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Controlled Hydrothermal Synthesis of NiSe Nanospheres and Nanorod Bundles

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Abstract: In our work, we report a simple and controllable hydrothermal synthetic approach of NiSe nanostructures with two different morphologies, namely the hollow nanospheres and nanorod bundles. We have preliminarily explored the growth process of the NiSe nanorod bundles based on our experimental observations depending on different amounts of additive. In addition, we have also preliminarily studied the Raman active modes and magnetic properties of the hollow nanospheres and nanorod bundles at room temperature. Therefore, we believe that it will accelerate the development of NiSe in its practical applications.

Keywords: Synthesis; NiSe; Nanorods Bundles; Growth Process

1. Introduction

In the past two decades, metal selenides have drawn considerable attention owing to their important optical, electrical, and transport properties [1–3]. To date, there have been extensive studied on exploring various approaches to synthesize the different morphology of metal selenides, and most of them so far can be categorized mainly as either chemical vapor deposition methods or solution-phase chemical routes. Among them, hydrothermal method has exhibited many outstanding advantages in cost, manipulation, large-scale production, control of objective products, environment-friendliness and so on [4]. Interestingly, owing to the immense scientific and technological interest, much effort has been devoted into the controlled synthesis of the transition metal selenides. However, the design and synthesis of these transition metal selenides via hydrothermal method of nanostructures with well-defined morphology, size and controlled properties is still an ongoing challenge.

NiSe, as an important VIII-VI semiconductor, is considered to be a promising material for lithium battery [5–6], It is also viewed as a less toxic and more environmentally responsible alternative to related narrow band gap lead or cadmium-based semiconductors. Until now, a few pioneering works on the NiSe nanostructures also have been developed [7–11]. However, few reports on the synthesis of NiSe nanostructures, especially nanorod bundles through hydrothermal method is reported to date, although they are desired strongly.

Herein, we have successfully synthesized two different morphologies of NiSe via a simple and controllable hydrothermal synthetic method, namely the hollow nanospheres and the nanorod bundles. Moreover, we have proposed the growth process of the NiSe nanorod bundles. In addition, the Raman active modes and magnetic properties of the hollow nanospheres and nanorod bundles are preliminarily studied at room temperature.

2. Experimental Section

All reagents were analytical grade and used without further purification and the water used was deionized.2.1.

2.1. Synthesis of Samples

The typical synthesis of NiSe nanorod bundles was as follows: 0.145 g Ni(NO3)2 6H2O (0.5 mmol), 0.08 g Polyvinyl Pyrrolidone (PVP, K-30) and 0.055 g SeO2 (0.5 mmol) were dissolved in deionized water (18 mL) at room temperature to get a clear solution under vigorous magnetic stirring. Then, 10 mL ammonia water (25~28%) and 12 mL N2H4·H2O (85%) were added into the above solution, and a dark-blue solution appeared immediately. The solution was continuously stirred for 10 min to get a well-dispersed status. Then, the mixture was sealed in a Teflon-lined stainless steel autoclave (50 mL) and maintained at 180 °C for 2 h under hydrothermal treatment. After heating, it was removed from the oven and naturally cooled to room temperature. The resulting black products were collected by centrifugation, washed with deionized water and absolute ethanol three times respectively, and the obtained sample was dried in vacuum at 60 °C for 12 h.

The typical synthesis of NiSe hollow nanospheres was carried out under the same condition as the preparation of NiSe hollow nanospheres without adding 0.08 g Polyvinyl Pyrrolidone (PVP, K-30).

2.2. Characterization

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The products were characterized by X-ray diffraction measurements carried out on X-ray diffractometer (XRD, Bruker D8 Advance diffractometer) with Cu-Ka radiation in the range of 10–80° at a scanning rate of 7 °min^{-1}. The morphology of the products was observed by a field emission scanning electron microscopy (SEM, S-4800) and a transmission electron microscope (TEM, JEOL, JEM-2100). Raman spectra were recorded on a Raman spectrometer (WITEC Spectra Pro 2300I) operating with 532 nm laser. Magnetic measurement was carried out by using a vibrating sample magnetometer (VSM, HH-15) under a magnetic field from -5 KOe to 5 KOe at room temperature.

