

Electronic Supplementary Information

An advanced high-energy sodium ion full battery based on nanostructured Na₂Ti₃O₇/VOPO₄ layered materials

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Experimental Section

Material preparation

Synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes: To obtain the $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes, 0.3 g nano-sized titanium powder (99.8% metals basis, 60 nm, Aladdin Industrial Co., China) was treated with 30 mL of 10 M NaOH solution in a sealed Teflon reactor at 160 °C for 72 h, soaked, washed with DI H_2O , and then dried in air.

Synthesis of VOPO_4 nanosheets: Bulk $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ chunks were synthesized according to previous literature.^{1, 2} Briefly, a mixture of V_2O_5 (4.8 g), H_3PO_4 (85%, 26.6 mL) and H_2O (115.4 mL) was refluxed at 110 °C for 16 h. The resulting yellow precipitate was collected by centrifugation, washed several times with water and acetone, then dried in oven at 80 °C. To obtain exfoliated VOPO_4 nanosheets, bulk $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ chunks were first ground to approximately 1 μm in size then dispersed in 2-propanol with concentration about 2 mg mL^{-1} . The yellow dispersion was ultrasonicated in water for 30 min, during which color of the dispersion became faded, indicating successful formation of VOPO_4 nanosheets.

Characterization

XRD patterns were performed on a Rigaku MiniFlex 600 equipped with Cu $\text{K}\alpha$ radiation. SEM/STEM and TEM observations were carried out on a Hitachi scanning electron microscope (S-5500) and JEOL transmission electron microscope (2010F), respectively.

Electrochemistry

Half cells were constructed using the CR2032 coin-type cells with Na metal as the counter and reference electrode and Waltman glassy fiber as the separator. The electrolyte was 1 mol L^{-1} NaClO_4 dissolved in propylene carbonate with 2 vol% fluorinated ethylene carbonate as an electrolyte additive. The VOPO_4 nanosheets electrode was prepared by adding Super P carbon and sodium carboxymethyl cellulose (CMC) directly into aforementioned 2-propanol dispersion after ultrasonication (weight ratio of VOPO_4 : Super P: CMC = 80: 15: 5). While heated to remove excess 2-propanol, the mixture was thoroughly mixed in Thinky centrifugal mixer to form a homogenous slurry, which was

then casted on aluminium foil. The $\text{Na}_2\text{Ti}_3\text{O}_7$ electrode was prepared by a slurry-coating procedure. The slurry consisted of 80 wt% active materials, 15 wt% Super P, and 5 wt% CMC dissolved in DI water. This slurry was spread on copper foil, which acted as a current collector. The aforementioned electrodes were dried at 115 °C for 12 h under vacuum and then pressed. Cyclic voltammetry (CV) curves were collected by Bio-logic potentiostat (VMP3) at 0.1 mV s^{-1} , Galvanostatic charge/discharge experiments were performed at different current densities on LAND battery cycler (CT2001A). Prior to full cells fabrication, the pre-sodiation of $\text{Na}_2\text{Ti}_3\text{O}_7$ anode and VOPO_4 cathode were performed to carry out the first cycle activation. The cell balance was achieved by setting the electrode mass ratio of cathode/anode to *ca.* 2.0.

