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Supporting Information

Ambient-Stable Two-Dimensional Titanium Carbide (MXene) Enabled by Iodine Etching

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Table of contents

1-Synthesis of 2D iodine-etched MXene

1.1-Iodine-assisted etching of Ti_3AlC_2

Ti_3AlC_2 powder (100 mg, 0.5 mmol) and iodine nanocrystals (I_2, 394 mg, 1.5 mmol) were added slowly into anhydrous acetonitrile (CH_3CN, 5 mL) in a glass ampoule. The ampoule was sealed under vacuum after three times freeze-pump-thaw cycles. After warming up to room temperature, the mixture was sonicated for 5 min, then heated up to 100 °C and kept for 4 days (**Figure S1**). Afterwards, the sediment was transferred to a centrifuge tube and washed several times with fresh anhydrous acetonitrile at 5100 rpm for 5 min until the supernatant became colorless (**Figure S2**). The sediment was then transferred into acetonitrile and sonicated for 5 min. Later the unreacted Ti_3AlC_2 was removed by means of centrifuging at 100 rpm for 2 min. The supernatant was collected and deployed for further characterization.
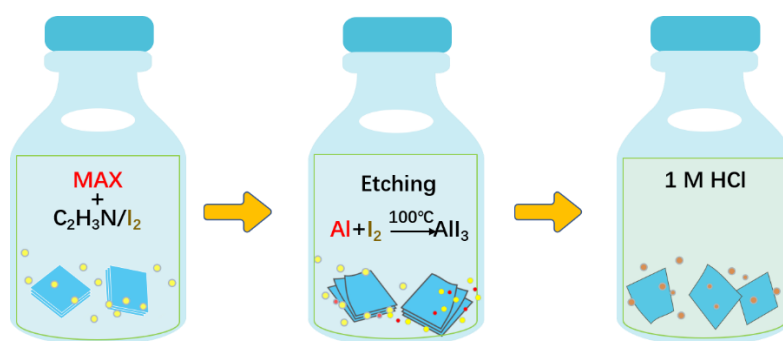

Figure S1. Schematic illustration of 2D IE-MXene sheets synthesis.

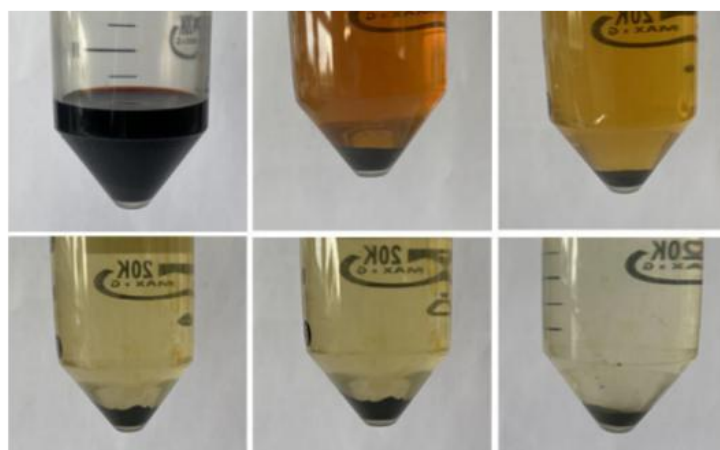**Figure S2**. Washing procedure of iodine-etched Ti_3AlC_2 powder with acetonitrile.

1.2-The delamination of 2D IE-MXene sheets

The collected I_2-etched Ti_3AlC_2 was delaminated in 1.0 M HCl solution by simple manual shaking (**Figure S3**). The delaminated MXene flakes were rinsed with distilled water to remove the possible contamination, and the aqueous MXene dispersion was deployed for further characterization.

Figure S3. (a) the delamination of I_2-etched Ti_3AlC_2 in 1.0 M HCl by manual shaking and (b) the aqueous dispersion of 2D IE-MXene.

