Facile synthesis of single-crystal tin oxide nanorods with tunable dimensions via hydrothermal process

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Abstract

Single-crystal SnO₂ nanorods with tunable diameters and lengths, ~42 × 197, ~5.5 × 19.3 and ~4.5 × 39.1 nm, have been synthesized through a simple hydrothermal process, using a mixture of water/ethanol (1:1 in volume), a mixture of water/ethanol (1:1 in volume) with cetyltrimethyl ammonium bromide, and pure ethanol as reaction media, respectively. X-ray diffraction, electron microscopy, UV–Visible spectroscopy and other techniques were used to characterize the nanorods. The as-synthesized SnO₂ nanorods exhibit preferential growth along the [001] direction. The related mechanisms of the oriented growth and dimensional tunableness are discussed.
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1. Introduction

Low-dimensional inorganic nanostructured materials are currently being exploited as active components in a wide range of technological applications in various fields, such as nanoelectronics [1], optoelectronics [2], chemical sensing [3], catalysis [4], biomedicine [5] and composite materials [6], due to their high surface-to-volume ratio, enhanced material characteristics because of quantum confinement effects, and the high fraction of chemically similar surface sites [7]. Motivated by the putative applications, scientists have developed lots of strategies, ranging from template-assisted synthesis [8] to conventional solution-phase routes [9], to fabricate multifarious low-dimensional nanostructured materials, including nanoparticles, nanotubes, nanowires, nanorods, nanocables, nanosheets, nanodisks, and so on [10–13]. Among them, metal oxide nanostructures are the most important ones, which exhibit excellent electrical, optical, magnetic and chemical properties, and high thermal stability.

Tin oxide (SnO₂), an important n-type semiconductor with a wide band gap (E_g = 3.6 eV), is a typical example. Many researches have shown that the semiconductor SnO₂ nanocrystals and related materials are of potential technological applicability in gas sensors [14,15], transparent conducting electrodes [16], solar cells [17] and transistors [18]. Recently, a series of groups have synthesized low-dimensional SnO₂ nanocrystals (e.g. nanowires, nanobelts, nanorods, nanotubes, nanodisks, nanoparticles, nanocables, etc.) by various routes, including thermal evaporation of SnO₂ or SnO powders at elevated temperature [19,20], refluxing the ethylene glycol solution of SnC_2O_4Æ2H_2O and poly(vinylpyrrolidone) [21], template-based synthesis [22], microemulsion-mediated growth [23], sol–gel process [24], polymeric precursor method [25], laser ablation synthesis [17], topotactic thermal oxidation of Sn [26], controlled aqueous growth [27], and so on [28–30]. However, it is still a great challenge for scientists to synthesize SnO₂...
nanocrystals with tunable dimensions by a wet chemical method.

Herein, we developed a hydrothermal process to prepare one-dimensional SnO$_2$ nanocrystals with tunable diameters and aspect ratios. The process is characteristic of facility, low-cost and easy control, which makes it possible to synthesize and apply this nanomaterials at large scale.

2. Experimental

All chemicals, purchased from Shanghai Chemical Reagent Co. Ltd., were analytically pure. For the synthesis of SnO$_2$ nanocrystals, three precursor mixtures were prepared beforehand: (I) 1.05 g of SnCl$_4$$\cdot$5H$_2$O and 1.40 g of NaOH dissolved in a solution consisting of 40 ml of H$_2$O and 40 ml of ethanol; (II) 1.05 g of SnCl$_4$$\cdot$5H$_2$O, 1.02 g of NaOH and 2.18 g of cetyltrimethyl ammonium bromide (CTAB) dissolved in a solution consisting of 40 ml of H$_2$O and 40 ml of ethanol; (III) 1.05 g of SnCl$_4$$\cdot$5H$_2$O and 1.30 g of NaOH dissolved in 80 ml of ethanol. The above three precursors were transferred into Teflon-lined stainless steel autoclaves, and then the autoclaves were heated in ovens at 180 $^\circ$C for 24 h, 180 $^\circ$C for 24 h and 200 $^\circ$C for 7.5 h, respectively. The obtained white or gray–white precipitates were carefully washed with water and ethanol repeatedly, and then dried in vacuum at 60 $^\circ$C for 24 h. The three final products derived from the precursors I, II and III were marked as sample-1, sample-2 and sample-3, respectively.

