

## Electronic Supplementary Information

for

### Bottom-up Method for Synthesis of Layered Lithium Titanate

#### Nanoplates using Ion Precursor

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## Experimental section

### Bottom-up process for the synthesis of lithium titanate nanoplates (LTNPs)

The peroxy titanium complex ion used as a precursor was synthesized as follows: Initially, 0.63 g of  $\text{TiH}_2$  (>99%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) was treated with 62.46 mL of a mixed solution containing  $\text{H}_2\text{O}_2$  (30%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) and a 4 M LiOH (>98.0%, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) aqueous solution for 6 h at 10 °C. The pH of the mixed solution was adjusted to 8 by adding the 4 M LiOH solution to the  $\text{H}_2\text{O}_2$  solution. A solution color change to yellow was indicative of the formation of the peroxy titanium complex ion. For the synthesis of the LTNPs, the prepared peroxy titanium complex ion solution was heated in a refluxing vessel at 100 °C while stirring at 200 rpm for 12 h without further addition of LiOH. Then, the yellowish LTNP precipitates were filtered using a vacuum pump (MDA-020C, ULVAC, Inc., Kanagawa, Japan) and dried on a freezing dryer (EYELA FDU-2200, TOKYO RIKAKIKAI CO, LTD., Tokyo, Japan). To investigate their morphological stability, the LTNPs were subjected to acid and thermal treatment as follows: (1) Acid treatment: the as-synthesized LTNP samples were treated with a 5 M HCl (30%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) solution until the pH stabilized at 5 and then washed by distilled water until the ion conductivity of the filtered solution became less than 5  $\mu\text{S}/\text{cm}$  using a vacuum pump. Finally, the acid-treated LTNP samples were dried. (2) Thermal treatment: the LTNPs were heated at 500 °C for 1 h under ambient conditions at a heating rate of 10 °C/min using a furnace.

### Hydrothermal treatment of anatase $\text{TiO}_2$ by LiOH solution

As a reference sample, another lithium titanate compound was synthesized as follows: 1 g of anatase  $\text{TiO}_2$  (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) was added into 15 mL of a 3.5 M LiOH solution, and the mixture was placed into a Teflon lined autoclave (100 mL) and heated at 200 °C for 10 h. Then, the white products were filtered and dried.

### Synthesis of layered sodium titanate using various methods

To compare their morphology and structure, sodium titanates ( $\text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_5$ ) were synthesized by the following two approaches: (1) Using the peroxy titanium complex ion as a precursor in the bottom-up method described above, using a 10 M NaOH (97%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) solution instead of the 4 M LiOH solution. (2) According to a previously reported procedure.<sup>1</sup> Briefly, 1 g of P25  $\text{TiO}_2$  powder was mixed with 400 mL of a 10 M NaOH solution and then heated in a refluxing vessel at 115 °C for 24 h while stirring at 200 rpm. The resulting white precipitates were washed by distilled water using the vacuum pump, and dried.

## Characterizations

The optical properties of the peroxo titanium complex ion were determined by ultraviolet–visible spectroscopy (UV–vis) (UVmini1240, SHIMADZU Corporation, Tokyo, Japan). The crystal structure and purity were examined by X-ray diffraction (XRD) (D8 ADVANCE, Bruker AXS Co. Ltd., Karlsruhe, Germany). The diffraction patterns were collected using a Scintag diffractometer operating in the Bragg configuration using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) from  $5^\circ$  to  $70^\circ$  at a scanning rate of  $0.02^\circ$ . The lattice parameters of the samples were calculated using the results of the XRD analysis and eq. (S1),

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (\text{S1})$$

where  $d$  is the interplanar spacing,  $h$ ,  $k$ , and  $l$  are the Miller indices, and  $a$ ,  $b$ , and  $c$  are the lattice constants of the crystal phase. The amount of lithium and titanium in the samples was measured using inductively coupled plasma optical emission spectrometry (Optima 8300, PerkinElmer Japan Co., Ltd., Yokohama, Japan). The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of Ti K-edge were measured in an ionization chamber in transmission mode on the Kyushu University Beamline (BL06) of the Kyushu Synchrotron Light Research Centre (SAGA-LS; Tosu, Japan). Pellet samples for the Ti K-edge XANES and EXAFS measurements were prepared as mixtures with boron nitride. As a reference sample, anatase TiO<sub>2</sub> (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) was used. The Ti K-edge spectra were collected over a photon energy range of 4635.2–5938.6 eV. The spectra were analyzed by ATHENA software (Ravel and Newville 2005).<sup>2</sup> The UV–vis absorbance was evaluated using the solid sample measurement mode (V-650, JASCO Co., Tokyo, Japan) within a wavelength range of 200–800 nm, and the diffuse reflectance spectroscopy and optical bandgap energy were measured by the Tauc-plot method using Kubelka–Munk transformation. For the O<sub>1s</sub> X-ray photoelectron spectra (XPS) (JPS-9010MX JEOL Ltd., Tokyo, Japan), the binding energy was standardized with the C<sub>1s</sub> energy. The morphology and particle size were observed using a field-emission scanning electron microscope (FE-SEM, SU-9000, Hitachi High-Technologies Corporation, Tokyo, Japan) with SEM and scanning transmission electron microscopy modes at an acceleration voltage of 30 kV. Transmission electron microscopy (JEM-ARM200F, JEOL, Tokyo, Japan) was performed at an acceleration voltage of 200 kV to further characterize the individual nanostructures of the titanate. Moreover, the lattice spacing was investigated using the Gatan Digital Micrograph software (Gatan Inc., CA, USA).<sup>3</sup> Without dispersing the dried samples in any solvent to minimize the reaction with water molecules, the samples were dropped on the surface of a carbon-coated copper grid as a solid powder.

