

Supporting Information

A Reversible Phase Transition for Sodium Insertion in Anatase TiO₂

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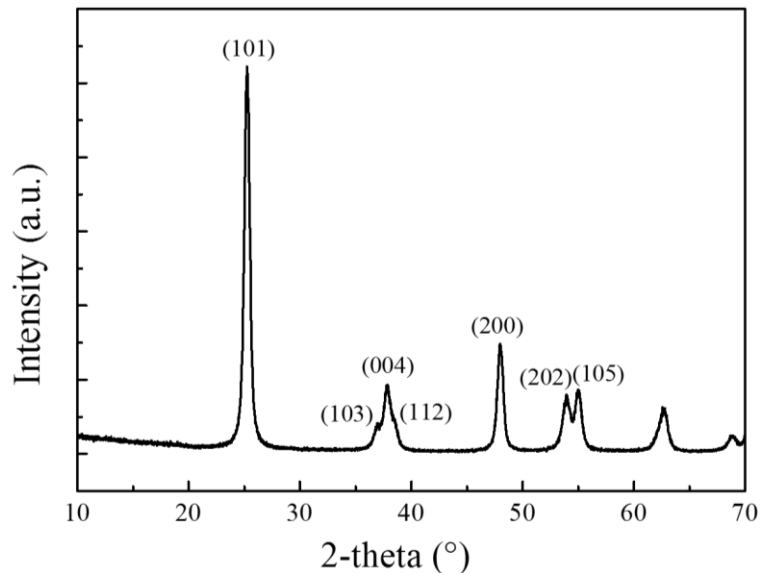


Figure S1. Powder x-ray diffraction pattern of anatase TiO₂.

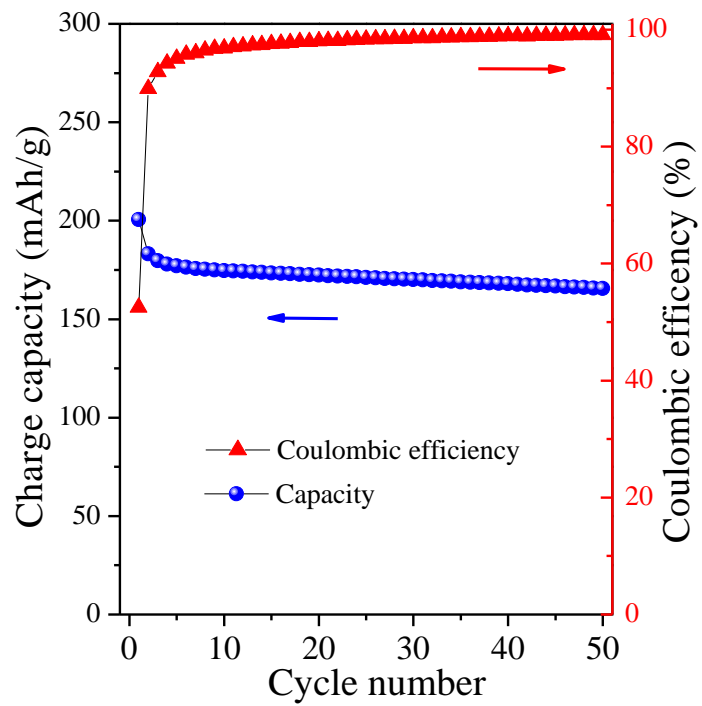


Figure S2. Cycling behavior of anatase TiO_2 upon Na insertion/de-insertion. The capacity obtained after 50 cycles is 165 mAh/g, corresponding to ca. 0.5Na^+ per TiO_2 .