The etching process by iodine has been performed in different reaction temperatures. The achieved samples after washing and delamination in HCl solution were investigated by SEM and energy-dispersive X-ray spectroscopy (EDS) (**Figure S4**) to confirm which temperature is much better to remove Al layer effectively.
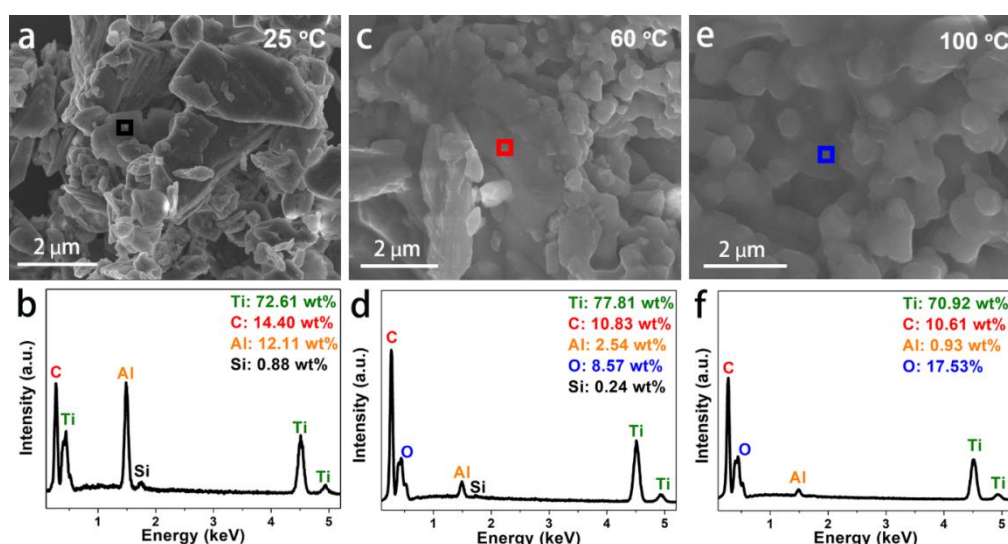

Figure S4. SEM images (a,c,e) and the corresponding element mapping (b, d, f) of the samples collected after etching at (a-b) 25 °C, (c-d) 60 °C, and (e-f) 100 °C and washing with HCl solution.

Table S1. The Al content of the MAX powder and the etched MAX after washing with HCl.

Etching temperature	Al content in Ti_3AlC_2	Al content in the etched Ti_3AlC_2 after washing with HCl
25 ℃	16.7 wt%	12.11 wt%
60℃	16.7 wt%	2.5 wt%
100 ℃	16.7 wt%	0.9 wt%

2-Synthesis of HF-etched MXene

Ti$_3$AlC$_2$ powder (1.0 g) was added slowly into 10 mL 30% HF. The mixture kept stirring at 40 °C for 15 h.[1] After that, it was washed with distilled water for 6 cycles by centrifugation (5100 rpm, 5 min for each cycle) until the supernatant reached a pH value of approximately 6. To delaminate the etched MAX powders, the precipitation was stirred vigorously in 20 mL tetramethylammonium hydroxide (TMAOH) for 5 hours. Then, the suspension was washed 3 times with distilled water to remove the excess amount of TMAOH. The remaining precipitation was further dispersed in fresh distilled water by sonication for 30 min. The delaminated MXene flakes were collected by centrifugation for further characterization.

3-Material Characterization

X-ray diffraction (XRD) patterns were collected via a PW1820 X-ray diffractometer with Cu Kα radiation. The morphology and structure of the samples were characterized by a ZEISS field-emission scanning electron microscope (FESEM), a Carl Zeiss Libra 200 high-resolution transmission electron microscope (TEM), and Bruker Multimode 8 system atomic force microscope (AFM). X-ray photoelectron spectroscopy (XPS) was performed using a PHI Quantum 2000 ESCA system with monochromatic Al Kα radiation. UV-vis spectra were measured in diffuse reflection mode on a BRUKER Cary 60.

4-Preparation of 2D IE-MXene electrodes

The 2D IE-MXene electrodes were prepared by mixing exfoliated MXene sheets, acetylene black, and polytetrafluoroethylene (PTFE) in a weight ratio of 8:1:1 with the help of ethanol. The mixture was pressed into a film and then dried at 80 °C overnight in vacuum. After drying, the film was cut into disks and were pressed onto a carbon paper to develop working electrodes. The mass loadings of Ti$_3$C$_2$T$_x$ electrodes range from ~1 to 4.5 mg cm^{-2}. The electrodes were soaked in a 1.0 M H$_2$SO$_4$ solution for over 12 h before electrochemical measurements.

5-Electrochemical studies

All electrochemical measurements were performed using a traditional three-electrode system with 1.0 M H$_2$SO$_4$ solution as the electrolyte. Ti$_3$C$_2$T$_x$ electrode, graphite rod, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) analyses were performed on an electrochemical workstation (CHI 660E). EIS measurements were performed in the frequency range of 0.1-100 kHz with 5 mV ac amplitude.

The specific capacitance (C, F g^{-1}) based on the CV curves were calculated according to the following equation (1):

$$C = \frac{1}{2 \times m \times v \times (V_\mathrm{f} - V_i)} \int_{V_i}^{V_\mathrm{f}} I(V)\, dV \tag{1}$$

where m is the total mass of each electrode (g), v is the scan rate (V s^{-1}), V_f and V_i are the integration potential limits of CV curves and $I(V)$ is the voltammetric current (in amperes). $\int_{V_i}^{V_f} I(V) \, dV$ is the integrated area of the CV curves.

