Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2022

Electronic Supplementary Information

Submicron Ti_2CT_x MXene Particulates as High-Rate Intercalation Anode Materials for Li-Ion Batteries

Cong Cui,[ab] Ruqiao Dai,[ab] Chao Zhang,[a] Bingbing Fan[c] and Xiaohui Wang*[a]

[a.] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China.*

[b.] *School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, China.*

[c.] *School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China*

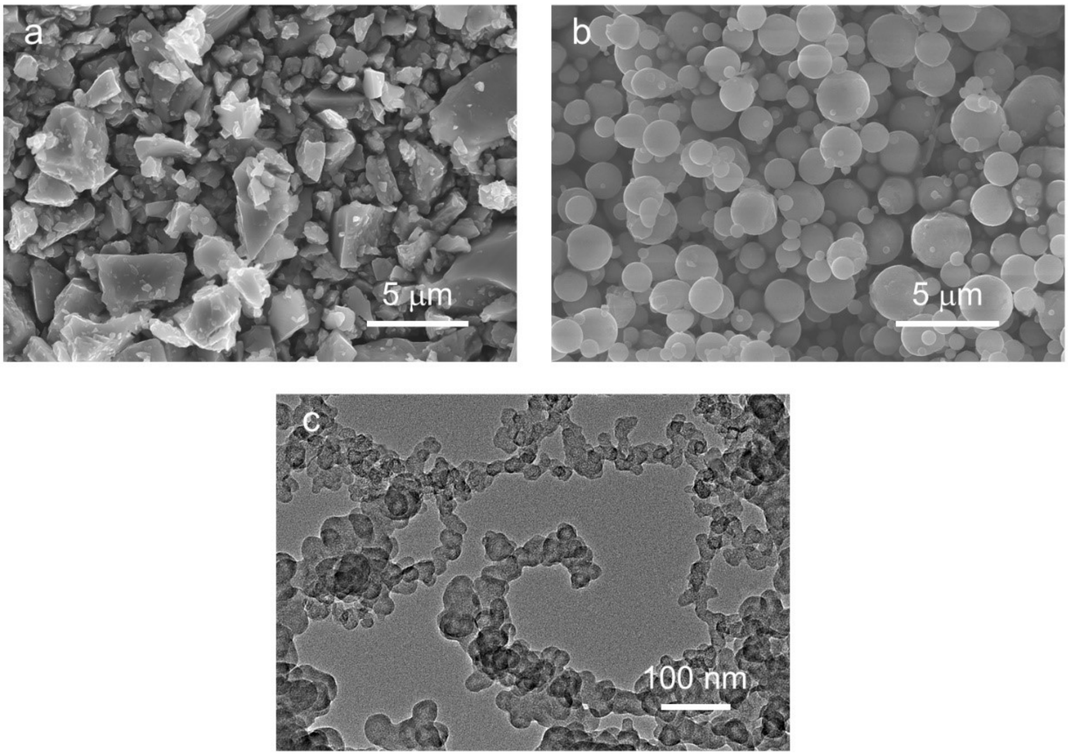

Fig. S1. SEM images of (a) TiH_2 and (b) Al and TEM image of (c) carbon black.

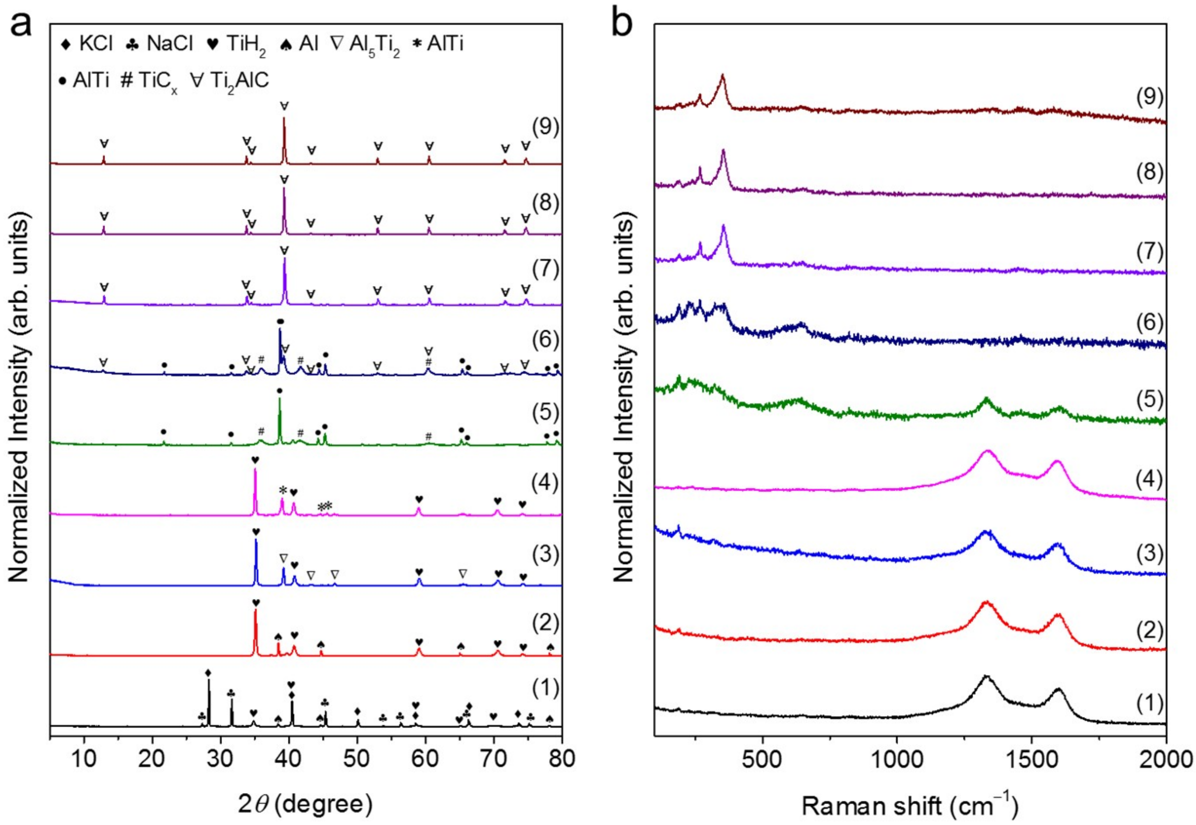

Fig. S2. (a) XRD patterns and (b) Raman spectra of samples. The numbers represent the (1) pristine mixed powder and the samples synthesized at (2) 500°C for 1 h, (3) 600°C for 1 h, (4) 700 °C for 1 h, (5) 800 °C for 1 h, (6) 900 °C for 1 h, (7) 1000 °C for 1 h, (8) 1000 °C for 3 h, and (9) 1000 °C for 5 h.

