

Supporting information

Spider web-like architecture assembled from Na₂Ti₃O₇ nanotubes as high performance anode for Sodium-ion battery

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1. Experimental section

1.1 Electrode preparation

The spider web-like Na₂Ti₃O₇ structure was assembled from Na₂Ti₃O₇ nanotubes, which were synthesized by alkaline treatment of Ti flake in a diluted sodium hydroxide solution. In a typical preparation, a piece of titanium foil (1 cm × 2 cm × 0.3 mm) was ultrasonically cleaned in acetone, ethanol and water for half an hour, respectively, and then placed against the inner wall inside a 40 mL Teflon-lined stainless steel autoclave, which was filled with 10 mL 1 M sodium hydroxide solution. The autoclave was sealed and kept at 220 °C for 16 h. After the hydrothermal growth, the autoclave was cooled down to room temperature, and the Ti plate was taken out, rinsed with flow distilled water for 2 minutes and dried at 60 °C for 8 hours. Then, the as prepared sample had been calcined at 300 °C under Ar atmosphere for 4 hours. Finally, the spider web-like Na₂Ti₃O₇ architecture assembled from Na₂Ti₃O₇ nanotubes on the Ti substrate was obtained.

1.2 Materials Characterization

The crystal structure of the as obtained product was characterized by X-ray powder diffraction (XRD) using a Shimadzu X-Lab6000 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5416 \text{ \AA}$). The morphology of the spider web-like Na₂Ti₃O₇ structure was studied by a JEOL JSM-7001F field emission scanning electron microscope (FESEM). The elemental composition of as-prepared samples was analyzed by a JEOL JSM-7500F cold-field emission scanning electron microscope

(CFESEM) and its affiliated energy dispersive X-ray diffraction spectroscopy (EDS). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a JEOL JEM-2100F microscope.

XAFS measurements were carried out at beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF) using a ring current of 150-250 mA at the energy of 2.5 GeV within 8 hours. XAFS spectra of Ti foil was recorded on transmission mode, and the others were recorded on fluorescence mode with an 45° angle. During the measurements, all battery electrode of initial, charged or discharged NTO electrode were clamped down on an aluminium sample holder. Before the test, the charged or discharged NTO electrode were disassembled from fresh cells in an Ar-filled glove box, then the NTO electrode was wash with ethylene carbonate several times and dried using a hair drier.

1.3 Electrochemical Measurement

Electrochemical experiments were performed by using coin cells (CR 2032). Before assembly, the electrode was put into vacuum drying oven at 120 °C for 24 hours. One side of the spider web-like $\text{Na}_2\text{Ti}_3\text{O}_7$ structures was scraped off by doctor blade so as to expose the Ti substrate as current collector. The as prepared Ti flake was cut into two pieces with dimension of 1 cm in length and 1 cm in width, one piece was used to calculated the mass of active material on Ti substrate, and the other was used to assembly for sodium cell. Then, it was used as the working electrode. Sodium metal acted as the counter electrode. The electrolyte was prepared by dissolving 1.0 M NaClO_4 in ethylene carbonate/dimethyl carbonate (EC/DMC=1:1). Glass fibers (GF/D) from Whatman were used as separators, and the cells were assembled in an Ar-filled glove box. Charge–discharge measurements were carried out on CT2001A Land battery testing systems (Jinnuo Electronics Co. Ltd., China) at different current densities in a potential range of 0.01-2.5 V vs. Na/Na^+ . The fresh cells used for XAFS measurement were charged/discharged at a current density of 20 mA g^{-1} at different potential points. Cyclic voltammetry (CV) curves were collected on a CHI660D electrochemical workstation at 0.1, 0.5 and 1 mVs^{-1} within the range of 0.005-2.5 V. Electrochemical impedance spectroscopy (EIS) was performed on the CHI660D electrochemical workstation at an open circuit voltage, with an AC voltage of 5 mV, and in the frequency range of 100 kHz to 0.01 Hz.

