Supporting Information

Self-assembly of SnO_2 dots into hierarchically ordered structure assisted by multistep oriented attachment

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Experimental Section

1.1 Materials and Reagents Stannic chloride ($SnCl_4 \cdot 5H_2O$), sodium hydroxide (NaOH) and ammonium hydroxide ($NH_3 \cdot H_2O$, 28 %) are of analytical grade. All chemicals were purchased from Alfa Aesar and used without further purification.

1.2 Preparation of primary SnO_2 nanoparticles. Using a typical procedure after minor modifications, SnO_2 nanoparticles were prepared by the hydrolysis of stannic chloride. To an aqueous solution of $SnCl_4 \cdot 5H_2O$ (30 g/L) was added $NH_3 \cdot H_2O$ until pH value came to ~ 5. At room temperature, a white turbid suspension was produced immediately. No surfactant was used to minimize external effects on the crystal growth in the following. The suspension was centrifuged at the speed of 8000 rpm for 2 minutes. The white precipitate was washed repeatedly with distilled water till Cl- was beyond the detection by 0.1 M AgNO3 solution. Finally, the product was dried under 80 ^oC for 48 h ($Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$) and ground into powder for kinetic measurements.

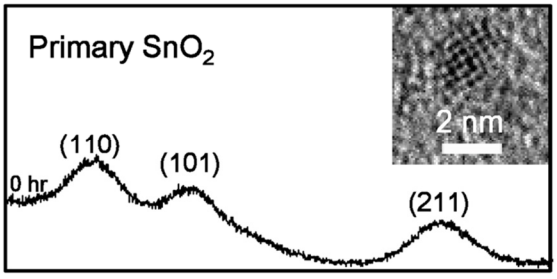

Figure S. XRD pattern and HRTEM image of as-synthezed SnO_2 nanoparticles.

Figure S shows the typical XRD pattern and HRTEM image of as-prepared SnO_2 nanoparticles. Primary nanoparticles are in tetragonal phase, with a calculated average size of ～1.9 nm.

1.3 Growth kinetics of SnO_2 nanoparticles in NaOH solution.

An amount of primary SnO_2 (0.1 g) and distilled water (10 mL) were loaded into a Teflon-lined stainless steel autoclave with 23 mL capacity. Later, the autoclaves were put in a large oven under 250 ^oC for 50 h, by which SnO_2 nanocrystals grew to a limited size of 4-5 nm in water. The suspension was centrifuged at the speed of 8000 rpm for 2 minutes. The white precipitate was mixed with 1.2 M NaOH (10 mL). Later, the autoclaves were put in a large oven under 250 ^oC again. For the time series experiment, autoclave containers were taken out at the appropriate time interval, and quenched to room temperature with ice water immediately. The precipitates were centrifuged, wash by ethanol, dried and characterized by X-Ray Diffraction, (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

1.4 Characterization.

XRD. The crystal structures and the average sizes of samples were identified by a PANalytical X'Pert PRO diffractometer with Cu Kα radiation (40 kV, 40 mA) in the continuous scanning mode. The scanning range of 2θ was from 15 ° to 75 ° in steps of 0.02 ° with a collection time of 100 s per step. The average crystallite size of nanocrystals was calculated from peak broadening by using the Scherrer equation.

TEM and SEM. To confirm the sizes and morphologies of SnO_2 nanoparticles, TEM and SEM images were taken on a JEOL JEM2010 at 5.0 kV and an JSM-6700F at 5.0 kV, respectively. All samples were prepared by depositing a drop of ethanol solution containing the nanocrystals onto holey carbon-coated grids.

Results

Table S1 Average particles size of SnO_2 nanocrystals along [110] and [002] directions, after coarsened in 1.2 M NaOH solution for 1.5, 24, 48 and 96 h, respectively.

Time (h)	1.5	24	48	96
[110] (nm)	5.0	5.1	5.5	5.4
[002] (nm)	14.8	25.8	29.1	36.0

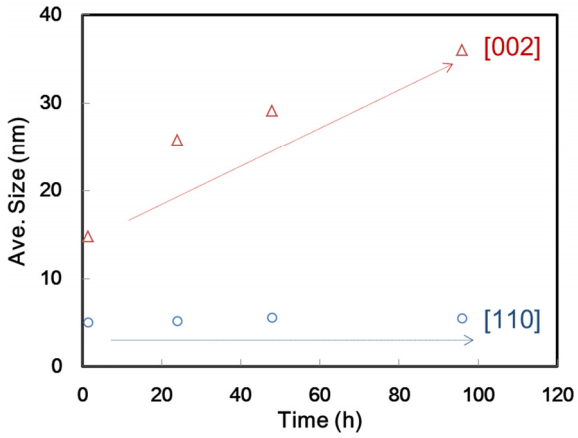

Figure. S1 Experimental data showing the average size of SnO_2 nanocrystals along [110] and [002] directions, after coarsened in 1.2 M NaOH solution for 1.5, 24, 48 and 96 h, respectively.

