

## Supporting Information

### **Structural evolution from layered Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> to Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> nanowires enabling a highly reversible anode for Mg-ion batteries**

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## **Experimental Section**

### *Materials Characterization*

X-ray diffraction (XRD) patterns were acquired on a Rigaku Ultima IV diffractometer using Ni filtered Cu K $\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ). The morphology and structure of the samples were studied using scanning electron microscopy (SEM, S8010 instrument) and transmission electron microscopy (TEM, TECNAI G2 F20). Raman spectra were obtained using a LabRAM HR Evolution (HORIBA Jobin Yvon) instrument with a 532 nm laser in ambient air. The TG was taken on a TA-60WS in air from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup>.

### *Electrochemical Measurements*

The CR 2025 coin cells were assembled in an argon-filled glovebox. The working electrode were fabricated to form a freestanding film with 70 wt% active material, 20 wt% conductive carbon (Super P),

and 10wt% polytetrafluoroethylene (PTFE) binder by milling in agate mortar and then dried at 120 °C in the vacuum drying oven about 12 h. Then it was cut and pressed on Ti mesh and the loading for each electrode is approximately 1.5-2 mg cm<sup>-2</sup>. Polished Mg foil was used as the counter electrode and glass fiber separator (WhatmanGF/F) was used as the separator. The 0.4M (PhMgCl)<sub>2</sub>-AlCl<sub>3</sub>/tetrahydrofuran (APC/THF) electrolyte was used as the electrolyte. Galvanostatic charge–discharge measurement was tested on a multichannel battery testing system (Land CT 2001A, China) in the potential range 0.01-2 V versus Mg<sup>2+</sup>/Mg at room temperature. Cyclic voltammetry (CV) were measured on Zennium (Zahner) at a scan rate of 0.5 mV s<sup>-1</sup>.

