# **Supporting Information**

## Intercalation pseudocapacitance of sodium-ion storage in TiO<sub>2</sub>(B)

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## **Experimental Section**

## *Synthesis of TiO*<sub>2</sub>(*B*) *nanosheets*

The synthesis of TiO<sub>2</sub>(B) nanosheets (NSs) based on the hydrothermal method.<sup>S1</sup> In detail, 2 mL of TiCl<sub>3</sub> was added to 60 mL glycol, and followed by the addition of 2 mL deionized water, and stirring for 30 minutes until the solution turned into pale purple. The solution was then transferred to a 100 ml Teflon-lined stainless-steel reactor, and heated at 150°C for 24 hours. After cooling to room temperature, the white precipitates were washed alternately with deionized water and anhydrous ethanol, and then dried at 80°C for 12 hours. Finally, TiO<sub>2</sub>(B) NSs were obtained after annealing at 250°C for 24 hours at a heating rate of 1 C min<sup>-1</sup> under air atmosphere.

#### Synthesis of $TiO_2(B)$ nanowires

TiO<sub>2</sub>(B) NWs were synthesized by hydrothermal and ion-exchange method.<sup>S2</sup> P25 (0.5 g) was added to NaOH aqueous solution (10 M, 50 mL) under continuous stirring. Then, the mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated at 180°C for 72 hours. After cooling to room temperature, the obtained powder was thoroughly washed with deionized water. The sediment was collected and immersed in 0.1 M HCl for 4 days, and then washed with deionized water and dried at 80°C for 12 hours. Finally, TiO<sub>2</sub>(B) NWs were obtained after calcination at 400 °C in air for 2 hours at a heating rate of 2 °C min<sup>-1</sup>.

## **Material Characterizations**

Powder XRD was characterized on Bruker D8 Advance X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5406$  Å). BET specific surface area was measured by nitrogen sorption isotherms (3H-2000PM2) at 77 K after degassing under vacuum at 200 °C for over 6 h. Scanning electron microscopy (SEM) images were recorded using SU-70. TEM images were recorded using Talos F200s. For ex-situ XRD and TEM measurements, the coin cell was disassembled in the Ar-filled glove box after being electrochemically cycled at different states, and the TiO<sub>2</sub>(B) electrode was washed with the diglyme solvent.

## **Electrochemical measurements**

All the electrodes were made from an aqueous slurry consisting of 85 wt.% active materials, 7 wt.% ketjen black, 4 wt.% carboxyl methyl cellulose (CMC) and 4 wt.% styrene butadiene rubber (SBR). The slurry was cast onto Al foils (changes to copper foils for Li<sup>+</sup> storage

measurements). The electrode was dried at 80°C under vacuum for 12 hours. The active mass loading was 1.5-2.0 mg cm<sup>-2</sup>. Coin cells (CR2032) were assembled in Ar filled glove box. For Na<sup>+</sup> storage, sodium metal was used as the counter and reference electrode, and 1 M NaPF<sub>6</sub> in diglyme as electrolyte. The potential range was 0.01-3.0 V vs. Na<sup>+</sup>/Na. For Li<sup>+</sup> storage, lithium metal was used as the counter and reference electrode, and 1 M LiPF<sub>6</sub> in EC/EMC/DMC (1:1:1 by weight) as electrolyte, and the potential range was 1.0-3.0 V vs. Li<sup>+</sup>/Li. Cyclic voltammetry (CV) was carried out on Bio-Logic VSP potentiostat. Rate capability and cycling performance were measured by using Neware BTS-4008. All the electrochemical tests were carried out in an oven at 25 °C.

## **DFT calculations**

All calculations on TiO<sub>2</sub>(B) were executed by the projector augmented wave (PAW) method<sup>S3</sup> within density functional theory (DFT), which was conducted in the Vienna ab initio Simulation Package (VASP).<sup>S4,S5</sup> The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE)<sup>S6</sup> was used to treat the exchange-correlation energy. The monoclinic TiO<sub>2</sub>(B) was selected as the host for Na<sup>+</sup> (and Li<sup>+</sup>) storage. A kinetic energy cutoff of 500 eV was used for wave functions expanded on the plane wave basis. Besides, spin polarization was considered. The energy (converged to  $1.0 \times 10^{-6}$  eV atom<sup>-1</sup>) and force (converged to 0.05 eV Å<sup>-1</sup>) were set as the convergence criteria for geometry optimization. For the Brillouin-zone sampling, a 4×4×4 k-point mesh was used to ensure convergence of the total energy. The formation energies of various compositions (i.e. M<sub>x</sub>TiO<sub>2</sub> in C, C+A1 and C+A1+A1 (M = Na or Li) were calculated to obtain stable crystal structures. The formation energy ( $\Delta E_{for}$ ) is estimated by the following formula:<sup>S7,S8</sup>

