Electronic Supplementary Information for

In-situ TEM observation of the structural transformation of rutile TiO_2 during electrochemical lithiation

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1. Experimental

Characterization: High-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (HR-STEM) images of TiO_2 NWs were taken using JEOL JEM-3010F and aberration-corrected JEOL-JEM2100F transmission electron microscopes, operating at accelerating voltages of 300kV and 200kV, respectively.

Assembly of the TiO_2 nanowire based Li-cell: A TEM specimen was prepared by embedding NWs in Ag-based paste on a Cu post. A prepared specimen was loaded onto a single-tilt in-situ Nanofactory Instruments TEM-STM holder to be part of an electro-chemical cell assembly as an anode in a JEOL JEM-3010F microscope. Bulk Li metal, as a cathode counter-part, was scrapped onto a tungsten STM tip that was loaded on a piezo-drive of the holder inside the glove box. A naturally formed Li_2O layer on the Li metal from the 3-6 sec exposure to air during transportation from an Ar-filled bag into the TEM column, acted as a solid electrolyte. The complete electro-chemical assembly was made by having the STM tip piezo-driven towards the NW. Relatively fast electro-chemical cycling, at the rate of 2V/s, was adopted in order to both restrict the quantity of Li inserted into the NW and avoid possible amorphous carbon contaminant deposition around the NW.

2. Supporting Figures Information

A. Atomic structure of a rutile TiO_2 NW

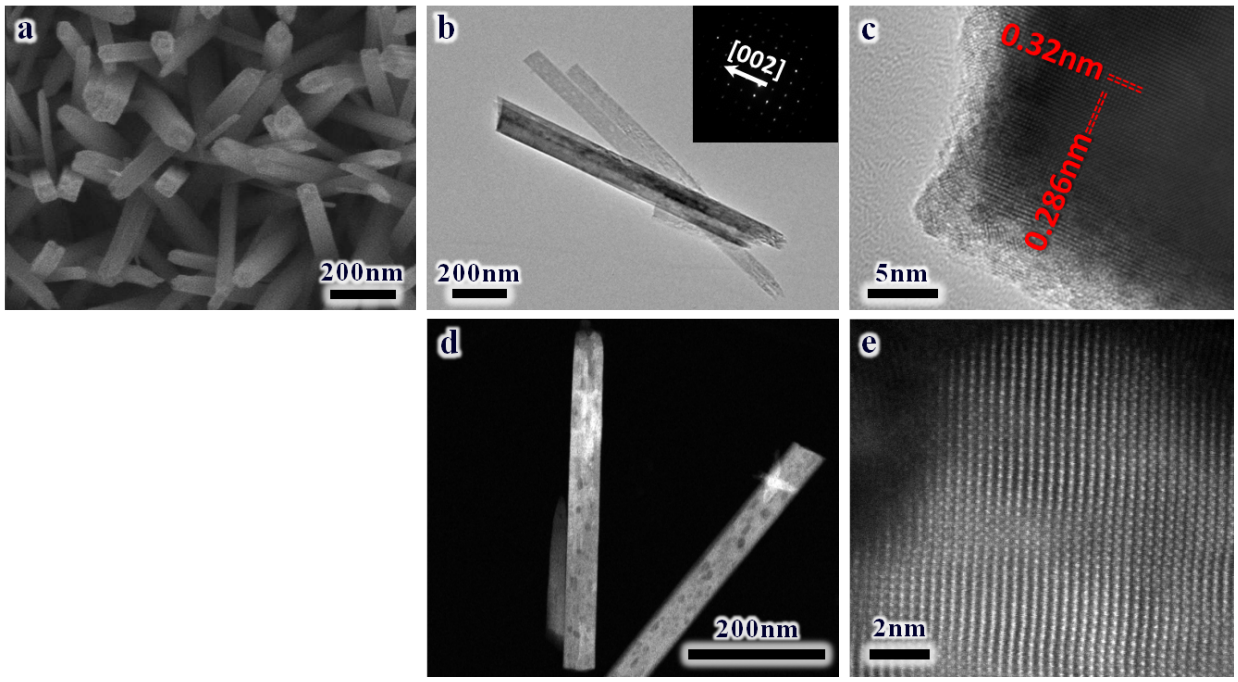

Fig. S1. (a) SEM image of rutile TiO_2 NWs grown on a fluorine-doped tin oxide substrate. **(b-e)** TEM and HR-TEM images of a rutile TiO_2 NW