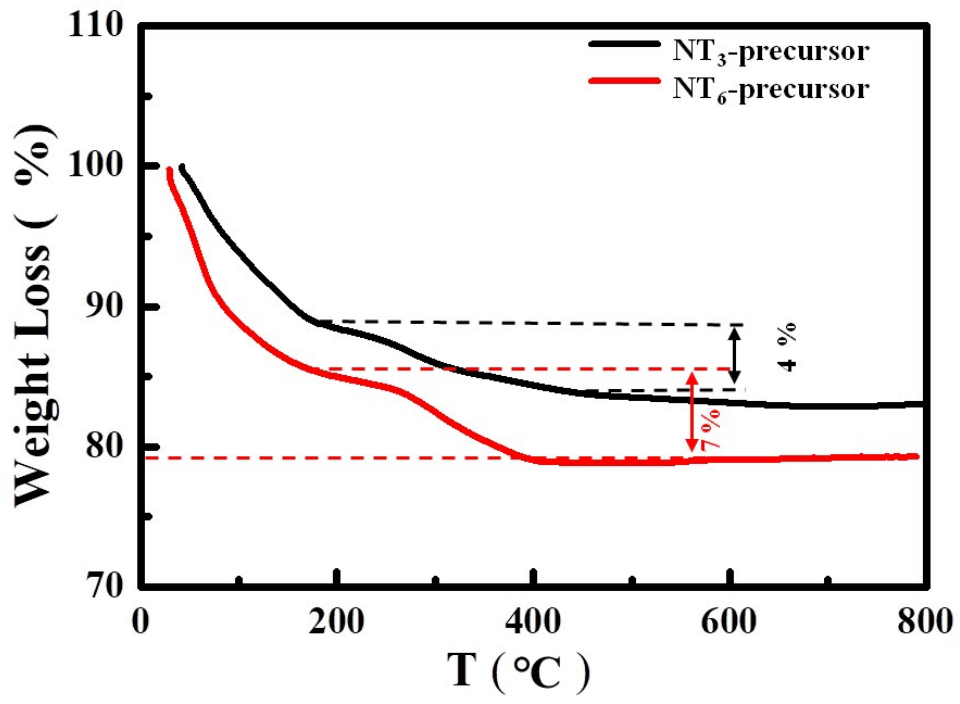
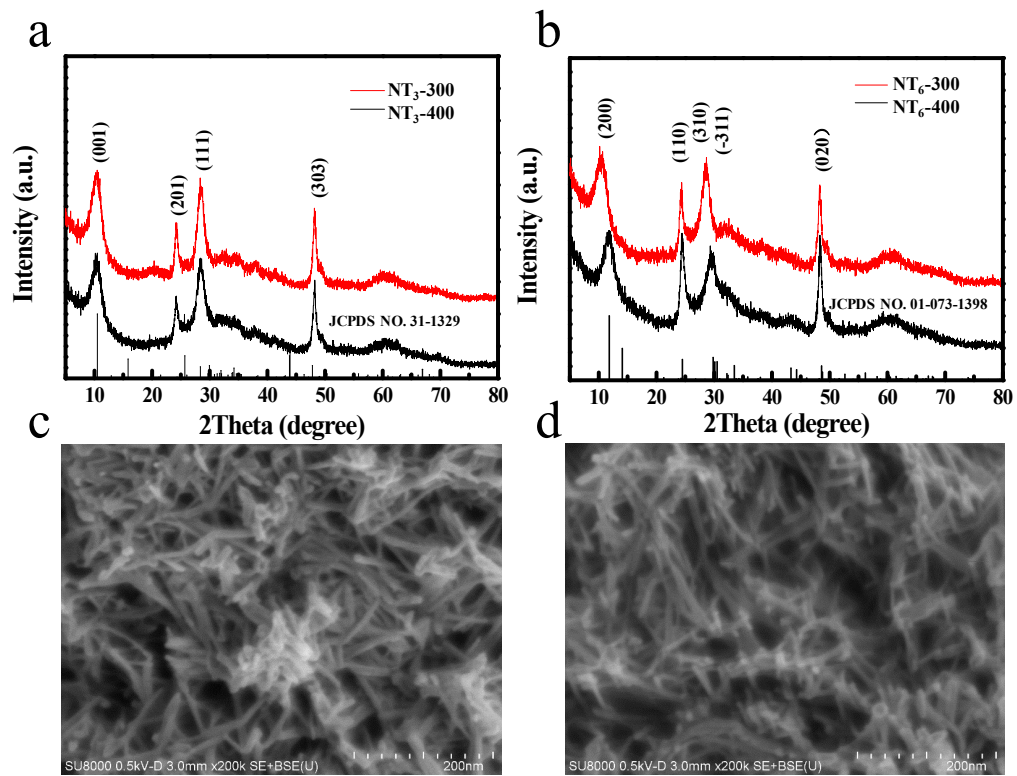
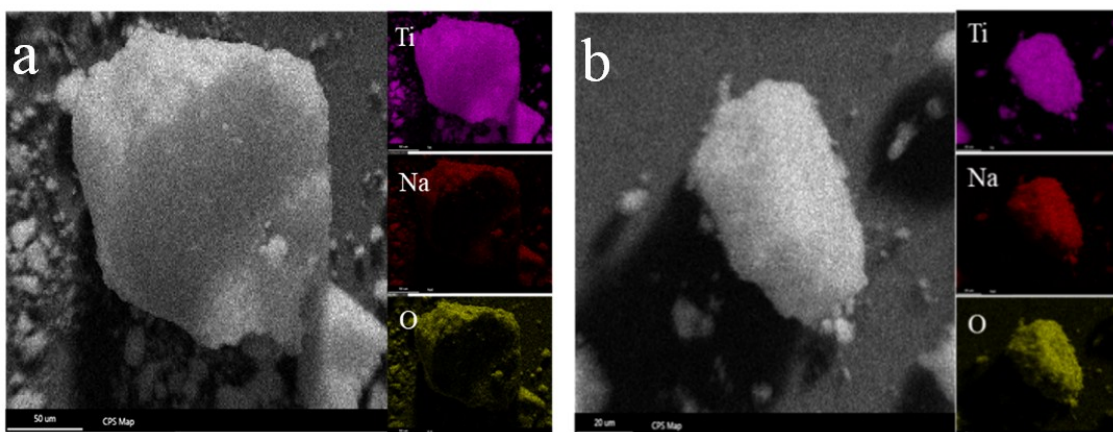


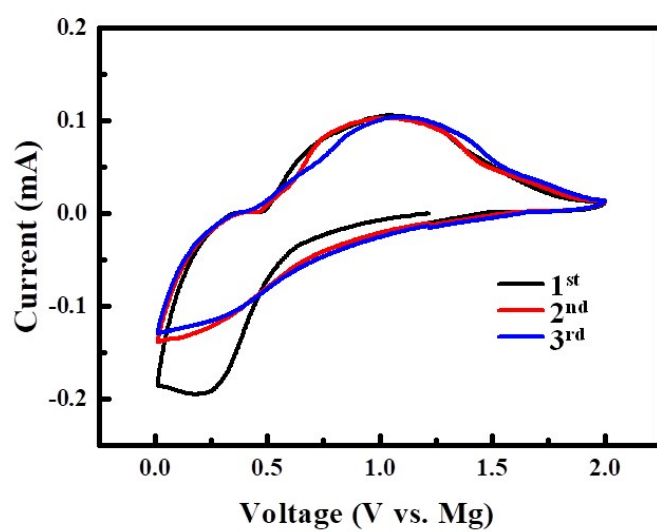
Fig.S1 TGA curve of different titanate precursors heated under air condition.



