Solution route to single crystalline SnO platelets with tunable shapes

Shuai Wang,[a] Songhai Xie,[a] Hexing Li,[b] Shirun Yan,[a] Kangnian Fan[a] and Minghua Qiao*[a]

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Square and round single crystalline SnO platelets have been prepared in a solution-based chemical route aided with sonication at room temperature.

In this communication, we report a facile solution route to single crystalline SnO platelets with controllable shapes from square to round. It is known that SnO is technologically important as a *p*-type semiconductor and in high energy density rechargeable lithium batteries,[1] storage of solar energy,[2] and organic synthesis.[3] Moreover, SnO is a versatile intermediate to metallic Sn, Sn_3O_4 and SnO_2.[4a] Much effort has been devoted to the synthesis of SnO materials with different dimensions and morphologies.[4–9] For example, by thermally evaporating SnO or SnO_2 powders under controlled conditions without the presence of catalyst, Wang *et al.* obtained SnO crystals with uniform nanostructures such as diskettes,[4a,4b] nanoribbons[4c] and blocks.[4b] On the other hand, although solution-phase growth has distinct advantages, using this route to produce regular SnO single crystals was less successful. Hydrothermal synthesis,[7] microwave-[8] or ultrasound-assisted solution methods[9] led to either amorphous or multiple sized and shaped SnO particles. Herein, by systematic variation of experimental parameters, we found that SnO single crystal platelets with either square or round contour can be readily prepared by a solution-based chemical route at room temperature. The process directly leads to relatively uniform products without fractionation procedure and is readily scaled up for mass production.

In a typical synthesis, Sn^{2+} precursor ($SnCl_2 \cdot 2H_2O$, 15 mmol), tri-sodium citrate ($Na_3C_6H_5O_7 \cdot H_2O$, 20 mmol) and a desired amount of cetyltrimethyl ammonium bromide (CTAB) were dissolved in 25 mL of deionized water with magnetic stirring. Then 10 mL of potassium hydroxide solution (KOH, 64.2 mmol) was added within 2 min under sonication (CQX25-6, 25 kHz, 250 W). After addition, the solution was removed from the sonication bath. The color of the solution turned to gray–black, indicating the formation of the SnO platelets. After standing, the black precipitate was separated *via* centrifugation and sequentially washed with deionized water and ethanol. All the procedures were conducted at room temperature. The products were characterized by scanning electron microscopy (SEM; Philips XL30 at 30 kV) fitted with an energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM; JEOL JEM2011 at 200 kV), and X-ray powder diffraction (XRD; Bruker AXS D8 Advance X-ray diffractometer, Cu Kα radiation at 40 kV and 40 mA).

Fig. 1 shows the SEM images of three types of SnO platelets synthesized with different amounts of CTAB (type I, without CTAB; type II, with 0.75 mmol of CTAB; type III, with 3.0 mmol of CTAB). It is readily observed that SnO platelets were obtained in large quantity and good uniformity by this route. Moreover, the shape of the SnO platelets can be easily tuned from square (Fig. 1A and C) to round (Fig. 1B) by simply adjusting the amount of CTAB added. However, it should be noted that although type I and III SnO platelets have a similar contour, they are enclosed by different side planes, as will be elaborated by TEM and selected area electron diffraction (SAED) characterizations.

Aside from the evolution in morphology, when increasing the amount of CTAB, the SnO platelets became larger and thinner on the whole. According to Fig. 1, the mean edge length of type I SnO platelet is ~7 μm, and edge length-to-thickness aspect ratio maintains around 3 irrespective of the dimension of the platelets. For type II and type III SnO platelets, the diameter/edge length and aspect ratio increase to ~9 μm and 8, and ~11 μm and 12, respectively.

EDX microanalysis and XRD measurements (inset in Fig. 1) reveal that these three types of SnO platelets are exclusively tetragonal SnO (*P4/nmm*, a = 3.802 Å and c = 4.836 Å, JCPDS 06-0395). No diffraction peaks due to metallic Sn or other tin oxides were discerned, indicating the high purity of the platelets. The intensity ratios between the (002) and (101) peaks of the platelets (0.8, 1.5 and 2.0 for type I, II and III, respectively) are much higher than the conventional value of 0.14 (JCPDS 06-0395), suggesting that the most abundant planes of the SnO platelets are {001} planes, thus their {001} planes tend to lie against the surface

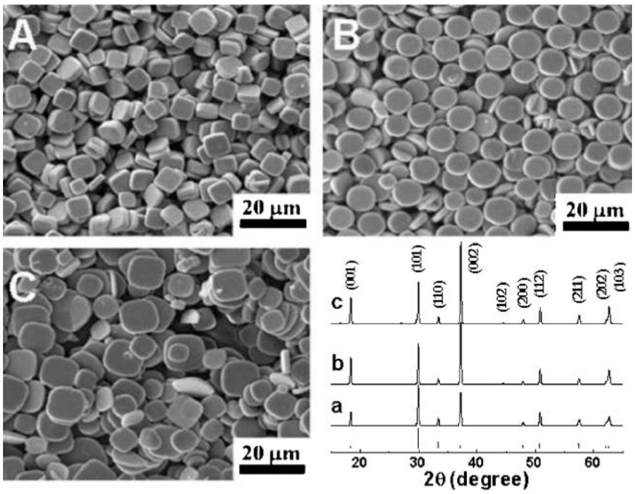

Fig. 1 SEM images of type I square SnO platelets (A), type II round SnO platelets (B), and type III square SnO platelets (C). XRD spectra of type I (a), type II (b), and type III (c) SnO platelets are shown in the inset. The standard XRD pattern of tetragonal SnO is illustrated in the form of a bar graph at the bottom of the graph.

