Supporting Information

Improved sodium-ion storage performance of $Ti_3C_2T_x$ MXene by sulfur doping

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Supplementary figures

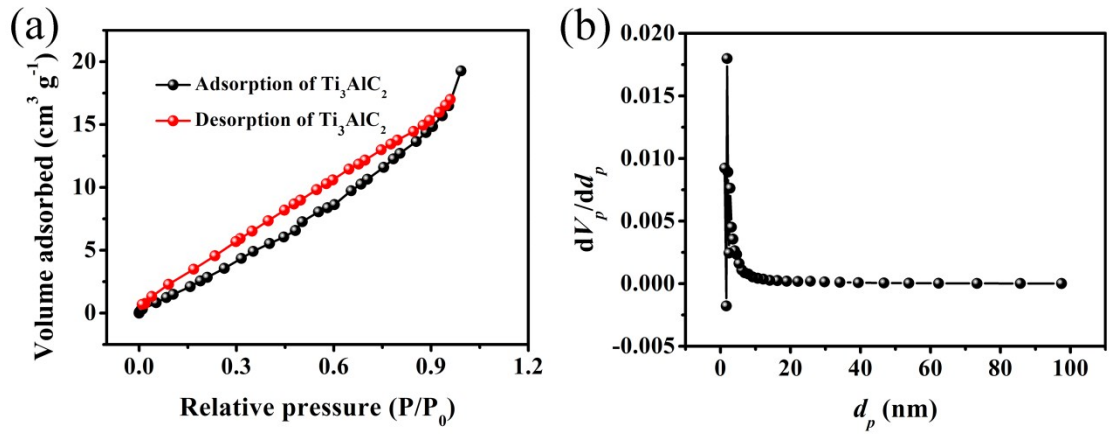

Fig. S1 N_2 adsorption/desorption isotherms (a) and pore size distribution (b) of Ti_3AlC_2.

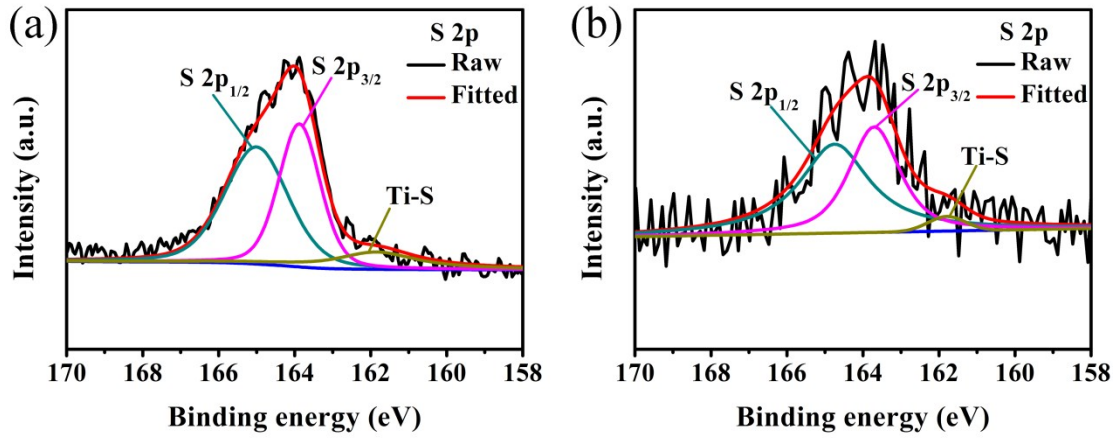

Fig. S2 High-resolution S 2p spectra of ST-1 (a) and ST-2 (b).

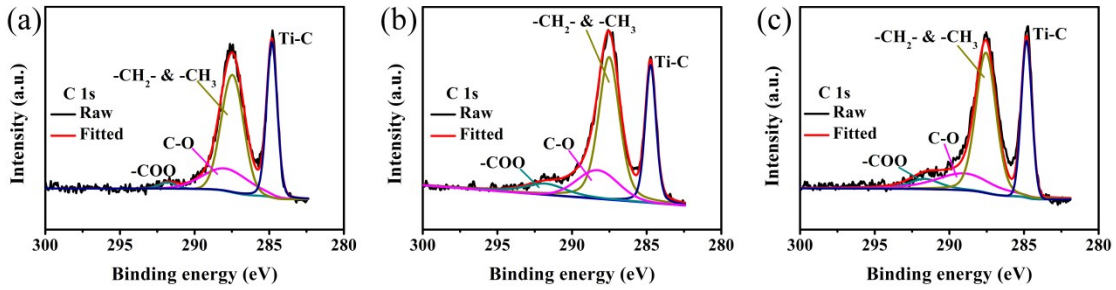

Fig. S3 High-resolution C 1s spectra of $Ti_3C_2T_x$ (a), ST-1 (b) and ST-2 (c).

