

## Supporting information

### **In-situ Formation of $\text{NaTi}_2(\text{PO}_4)_3$ Cubes on $\text{Ti}_3\text{C}_2$ MXene for Dual-mode Sodium Storage**

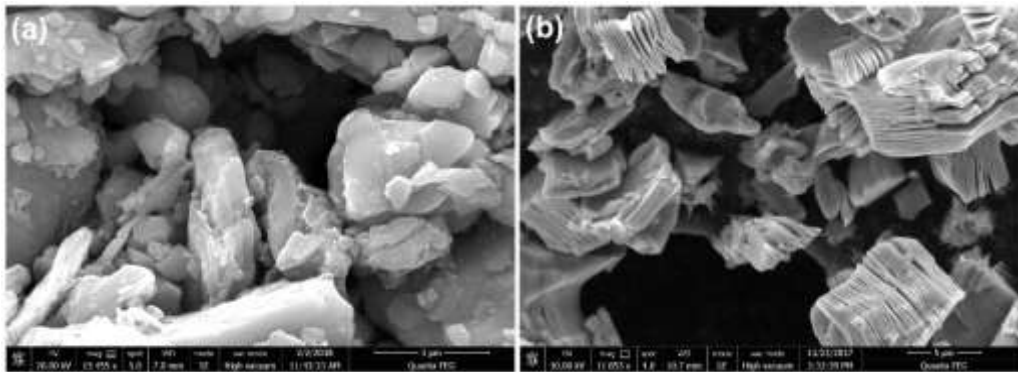
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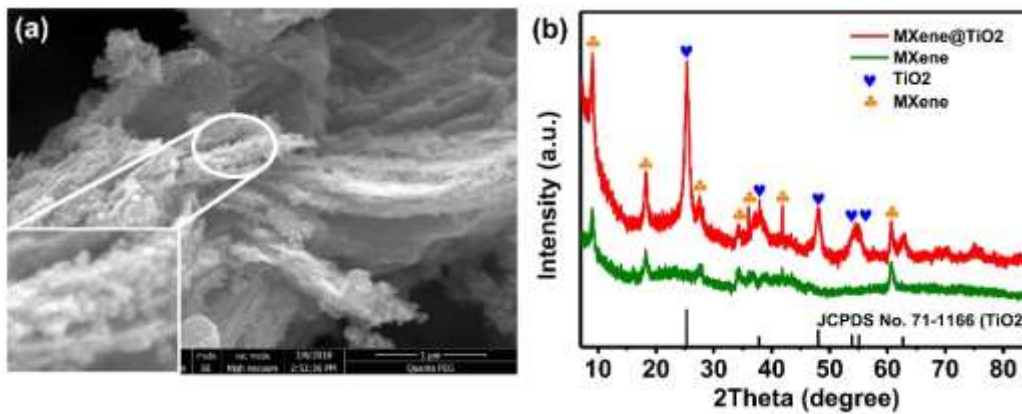
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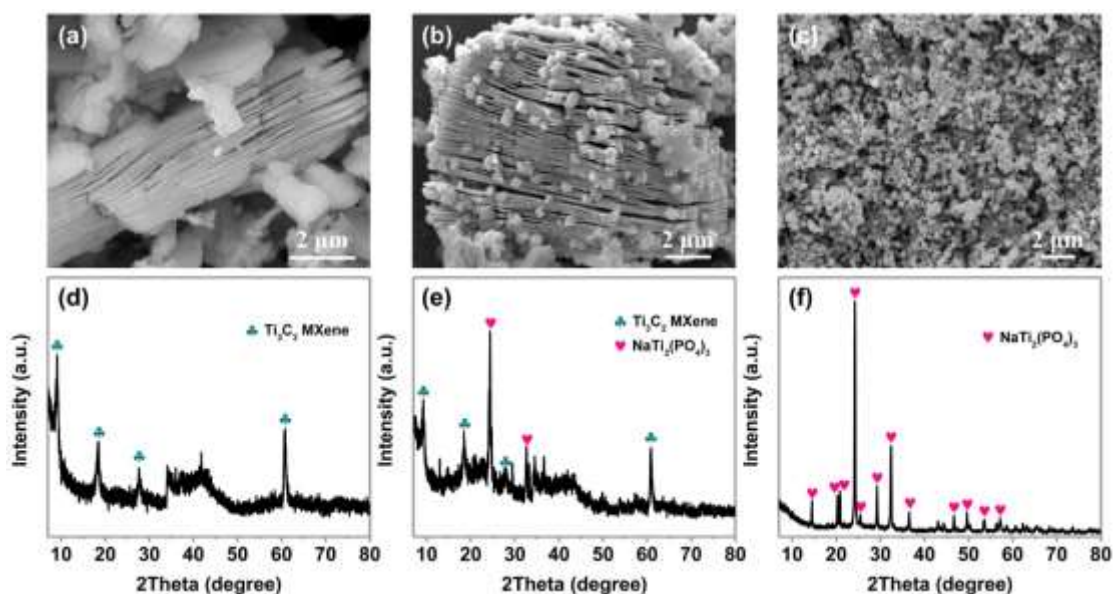
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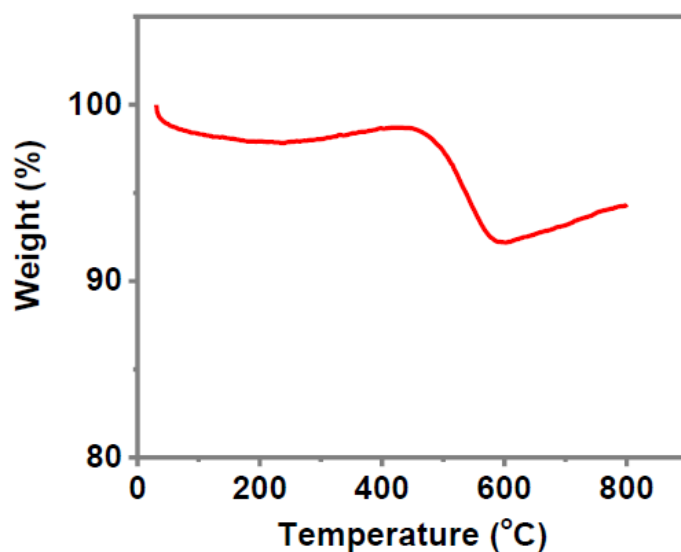
**Figure S1.** SEM images of layered Ti<sub>3</sub>AlC<sub>2</sub> MAX phase (a) and Ti<sub>3</sub>C<sub>2</sub> Mxene nanosheets (b) fabricated by a mature HF etching method.



