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Mixed Solvothermal Synthesis of Sb_2Se_3 Whiskers Assembled by Nanobelts†

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By adopting mixed solvothermal synthesis technology, nanobelt-based Sb_2Se_3 whiskers were fabricated in the mixed solvent of C_2H_5OH and $N_2H_4{\cdot}H_2O$ with the volume ratio of 2:1 at 160-180 ºC for 12 h, using $SbCl_3$ and SeO_2 as starting reactant. The products are characterized by X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy. The volume ratio of ethanol and hydrazine hydrate influences the morphology of Sb_2Se_3 products. The diameters of Sb_2Se_3 whiskers range from 0.4 to 1.2 μm and length is up to 30 μm. The whisker is assembled by multi-layered Sb_2Se_3 nanobelts and the growth mechanism is simply studied.

Key Words: Sb_2Se_3, Whisker, Nanobelt, Solvothermal synthesis.

INTRODUCTION

As an important *p*-type semiconductor with direct band gap of 1.3 eV, antimony triselenide (Sb_2Se_3) has received a great deal of attention due to its many potential applications in photo-electrochemical devices[1], photoconducting devices[2], solar selective and decorative coatings[3], thermoelectric cooling devices[4]. Various methods have been adopted to synthesis Sb_2Se_3 micro/nano crystals, such as polymer-controlled growth of Sb_2Se_3 nano-ribbons *via* a hydrothermal process[5], solvothermal growth of bulk polygonal tubular Sb_2Se_3 crystals *via* a solvent-relief-self-seeding process[6], solvothermal synthesis of Sb_2Se_3 hollow nanospheres in the presence of CTAB 7, Microwave-enhanced rapid and green synthesis of Sb_2Se_3 nanorods[8], Microwave-assisted polyol method to prepare Sb_2Se_3 submicron tetragonal tubular and spherical crystals[9], solvothermal route to synthesize Sb_2Se_3 nanowires form a single source precursor[10], solvent-assisted growth of Sb_2Se_3 nanocompounds from a single-source precursor[11], solvothermal preparation of Sb_2Se_3 ultralong nanobelts and hierarchical urchin-like nanostructures in the presence of citric acid[12], *etc*. In this paper, using $SbCl_3$ and SeO_2 as starting reactant, large-scale uniform Sb_2Se_3 whiskers assembled by thin nanobelts were prepared in the mixed solvent of ethanol and hydrazine hydrate through a convenient solvothermal technique. The volume ratio of ethanol and hydrazine hydrate influences the morphology of Sb_2Se_3 products, which is discussed.

EXPERIMENTAL

In a typical experimental procedure, 1 mmol $SbCl_3$, 1.5 mmol SeO_2 were successively added into a 50 mL Teflon-lined stainless steel autoclave, which was then filled with 40 mL mixed solvent of ethanol and hydrazine hydrate (2:1, v/v). The obtained reaction mixture was stirred for 0.5 h. The autoclave was sealed and maintained at 160-180 ºC for 12 h. The resulting solid products were filtered off, washed with absolute ethanol and distilled water for several times and then finally dried in a vacuum at 60 ºC for 6 h.

The phase purity of the as-synthesized products was examined by X-ray diffraction using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized Cu K_α radiation (λ = 1.54178Å). Field-emission scanning electron microscope (FESEM) images of the sample were taken on a field-emission microscope (JEOL JSM-6700F). The transmission electron microscope (TEM) images of the samples were performed on a H-7650 transmission electron microscope.

RESULTS AND DISCUSSION

The typical XRD pattern of the prepared sample is shown in Fig. 1. All the diffraction peaks can be well indexed to orthorhombic phase of Sb_2Se_3 with *Pbnm* space group symmetry (cell constants a = 11.62 Å, b = 11.77 Å, c = 3.962 Å; JCPDS 72-1184). The shape of the diffraction peaks suggests that the obtained products should be well crystallized.