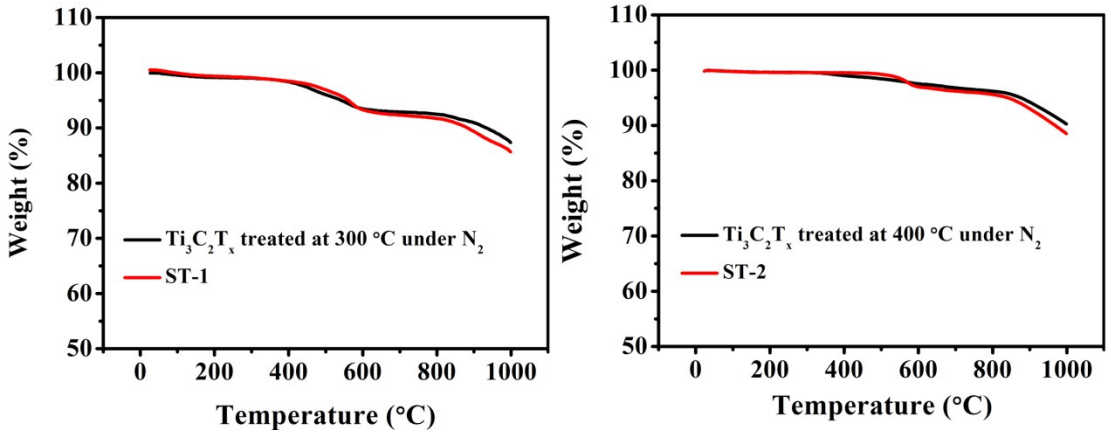

Fig. S4 TG analysis: (a) $Ti_3C_2T_x$ thermally treated at 300 °C under N_2 for 3 h and ST-1; $Ti_3C_2T_x$ thermally treated at 400 °C under N_2 for 3 h and ST-2.

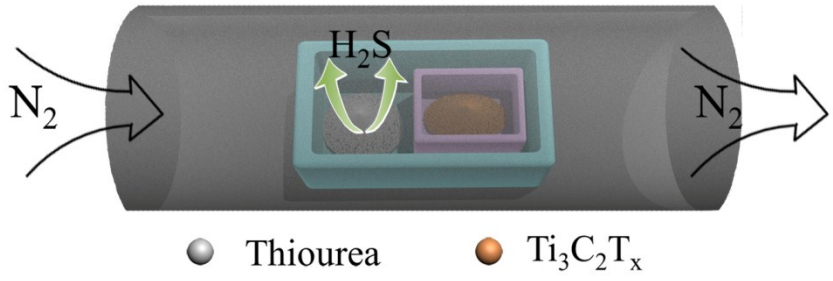

Fig. S5 The preparation process of S-doped $Ti_3C_2T_x$ from $Ti_3C_2T_x$: During the thermal treatment under N_2, H_2S generated from the decomposition of thiourea reacts with $Ti_3C_2T_x$, resulting in the formation of S-doped $Ti_3C_2T_x$.

