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## Scalable synthesis of Sb(III)Sb(V)O<sub>4</sub> nanorods from Sb<sub>2</sub>O<sub>5</sub> powder via solvothermal processing

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## Abstract

Scalable Sb(III)Sb(V)O<sub>4</sub> nanorods from Sb<sub>2</sub>O<sub>5</sub> powder were prepared using solvothermal route. XRD and HRTEM demonstrate that the nanorods are single-crystal orthorhombic-Sb<sub>2</sub>O<sub>4</sub> phase with several micrometers long and 200–300 nm diameter size. XPS result further shows that the antimony cations in the nanorods are composed of three valence and five valence antimony ions. The emission of the nanorods appears around 450 nm wavelength. The formation mechanism of the Sb(III)Sb(V)O<sub>4</sub> nanorods was discussed in detail.

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Nanometer-sized semiconductor oxides of nanowires or nanorods have stimulated intensive research activities due to their high stability and potential values for fundamental studies of dimensionality and size in the physical properties as well as for the application in optoelectronic nanodevices [1]. Recently, the nanowires or nanorods of several binary oxides, such as  $In_2O_3$  [2],  $Ga_2O_3$  [3],  $SnO_2$  [4], ZnO [5] or  $TiO_2$  [6], have been successfully prepared. However, until now, a large scale of nanorods or nanowires of antimony oxides have not been obtained yet.

The antimony oxides of  $Sb_2O_3$  and  $Sb_2O_5$  have been widely used in many applications. They are additive materials of flame retardant [7,8] and they are also used as an optical materials due to its high refractive index and high abrasive resistance [8]. As a kind of Lewis acid catalyst, the  $Sb_2O_5$  has shown good active for the transformation of propene into acrylonitrile [9]. Recently, hydrous antimony oxide has been reported to exhibit high proton conductivity, so it has potential application in humidity-sensing material [10]. Herein we utilized the Sb<sub>2</sub>O<sub>5</sub> powder directly and simply to synthesize a large scale of Sb(III)Sb(V)O<sub>4</sub> (denoted as SSO) nanorods under mild condition by solvothermal method. General SSO powder material can be prepared using Sb<sub>2</sub>O<sub>5</sub> at about 750 °C for a long time [11] or at high temperature and high pressure (300–500 °C, 100–1800 atm) by the mixture of Sb<sub>2</sub>O<sub>3</sub> with Sb<sub>2</sub>O<sub>5</sub> in NaOH and H<sub>2</sub>O<sub>2</sub> aqueous solutions [12], whereas the synthesis and characterization of the SSO nanorods have hardly been studied except for the microemulsion preparation of only single low-quality SSO nanowire (shown in TEM image) reported in the literature [13].

In this communication, ball-milled Sb<sub>2</sub>O<sub>5</sub> powder was chosen as starting compound to synthesis the SSO nanorods, since it can be easily bought and long-time stored as well as considered on the basis of structural transformation from general powder to special shape materials which have special applications in many fields. Additionally, more importance is that it can slowly dissolve in warm alkali

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solution, so in soft template of the mixture of ethylenediamine (EA) with ethylene glycol (EG) and part reduction of the Sb<sup>5+</sup> to Sb<sup>3+</sup> cations by the EA, a large scale of the SSO nanorods can be obtained. Under high temperature of solvothermal process, the reductive property of the EA has been confirmed [14].

Fig. 1 is the schematic illumination of the SSO nanorods and metal antimony particles prepared from the ball-milled Sb<sub>2</sub>O<sub>5</sub> powder. The SSO nanorods were obtained in the mixture solution of the EA and EG with a little bit oleic acid and water at 200 °C for reaction time of 24 h, whereas over reaction time of 65 h, metal antimony particles were prepared due to the completely reduction of precursor Sb<sub>2</sub>O<sub>5</sub>. The SSO nanorods were also obtained when the reaction temperature was decreased to 150 °C, but reaction time needs much longer than that at 200 °C. This is because at low temperature the dissolution and part reduction of the used Sb<sub>2</sub>O<sub>5</sub> powder are relative slower and the formation of the SSO nanorods needs the longer time. Many experiments for the preparation of the SSO nanorods and the metal Sb particles using Sb<sub>2</sub>O<sub>5</sub> powder were performed by changing reaction conditions, such as reaction temperature and time, and the mixture of the nanorods and the metal Sb could also be prepared, but any core-shell structural Sb-coated SSO nanorods could not be observed.