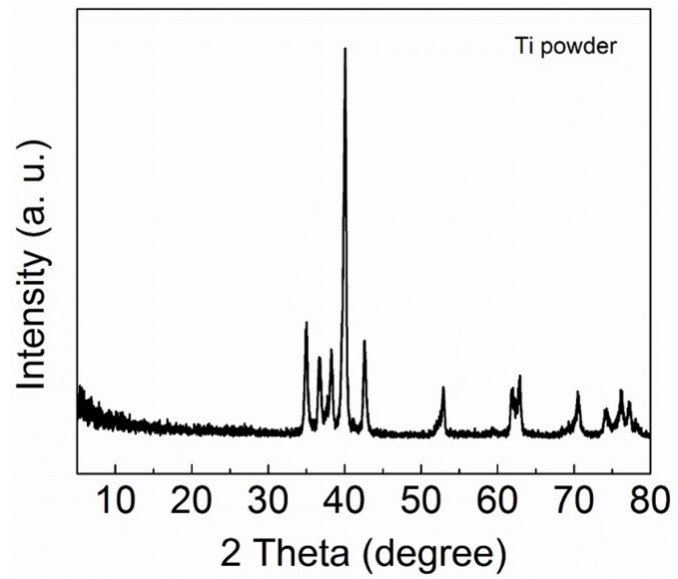


Fig. S1 XRD patterns of the commercial Ti powder

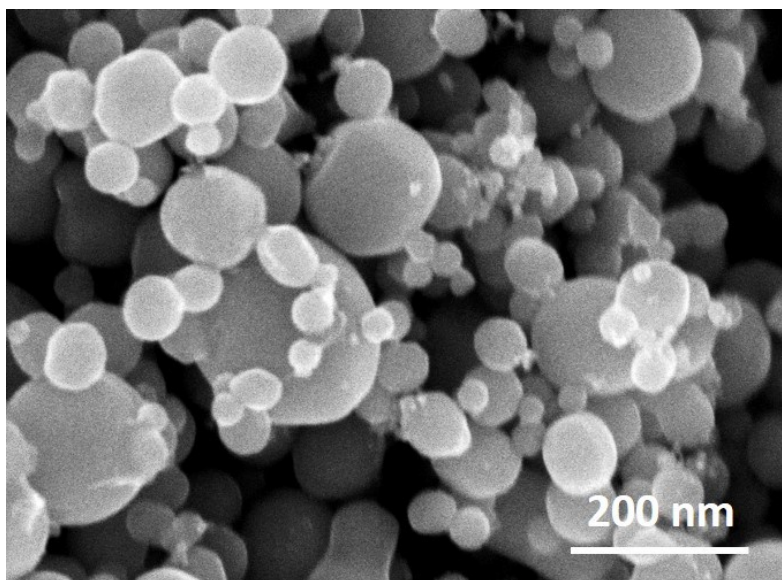


Fig. S2 SEM image of the commercial Ti powder

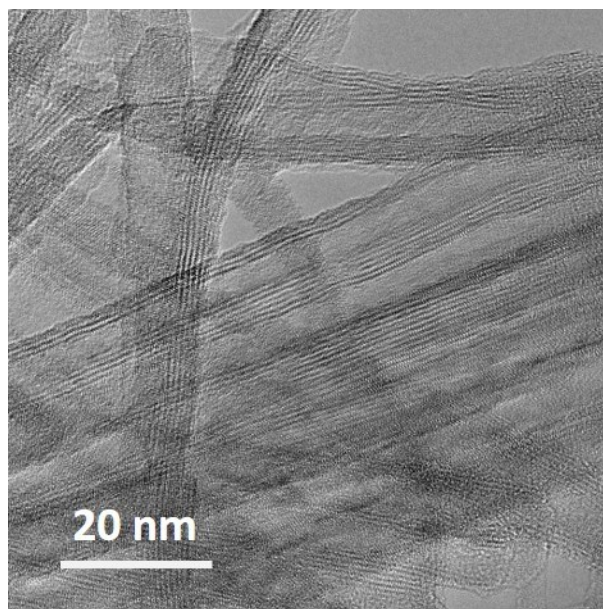


Fig. S3 TEM image of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes

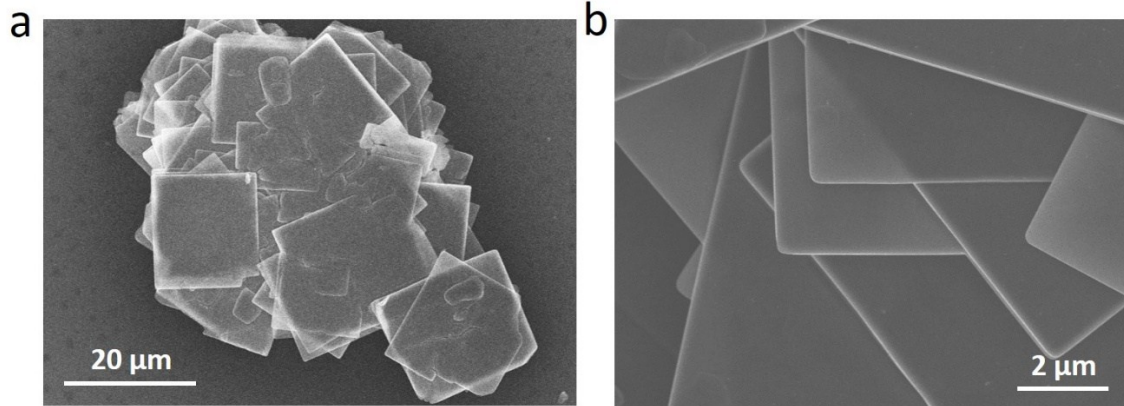


Fig. S4 Top-view and side-view SEM image of the bulk $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ chunks

