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# Growth of tetragonal $SnO_2$ microcubes and their characterization

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ABSTRACT

Single-crystalline $SnO_2$ microcubes were grown using the hydrothermal method without any catalyst. X-ray diffraction (XRD) patterns and energy dispersive X-ray (EDX) analysis verified that the cubes are tin dioxide $SnO_2$. Their morphology and structure was studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and Raman spectroscopy. It is revealed that the cube-shaped $SnO_2$ crystal have dimension varying from 500 nm to 5 μm as a function of chemical concentration and hydrothermal temperatures regimes. According to TEM results the cube axes are [0 0 1] direction and the side surfaces are {1 1 0} planes. A growth mechanism of $SnO_2$ cube-shaped crystals has been proposed.



## 1. Introduction

Tin oxide ($SnO_2$) microcrystals have attracted researchers attention due to their unique properties [1] and because of their wide applications in the field of optical waveguides [2], ultra-sensitive gas sensors [3], transistors [4], photosensors and solar cells [3,5]. Uniform shape and size controls are of fundamental and practical importance due to their unique shape-dependent properties of material [6–8]. Different strategies, such as, laser ablation, thermal evaporation, carbothermal reduction have been investigated in order to grow cubes of transition metal oxides [9,10], chalcogenides [11], transition metals [12]. So far only one report on $SnO_2$ microcubes from self-assembled nanorods [13] was reported. Recently, researchers' attention were focused on the hydrothermal technique and aqueous solution synthesis of various metal oxides [14,15]. These methods have been noteworthy as a new fabrication technique of functional materials at relatively low-processing temperatures. By controlling the nucleation sites, the coordination states of coexisting species, supersaturated and kinetic growth regime in aqueous system it is possible to enable the construction of novel architecture through crystal growth.

In this paper, we report the results of a hydrothermal synthesis of $SnO_2$ cubes (which are not reported till date) and size-control of these cubes by varying reaction condition. The importance of the present technique is its simplicity and no sophisticated equipments are required.

## 2. Experimental procedure

In a typical synthesis route, $SnCl_2 \cdot 2H_2O$ and $NH_4OH$ (29.5%) solution (from Fisher Scientific) were dissolved in a 100 ml aqueous solution (deionized water with resistivity about 18.2 MΩ cm added with a 5 ml of HCl (36%)). The solution was stirred for 5 min at room temperature until it became homogeneous. A silicon wafer and microscopic glass slide cleaned according to previous work [16,17] were used as substrates. After mixing, the

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solution was transferred in a glass beaker with a sphericalconcave cap with the radius of curvature of the surface of 10 cm and an orifice (1 mm in radius) on the side [14]. The system was heated to 98 °C and kept for 15 min, then was allowed to cool to 40 °C naturally. The products synthesized by described method were then annealed at 370 °C for 10 min.

Synthesized material was analyzed and characterized by scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM) (a FEI Tecnai F30 TEM), X-ray diffraction (XRD), (Rigaku) and Raman spectroscopy. For the TEM observation, the products were collected on a carbon holey grid. The Raman spectra were obtained using a Horiba Jobin Yvon LabRam IR system with a spatial resolution of 2 μm. He–Ne laser was used as an exciting source. This unit delivers $<4$ mW at the sample at 633 nm and was used in this study with a spectral slit width of approximately 2 $cm^{-1}$.

## 3. Results and discussion

Fig. 1(a) displays SEM images of the cube-shaped $SnO_2$ crystals grown by a hydrothermal method on silicon (1 0 0) substrates using 15–25 mM $SnCl_2 \cdot 2H_2O$. Fig. 1(a) and (b) shows, respectively, SEM of tin oxide microcubes with length of each side about 5–8 μm and smaller cubes with length of each side about 500 nm. Different sizes were obtained by changing the concentration using 30–40 mM $SnCl_2 \cdot 2H_2O$ and by varying the kinetic growth regime, thus for sample shown in Fig. 1(b) temperature gradient was lower by 0.5 °C/s, than for sample shown in Fig. 1(a).

Each face of the $SnO_2$ microcubes is a square. Evidence of the faultless shape is given by the SEM image (Fig. 1(a) and (b)) where eight vertices and six faces can be observed. Every face is not only flat and smooth, but also is perpendicular to its adjacent faces.