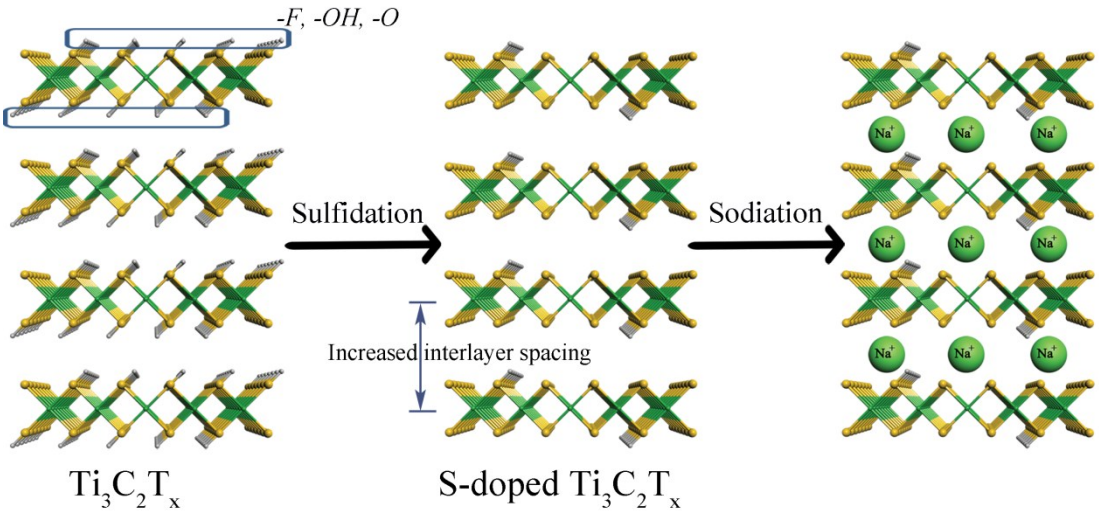

Fig. S6 Schematic illustration of the solidation process of S-doped $Ti_3C_2T_x$.

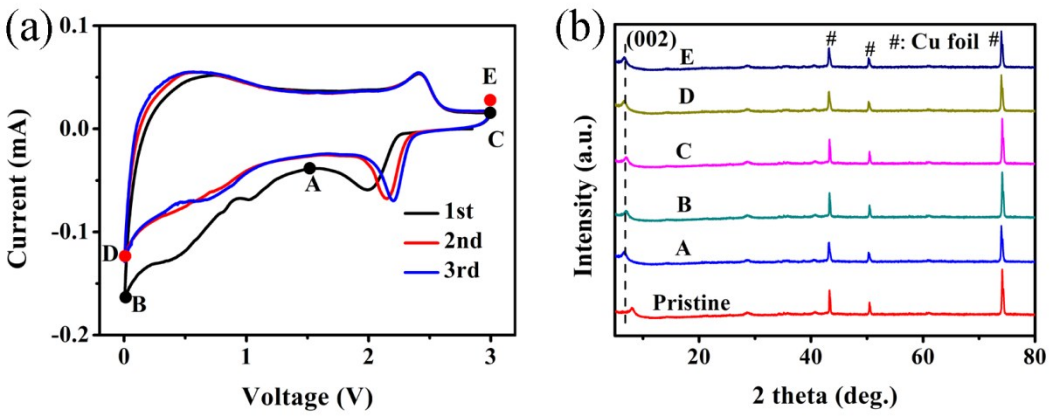

Fig. S7 (a) CV curves of ST-1 from 3 to 0.005 V at 0.2 mV s^{-1}. (b) Ex-situ XRD patterns during CV cycles: A (discharged to 1.5 V in the first cycle), B (discharged to 0.005 V in the first cycle), C (charged to 3.0 V in the first cycle), D (discharged to 0.005 V in the second cycle), E (charged to 3.0 V in the second cycle).

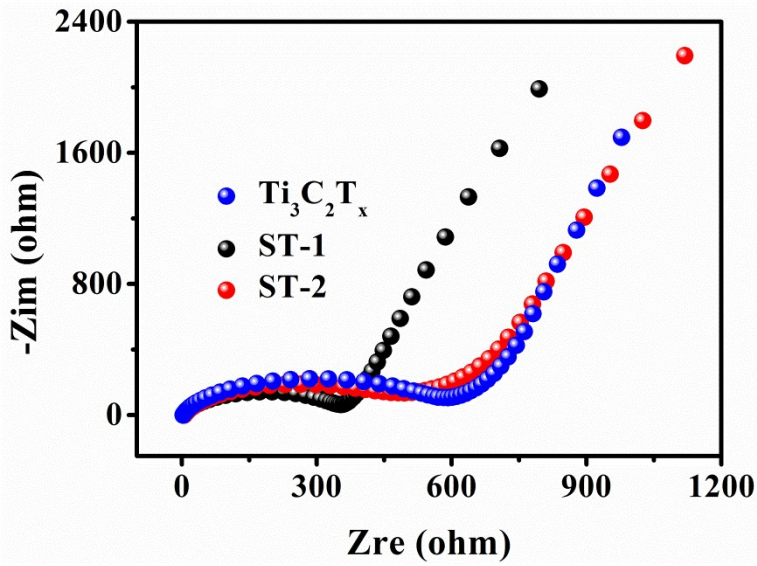

Fig. S8 Nyquist plots of $Ti_3C_2T_x$, ST-1 and ST-2 before cycling.