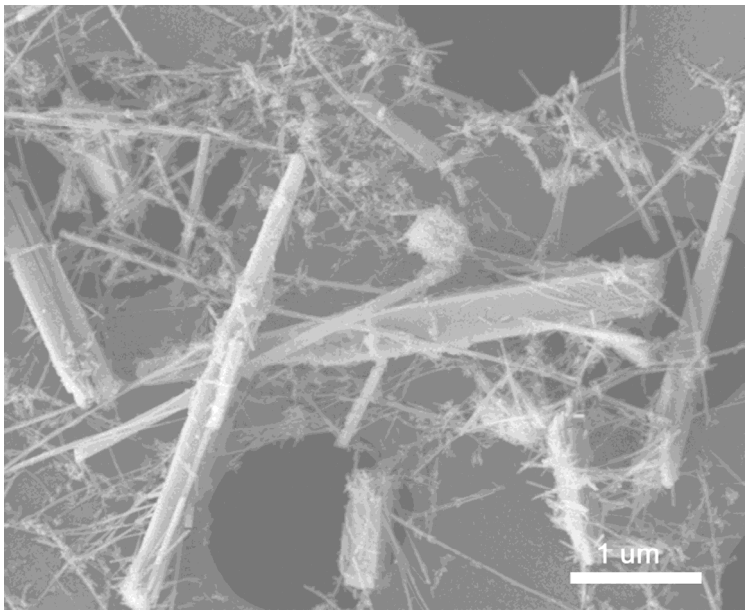

Figure S2. Typical SEM image of a big elongated SnO_2 crystal after coarsened in 1.2 M NaOH at 250 ^{o}C for 310 h.

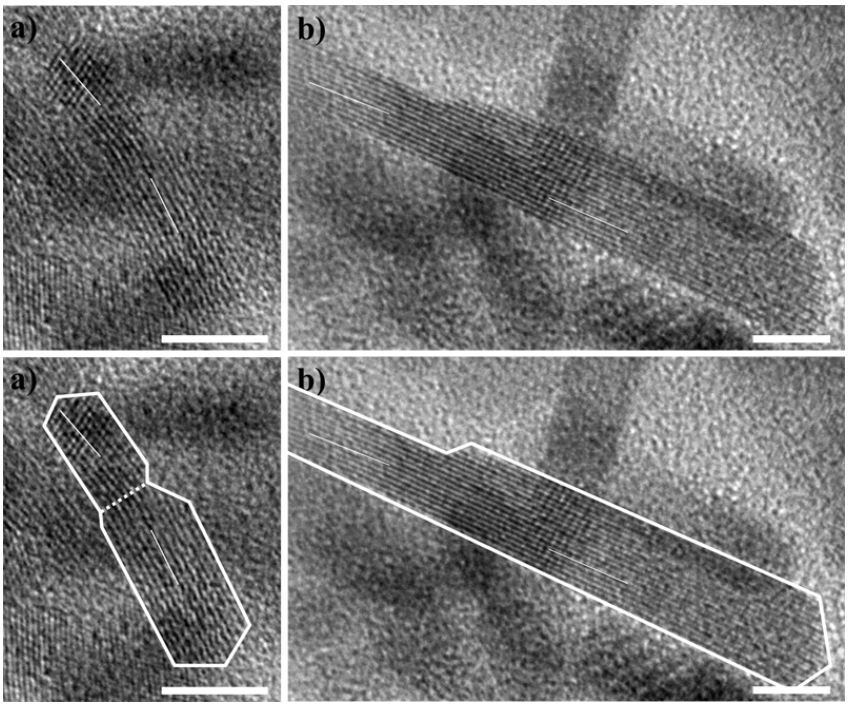

Figure S3. HRTEM images with lines to indicate the shape and interface positions, showing the growth trace of nanorods with common crystallographic orientation. Small SnO_2 nanorods as "building block" attached with each other via a common crystallographic orientation. The produced particles are with irregular shapes, exhibiting the character of crystal growth of nanowires by OA mechanism. Scale bars: 5nm.