The specific capacitance (C, F g^{-1}) was also calculated from the GCD curves according to the following equation (2):

$$C_A = \frac{I}{m} \times \frac{t}{v} \tag{2}$$

where I/m is the current density (A g^{-1}) and t is the discharge time (s). v is the voltage.

6-Mechanistic study of etching/delamination processes

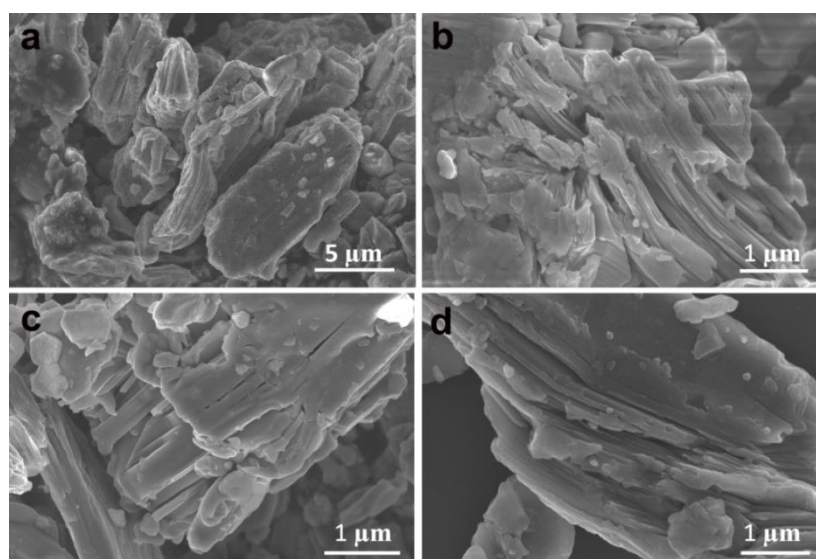**6.1-Element mapping of I$_2$-etched Ti$_3$AlC$_2$, delaminated IE-MXene, and HF-etched MXene**

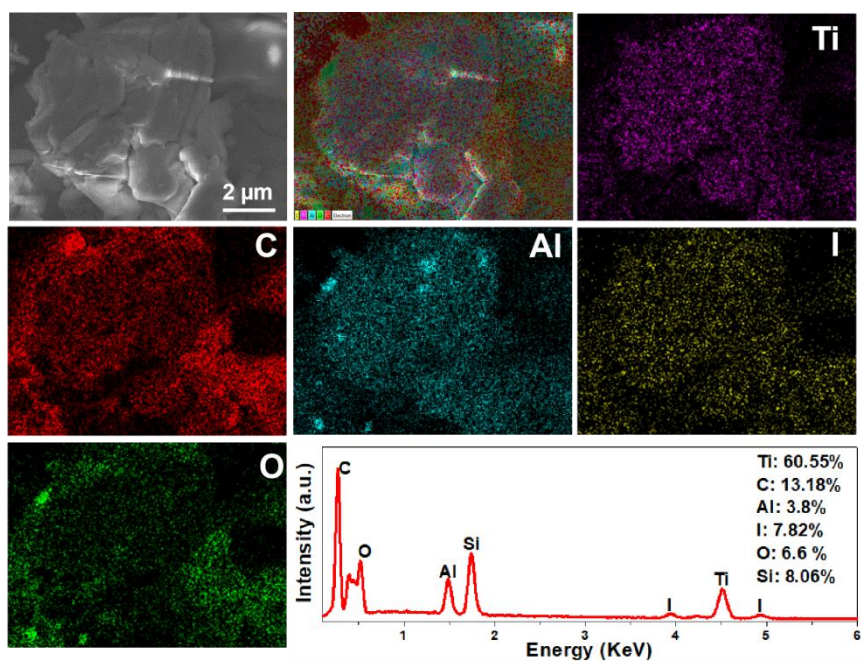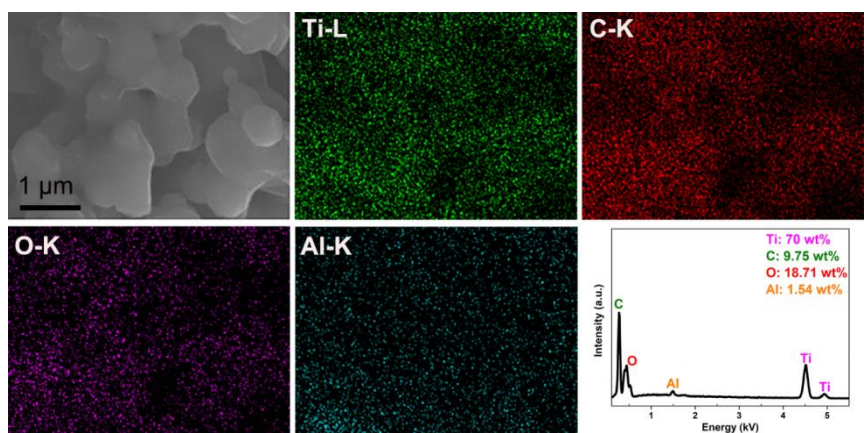**Figure S5.** SEM images of I$_2$-etched Ti$_3$AlC$_2$.