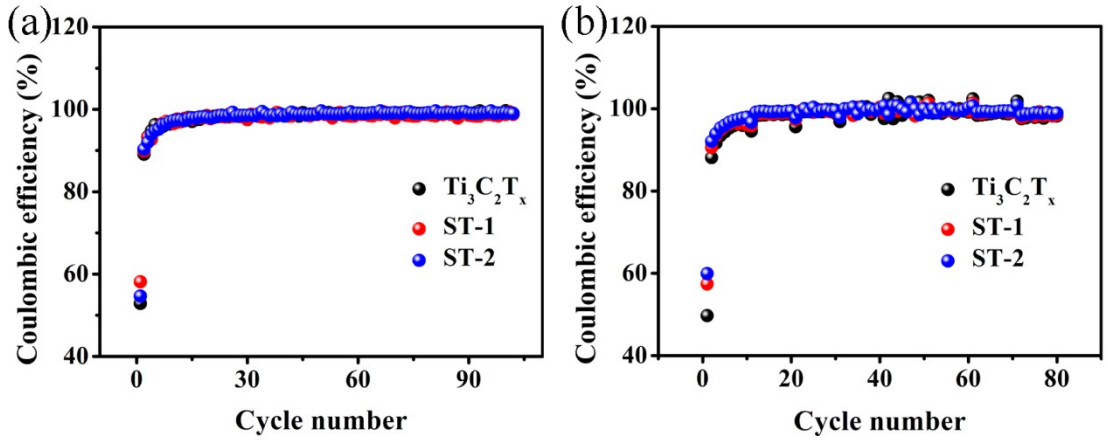

Fig. S9 Coulombic efficiencies at 0.1 A g^{-1} (a) and rate performances (b) of $Ti_3C_2T_x$, ST-1 and ST-2.

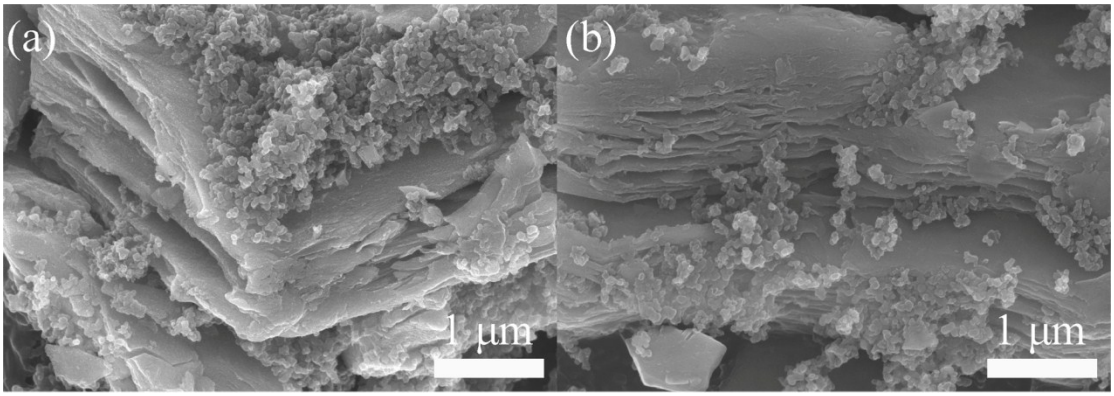

Fig. S10 FESEM images of $Ti_3C_2T_x$ (a) and ST-1 (b) after 100 cycles at 0.1 A g^{-1}.

