Supplementary Information

High-capacitance $Ti_3C_2T_x$ MXene enabled by etching submicron Ti_3AlC_2 grains grown in molten salt

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Experimental Section

1. Materials

1.1 Synthesis of $Ti_3AlC_2$by molten salt method

The submicron Ti_3AlC_2grains were prepared by molten salt method using elemental powders of Ti (99%, −325 mesh), Al (99%, −200 mesh) and carbon black (99%,primary particles size: 60nm) in a molar ratio of 3:1.1:1.8 along with the reaction medium of mixed salts composed of NaCl and KCl (NaCl:KCl = 50:50mol%). The mixture was mixed for 12hours with agate balls and absolute alcohol in an agate jar, followed by drying at 60 °C for 8 hours in air. The homogenized mixture was then heated in a tube furnacein a flowing Ar atmosphere. Finally, the sample was naturally cooled down to room temperature. Then Ti_3AlC_2 was obtained by washing the mixture of Ti_3AlC_2 and salts with water for several times.

1.2 Synthesis of porous Ti_3AlC_2monolith

The porous Ti_3AlC_2 monolith (porosity, ~40%) used in this work was prepared in the authors' laboratory by the solid–liquid reaction synthesis method[1] using elemental powders of Ti (99%, −300 mesh), Al (99%, D50 = 10 μm) and graphite (99%, D90 = 6.5 μm) in a molar ratio of 3:1.1:1.8. Briefly, the powders were mixed for 12 hours with agate balls and absolute alcohol in an agate jar, followed by drying at 60 °C for 8 hours in air. The homogenized mixture was then uniaxially cold pressed into a green compact in a graphite mould. Subsequently, the green compact together with the mould was heated in a furnace up to 1550 °C and hold at that temperature for 2 hours in a flowing Ar atmosphere. Finally, the sample was naturally cooled down to room temperature.

1.3 Synthesis of $Ti_3C_2T_x$ MXene

Two kinds of the as-prepared Ti_3AlC_2 (~1.0 g), powder of submicron Ti_3AlC_2 grains and porous Ti_3AlC_2 monolith,were immersed respectively in an aqueous HF solution (10 mL, 6 mol L^{-1}) at room temperature until no bubbles generated. The resulting particulates were separated by vacuum filtration with a porous membrane filter (0.22 μm pore size) and washed with deionized water until the pH value of the supernatant is higher than 5.

2. Materials Characterization

XRD data were collected on an X-ray diffractometer (D/max-2400, Rigaku) using Cu K_α radiation. Microstructural characterization ofs-$Ti_3C_2T_x$ materials was conducted by transmission electron microscopy (TEM) on an analytic transmission electron microscope (Tecnai G2 F30, FEI) working at 300 kV. Scanning electron microscopy (SEM) characterization was performed on a scanning electron microscope (LEO Supra35, Zeiss).

3. Fabrication of $Ti_3C_2T_x$film electrodes

The fabrication of film electrodes follows the method reported in the literature[2]. In a typical fabrication, a mixture of 100 mg $Ti_3C_2T_x$, 12.5 mg polytetrafluoroethylene (PVDF) binder and 12.5 mg carbon black were grinded finely with N-Methyl pyrrolidone (NMP) as the organic solvent. Then the slurry was coated on a copper foil and dried in a vacuum electric drying oven at 140 °C for 10hours.

4. Configuration of three-electrode system

The s-$Ti_3C_2T_x$ or l-$Ti_3C_2T_x$ coated copper foil were cut into circular shape as the working electrodes in this study.The mass loadingsof s-$Ti_3C_2T_x$ and l-$Ti_3C_2T_x$ are 0.368 mg and 0.304 mg, respectively, to ensure the results are comparable. The thickness of each electrode is about 9 μm (Fig. S6).The counter electrode wasplatinum foil and the reference electrodewas Ag/AgCl electrode.

5. Electrochemical measurements

The electrochemical performance of the $Ti_3C_2T_x$ material was evaluated using a three-electrode test cell at room temperature. The electrolyte was aqueous H_2SO_4 solution (1 mol L^{-1} H_2SO_4). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were all performed on an electrochemical workstation (PARSTAT 2273, Princeton Applied Research). The voltage ramp rates ranged from 2 to 100 mVs^{-1}.

