## Tunable Pseudocapacitance Storage of MXene by Cation Pillaring for High-Performance Sodium Ion Capacitors

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Fig. S1 Energy dispersive spectroscopy of (a) Ti<sub>3</sub>C<sub>2</sub>, (b) Li-Ti<sub>3</sub>C<sub>2</sub>, (c) Na-Ti<sub>3</sub>C<sub>2</sub>, (d) K-Ti<sub>3</sub>C<sub>2</sub>, (e) Na-Ti<sub>3</sub>C<sub>2</sub>-450, (f) Na-Ti<sub>3</sub>C<sub>2</sub>-700.



Fig. S2a (a-e) SEM image of Ti<sub>3</sub>C<sub>2</sub> and elemental mapping of Ti, C, O and F, which confirm the homogeneously distribution of –OH and –F groups in all MXene sheets.



Fig. S2b (a-e) SEM image of Li-Ti<sub>3</sub>C<sub>2</sub> and elemental mapping of Ti, C, O and F. After Li<sup>+</sup> pillaring, the –F groups was replaced by –OH due to the decrease intensity of the F signal and the increase intensity of the O signal compared with those in Ti<sub>3</sub>C<sub>2</sub>, while the signal of Li can't be detected by EDS.



Fig. S2c (a-f) SEM image of Na-Ti<sub>3</sub>C<sub>2</sub> and elemental mapping of Ti, C, O, F, and Na, which confirm the homogeneous distribution of Na in all MXene sheets. After Na<sup>+</sup> pillaring, the -F groups was replaced by -OH due to the decrease intensity of the F signal and the increase intensity of the O signal compared with those in Ti<sub>3</sub>C<sub>2</sub>.



Fig. S2d (a-f) SEM image of K-Ti<sub>3</sub>C<sub>2</sub> and elemental mapping of Ti, C, O, F, and K, which confirms the homogeneous distribution of K in all MXene sheets. After K<sup>+</sup> pillaring, the –F groups was replaced by –OH due to the decrease intensity of the F signal and the increase intensity of the O signal compared with those in Ti<sub>3</sub>C<sub>2</sub>.



Fig. S2e (a-f) SEM image of Na-Ti<sub>3</sub>C<sub>2</sub>-450 and elemental mapping of Ti, C, O, F, and Na, which confirms the homogeneous distribution of Na in all MXene sheets after calcinations at 450 °C. The O signal decreased compared with Na-Ti<sub>3</sub>C<sub>2</sub>.



Fig. S2f (a-f) SEM image of Na-Ti<sub>3</sub>C<sub>2</sub>-700 and elemental mapping of Ti, C, O, F, and Na, which confirms the homogeneous distribution further of Na in all MXene sheets after calcinations at 700 °C. The O signal decreased further compared with Na-Ti<sub>3</sub>C<sub>2</sub>-450.



Fig. S3 (a, b) Surface wetting of the water droplet on the Li-Ti<sub>3</sub>C<sub>2</sub>, K-Ti<sub>3</sub>C<sub>2</sub>.



Fig. S4 The galvanostatic charge/discharge profiles of (a) Ti<sub>3</sub>C<sub>2</sub>, (b) Li-Ti<sub>3</sub>C<sub>2</sub>, (c) Na-Ti<sub>3</sub>C<sub>2</sub>, (d) K-Ti<sub>3</sub>C<sub>2</sub>, (e) Na-Ti<sub>3</sub>C<sub>2</sub>-450, and (f) Na-Ti<sub>3</sub>C<sub>2</sub>-700 at a current density of 0.1 A g<sup>-1</sup>.



Fig. S5 CV curves of (a)  $Ti_3C_2$ , (b) Li- $Ti_3C_2$ , (c) K- $Ti_3C_2$ , (d) Na- $Ti_3C_2$ -450, and (e) Na- $Ti_3C_2$ -700 at 0.1 mV s<sup>-1</sup>.



Fig. S6 (a-c) CV curves of Li-Ti<sub>3</sub>C<sub>2</sub>, K-Ti<sub>3</sub>C<sub>2</sub>, and Na-Ti<sub>3</sub>C<sub>2</sub>-700 electrodes at different scan rates. (d-f) Capacitive and diffusion currents (blue) contributed to charge storage of Li-Ti<sub>3</sub>C<sub>2</sub>, K-Ti<sub>3</sub>C<sub>2</sub>, and Na-Ti<sub>3</sub>C<sub>2</sub>-700 at a scan rate of 2.0 mV s<sup>-1</sup>. (g-i) The percentage of capacitance contribution of Li-Ti<sub>3</sub>C<sub>2</sub>, K-Ti<sub>3</sub>C<sub>2</sub>, and Na-Ti<sub>3</sub>C<sub>2</sub>-700 at different scan rates (0.1-2.0 mV s<sup>-1</sup>).



Fig. S7 Ex situ XPS studies for the  $Ti_3C_2$ . (a) The ex situ XPS spectra of the Ti 2p peaks to survey the changes in valence states of Ti during the sodiation and de-sodiation processes about  $Ti_3C_2$ . (b) Voltage profiles of  $Ti_3C_2$  in different states of sodiation/desodiation at which the samples were taken for ex situ XPS test. (c) The Ti 2p peaks of  $Ti_3C_2$  samples at pristine state, 0.01 V discharge state, 3.0 V charge state.



Fig. S8 (a) The CV Curves of AC at different scan rates between 3.0-4.2V. (b) The charge-discharge curves of AC at 0.2 A  $g^{-1}$  between 3.0-4.2V. (c) The cycling performance of AC at 0.2 A  $g^{-1}$  between 3.0-4.2V.