Electronic Supplementary information

Sn-doped TiO_2 nanotube as a superior anode material for sodium ion battery †

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Experimental Section

Preparation

Sn-doped TiO_2 nanotubes (STNTs) were synthesized through sol-gel method and subsequent hydrothermal process. Firstly, 5 ml of titanium butoxide (TBT, 99.9%, Aladdin, Shanghai) was added dropwise into ethanol to get the TBT solution. Meanwhile, a certain amount of $SnCl_4 \cdot 5H_2O$ (99.9%, Aladdin, Shanghai) was added to the acetylacetone-ethanol mixture under magnetic stirring. Then, the obtained solution was slowly dropped into the TBT solution under constant stirring to get the sol. After aged for 48 h, the gel was dried at 70 °C, and then calcined at 400 °C for 2 h in air. Secondly, the obtained powders were mixed with 10 mol l^{-1} NaOH aqueous solution in a Telflon autoclave and experienced a subsequent hydrothermal reaction at

120 °C for 24 h. After cooled to room temperature, the product was isolated by centrifugation and rinsed for several times, and then dried at 70 °C under vacuum overnight. The powders were finally annealed at 400 °C for 2 h in an Ar gas atmosphere. Pristine TiO_2 nanotubes (TNTs) were also prepared for comparison according to similar procedure without the use of $SnCl_4 \cdot 5H_2O$.

Characterizations

The crystalline phase of the samples was characterized by X-ray diffraction (DX-2700, Fangyuan) measurement using Cu Kα radiation with λ=1.54145 Å. Raman spectra were recorded on a Raman Spectrometer (RM-1000, Renishaw) with 632.8 nm He-Ne laser as irradiation source. The X-ray photoelectron spectroscopy analysis (XPS) was carried out on Kratos Axis Ultra using a monochromatic Al Kα radiation and the binding energies were calibrated with that of C1s at 284.8 eV as the reference. The morphology of the samples was characterized by field-emission scanning electron microscopy (SEM, JSM-7001F, JEOL) and high resolution transmittance electron microscopy (HRTEM, JEM-2010, JEOL). Element mapping was collected on energy dispersive X-ray spectroscopy (EDS, Oxford, 6498) attached to HRTEM to determine the element distribution. The specific surface area was evaluated with a BELSORP-mini surface analyzer (V-Sorb2800, Beijing, Gold App) based on the Brunauer-Emmett-Teller multipoint method. Electrical conductivity of the samples after 50 charge/discharge cycles was measured using Hall effect measurement system (HMS-300, Ecopia).

Electrochemical measurements

For electrochemical testing, the samples, Super-P carbon black and polyvinyldiuoride were mixed in N-methylpyrrolidone solvent with weight ratio of 70:15:15 to form a homogenously slurry and coated on a copper foil followed by

drying at 120 °C overnight in vacuum oven. Coin type cells (CR2032) were assembled in a glove box (MB-10-compact, MBRAUN) under Ar atmosphere, with oxygen and water contents less than 0.5 ppm, where sodium metal foil and Whatman glass fiber membrane were used as the counter electrode and separator, respectively. The electrolyte was 1 M $NaClO_4$ solution in ethylene carbonate and propylene carbonate (1:1, w/w) with the addition of 5 % fluoroethylene carbonate. Galvanostatic charge-discharge test was conducted on a LAND2001A battery test system in a voltage range of 0.005-3 V at a current density of 50 mA g^{-1} unless otherwise specified. Cyclic voltammetry was performed using an electrochemical workstation (AUTOLAB PGSTAT302N) in a voltage range of 0.005-3 V at a scan rate of 0.2 mV s^{-1} at room temperature. Electrochemical impedance spectroscopy measurement was carried out on the same electrochemical workstation in a frequency range of 0.01 Hz to 100 kHz, and the applied bias voltage and ac amplitude were set at the open circuit voltage of the cells and 5 mV, respectively.

