Synthesis of Nickel Selenide Nanocables and Nanotubes

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(Received May 18, 2005; CL-050655)

Se@$NiSe_2$ nanocables were synthesized using a procedure that combines self-sacrificing template method and hydrothermal method, in which nanorodes of trigonal selenium served as template. The nickel selenide nanotubes were obtained by appropriate evaporation to remove Se cores.

In the past decades, a considerable number of experimental and theoretical studies on transition metal dichalcogenides have been reported because of their interesting electrical and magnetic properties and promising applications in many fields, such as conductivity, and catalytic fields.[1] Nickel selenides are the typical Pauli paramagnets with metallic conductivity. They now have been regarded as typical materials for studies of the physical characteristics associated with a narrow band electron system.[2] Many methods have been employed for synthesis of nickel selenides, such as molecular precursor,[3] elemental reactions,[4] and mechanical alloying.[5] According to previous investigation, the properties of nickel selenides sensitively depend on their compositions and morphologies. Our group has successfully synthesized a series of nickel selenide nanocrystal by hydrothermal method. Octahedral, spherical, and irregular $NiSe_2$ particles with micrometer or nanometer size have been produced.[6] Recently, Li group synthesized hollow submicrometer spheres of nickel selenide.[7] To our knowledge, tubular nanostructures of nickel selenide has not been reported so far. It is significant challenges to fabricate nickel selenides with tubular morphologies. In this letter, we demonstrate a synthesis of Se@$NiSe_2$ nanocables and $NiSe_2$ nanotubes using a procedure that combines self-sacrificing template method with hydrothermal method, in which nanorodes of trigonal selenium served as template. The disproportionating reaction of selenium was fulfilled on the surface of Se nanorod template under alkaline condition. Subsequently, a $NiSe_2$ shell was produced on the surface of the nanorod in $NiCl_2$ solution by hydrothermal treatment at 110 °C. The reactions in our route can be summarized as the following:

$$3Se + 6NaOH = 2Na_2Se + Na_2SeO_3 + 3H_2O, \qquad (1)$$

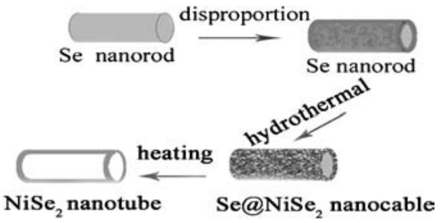
$$Na_2Se + (x-1)Se = Na_2Se_x, \qquad (2)$$

$$Na_2Se_x + Na_2SeO_3 + 2Ni^{2+} = NiSe_2\downarrow + NiSeO_3 + 4Na^+ + (x-2)Se. \qquad (3)$$

When newly produced Se nanorods were mixed with NaOH solution, the disproportional process[8] would occur at the surface of Se nanorods (see: eq 1). Following that, multinary selenide materials were formed because of the existence of excessive active Se on the surface of Se nanorods (see: eq 2). This is just like the formation of polysulfide ions in aqueous solution.[9] In the hydrothermal process, the $[Se_x]^{2-}$ and $SeO_3{}^{2-}$ reacted with Ni^{2+} (see: eq 3). The $NiSeO_3$ dissolved into solution owing to $NiSeO_3$ has good solubility at above 100 °C during hydrothermal process. So $NiSe_2$ deposited on the surface of Se nanorods without $NiSeO_3$ and gradually formed the dense shell. When the reaction mixture was cooled to room temperature, the $NiSeO_3$ precipitated out. But it can be removed by hot water.

Our strategies to fabricate the Se@$NiSe_2$ nanocables and $NiSe_2$ nanotubes are summarized in Scheme 1. Firstly, single crystal Se nanorods were prepared using a similar method to those in previous works.[10] The Se nanorods (5 mmol) were added into a solution of NaOH (0.7 mol L^{-1}) under magnetic stirring for 15 min and then were collected by centrifuging. The precipitate was put into a solution of $NiCl_2$ (0.3 mol, 45 mL) with magnetic stirring for 5 min. Then the solution was placed in a Teflon-lined stainless steel autoclave of 50 mL capacity. The autoclave was maintained at 110 °C for 10 h and then cooled to room temperature on standing. A black precipitate was collected by centrifuging and washed with hot water several times. Finally, the as-produced sample was heated at 230 °C for 20 min under argon atmosphere in order to remove unreacted Se. Almost all of Se can be removed by heating the as-produced sample because of relatively low melting point of Se (217 °C), and the $NiSe_2$ is stable at temperatures below 500 °C.[6]

Figure 1 shows the powder X-ray diffraction (XRD) patterns of the products obtained at different stages of preparation process. Figure 1a shows the XRD pattern of pure trigonal selenium nanorods served as template. All the peaks could be indexed as trigonal selenium (JCPDS 06-0362). Figure 1b shows the XRD pattern taken from the sample after a 10 h hydrothermal process and washing with hot water. Except for Se peaks, some new peaks appeared, and all of the new peaks can be indexed to be cubic $NiSe_2$ (JCPDS card No. 41-1495). It indicated that a part of Se has reacted with $NiCl_2$ under hydrothermal condition. Figure 1c shows the XRD pattern taken from the sample after



Scheme 1. Schematic illustration of experimental procedure for preparation of Se@$NiSe_2$ nanostructures and $NiSe_2$ nanotubes. (a) The preparation of single crystal Se nanorods. (b) The disproportion reaction on the surface of nanorods. (c) The synthesis of nickel selenide on the surface of Se nanorods. (d) The as-obtained sample was heated.