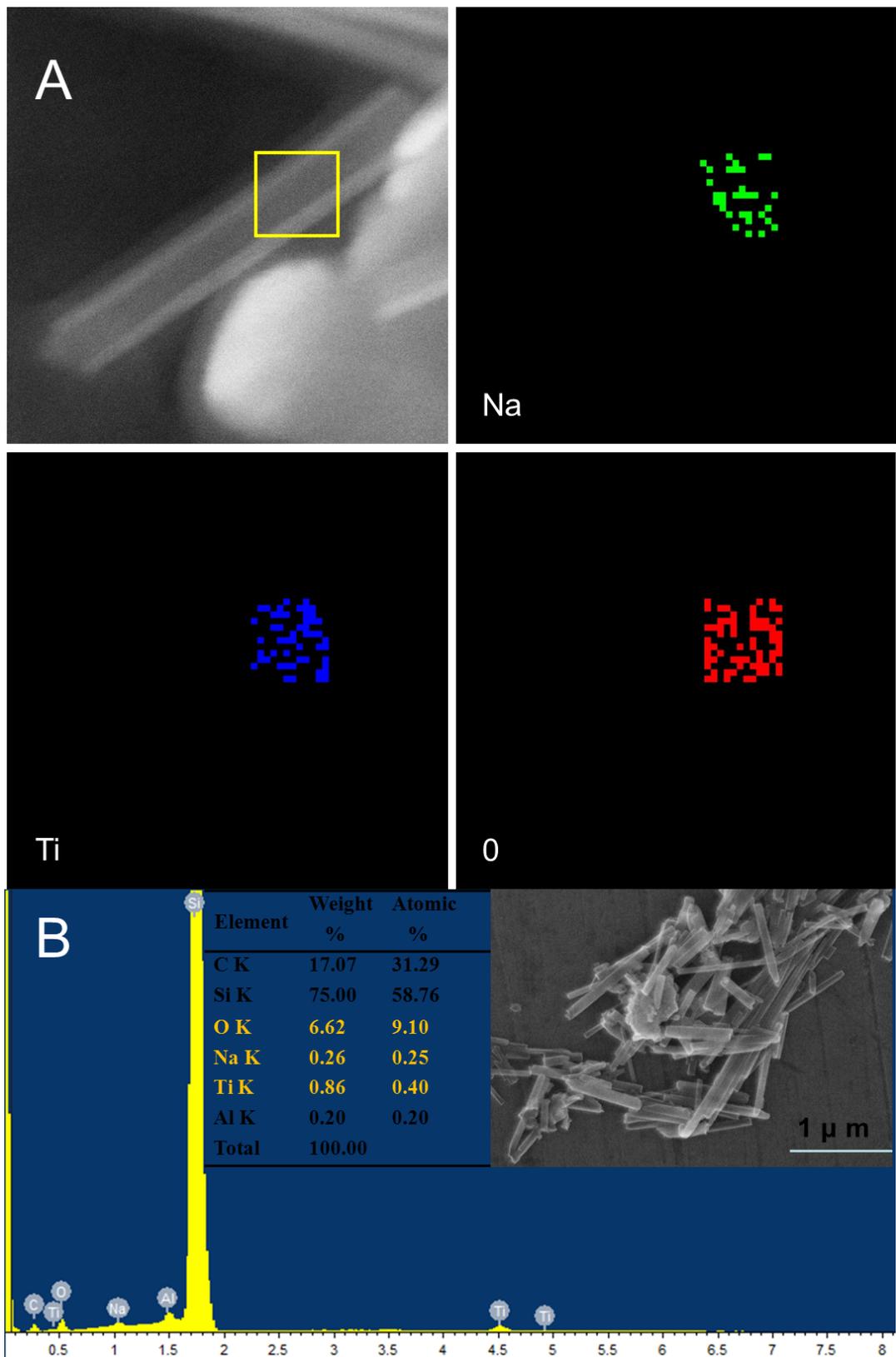


Figure S1. A) EDX mapping images of Na, Ti and O in the yellow square region. B) EDX spectrum of the $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes (inset is an SEM image). The chemical composition and respective atomic percentage of as prepared NTO nanotube was analyzed by EDX, as shown in Fig. S1, the EDX mapping image of Ti, Na and O are

