Rapid Synthesis of SnSe Nanowires via an Ethylenediamine-assisted Polyol Route

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A rapid ethylenediamine-assisted polyol (ENAP) process has been proposed to synthesize SnSe nanowires with high aspect ratio for the first time. The product was characterized by X-ray powder diffraction and transmission electron microscope. It was found that ethylenediamine has a great influence on the morphology and purity of the final products.

Currently, developing well-controlled synthesis methods of low-dimensional semiconductor nanomaterials such as nanowires and nanotubes[1–3] has sparked increasing interest because of their great potential applications to optoelectronic devices,[4] such as nanowires light-emitting devices with extremely low power consumption.[5]

Tin monoselenide, SnSe, belongs to the interesting class of isomorphic materials that are in many ways between two-dimensional (layer type) systems and three-dimensional crystals, and it exhibits a strong anisotropy of optical properties.[6] The energy gap of SnSe is about 0.9 eV and it can be widely used in infrared optoelectronic devices,[7] memory switching devices[8] and holographic recording system.[9] SnSe is commonly synthesized by the solid state reaction of the elements at high temperature,[10] Bridgman methods[11] and vapor phase methods,[6,7,12] which need high temperature, toxic reagents or long reaction time. Recently, solution routes, such as hydrothermal,[13,14] solvothermal,[15] and organometallic precursor methods,[16] etc.[17] have been developed for the synthesis of SnSe nanoparticles. However, to the best of our knowledge, no report could be found on the synthesis of SnSe nanowires with high aspect ratio.

In this study, we reported the synthesis of SnSe nanowires, for the first time, via a novel ethylenediamine-assisted polyol (ENAP) route. The addition of ethylenediamine avoids the occurrence of impurities and can effectively control the morphology of the final products. Compared with previous reports, the present method is relatively simple, rapid and provide a new strategy for the synthesis of metal chalcogenides with special morphology.

All reagents were of analytical purity from Shanghai Chemistry Co. and were used without further purification. Manipulations and reactions were carried out in air. In a typical procedure, 0.01 mol Se powder and 50 mL diethylene glycol (DEG) were added to a one-necked round-bottomed flask of 100 mL capacity, then 2 mL ethylenediamine was added at room temperature on magnetic stirring. After about 20 min, elemental Se was dissolved completely. Then 0.01 mol $SnCl_2 \cdot 2H_2O$ was added to the solution and the solution was refluxed at 200 °C for 1.5 h. A black precipitate was collected and washed with absolute ethanol and then distilled water to remove any impurities. The final product was dried in vacuum at 55 °C for 2 h. The yield is about 85% based on $SnCl_2$. The obtained powder was identified by X-ray powder diffraction (XRD). The pattern was recorded on a Rigaku D/max γA diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). TEM images were taken with a Hitachi Model H-800 transmission electron microscope using an accelerating voltage of 200 kV.

All the peaks of XRD pattern shown in Figure 1 could be indexed to the orthorhombic phase SnSe with cell parameters comparable to the reported values (JCPDS 32-1382). On the XRD pattern, some very weak peaks (26–29 °, 34–36 °) were also detected, which may be attributed to tin oxides. In the present process, our experiments were conducted in air and the reagent is $SnCl_2 \cdot 2H_2O$, so it is inevitable to avoid the formation of a few oxides.

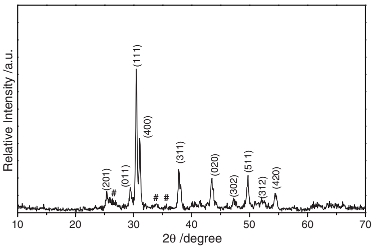


Figure 1. XRD pattern of as-prepared SnSe. The weak peaks marked with # are that of tin oxide.

Figure 2a–b are the TEM images of the as-prepared product, which indicates the morphology of SnSe is mainly uniform nanowires having a narrow size distribution with a mean diameter of 50 nm (Figure 2c). The length of these nanowires can be as long as 10 µm. The average aspect ratio of these nanowires is about 150. The electron diffraction pattern (Figure 2b inset) taken from the selected area of SnSe nanowires shown in Figure 2b shows that the as-prepared SnSe nanowires are well crystallized.

Energy-dispersive X-ray (EDX) analysis was used to determine the composition of these nanowires. The results (Figure 2d) show that these nanowires are composed of the elements Sn and Se and the ratio of Sn:Se is 1:1.02, in agreement with the expected values (the Cu peaks arise from the copper grid).

