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Synthesis and characterization of hexagonal nano-sized nickel selenide by simple hydrothermal method assisted by CTAB

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ABSTRACT

Nano-sized nickel selenide powders have been successfully synthesized via an improved hydrothermal route based on the reaction between $NiCl_2{\cdot}6H_2O$, $SeCl_4$ and hydrazine ($N_2H_4{\cdot}H_2O$) in water, in present of cetyltrimethyl ammonium bromide (CTAB) as surfactant, at various conditions. The products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray energy dispersive spectroscopy analysis. Effects of temperature, reaction time and reductant agent on the morphology, the particle sizes and the phase of the final products have been investigated. It was found that the phase and morphology of the products could be greatly influenced by these parameters. The synthesis procedure is simple and uses less toxic reagents than the previously reported methods. Photoluminescence (PL) was used to study the optical properties of NiSe samples.

1. Introduction

Over recent years, a great deal of research effort has been devoted to the research in nanocrystallites of semiconductors because of their quantum size effects and potential applications [1,2]. Hence, investigations on the synthesis and modification of nanosized NiSe have attracted tremendous attentions. Nickel selenide semiconductors exhibit interesting electronic and magnetic properties and have found several applications in the field of materials science, which has attracted considerable research attention over the last 10 years or so [3–10]. Traditionally, nickel selenides were synthesized by using a variety of methods, such as solid-state synthesis [11], molecular precursors [12], elemental direct reactions [13], ultrasonic synthesis [14] and mechanical alloying [15]. However, these methods often need a high temperature or use toxic metallorganic reagents as precursors and usually need a special device. Few of these methods can be used to controllably and systematically synthesize a series of nickel selenides. The solvothermal method is by far the most reported [16]. However, it is still a challenge to obtain a series of nickel selenides ($NiSe_2$, $Ni_{1+x}Se$ and Ni_3Se_2) and systematically control their compositions, phase structures, and morphologies in aqueous solution. Recently, the hydrothermal method has been also reported to prepare metal chalcogenide nanostructural materials, which have potential advantages of relatively low cost, high purity, and controlled morphology [17–20].

Na_2SeO_3 [21,22], NaHSe, H_2Se, $Se(C_2H_5)_2$, selenium powder [23], bis(trimethylsilyl)selenium $Se(TMS)_2$ [24], selenourea ($H_2NC(Se)NH_2$) [25] and SeO_2 [26] have been introduced as selenium reagents for the synthesis of metal selenides. $SeCl_4$ was selected in our experiments to provide a highly reactive selenium source in aqueous solution and has given good results. Following this method, we herein report a convenient and controllable synthetic method for obtaining a series of nickel selenides. By simply adjusting the molar ratio of the reactants, capping agent, metal salts, reductant agent, the temperature or the reaction times, we could obtain NiSe samples with the best size and morphology. 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 [27].

Herein, we developed a facile method to prepare NiSe in an aqueous solution using hydrazine as reductant and CTAB as surfactant under hydrothermal conditions. 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 optical properties of the new materials are reported. This study also describes a comparison of features observed from the products obtained from various conditions.

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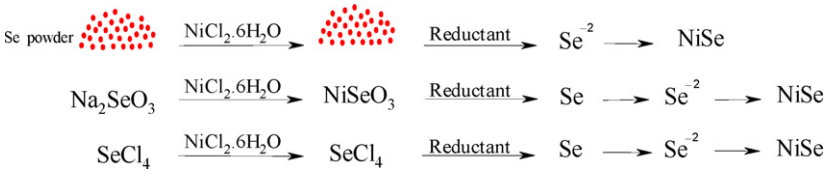

Scheme 1. Comparison of different Se sources to synthesize nickel selenides.

2. Experimental

2.1. Chemicals and equipment

All the chemicals reagents used in our experiments were of analytical grade, were purchased from Merck and were used as received 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. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscopy (TEM) image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Room temperature photoluminescence (PL) was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer.

2.2. Synthesis of nano-sized NiSe

Nano-sized NiSe were synthesized by simple hydrothermal method. In a typical synthesis a mixed aqueous solution composed of $NiCl_2{\cdot}6H_2O$ and $SeCl_4$ (with a stoichiometric ratio of 1:1) was added to CTAB aqueous solution under strong magnetic stirring at room temperature for 15 min. Then, 2 ml of hydrazine was added drop-wise to the above solution, the color of the colorless solution changed to black, indicating that Se^{4+} was reduced to Se and then Se^{2-} and NiSe was generated. After stirring, the reactants were put into a Teflon-lined autoclave of 100 ml capacity. The autoclave was maintaining at 180 °C for 12 h and then cooled down to room temperature naturally. The black precipitate was centrifuged, washed out with alcohol and distilled water for three times and dried under vacuum at 60 °C for 8 h. The purity and morphology of the as-prepared product was characterized by XRD, SEM and TEM.

