

Supporting Information

Black Titanium Oxide Nanoarray Electrodes for High Rate Li-ion Microbatteries

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Experimental Procedure

Material preparation and characterization: A commercially pure titanium sample (0.05-mm thick foil, 99.5% purity, Niraco, Japan) was degreased with acetone and then rinsed with deionized water and dried in a nitrogen stream. The electrochemical cell for anodization of Ti consisted of a specimen with an area of 1 cm² as a working electrode and platinum as a counter electrode in a two-electrode system. Electrochemical anodization experiments were conducted at a constant potential with a DC power supply. The time variable current was monitored using a digital multimeter (Model 34401A, Agilent Technologies, Inc.) interfaced with a computer. The electrolytes were 0.05 wt% NH₄F in ethylene glycol (99.8%, anhydrous). All the tests were performed at ambient temperature (22 ± 2 °C). The as-prepared TiO₂ nanotubes were thoroughly washed with ethanol and deionized (DI) water and then dried at 80 °C in a drying oven overnight. Black TiO₂ NTs were obtained by subsequent thermal treatment of the as-prepared TiO₂ NTs in a hydrogen atmosphere at 450 °C for 2 h. Thermal treatment was performed in a quartz tube furnace filled with ultrahigh purity hydrogen gas. For comparison purposes, anatase TiO₂ NTs were also prepared by thermal treatment of the as-prepared samples at 450 °C for 2 h in air. The morphological evolution of the TiO₂ NTs prepared in different atmospheres was observed by scanning electron microscopy (SEM, Philips, XL 30 SFEG). Cross-sectional

measurements of the samples were performed on mechanically bent samples in which cracking and partial lift-off of the porous layer occurs. The crystal structures of the samples were analyzed by X-ray diffraction (XRD, Rigaku, D/MAX-IIIC). The Ti 2p and O 1s core binding energies of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Thermo, MultiLab 2000).

Cell fabrication and electrochemical analysis: The Li/TiO₂ NTs cells were assembled in a 2016 coin-type cell configuration in an argon-filled glove box. A polypropylene separator soaked with a liquid electrolyte (Panax Etec[®]) of 1 M LiPF₆ dissolved in a 1:1:1 volume ratio of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) was placed between the electrode and Li metal foil in the cell. The cells were galvanostatically charged and discharged using a battery cycler (WBCS3000, Won-A Tech[®]) between 1.0 and 3.0 V (vs. Li/Li⁺) at various currents. All of the potentials refer to Li/Li⁺. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a FRA2 and PGSTAT20 system (Autolab[®]) over the frequency range 100 kHz to 0.01 Hz.

[Supporting information 1]

We conducted TEM analysis to further confirm morphological features of the anatase TiO_2 NT and black TiO_{2-x} NT electrodes (Figure S1). Both cross-sectional morphologies are almost similar without significant change and the diameter of the both NTs was about 50 nm, which is consistent with SEM observations. This result indicates that there was negligible effect of morphology change after calcination in different atmospheres.

