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Synthesis and characterization of a nickel selenide series via a hydrothermal process

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ABSTRACT

A series of nickel selenides (NiSe and $NiSe_2$) has been successfully synthesized from the reaction of $SeCl_4$ with $NiCl_2{\cdot}6H_2O$ in the presence of cetyltrimethyl ammonium bromide (CTAB) as surfactant and hydrazine hydrate ($N_2H_4{\cdot}H_2O$) as reductant at 180 °C for 12 h through a simple hydrothermal method. The morphology, phase structure and composition of Ni_xSe_y can be controlled by adjusting the Ni/Se ratio of the raw materials, the quantity of reductant, the reaction temperature and so forth. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) analysis. It was found that when the ratio of Ni/Se is 1:1 or 3:2, flower-like assemblies of NiSe nanosheets are formed, at 180 °C for 12 h. When the ratio of Ni/Se is 1:2 at 180 °C, the products are found to be the mixture of hexagonal NiSe and cubic $NiSe_2$. With decrease of nickel content in molar ratio of 1:2 (Ni:Se), nanospheres are agglomerated and microstructures are formed. With the reaction temperature decreasing from 180 °C to 120 °C, we reach pure $NiSe_2$ nanoparticles. The formation mechanism of the nickel selenides has been investigated in detail by means of XRD and SEM analyses.

1. Introduction

The metal chalcogenides form a vast, almost infinite area of research. It is practically impossible in a single article to cover all the aspects of this chemistry. The task is made easier since reviews devoted

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to different aspects of the metal chalcogenide chemistry have been appearing continuously, trying to keep up with the new compounds, while the synthesis and characterization of chalcogenides continues unabated [1–9]. The efforts in this area are constantly driven by important technological applications found for many of these materials as well as their remarkable diversity in structure and properties [10]. With increased access to sophisticated structural tools and solution methods, more and more complicated compounds are prepared and characterized. A vast amount of research was dedicated also to the intercalation of innumerable guests into the chalcogenide hosts [7].

Nickel selenide semiconductors exhibit interesting electronic and magnetic properties and have found several applications in the field of materials science. Recently, $NiSe_2$ has been found new applications as a kind of storage energy material due to its electrochemistry properties [11]. Therefore, enormous research attention has been focus on these semiconductors over the last 10 years or so [12–18]. The metal selenides, similar to those of sulfides and tellurides, tend to form covalent, often low-dimensional structures in contrast to the ionic, 3D-type structures of the oxides. The greater covalency of the metal–selenides interactions reduces the relative charge on the metal ion thus enhancing metal orbital diffuseness and favors M–M bonding.

Traditionally, CVD method [19], molecular precursors [20,21], Chemical method [22], solid-state synthesis [23–25] elemental direct reactions [26] ultrasonic synthesis [27], mechanical alloying (MA) [28–30], hydrothermal [31] and solvothermal process [32] were employed to synthesize nickel selenides. Herein, we develop a hydrothermal method to prepare nickel selenides in an aqueous solution using hydrazine as reductant and CTAB as surfactant. This method is simple, convenient and effective controlled synthetic procedure and provided an effective way to the synthesis of selenides and tellurides materials. For a few years, we have been interested in the synthesis of metal, metal oxide, sulfide, selenide and telluride nanostructures, using this method [33–38]. In the present work, the physical properties as well as the optical properties of the new materials have been reported.

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and were used as received without further purification. The XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu Kα radiation ($\lambda = 1.54$ Å). X-ray diffraction is used to determine the structure of small molecules and proteins at high resolution. Applications include chemistry, geology, physics, structural biology and pharmaceutical research. The trend in crystallography is towards the ability to analyze smaller, poorer crystal samples and to increase the speed of sample throughput. The XRD is typically set up with an Ag or Mo anode tube and a scintillation detector. Experiments with a sample of SiO_2 have demonstrated that the statistical error across the angular range varies greatly, and good data typically requires 24 h to collect. Scan times of this length are made on the assumption that the signal is sufficiently good; a range of capillary sizes, from 0.5 to 2.5 mm, are available to allow the balance between scattering intensity and absorption to the optimized. The significant improvement in the intensity of X-ray radiation placed on the sample from the dual Nova(TM) and Mova(TM) X-ray micro-sources makes both higher resolution and higher throughput possible. The system is ideal for the study of challenging samples in small molecule and protein crystallography. It includes co-mounted, dual wavelength and high intensity X-ray micro-sources of both molybdenum and copper wavelength. It is the first dual wavelength system incorporating purely high intensity Mo and Cu micro-source X-ray technology. The system improves throughput in several ways. The high intensity X-ray radiation allows for shorter X-ray exposure, as does the high sensitivity, large area Atlas CCD (charge-coupled device). Both enable faster data collection. In addition, the duty cycle (the dead time required for the CCD detector to transfer data to the computer), has been substantially reduced. Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope. The SEM employs a Schottky based gun design using a point-source cathode of tungsten which has a surface layer of zirconia (ZrO_2). The working