**Fig.S2** XRD patterns of (a) NT<sub>3</sub>-300 and NT<sub>3</sub>-400, (b) NT<sub>6</sub>-300 and NT<sub>6</sub>-400. SEM images of (c) NT<sub>3</sub>-400 and (d) NT<sub>6</sub>-400.



**Fig.S3** Corresponding EDX element mapping images of (a) NT<sub>3</sub> and (b) NT<sub>6</sub>.



**Fig.S4** Cyclic voltammograms for NT<sub>3</sub>-300 at a scan rate of 0.5 mV s<sup>-1</sup> between 0.01-2 V .

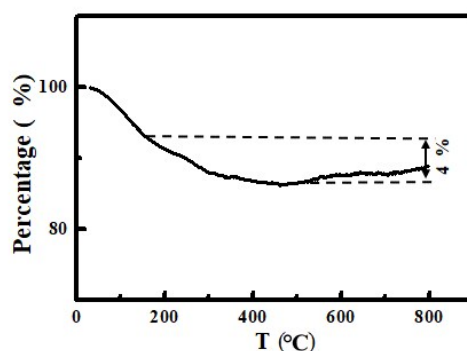
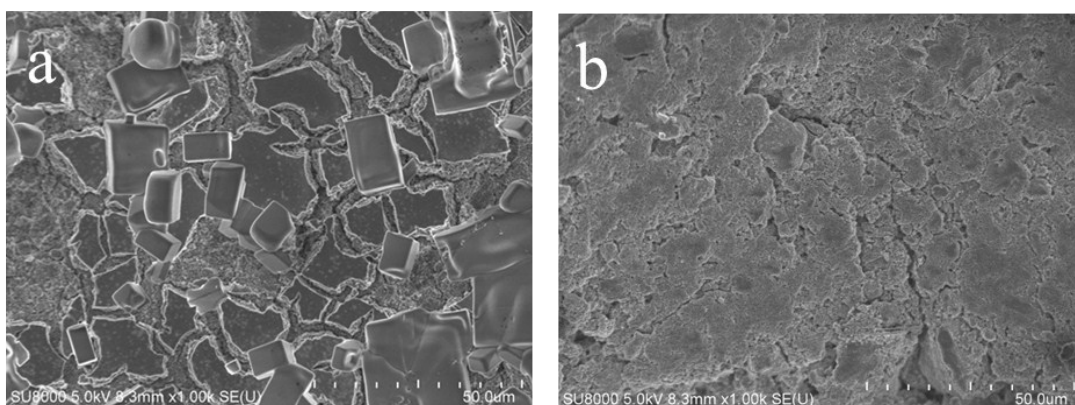


Fig. S5 TG curves of  $\text{NT}_6$  obtained under  $300^\circ\text{C}$ .

**Table S 1** Comparison of Mg storage performance of related anodes.

Materials <sup>reference</sup>	Electrolyte	Potential range (vs. Mg 2+ /Mg)	ICE	Reversible capacity
$\text{NaMgTi}_3\text{O}_7$ <sup>19</sup>	0.25 M $(\text{PhMgCl})_2 - \text{AlCl}_3 / \text{THF}$ (APC)	0.01-2.00 V	67.4%	91 mA h/g at
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ <sup>21</sup>	0.25M $\text{Mg}(\text{AlCl}_2\text{BuEt}_2)_2 / \text{THF}$	0.01-2.00 V	71.4%	25 mAh/g at 15 mA/g
$\text{TiO}_2 - \text{B}^{20}$	0.4 M APC in THF	0.01-2.00 V	55.6%	79 mAh/g at 10 mA/g
cation-deficient anatase $\text{TiO}_2$ <sup>22</sup>	0.2 M APC in THF	0.05–2.3 V	84.8%	140mAh/g at 20 mA/g
B- $\text{TiO}_{2-x}$ <sup>23</sup>	0.4 M APC in THF	0.05–2.1 V	70.5%	134mAh/g at 50 mA/g (from the rate performance)
$\text{Na}_2\text{Ti}_6\text{O}_{13}$ <sup>This work</sup>	0.4 M APC in THF	0.01-2.00 V	89.1%	165.8 mAh/g at 10mA/g



**Fig.S6** SEM images of (a)NT<sub>3</sub> and (b) NT<sub>6</sub> electrodes after the first cycle.

Table S2 The contents of the elements for different electrodes after first cycle.

Actom%	Na	Ti	Cl	O	Mg
NT <sub>3</sub>	22.29	18.23	8.1	46.17	5.21
NT <sub>6</sub>	14.43	17.15	6.32	53.44	8.67