# **Supplementary Information**

## Conductive Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> networks to optimize Na<sub>3</sub>V<sub>2</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F cathode

### for improved rate capability and low temperature operation

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#### **Experimental section**

**Preparation of Na<sub>3</sub>V<sub>2</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F NPs.** 1 mmol of vanadyl acetylacetonate was dissolved into a mixed solution of ethanol and water (volume ratio of 1:1) with 30 min ultrasonic treatment. Then, 1.7 mmol NaF powder and 1.5 mmol H<sub>3</sub>PO<sub>4</sub> (85 wt%) were slowly added to the above solution under magnetic stirring. In an oil bath at 40 °C, the obtained solution was transferred into a 150 mL round-bottom flask connected with a spherical condenser under continuous stirring for 10 h. Finally, the product was collected by centrifugation, washed alternately with deionized water and ethanol, and vacuum dried at 80 °C for 6 h.

**Preparation of Ti**<sub>3</sub>**C**<sub>2</sub>**T**<sub>x</sub> **nanosheets.** Typically, 0.998 g LiF was added into 10 mL concentrated hydrochloric acid (12 M) and stirred until dissolved. Then, 1 g Ti<sub>3</sub>AlC<sub>2</sub> was slowly added to the above solution, and the mixture was magnetically stirred at 36 °C for 24 h. After the reaction, the acidic mixture was washed with deionized water by centrifugation at 3500 rpm for 5 min until the pH was above 6.0. Subsequently, the mixture was re-dispersed into deionized water and sonicated for 1 h in an ice bath under inert gas protection. Finally, the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheet suspension was collected by centrifugation at 3500 rpm for 1 h.

**Preparation of Na<sub>3</sub>V<sub>2</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>).** The obtained NVOPF nanoparticles (100 mg) were re-dispersed into 20 mL deionized water under magnetic stirring and then ultrasonic for 1 h until a uniformly blue solution was obtained. Then, 17 mL of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> suspension (2 mg mL<sup>-1</sup>) was added to the above solution, followed by sonicating for 1 h in an ice bath under inert gas protection. After that, the mixed solution was filtrated through a Celgard membrane. Finally, the product (NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) was obtained after drying overnight in a vacuum at room temperature. For comparison, 8.5 mL and 25.5 mL of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> suspension were added under the same conditions and denoted NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-L and NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-H, respectively.

**Preparation of NaTi2(PO4)3.** In a typical procedure, 3.4 mL tetrabutyl titanate and 10 mL concentrated ammonia was added to 40 mL of glycol and stirred for 1 h to form a

homogeneous milky white solution. Then, 15 mmol ammonium dihydrogen phosphate and 2.5 mmol sodium carbonate were added to the above solution and contiguously stirred to form a white gel. Subsequently, the gel was transferred to a Teflon-lined autoclave and kept at 150 °C for 24 h. The resultant precursor was then collected after freeze-drying. Finally, the final product was obtained by pre-annealing at 400 °C for 3 h and then calcination at 700 °C for 2 h under N<sub>2</sub> atmosphere with a heating rate of 2 °C min<sup>-1</sup>.

Material Characterizations. The crystal structure of samples was measured by X-ray powder diffraction (XRD, Bruker D8 Advance) with Cu-Kα radiation ( $\lambda \approx 0.154$  nm) at 40 kV and 40 mA. The morphology and structure of samples were obtained using a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) and transmission electron microscopy (TEM; JEOL JEM-2010) coupled with energydispersive spectroscopic (EDS) analysis. The specific surface area and pore size distribution of samples were measured using the Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods under N<sub>2</sub> physisorption at 77 K. The element valence information was obtained using UV-visible spectroscopy (UV-vis, HITACHI U4100). The molecular structure and chemical bonds were obtained using Fourier transform infrared spectroscopy (FTIR, Bruker VECTOR 22). The element content was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). Xray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250 spectrometer (Perkin–Elmer). The contact angle was measured by optical surface analyser (OSA 100).

**Electrochemical Measurements.** For half-cell testing, CR2025-type coin cells were assembled in a glove box filled with argon gas, and Na foil was used as the counter electrode. The cathode was prepared by mixing 70% active materials, 20% acetylene black and 10% sodium carboxymethyl cellulose binder (CMC) in water. The obtained mixture was coated on aluminum foil and dried in a vacuum oven at 60 °C and 120 °C for 12 h, respectively. The loading of active material was about 0.8-1.2 mg. The coin cell selects 1 M NaClO<sub>4</sub> in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 v/v

ratio) with 5% fluoroethylene carbonate (FEC) as the electrolyte and glass fiber (GD/C, Whatman) as the separator. All galvanostatic charge/discharge tests were recorded using a LAND CT2001A testing system. Cyclic voltammetry (CV) curves were tested on a CHI-760E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) is measured over a frequency range from 100 kHz to 10 mHz with an amplitude of 5 mV. The galvanostatic intermittent titration technique (GITT) was carried out by applying a pulsed current of 0.065 C for 20 min, followed by standing for 2 h in an open circuit state. In addition, it should be noted that the specific capacity of the electrodes is calculated based on the content of NVOPF due to its dominance in capacity.