3. Results and Discussion

The phase purity of as-synthesized two different NiSe samples was characterized by X-ray diffraction (XRD, Fig. 1a). All the peaks displayed in XRD pattern can be readily indexed to the hexagonal phase of NiSe with lattice constants a = 3.66 Å, b = 3.66 Å and c = 5.33 Å, which are in good agreement with the literature values (JCPDS 02-0892). In addition, the obtained NiSe nanorod bundles in Fig. 1b shows that the peaks readily indexed to the rhombohedral phase of NiSe with lattice constants a = 10.01 Å, b = 10.01 Å and c = 3.315 Å, which are in good agreement with the literature values (JCPDS 18-0887). These two results indicate that the two NiSe samples obtained via our synthetic system are both consisted of pure phases.The morphology and size of the products prepared by the procedure described in the experimental section are visualized by SEM as shown in Fig. 1c-d. As can be seen at Fig. 1c, the as-obtained NiSe product in the reaction system consists almost entirely of 300–400 nm nanospheres formed by lots of nanoparticles. With adding the PVP, the obtained sample is consisted of nanorod bundles with the length of 0.5–1.0 μm (Fig. 1d). In addition, transmission electron microscopy (TEM) provides further insight into the microstructural details of NiSe samples. Fig. 1e-f shows TEM images of two different kinds of NiSe samples which display the sphere is hollow and nanorod bundles are also to be further demonstrated.

To better understand the formation processes, a series of contrast experiments were carried out to determine the parameters, such as reaction time, that might influenced the formation of hollow NiSe nanospheres in our previous paper [12]. The main chemical reactions are as follows:

$$SeO_2 + N_2H_4 \cdot H_2O \rightarrow Se\downarrow + N_2\uparrow + 3H_2O \quad (1)$$

$$3Se + 6OH^- \rightarrow 2Se^{2-} + SeO_3^{2-} + 3H_2O \quad (2)$$

$$Ni^{2+} + Se^{2-} \rightarrow NiSe\downarrow \quad (3)$$

In addition, we have found that the Polyvinyl Pyrrolidone (PVP) played an important role in effective controlling the shape of NiSe nanocrystals. Fig. 2 shows SEM images of the samples obtained by adding the different amounts of PVP. When adding 0.03 g PVP (Fig. 2a), the obtained product consists of numerous nanoparticles with size of ca. 30–50 nm, whereas it is different with the typical NiSe hollow nanospheres obtained under the same condition without adding PVP. Fig. 2b also shows that the sample is the hexagonal phase of NiSe (JCPDS 02-0892). When the amount of PVP is increased to 0.06 g, the product is composed of almost entirely of nanorod bundles. Only a small portion (< 5%) of nanoparticles can be found. The length of rod bundles is increased into 500–800 nm with the diameter of 100–200 nm, which results in the shape of NiSe products is close to the nanorod bundles morphology. But the XRD analysis in Fig. 2d shows that the sample is not the pure phase which is contained of the hexagonal phase of NiSe (JCPDS 02-0892) and rhombohedral phase of NiSe (JCPDS 18-0887). Up to 0.09 g PVP, a bit more than the optimum value, the monodispersity of the sample becomes to be worse (Fig. 2c). These results clearly indicate that the PVP in our reaction system can act as a shape controller to change the NiSe nanostructures and crystal types. In this process, due to the effect with the surfactant (PVP), the type of crystal has been strongly influenced and turned to the rhombohedral phase. The PVP promotes the transaction of crystal types in our synthetic process. This phenomenon is very similar to the previous reports [9]. The PVP could stimulate the crystal change of the NiSe (From hexagonal phase to rhombohedral phase). The further study of the process is still in process.

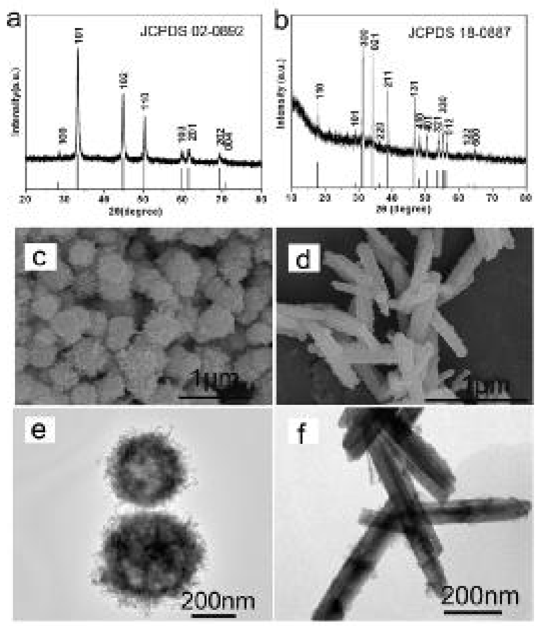

Figure 1. XRD patterns of the as-synthesized NiSe products: (a) hollow nanospheres; (b) nanorod bundles; (c)–(d) SEM images of as-synthesized NiSe hollow spheres and nanorod bundles; (e)–(f) TEM images of NiSe hollow sphere and nanorod bundles

