of other metal selenides.

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Fig. 5. XRD patterns of samples prepared in the presence of: (a) SDS at 180 °C for 18 h (sample no. 4), (b) PVA at 180 °C for 18 h (sample no. 3), (c) PVA at 200 °C for 36 h (sample no. 7).

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Fig. 6. XRD patterns of samples prepared in the presence of CTAB: (a) at 120 °C for 18 h (sample no. 5), (b) at 180 °C for 18 h (sample no. 8), (c) at 200 °C for 24 h (sample no. 9).



Fig. 8. EDS spectrum of the as-synthesized cobalt selenide.



Fig. 7. M-H hysteresis at 300 K for: (a) sample no. 4, (b) sample no. 7.