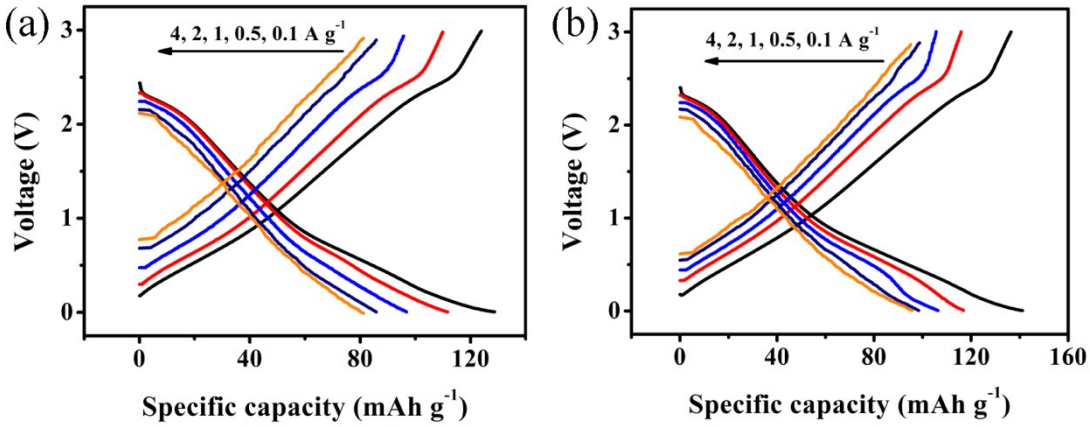

Fig. S11 Discharge/charge profiles of $Ti_3C_2T_x$ (a) and ST-2 (b) at different current densities.

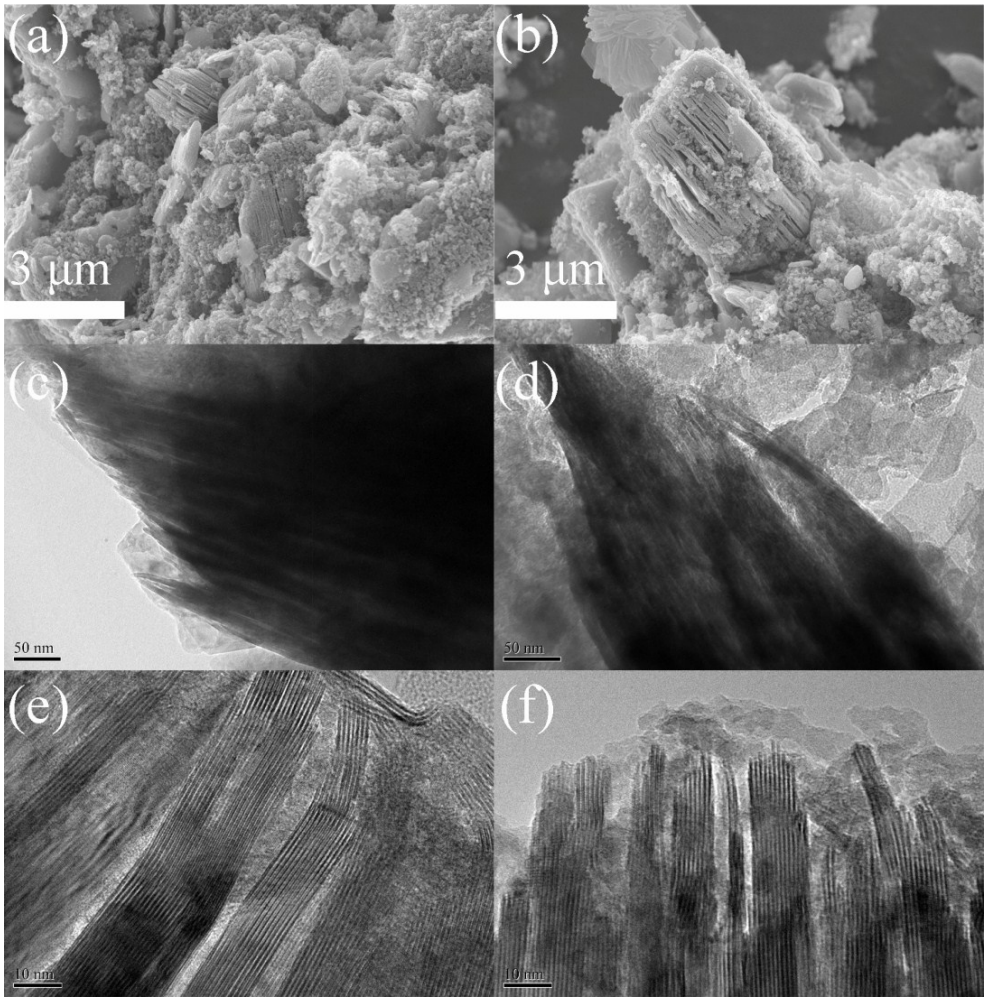

Fig. S12 FESEM, TEM and HRTEM images of $Ti_3C_2T_x$ (a, c and e) and ST-1 (b, d, and f) electrodes after 2000 cycles at 0.5 A g^{-1}.