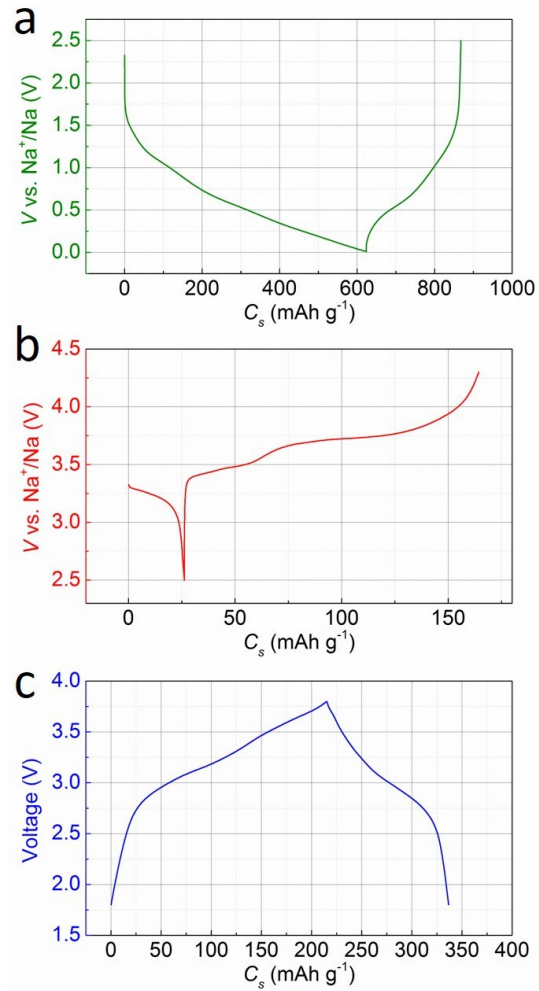


Fig. S5 (a) The first discharge-charge profile of the $\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}$ half cells with the voltage range of 0.01-2.5 V. (b) The first discharge-charge profile of the VOPO_4/Na half cells with the voltage range of 2.5-4.3 V. (c) The first charge-discharge profile of the $\text{Na}_2\text{Ti}_3\text{O}_7/\text{VOPO}_4$ based sodium ion full cells with the voltage range of 1.8-3.8 V.

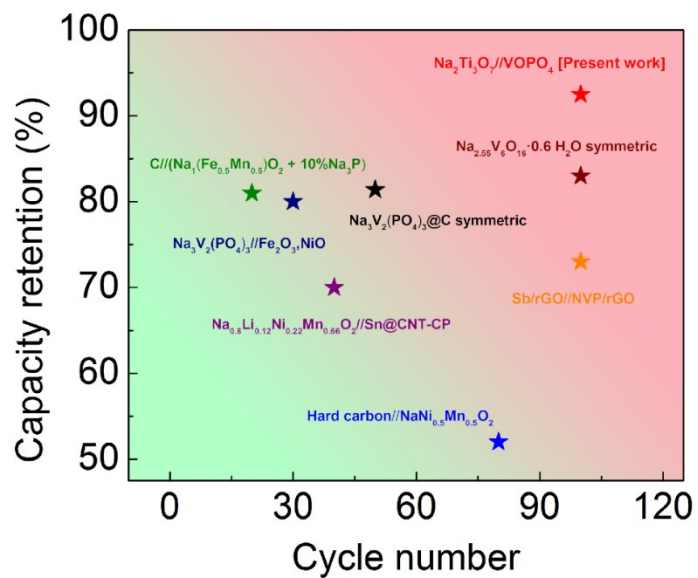


Fig. S6 The Sodium ion storage properties of the $\text{Na}_2\text{Ti}_3\text{O}_7//\text{VOPO}_4$ full cell and other recently reported literature.³⁻⁹