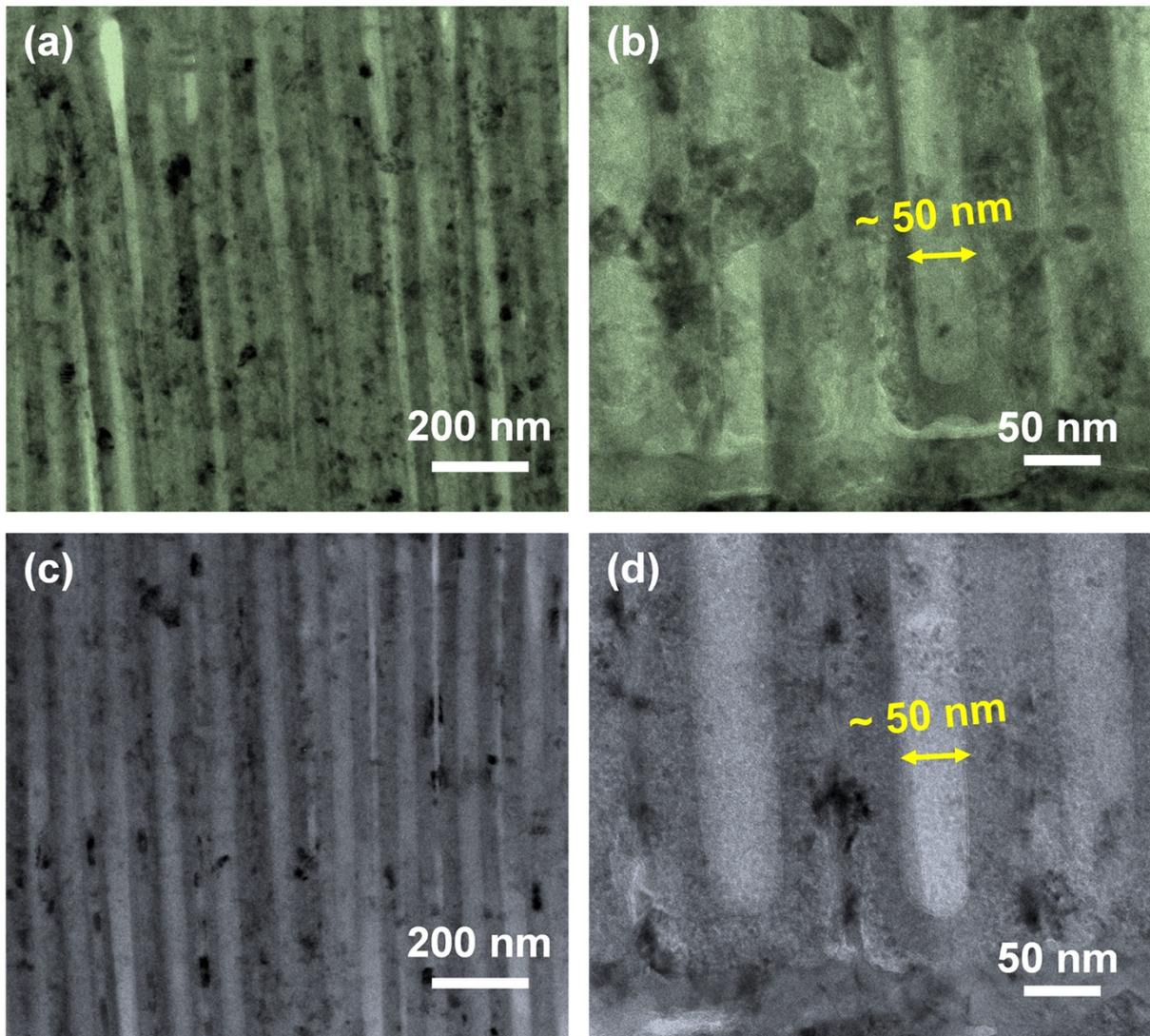


Figure S1. TEM cross-sectional morphologies of (a,b) anatase TiO_2 NTs and (c,d) black TiO_{2-x} NTs with different magnifications. Both cross-sectional morphologies obtained by TEM are almost similar without significant change and the diameter of the both NTs was about 50 nm.

[Supporting information 2]

The capacity value of black TiO_{2-x} NT electrode (0.129 mAh/cm² of initial capacity at 0.1 mA/cm², 0.101 mAh/cm² of initial capacity at 1 mA/cm²) was much higher than that of anatase TiO_2 NT electrode (0.112 mAh/cm² of initial capacity at 0.1 mA/cm², 0.078 mAh/cm² of initial capacity at 1 mA/cm²) as shown in Figure S2. At low current density of 0.1 mA cm⁻², the anatase TiO_2 NTs and black TiO_{2-x} NTs showed very stable and similar cycling retention (~99 %) after 100 cycles (Figure S2a). On the other hand, at the 100-fold higher current density of 1 mA cm⁻², the black TiO_{2-x} NTs exhibited much higher capacity than the anatase TiO_2 NTs compared with their initial discharge capacity after 300 cycles (Figure S2b).