shown in Fig. S1A, this is a qualitative analysis for chemical composition determination of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotube, moreover, the chemical composition of the as prepared $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotube can be further quantitative analyzed by EDS, as shown in Fig. S1B, the atomic ration of Na:Ti is calculated to be approaching 2:3, which is mostly matched with stoichiometric ratio of Na and Ti in $\text{Na}_2\text{Ti}_3\text{O}_7$, the elements Al and Si are come from the substrate of Al and Si used in the measurement, and the C element should be derived from the pollution of electrically conductive adhesive, which was used for binding the Si substrate and Al platform in EDS test.

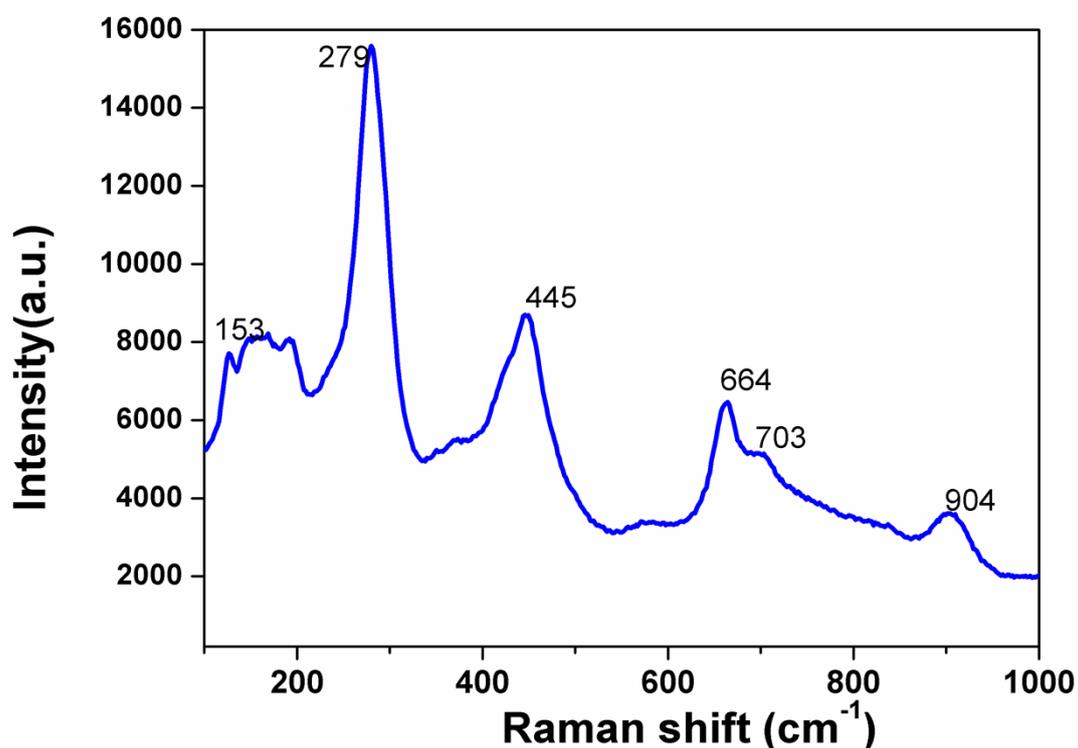


Fig. S2 Raman spectra of nanotube $\text{Na}_2\text{Ti}_3\text{O}_7$. The Raman band at about 277, 445, 664 and 904 cm^{-1} feature of sodium tirtianate nanostructure, the 445 cm^{-1} peak can be assigned to pure framework of Ti-O-Ti vibration. The Raman bands at 277, 445 and 664 cm^{-1} can be ascribed to Na-O-Ti stretching, while the broad peak at 153 and 904 cm^{-1} is assigned to the symmetric stretch of short Ti-O bonds involving nonbridging oxygen coordinated with sodium ions. The peak at 703 cm^{-1} , representing the Ti-O-Ti stretching in edge shared TiO_6 .^[1-3]