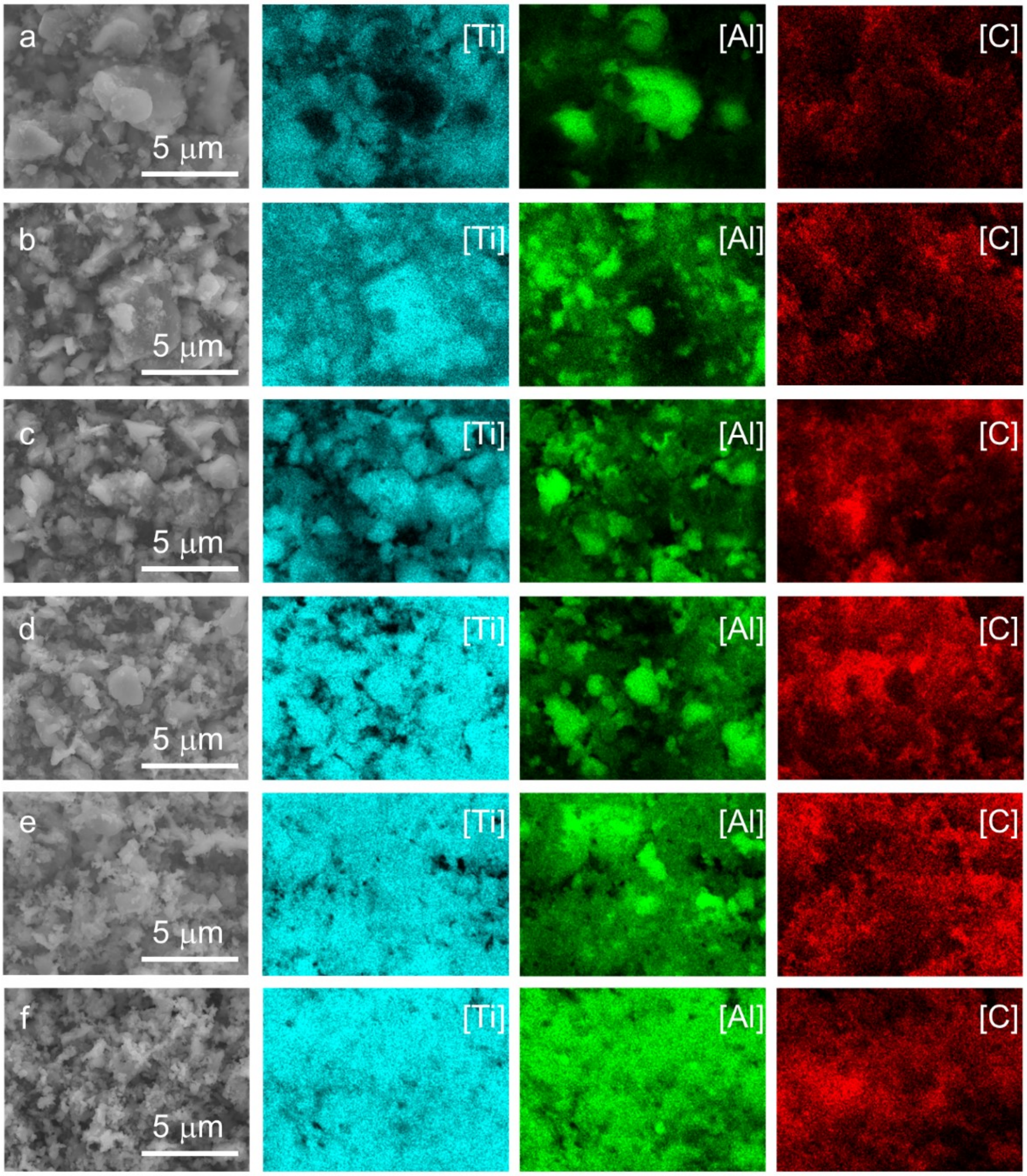

Fig. S3. SEM images and corresponding EDS mappings of the samples synthesized at (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, and (f) 1000 °C for 1 h.

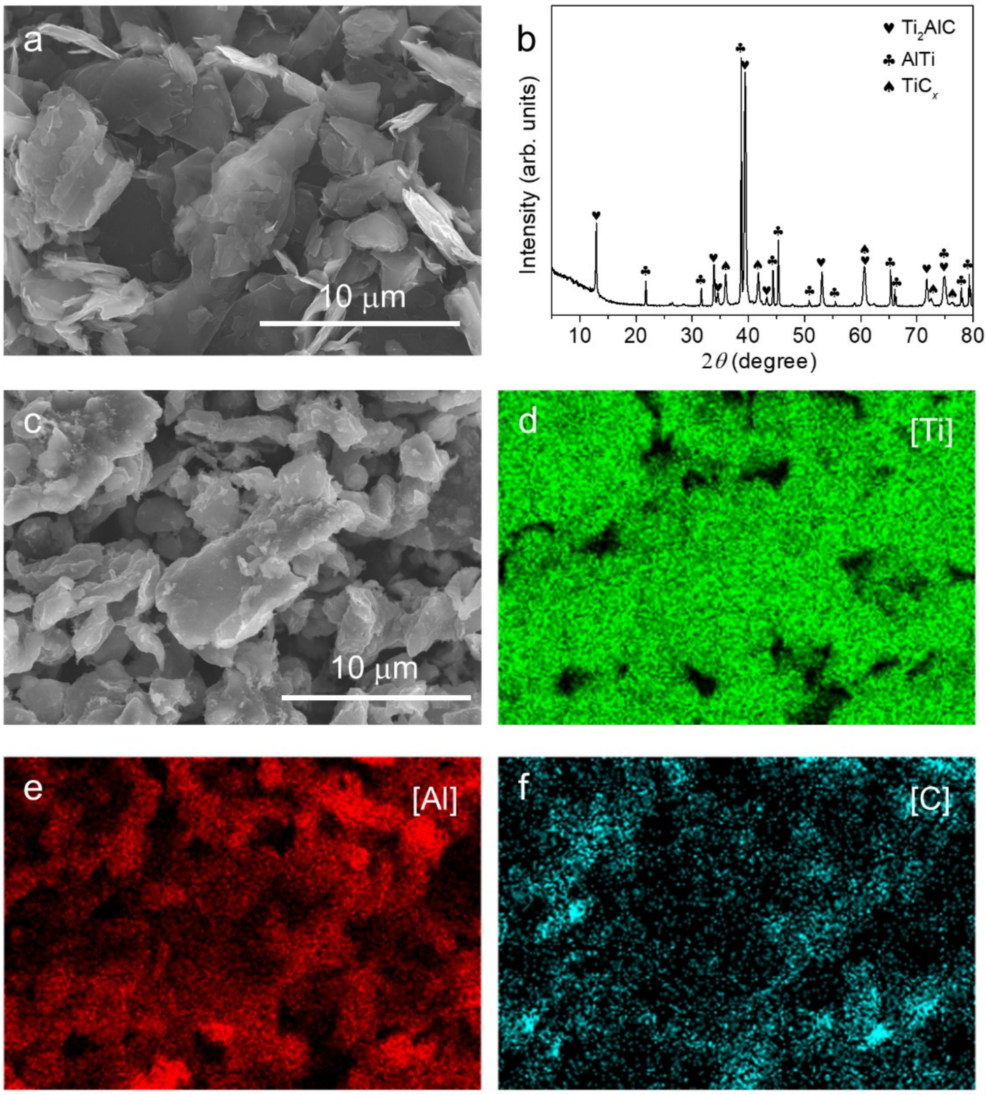

Fig. S4. (a) SEM image of micron graphite, (b) XRD pattern of the sample synthesized at 1000 °C for 1 h using micron graphite as carbon source, (c) SEM image of the as-prepared sample and corresponding EDS mapping results of (d) Ti, (e) Al, and (f) C

