

## SUPPLEMENTARY INFORMATION

### **A new sodiation-desodiation mechanism of titania-based negative electrode for sodium-ion battery**

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## Experimental

### Synthesis of cubic Na<sub>2</sub>TiO<sub>3</sub> powders

NaOH (Wako) and anatase TiO<sub>2</sub> nanopowders (Sigma Aldrich) were used as raw materials to synthesize cubic Na<sub>2</sub>TiO<sub>3</sub> ( $\alpha$ -Na<sub>2</sub>TiO<sub>3</sub>) powders. The NaOH was first dissolved with pure water to form a 70 wt% solution in an Al<sub>2</sub>O<sub>3</sub> crucible. The TiO<sub>2</sub> nanopowders were then dispersed into the NaOH solution by stirring. The mass ratio of NaOH and TiO<sub>2</sub> is 1.3:1. Finally, the mixture was put into an electric furnace and heated at 550 °C for 1 h. The calcined white sample was ground using a mortar and pestle to obtain Na<sub>2</sub>TiO<sub>3</sub> powders, which were stored in an Ar-filled glove box until use.

### Heating of Na<sub>2</sub>TiO<sub>3</sub>-TiO powders

Cubic TiO powders (High Purity Chemicals) and cubic Na<sub>2</sub>TiO<sub>3</sub> powders with a molar ratio of 1:1 were ball-milled with dry type for 12 h at 600 rpm. The ball-milled mixture was heated at 200-600 °C for 5 h in Ar gas flow. The structure of the heated powders was investigated by means of X-ray diffraction (XRD, Rigaku SmartLab).