The gravimetric capacitance was calculated from the CV curves according to $C_g = (\int i dV)/(2vMV)$, where i is the current, v the voltage scan rate, M themass of $Ti_3C_2T_x$ in electrode, and V the voltage window. EIS spectra were recorded from 100kHz to 10 mHz at open circuit with an amplitude of 10 mV.

6. Electrical conductivity measurements

Both of two kinds of MXene particulates, s-$Ti_3C_2T_x$ and l-$Ti_3C_2T_x$, were first pressed into pellets with a diameter of 8 mm under an identical pressure of 200 MPa, and then subjected to conductivity measurements by means of four-point colinear probe method (PTS-9, Guangzhou Four Probe Technology Co., Ltd.).

References

1. X. Wang and Y. Zhou, *J. Mater. Chem.*, 2002, **12**, 455-460.
2. M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum and Y. Gogotsi, *Science*, 2013,

341, 1502-1505.

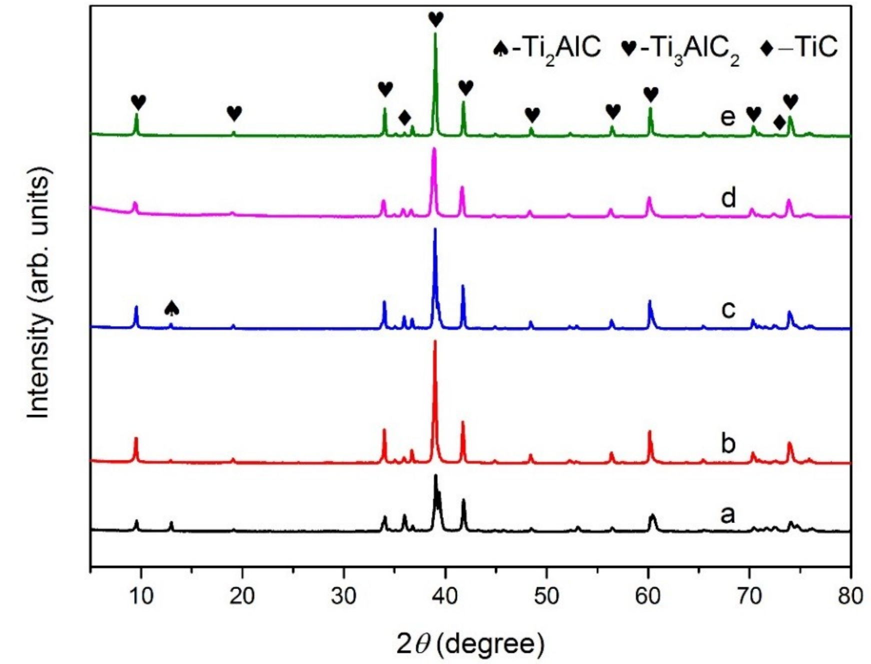

Fig. S1 XRD patterns of submicron Ti$_3$AlC$_2$ grains synthesized at (a) 1150 °C for 1h,(b)1150°C for 3h, (c) 1250 °C for 1h, (d)1250 °C for 2h, and (e)1250 °C for 3h.