## Supplementary Figures

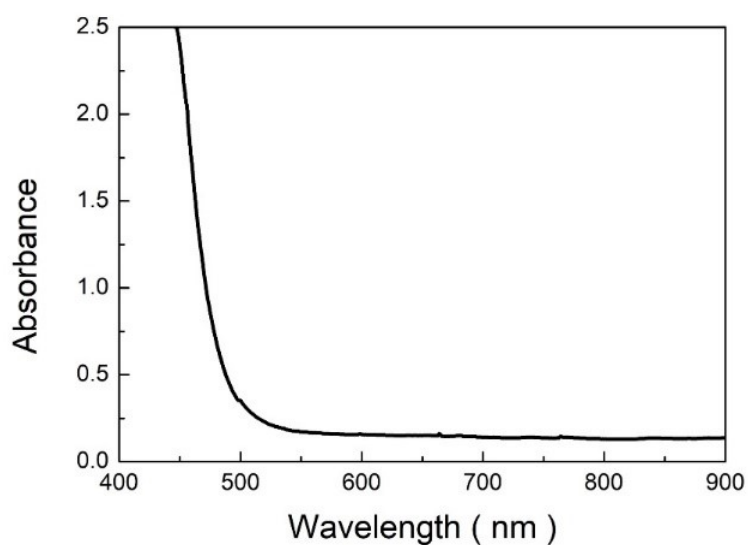


Fig. S1. Ultraviolet–visible spectrum of the peroxy titanium complex ion solution obtained by treating  $\text{TiH}_2$  with an  $\text{H}_2\text{O}_2/\text{LiOH}$  solution at  $10^\circ\text{C}$  for 6 h.

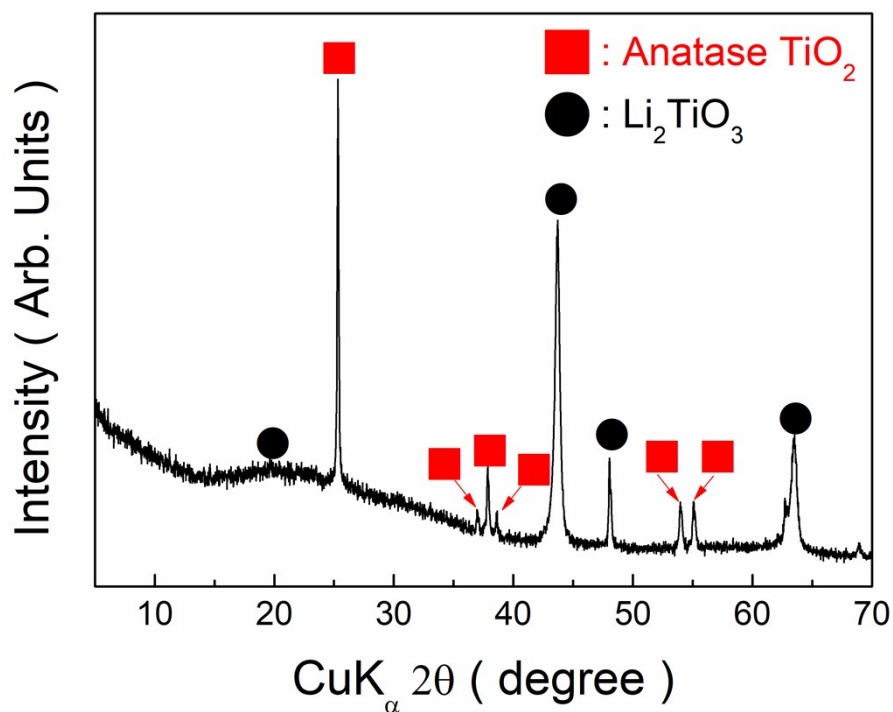


Fig. S2. X-ray diffraction pattern of the powder synthesized by hydrothermally treating anatase  $\text{TiO}_2$  using a 3.5 M  $\text{LiOH}$  solution. The mixed phases of anatase  $\text{TiO}_2$  (PDF card# 00-021-1272) and  $\text{Li}_2\text{TiO}_3$  (PDF card# 00-033-0831) can be observed.