The phases of the samples were identified by powder X-ray diffraction (XRD) analysis using a D/max 2550 V diffractometer with Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å). The morphology, microstructure and composition of the products were determined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) using a field emission electron microscope (JEM-2100F). UV–Visible absorption spectra were obtained on a Shimadzn UV-3101PC spectrophotometer using dry powders as samples in an absorbance mode. The diameter and length distributions of the obtained nanorods were determined by measuring the diameters and lengths of over 200 nanorods from each sample based on the TEM images.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples obtained at various conditions. All the diffraction peaks can be well indexed to the tetragonal rutile structure of SnO$_2$, which belongs to the space group of P4$_2$/mmm according to the JCPDS file No. 41-1445. The lattice parameters of the samples were calculated according to the equation of $1/d^2 = (h^2/k^2)/a^2 + l^2/c^2$ based on the crystal planes of (110) and (101), and the results were listed in Table 1. Here, $h$, $k$ and $l$ are the indices of crystallographic plane, $a$ and $c$ are lattice parameters, and $d$ is the interplanar distance of ($hkI$). The calculated values are in good agreement with the data from the JCPDS file No. 41-1445 in the error range. The diffraction peaks become broader from sample-1 to sample-3, which indicates that their sizes become smaller according to the Scherer equation. Comparing the relative intensity of the diffraction peaks, one can easily find that the diffraction intensity ratios of (002) to (110), and (101) to (110), i.e. $(I_{002}/I_{110})$ and $(I_{101}/I_{110})$, of the as-synthesized samples are much larger than those of the standard pattern from JCPDS 41-1445 (as shown in Table 1). This indicates the anisotropic growth of the SnO$_2$ nanocrystals.

Fig. 2 presents the morphology and size distributions of sample-1, obtained in ethanol/water media without surfactant CTAB. Fig. 2a shows the low-magnification TEM image, which indicates that there are two morphologies: nanospheres and nanorods. Another interesting phenomenon is that the obtained nanorods take on sharp ends, which is similar to nanoneedles. Figs. 2c,d show the histograms of the nanorod diameter distribution and the nanorod length distribution, respectively. The diameter of the nanorods is 41.6 ± 5.6 nm and their length is 197.0 ± 47.1 nm. The average aspect
ratio is ~4.74. Fig. 2b shows a single SnO$_2$ nanorod with a diameter of ~42 nm. The upper left inset in Fig. 2b is the corresponding SAED pattern along the $\{1\ 1\ 0\}$ zone axis. The well-defined SAED pattern shows that the obtained SnO$_2$ nanorod is single-crystal structure, and grows along the [001] direction. Fig. 2e shows the HRTEM image of the nanorod tip. The spacing between the adjacent lattice planes parallel to the nanorod growing direction is ~3.35 Å, which belongs to the (110) planes of rutile SnO$_2$. And the adjacent plane spacing perpendicular to the preferential growth direction is ~3.19 Å, which belongs to the (001) planes. So, the clear lattice fringes in the HRTEM image confirm that the nanorod is single-crystalline and the preferential growth direction of the nanorods is [001]. The EDS spectrum (the lower right inset in Fig. 2b) of the nanorod shows that there are only elemental O and Sn, except the elements of C and Cu, which come from the supported grid for TEM measurement. The atomic ratio of O to Sn according to the EDS semi-quantitative assessment is about 1.8, which indicates the existence of oxygen deficiencies in SnO$_2$ nanocrystals.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$/Å</th>
<th>$c$/Å</th>
<th>$I_{{1\ 0\ 1}}/I_{{1\ 1\ 0}}$</th>
<th>$I_{{0\ 0\ 2}}/I_{{1\ 1\ 0}}$</th>
<th>Diameter/nm</th>
<th>Length/nm</th>
<th>Aspect ratio</th>
</tr>
</thead>
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<tr>
<td>Sample-1</td>
<td>4.7421</td>
<td>3.1791</td>
<td>1.40</td>
<td>0.21</td>
<td>41.6 ± 5.6</td>
<td>197.0 ± 47.1</td>
<td>4.74</td>
</tr>
<tr>
<td>Sample-2</td>
<td>4.7423</td>
<td>3.1897</td>
<td>1.26</td>
<td>0.19</td>
<td>5.51 ± 1.06</td>
<td>19.34 ± 6.43</td>
<td>3.51</td>
</tr>
<tr>
<td>Sample-3</td>
<td>4.7414</td>
<td>3.1845</td>
<td>1.96</td>
<td>0.37</td>
<td>4.47 ± 0.83</td>
<td>39.1 ± 26.0</td>
<td>8.75</td>
</tr>
<tr>
<td>Std. file</td>
<td>4.7382</td>
<td>3.1871</td>
<td>0.75</td>
<td>0.06</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 3 shows the morphology of sample-2, synthesized in the presence of CTAB in ethanol/water media. The TEM image in Fig. 3a shows that the products mainly take on short nanorod shape. The histograms in Figs. 3c, d indicate that the as-obtained SnO$_2$ nanorods have diameters of 5.51 ± 1.06 nm and lengths of 19.34 ± 6.43 nm, which are much smaller than those of sample-1. Unfortunately, the average aspect ratio of
sample-2, ~3.51, also become less than that of sample-1. Fig. 3b shows the HRTEM image of several nanorods. The lattice fringes indicate the nanorods are single-crystalline, and the crystal planes along the growth direction of the nanorods belong to the \{110\} planes with an interplanar distance of 3.35 Å, which is similar to sample-1. The nanorods have almost flat ends. Fig. 3e shows the SAED pattern of a nanorod aggregate, whose diffraction rings from inside to outside can be indexed as \( (110), (101), (200), (211) \) and \( (112) \) planes of rutile \( \text{SnO}_2 \), respectively.