X-ray diffraction (XRD) analyses was used to determine the phases of the SSO and metal antimony (Fig. 2). The pattern a in the Fig. 2 is the XRD pattern of the SSO phase. All the peaks could be indexed to SSO compound according to the reported data (JCPDS No. 11-694) [12] of bulk orthorhombic-Sb<sub>2</sub>O<sub>4</sub>. No peaks of any other phase were detected, indicating that the main product is the SSO phase. It is noted that the relative intensities of some diffraction peaks are greatly changed comparing with the standard values. Its strongest diffraction peak is indexed to (202) plane, not reported (112) plane of bulk Sb<sub>2</sub>O<sub>4</sub>, indicating that the nanorods may have a preferential [101] growth direction. The pattern b in the Fig. 2 is the XRD pattern of the metal antimony material. It could be indexed to hexagonal lattice of metal Sb with cell constants a=b=4.30, c = 11.27 Å, which are in excellent agreement with the reported data (JCPDS No. 5-0562) of bulk hexagonal-Sb. In comparison with the XRD pattern of Sb<sub>2</sub>O<sub>5</sub> powder in the



Fig. 1. Schematic mechanism for  $Sb(III)Sb(V)O_4$  nanorods and metal Sb particles prepared from ball-milled  $Sb_2O_5$  powder using solvothermal processing.



Fig. 2. XRD patterns of (a) the orthorhombic  $Sb(III)Sb(V)O_4$  nanorods, (b) the hexagonal metal Sb particles and (c) the used precursor  $Sb_2O_5$  powder.

pattern c of the Fig. 2, the crystallinity of the SSO nanorods and Sb particles is very high. It demonstrates that the reaction processing from  $Sb_2O_5$  powder to the products SSO and metal Sb phases is not only phase and shape transformation processing, but also a kind of crystalline processing.

Representative scanning electron microscopy (SEM) of the SSO nanorods and metal Sb particles are shown in Fig. 3. A majority of the SSO nanorods with smooth surface were observed (Fig. 3(a)). Typically they have several micrometers long and 200–300 nm diameter size. Their atomic ratio of O/Sb measured on SEM-energy-dispersive X-ray analyses is about 2.1, close to the chemical composition ratio of the SSO (O/Sb=2). The excess of oxygen atoms may be caused by the surfactant oleic acid on the surface of the SSO. In Fig. 3(b), the metal Sb particles with several micrometers can also be observed.

A high-resolution transmission microscope (HRTEM) image provides an insight into the structure of the prepared SSO nanorods (Fig. 4). Generally Sb<sub>2</sub>O<sub>4</sub> has two types of structures of orthorhombic [12] and monoclinic [15] which are also called as  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> and  $\beta$ -Sb<sub>2</sub>O<sub>4</sub>, respectively. Herein, the prepared SSO nanorods are orthorhombic crystal of the  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub>. The HRTEM image (Fig. 4(b) and (c)) of the end of the individual nanorods shows that it is the single crystal with the presence of few dislocations and defects, whereas the side surfaces of the nanorods are covered with thin and relatively smooth amorphous layers (about 3 nm). The amorphous layer may be resulted mainly from the surfactant oleic acids. Perpendicular to c-axis, the layerperiodically packed lattice with about 1.15 nm distance corresponding to four-atom layer unit along [001] direction can be seen. This distance is close to the c value of the cell constant of the  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> (a=5.436, b=4.810 and c= 11.76 Å). The corresponding selected area electron



Fig. 3. SEM images of (a)  $Sb(III)Sb(V)O_4$  nanorods (scale bar 1.5 µm); (b) metal Sb particles (scale bar 5 µm).



Fig. 4. Structural characterization of Sb(III)Sb(V)O<sub>4</sub> nanorods. (a) TEM image of Sb(III)Sb(V)O<sub>4</sub> nanorods. (b) and (c) HRTEM images of the top end of Sb(III)Sb(V)O<sub>4</sub> nanorods. In (c) image, Perpendicular to *c*-axis ([001] direction), a periodic layer packed can be seen. (d) Electron diffraction pattern of the nanorod.

diffraction pattern (Fig. 4(d)) of the nanorod can also be indexed as the reflections of the orthorhombic phase  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub>.