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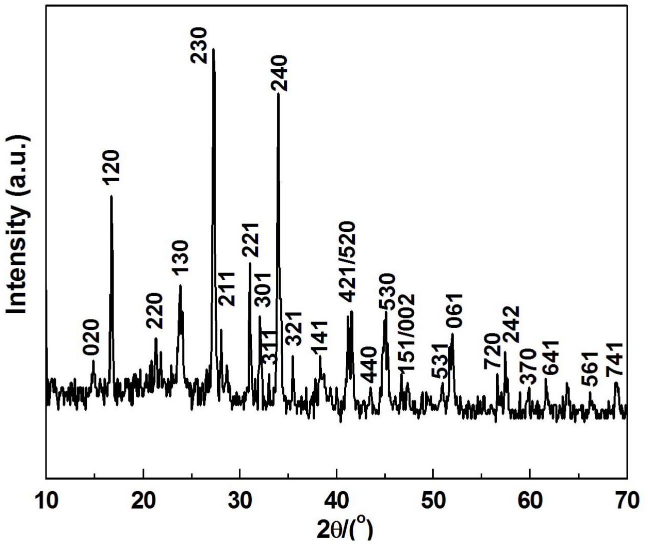

Fig. 1. Typical XRD pattern of Sb_2Se_3 whiskers assembled by nanobelts

The morphology and microstructure of as-synthesized Sb_2Se_3 products are detected by field-emission scanning electron microscope and TEM technology. Fig. 2(a) is the low magnification field-emission scanning electron microscope image of the products, which indicates that the products are mainly composed of uniform whisker-like microcrystals having diameters in the range of 0.4-1.2 μm and lengths up to 30 μm. By increasing the field-emission scanning electron microscope magnification, more detailed microstructures can be clearly seen. We find that these whiskers are actually constructed by multi-layered thin nanobelts (also called as nanobelt bundles), as shown in the inset image of Fig. 2(a). Fig. 2(b) gives the magnified picture. Most of whisker-like products are smooth and straight throughout their lengths. From the side view of a single Sb_2Se_3 whisker, we can deduce that the whisker is assembled by overlapped nanobelts [indicated by the white arrow in Fig. 2(b)]. The width and thickness of Sb_2Se_3 nanobelt building units are estimated to be 300-1000 nm and 60-80 nm. In addition, the tips of these nanobelt bundles are fused into solid cross section of each whisker [indicated by the black dashed circle in Fig. 2(b)]. Fig. 2(c) and (d) are the TEM images of Sb_2Se_3 whiskers. These nanobelt bundles were not been separated into discrete nanobelts even by the long time untrasonic vibration, indicating that these nanobelts were closely connected by chemical bond. The contrast between the dark edge and the relatively light fringe [indicated by the white dashed circle in Fig. 2(d)] further reveals that the whisker is comprised of nanobelts.

Based on the above results, a possible formation mechanism of the nanobelt-based Sb_2Se_3 whiskers in the mixed solvothermal system of ethanol and hydrazine hydrate is described as follows: First, metal ions Sb^{3+} and SeO_2 are respectively reduced to colloid Sb and Se by hydrazine hydrate [eqns. (1) and (2)]. The freshly-produced colloid Sb and Se are much more reactive than Sb and Se powder. Then, colloid Sb react with colloid Se to form Sb_2Se_3 nuclei [eqn. (3)] and further grow into nanobelts because that Sb_2Se_3 is a highly anisotropic crystal with a unique layered structure (Sb and Se atoms are bound in infinite hexagonal sheets)[5,8]. Finally, the preformed nanobelts tend to pile up plane by plane through

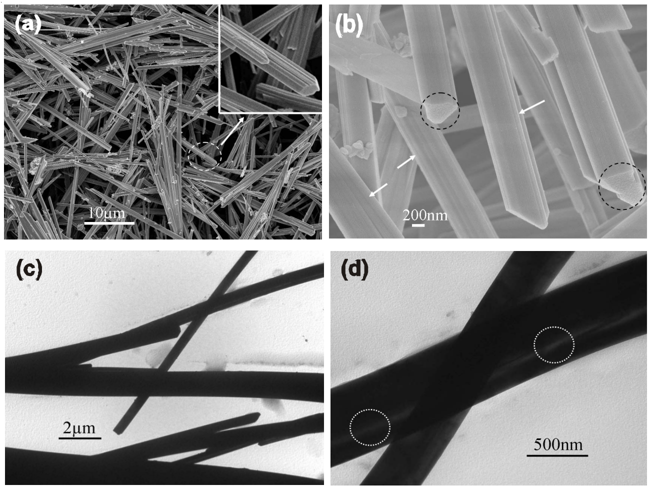

Fig. 2. Sb_2Se_3 whiskers assembled by nanobelts: (a, b) field-emission scanning electron microscope image, (c, d) TEM image

oriented-overlapping to decrease the high specific surface energy. With the prolongation of crystallization time, nanobelt-based Sb_2Se_3 whiskers are successfully fabricated under the proper solvothermal conditions.