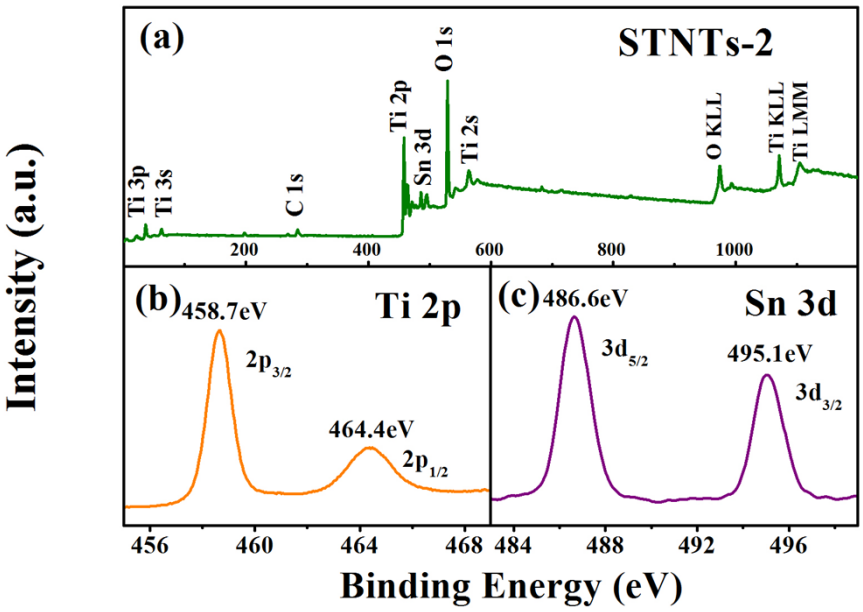

Fig. S1 XPS survey (a), Ti 2p (b) and Sn 3d (c) for STNTs-2.

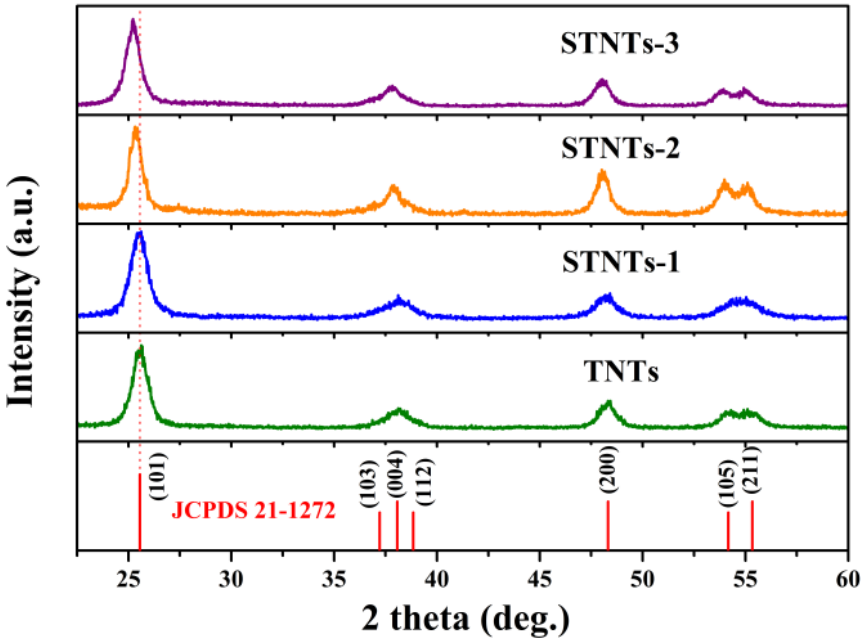

Fig. S2 XRD profiles of TNTs and STNTs.

Table S1 The lattice parameters calculated from XRD.