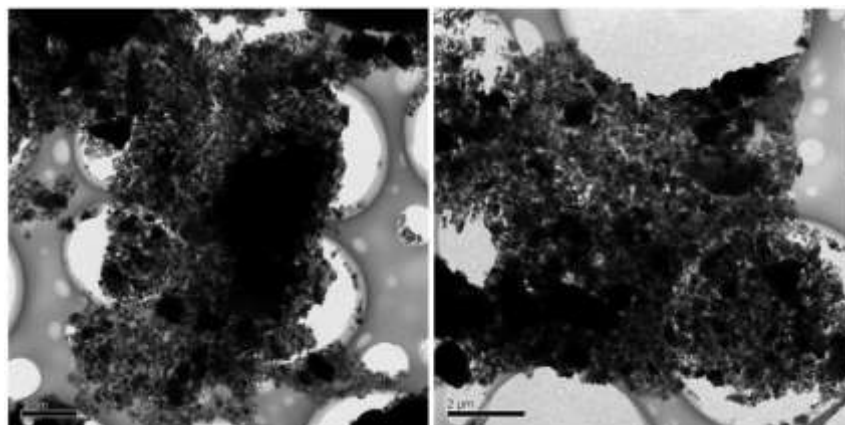
**Figure S2.** SEM image (a) and XRD pattern (b) of MXene@TiO<sub>2</sub> prepared by oxidizing MXene using H<sub>2</sub>O<sub>2</sub> without adding sodium acetate trihydrate and phosphoric acid. The SEM image reveals that large amounts of TiO<sub>2</sub> nanoparticles in-situ appear in nanogaps between the adjacent MXene nanosheets. The coexistence of characteristic peaks of both MXene and TiO<sub>2</sub> in the XRD pattern further verifies the formation of TiO<sub>2</sub> on MXene nanosheets.