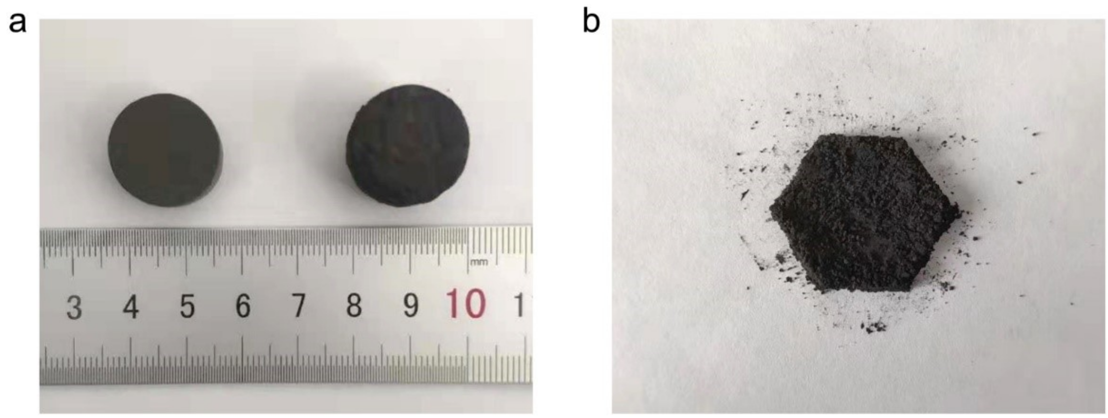

Fig. S5. Optical photographs of (a) cold-isostatic-pressing-treated reactant before (left) and after (right) heating at 1000 °C for 1 h, and (b) Ti_2AlC powder synthesized at 1000 °C for 1 h.

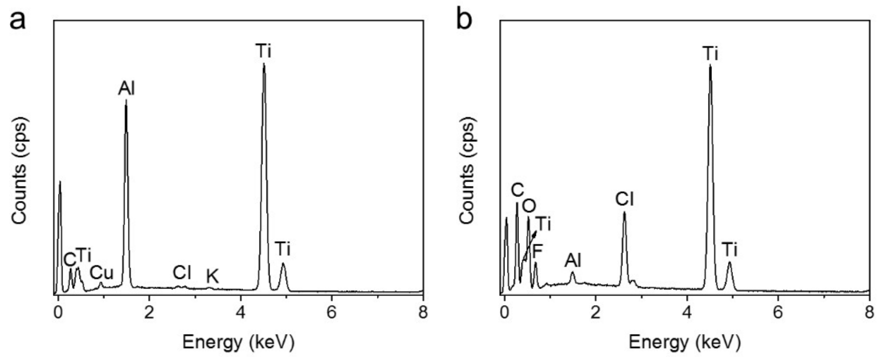

Fig. S6. EDS spectra of (a) Ti_2AlC synthesized by molten salt method at 1000 °C for 1 h and (b) etched Ti_2CT_x at 35 °C for 36 h. The signal of Cu is from copper sample holder.

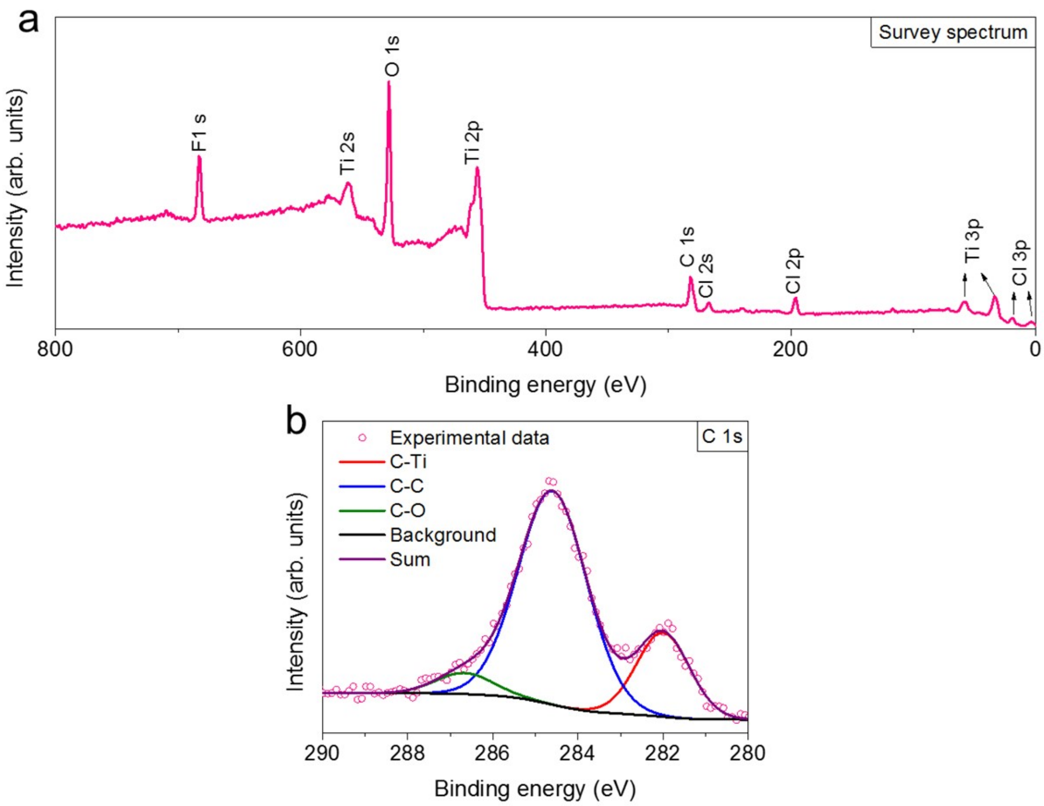

Fig. S7. (a) XPS survey spectrum of Ti_2CT_x. (b) High-resolution XPS spectrum of C 1s.

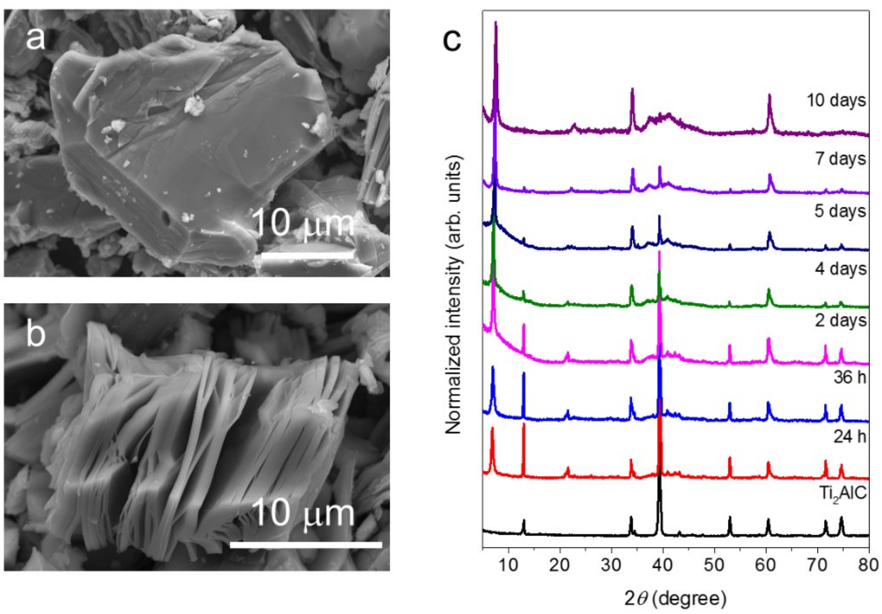

Fig. S8. SEM images of (a) −200 mesh Ti_2AlC and (b) l-Ti_2CT_x etched for 10 days. (c) Phase evolution of −200 mesh Ti_2AlC along with etching time.