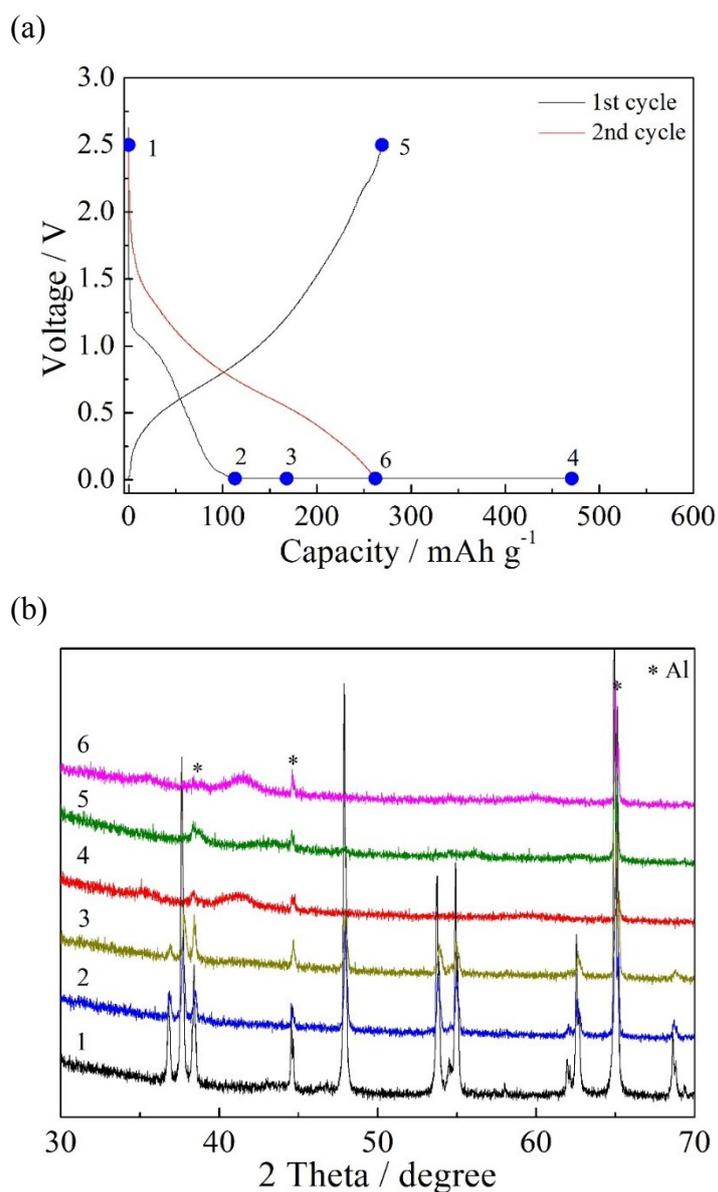
### Electrode fabrication

Amorphous TiO<sub>2</sub> nanopowders (Alfa Aesar), cubic TiO powders and cubic Na<sub>2</sub>TiO<sub>3</sub> powders with a molar ratio of 8:1:1 were ball-milled with dry type for 12 h at 600 rpm. The ball-milled TiO<sub>2</sub>-Na<sub>2</sub>TiO<sub>3</sub>-TiO powders were then dried in vacuum at 120 °C overnight before being transferred into an Ar-filled glove box. And then, the TiO<sub>2</sub>-Na<sub>2</sub>TiO<sub>3</sub>-TiO powders was mixed well with graphite and polytetrafluoroethylene (PTFE) at a weight ratio of 75:15:10 using a mortar and pestle to form a thin film, which was pressed onto an aluminium mesh current collector to form TiO<sub>2</sub>/Na<sub>2</sub>TiO<sub>3</sub>/TiO working electrode. Na<sub>2</sub>TiO<sub>3</sub>/TiO working electrode was fabricated using the same method.

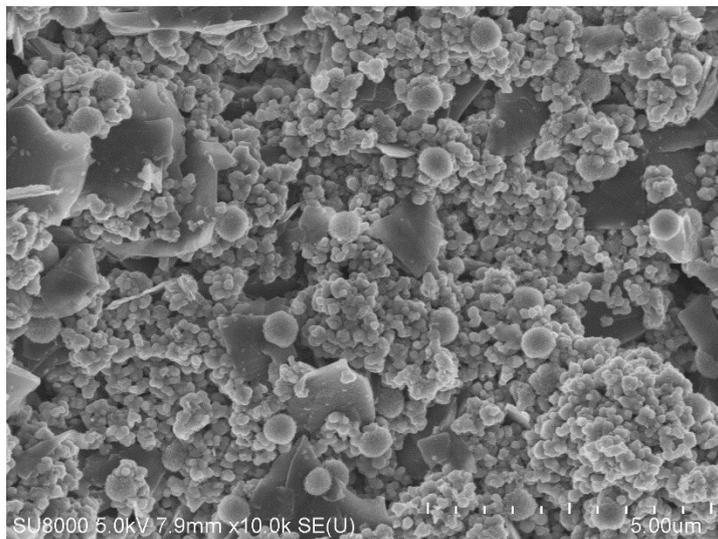
For comparison, amorphous TiO<sub>2</sub> working electrode was also fabricated using a conventional coating method. A slurry consisting of TiO<sub>2</sub> active material (75 wt%), graphite (15 wt%), and polyamide-imide (10 wt%) in *N*-methyl-2-pyrrolidone (NMP) was uniformly spread onto an Al foil. The electrodes were dried in vacuum at 120 °C overnight before being transferred into an Ar-filled glove box.

