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Evidencing the Structural Conversion of Hydrothermal-synthesized Titanate Nanorod by *in-situ* Electron Microscopy

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S1. Experimental methods

Synthesis of titanate nanorods. The titanate nanorods were synthesized according to previous report.[1] 1 g TiO_2 (anatase) and 10 M NaOH aqueous solution (total volume of 40 ml) was heated in a 50 ml Teflon-lined autoclave, maintained at 200 ^oC for 24 h. After the autoclave was naturally cooled down to room temperature, the product was sequentially washed with dilute HCl solution, distilled deionized water, and absolute ethanol for several times. The product was then dried in a vacuum oven for 12 h at 60 ^oC.

TEM observations. The in-situ heating experiment described in this work was conducted on a Protochips Aduro platform with heating E-Chip specimen support that provides atomic resolution at a thermal ramp rates of up to 10^6 $^oC/s$ with highly accurate temperature control over specimen inside a TEM. The TEM sample was prepared for in-situ experiment by drop-casting titanate nanorod onto a Si_3N_4 thin-film supported by a ceramic membrane from a nanoparticle-ethanol suspension and was allowed to dry in air. TEM observation was conducted on a JEOL JEM-2100F field-emission transmission electron microscope operated at 200 kV, equipped with Oxford INCA x-sight EDS and ENFINA 1000 EELS. During the observation, the sample was irradiated by a focused electron beam with a current density of ca. 65 pA/cm^2 (measured from the fluorescent screen), and the image was captured using a Gatan SC1000 ORIUS CCD with a short exposure time (0.1 s). The electron beam was blanked whenever possible to minimize beam effects on the nanorod.

Theoretical calculations. To calculate the electronic structure and Mulliken bond populations of $Na_{0.8}Ti_4O_8$ and β-TiO_2,[2,3] we used local density approximation (LDA) as implemented in the CASTEP code.[4] All results are obtained by using the ultrasoft pseudopotential with a plane wave basis set. An energy cutoff of 410 eV and 1x4x2 Monkhorst-pack k points in the Brillouin zone were used for both $Na_{0.8}Ti_4O_8$ and β-TiO_2.

S2. Morphology evolved with heating temperature

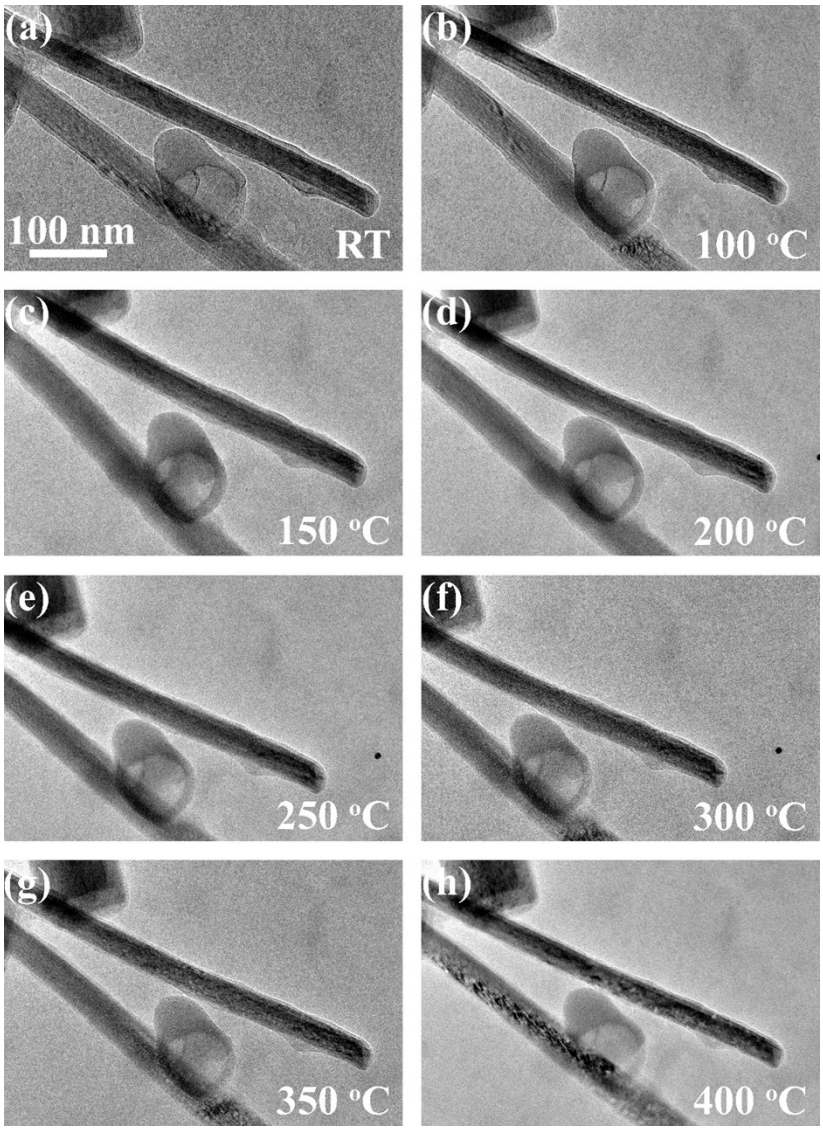

Figure S1 Typical TEM image sequence showing the temperature-dependent morphologies for two nanorods. The scale bar in (a) also applies to (b - h).