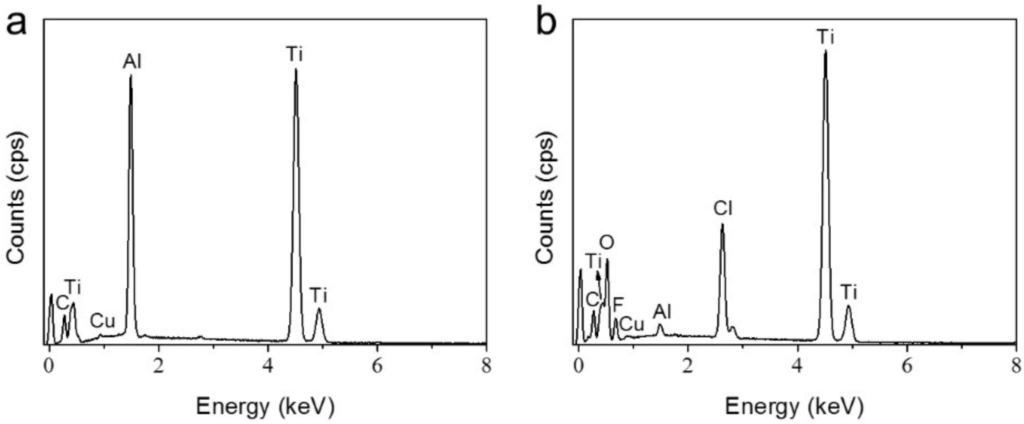

Fig. S9. EDS spectra of (a) Ti_2AlC synthesized by solid-liquid reaction and (b) l-Ti_2CT_x etched at 35 °C for 10 days. The signal of Cu is from copper sample holder.

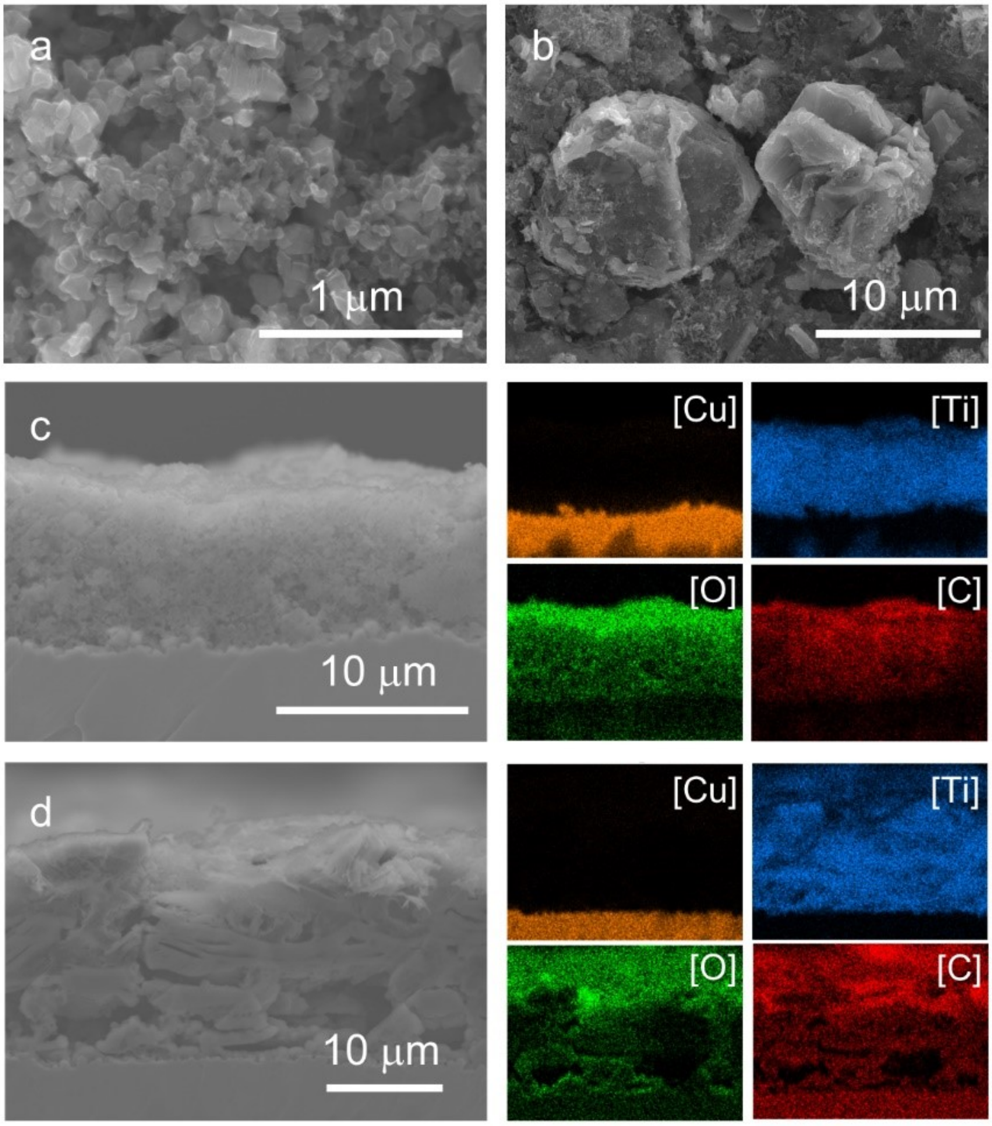

Fig. S10. SEM images of (a) s-Ti_2CT_x and (b) l-Ti_2CT_x. Cross section morphologies and EDS mapping results of (c) s-Ti_2CT_x and (d) l-Ti_2CT_x.