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*mhqiao@fudan.edu.cn

of the supporting substrate, as implied by SEM images. Moreover, the increased intensity ratios are in line with the increased aspect ratios of the platelets. It is observed that the intensity ratios between the (110) and (200) peaks decrease in the order of $2.20 > 2.09 > 1.68$ with the increment of CTAB, being an indication of the relative abundance of the {100} planes, which is closely related to the change of the shapes of the SnO platelets.

A series of electron diffraction patterns have been recorded from the same SnO platelets while tilted along different crystallographic orientations, which indicate that the SnO platelets are single crystals. By combining the TEM images and their corresponding SAED patterns (Fig. 2A, C and D), it is determined that the normal direction of the SnO platelets is [001]. The spacing between adjacent lattice fringes in Fig. 2B is 0.265 nm, corresponding to (−110) planes of tetragonal SnO. For square SnO platelets, although the edges are slightly truncated, the type I SnO is primarily enclosed by {110} facets, while the type III SnO is mainly enclosed by {100} facets.

The synthetic results seem to support the shape transformation mechanism illustrated in Fig. 3. According to Wang,[10] the shape of the tetragonal SnO single crystal is mainly determined by the growth rates along the <001>, <100> and <110> directions. Owing to the slowest growth rate along the <001> direction, {001} planes are always the most plentiful surfaces for all three types of SnO, while the shape of the (001) surface is determined by the relative ratio R between the growth rates along the <100> and <110> directions. For type I SnO square platelet without the addition of CTAB, the ratio R is 1.41. For the type II SnO platelet, R equals 1 and thus a round contour is obtained. For the type III SnO platelet with square contour again, R is further decreased to 0.71. It seems that tri-sodium citrate tends to suppress the growth rate of the {110} planes more than that of the {100} planes, which is the reverse to the effect observed for CTAB. The synergistic effect of tri-sodium citrate and CTAB thus controls the morphologies of the SnO platelets.

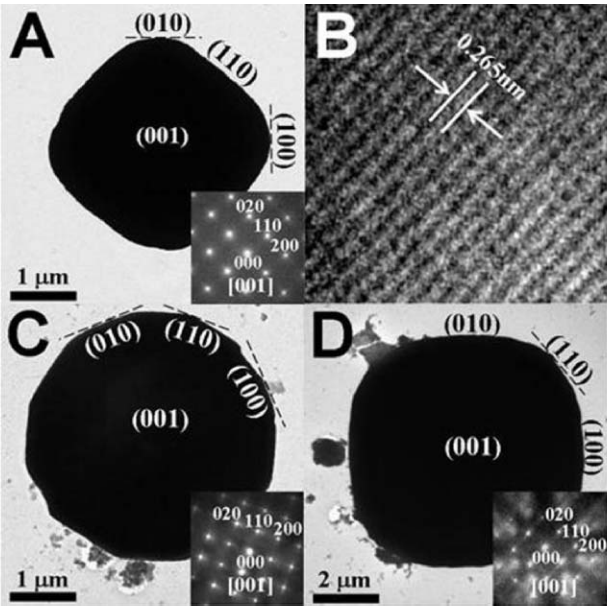

Fig. 2 TEM images of type I square SnO platelet (A), type II round SnO platelet (C), and type III square SnO platelet (D) recorded with the electron beam parallel to the [001] crystal direction. (B) HRTEM image of (A). The insets in (A), (C) and (D) are corresponding SAED patterns taken from the same SnO platelet in the [001] orientation, based on which the planes of the SnO platelets are indexed.

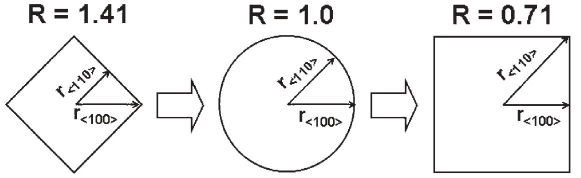

Fig. 3 Schematic illustration of the transformation in crystal shapes as a function of the ratio R between the growth rates along the <100> and <110> directions.

In addition, the morphology and dimension of SnO were found to strongly depend on reaction parameters such as sonication, molar ratio between tri-sodium citrate and tin dichloride, and the concentration of tin dichloride. For example, without sonication, SnO was hardly acquired and the morphology was irregular. If the molar ratio between tri-sodium citrate and tin dichloride was decreased, the particles with multiply intersected facets became the dominant product. And the dimension of the platelets increased accompanying the decrease of the concentration of tin dichloride. Moreover, when using CTAB instead of tri-sodium citrate in the synthesis, large SnO sheets with a side length of 25 μm and thickness of ∼20 nm were obtained. These demonstrations suggest that the present route is able to provide SnO materials with diversified morphologies and dimensions.

In brief, shape-controlled single crystalline SnO platelets have been prepared in solution at room temperature aided with sonication. The synergistic effect of tri-sodium citrate and CTAB is suggested to be essential for tuning the growth rates along different crystallographic planes of tetragonal SnO. Due to their defined shapes and crystal planes, these SnO platelets can be employed as model materials in a variety of areas such as anode materials, storage of solar energy and catalysis.

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Shuai Wang,[a] Songhai Xie,[a] Hexing Li,[b] Shirun Yan,[a] Kangnian Fan[a] and Minghua Qiao*[a]
[a]*Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China. E-mail: mhqiao@fudan.edu.cn; Fax: 86-21-65641740; Tel: 86-21-65643792*
[b]*Department of Chemistry, Shanghai Normal University, Shanghai 200234, P. R. China*

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