Supporting Information

High-Temperature Behavior and Surface Chemistry of Carbide MXenes Studied by Thermal Analysis

Mykola Seredych, Christopher Eugene Shuck, David Pinto, Mohamed Alhabeb, Eliot Precetti, Grayson Deysher, Babak Anasori, Narendra Kurra, and Yury Gogotsi*

A.J. Drexel Nanomaterials Institute, and Department of Material Science and Engineering, Drexel University, Philadelphia, PA 19104, USA

*Corresponding author. E-mail address: gogotsi@drexel.edu (Y. Gogotsi)

Safety Measures

It is very important to be fully aware of safety and emergency protocols when working with HF acid or HF containing solutions regardless of their concentrations.

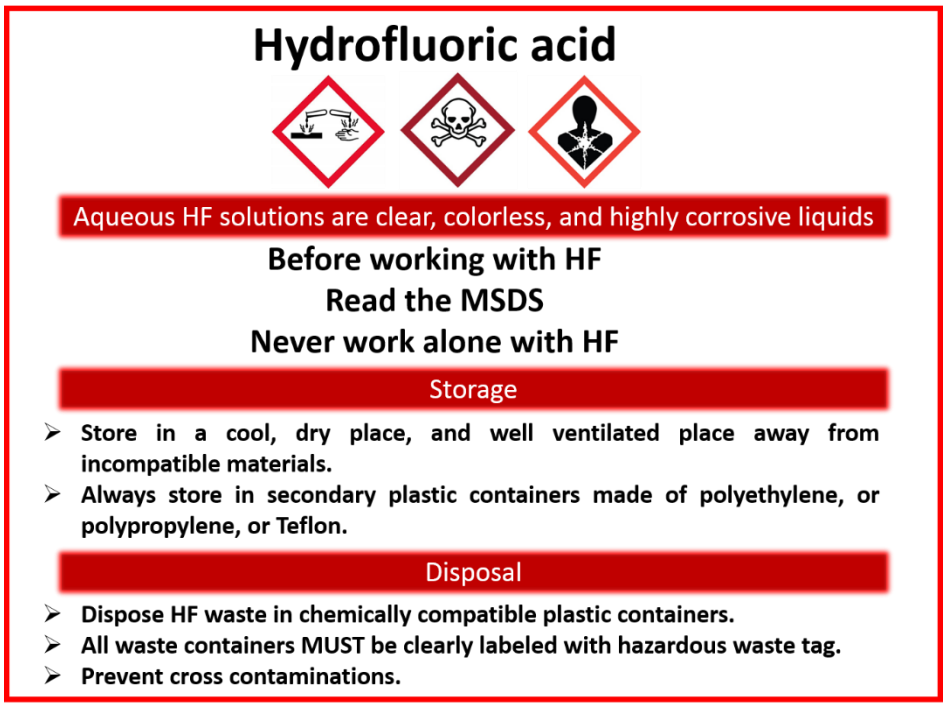

Table S1. Synthesis conditions of multilayer MXene powders discussed in this paper.

MAX phase	Etching methods	MXene
Ti_3AlC_2	5 wt % HF, 24 h, RT	$Ti_3C_2T_x$-5HF
	10 wt % HF, 18 h, RT	$Ti_3C_2T_x$-10HF
	30 wt % HF, 4 h, RT	$Ti_3C_2T_x$-30HF
	5/25/70 wt % $HF/H_2SO_4/H_2O$, 24 h, RT	$Ti_3C_2T_x$-HF/H_2SO_4
	5/25/70 wt % $HF/HCl/H_2O$, 24 h, RT	$Ti_3C_2T_x$-HF/HCl
Mo_2Ga_2C	50 wt % HF, 120 h, 50°C	Mo_2CT_x
Nb_2AlC	50 wt % HF, 48 h, 50°C	Nb_2CT_x

RT – room temperature; HF – hydrofluoric acid; HCl – hydrochloric acid; H_2SO_4 – sulfuric acid

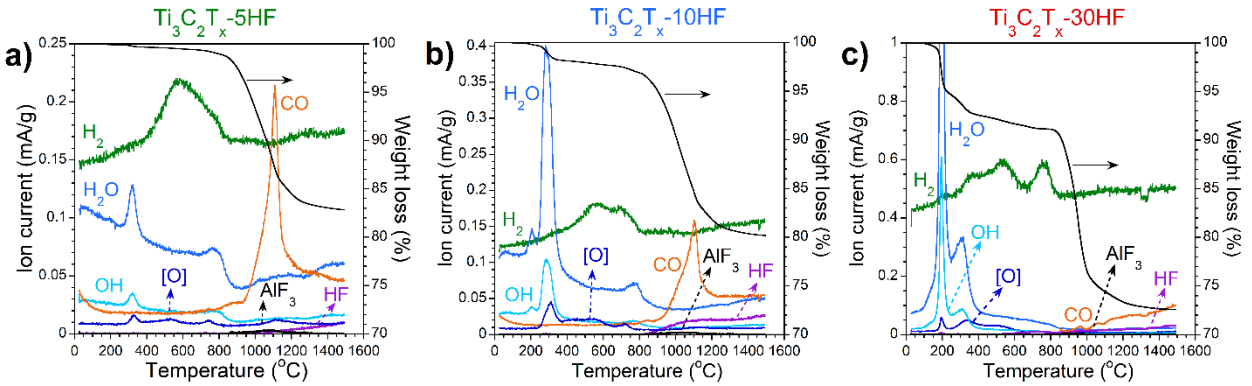

Figure S1. Thermal gravimetric (TG) curves with mass spectrometry analysis for $Ti_3C_2T_x$ MXene: $Ti_3C_2T_x$-5HF (5 wt.% HF for etching) (a), $Ti_3C_2T_x$-10HF (10 wt.% HF for etching) (b) and $Ti_3C_2T_x$-30HF (30 wt.% HF for etching) (c). Ion currents for atomic mass unit (amu) 28 (corresponding to either CO or N_2) is not shown at low temperature (c) due to trace of N_2 in the He tank (see explanation below).