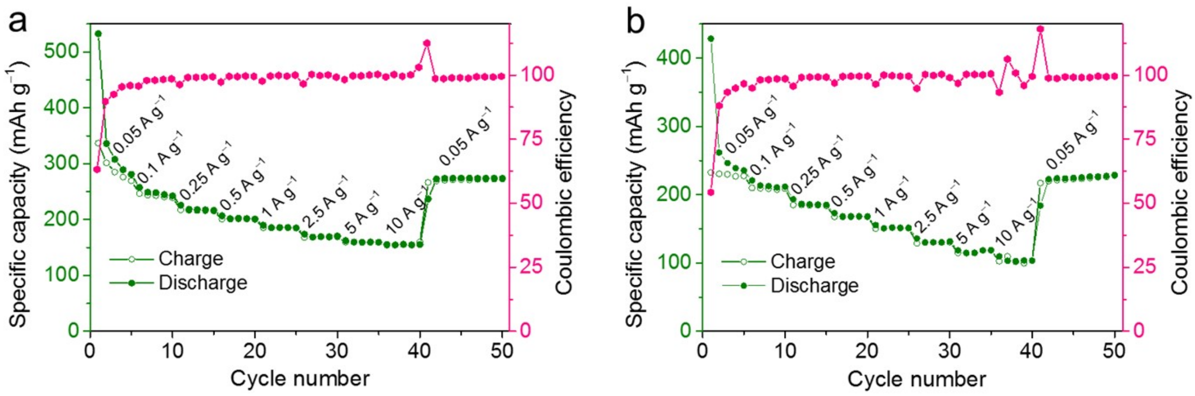

Fig. S11. Rate performances of (a) s-Ti_2CT_x and (b) l-Ti_2CT_x.

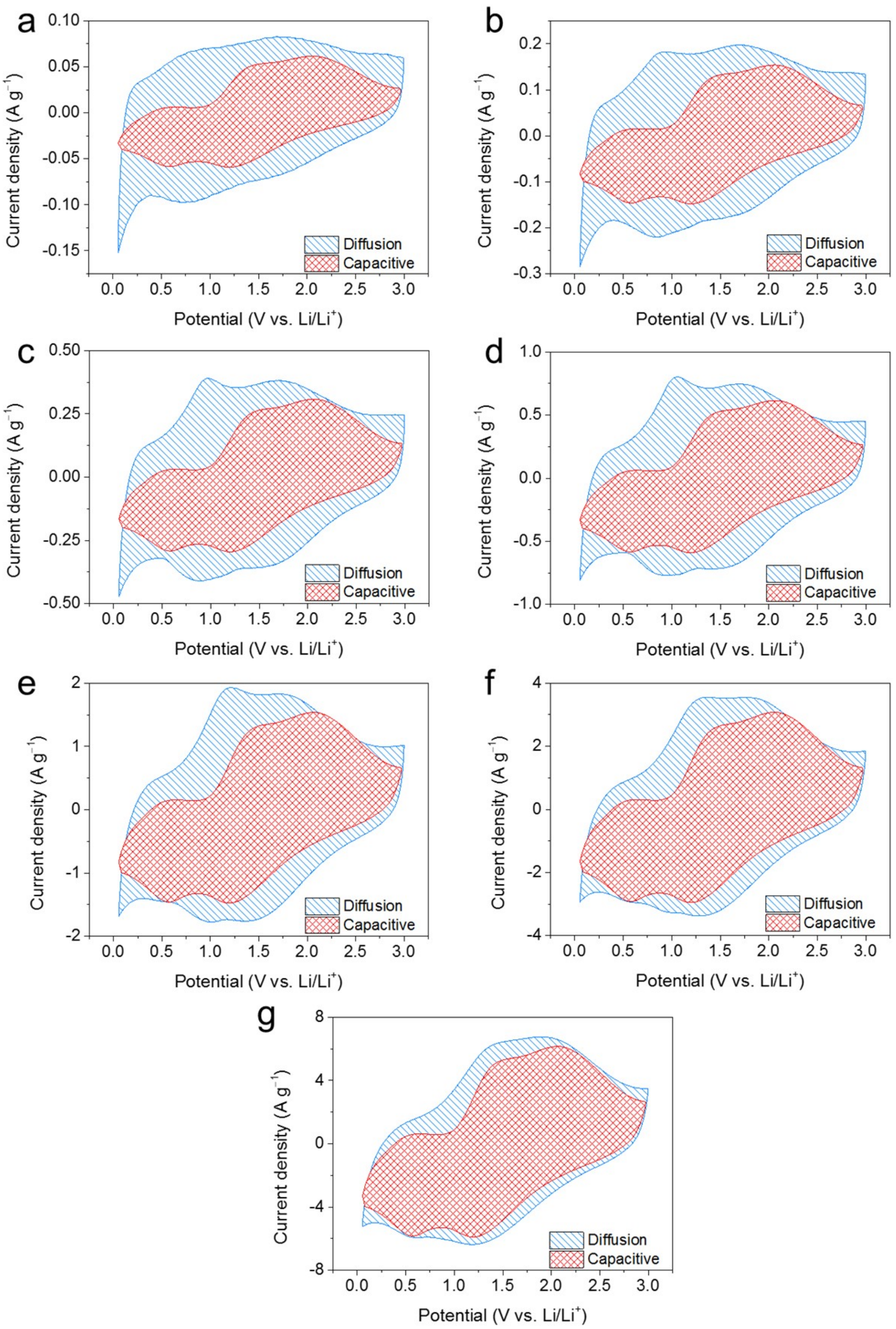

Fig. S12. Determination of capacitive contribution of s-Ti_2CT_x from the CV data. (a) 0.2 mV s^{-1}, (b) 0.5 mV s^{-1}, (c) 1 mV s^{-1}, (d) 2 mV s^{-1}, (e) 5 mV s^{-1}, (f) 10 mV s^{-1}, and (g) 20 mV s^{-1}.