Note that the EELS and EDS spectra as well as the SAED patterns throughout **Figure 2** were all captured from the upper nanorod.

It is also worthy of note that, after intensive irradiation of electron beam, the upper nanorod didn't show any difference with the lower one (see **Figure S1h**), implying that the electron beam has little influence throughout our in-situ experiment.

S3. Zero-loss EELS spectra

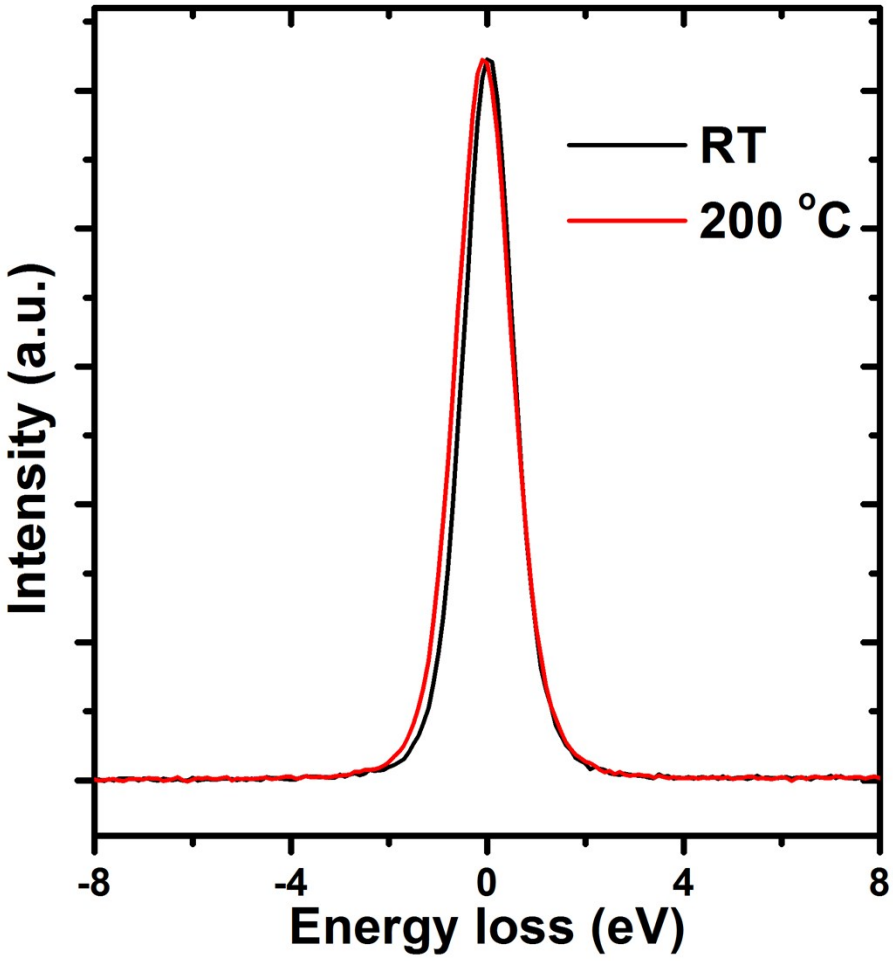

Figure S2 The corresponding EELS zero-loss peaks for the Ti L-edge spectra in **Figure 2a**.

Table S1. Bonding atoms, population analysis and bond length in NT phase.

Bond	population	Length (Å)
O -- Ti	0.60	1.79875
O -- Ti	0.50	1.87381
O -- Ti	0.52	1.88193
O -- Ti	0.53	1.91884
O -- Ti	0.36	1.98874
O -- Ti	0.24	2.06919
O -- Ti	0.22	2.08200
O -- Ti	0.17	2.21020
O -- O	-0.04	2.58580
O -- O	-0.04	2.65617
O -- O	-0.04	2.68253
O -- O	-0.03	2.74037
O -- Na	-0.05	2.86194
O -- O	-0.02	2.89390
O -- O	-0.01	2.92479
Ti -- Ti	-0.32	2.98314

References

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