$$4Sb^{3+} + 3N_2H_4{\cdot}H_2O + 12OH^- \rightarrow 4Sb\ (colloid) + 3N_2 + 15H_2O \quad (1)$$

$$SeO_2 + N_2H_4{\cdot}H_2O \rightarrow Se\ (colloid) + N_2\uparrow + 3H_2O \quad (2)$$

$$2Sb\ (colloid) + 3Se\ (colloid) \rightarrow Sb_2Se_3 \quad (3)$$

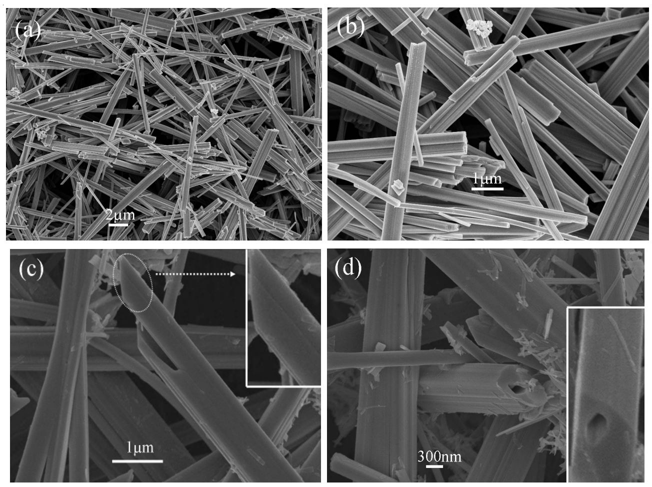

Fig. 3. Morphology of Sb_2Se_3 products prepared in mixed solvent of ethanol and hydrazine hydrate with different volume ratio: (a,b) C_2H_5OH : $N_2H_4{\cdot}H_2O$ = 1:2, (c,d) C_2H_5OH : $N_2H_4{\cdot}H_2O$ = 3:1

During the process of mixed-solvothermal reaction, we discover that the morphology of Sb_2Se_3 products was influenced by volume ratio of ethanol and hydrazine hydrate to some extent. Fig. 3(a) and (b) present the morphology of Sb_2Se_3 products acquired in the mixed solvent of C_2H_5OH and $N_2H_4{\cdot}H_2O$ with the volume ratio of 1:2, which indicates that products still take on whisker-like microstructures consisting of nanobelts, but the lengths of microwhiskers are shortened. Fig. 3(c) and (d) exhibit the morphology of Sb_2Se_3 products fabricated in the mixed solvent of C_2H_5OH and $N_2H_4{\cdot}H_2O$ with the volume ratio of 3:1. One can see, in addition to nanobelt-based whiskers, some tetragonal microtubes are interestingly found in the products. Based on the field-emission scanning electron microscope observation, the individual microtube is also made up of thin nanobelts [See the enlarged part of Fig. 3(c)]. Similar to the reported literature[5,8], the growth of tetragonal Sb_2Se_3 microtubes may attribute to the linkage of different sheets at certain angles by the Sb-Se interactions. By crystallization and Ostwald ripening, nanobelt-based microtubes can also develop into completed microtubes with comparatively smooth surface, as shown in the inset image of Fig. 3(d).

Conclusion

Using $SbCl_3$ and SeO_2 as starting reactant and ethanol and hydrazine hydrate as mixed solvent, uniform Sb_2Se_3 whiskers constructed by thin nanobelts were prepared on a large scale through a mixed solvothermal route. The whisker is constructed by overlapped Sb_2Se_3 nanobelts. Most of whisker-like products are smooth and straight throughout their lengths. The comparative experimental results reveal that the morphology of Sb_2Se_3 products were influenced by solvent effect to some extent derived from different volume ratio of ethanol and hydrazine hydrate. The present route is convenient, eco-friendly and reproducible.

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