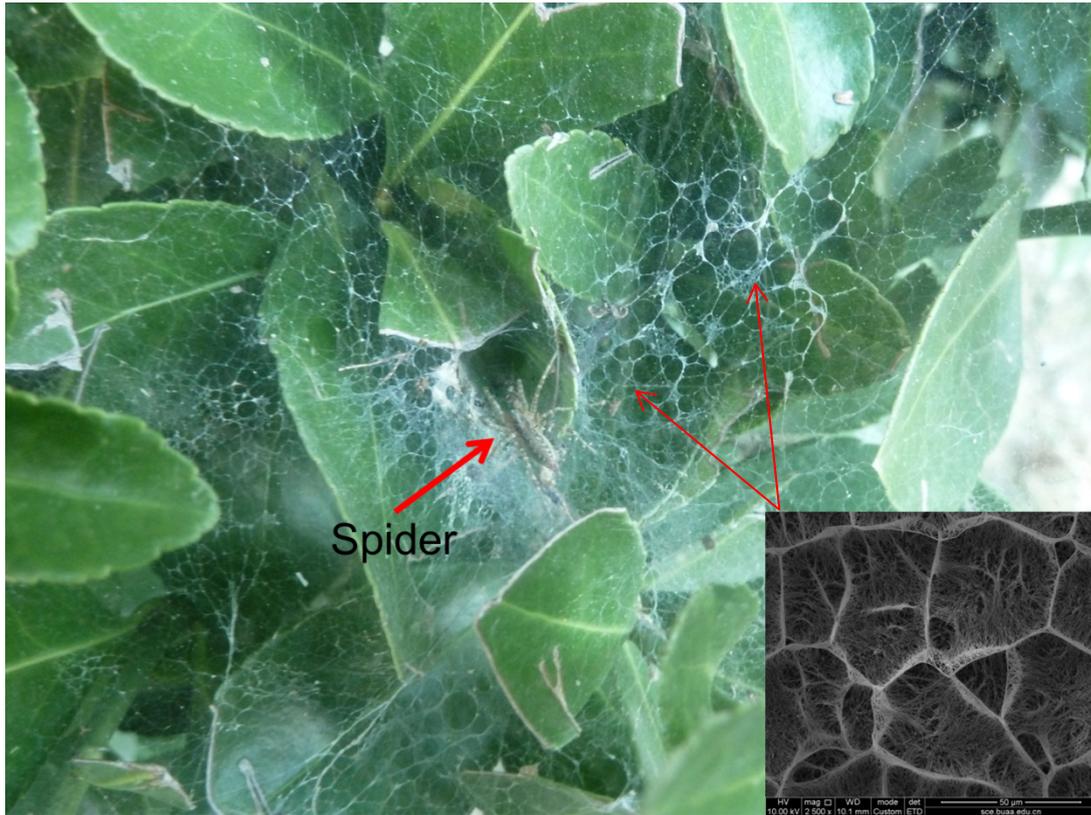


Fig. S3 Photograph of spider web, inset is SEM image of spider web-like $\text{Na}_2\text{Ti}_3\text{O}_7$ nanoarchitecture.