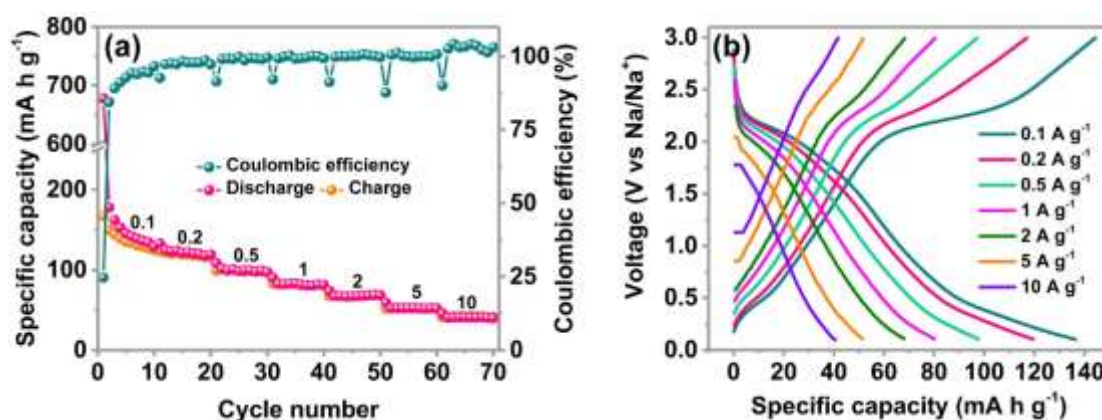
**Figure S3.** Morphology and composition transition from neat MXene (zero transformation rate) to MXene@NTP-L (low transformation rate) and NTP-C (100% transformation rate). SEM image and XRD data of neat MXene (a, d); SEM image and XRD data of MXene@NTP-L (b, e); SEM image and XRD data of neat NTP (c, f).



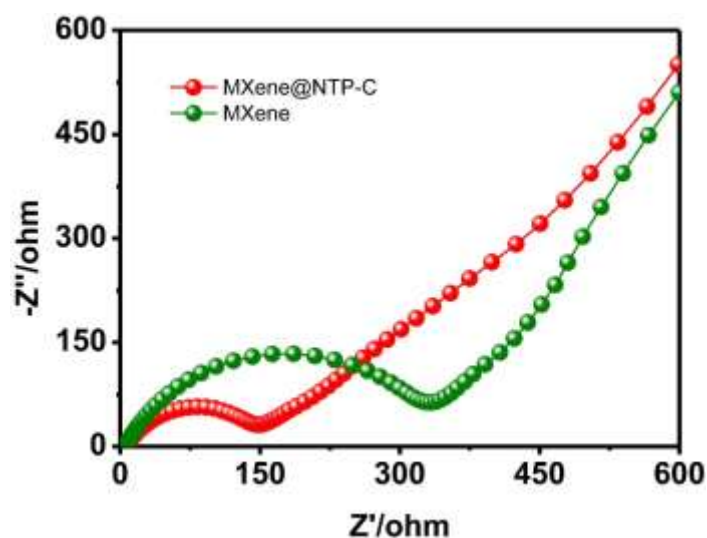
**Figure S4.** Thermal gravimetric analysis of MXene@NTP-C in oxygen, which suggests that the carbon layer accounts for about 8 wt% of the whole weight of MXene@NTP-C. The tiny increase of weight after 600 °C is attributed to the oxidation of  $\text{Ti}_3\text{C}_2$  MXene by oxygen.



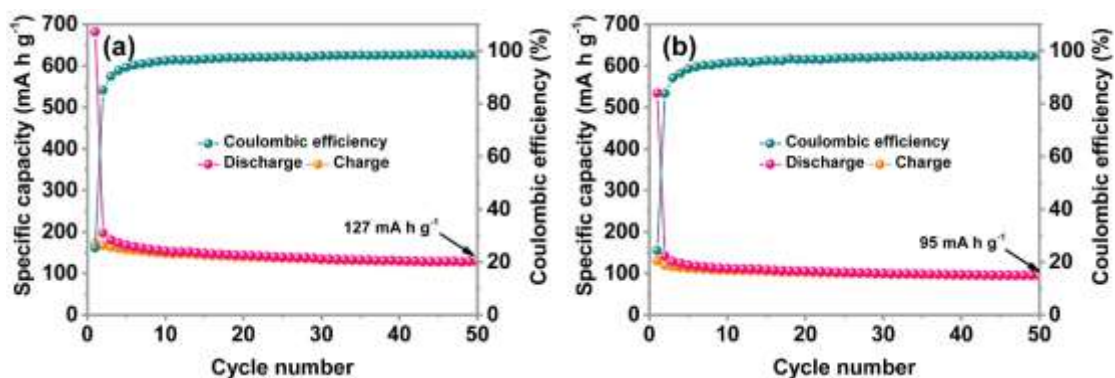
**Figure S5.** TEM images of MXene@NTP-C nanohybrids with a sheet-like topological structure decorated by enormous  $\text{NaTi}_2(\text{PO}_4)_3$  cubes. It should be noted that the ultrasonic exfoliation must be conducted to decrease the thickness of MXene@NTP-C hybrids before TEM observation.