$$\Delta E_{for} = \frac{E_M x^{\text{TiO}} 2}{2} - \frac{E_{\text{TiO}} 2}{2} - x^E M$$
(S1)

where  ${}^{E_{M_x \text{TiO}_2}}$  is the energy for the intercalation systems,  ${}^{E_{\text{TiO}_2}}$  is the energy for TiO<sub>2</sub>(B), *x* is the intercalation number of Li<sup>+</sup>/Na<sup>+</sup> ions, and  ${}^{E_M}$  is the energy of isolated Na/Li.



**Fig. S1** CV curves of NSs (a) and NWs (b) for  $Li^+$  storage at 0.2 mV s<sup>-1</sup>. The charge-discharge curves of the NSs (c) and NWs (d) for  $Li^+$  storage at 0.1 A g<sup>-1</sup>.



**Fig. S2** Electrochemical Na<sup>+</sup> storage of TiO<sub>2</sub>(B) in ester electrolyte (1 M NaPF<sub>6</sub> in EC/EMC/DMC in a 1:1:1 ratio by weight). The CV curves of (a) TiO<sub>2</sub>(B) NSs and (b) NWs at 0.2 mV s<sup>-1</sup>. (c) The initial discharge and charge curves of TiO<sub>2</sub>(B) NSs and NWs at 0.1 A g<sup>-1</sup>.



Fig. S3 Ex-situ XRD patterns of (a) NSs and (b) NWs for  $Li^+$  storage at different states.



**Fig. S4** The  $d_{110}$  value variation for Li<sup>+</sup> storage.



Fig. S5 Ex-situ TEM images of (a)  $TiO_2(B)$  NSs and (b) NWs after sodiation to 0.01 V vs. Na<sup>+</sup>/Na.



Fig. S6 (a) TEM image and (b-d) EDS mappings of  $TiO_2(B)$  NSs after sodiation to 0.01 V vs. Na<sup>+</sup>/Na. The element mapping of (b) titanium (green), (c) oxygen (yellow) and (d) sodium (purple).



Fig. S7 (a) TEM image and (b-d) EDS mappings of  $TiO_2(B)$  NWs after sodiation to 0.01 V vs. Na<sup>+</sup>/Na. The element mapping of (b) titanium (green), (c) oxygen (yellow) and (d) sodium (purple).



**Fig. S8** CV curves of (a)  $TiO_2(B)$  NSs and (b) NWs for Li<sup>+</sup> storage at various sweep rates ranging from 0.2 to 1 mV s<sup>-1</sup>. Calculated capacitive contributions of (c)  $TiO_2(B)$  NSs and (d) NWs for Li<sup>+</sup> storage.



Fig. S9 The calculated  $Li^+$  diffusion coefficient of the  $TiO_2(B)$  NSs and NWs based on the GITT method.



Fig. S10 The Nyquist plots of  $TiO_2(B)$  NSs during the electrochemical (a) sodiation and (b) desodiation at 5th cycle. (c) 3D Bode of  $TiO_2(B)$  NSs. The Nyquist plots of  $TiO_2(B)$  NWs during the electrochemical (d) sodiation and (e) desodiation at 5th cycle. (f) 3D Bode of  $TiO_2(B)$  NWs.