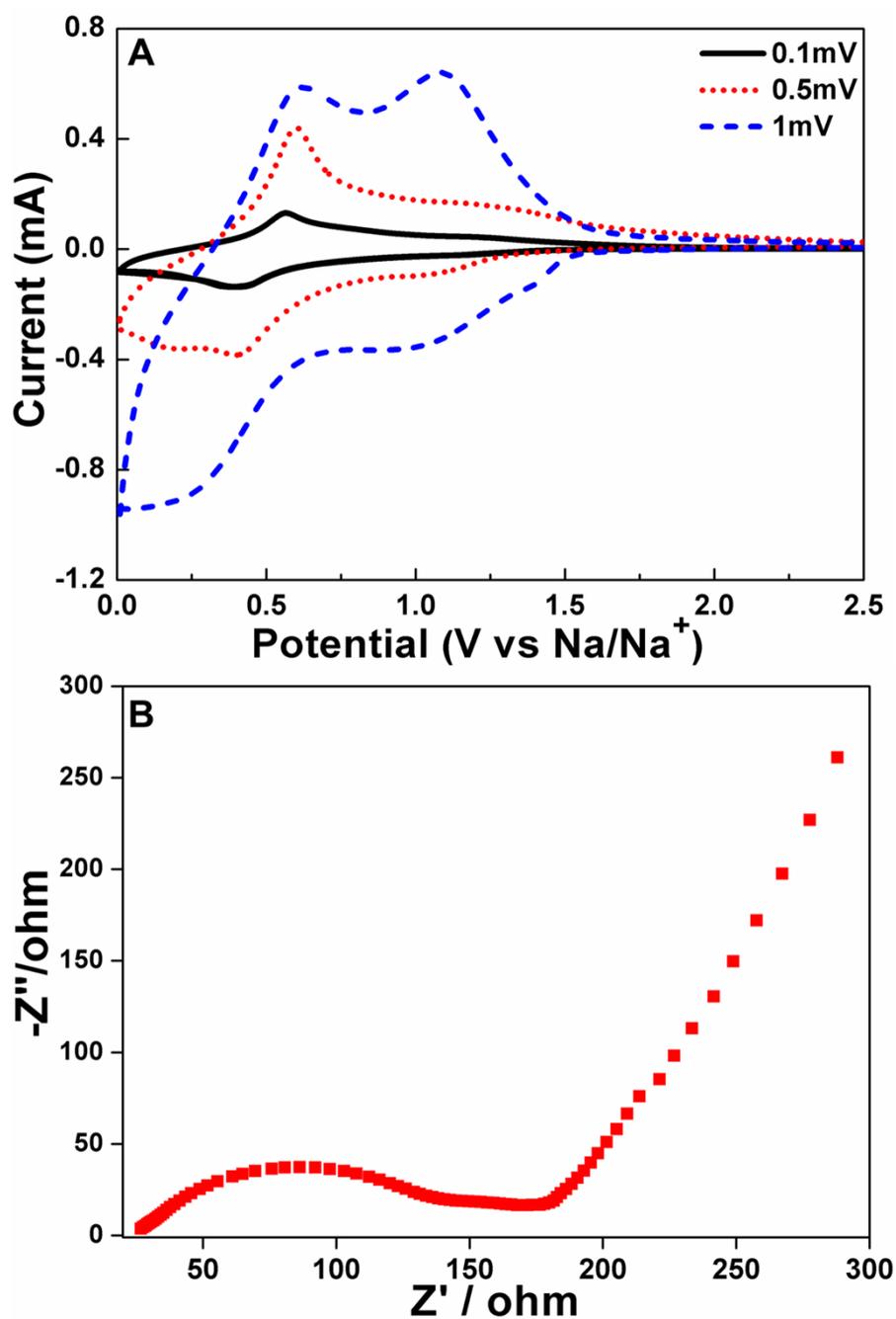


Fig. S4 A) Cyclic voltammograms (CV) curves of the $\text{Na}_2\text{Ti}_3\text{O}_7$ electrode at different scan rate of $0.1\text{-}1\text{ mV S}^{-1}$ in a voltage range of $0.005\text{-}2.5\text{ V}$, from the CV profile, it is clearly observed that a pair of oxidation and reduction peak were located at ca. 0.6 V and 0.4 V , respectively, indicating that good reversibility of the spider web-like $\text{Na}_2\text{Ti}_3\text{O}_7$ electrode. However, the peak obvious increase when scanning rate increased to 1 mV S^{-1} , a new pair of cathode and anode peak was prominent in CV

curve, which located at about 1.0-1.2 V, the appearance of the new peaks is probably attributed to the structure change. The oxidation current peak was as same as that of reduction peak means that the Na⁺ ion inserting into Na₂Ti₃O₇ is great kinetically fast.^{4,5} B) Nyquist impedance plot of the as prepared electrode. The diameter of semicircle in high frequency region is small, indicating that the contact resistance between electrode and the electrolyte is not very strong. Moreover, the semicircle in medium frequency is attributed to the charge-transfer resistance on electrode/electrolyte interface, the small diameter of semicircle in medium frequency indicates the low charge-transfer resistance, inclined line is related to Na⁺ ions diffusion process means sodium ion extracted or inserter into Na₂Ti₃O₇ structure is feasibly.