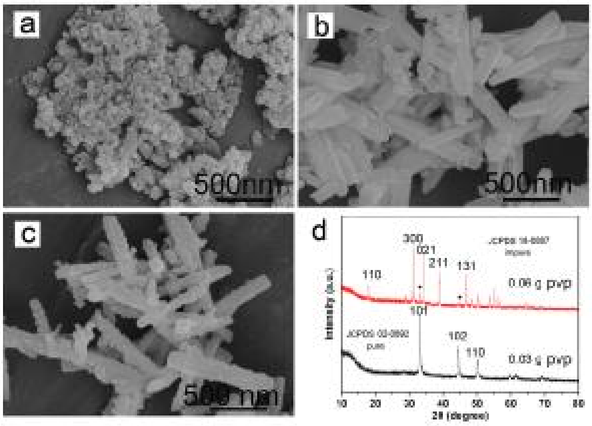

Figure 2. SEM images of the as-prepared NiSe with different amounts of PVP in the same reaction condition: (a) 0.03 g; (b) 0.06g; (c) 0.09 g; (d) the XRD patterns of the samples (a) and (b)

Figure. 3 shows the Raman spectra of the as-synthesized two different NiSe samples. For NiSe hollow nanospheres, there are three Raman peaks at 534, 697, and 1070 cm-1. The peaks at 534 cm-1 can be assigned to the longitudinal optical (LO) one-phonon (1P) modes of NiSe. The peaks at 697 and 1070 cm-1 can be assigned as two-phonon (2P) modes of 2TO and 2LO, respectively [13]. In the spectra, the 1P band is pronounced in our prepared NiSe nanospheres due to the presence of defects or surface effect [14]. In addition, the NiSe nanorod bundles have integral red shift (528, 694 and 1060 cm-1). It also indirectly there is a possible that we could realize the transition of the crystal types in the certain hydrothermal condition. Meanwhile, the peaks, observed at 202 cm-1, 384 cm-1 (202 cm-1, 358 cm-1) might be attributed to Se–Se librational and stretching vibrations or their combination. It is close to the value observed in other metal selenides [15]. The difference in the absorption peaks of NiSe hollow nanospheres and nanorod bundles is possible due to the different crystal phases of the NiSe, the anisotropy of morphology and quantum effects.

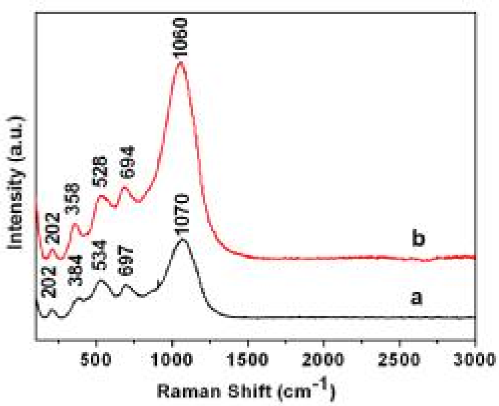

Figure 3. Raman spectra of NiSe samples at room temperature: (a) hollow nanospheres; (b) nanorod bundles

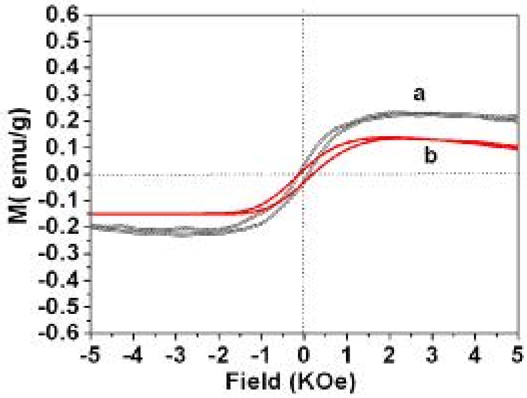

Figure 4. Magnetic hysteresis curves of NiSe samples measured at room temperature: (a) nanorod bundles; (b) hollow nanospheres

In addition, we have studied the magnetic properties of the two different morphologies of NiSe samples at room temperature. As shown in Fig. 4, we could found that the saturation magnetization (Ms) and coercivity (Hc) values of as-obtained nanorod bundles are 0.223 emu/g and 110 Oe, and NiSe nanospheres are 0.142 emu/g and 180 Oe, respectively. In our work, the coercivity of the nanorod bundles is lower than the nanospheres. It is mainly possible due to the different crystal phases of the NiSe. Then, these studies will be utilized as building blocks in future of research and development of materials.

Conclusion

In summary, we have successfully fabricated the NiSe nanostructures with two different morphologies, namely the hollow nanospheres and nanorod bundles through a simple and controllable hydrothermal synthetic route. We have preliminarily studied the growth mechanisms of the nanorod bundles based on a series of contrast research observations depending on different reaction conditions. Moreover, the magnetic properties of the as-obtained two different NiSe nanocrystals are measured at room temperature. In addition, we believe that our study may extend the applications of the NiSe and provide alternative synthetic approach for other metal selenides and in the future.

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