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Facile synthesis of boscage-like SnO_2 nanorods by hydrothermal method

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ABSTRACT

Boscage-like SnO_2 nanorods were successfully synthesized by a facile one-step hydrothermal route only using the sodium stannate trihydrate solution of alcohol and water, without any surfactants and substrates. X-ray diffraction spectra, scanning electron microscopy, transmission electron microscopy and high-resolution transmission electron microscopy were used to examine the morphology and microstructure of SnO_2 nanorods boscages. The results show that the SnO_2 nanorods boscage consists of single crystalline, rutile SnO_2 nanorods with a diameter of 4–10 nm and length of about 200 nm. The formation and growth of the boscage-like SnO_2 nanorods can be rationally expressed by the Ostwald-ripening assisted oriented attachment mechanism as a kinetically controlled nonclassical crystallization process.

1. Introduction

As a wide band-gap (E_g=3.6 eV at 300 K) n-type semiconductor functional materials, SnO_2 has been widely investigated in many fields, such as optical waveguides, gas sensors, gas conversion catalysts, photocatalysts, battery materials and solar cells. Since the discovery of SnO_2 nanobelts in 2001 [1], the synthesis and assembly of 1D SnO_2 nanostructures have attracted great interest and are expected to lead to novel device application due to their excellent properties and unique applications in gas sensors [2], UV detectors [3], field-effect transistors [4] and so on. In the past decade, due to the wide variety of important applications required for fabricating morphologically and functionally distinct nanostructures, the synthesis of one-dimensional (1D) SnO_2 nanoscale structure with controllable morphology has become the subject of intense researches [5]. Various chemical and physical methods including thermal evaporation [6], chemical vapor deposition (CVD) [7], molten salt method [8], laser ablation [9] and thermal decomposition [10], were generally employed to prepare one-dimensional SnO_2 nanostructure. Compared with these methods, which all require a high reaction temperature or rigorous conditions and are complex to perform, the hydrothermal approach is more convenient and may lead to SnO_2 nanomaterials of controlled morphology. Recently, hydrothermal procedure has been used widely to synthesize one-dimensional nanostructured SnO_2 materials with specific morphology since the anisotropic growth of the crystal can be favored under high pressure and temperature. Fu synthesized a novel nanostructure built by numerous one-dimensional tetragonal prism SnO_2 nanorods using the hydrothermal route in the presence of cetyltrimethylammonium bromide (CTAB) [2]. Shi prepared SnO_2 nanotubes by a facile hydrothermal method, adding HCl and using polycarbonate (PC) membrane as a hard template at low temperatures [11]. Zhang reported a hydrothermal synthesis of crystalline SnO_2 nanorods by using organic reagents [12]. Single crystalline small SnO_2 nanorods were fabricated by Samulski [13]. Lupan Synthesized SnO_2 nanorods via a hydrothermal technique, adding HCl and NH_4OH [14]. Using oleylamine as solvent and oleic acid as surfactant, Li synthesized SnO_2 single-crystalline nanorods based on the oleylamine-assisted hydrolysis of tin alkoxide in the presence of high content of oleic acid [15]. Wang demonstrated twisted and branched SnO_2 poly crystalline nanowires fabricated by a solvothermal process, combined with the introduction of oleylamine and oleic acid used as surfactants [16]. However, special alkaline or acid solution conditions, surfactants, templates and catalysts are required in the hydrothermal process. Some organic reagents, such as heptane, hexanol, sodium dodecyl sulfate, NaOH, KOH, $NH_4(OH)$ and HCl are used in the growth process, leading to significantly negative effects on human healths and on the environments.

In this study, we synthesized boscage-like single crystalline SnO_2 nanorods with diameters of 4–10 nm by a template-free

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hydrothermal route, using $Na_2SnO_3 \cdot 3H_2O$ as the sole precursor. In the synthesis process, alcohol and water, which are friendly to the environments, were used as the solvents. Furthermore, the growth mechanism of nanorods boscage was preliminarily proposed and discussed from the valuable insights.

2. Experimental

All chemical reagents utilized in the present study are of analytical grade and used as purchased without further purification. The boscage-like SnO_2 nanorods were fabricated by a hydrothermal route. In a typical experiment, 6 mmol sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$) was dissolved in 20 ml deionized water under magnetic stirring for 30 min. Subsequently, 60 ml absolute ethanol was slowly added into the solution to make the white precipitation stirring for 60 min, and then transferred into 100 ml Teflon-lined stainless steel autoclave, followed by heating at 210 °C in an airflow electric oven for 48 h. After heating, the autoclave cooled naturally to room temperature. The white precipitate was collected by centrifugation and washed with deionized water and absolute ethanol several times, then dried at 60 °C for 24 h in an oven for further characterization.