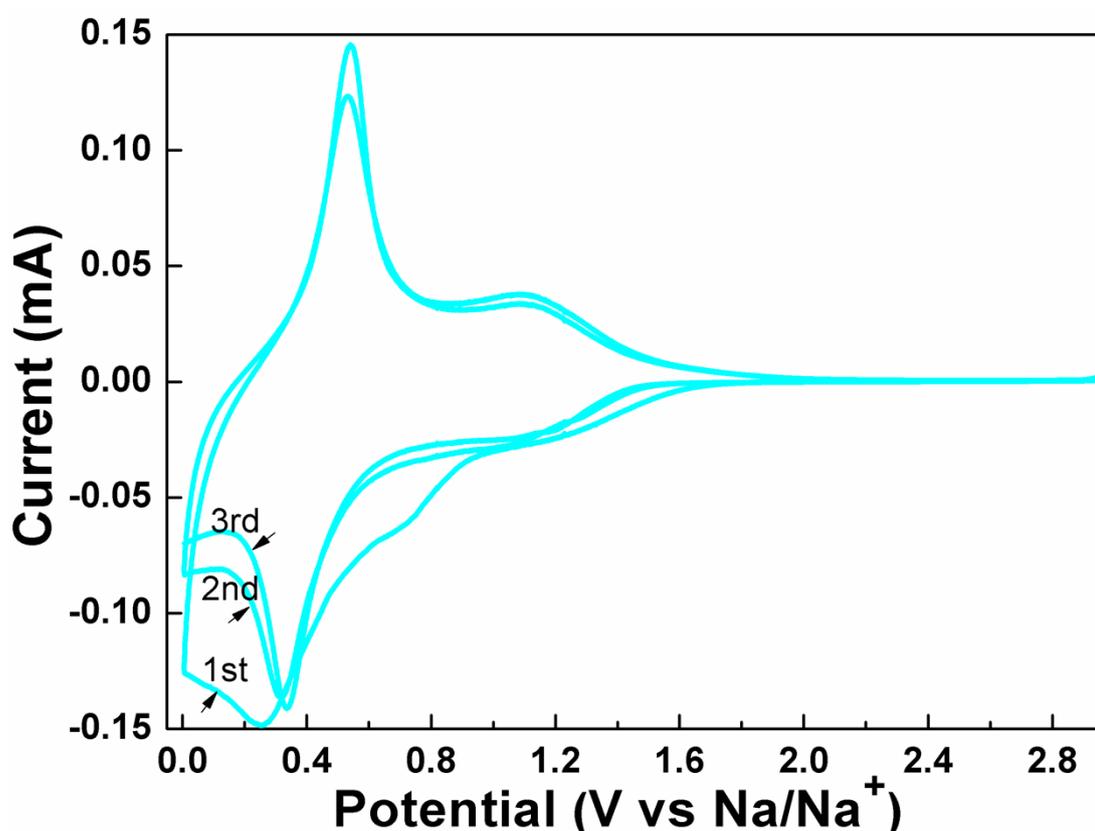


Fig. S5. Cyclic voltammograms (CV) curves of the Na₂Ti₃O₇ electrode at scanning

rate of 0.1 mV/s from the cell that assembled fresh without experiencing discharge-charge test.

Form the CV curve, some irreversible reductive peaks were present in the first circle. One fixed peak was located at 0.25 V, which was assigned to decomposition of electrolyte for formation of SEI film, and this reductive peak at this location were vanished in the subsequent circles, which is a another proof to testify the reductive peak at 0.25 V was derived from the formation of SEI film. Another reductive shoulder at about 0.7 V was possible ascribed to some side reaction related with SEI film that between electrode and electrolyte. This irreversible reductive peak appeared at initial circle is well consistent with that of huge discharge capacity in the initial cycle. In addition, a broad redox peaks between 1.0 and 1.2 V were probably ascribed to some low valence state of Ti atoms join in the sodium insertion/extraction reaction.

Reference

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