B. Lattice expansion of rutile TiO_2 upon intermediate phase transformation

Figure S2 shows lattice expansion of a rutile TiO_2 NW upon intermediate phase transformation ($TiO_2 \rightarrow Li_xTiO_2$) in both low- and high-magnification images. The measured lattice spacings (d(202)) for TiO_2 and Li_xTiO_2 are 0.248nm and 0.250nm, respectively, the difference of which is slightly larger than that theoretically calculated. (d_{101} for TiO_2 and Li_xTiO_2 are 0.2487nm and 0.2489nm)

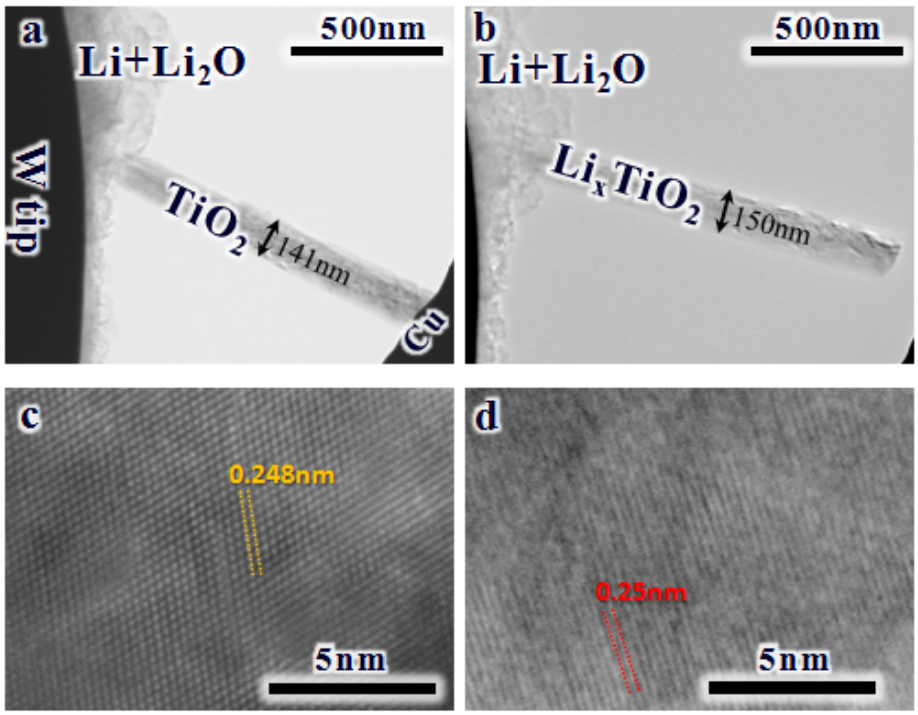

Fig. S2 Low- and high-magnification TEM images of (**a and c**) a TiO_2 NW in primitive state and (**b and d**) a Li_xTiO_2 NW in transition to intermediate state.

C. Selected area diffraction of TiO_2 NW before and during the phase transformation

Figure S3 shows selected area diffraction patterns of the TiO_2 NW (ZA: 100) before and during the phase transformation. Notice that there is a secondary diffraction pattern (yellow) overlaying the original diffraction pattern (red) (Figure S3 (b)) from the rutile phase. This agrees very well with the monoclinic phase, which marks the phase transformation from TiO_2 to Li_xTiO_2.