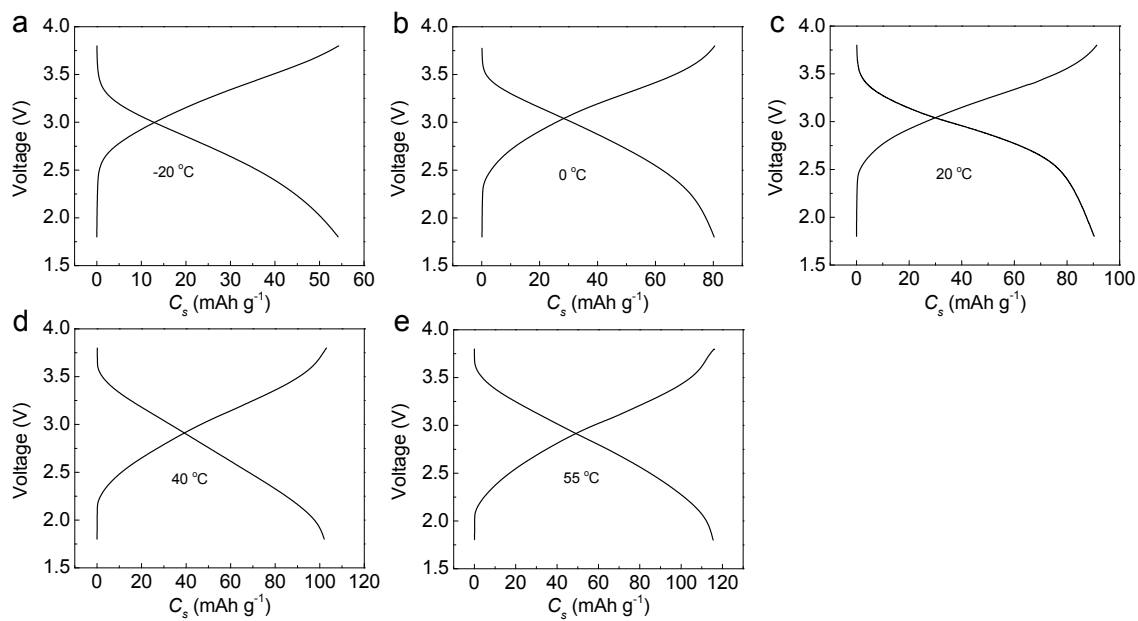


Fig. S7 Electrochemical performance of the $\text{Na}_2\text{Ti}_3\text{O}_7/\text{VOPO}_4$ based full cell tested at different temperatures at 1 C rate.

Table S1 The sodium storage properties for reported sodium full cells.

Configuration	Voltage [V]	Specific capacity [mAh g ⁻¹]	Cycle life (corresponded capacity retention)	(A)Symmetric
Na ₂ Ti ₃ O ₇ //VOPO ₄ (present work)	3.2	113.9	100 (92.4%)	asymmetric
C//(Na ₁ Fe _{0.5} Mn _{0.5} O ₂ + 10%Na ₃ P) ³	3.2	110	20 (81%)	asymmetric
Fe ₂ O ₃ ,NiO//Na ₃ V ₂ (PO ₄) ₃ ⁴	2.5	100	30 (80%)	asymmetric
Sn@CNT-CP //Na _{0.8} Li _{0.12} Ni _{0.22} Mn _{0.66} O ₂ ⁵	3.1	445 ^[a]	40 (70%)	asymmetric
Sb/rGO// Na ₃ V ₂ (PO ₄) ₃ /rGO ⁶	2	400 ^[a]	100 (73%)	asymmetric
Hard carbon//NaNi _{0.5} Mn _{0.5} O ₂ ⁷	3	120	80 (52%)	asymmetric
Na _{2.55} V ₆ O ₁₆ ·0.6H ₂ O ⁸	1.25	140	100 (83%)	symmetric
Na ₃ V ₂ (PO ₄) ₃ @C ⁹	1.7	90.9	50 (81.4%)	symmetric
Na _{0.8} Ni _{0.4} Ti _{0.6} O ₂ ¹⁰	2.8	82	150 (75%)	symmetric
Na _{0.66} Ni _{0.17} Co _{0.17} Ti _{0.66} O ₂ ¹¹	3.1	92	100 (94.8%)	symmetric
Hard carbon//NaNi _{0.5} Ti _{0.5} O ₂ ¹²	2.75	95	100 (72%)	asymmetric
Na ₃ V ₂ (PO ₄) ₃ /C //Na _{0.66} [Li _{0.22} Ti _{0.78}]O ₂ ¹³	2.5	98	--	asymmetric
Fe ₃ O ₄ //Na ₂ FeP ₂ O ₇ ¹⁴	2	90	--	asymmetric
Na _{1.0} Li _{0.2} Ni _{0.25} Mn _{0.75} O ₆ //TiO ₂ NT ¹⁵	1.8	78	--	asymmetric

[a] The specific capacity is calculated based on the mass of the anode materials, while the other data in the same column is calculated based on the mass of the cathode materials.

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