Supporting Information

A Reversible Phase Transition for Sodium Insertion in Anatase TiO_2

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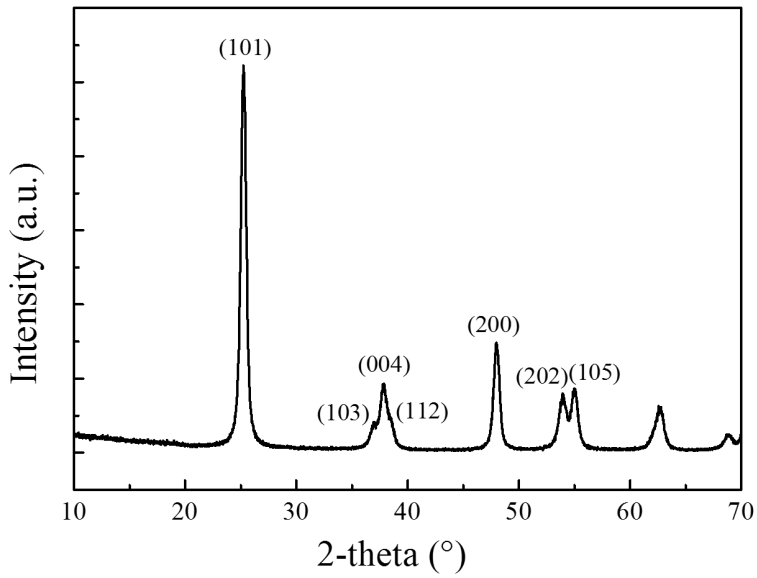

Figure S1. Powder x-ray diffraction pattern of anatase TiO_2.

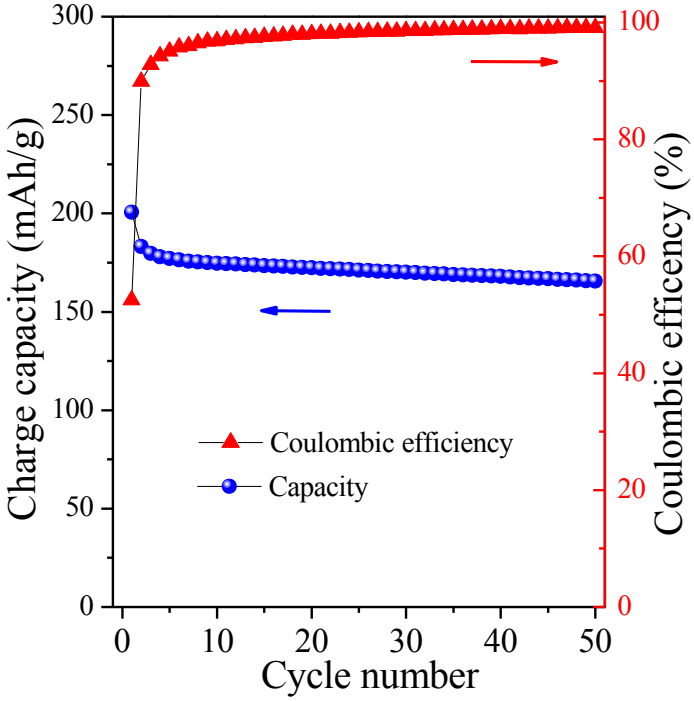

Figure S2. Cycling behavior of anatase TiO_2 upon Na insertion/de-insertion. The capacity obtained after 50 cycles is 165 mAh/g, corresponding to ca. 0.5 Na^+ per TiO_2.