In the ethylenediamine-assisted polyol (ENAP) route, the addition of ethylenediamine (EN) is the key factor to purity. The presence of EN results in the formation of phase pure SnSe nanowires. But without EN, unreacted elemental selenium presents in the final products. It is well known that EN is strongly basic[18] and we speculate that selenium is activated by a nucleophilic attack of the amine to form Se^{2-} in the polyol route, which may be similar to the way that the sulfur is activated by amine or hydroxide.[19] This is confirmed by the fact that the solution color changed from opaque to dark-brown and selenium disappeared soon after the addition of EN.

In our synthetic system, the addition of EN is also impor-

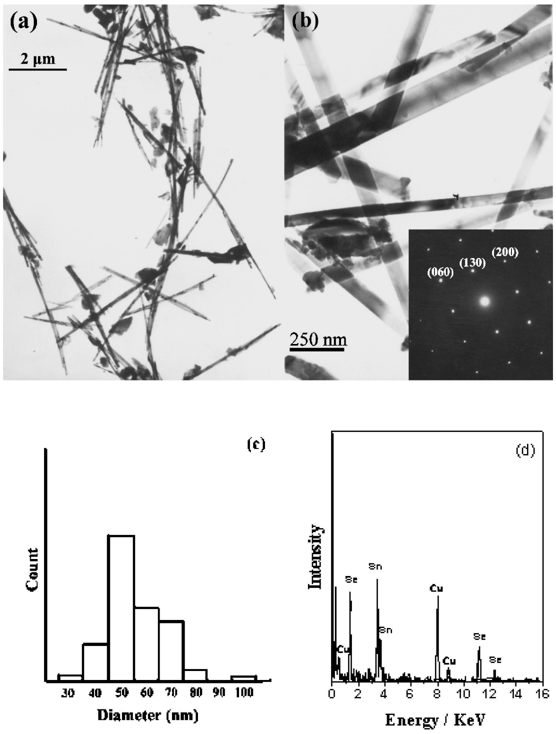
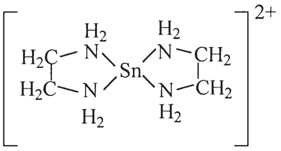


Figure 2. (a)-(b) TEM images of as-prepared SnSe (inset is the ED pattern of SnSe nanowires); (c) diameter distribution of SnSe nanowires; (d) EDX spectrum of the SnSe nanowires.

tant to the product's morphology. With no addition of EN, all the products show flake or particle morphology. As reported in the literature,[18] EN is a bidentate ligand and it can react with metal ions to form relatively stable metal complexes, Sn^{2+}-EN complexes in the present route,



which may serve as molecular templates in control of the crystals growth.[20] The stability of the complexes is expected to decrease with the increase of the temperature.[20] At some relatively high temperature, selenium ions may coordinate with the complexes to form a one-dimensional SnSe nanorod structure and the volatile coordinated ligands are lost gradually.[20] To improve the understanding of the effect of EN, we substituted EN with NaOH, diethylamine, and pyridine. Unfortunately, we can't get pure SnSe nanowires even the reaction was kept for as long as 8 h. Experiments show that EN is an excellent additive to control the purity and morphology of as-prepared sample.

The solvent diethylene glycol (DEG) also has great influence on the as-prepared samples. The use of DEG can efficiently complex and stabilize the surface of the nanoparticles,[21] thus avoids the agglomeration of the initial formed nuclei. DEG is a weak bidentate ligand and can react with metal ions to form metal complexes similar to the metal-EN complexes, which are also favorable for the oriented growth of the nanowires. But compared with the effect of EN, the influence of DEG is much weaker for that rodlike crystals with a large number of nanoparticles and nanoflakes were obtained without the addition of EN. The results are shown in Table 1. The exact influence of EN and the polyol solvent on the morphology undoubtedly needs further investigation.

Table 1. The influence of solvents on the final products

Solvent	Product	Morphology
EN	Very few products	Irregular crystals
EN/DEG	SnSe	Nanowires
DEG	SnSe + unreacted Se	Nanoparticles (nanoflakes) with very few nanowires

In summary, SnSe nanowires have been successfully prepared through a rapid ethylenediamine-assisted polyol (ENAP) route for the first time. The experiments show that ethylenediamine is the key factor to the purity and morphology of the final product.

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