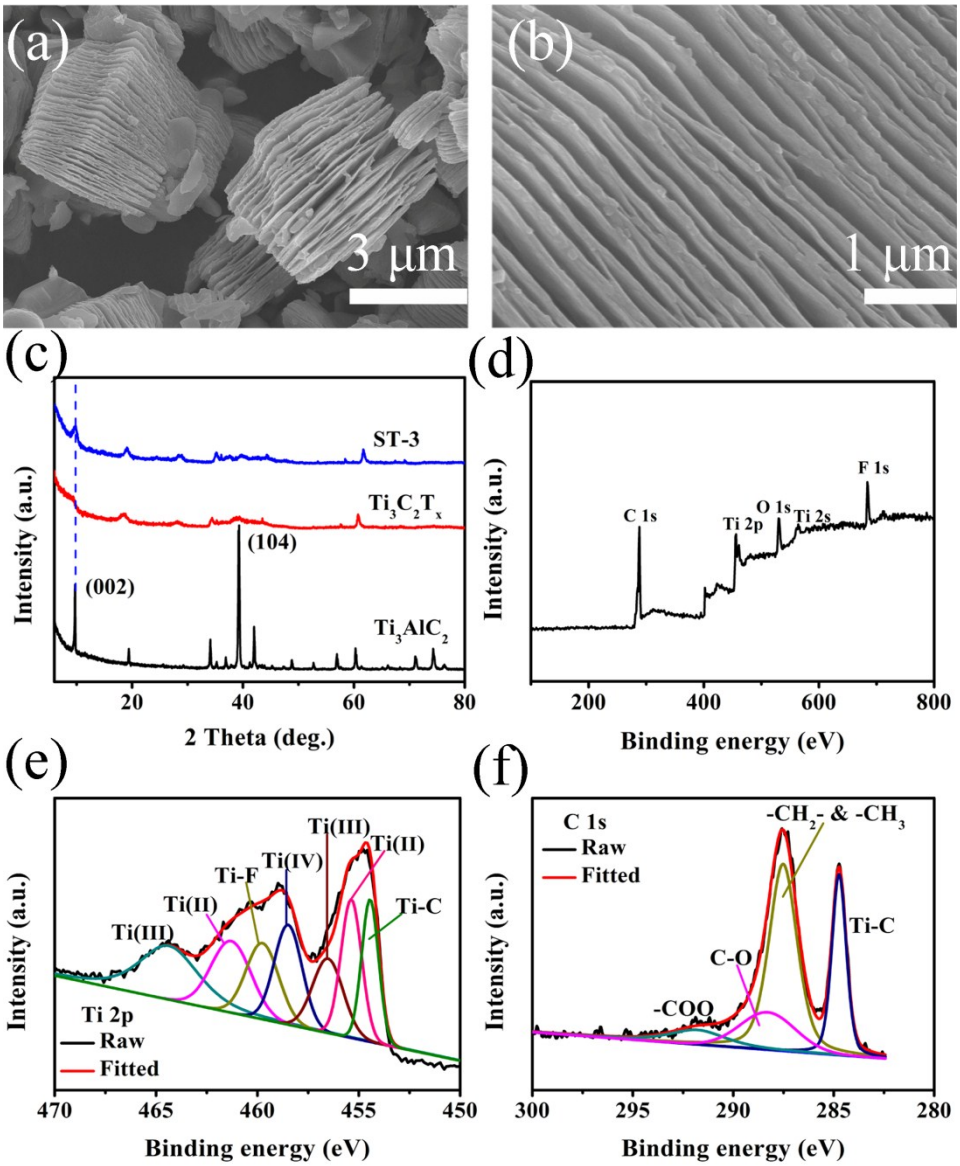

Fig. S13 FESEM images of ST-3 (a and b). XRD patterns of Ti_3AlC_2, $Ti_3C_2T_x$ and ST-3 (c). XPS spectrum (d) and corresponding high-resolution Ti 2p (e) and C 1s (f) spectra of ST-3.