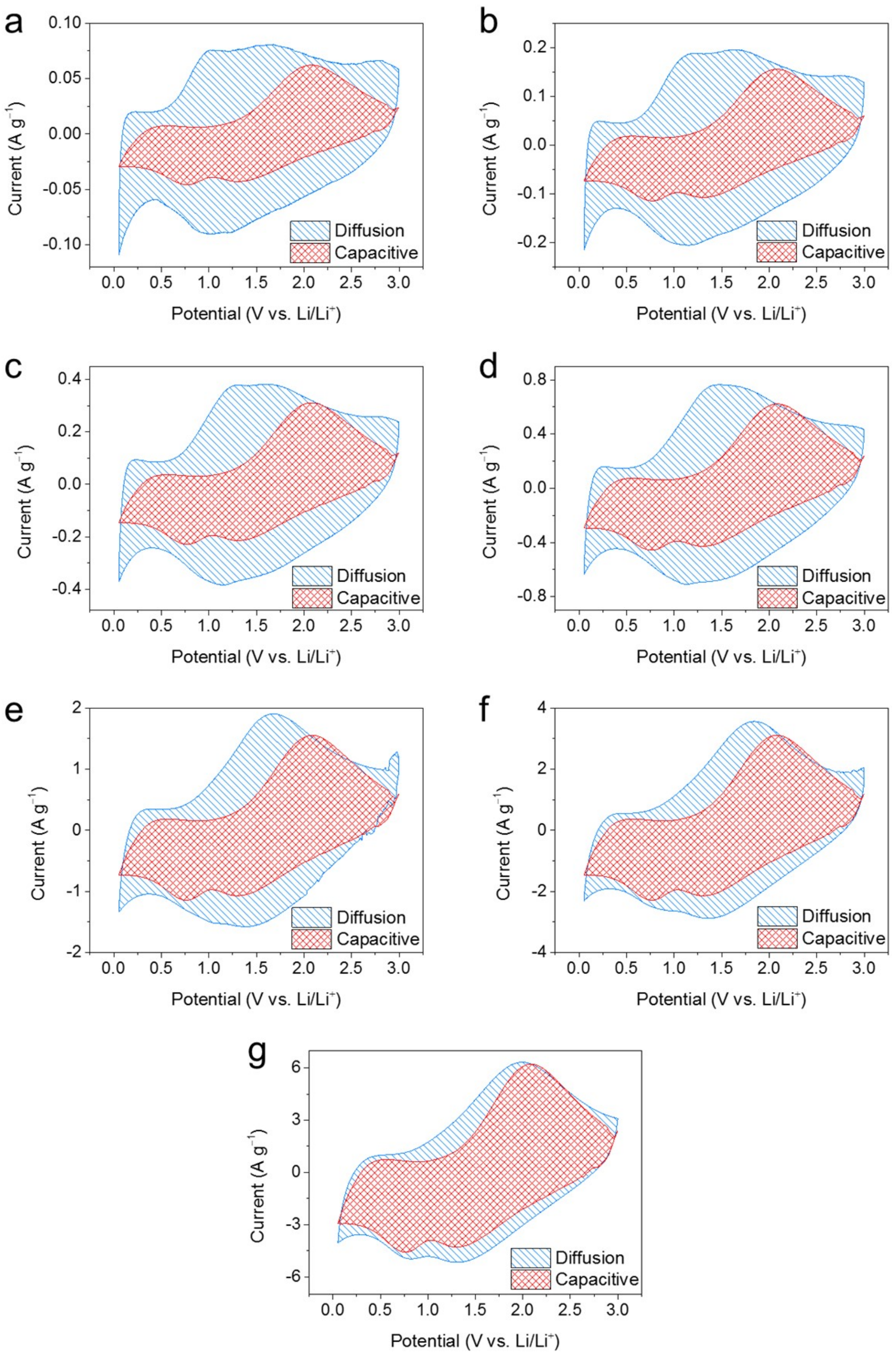

Fig. S13. Determination of capacitive contribution of l-Ti_2CT_x from the CV data. (a) 0.2 mV s^{-1}, (b) 0.5 mV s^{-1}, (c) 1 mV s^{-1}, (d) 2 mV s^{-1}, (e) 5 mV s^{-1}, (f) 10 mV s^{-1}, and (g) 20 mV s^{-1}.

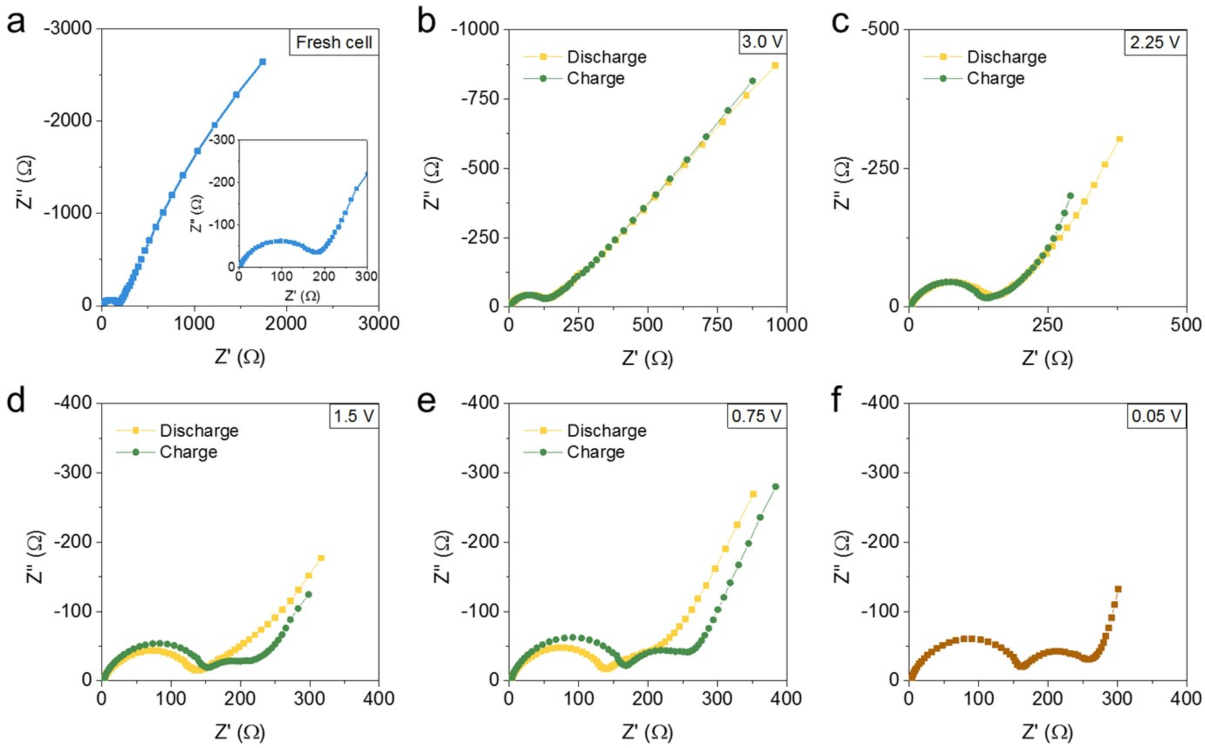

Fig. S14. EIS spectra of l-Ti_2CT_x collected at designed potentials. (a) Fresh cell. (b) 3.0 V. (c) 2.25 V. (d) 1.5 V. (e) 0.75V. (f) 0.05V.

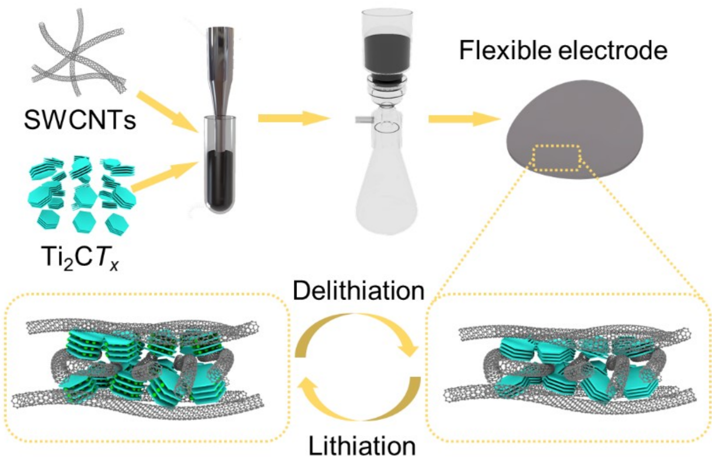

Fig. S15. Schematic illustration of fabricating free-standing s-Ti_2CT_x/SWCNTs flexible electrode.