Samples	a(Å)	b(Å)	c(Å)
TNTs	3.754(6)	3.754(6)	9.255(7)
STNTs-1	3.767(3)	3.767(3)	9.266(4)
STNTs-2	3.776(1)	3.776(1)	9.277(8)
STNTs-3	3.788(3)	3.788(3)	9.280(4)

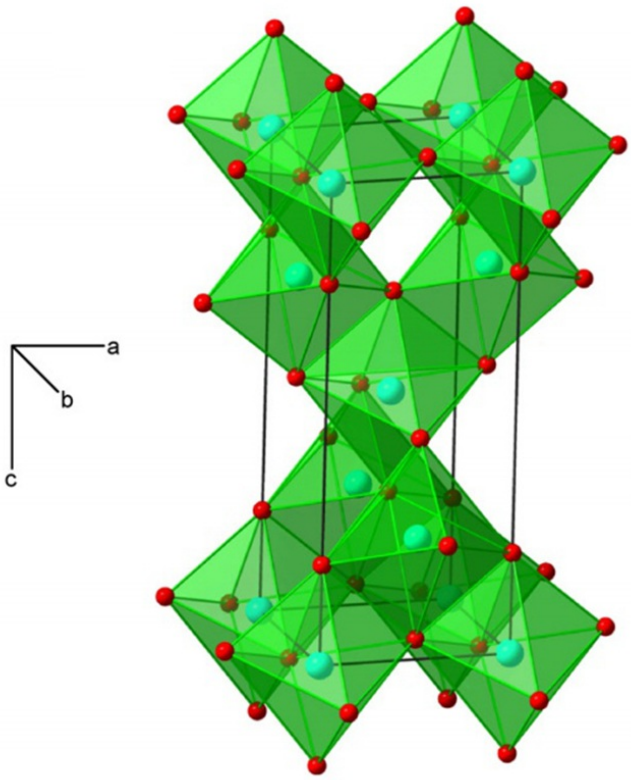

Fig. S3 Crystal structure of anatase TiO_2. Blue and red spheres are Ti and O atoms respectively.[1]

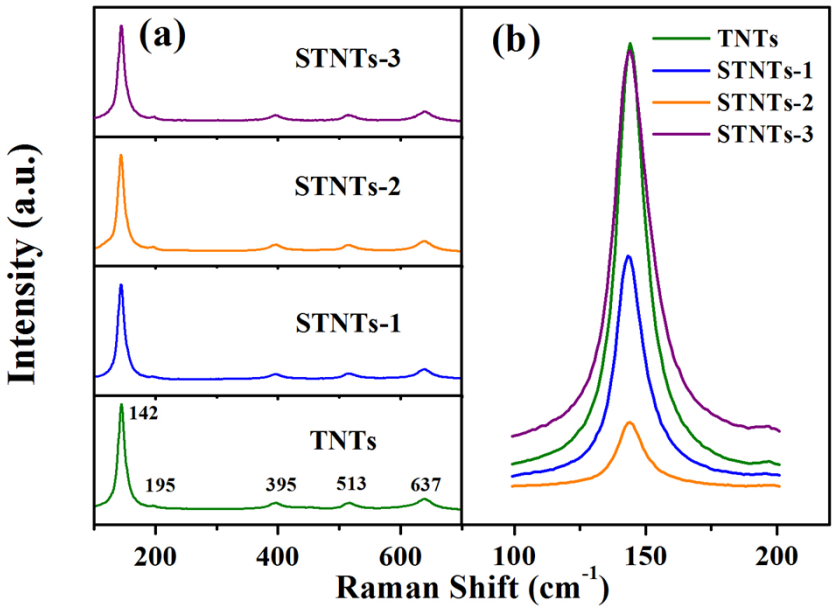

Fig. S4 Raman spectra of TNTs and STNTs (a) and partial enlarged view near 142 cm^{-1} (b).