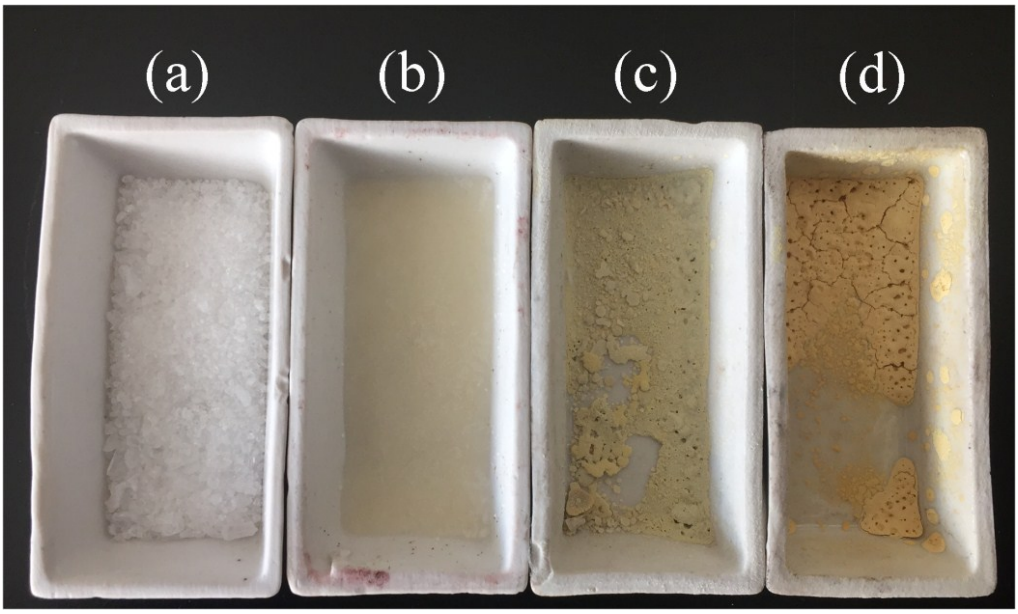

Fig. S14 Comparison of commercial thiourea (2 g, a) after thermal treatment under N_2 at 200 °C (b), 300 °C (c) and 400 °C (d) for 3 h with a heating rate of 2 °C min^{-1}.