### Electrochemical characterization

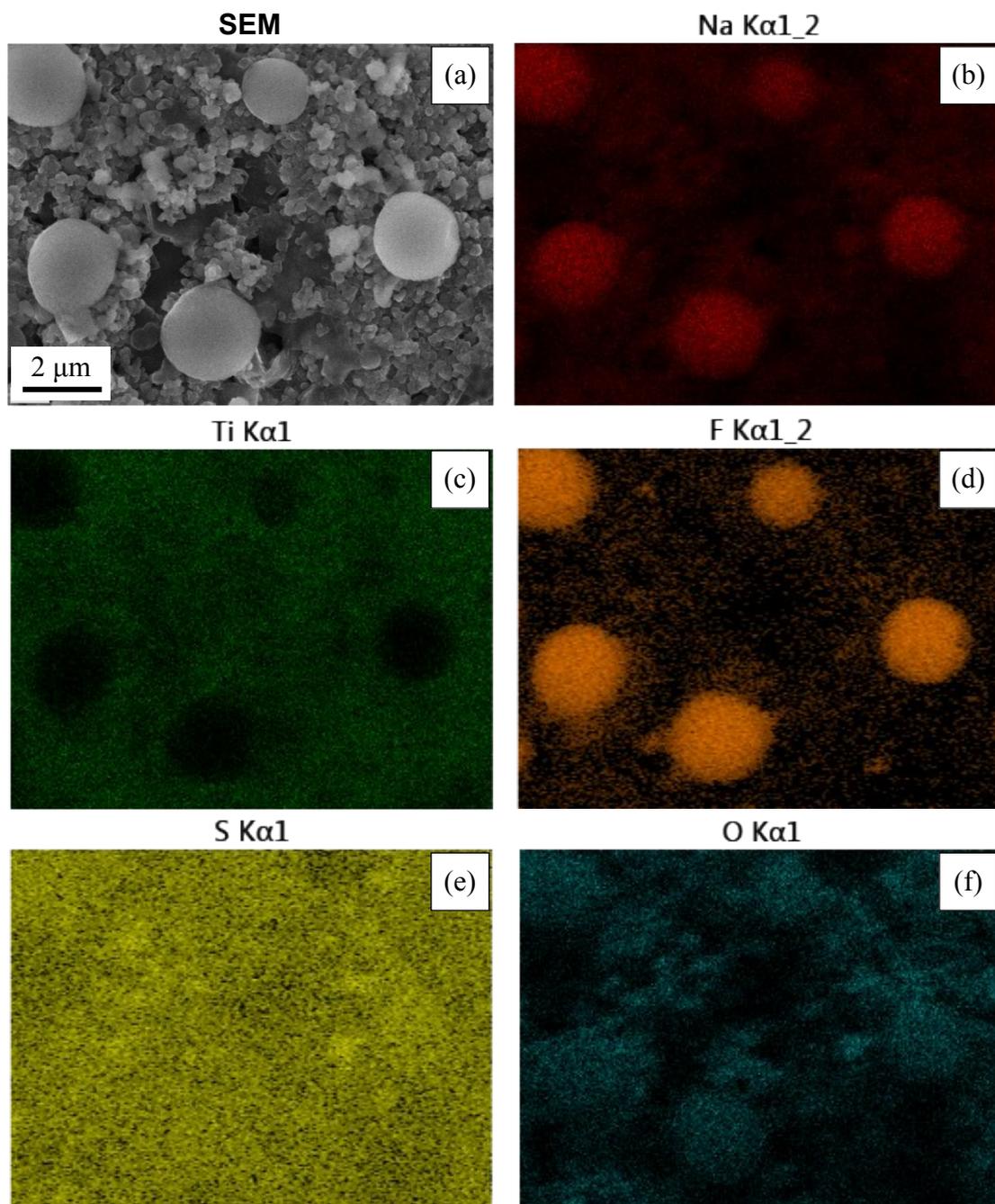
Charge-discharge tests were performed using a coin-type 2032 cell with a sodium foil counter electrode. The electrolyte used was the Na[FSA]-[C<sub>3</sub>C<sub>1</sub>pyrr][FSA] ionic liquid with molar ratio of 2:8. A glass fiber filter (Whatman, GF-A, 260 mm) was used as a separator. The working electrodes and separators were vacuum-impregnated with Na[FSA]-[C<sub>3</sub>C<sub>1</sub>pyrr][FSA] at 60 °C before assembling the cells. Charge-discharge testing was conducted at constant current rates of 20 mA g<sup>-1</sup> in the voltage range of 0.01-2.5 V at 90 °C.