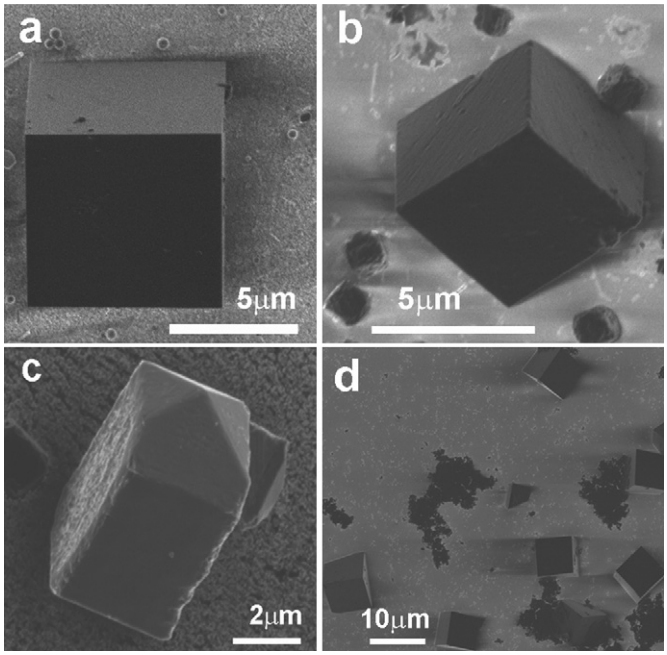


**Fig. 1.** SEM images of the (a) typical as-synthesized $SnO_2$ microcube grown by using 15–25 mM $SnCl_2 \cdot 2H_2O$ in aqueous solution; (b) different sizes $SnO_2$ microcubes grown by using 30–40 mM $SnCl_2 \cdot 2H_2O$ in aqueous solution; (c) $SnO_2$-pyramided architecture obtained by second process at 80 °C and (d) lower magnification view showing monodisperse $SnO_2$ cubes distributed on substrate surface.

The general morphology of the different sizes microcubes are shown in Fig. 1(b), which shows that in addition to the larger microcubes, there are also smaller cubes. Growth of two types of cubes bigger (length of each side 5–8 μm) and smaller (length of each side 0.5 μm) for the anisotropic crystal can be adjusted by balance between the thermodynamic and the kinetic growth regimes. Also, as the quantity of the nuclei depends on the concentration of the precursor we observed that by increasing the concentration of $Sn(OH)_6^{2-}$ generated more nuclei, which benefits the formation of nanocrystals with smaller cubes as displayed in Fig. 1(b). The hydrothermal route was performed at 80 and 98 °C. The crystals grown at 80 °C have curved and imperfect faces, irregular shape, corners and rough surface (Fig. 1(c)). Fig. 1(c) shows the SEM image of a tin oxide pyramided architecture grown at 80 °C for the same duration of heating. In Fig. 1(d) a lower magnification image of $SnO_2$ cubes synthesized on silicon substrate is presented.

The chemical composition of the microcubes was determined by EDX to be pure tin oxide. The XRD pattern is shown in Fig. 2, which reveals the crystal structure and phase purity of the as-synthesized microcubes. All of the diffraction peaks can be indexed to the tetragonal $SnO_2$ structure with lattice parameters $a = b = 4.738$ Å and $c = 3.188$ Å (JCPDS 041-1445). No characteristics peaks of other forms of tin oxide were detected.

Fig. 3(a) shows a typical high-resolution (HRTEM) image of one edge of the cube-shaped $SnO_2$ crystal. In the inset in Fig. 3 is the selected area electron diffraction (SAED) pattern of $SnO_2$ microcubes. The spacing between the lattice planes along the cube height and the width are 0.32 and 0.33 nm, which are in agreement with distance between (0 0 1) and (1 1 0) planes of rutile $SnO_2$, respectively. The growth direction for the cubes can be determined from SAED patterns. This confirmed that it grew along [1 1 0] direction in lateral sides (indicated with an arrow, perpendicular to the axis of a microcube). The distance separation between lattice layers are found to be 0.33 nm corresponding to lattice parameters of the rutile structure of $SnO_2$ [1 1 0] reflection. No dislocations or other planar defects were detected in the examined area of $SnO_2$ cubes. The growing is along [0 0 1] and [1 1 0] directions in vertical and horizontal planes, respectively, which is in accordance with the "lowest energy" argument.

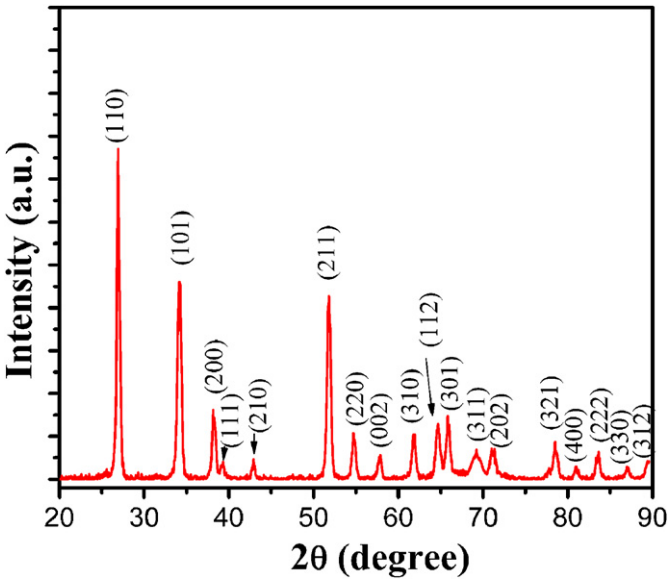


**Fig. 2.** A typical X-ray diffraction (XRD) pattern obtained by using CuKα radiation 1.5406A of $SnO_2$ microcubes obtained by the aqueous solution method.