Controlled Synthesis of Sb_2O_3 Nanoparticles, Nanowires, and Nanoribbons

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Sb_2O_3 nanoparticles, nanowires, and nanoribbons have been selectively synthesized in a controlled manner under mild conditions by using CTAB as a soft template. By adopting $\text{Sb}(\text{OH})_4^-$ as an inorganic precursor and the concentration of CTAB as an adjusting parameter, morphologies of Sb_2O_3 nanostructures can be selectively controlled. Typically, $C_{\text{CTAB}} < 0.15$ mmol favors the formation of nanoparticles (product one or short form P1); when the concentration of CATB is in the range 0.15–2.0 mmol, nanowires (P2) dominate the products; nanoribbons (P3) form above the concentration of 2.0 mmol, and when the concentration of CTAB goes further higher, treelike bundles of nanoribbons could be achieved. The method in the present study has potential advantages of easy handling, relatively low-cost, and large-scale production. The facile and large-scale synthesis of varied Sb_2O_3 nanostructures is believed to be useful for the application of catalysis and flame retardance.

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1. INTRODUCTION

Antimony trioxide (Sb_2O_3) is a semiconducting material and possesses excellent catalytic performance in photochemistry and superior chemical stability in flame retardance [1, 2]. So far, much attention has been focused on the synthesis of Sb_2O_3 films, and the exploration of their novel properties [3, 4]. By comparison, low-dimensional Sb_2O_3 , such as nanoparticles, nanowires, nanotubes, and nanoribbons, can be expected to exhibit special properties. It is well known that many of the properties of nano-scaled materials are shape-dependent [5]; therefore, controlled synthesis of desired morphologies of nanomaterials is exceedingly important. Although much effort has been invested in this direction, it is still a challenging task for the scientists to controllably synthesize a predetermined material morphology in a facile way.

Recently, we successfully synthesized Sb_2O_3 nanotubes and nanowires, and several other groups prepared Sb_2O_3 nanorods and/or whiskers [6–8]. In this communication, we introduce a room temperature solution method to synthesize a variety of morphologies of Sb_2O_3 nanostructures using a structure-directing surfactant cetyltrimethylammo-

nium bromide (CTAB) as soft template by varying reaction conditions and employing $\text{Sb}(\text{OH})_4^-$ as an inorganic precursor (produced by adjusting a SbCl_3 solution to a pH value of 14 [9]). Via this method, the morphologies could be selectively controlled. Control over the morphology of the products was achieved by surfactant assembly, which may form different conformations by self-assembly and lead to the formation of different nanostructures [10].

2. RESULTS AND DISCUSSIONS

In a typical synthesis, cetyltrimethylammonium bromide of varied concentrations (CTAB; P1 < 0.15 mmol, P2 0.15 mmol–2.0 mmol, P3 > 2.0 mmol, and for treelike bundles of Sb_2O_3 nanoribbons ~ 10.0 mmol) was added to a 0.01 M SbCl_3 (100 mL) solution under vigorous stirring for 2 h until CTAB being fully dissolved. Subsequently, 1 M NaOH solution was added dropwise to the above solution to reach a pH value of 14. After the resulting solution was stirred for 24 h at room temperature, it was put into an oven. After the solution was maintained at 60°C for 4 h, the resulting light brown precipitate was centrifuged, washed several times using absolute ethanol and distilled

FIGURE 1: SEM images of Sb_2O_3 : (a) nanoparticles; (b) nanowires; and (c) nanoribbons.

water, and dried under vacuum at room temperature gradually.

The morphologies of the product were examined under a scanning electron microscope (SEM), and typical SEM images of P1, P2, and P3 are shown in Figure 1. In Figure 1(a), Sb_2O_3 nanoparticles with narrow dispersity (diameter of 17 ± 1 nm) are displayed. Figure 1(b) shows Sb_2O_3 nanowires in a large quantity. The diameter of the nanowires is in the range 20–100 nm and length of several tens of micrometers. Sb_2O_3 nanoribbons are exhibited in Figure 1(c). The nanoribbons have length of hundreds of micrometers and width in the range of tens of nanometers to 2 micrometers. The treelike bundles of Sb_2O_3 nanoribbons are shown in Figure 2. In Figures 2(a) and 2(b), the stem and the end of the treelike bundles of nanoribbons are displayed, respectively. Figure 2(c) is the close view of the end of the dendrite. Figure 2(d) is a high-magnification view near the end of a bundle. The nanoribbons are as long as several hundred of micrometers judged from the SEM images.

Transmission electron microscopy (TEM) was also employed to study the structure and morphology of the nanostructures. Figure 3(a) exhibits the typical morphology of the Sb_2O_3 nanoribbons. The dark lines across the nanoribbons are bending contours as generally observed in many other nanobelts or nanoribbons. A closer view of the nanoribbon is shown in Figure 3(b). The width of the nanoribbons is in the range of tens of nanometers to $1 \mu\text{m}$, and the thickness is as thin as several tens of nanometers on the basis of the TEM characterizations.

To further study the crystallinity and phase of the products, X-ray diffraction (XRD) measurement was carried out.

FIGURE 2: SEM images of the treelike bundles of Sb_2O_3 nanoribbons: (a) and (b) the stem and the end of the treelike bundles of nanoribbons; (c) the close view of the end of the bundle; (d) a high-magnification view near the end of a bundle.