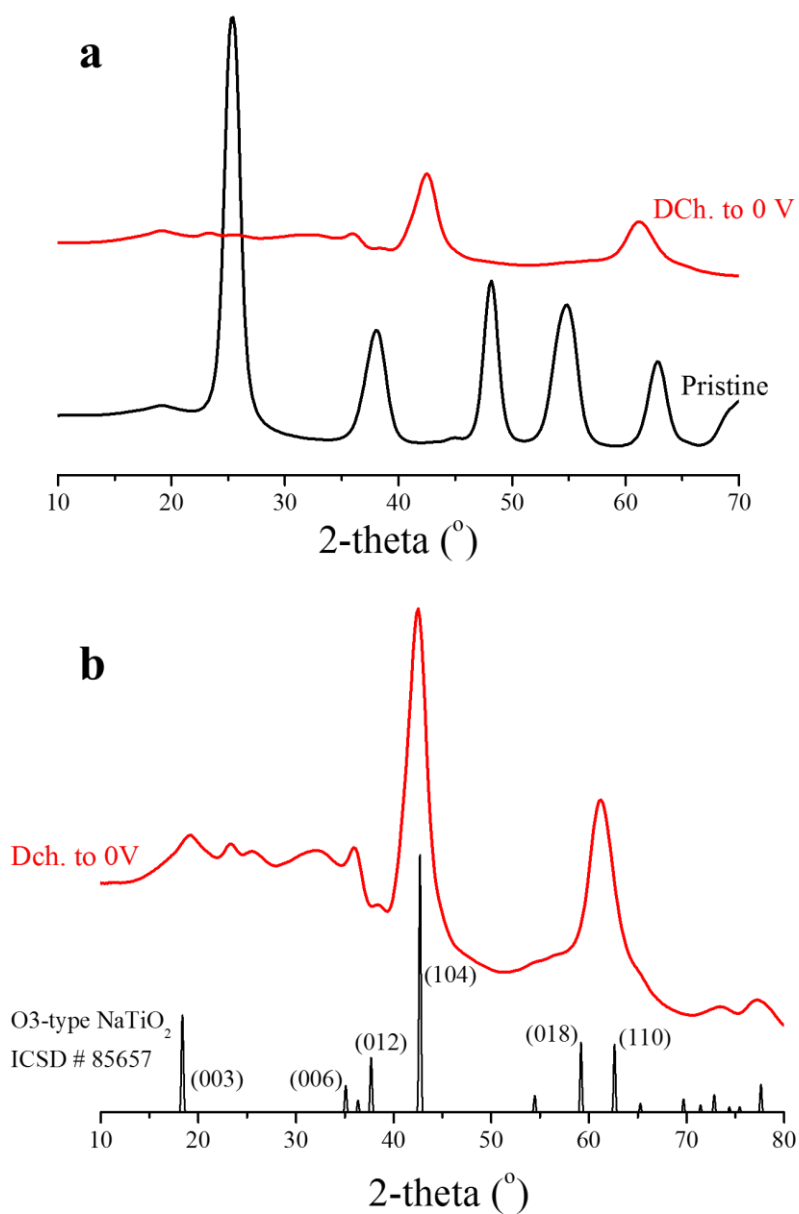


Figure S3.(a) High-energy X-ray diffraction pattern of the pristine and fully discharged TiO₂ electrodes. (b) The X-ray diffraction pattern of the fully discharged electrode was indexed with an O3-type NaTiO₂ rhombohedral structure (space group: R-3m).

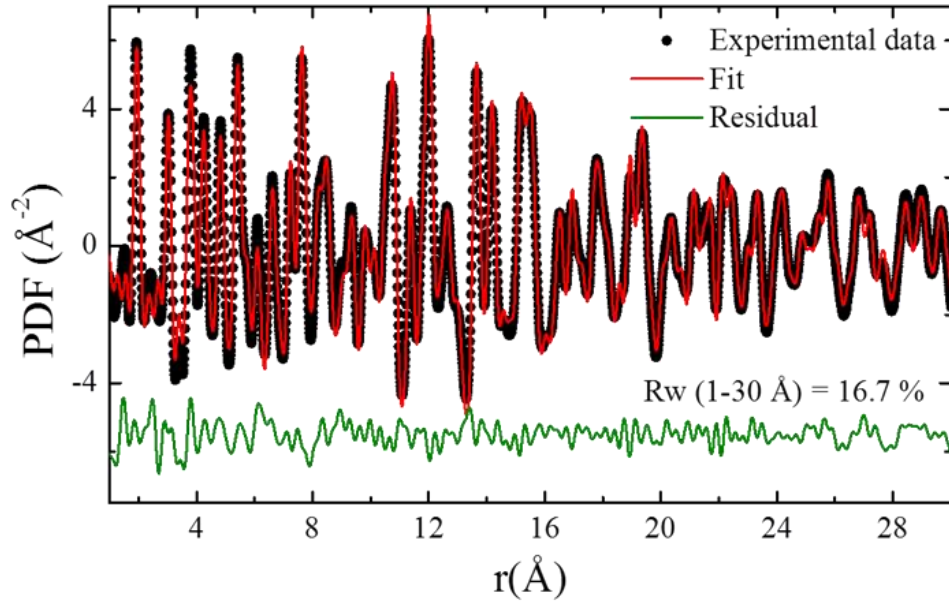


Figure S4. PDF refinement of the electrode discharged to 0.3V, *i.e.* 0.3Na⁺ per TiO₂, using the tetragonal symmetry characteristic of anatase. The refinement of the sodium occupancy in the interstitial site showed that no insertion of sodium occurs suggesting that the region observed prior to the plateau region arises from the decomposition of the electrolyte.