The phase and crystalline structure of SnO_2 product was identified by X-ray diffraction (XRD) employed using a D/MAX-RA diffractometer equipped with graphite monochromatized Cu-$K\alpha$ radiation (λ=0.154 nm, 40 kV, 30 mA). The morphologies of the sample were examined with an FEI Quanta 200 scanning electron microscope (SEM). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were carried out on a JEM-2010 at an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows a typical powder X-ray diffraction (XRD) pattern of the as-prepared SnO_2 product. The distinct and sharp reflection peaks suggest that the product is highly crystalline. All of the diffraction peaks are corresponding to (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 1), (2 2 0), (0 0 2), (3 1 0), (1 1 2), (2 0 2), (3 2 1), (2 2 2) and (3 1 2) planes match well with the standard data file of rutile structured SnO_2 crystal with tetragonal lattice constants of $a=b=4.732$ Å and $c=3.186$ Å (JCPDS file no. 41-1445). No signals of side products, such as Sn $(OH)_4$ and SnO are detected in the product. The obviously broadening of XRD peaks suggests that the as-prepared SnO_2 crystals are of small sizes. Based on the Debye–Scherrer formula, the average crystal size of as-prepared SnO_2 is calculated to the (1 1 0) plane diffraction peak

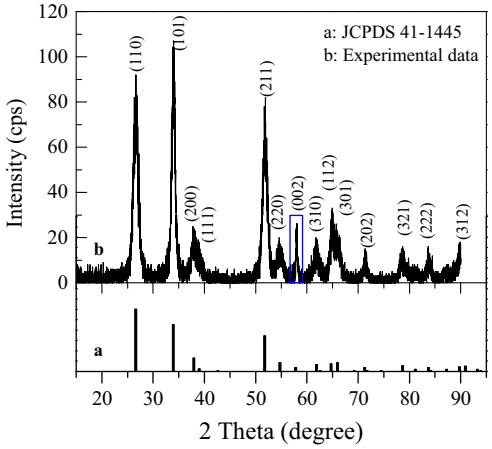

Fig. 1. XRD pattern of as-synthesized SnO_2 sample.

(2θ=30.98°) to be 6.8 nm, which is in good agreement with the average particle size obtained from TEM images. Moreover, the remarkably enhanced (0 0 2) peak and weakened (1 1 0) peak are also observed, indicating that the nanorods grew along [0 0 1] direction and relatively orient with their *c*-axis [17].

The morphology and microstructure of SnO_2 nanorods boscages are shown in Fig. 2. Fig. 2(a) displays SEM image of a flocky assembling architecture of boscages with countless spinule-like nanoparticles on the surfaces. An enlarged SEM survey on the top of SnO_2 architecture as shown in Fig. 2(b) depicts the remarkable feature of the boscages. Numerous one-dimensional nanorods grew homocentrically from their roots. Fig. 2(c) shows the morphologies of a section removed from the boscage-like SnO_2 nanorods with a diameter of about 4–10 nm and lengths of about 200 nm. A typical HRTEM image of individual nanorods as shown in Fig. 2(d) displays structure uniform and clear lattice fringe, indicating the single crystal nature of the SnO_2 nanorods. The space between adjacent lattice fringes is 0.348 nm, which can be indexed as the (1 1 0) plane of rutile SnO_2. The HRTEM reveals that the growth of the nanorod is along [0 0 1] direction with the (1 1 0) facet.

To explore the formation of nanorod in detailed, a higher magnification TEM image of a few nanorods is obtained as shown in Fig. 3(a). It obviously shows that nanorods consisted of sphere-like SnO_2 nanoparticles about 4–10 mm in diameter. It should be noted that the size of the sphere-like nanoparticles is consistent with the diameter of the final SnO_2 nanorods. As shown in Fig. 3(b), the HRTEM image of the nanorods indicates that the SnO_2 nanoparticles in one nanochain are bound to each other, leading to the particle attachment along the [0 0 1] direction (as shown in the sign), which is consisted with the growth direction of the final nanorods. These results are in agreement with the results of XRD as shown in Fig. 1.

From the above experimental observation, as a kinetically controlled nonclassical crystallization process, the formation and growth of the boscage-like SnO_2 nanorods can be rationally expressed by the Ostwald-ripening assisted oriented attachment mechanism, which explains the observed growth behavior of nanocrystals [18]. $Na_2SnO_3 \cdot 3H_2O$ is a compound with unstable chemical properties in the aqueous solution. After being added into the deionized water, $Na_2SnO_3 \cdot 3H_2O$ hydrolyze and oxidize rapidly to form Sn^{4+} ions. When the hydrothermal reaction was carried out, numerous SnO_2 nuclei were rapidly formed and grew up to SnO_2 small nanoparticles through a homogeneous nucleation process. To minimize the total interfacial energy, these small SnO_2 nanoparticles grew and aggregated via the Ostwald ripening mechanism to assemble irregular nanocrystal SnO_2 architecture. Because of the ripening, the SnO_2 nanoparticles gradually evolved into sphere-like nanoparticles. For rutile phase SnO_2, computer simulation studies have demonstrated that the sequence of surface energy in different crystallographic orientations is (0 0 1) > (1 0 1) > (1 0 0) > (1 1 0), that is, the (0 0 1) crystal face has the highest surface energy [19]. Therefore, according to the Lowest Energy principle, the [0 0 1] direction theoretically is a preferential growth direction of the SnO_2 nanocrystals. As a consequence of the kinetic limitations, the nanoparticles oriented assembled into short nanochains by binding to each other along the [0 0 1] direction with the (1 1 0) facet. Finally, the linear aggregates recrystallized into single-crystalline nanorods whose diameter was determined by the diameter of the sphere-like nanoparticles. The formation process of the nanorods is summarized in Fig. 4. These nanocrystals grew orientally from their roots, resulting to the boscage-like clusters. Consequently, the present boscage-like SnO_2 nanorods were prepared through the synergic effect of ripening mechanism and oriented attachment. The grown progress of nanorods relates to the intrinsic anisotropic characters of hexagonal rutile SnO_2 crystal structure.