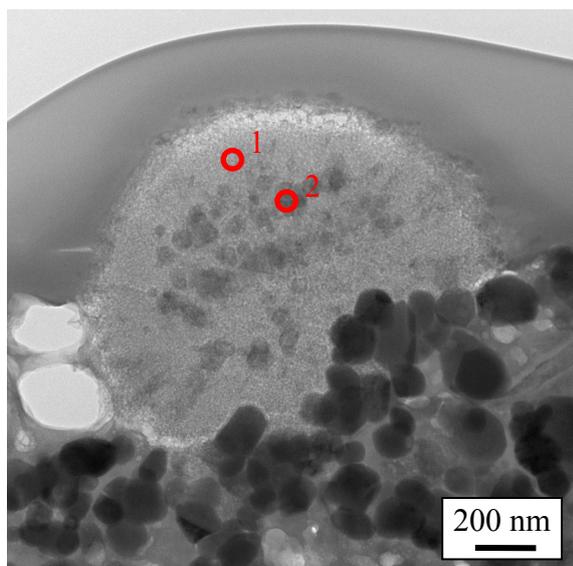
**Fig. S1.** Electrochemical and structural characterization of the TiO<sub>2</sub>/C electrode: (a) Charge-discharge curves by means of CC-CV charge (CC: 1000 mA g<sup>-1</sup> to 0.01 V; CV: 0.01 V until 1 mA g<sup>-1</sup> cutoff current), CC discharge (20 mA g<sup>-1</sup>), and subsequent CC charge-discharge at 20 mA g<sup>-1</sup>. (b) Ex-situ XRD patterns of the TiO<sub>2</sub>/C electrodes at various charge/discharge stages as indicated in (a).



**Fig. S2.** SEM image of the  $\text{TiO}_2/\text{C}$  electrode charged to 0.01 V by CC-CV mode.



**Fig. S3.** EDX mapping analysis of the  $\text{TiO}_2/\text{C}$  electrode charged to 0.01 V: (a) SEM image, (b-f) The elemental mappings for Na, Ti, F, S and O, respectively.

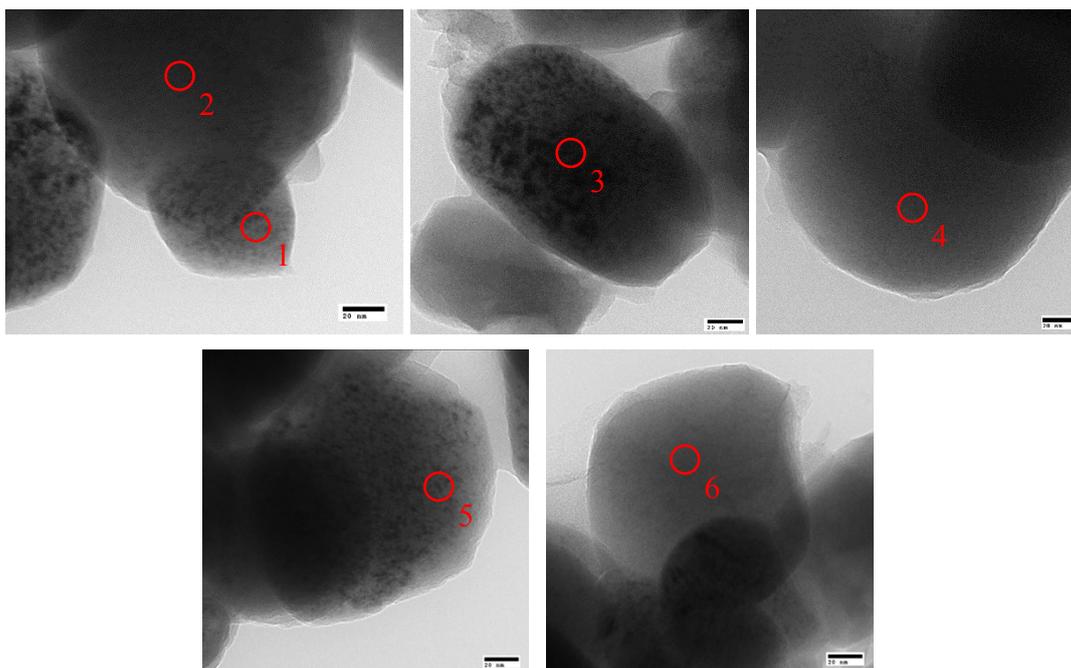


Element	Point 1	Point 2
O	10.5	6.1
F	30.2	36.7
S	7.3	8.4
Na	52.0	48.8

**Fig. S4.** TEM-EDX point analysis of the TiO<sub>2</sub>/C electrode charged to 0.01 V.

**Table S1:** The d values calculated from electron diffraction pattern of the TiO<sub>2</sub>/C electrode discharged to 2.5 V.

