Supplementary Information

Free-standing $Ti_3C_2T_x$ electrode with ultrahigh volumetric capacitance

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Fig. S1 A digital photograph of a free-standing $Ti_3C_2T_x$ -Li paper obtained from vacuum filtration. Inset presents a digital photograph of such a flexible paper.



Fig. S2 A TEM image of carbon particle clusters. It can be produced by etching Ti_3AlC_2 powder. In particular, some nanoparticles tightly adhere to the ultrathin $Ti_3C_2T_x$ -Li sheet edge.



Fig. S3 Measured thicknesses at different positions of the TCTL-I sample. The average thickness of the paper is calculated to be approximately $8.8 \mu m$.



Fig. S4 EDX spectrum of the TCTL-I is mainly composed of Ti, C, O, F, and Cl as well as trace Al content. Their atom percentages are 33.5, 30.5, 22.1, 10.4, 3, 0.5%, respectively. The carbon content in the TCTL-I is about 8.2% according to the stoichiometry of Ti_3C_2 .



Fig. S5 Raman scattering spectrum of the TCTL-II with the typical D and G bands of graphitic carbon located at 1371 cm⁻¹ and 1573 cm⁻¹, respectively. The intensity ratio (I_D/I_G) of D and G bands is 0.74, indicating that these clusters are well graphitized, which is consistent with HRTEM results. However, D and G bands of graphitic carbon are not found in the Raman spectrum of the Ti₃AlC₂ powder.



Fig. S6 CV curves of the other paper electrode sample (a) at a scan rate of 2 mV/s and (b) at different scan rates.



Fig. S7 Galvanostatic charge-discharge (GCD) curves of the TCTL-II electrode at various current densities with the nearly triangular shape. It confirms the high reversibility of the redox reactions of the tested electrode.



Fig. S8 A EIS spectrum of the TCTL-II electrode. Inset is the magnified section in the high frequency region.



Fig. S9 We have designed two different experiments to explore the effect of the posttreatment of as-prepared MXenes in LiCl solution on the interlayer space. The XRD peak (0002) of the as-prepared MXenes washed by LiCl solution locates at 6.16°, the corresponding the c-LP is 28.7 Å (Red curve). However the XRD peak (0002) of the sample unwashed by LiCl solution locates at 6.76°, the corresponding the c-LP is 26.1 Å (Black curve). So, it is essential to immerse the as-prepared MXenes in LiCl solution in order to increase the interlayer space. Red and black curves represent the XRD patterns of the as-prepared MXenes washed and unwashed by LiCl solution, respectively.

Region	BE[eV]	Assigned to	Substance	Reference
Ti 2p _{3/2} (2p _{1/2})	454.9 (461.1)	Ti-C	Ti ₃ C ₂ T _x	[1]
	455.8 (462.4)	Ti-O	$TiO_{x}(1.5 < x < 2)$	This work
	456.6 (463.2)	Ti-O	$TiO_x(1.5 < x < 2)$	This work
	458.5 (464.5)	Ti-O	TiO ₂	[2,3]
C 1s	281.9	C-Ti	$Ti_3C_2T_x$	[1]
	285.1	C-C	С	[4]
	286.4	C-0	С	[5]
	287.1	C=O	С	[5]
	288.9	O-C=O	С	[5]
O 1s	529.5	O-Ti	TiO ₂	[2]
	530.5	O-Ti	$TiO_x(1.5 < x < 2)$	This work
	531.1	O-Ti	$TiO_{x}(1.5 < x < 2)$	This work
		-0	$Ti_3C_2O_x$	[1,6]
	531.6	C=O	С	[7,8]
	532.2	О-Н	Ti ₃ C ₂ (OH) _x	[7,8]
	533.5	O-C, O-C=O	С	[7,8]
		Н-О-Н	Ti ₃ C ₂ (OH) _x -H ₂ O _{ads}	[6]
F 1s	684.6	-F	$Ti_3C_2F_x$	[9]
Li 1s	59.8	-Li	$Ti_3C_2Li_x$	This work

Table S1. XPS peak fitting results for $Ti_3C_2T_x$ -Li. The numbers in brackets in column II are peak positions of Ti $2p_{1/2}$.

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