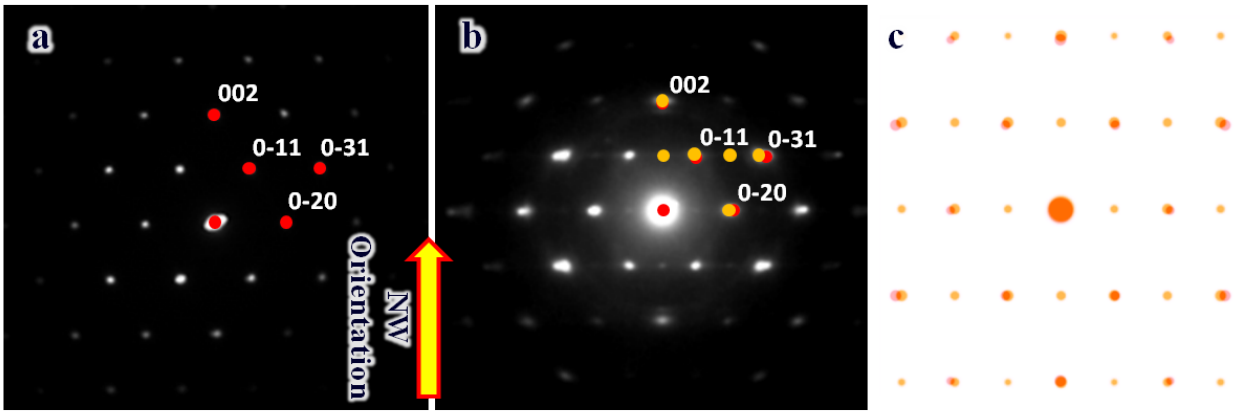

Figure S3. (a and b) Selected area diffraction of a primitive TiO_2 NW (figure S2a) and a Li_xTiO_2 NW (figure S2b) under transition from rutile to intermediate state. Red and orange dots are the representative reciprocal spots for primitive TiO_2 and transformed Li_xTiO_2, respectively. **(c)** Simulated electron diffraction pattern showing phase overlap between rutile TiO_2 and monoclinic Li_xTiO_2.

D. Current-voltage characteristics of Li_xTiO_2 upon electrochemical cycling

Lithiation (during the low-resistance branch of the voltage sweep from 0 to –5V) of the NW (e.g., $TiO_2 + xLi^+ + xe^- \rightarrow Li_xTiO_2$) induces the NW to go through the transition from a low-resistance to a high-resistance state, while the opposite is true for de-lithiation (during the high-resistance branch of the voltage sweep from 0 to 5V), as shown in Figure S4. Li-rich Li_xTiO_2 exhibits Schottky-type semiconductor behavior, while Li-deficient Li_xTiO_2 exhibits close-to-ohmic behavior, as reported in many literature references for other Li intercalation systems.[1] This transition, despite some difference in magnitude in each cycle, repeats throughout the continuous electrochemical cycling at this stage of Li intercalation.

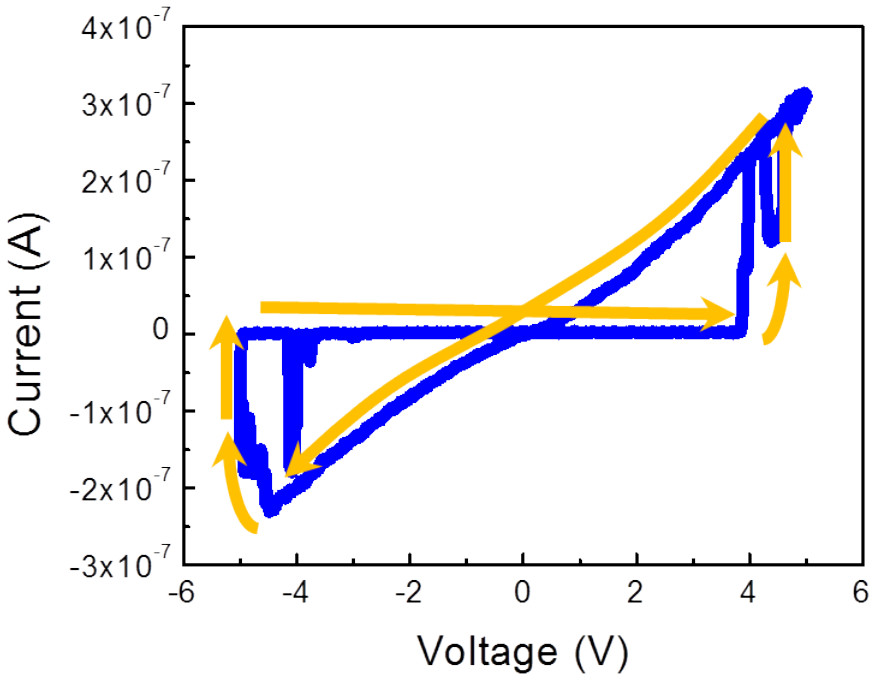

Figure S4. Representative graph showing the lithiation and de-lithiation behavior of the Li_xTiO_2 NW under standard voltage sweep.

1 P. G. Bruce, *Chemical Communications*, 1997, 1817.

3. Supporting Movie Information

Movie S1. An in-situ TEM movie showing the fast lithiation and de-lithiation cycle of a Li_xTiO_2 NW at the monoclinic phase. There is no obvious structural change observed in this intermediate regime.

Movie S2. An anisotropic dilation of TiO2-B upon full lithiation at -4V, showing a bubble-like form of dilation of the Li_xTiO_2 NW