Samples	$\frac{\text{SSA}}{(\text{m}^2 \text{ g}^{-1})}$	Specific capacity (mAh g <sup>-1</sup> )	Testing conductions	Electrode composite	Electrolyte	Refs.
TiO <sub>2</sub> (B)-	47	107	at 0.1 A g <sup>-1</sup>	TiO <sub>2</sub> (B):KJB:CM	1 M NaPF <sub>6</sub> in DGDE	This
nanowires			in 0.01-3 V	C:SBR=85:/:4:4		work
T1O <sub>2</sub> (B)-	240	119	at 0.1 A $g^{-1}$	T <sub>1</sub> O <sub>2</sub> (B):KJB:CM	1 M NaPF <sub>6</sub> in DGDE	This
nanosheets			in 0.01-3 V	C:SBR=85:7:4:4		work
TiO <sub>2</sub> (B)-noddle	216.9	102	at 0.15 A $g^{-1}$	TiO <sub>2</sub> (B):SuperC6	1 M NaClO <sub>4</sub> in PC/EC	S9
like morphorlogy			in 0.02-2 V	5:CMC=70:20:10	(1:1)	
TiO <sub>2</sub> (B) bunchy	198	131	at $0.168 \text{ A g}^{-1}$	TiO <sub>2</sub> (B):SP:PVdF	1 M NaClO <sub>4</sub> in EC/DMC	S10
hierarchical	190		in 0-2.5 V	=70:20:10	(1:1)	
TiO <sub>2</sub> (B)		102.7	at 0.168 A g <sup>-1</sup>	TiO <sub>2</sub> (B):SP:CMC	1 M NaClO <sub>4</sub> in PC/FEC	S11
nanobelts	125.9		in 0.01-3 V	=70:15:15	(95:5)	
TiO <sub>2</sub> (B)		108	at 0.1 A g <sup>-1</sup>	TiO <sub>2</sub> (B):SP:CMC	$1 \text{ M NaPF}_6 \text{ in PC}$	S12
nanosheets	124		in 0-3 V	:CA=70:20:5:5		
TiO <sub>2</sub> (A)-5 nm	303	236				
TiO <sub>2</sub> (A)-10 nm	133	229				
TiO <sub>2</sub> (A)-18 nm	80	193	at $0.1 \text{ A g}^{-1}$	TiO <sub>2</sub> (A):KJB:CM		~ 1 •
TiO <sub>2</sub> (A)-25 nm	57	160	in 0.01-3 V	C:SBR=85:7:4:4	$1 \text{ M NaPF}_6 \text{ in DGDE}$	S13
TiO <sub>2</sub> (A)-40 nm	40	87				
TiO <sub>2</sub> (A)-100 nm	11	33				
TiO <sub>2</sub> (A)		147.3	at $0.168 \text{ A g}^{-1}$	TiO <sub>2</sub> (A): SP:	1 M NaClO <sub>4</sub> in PC with	S14
nanoparticles	80.72		in 0.01-3 V	CMC=70:15:15	5% FEC	
TiO <sub>2</sub> (A)	74.9	140.6	at 0.1 A $g^{-1}$	TiO <sub>2</sub> (A):SP:PVd	1 M NaClO <sub>4</sub> in EC/DMC	S15
nanocrystals			in 0.01-2.5 V	F=80:10:10	(1:1)	
TiO <sub>2</sub> (A)	33.4	127	at $0.168 \ A \ g^{-1}$	TiO <sub>2</sub> (A):SP:PVd	1 M NaClO <sub>4</sub> in EC/DMC	S16
nanocubes			in 0.01-3 V	F=70:20:10	(1:1) with 5% FEC	
TiO <sub>2</sub> (A)	20.39	94	at 0.1 A $g^{-1}$	TiO <sub>2</sub> (A):SP:CMC	1 M NaClO <sub>4</sub> in EC/DMC	S17
yolk@shell			in 0.01-3 V	=60:30:10	(1:1) with 5% FEC	

Table S1 The specific capacities of the  $TiO_2(B)$  (this work) and previously reported  $TiO_2$  nanomaterials for Na<sup>+</sup> storage.

\* KJB: ketjen black; CMC: carboxymethyl cellulose; SBR: polymerized styrene butadiene rubber; SP: acetylene black carbon; CA: citric acid; PVDF: polyvinylidene fluoride; DGDE: diglyme; PC: propylene carbonate; EC: ethylene carbonate; DMC: dimethyl carbonate; FEC: fluoroethylene carbonate; .

Storage ions	Sample	Specific capacity (mAh g <sup>-1</sup> )
Na <sup>+</sup> storage	NSs	119 (Na <sub>0.355</sub> TiO <sub>2</sub> )
Iva" storage	NWs	107 (Na <sub>0.319</sub> TiO <sub>2</sub> )
T '+ /	NSs	217 (Li <sub>0.648</sub> TiO <sub>2</sub> )
L1 <sup>+</sup> storage	NWs	211 (Li <sub>0.630</sub> TiO <sub>2</sub> )

**Table S2** The Na<sup>+</sup> and Li<sup>+</sup> storage capacities of TiO<sub>2</sub>(B) NSs and NWs at 0.1 A  $g^{-1}$ .

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