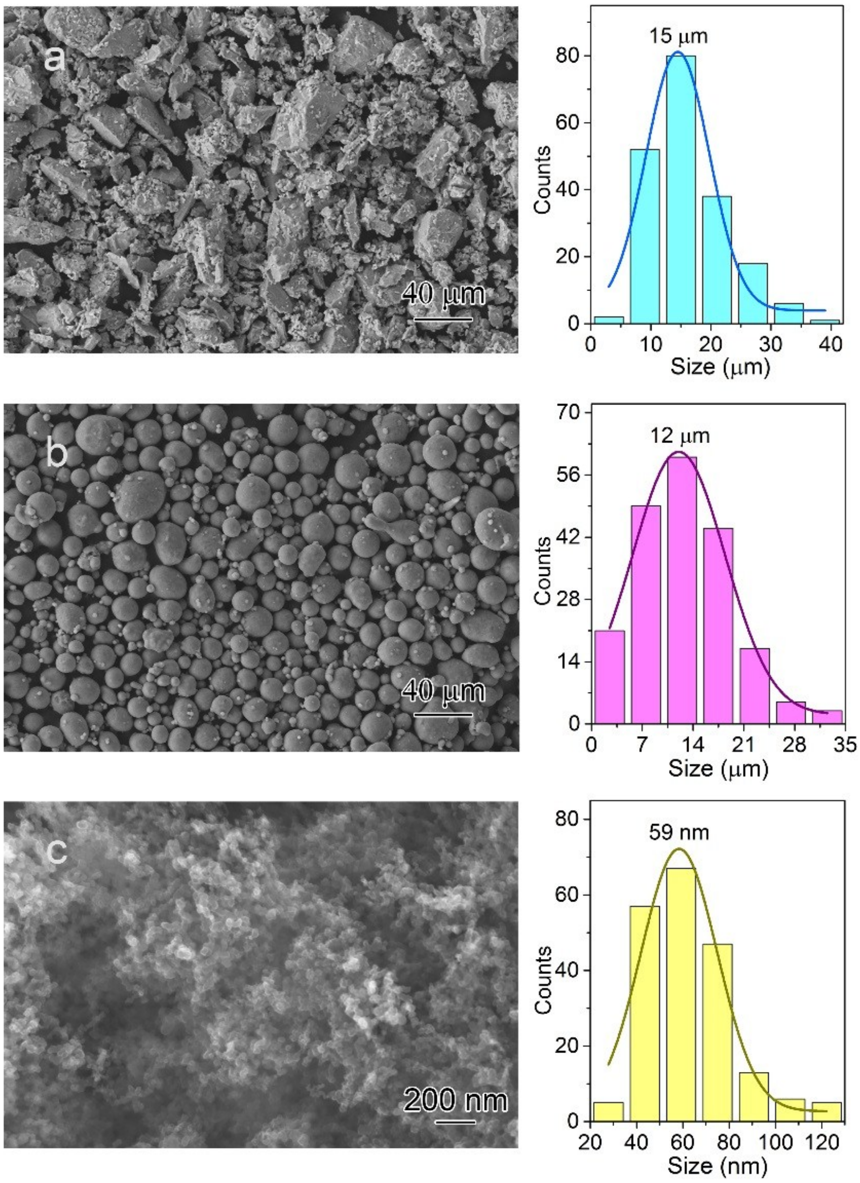

Fig. S2SEM images of reaction precursors. (a)Ti, (b) Al and (c) Carbon black.

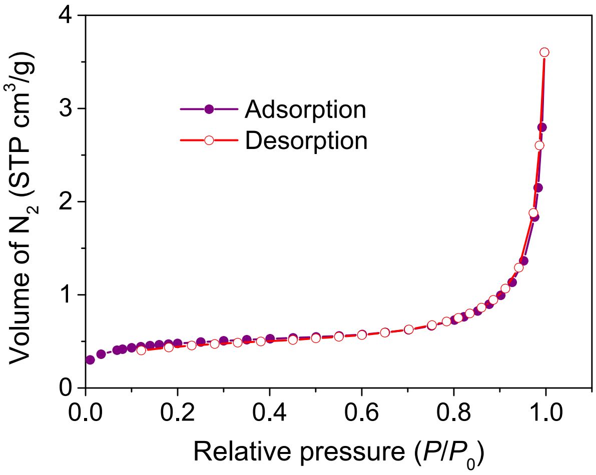

Fig. S3 Nitrogen adsorption/desorption isotherms of Ti_3AlC_2 synthesized in molten salt at 1250 °C for 3 h. The BET specific surface area of as-prepared Ti_3AlC_2 is 1.7 m^2g^{-1}.

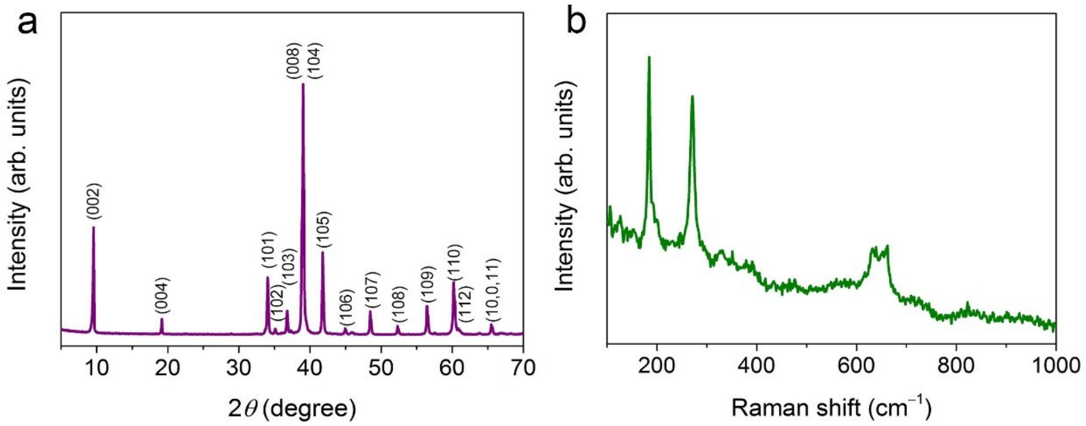

Fig. S4(a) XRD pattern and (b) Raman spectrum of porous Ti_3AlC_2monolith synthesized by high temperature reaction synthesis.