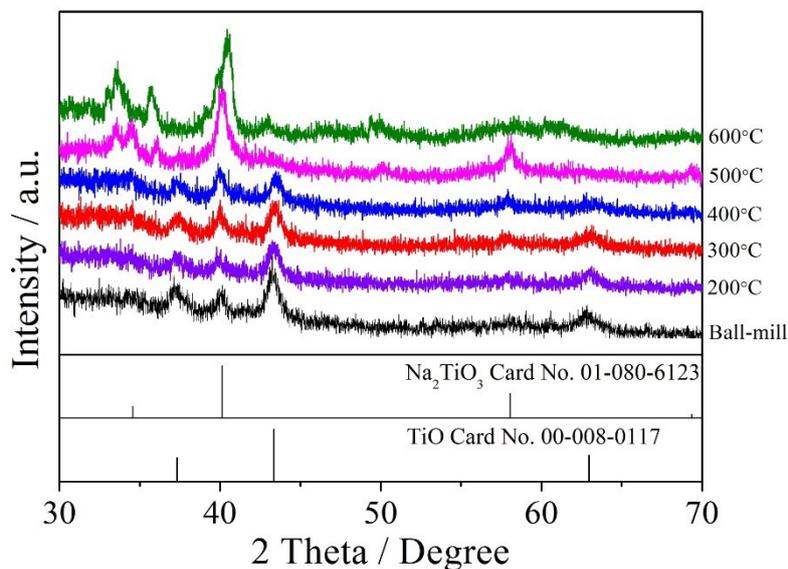
Discharged TiO <sub>2</sub> /C electrode		Cubic TiO Card No: 00-008-0117		
Spot	d	2theta	d	I
1	2.39	37.33	2.407	45
2	2.07	43.36	2.085	100
3	1.47	62.96	1.475	50
-	-	75.44	1.259	14
4	1.19	79.47	1.205	12
5	1.03	95.09	1.044	6



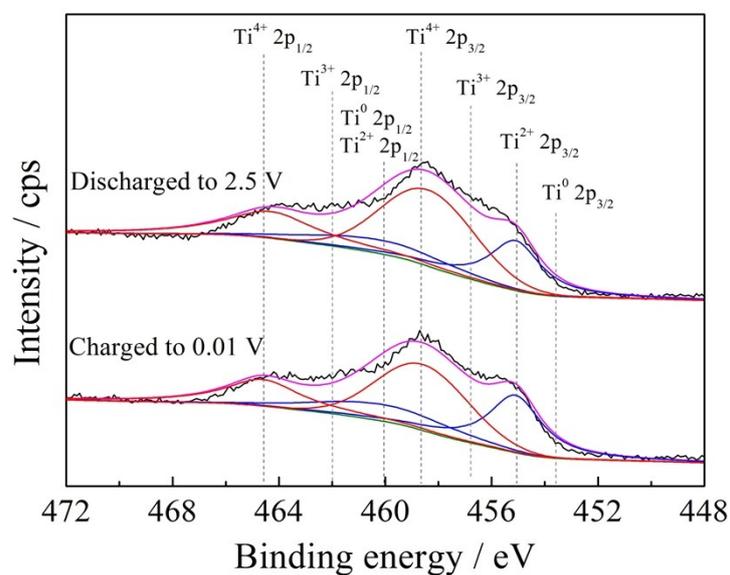
**Fig. S5.** TEM images of the TiO<sub>2</sub>/C electrode discharged to 2.5 V for EDX point analysis (Table S2).

**Table S2:** TEM-EDX point analysis results of the TiO<sub>2</sub>/C electrode discharged to 2.5 V, and calculated molar ratio of Na, Ti and O.