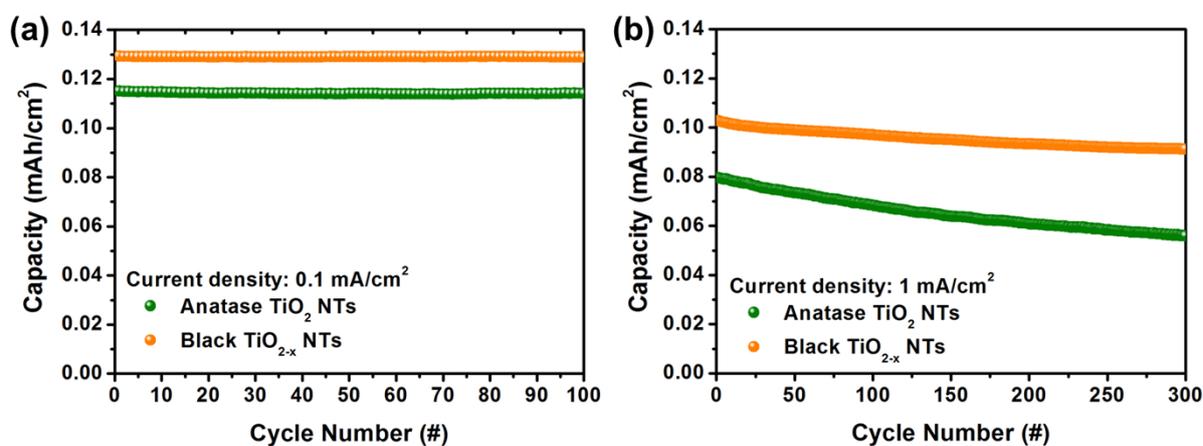


Figure S2. Cycling performance of the A- TiO_2 NTs and H- TiO_2 NTs at a current density of (a) 0.1 mA cm⁻² for 100 cycles, and (b) at 1 mA cm⁻² for 300 cycles. The cycle data were collected after 10 cycles. All electrochemical cycling experiments were performed over a voltage window between 1.0 and 3.0 V.

[Supporting information 3]

The donor density of reduced TiO_2 nanostructures proportional to electrical conductivity is significantly improved by the formation of oxygen vacancy/ Ti^{3+} sites and consequently relatively narrower bandgap of approximately 2.2 eV was found for black TiO_{2-x} NT structure. UV-vis absorption spectra for both NT electrodes were shown in Figure S3 to further verify the electronic structure of the black TiO_{2-x} NT structure. TiO_2 phase has no absorption band in visible range and shows the characteristic spectrum with its fundamental absorption of Ti–O bond in ultraviolet range from 350 to 400 nm. The sudden decrease in absorption band near 350 nm was found for anatase TiO_2 NTs. On the other hands, the black TiO_{2-x} NT sample showed a much stronger photoabsorption in the range of wavelengths from 400 to 700 nm, indicating low bandgap of black TiO_{2-x} structure resulted from the formation of oxygen vacancy/ Ti^{3+} sites.

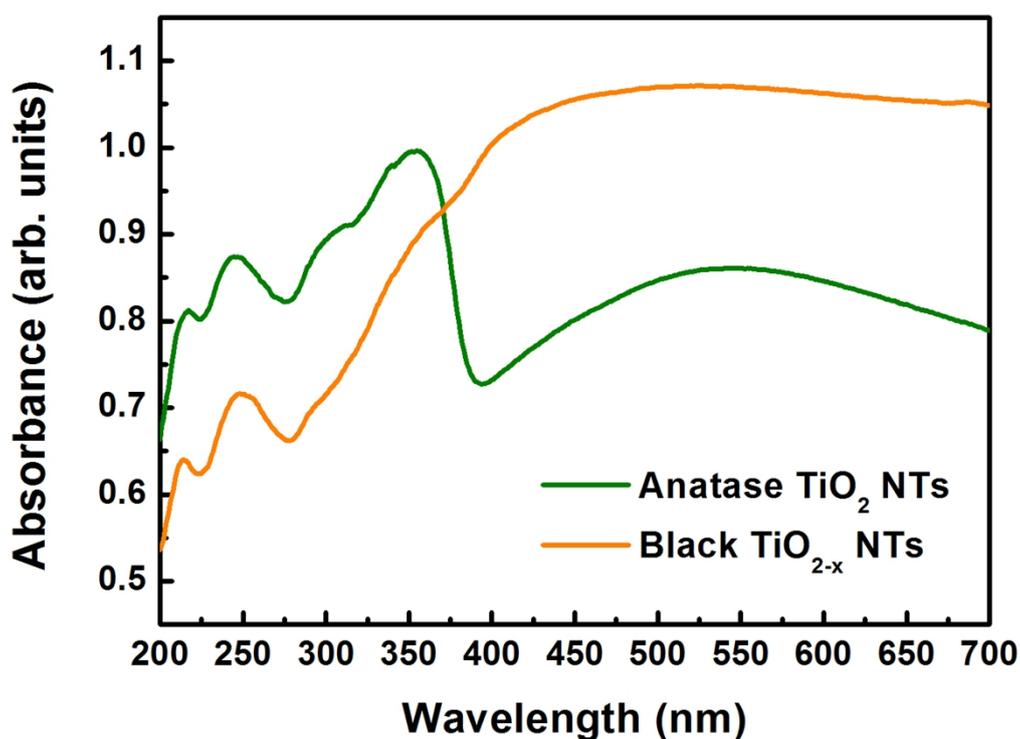


Figure S3. UV-vis absorption spectra of the anatase TiO_2 NTs and black TiO_{2-x} NTs.