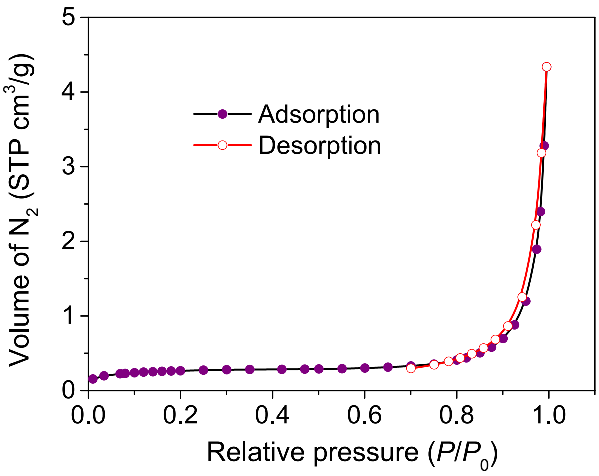

Fig. S5 Nitrogen adsorption/desorption isotherms of Ti_3AlC_2 powders. The powders were obtained by drilling Ti_3AlC_2monolith that was synthesized by high temperature reaction synthesis. The BET specific surface area of the powders is 0.9 m^2 g^{-1}.

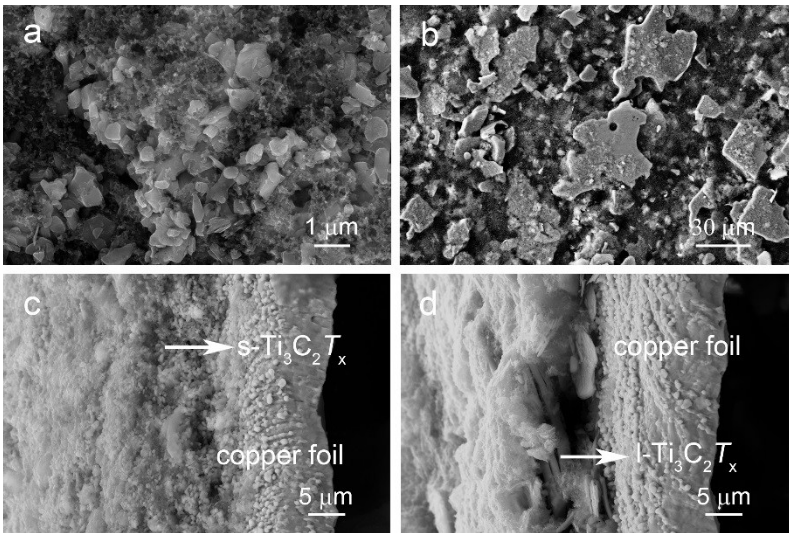

Fig. S6SEM images of as-fabricated electrodes. Top view of (a) s-$Ti_3C_2T_x$, and (b) l-$Ti_3C_2T_x$,andside viewof (c) s-$Ti_3C_2T_x$, and (d) l-$Ti_3C_2T_x$.