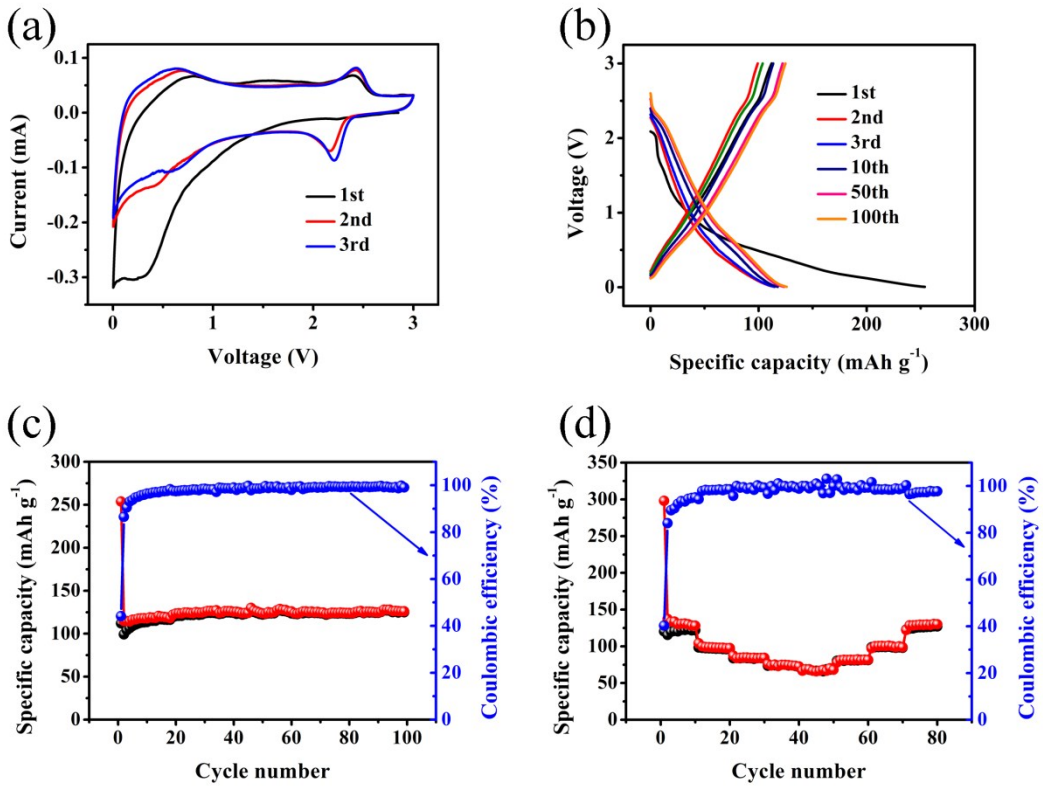

Fig. S15 Sodium storage performance of ST-3: (a) CV curves from 3 to 0.005 V at a scan rate of 0.2 mV s^{-1}. (b) Discharge/charge profiles at 0.1 A g^{-1}. (c) Cycle performance at 0.1 A g^{-1}. (d) Rate performance.

Table S1 Pore parameters of Ti_3AlC_2, $Ti_3C_2T_x$, ST-1 and ST-2.

Sample	Pore parameters		
	Specific surface area ($cm^2\ g^{-1}$)	Average pore size (nm)	Pore volume ($cm^3\ g^{-1}$)
Ti_3AlC_2	10.802	6.284	0.02953
$Ti_3C_2T_x$	83.061	24.362	0.5059
ST-1	57.983	29.101	0.4218
ST-2	29.879	24.393	0.1709

Table S2 Atomic concentration (at.%) of elements detected from XPS measurement for $Ti_3C_2T_x$, ST-1 and ST-2 and ST-3.

Samples	Ti	C	S	O	F
$Ti_3C_2T_x$	19.8	41.08	-	23.65	15.48
ST-1	20.1	36.94	4.01	29.09	9.86
ST-2	20.2	35.65	1.89	35.42	6.84
ST-3	19.8	39.92	-	28.86	11.32

Table S3 Comparison of sodium storage performance of ST-1 with other $Ti_3C_2T_x$ based anodes.

Sample	Voltage range (V)	Cycling performance	Long-term cycling performance at high current density	Ref.
Multilayered $Ti_3C_2T_x$ MXene	0.01-2.5	About 100 mAh g^{-1} after 100 cycles at 0.05 A g^{-1}	68.3 mAh g^{-1} after 1000 cycles at 0.2 A g^{-1}	1
Ti_2CT_x MXene	0.1-3.0	142 mAh g^{-1} after 100 cycles at 0.02 A g^{-1}	/	2
$Ti_3C_2T_x$ MXene/CNT paper	0.01-3.0	175 mAh g^{-1} after 100 cycles at 0.02 A g^{-1}	/	3

$Ti_3C_2T_x$ MXene	0.1-3.0	100 mAh g^{-1} after 100 cycles at 0.02 A g^{-1}	/	4
$Ti_3C_2T_x$ MXene derived $NaTi_{1.5}O_{8.3}$	0.01-3.0	136 mAh g^{-1} after 150 cycles at 0.2 A g^{-1}	/	5
S-doped $Ti_3C_2T_x$ MXene	0.005-3.0	183.2 mAh g^{-1} after 100 cycles at 0.1 A g^{-1}	138.2 mAh g^{-1} after 2000 cycles at 0.5 A g^{-1}	This work

References

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3. X. Xie, M.-Q. Zhao, B. Anasori, K. Maleski, C. E. Ren, J. Li, B. W. Byles, E. Pomerantseva, G. Wang and Y. Gogotsi, *Nano Energy*, 2016, **26**, 513-523.
4. Y. Xie, Y. Dall'Agnese, M. Naguib, Y. Gogotsi, M.W. Barsoum, H.L. Zhuang, P.R.C. Kent, *ACS Nano*, 2014, **8**, 9606-9615.
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