3. Results and discussion

In our experiment, when $NiCl_2{\cdot}6H_2O$ and $SeCl_4$ are added in the deionized water, a completely clear acidic solution is obtained that contain H_2SeO_3 (Eqs. (1); however, H_2SeO_3 can be converted to Se, by $N_2H_4{\cdot}H_2O$, quickly up on heating, which has high reactivity and is easy to be disproportionate into Se^{2-} ion under alkaline conditions (Eqs. (2) and (3)). Under given condition, free Ni^{2+} ions can react with Se^{2-} ions (Eq. (4)) to form NiSe. The proposed mechanism for the synthesis of NiSe can be expressed in the following equation:

$$SeCl_4 + 3H_2O \rightarrow H_2SeO_3 + 4HCl \quad (1)$$

$$H_2SeO_3 + N_2H_4{\cdot}H_2O \rightarrow Se\downarrow + N_2\uparrow + 3H_2O \quad (2)$$

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

$$Ni^{2+} + Se^{2-} \rightarrow NiSe\downarrow \quad (4)$$

Traditionally, Na_2SeO_3 and Se powder were commonly employed in the synthetic systems of nickel selenides. Compared with the commercial Se powder, the newly produced Se reduced from $SeO_3{}^{2-}$ ions of Na_2SeO_3 is much more reactive [21,22]. However, when Na_2SeO_3 was employed to prepare M_xSe_y (M = metal), $SeO_3{}^{2-}$ should be slow-released from $MSeO_3$ (M = metal) precipitation and then be reduced to Se, which would hinder the formation of M_xSe_y nuclei [28]. In this work, $SeCl_4$ as the Se source have been chosen to prepare the NiSe. $SeCl_4$ not only can be reduced to Se with high reactivity but also not react with Ni^{2+} to form precipitation. Furthermore, we find that the application of $SeCl_4$ can affect the size of NiSe nanocrystals. Reentry, our group reported synthesis of nanostructures containing telluride ion [29–31], These samples have applications similar to the samples containing selenide ions. In Scheme 1 different Se sources to synthesize nickel selenides have been compared. The effects of temperature, reaction time and reductant agent on the morphology, the particle sizes and the phase of NiSe samples have been investigated. The results have been listed in Table 1.

The XRD patterns of as-synthesized products are shown in Fig. 1. All peaks in the patterns correspond to the reflections of hexagonal phase NiSe [space group: *P*63/*mmc*], with lattice constants $a = b = 0.366$ nm and $c = 0.533$ nm (JCPDS 75–0610). No remarkable diffractions of other phases such as selenium, nickel or their other compounds can be found in Fig. 1, indicating that a pure NiSe phase has been formed after the synthesis for all samples. According to Fig. 1, with increases at the reaction time from 12 h (sample no. 3) to 24 h (sample no. 5), the crystallinity of the as-prepared products is increased and with the elongation of reaction time up to 70 h (sample no. 6), the crystallinity is decreased. In sample no. 3 the average particle size of the sample is about 22 nm, estimated through the Scherrer formula. In comparison with sample no. 3, sample no. 5

Table 1
The reaction conditions of nickel selenides synthesized from $NiCl_2.6H_2O$ and $SeCl_4$ (molar ratio = 1:1).

Sample no.	Effect	Surfactant	Time (h)	*T* (°C)	Reductant agent	Morphology	Size
1	Temperature	CTAB	12	80	$N_2H_4{\cdot}H_2O$	Particle	<70 nm
2		CTAB	12	110	$N_2H_4{\cdot}H_2O$	Particle	<50 nm
3		CTAB	12	180	$N_2H_4{\cdot}H_2O$	Flower-like	Non uniform
4	Time	CTAB	6	180	$N_2H_4{\cdot}H_2O$	Aggregated particle	>100 nm
5		CTAB	24	180	$N_2H_4{\cdot}H_2O$	Particle	<100 nm
6		CTAB	70	180	$N_2H_4{\cdot}H_2O$	Flower-like	500 nm– 2 μm
7	Reductant	CTAB	12	180	Zn	Particles elongated along the *c*-axis	Lengths of 500 nm–2 μm
8		CTAB	12	180	KBH_4	Rod-like particles	Diameters of 150–600 nm <100 nm