To assemble the full cell, the anode was prepared by mixing  $NaTi_2(PO_4)_3$  powder, acetylene black and poly(vinylidene fluoride) (PVDF) in an N-methyl-2-pyrrolidone (NMP) solvent with a mass ratio of 8:1:1. Except for using copper foil as a collector, other conditions are consistent with the cathode preparation process. The mass loading of the anode is matched according to the reversible capacity of the cathode and anode. Generally, the capacity ratio of the cathode and anode is 1:1.2. For the  $NaTi_2(PO_4)_3$  half-cell, the electrochemical performance was tested in the voltage range of 1.00-3.00 V, where the current density 1 C represents 133 mA g<sup>-1</sup>. Finally, the assembled full cell was tested for galvanostatic charge/discharge in the voltage range of 0.50-3.00 V.

### **Supplementary Figures**



**Fig. S1** (a) XRD patterns of NVOPF NPs at different synthesis temperatures. (b) XRD patterns of  $Ti_3AlC_2$  and as-synthesized  $Ti_3C_2T_x$ .

In XRD pattern of  $Ti_3C_2T_x$ , the characteristic (002) peak shifted to the lower angles of 6.7°, accompanied by the disappeared (104) plane peak of  $Ti_3AlC_2$ . This indicates the successful synthesis of  $Ti_3C_2T_x$  nanosheets from the MAX phase.



**Fig. S2** FE-SEM images of (a and b) NVOPF NPs and (c) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. (d) TEM image of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.



Fig. S3 The initial three CV curves of pristine NVOPF electrode at 0.1 mV s<sup>-1</sup>.



Fig. S4 Cycling performance of  $Ti_3C_2T_x$  at 1 C (1 C=130 mA g<sup>-1</sup>).



Fig. S5 XRD patterns of NVOPF/ $Ti_3C_2T_x$  samples with different mass ratios.



Fig. S6 (a) Charge-discharge curves of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with different cycles at 1 C. (b) Charge-discharge curves of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> at different rates.



Fig. S7 Galvanostatic charge-discharge voltage profiles of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and NVOPF over the temperature range between 40 and -20  $^{\circ}$ C.



**Fig. S8** (a) The equivalent circuit for fitting different EIS spectra, where the  $R_s$  represents the resistance of the electrolyte between the electrodes, the  $R_{ct}$  represents charge transfer resistance, the CPE stands for a constant phase element related to the capacitive behavior of the electrodes, and the  $Z_w$  is a Warburg impedance related to ion diffusion. (b) Nyquist impedance plots of samples with different NVOPF contents.



**Fig. S9** GITT curves of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and NVOPF under (a) RT and (b) -20 °C. (c) The calculated  $D_{\text{Na}}^+$  of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and NVOPF from GITT of -20 °C.



Fig. S10 The voltage gaps extracted from related redox pairs of the first CV curves of NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and NVOPF recorded at 0.1 mV s<sup>-1</sup>.



**Fig. S11** (a) CV curves at different scan rates, (b) the linear relationship of log ( $I_p$ ) vs. log (v), and (c) capacitive contribution at 0.8 mV s<sup>-1</sup> of NVOPF.



Fig. S12 Contact angles of the electrolyte on (a) NVOPF/ $Ti_3C_2T_x$  and (b) NVOPF.



Fig. S13 XRD patterns of  $Ti_3C_2T_x$  before and after immersion in electrolyte.



**Fig. S14** (a) XRD pattern, (b) FE-SEM image, (c) cycling performance at 1 C, and (d) rate capability of the homemade  $NaTi_2(PO_4)_3$  anode (1 C=133 mA g<sup>-1</sup>).

Samples	NVOPF/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -H	NVOPF/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	NVOPF/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -L
Mass ratio (wt%)	82.3	71.7	62.4

 Table S1. The contents of NVOPF in different samples determined by ICP-OES.

**Table S2.** The  $R_{ct}$  values of samples with different NVOPF contents.

Samples	R <sub>ct</sub> (ohm)		
NPs	650.4		
NVOPF/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -H	528.8		
NVOPF/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	448.2		
NVOPF/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -L	305.4		
$Ti_3C_2T_x$	203.9		

Charge	$R_{\rm ct}$	Angle	Discharge	$R_{\rm ct}$	Angle
(V)	(ohm)	(degree)	(V)	(ohm)	(degree)
OCV	336.7	72.5	4.1	355.4	57.7
3.1	422.5	70.5	3.9	428.1	29.7
3.3	472.4	46.2	3.7	457.4	49.5
3.5	440.6	51.2	3.5	568.8	33.1
3.7	376.4	54.8	3.3	502.8	43.9
3.9	356.0	55.3	3.1	428.1	65.0
4.1	309.1	52.0	2.9	418.8	63.8
4.3	317.7	64.9	2.7	415.1	63.4
			2.5	414.1	60.7

**Table S3.** The fitted  $R_{ct}$  and the tilt angle values of the linear Warburg region for the NVOPF/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> during the initial charge/discharge process at various voltages.