The diffraction peaks in the XRD spectrum (Figure 4) could be indexed to the cubic phase of Sb_2O_3 according to the literature (JCPDS NO. 42-1466). No other phases were detected from the spectrum.

High-resolution electron microscopy (HREM) was used to characterize the microstructure of the nanoribbons. Figure 5 shows an HREM image of a typical Sb_2O_3 nanoribbon. The lattice fringes are clearly exhibited. The spacing of 0.64 nm between two neighboring fringes corresponds well to the separation between (111) lattice planes. The selected area electron diffraction (SAED) pattern (inset) taken along the [011] zone axis further demonstrates the crystallinity of the nanoribbons. The nanoribbon is determined to be bound by pairs of $(11\bar{1})$ end, $(01\bar{1})$ side, and (011) top surface planes. The growth direction is along the $[11\bar{1}]$ direction.

There are many reports about the synthesis of nanomaterials in micellar or inverse micellar solutions [11–19], and CTAB has been systematically studied in the synthesis of nanostructured materials [20–22]. Recently, Cao et al. [10] reported the controlled synthesis of Cu, Cu_2O , and CuO nanorods and nanotubes using CTAB as soft template and the concentration of $\text{Cu}(\text{OH})_4^{2-}$ anions as the adjusting parameter. However, the controlled synthesis of higher-order phase nanostructures such as nanoribbons have never been reported. The growth mechanism of Sb_2O_3 nanostructures by templating CTAB surfactant and the concentration of CTAB as the adjusting parameter in the present study may be similar to their case. However, the change of molar ratio of water to CTAB (denoted as ω) may play a critical role in our case [11–14], which differs from Cao's case where ω

FIGURE 3: TEM images of Sb_2O_3 nanoribbons: (a) low-magnification view of several nanoribbons; (b) high-magnification view of a 350 nm wide nanoribbon.

FIGURE 4: XRD pattern of the treelike bundles of Sb_2O_3 nanoribbons. All the diffraction peaks could be indexed to cubic phase Sb_2O_3 .

FIGURE 5: HREM image of an Sb_2O_3 nanoribbon. The inset is the SAED pattern taken along the $[011]$ zone axis.

is fixed. Therefore, in our system, we believe that the determinants of the formation of various nanostructure morphologies are twofold, namely, lower CTAB concentration (high ω value) favors the formation of lower-order phases such as spherical and cylindrical structures, and higher CTAB concentration higher-order phases such as layered structures and hexagonally packed arrays, and these statements have been confirmed by other researchers [11–14]; the electrostatic interactions between $\text{Sb}(\text{OH})_4^-$ anions and cationic surfactant CTAB promote the formation of different conformational inorganic-surfactant composites. The $\text{Sb}(\text{OH})_4^-$ anions present in the reaction mixture electrostatically interact with the surfactant cationic head groups, CTA^+ , to form $\text{CTA}^+ - \text{Sb}(\text{OH})_4^-$ ion pairs [10]. When the concentration of CTA^+ cations is lower, the number of necessary charge compensating anions decreases and the system finds its minimum energy configuration by adopting the spherical or rod-like micelle structure [23]. Thus, Sb_2O_3 nanoparticles and nanowires are formed after the following thermal treatment. As the concentration of CTA^+ cations increases to a higher value, the required number of charge compensating anions remarkably increases as well. So, the system favors a complete lamellar phase structure and even hexagonally packed arrays to obtain its minimum energy configuration [23]. The inter-layer might serve as microreactors and are responsible for the ultimate formation of nanoribbons. During increasing the

concentration of CTAB, the mesophase structure should be in the transition from a micellar to a lamellar phase and then leads to the coexistence of both phases in the mixture, which explains the coexistence of nanowires and nanoribbons at a moderate concentration of CTAB. The formation mechanism of the Sb_2O_3 nanostructures is schematically illustrated in Figure 6.

The treelike bundles of nanoribbons may form to lower the free energy of the system. Wen et al. [24] also observed the formation of bundled $\text{Cu}(\text{OH})_2$ nanoribbons when using Cu_2S nanowire arrays as a template, and they proposed that the nanoribbons intergrew from single nanoribbons. The nanoribbons in the present study are possibly bound together with weak forces, which is supported by the evidence of the TEM imaging where a brief ultrasonication of 30 min in ethanol was sufficient to completely separate the nanoribbon bundles to freestanding single nanoribbons.

3. CONCLUSIONS

In summary, we have controllably synthesized a variety of Sb_2O_3 nanostructure via a mild solution approach by adopting CTAB as a soft template. The facile and selective synthesis of Sb_2O_3 nanostructures is believed to be useful for the application of catalysis and flame retardance. The exploration of properties and interaction with inorganic species of

FIGURE 6: Schematic diagrams of the formation of various Sb_2O_3 nanostructures: (a) spherical nanoparticles; (b) nanowires; (c) nanoribbons. $\oplus$ denotes positively charged head group of the surfactant CTAB molecules, CTA^+ (i.e., $(\text{CH}_3)_3\text{N}^+$ here);—denotes the tail of the surfactant CTAB molecules, $\text{CH}_3(\text{CH}_2)_{15}$ here;—near the head of the micelle denotes negatively charged $\text{Sb}(\text{OH})_4^-$ ions.

the so-called soft matter in nanometer environment is also made possible. In addition, preliminary results show that the present method could be easily extended to controllably synthesize other oxide nanostructures, such as SnO_2 [25].

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