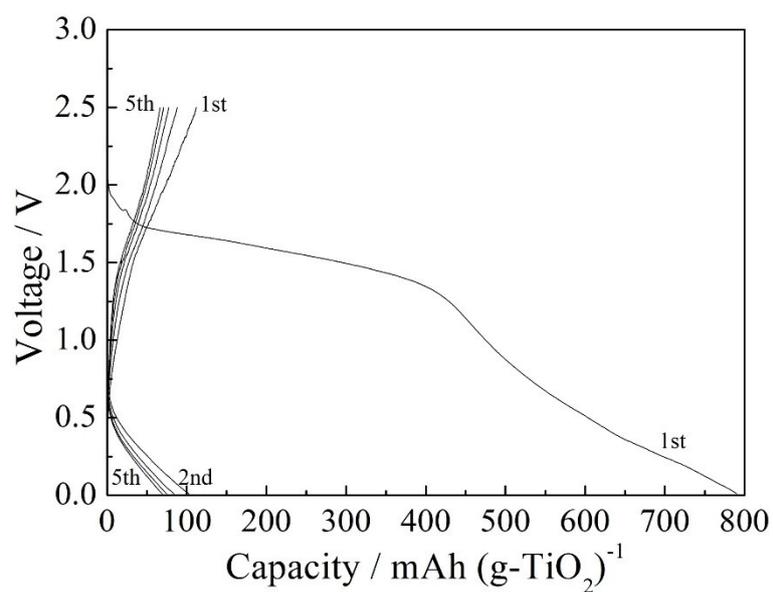
	<b>O-K</b> at%	<b>Na-K</b> at%	<b>Ti-K</b> at%	<b>Na</b>	<b>Ti</b>	<b>O</b>
				<b>molar ratio</b>		
Point 1	66.5	7.7	25.9	0.30	1	2.6
Point 2	54.9	9.6	35.5	0.27	1	1.5
Point 3	63.8	8.4	27.9	0.30	1	2.3
Point 4	61.6	10.5	27.9	0.38	1	2.2
Point 5	60.5	10.1	29.4	0.35	1	2.1
Point 6	65.7	8.1	26.2	0.31	1	2.5



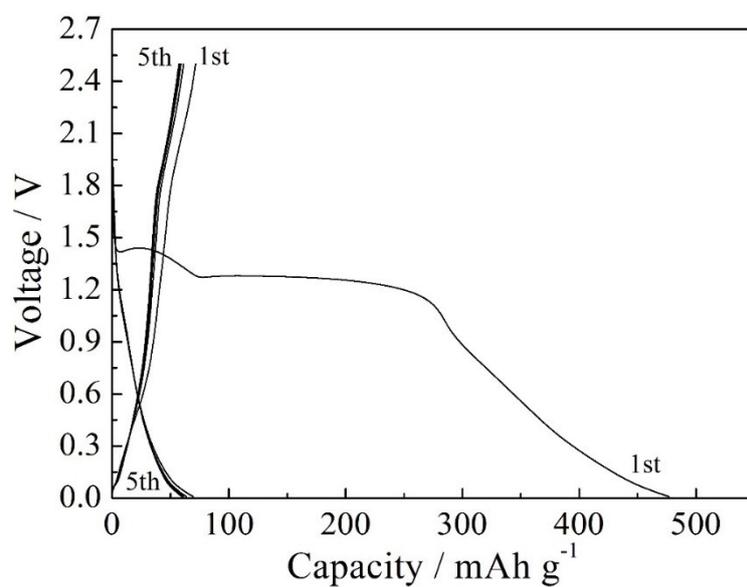
**Fig. S6.** XRD patterns of ball-milled cubic  $\text{Na}_2\text{TiO}_3$  and  $\text{TiO}$  powders heated at 200-600 °C in Ar gas flow.



**Fig. S7:** Ti 2p XPS spectra of  $\text{TiO}_2/\text{C}$  electrode charged to 0.01 V and  $\text{TiO}_2/\text{C}$  electrode discharged to 2.5 V, after  $\text{Ar}^+$  etching. (The binding energies of  $\text{Ti}^{4+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ti}^{2+}$  and  $\text{Ti}^0$  come from NIST X-ray Photoelectron Spectroscopy Database.)



**Fig. S8.** Charge-discharge curves of the TiO<sub>2</sub> (amorphous) electrode at 20 mA g<sup>-1</sup>.



**Fig. S9.** Charge-discharge curves of the Na<sub>2</sub>TiO<sub>3</sub>/TiO electrode at 20 mA g<sup>-1</sup>.