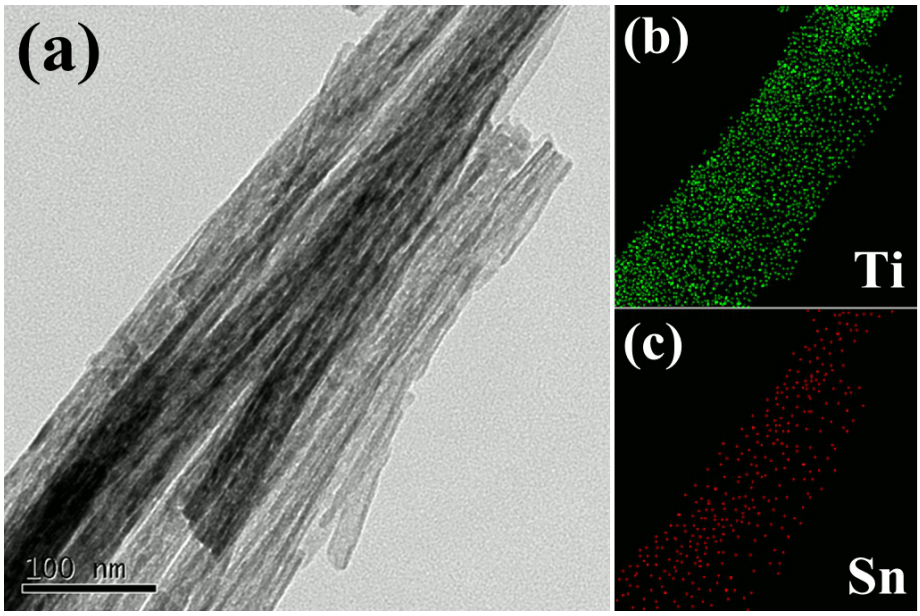

Fig. S5 HRTEM image of STNTs-2 (a) and corresponding EDS mapping images of Ti (b) and Sn (c).

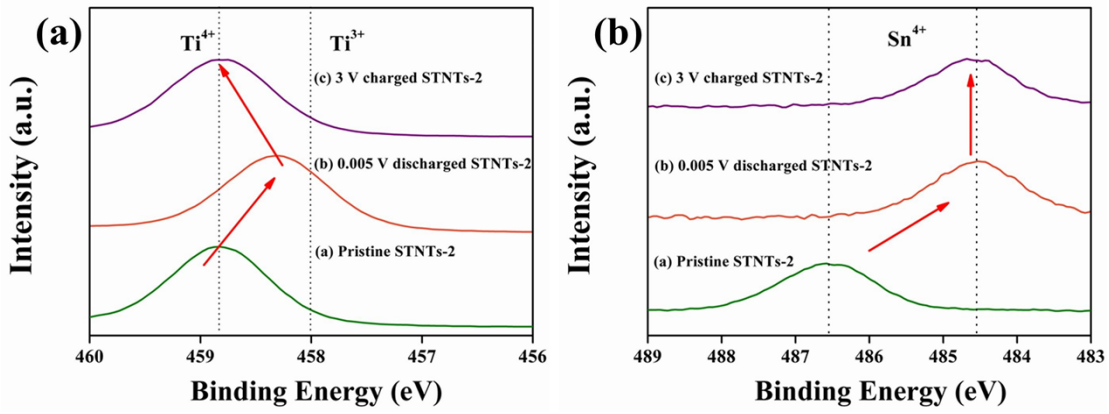

Fig. S6 Ex-situ XPS survey of Ti 2p (a) and Sn 3d (b) for STNTs-2 at fully discharged and charged state at 20th cycle.