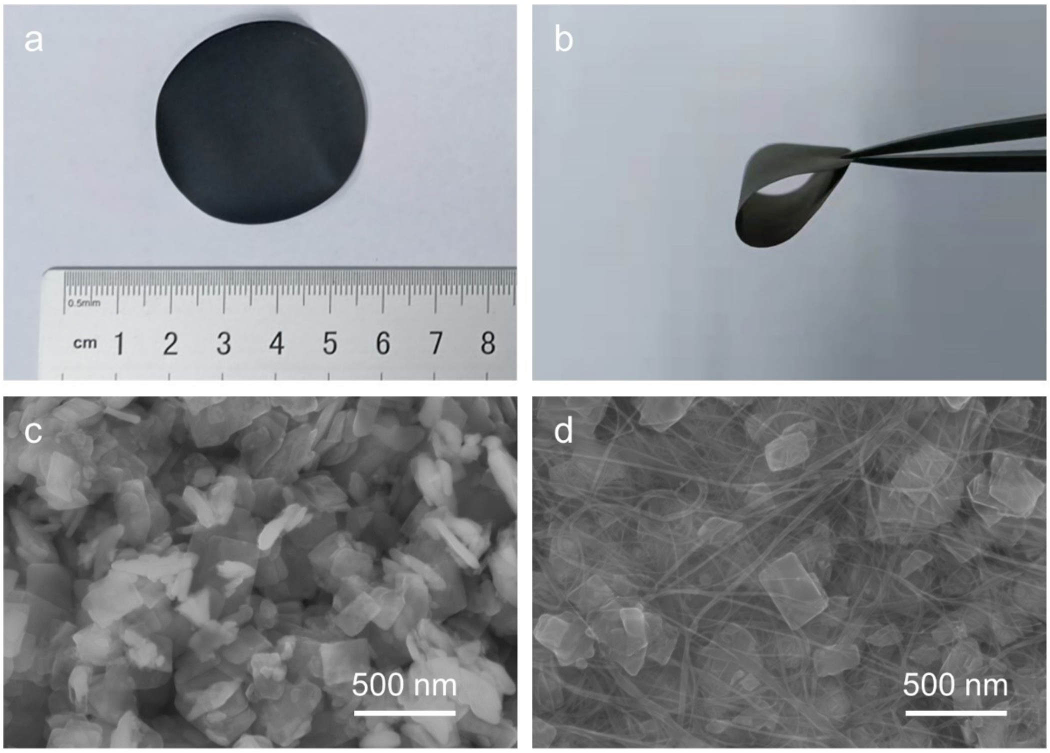

Fig. S16. (a-b) Optical photographs of [100]-$LiFePO_4$/C/SWCNTs flexible electrode, (c) SEM image of [100]-$LiFePO_4$/C, (d) SEM image of [100]-$LiFePO_4$/C/SWCNTs free-standing flexible electrode.

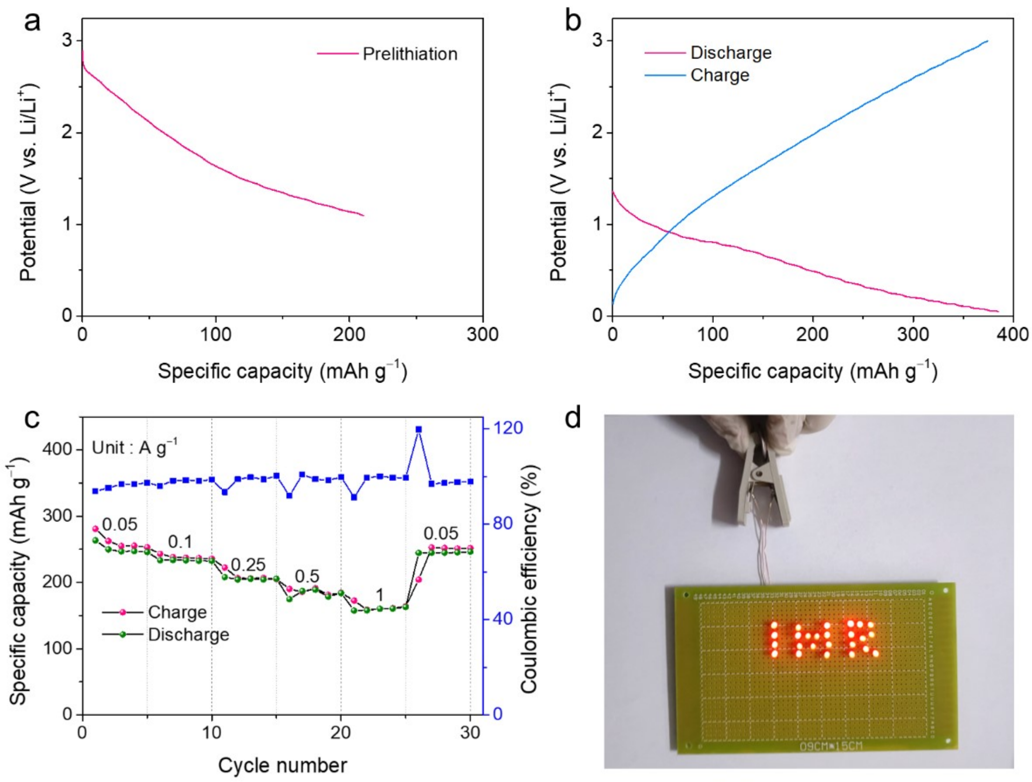

Fig. S17. (a) Discharge curve of s-Ti_2CT_x/SWCNTs electrode in the process of prelithiation, (b) initial discharge-charge curve of s-Ti_2CT_x/SWCNTs electrode, (c) rate performance of a full cell based on prelithiated s-Ti_2CT_x/SWCNTs anode and [100]-$LiFePO_4$/C/SWCNTs cathode, and (d) optical photograph of the full cell lighting up 25 LED lights.

Table S1. Atomic percentage of small-sized Ti_2AlC synthesized by molten salt method at 1000 °C for 1 h and s-Ti_2CT_x MXene.

Samples	C	Al	Cl	K	Ti	Cu	O	F
Ti_2AlC	33.73	19.96	0.24	0.23	44.8	1.05	-	-
s-Ti_2CT_x	38.40	0.54	3.39	-	19.38	-	29.84	8.45

Table S2. Binding energies for s-Ti_2CT_x.

Binding Type	Binding energy (eV)	
C–Ti	282.0 (C 1s)	
C–C	284.6 (C 1s)	
C–O	286.7 (C 1s)	
Ti–C	454.5 (Ti $2p_{3/2}$)	460.0 (Ti $2p_{1/2}$)
Ti–T_x (II)	455.5 (Ti $2p_{3/2}$)	461.0 (Ti $2p_{1/2}$)
Ti–T_x (III)	457.0 (Ti $2p_{3/2}$)	462.5 (Ti $2p_{1/2}$)
Ti (IV)	458.6 (Ti $2p_{3/2}$)	464.1 (Ti $2p_{1/2}$)
O–Ti (TiO_2)	530.1 (O 1s)	
O–Ti	531.0 (O 1s)	
OH–Ti	532.2 (O 1s)	
O–H (H_2O)	533.7 (O 1s)	
F–Ti	685.2 (O 1s)	
Cl–Ti	198.4 ($2p_{3/2}$)	200.0 ($2p_{1/2}$)

Table S3. Atomic percentage of Ti_2AlC synthesized by solid-liquid reaction method and l-Ti_2CT_x MXene.

Samples	C	Al	Cl	K	Ti	Cu	O	F
Ti_2AlC	28.63	24.23	-	-	46.67	0.47	-	-
l-Ti_2CT_x	18.56	0.59	5.72	-	27.55	0.12	38.72	8.73

Table S4. Simulation results of the EIS spectra in **Fig.** 6.