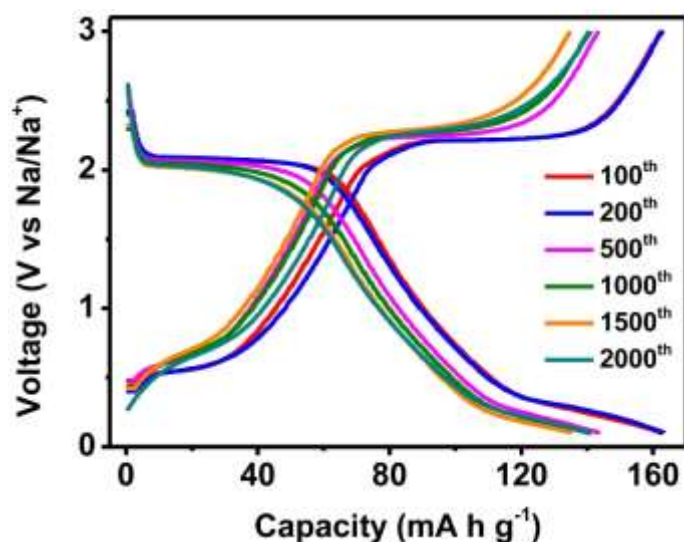
**Figure S6.** Rate capabilities (a) and the corresponding discharge-charge curves (b) of MXene@NTP without carbon coating. It is obviously that MXene@NTP showed a lower specific capacities at current densities of 0.1-10  $\text{A g}^{-1}$ . This phenomena can be illustrated by the shortened voltage platforms caused by the inferior conductivity without carbon coating.



**Figure S7.** Nyquist plots of MXene@NTP-C and the original MXene, and their expanded high-frequency regions. The semicircle with a much smaller radius at the high-frequency region suggests that MXene@NTP-C electrode exhibits much lower charge transfer resistance compared to that of MXene.



**Figure S8.** Cycle performance at the current density of  $0.1 \text{ A g}^{-1}$  of NTP-C (neat  $\text{NaTi}_2(\text{PO}_4)_3$ ) (a) and the mixture of MXene and NTP-C (b). Both NTP-C and the simple mixture show lower specific capacities than MXene@NTP-C



**Figure S9.** Discharge/charge profiles of MXene@NTP-C from the 100<sup>th</sup> to the 2000<sup>th</sup> cycle at a current density of 1 A g<sup>-1</sup>.

**Table S1.** Comparison of current density, specific capacity, and lifespan between this work and the related ones in previous literature.

Sample	Current density (mA g <sup>-1</sup> )	Specific capacity (mA h g <sup>-1</sup> )	Lifespan (cycles)	Reference
MXene@NTP-C	1,000	143	2,000	This work
	5,000	109	10,000	
NaTi <sub>1.5</sub> O <sub>8.3</sub> nanoribbons	200	136	150	Ref. <sup>1</sup>
Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> nanosheets	1,000	130	1,000	Ref. <sup>2</sup>
Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> nanotubes	354	108	100	Ref. <sup>3</sup>
Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> /C	178	112	100	Ref. <sup>4</sup>
TiO <sub>2</sub>	50	150	600	Ref. <sup>5</sup>
TiO <sub>2</sub> /graphene	500	120	4,300	Ref. <sup>6</sup>
B-doped TiO <sub>2</sub>	660	150	400	Ref. <sup>7</sup>
N-doped TiO <sub>2</sub>	3,350	110	500	Ref. <sup>8</sup>
Na <sub>0.23</sub> TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub>	2,000	56	4,000	Ref. <sup>9</sup>
Ti <sub>2</sub> C MXene	20	142	100	Ref. <sup>10</sup>
Ti <sub>3</sub> C <sub>2</sub> MXene	200	68.3	1,000	Ref. <sup>11</sup>

## Reference

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