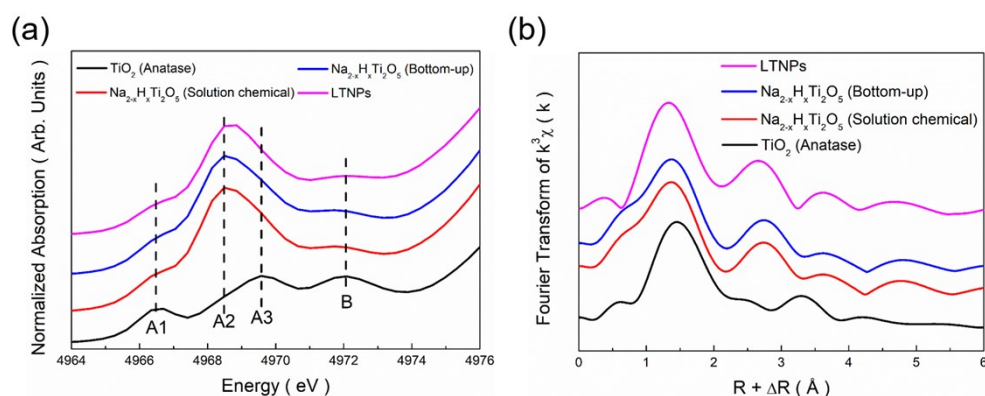


Fig. S3. X-ray absorption fine structure (XAFS) spectra of anatase, sodium titanate prepared by the bottom-up method ( $\text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_5$  (Bottom-up)), sodium titanate prepared following a previously reported procedure ( $\text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_5$  (Solution chemical)), and lithium titanate nanoplates (LTNPs): (a) pre-edge regions of the X-ray absorption near edge structure spectra and (b) Fourier transform extended XAFS spectra. Radial distribution functions were not corrected for the phase shift.

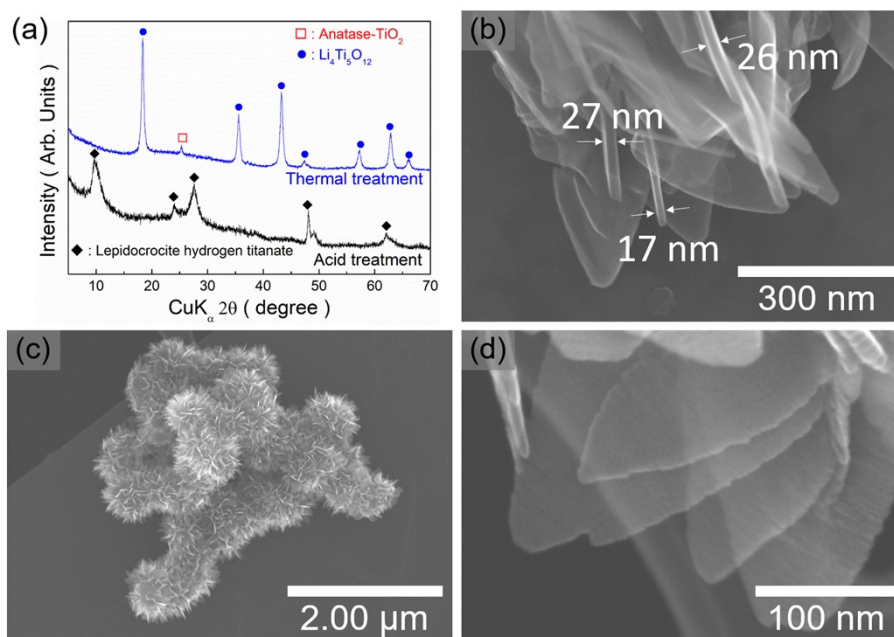


Fig. S4. (a) X-ray diffraction pattern of the powder prepared by acid treatment and thermal treatment of the lithium titanate nanoplates. The pattern of the acid-treated sample (black line) can be assigned to lepidocrocite-type hydrogen titanate. The lattice constants were determined to be  $a_0 = 17.0 \text{ \AA}$ ,  $b_0 = 3.8 \text{ \AA}$ , and  $c_0 = 2.9 \text{ \AA}$ . The pattern of the thermally treated sample (blue line) exhibits the mixed phase of anatase  $\text{TiO}_2$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (PDF card# 00-049-0207). Scanning electron microscopy (SEM) image of (b) acid-treated sample and (c) thermally treated sample. (d) Magnified SEM image of the thermally treated sample.

## Reference

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- 2 B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537–541.
- 3 D. R. G. Mitchell, *Microsc. Res. Tech.*, 2008, **71**, 588–593.