Fig. 4 shows the morphology and size distribution of sample-3, prepared by hydrothermal treatment in ethanol. TEM image in Fig. 4a shows the obtained products are long interlaced nanorods, with diameters of \( 4.47 \pm 0.83 \) nm (Fig. 4c) and lengths of \( 39.1 \pm 26.0 \) nm (Fig. 4d). The average aspect ratio reaches 8.75. The HRTEM image in Fig. 4b shows the obtained nanorods are monocrystalline, and crystal planes parallel to the nanorods also belong to the \{110\} planes (adjacent lattice spacing of 3.35 Å). The growth direction of the nanorods in sample-3 can be determined to be \[001\] by the similar HRTEM and XRD results to sample-1 and sample-2. Fig. 4e shows the SAED pattern of a nanorod bundle, and the diffraction rings from inside to outside belong to \( (110), (101), (200), (211) \) and \( (112) \) planes, respectively.

As the above results show, the tetragonal structured \( \text{SnO}_2 \) nanorods obtained by hydrothermal process in water/ethanol solution present preferential growth along \[001\] direction, and are enclosed by \{110\} crystal planes. The aspect ratios of the \( \text{SnO}_2 \) nanorods can be forecasted by the values of \( I_{002}/I_{110} \). The larger the value of \( I_{002}/I_{110} \) the larger the average aspect ratio of the \( \text{SnO}_2 \) nanorods, which is clearly shown in Table 1. The preferential growth can be well understood by the surface energy difference of the various crystallographic orientations. For the rutile structure of \( \text{SnO}_2 \), the low-index \( (110) \) face is the thermodynamically most-stable bulk termination and has the lowest surface energy [27]. The sequence of surface energy per crystal face can be described as \( (110) < (100) < (101) < (001) \) according to the calculated data [29]. So, the surfaces of \( (110) \) and \( (001) \) have the lowest and the highest surface energy, respectively, which can properly explain the preferential growth of \( \text{SnO}_2 \) along the \[001\] direction in thermodynamic aspects [30]. However, the previous reports show that the one-dimensional \( \text{SnO}_2 \) nanocrystals obtained by high-temperature process seldom grow along the \[001\] direction, but along the \[100\], \[101\] and \[301\] directions [18–20,31,32]. According to the opinion of Vayssieres and Graetzel [27], the \( (110) \) stoichiometric surface is a nonpolar surface with no net
dipole moment in the [110] direction, and the centrosymmetric structure of low-axial ratios \((c/a = 0.67)\) reduces substantially the possibility of anisotropic growth of the crystals along the [001] direction. In our experiments, the hydrothermal process using water/ethanol as the reaction media allows a slow nucleation and growth at low-interfacial tension conditions, which favors the generation of \(c\)-elongated anisotropic SnO\(_2\) nanocrystals, enclosed by the stable (110) facets [27].

The adjustment of the diameters and their aspect ratios is carried out by adding CTAB or changing the reaction media. Besides the steric effect, the adsorption of CTAB molecules on the surfaces of SnO\(_2\) nanocrystals can change the surface energies of some special surfaces, which may influence the morphology and dimension of nanocrystals. This reduces the diameters of SnO\(_2\) nanorods from \(~42\) to \(~5.5\) nm, but their aspect ratios are all less than 5. But, the obtained SnO\(_2\) nanorods in ethanol not only have a small average diameter (<5 nm), but also present a large aspect ratio (>8), which probably results from the lower interfacial tension of the ethanol media [27].

Fig. 5 shows the UV–Visible absorption spectra of the as-synthesized SnO\(_2\) nanorods. The absorption bands of the nanorods are very close to that of the bulk materials (345 nm), which can be attributed to the fact that the diameters (>4.5 nm) of the obtained nanorods are much larger than the excitation Bohr radius (~2.7 nm) of SnO\(_2\), and the weak quantum confinement effect can be negligible [33].

4. Conclusions

Single-crystal SnO\(_2\) nanorods with tunable diameters and lengths have been synthesized through a simple hydrothermal process. SnO\(_2\) nanorods with a dimension of \(~42 \times 197\) nm are formed in an isometric mixture of water and ethanol, and the smaller SnO\(_2\) nanorods of
~5.5 × 19.3 nm are obtained in the presence of CTAB. When the ethanol is used as reaction media, the SnO$_2$ nanorods with large aspect ratio (~4.5 × 39.1 nm) are achieved. The HRTEM images and SAED pattern show that the as-synthesized SnO$_2$ nanorods exhibit preferential growth along the [001] direction, which is different from the anisotropic SnO$_2$ nanocrystals obtained via high-temperature process. The facile synthesis of SnO$_2$ nanorods with tunable dimensions will pave the way for their large-scale applications in various technological fields.

References