Figure S6. EDS mapping of I_2-etched Ti_3AlC_2.

Figure S7. EDS mapping of 2D IE-MXene.

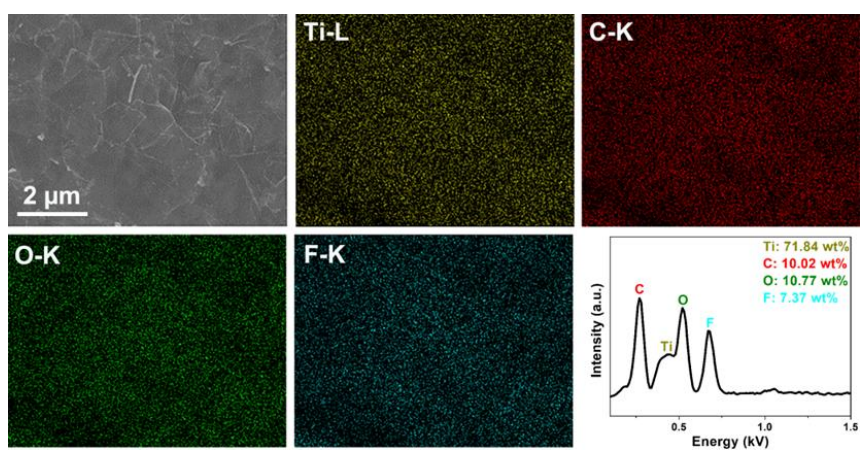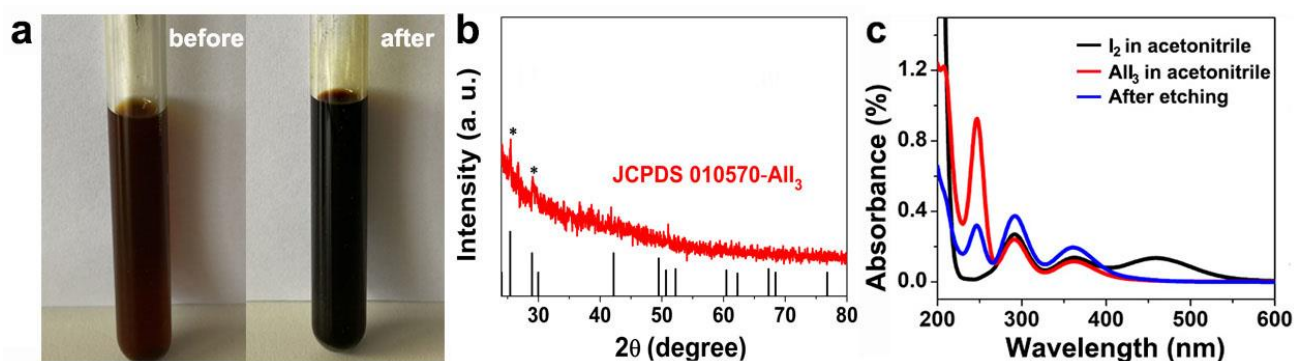**Figure S8**. EDS mapping of HF-etched MXene sheets.

6.2-Evidences of AlI₃ formation during the etching process

Figure S9. (a) The optical images of the solution before and after etching, (b) XRD pattern of the powder collected from the etching solution, (c) UV-vis spectra of I_2 and AlI_3 in acetonitrile as well as the etching solution.
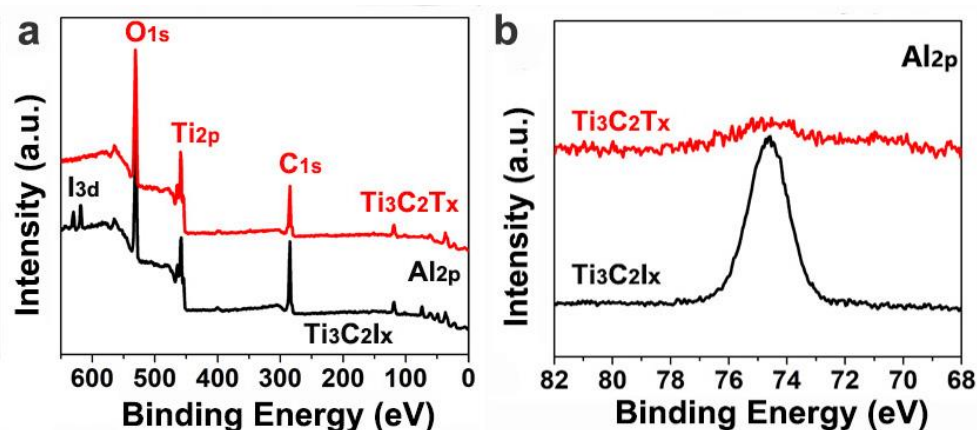
6.3-XPS characterization of I₂-etched Ti₃AlC₂ and delaminated IE-MXene

Figure S10. (a) XPS survey spectra and (b) high-resolution XPS spectra of Al 2p of I_2-etched Ti_3AlC_2 and 2D IE-MXene flakes.