	R_s/Ω	CPE_1-T/F	CPE_1-P	R_{ct}/Ω	CPE_2-T/F	CPE_2-P	R_m/Ω	CPE_3-T/F	CPE_3-P
Fresh cell	5.48E+00	1.90E-05	8.50E-01	8.11E+01	2.47E-03	7.83E-01			
Error/%	1.51E-02	7.19E-02	9.15E-03	1.20E-02	9.84E-03	6.00E-03			
3 V-Discharge	2.82E+00	1.30E-05	8.49E-01	1.45E+02	3.61E-03	5.39E-01			
Error/%	2.67E-02	7.37E-02	9.29E-03	1.86E-02	1.88E-02	1.57E-02			
2.25 V-Discharge	2.65E+00	1.45E-05	8.44E-01	1.41E+02	3.30E-03	6.52E-01	6.04E+01	3.09E-02	7.85E-01
Error/%	2.16E-02	7.70E-02	1.29E-02	4.70E-02	2.33E-01	2.07E-01	2.43E-01	9.47E-02	3.93E-02
1.5 V-Discharge	2.69E+00	1.46E-05	8.43E-01	1.30E+02	1.41E-02	5.43E-01	6.48E+01	1.08E-01	8.06E-01
Error/%	2.02E-02	5.99E-02	8.33E-03	2.08E-02	1.39E-01	1.21E-01	Fixed	1.73E-01	7.39E-02
0.75 V-Discharge	2.87E+00	1.34E-05	8.54E-01	1.24E+02	3.32E-03	7.52E-01	5.17E+01	4.04E-02	6.73E-01
Error/%	1.69E-02	5.53E-02	7.13E-03	2.30E-02	2.09E-01	1.35E-01	1.75E-01	1.33E-01	6.12E-02
0.05 V	2.99E+00	1.34E-05	8.56E-01	1.17E+02	2.91E-03	7.69E-01	6.48E+01	8.61E-02	7.45E-01
Error/%	1.69E-02	5.58E-02	6.98E-03	1.99E-02	1.52E-01	9.35E-02	1.12E-01	1.93E-01	8.28E-02
0.75 V-Charge	3.42E+00	1.31E-05	8.56E-01	1.28E+02	2.66E-03	7.81E-01	6.51E+01	4.47E-02	6.86E-01
Error/%	1.51E-02	5.21E-02	6.57E-03	1.91E-02	1.56E-01	9.61E-02	1.25E-01	1.35E-01	6.17E-02
1.5 V-Charge	3.12E+00	1.32E-05	8.54E-01	1.27E+02	2.81E-03	7.30E-01	6.25E+01	1.04E-01	8.07E-01
Error/%	1.57E-02	5.43E-02	7.20E-03	2.39E-02	1.67E-01	1.09E-01	1.17E-01	1.74E-01	7.11E-02
2.25 V-Charge	3.10E+00	1.33E-05	8.45E-01	1.34E+02	3.12E-03	6.87E-01	5.22E+01	3.71E-02	7.65E-01
Error/%	1.65E-02	6.04E-02	9.02E-03	3.37E-02	2.29E-01	1.69E-01	1.91E-01	8.85E-02	3.80E-02
3 V-Charge	3.00E+00	1.33E-05	8.47E-01	1.52E+02	3.88E-03	5.35E-01			
Error/%	2.27E-02	6.35E-02	8.07E-03	1.62E-02	1.75E-02	1.44E-02			

Table S5. Simulation results of the EIS spectra in **Fig.** S13.

	R_s/Ω	CPE_1-T/F	CPE_1-P	R_{ct}/Ω	CPE_2-T/F	CPE_2-P	R_m/Ω	CPE_3-T/F	CPE_3-P
Fresh cell	1.77E+00	1.32E-05	8.10E-01	1.73E+02	2.34E-03	7.00E-01			
Error/%	4.13E-02	6.37E-02	7.82E-03	1.37E-02	1.47E-02	9.74E-03			
3 V-Discharge	2.01E+00	1.91E-05	7.61E-01	1.22E+02	3.41E-03	4.93E-01			
Error/%	4.92E-02	7.92E-02	1.06E-02	1.98E-02	1.58E-02	1.43E-02			
2.25 V-Discharge	2.17E+00	1.93E-05	7.57E-01	1.31E+02	5.63E-03	5.40E-01	7.87E+01	1.92E-02	6.80E-01
Error/%	4.97E-02	9.53E-02	1.61E-02	5.04E-02	1.84E-01	2.19E-01	2.31E-01	3.82E-02	Fixed
1.5 V-Discharge	2.23E+00	1.76E-05	7.62E-01	1.28E+02	9.34E-03	6.00E-01	7.97E+01	3.06E-02	6.50E-01
Error/%	3.88E-02	6.33E-02	8.16E-03	1.31E-02	1.18E-01	Fixed	8.69E-02	4.81E-02	Fixed
0.75 V-Discharge	2.42E+00	1.12E-05	8.07E-01	1.30E+02	4.11E-03	6.53E-01	8.36E+01	2.37E-02	6.93E-01
Error/%	2.93E-02	6.42E-02	8.34E-03	2.32E-02	1.59E-01	1.32E-01	2.24E-01	1.44E-01	6.04E-02
0.05 V	2.53E+00	7.86E-06	8.38E-01	1.56E+02	1.91E-03	7.84E-01	1.08E+02	7.23E-02	8.22E-01
Error/%	2.41E-02	5.00E-02	5.90E-03	1.39E-02	1.06E-01	6.00E-02	6.96E-02	1.51E-01	6.14E-02
0.75 V-Charge	2.51E+00	8.16E-06	8.33E-01	1.61E+02	1.72E-03	8.04E-01	9.58E+01	2.57E-02	7.41E-01
Error/%	2.35E-02	4.75E-02	5.63E-03	1.39E-02	1.24E-01	6.65E-02	8.41E-02	7.76E-02	3.51E-02
1.5 V-Charge	2.42E+00	1.01E-05	8.16E-01	1.42E+02	2.96E-03	6.76E-01	7.74E+01	4.32E-02	6.46E-01
Error/%	2.62E-02	5.61E-02	7.15E-03	2.06E-02	1.33E-01	9.22E-02	8.16E-02	4.67E-02	Fixed
2.25 V-Charge	2.26E+00	1.40E-05	7.88E-01	1.24E+02	5.93E-03	5.50E-01	7.18E+01	3.18E-02	7.00E-01
Error/%	3.17E-02	5.97E-02	7.55E-03	1.56E-02	1.31E-01	Fixed	5.40E-02	3.20E-02	Fixed
3 V-Charge	1.98E+00	2.02E-05	7.58E-01	1.21E+02	3.76E-03	4.93E-01			
Error/%	4.91E-02	7.82E-02	1.05E-02	1.96E-02	1.67E-02	1.49E-02			

Table S6. Formation energy of $Ti_2CO_2Li_x$ super cell.

Li coverage	E_f
0	0.00E+00
0.25	-1.86E+00
0.5	-3.76E+00
0.75	-5.09E+00
1	-6.40E+00
1.25	-7.29E+00
1.5	-8.27E+00
1.75	-9.11E+00
2	-9.90E+00