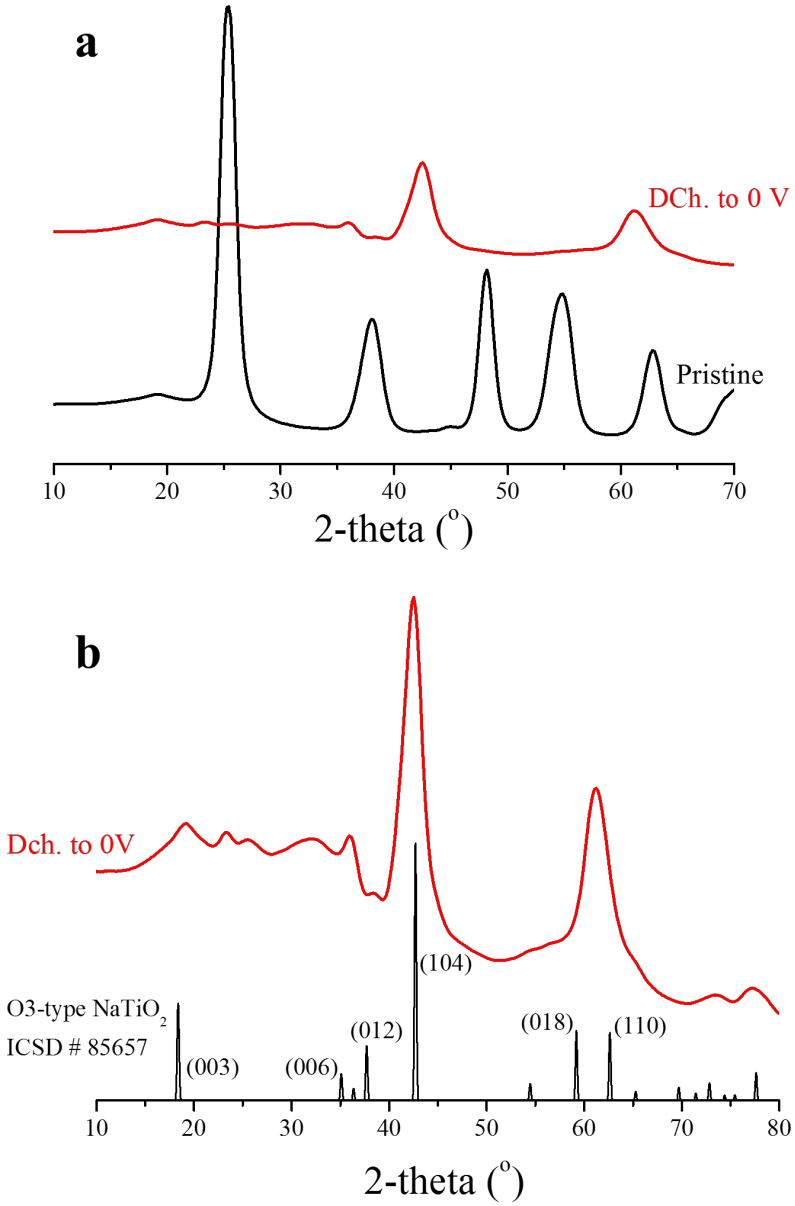

Figure S3. (a) High-energy X-ray diffraction pattern of the pristine and fully discharged TiO_2 electrodes. **(b)** The X-ray diffraction pattern of the fully discharged electrode was indexed with an O3-type $NaTiO_2$ rhombohedral structure (space group: R-3m).

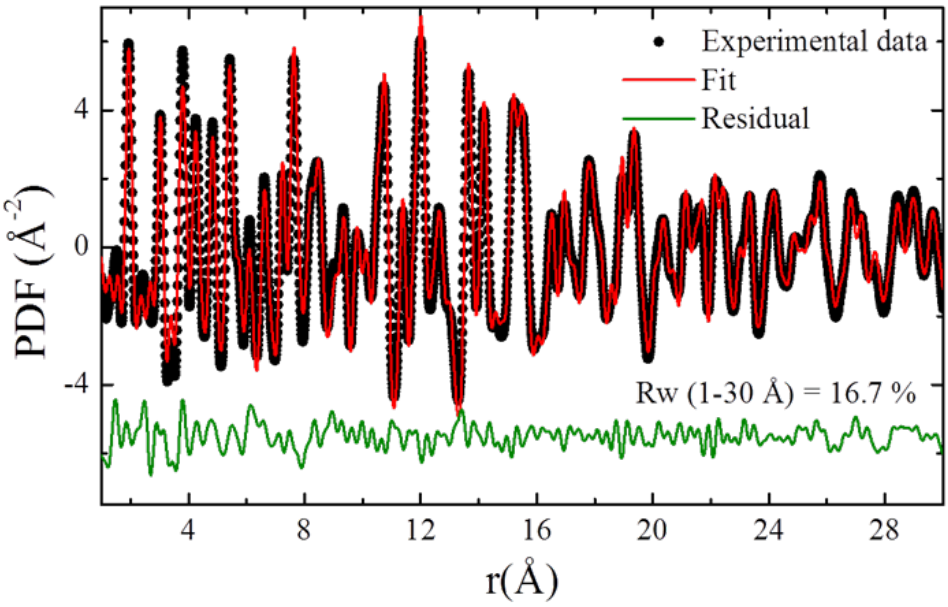

Figure S4. PDF refinement of the TiO_2 electrode discharged to 0.3V, *i.e.* 0.3 Na^+ per TiO_2.