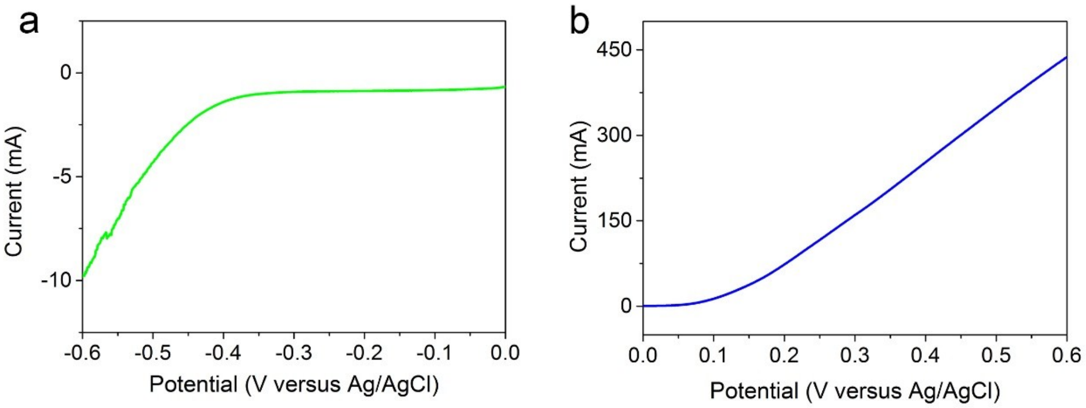

Fig. S7 (a) Hydrogen evolution curve and (b) oxygen evolution curve of s-$Ti_3C_2T_x$ at a scan rate of 10 mV/s. Graphite rod was used as the counter electrode.

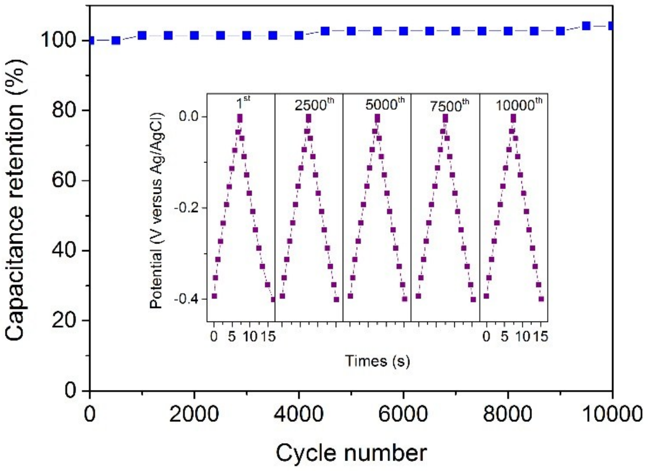

Fig. S8 Capacitance retention of s-$Ti_3C_2T_x$ film electrode in 1 mol L^{-1} H_2SO_4 solution. Inset shows galvanostatic cycling data collected at 10 A g^{-1}. The mass of active material is 0.264 mg. Graphite rod was used as the counter electrode.

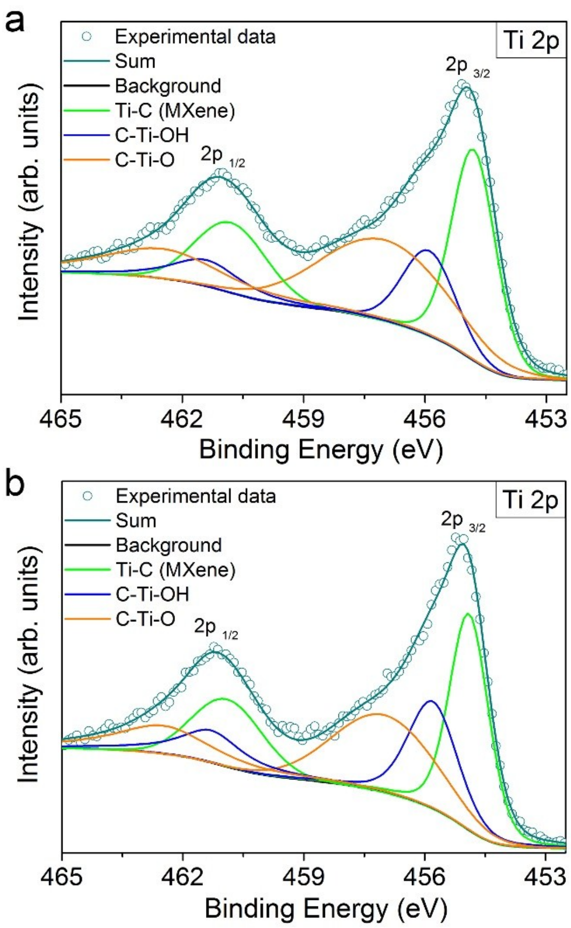

Fig. S9XPS spectra of Ti 2p in (a) s-$Ti_3C_2T_x$ and (b) l-$Ti_3C_2T_x$. The Ti 2p spectra are deconvolved with three doublets (Ti 2p $2p_{3/2}$–Ti $2p_{1/2}$) with a set area ratio equal to 2:1.