6.4-Density functional theory (DFT) calculation of etching/delamination processes

DFT-based theoretical calculations were performed with the CASTEP package within the generalized gradient approximation (GGA) as formulated by the Perdew–Burke–Ernzerhof (PBE) functional (*J. Phys. Chem.*, **1990**, 92, 508; *Phys. Rev. B,* **1994**, 90, 17953; *First Principles Methods Using CASTEP. Z. Kristallogr*, **2005**, 220, 567). The final set of energies for all calculations was computed with an energy cut-off of 440.0 eV. The convergence criteria for energy were set to be 10^{-5} eV, and the residual forces on each atom became smaller than 0.01 eVÅ^{-1}. The Brillouin zone integration was performed with 8×1×1 Γ-centred Monkhorst-Pack k-point meshes in geometry optimization calculations.
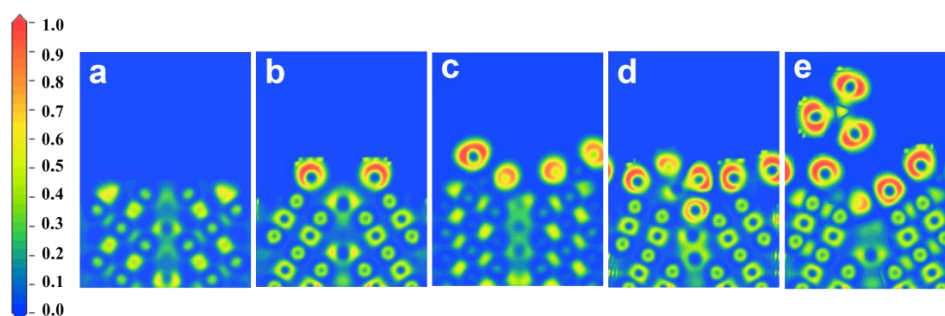
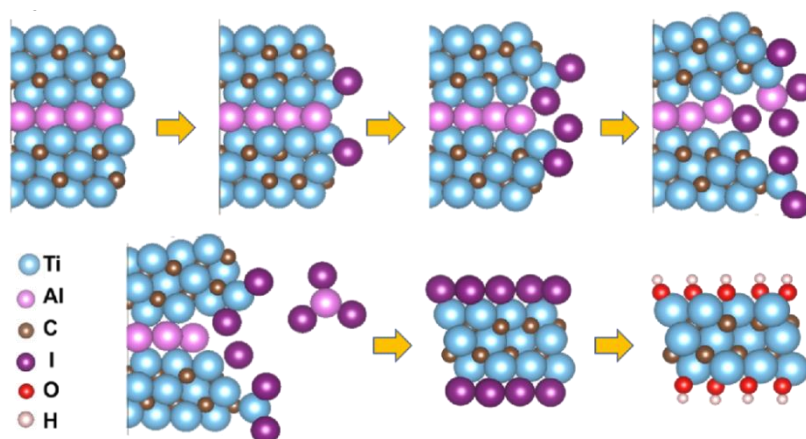**Figure S11.** ELF plots without atoms for the etching process.

Figure S12. Lowest energy atomic configuration for the etching and delamination processes.
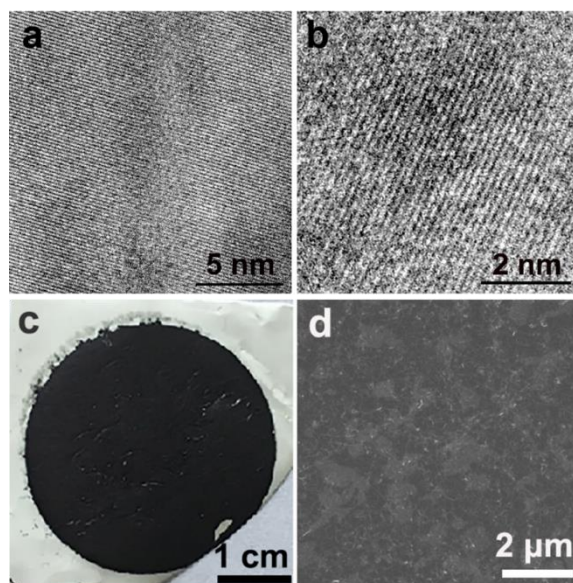
7-Morphology of 2D IE-MXene

Figure S13. (a, b) HR-TEM of 2D IE-MXene flakes, (c) the optical, and (d) SEM image of prepared 2D IE-MXene film via filtration of the dispersion.