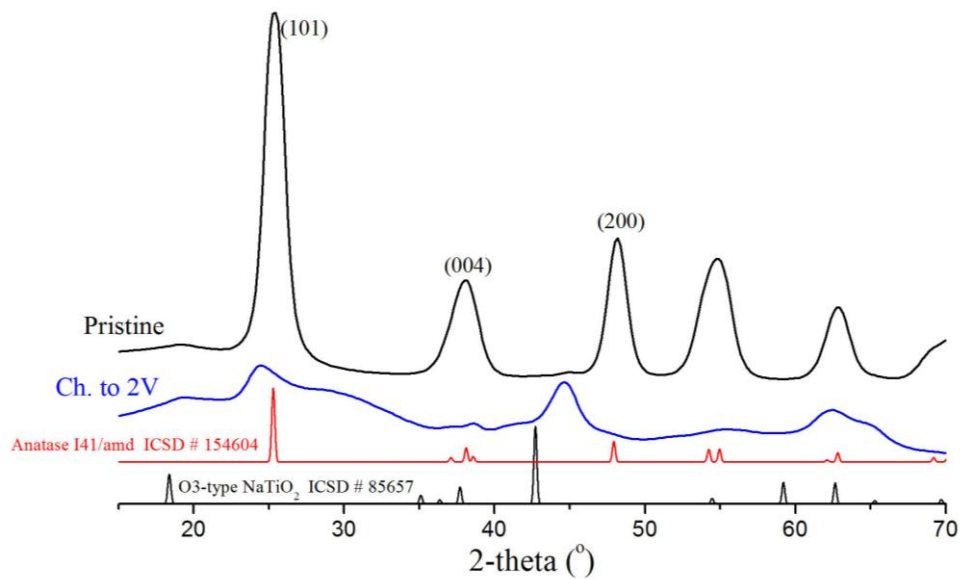


Figure S5. High-energy X-ray diffraction pattern of the fully charged electrode. The peak at 2-theta $\approx 25^\circ$ can be assigned to the (101) of the anatase type structure, indicating the recovery of anatase framework upon charging.

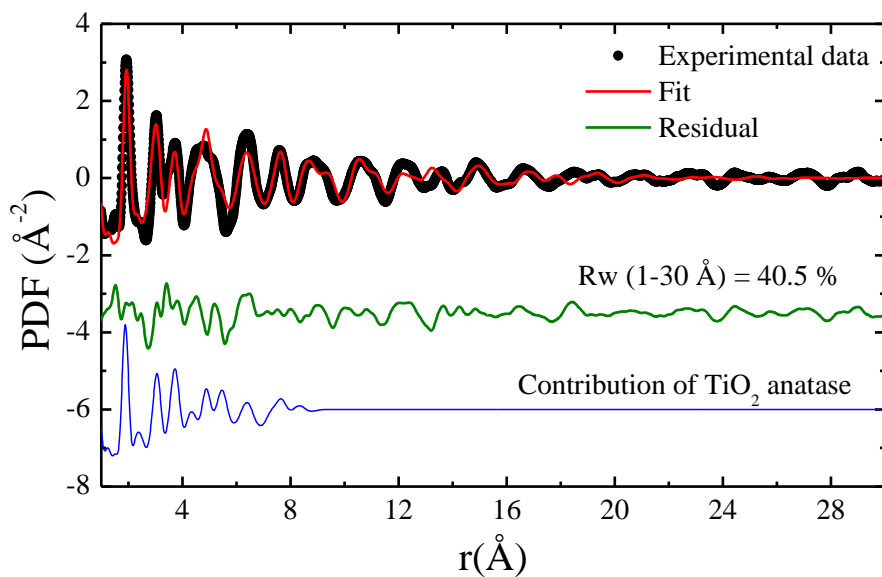


Figure S6. PDF refinement of the electrode charged to 2 V using O3-type NaTiO_2 (space group: R-3m) and TiO_2 (space group: $I4_1/amd$) models. The results show that the desodiated electrode is composed by 20 % O3-type Na_xTiO_2 and 80 % TiO_2 , which agrees with the capacity delivered during the 1st charge. Note that the high value of the Rw is due to strong disorder occurring in Na_xTiO_2 phase.