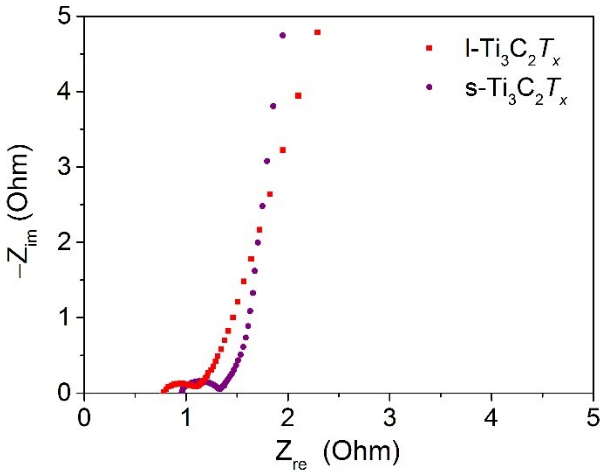

Fig. S10 Nyquist plots of s-$Ti_3C_2T_x$ and l-$Ti_3C_2T_x$ electrodes at high frequency region.

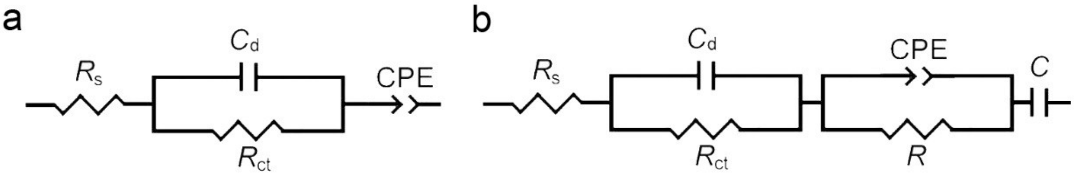

Fig. S11 Equivalent circuit adopted in the simulation of EIS spectra of (a) s-$Ti_3C_2T_x$(b) and l-$Ti_3C_2T_x$.R_s: electrolyte resistance; C_d: electrical double layer capacitor; R_{ct}: charge transfer resistance; CPE: constant phase angle element, R: migration resistance of hydrated hydrogen ion within l-$Ti_3C_2T_x$interlayer space, C: charge accumulation capacitor.

Table S1 Simulation results of the EIS spectra in Figure 3d.

Element	s-$Ti_3C_2T_x$		l-$Ti_3C_2T_x$	
	Values	Error/%	Values	Error/%
R_s (ohm)	1.0	2.0	0.8	1.7
C_d (F)	1.4E–4	14.1	1.4E–4	12.7
R_{ct} (ohm)	0.4	5.6	0.3	5.1
CPE-T	0.1	0.9	3.7E–2	1.1
CPE-P	0.9	0.5	0.84	0.5
C (F)			0.4	14.0

Table S2 Conductivity measurements for l-$Ti_3C_2T_x$ MXene.

Test conditions

Sample	Range (mA)	Current (mA)	Mean distance of probe (mm)	Thickness (mm)	Thickness correction factor
l-$Ti_3C_2T_x$	100	45.32	1.0	1.91	0.6562

Results

No.	V23+ (mV)	V23– (mV)	V24+ (mV)	V24– (mV)	Resistivity (mΩ·cm)	Conductivity (S/cm)
1	21.57	21.57	17.26	17.29	266.2	3.757
2	24.76	24.77	19.61	19.65	310.4	3.222
3	22.10	22.11	17.16	17.22	284.7	3.512
4	22.50	22.51	18.20	18.21	273.4	3.658
5	23.01	23.00	18.20	18.23	288.9	3.461
					277.5±16.9	3.522±0.205

Table S3 Conductivity measurements for s-$Ti_3C_2T_x$ MXene.

Test conditions

Sample	Range (mA)	Current (mA)	Mean distance of probe (mm)	Thickness (mm)	Thickness correction factor
s-$Ti_3C_2T_x$	100	45.32	1.0	2.24	0.5789

Results

No.	V23+ (mV)	V23– (mV)	V24+ (mV)	V24– (mV)	Resistivity mΩ·cm	Conductivity (S/cm)
1	13.72	13.73	11.33	11.35	166.5	6.006
2	13.41	13.41	10.89	10.90	167.4	5.974
3	14.13	14.13	11.80	11.81	168.1	5.949
4	13.14	13.22	10.75	10.76	163.3	6.124
5	13.45	13.45	10.90	10.91	168.4	5.938
					166.7±2.1	5.998±0.075