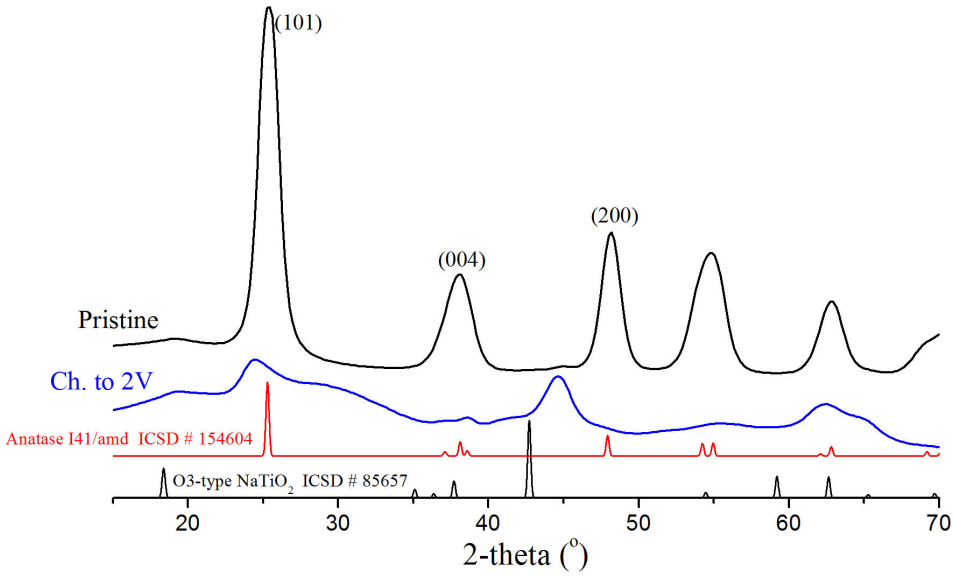

Figure S5. High-energy X-ray diffraction pattern of the fully charged electrode. The peak at 2-theta ≈ 25° can be assigned to the (101) of the anatase type structure, indicating the recovery of anatase framework upon charging.

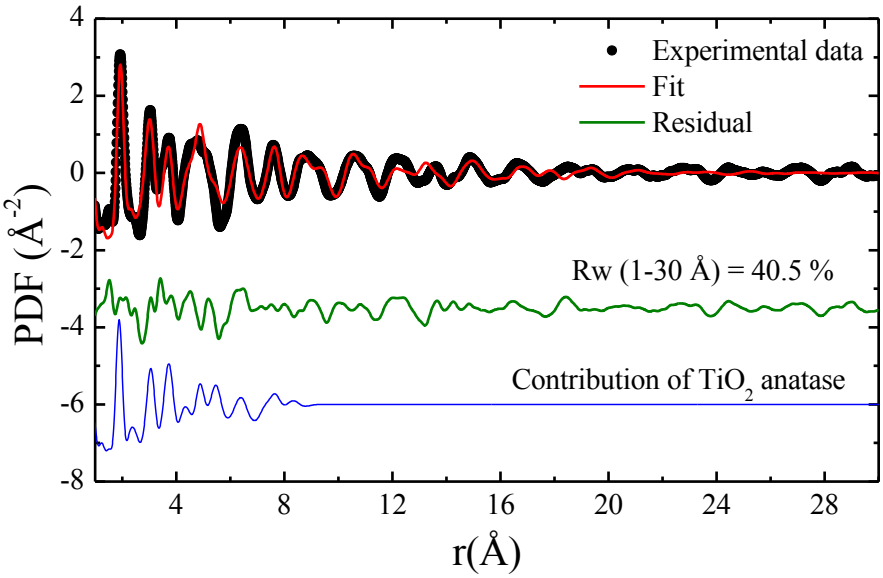

Figure S6. PDF refinement of the electrode charged to 2 V using O3-type $NaTiO_2$ (space group: R-3m) and TiO_2 (space group: $I4_1/amd$) models. The results show that the de-sodiated electrode is composed by 20 % O3-type Na_xTiO_2 and 80 % TiO_2, which agrees with the capacity delivered during the 1st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