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Hydrothermal synthesis of CoSe nanostructures without using surfactant

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ABSTRACT

CoSe nanostructures are synthesized by hydrothermal route in the presence of reductant, without using surfactant. In this work, we use from $SeCl_4$ 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 nanostructures.

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, $CoSe_2$ and CoSe, and two other possible compositions: Co_3Se_4 and Co_2Se_3. 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, $SeCl_4$ is used as a new selenium source. To the best of our knowledge, studies on the synthesis of cobalt selenide nanostrucrures by using $SeCl_4$ 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 Kα 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 magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

2.2. Synthesis of CoSe nanostructures

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, $SeCl_4$ was dissolved in 20 ml of distilled water and added into the solution under strong magnetic stirring at room temperature. Then reductant ($N_2H_4\cdot H_2O$, KBH_4,·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	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
2	1:1	12	180	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
3	1:1	18	180	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
4	1:1	12	220	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
5	1:1	12	150	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
6	1:1	12	120	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
7	1:1	12	180	$N_2H_4 \cdot H_2O$	–	$SeCl_4$	$CoSO_4 \cdot 7H_2O$
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	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$
10	1:1	12	180	Zn	–	$SeCl_4$	$CoCl_2 \cdot 6H_2O$

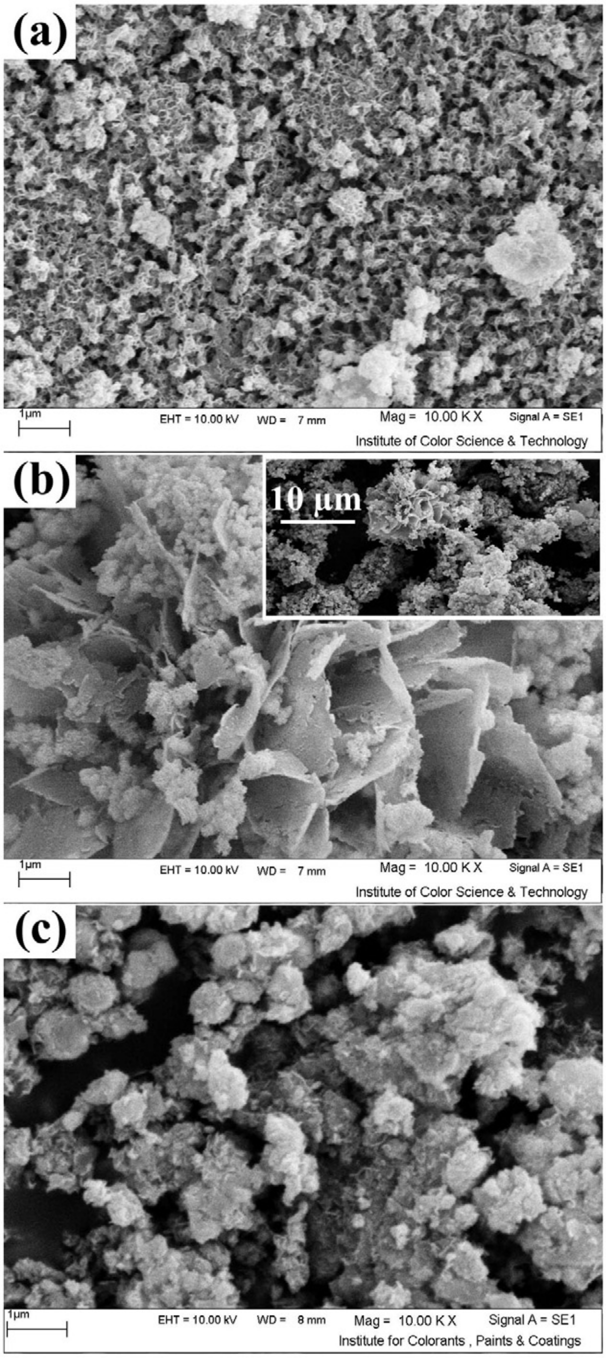

Fig. 1. SEM images of samples prepared from $CoCl_2 \cdot 6H_2O$ and $SeCl_4$ in the presence of hydrazine at 180 °C for: (a) 6 h (sample no. 1), (b) 12 h (sample no. 2) (inset: low-magnification SEM image of sample no. 2), (c) 18 h (sample no. 3).

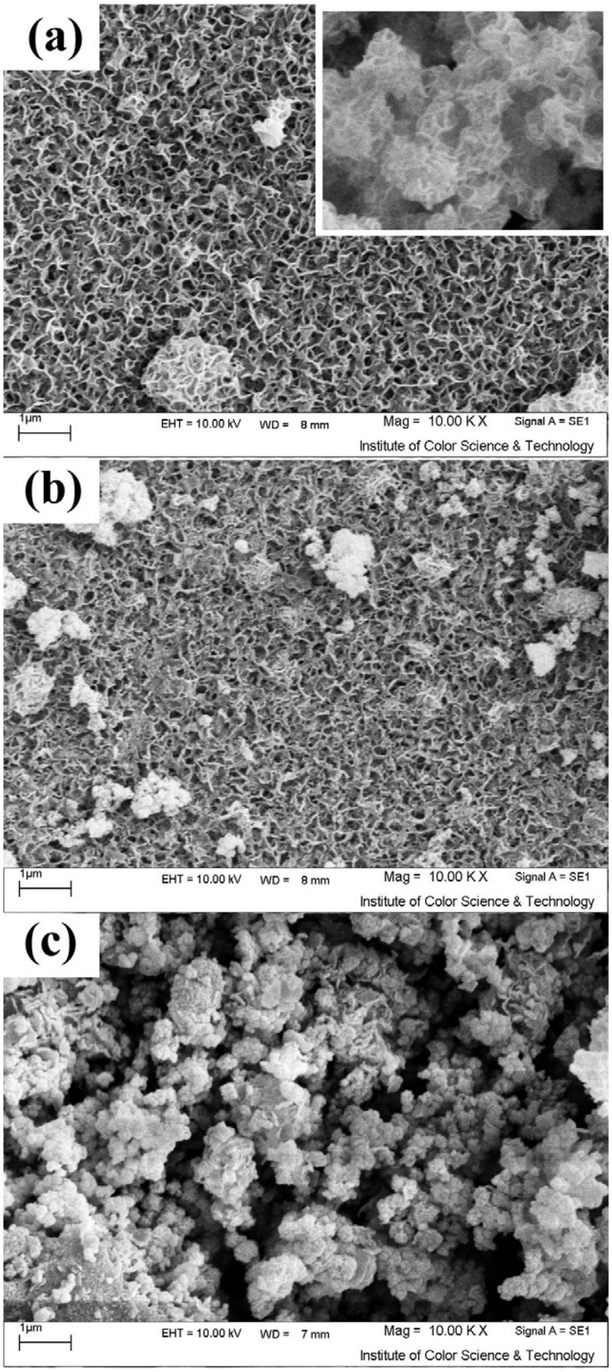

Fig. 2. SEM images of samples prepared from $CoCl_2 \cdot 6H_2O$ and $SeCl_4$ in the presence of hydrazine after 12 h hydrothermal reaction at: (a) 220 °C (sample no. 4) (inset: low-magnification SEM image of sample no. 4), (b) 150 °C (sample no. 5), (c) 120 °C (sample no. 6).