8-Stability of HF-etched MXene and IE-MXene in aqueous dispersion

8.1-Stability of HF-etched MXene in aqueous dispersion

HF-etched MXene stored in H_2O presents a dramatic color change from dark green to colorless within two weeks (**Figure S14a-d**). SEM and AFM images clearly show the oxidation process, which initiates from edge to center of flakes owing to the highly negatively charged edge (**Figure S14e-l**).[2] EDS mapping reveals that oxygen content has a dramatic increase from 10.77 to 37.49 wt% (**Figure S15a**). XRD pattern shows that HF-etched MXene has been completely oxidized to TiO_2 after 2 weeks (**Figure S15b**).
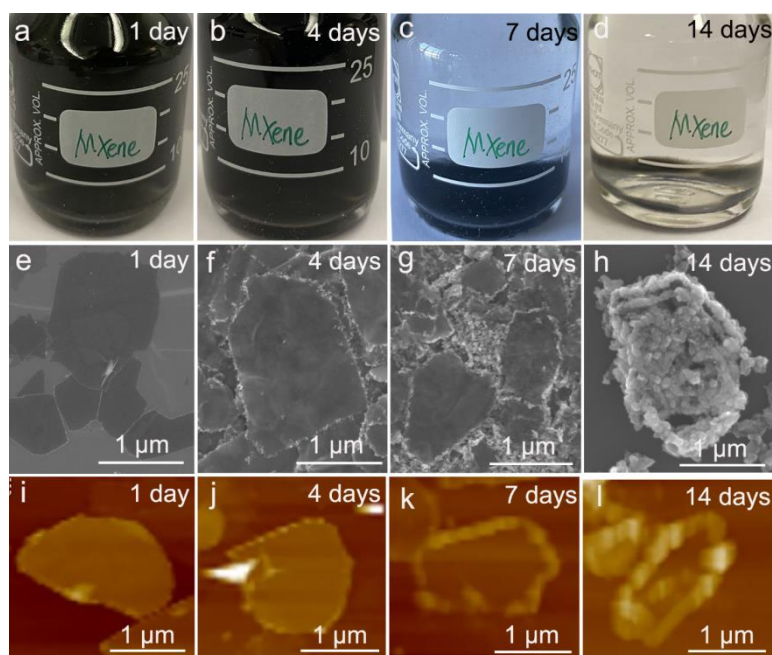

Figure S14. Long-term stability of HF-etched MXene in water. (a-d) the optical images, (e-h**)** SEM images, and (i-l) AFM images of the selected sheets as a function of time.
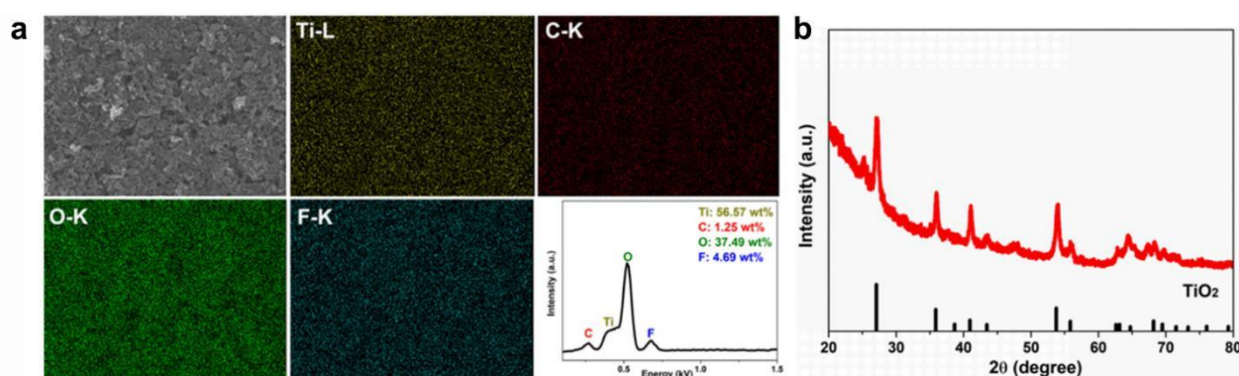

Figure S15. (a) EDS and (b) XRD of HF-etched MXene stored in water for 2 weeks.

Table S2. A brief summary of the stability of MXenes in water.