The X-ray photoelectron spectroscopy (XPS) was used to further examine the valence state and chemical composition of the SSO nanorods [16]. Fig. 5 shows the XPS survey (Fig. 5(a)) and Sb 3d5 (Fig. 5(b)) spectra of the SSO nanorods. Antimony and oxygen peaks are clearly resolved in the survey spectrum, which qualitatively provide antimony atom number 31.7% and oxygen 62.3%, respectively, in close agreement with the composition of Sb(III)Sb(V)O<sub>4</sub>. The binding energy of measured Sb 3d5 spectrum peak is at 530.2 eV. This region was simulated two regions of Sb<sup>3+</sup> and Sb<sup>5+</sup> cations which have the binding energies of Sb 3d5 of 529.9 and 530.6 eV, respectively. They have the similar peak area. In comparison with the standard binding energies of the Sb 3d5 of Sb<sub>2</sub>O<sub>3</sub> (529.5 eV) and Sb<sub>2</sub>O<sub>5</sub> (530.5 eV), the binding energies of the two



Fig. 5. XPS spectra of Sb(III)Sb(V)O<sub>4</sub> nanorods: (a) survey spectrum; (b) Sb 3d5 region. Sb 3d5 region has been simulated two regions (dash dot) of the Sb 3d5 of Sb<sup>3+</sup> and Sb<sup>5+</sup> cations which have the similar peak area.

simulated peaks have a slightly shift because of the different binding sites of the  $Sb^{3+}$  and  $Sb^{5+}$  cations of the SSO from those of  $Sb_2O_3$  and  $Sb_2O_5$  compounds. The results also demonstrate that the prepared nanorods are  $Sb(III)Sb(V)O_4$  material.

The formation mechanism of the SSO nanorods is suggested as follows. The existence of H<sub>2</sub>O in the mixture solution of organic compounds EA and EG directly leads to the formation of OH<sup>-</sup> groups. The OH<sup>-</sup> first reacts with Sb<sub>2</sub>O<sub>5</sub> powder to produce Sb–OH complexes (such as  $Sb(OH)_6^-$ ). The complex can also react with EG or EA which partly reduces the  $Sb^{5+}$  to  $Sb^{3+}$  cations [14]. Then, the partly reduced Sb(III)-OH further reacts with Sb(V)-OH complex to obtain the SSO nanorods in soft template of the EA and EG. As the dissolution of the Sb<sub>2</sub>O<sub>5</sub> powder is slow, it is beneficial to the formation of the SSO nanorods. However, with further increasing the reaction time, the slow dissolution of the nanorods in the alkali system causes the reduction of much more Sb5+ cations to the Sb3+ cations and also the reduction of the Sb3+ cations to metal antimony, and finally all the nanorods transfer into metal antimony particles.

The room temperature UV–vis spectra of the SSO nanorods and the  $Sb_2O_5$  powder in the 225–600 nm wavelength range are shown in Fig. 6. A shoulder peak (shown in arrow) of the absorption of the nanorods at 365 nm can be obviously observed due to two different valence antimony cations in the nanorods. For comparison, the absorption edge of the  $Sb_2O_5$  shifts to around 275 nm. The difference between their absorptions also demonstrates the distinct of their bandgap. The sharp absorption edge of



Fig. 6. The room temperature UV–vis spectra of Sb(III)Sb(V)O<sub>4</sub> nanorods and ball-milled Sb<sub>2</sub>O<sub>5</sub> powder. Arrow in Sb(III)Sb(V)O<sub>4</sub> absorption curve shows the shoulder peak caused by different valence antimony cations. Inset is UV–vis emission spectra of Sb(III)Sb(V)O<sub>4</sub> nanorods and ball-milled Sb<sub>2</sub>O<sub>5</sub> powder.

the nanorods indicates the present of a direct bandgap [17]. The photoluminescence (PL) of the SSO nanorods displays a weak blue emission around 450 nm, whereas it is much stronger than that of the  $Sb_2O_5$  powder.

In summary, we have successfully prepared Sb(III)Sb(V)O<sub>4</sub> nanorods mainly with several micrometers long and 200–300 nm diameter by a simple solvothermal process only using ball-milled Sb<sub>2</sub>O<sub>5</sub> powder in ethylenediamine and ethylene glycol with a little bit oleic acid and water. The possible formation mechanism of the nanorods is suggested as three stages: the dissolution of Sb<sub>2</sub>O<sub>5</sub> powder, the part reduction of Sb<sup>5+</sup> cations and the growth of the nanorods. Prolonging reaction time can lead to complete reduction of the Sb<sub>2</sub>O<sub>5</sub> powder to metal Sb particles. UV–vis emission spectrum of the SSO nanorods shows that emission appears around 450 nm wavelength.

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