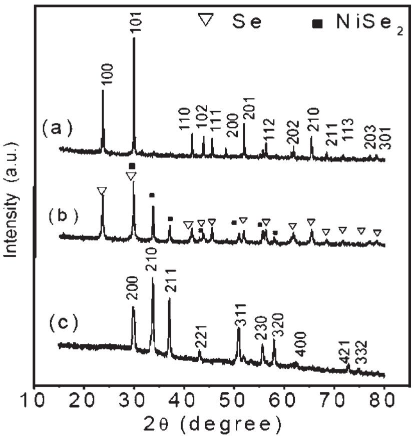


Figure 1. XRD patterns of product in three stages: (a) trigonal Se nanorods; (b) after a 10 h hydrothermal process and washing with hot water; (c) after thermal treatment at 230 °C under argon atmosphere.

thermal evaporation process. All the peaks could be indexed to be $NiSe_2$. It indicated that unreacted Se could be removed by evaporation.

The morphology and structure of the as-obtained samples in the different stages were observed by a field emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM), respectively (shown in Figure 2). Figure 2a shows the FESEM images of Se nanorods (80–125 nm in diameter). Figure 2b shows the FESEM image of the as-produced sample after disproportion process under alkaline condition. The surfaces of nanorods become coarse. Figure 2c shows the TEM image of the sample after hydrothermal process and washing with hot water. The surfaces of the nanorods in this stage become rougher owing to the formation of $NiSe_2$ shell from aggregated nanoparticles. The diameters of the nanorods were determined to be about 160 nm. Figure 2d shows the TEM image of the as-obtained sample after thermal evaporation. Many tubular structures (about 120–160 nm in outer diameter) were observed. It indicated that the Se core has been removed and the $NiSe_2$ shell was retained, which is in agreement with the result of the XRD pattern result of the samples. The insets of Figures 2c and 2d show the selected area electron diffraction pattern taken from the relevant sample, which indicated the polycrystalline wall. Figure 3 shows a typical HRTEM observation of the tube wall (approximate 18 nm in wall thickness), which indicated that the wall was composed of many nanocrystallites with different orientations. The fringe spacing (about 0.59 nm) observed in this image agrees with the separation between the (100) lattice planes of cubic $NiSe_2$.

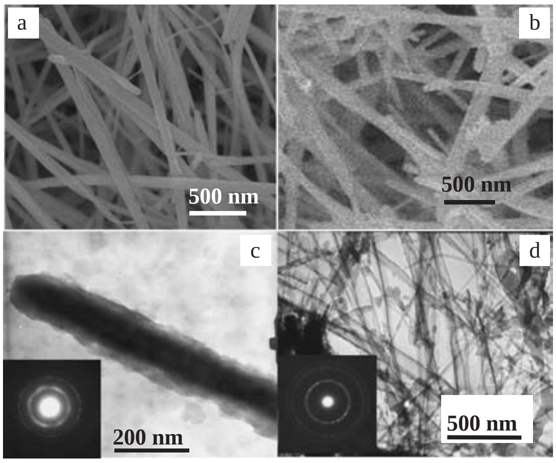


Figure 2. (a) FESEM image of Se nanorods. (b) FESEM image of as-obtained sample after disproportion process under alkaline condition. (c) TEM images of Se@NiSe2 composite. (d) TEM image of final product.

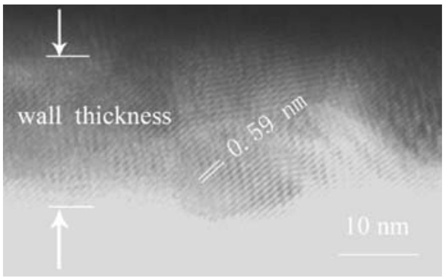


Figure 3. The HRTEM image of Se@NiSe2 composite, showing that the wall of nanotube was consisted of many nano-crystallites.

In summary, Se@$NiSe_2$ nanocables and $NiSe_2$ nanotubes were synthesized using a procedure that combines template method with hydrothermal methods. The high-resolution transmission electron microscopic observation indicated that the wall of $NiSe_2$ nanotube was formed of polycrystalline nanoparticles. Tubular nickel selenide perhaps provide some new characteristic for the theoretical and applied studies on a narrow band electron system owing to their relatively low densities and large surface areas.

The authors gratefully acknowledge China Postdoctoral Science Foundation and K. C. Wong Education Foundation, Hong Kong.

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Published on the web (Advance View) July 9, 2005; DOI 10.1246/cl.2005.1136