Materials/Synthesis method	Stability	Reference
$Ti_3C_2T_x/I_2$	2 weeks	This work
$Ti_3C_2T_x/HF$	< 1 week	This work
$Ti_3C_2T_x/LiF$-HCl	1 week	*Inorg. Chem.* **2019**, 58, 1958
$Ti_3C_2T_x$ orTi_2CT_x/LiF-HCl	< 1 week	*Chem. Mater.* **2017**, 29, 4848
$Ti_3C_2T_x/LiF$-HCl	< 10 days	*Matter,* **2019**, 1,513
$Ti_3C_2T_x$ films/LiF-HCl	< 10 days in air	*npj 2D Mater Appl*, **2019**, 3, 8

8.2-Stability of IE-MXene in aqueous dispersion

The aqueous dispersion of IE-MXene sheets does not show any sedimentation or color change within 2 weeks (**Figure S16a-c**). The morphology of water-dispersed IE-MXene sheets remains unchanged and well-defined in this timescale **(Figure S16d-f**). However, they still undergo slow degradation in water, which somehow resembles HF-etched MXenes. Based on the SEM and XRD results, IE-MXene sheets can be oxidized into nanometer-sized TiO_2 nanoparticles after two months (**Figure S17**).
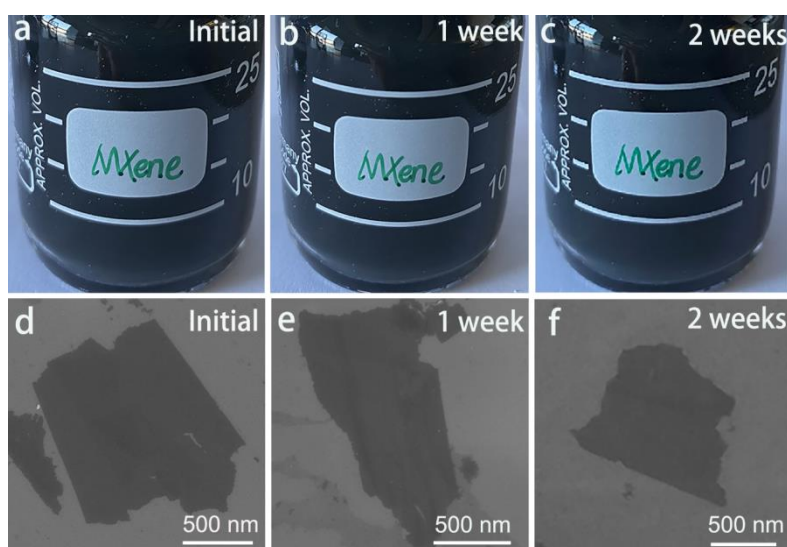
Figure S16. (a-c) The optical images and (d-f) SEM images of IE-MXene in water.
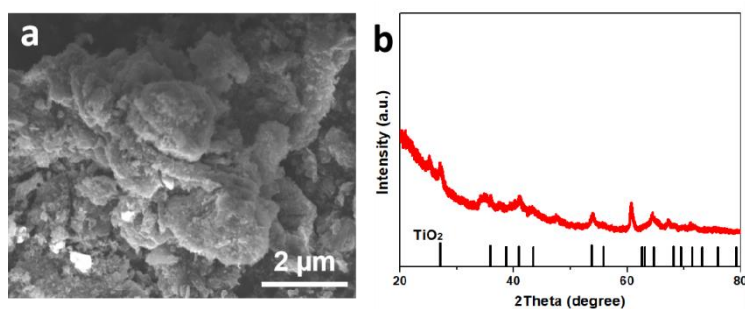
Figure S17. (a) SEM image and (b) XRD of IE-MXene stored in water for 2 months.

9-Electrochemical performance of 2D IE-MXene

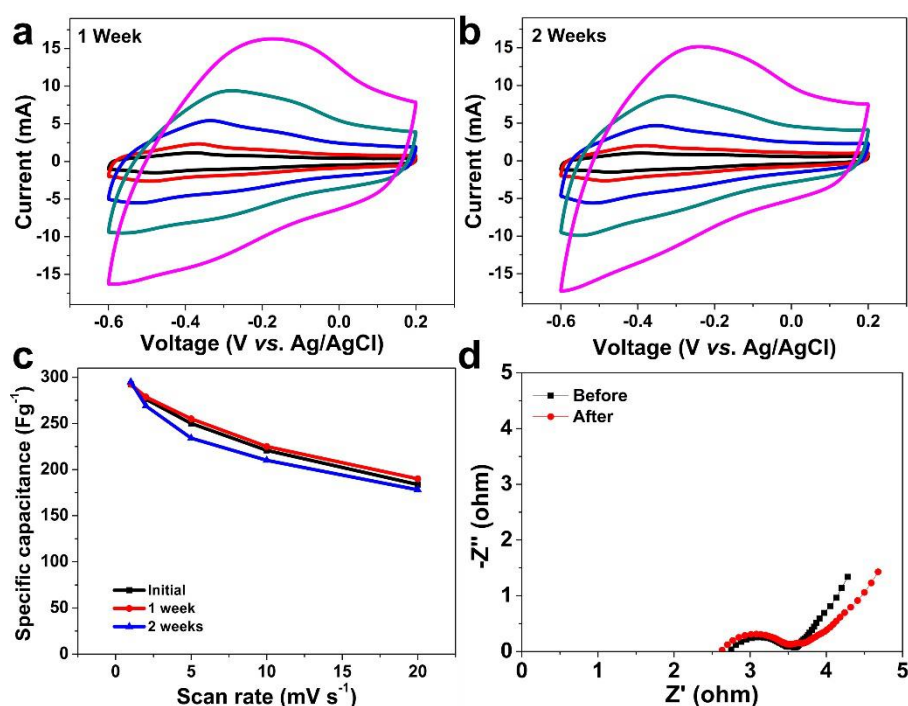**Figure S18**. The stability test of the IE-MXene electrode in water for two weeks. (a-b) CV curves of at different scan rates from 1 to 20 mV s^{-1}, (c) gravimetric capacitances, and (d) electrochemical impedance of the IE-MXene electrode before and after cycling test.

