

## *Experimental Section*

### *Synthesis*

All the chemicals were of analytical grade and used without further purification. In a typical synthesis, 5 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was dissolved 40 mL of distilled water. Then, the above solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 150 °C for 20 h. Finally, the sample was collected after being washed with absolute alcohol and distilled water, respectively.

### *Characterization*

The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu  $K\alpha$  source ( $\lambda = 0.15406$  nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The high-resolution transmission electron microscopy (HR-TEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. The specimen of HR-TEM measurement was prepared via spreading a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air.

### *Electrochemical Test*

The electrochemical Li intercalation performance was investigated in Li test cells for the  $\text{SnO}_2$  nanocrystals. Typically, the  $\text{SnO}_2$  electrode consisted of 80 wt% active material, 10 wt% conductivity agents (acetylene black), and 10 wt% binder (carboxyl methyl cellulose). After ethanol was evaporated, the mixture was rolled into a sheet and cut into circular strips of 8 mm diameter. The strips were then dried at 120 °C for 10 h in air. Lithium metal was used as the counter and reference electrodes. The electrolyte consisted of a solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, in weight percent). The above three parts were assembled into test cells in an argon-filled dry glovebox, and then the cells were measured at different current densities within a voltage range of 0.01-2.0 V with a Land CT 2001 battery tester.

**Fig. S1** TEM image of the as-synthesized SnO<sub>2</sub> nanocrystals with 1.4g SnCl<sub>4</sub>·5H<sub>2</sub>O.