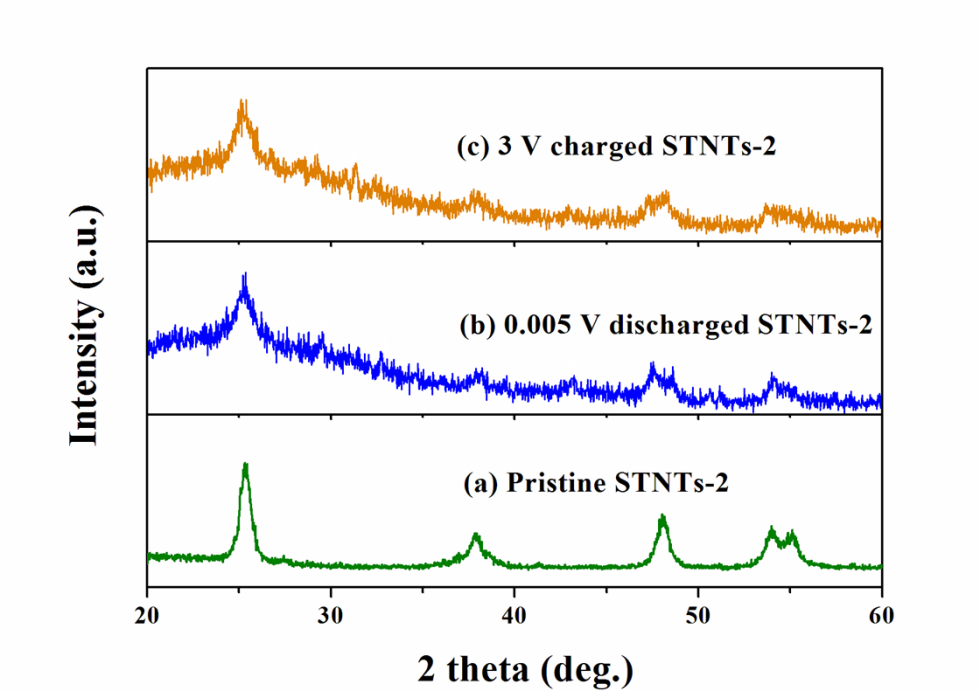

Fig. S7 Ex-situ XRD profiles of pristine (a) fully discharged (b) and charged state (c) of STNTs-2 at 20th cycle.

Table S2 The lattice parameters calculated from ex-situ XRD in Fig. S7.

Samples	a(Å)	b(Å)	c(Å)
STNTs-2	3.776(1)	3.776(1)	9.277(8)
20^{th} discharged state	3.818(4)	3.818(4)	9.301(1)
20^{th} charged state	3.778(5)	3.778(5)	9.280(3)

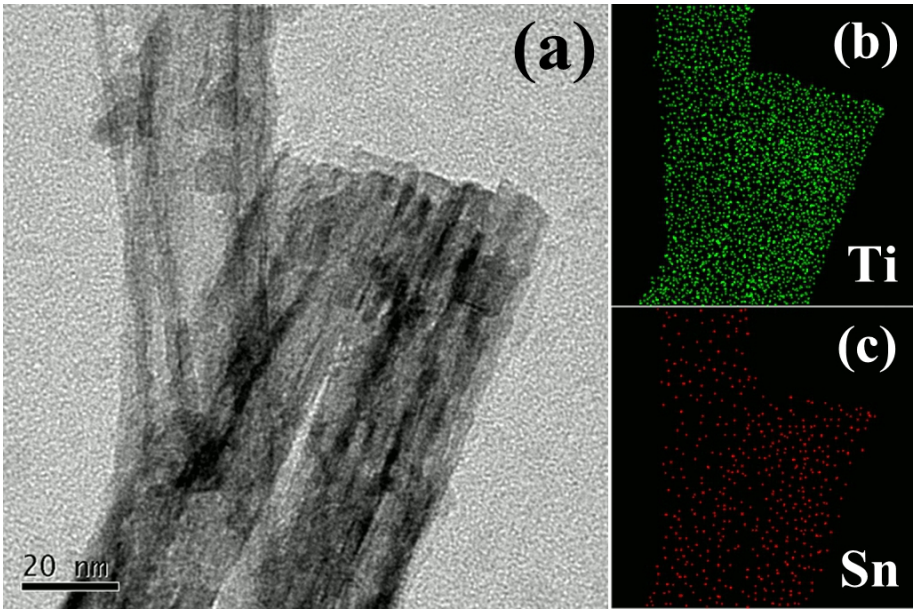

Fig. S8 HRTEM image of STNTs-2 after 50 galvanostatic charge/discharge cycles at a current density of 2.5 A g^{-1} (a) and corresponding EDS mapping images of Ti (b) and Sn (c).

Reference

1. Z. G. Yang, D. Choi, S. Kerisit, K. M. Rosso, D. H. Wang, J. Zhang, G. Graff, J. Liu, *J. Power Sources*, 2009, **192**, 588.