Table S3. A brief summary of $Ti_3C_2T_x$-based electrodes for supercapacitors.

Materials/Synthesis method	Electrolyte	Voltage window	Capacitance	Capacitance retention	Reference
$Ti_3C_2T_x/I_2$	1 M H_2SO_4	-0.6-0.2 V	293 F/g at 1 mV/s	95.8% after 10k cycles	This work
$Ti_3C_2T_x$/LiF-HCl	1 M H_2SO_4	-0.2-0.4 V	192 F/g at 1 mV/s	92% after 10k cycles	*Nano Energy*, **2017**, 38, 368
$Ti_3C_2T_x$/HF	1 M H_2SO_4	/	130 F/g at 2 mV/s	99% after 10k cycles	*Nature*, **2014**, 516, 78
$Ti_3C_2T_x$/LiF-HCl	1 M H_2SO_4	-0.2-0.6 V	88 F/g at 2 mV/s	/	*J. Mater. Chem. A*, **2019**,7, 269
$Ti_3C_2T_x$/LiF-HCl	1 M KOH	-1.0-(-0.4) V	170 F/g at 2 mV/s	/	*Proc. Natl. Acad. Sci.*, **2014**, 111, 16676
$Ti_3C_2T_x$/LiF-HCl	1 M H_2SO_4	-0.2-0.4 V	250 F/g at 5 mV/s	92% after 25k cycles	*Adv. Mater.* **2016**, 28, 1517
$Ti_3C_2T_x$/LiF-HCl	1 M H_2SO_4	-0.6-0 V	280 F/g at 2 mV/s	/	*Nanoscale*, **2020**, 12, 763
$Ti_3C_2T_x$/LiF-HCl	3 M H_2SO_4	-1.1-(-0.2) V	248 F/g at 1 mV/s	97.1% after 10k cycles	*Adv. Mater.* **2019**, 1902432
$Ti_3C_2T_x$/HF	6 M KOH	0-0.7 V	245 F/g at 1 mV/s	/	*Adv. Energy Mater.* **2018**, 8, 1703173
$Ti_3C_2T_x$/HF	1 M H_2SO_4	-0.45-(-0.1) V	255 F/g at 2 mV/s	90 % after 10k cycles	*ACS Nano*, **2019**, 13, 9449
$Ti_3C_2T_x$/HF	1 M TEA BF$_4$	-1.0-(-0.4) V	50 F/g at 2 mV/s	/	*Nat. Commun.*, **2017**, 8, 15717
$Ti_3C_2T_x$/HF	1 M H_2SO_4	-0.5-0.3 V	290 F/g at 1 mV/s	/	*Nanoscale*, **2018**, 10, 9642
$Ti_3C_2T_x$ clay/HF	1 M KOH	-0.55-0 V	130 F/g at 2 mV/s	100 % after 10k cycles	*Science*, **2013**, 314, 1502

Reference:

[1]   a）M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, *Adv. Mater.* **2011**, *23*, 4248-4253; b) M. Naguib, V. N. Mochalin, M. W. Barsoum, Y. Gogotsi, *Adv. Mater.* **2014**, *26*, 992-1005.

[2]   a) V. Natu, J. L. Hart, M. Sokol, H. Chiang, M. L. Taheri, M. W. Barsoum, *Angew. Chem.* **2019**, *58*, 12655-12660; b) X. Zhao, A. Vashisth, E. Prehn, W. Sun, S. A. Shah, T. Habib, Y. Chen, Z. Tan, J. L. Lutkenhaus, M. Radovic, M. J. Green, *Matter* **2019**, *1*, 513-526.