It was noticed that the background ionic current varies for different samples, starting from ambient temperature in the recorded TA-MS profiles. It should be noted that residual nitrogen from the ultra-high purity He tank can contribute to that ionic current, which often causes different backgrounds. Since N_2 and CO have similar *m/z* ratios, and given the high sensitivity for CO, if

the CO gas starts evolving from the surface terminations at high temperatures, the nitrogen background current gets suppressed. Therefore, to avoid confusion, we have excluded the background ionic current profile from nitrogen gas and only focused on CO signal at high temperature regime.

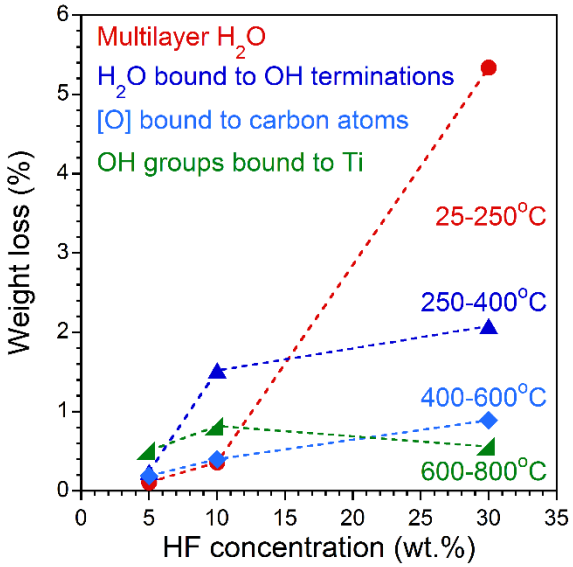

Figure S2. The changes in the weight loss after etching with 5, 10 and 30 wt % HF in the different temperature regimes.

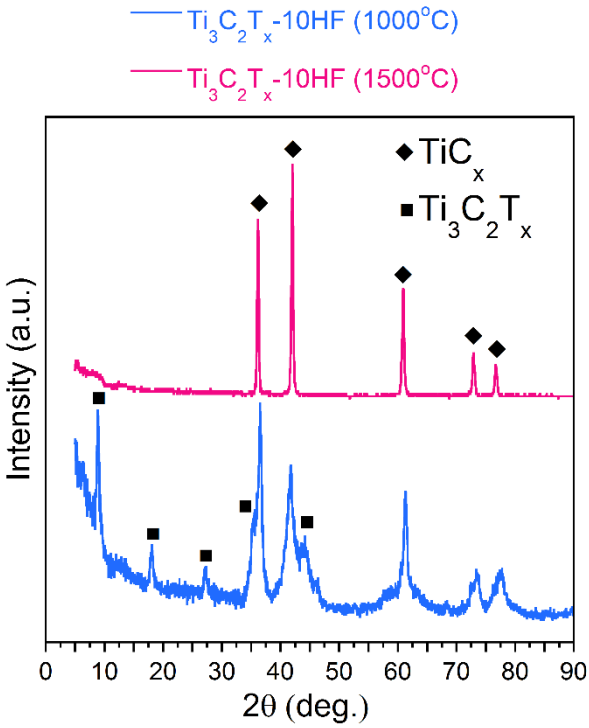

Figure S3. X-ray diffraction (XRD) patterns for $Ti_3C_2T_x$-10HF obtained by etching Ti_3AlC_2 with 10 wt.% HF MXene after heating to 1000 °C and 1500 °C.

The XRD pattern indicates that after initial heating to 1000 °C, MXene is transformed into cubic TiC. This conversion is accompanied by the release of CO species. At 1500 °C, the $Ti_3C_2T_x$ is completely transformed into cubic carbide, with no evidence of any other phases in the XRD pattern.

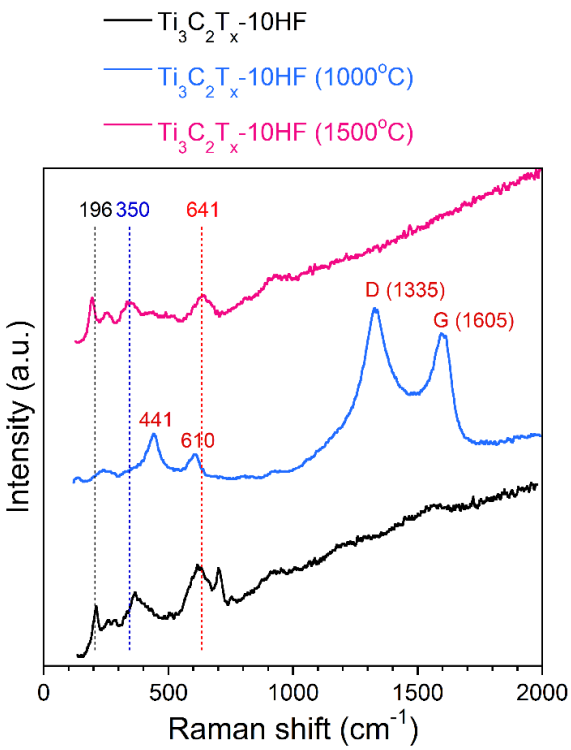

Figure S4. Raman spectra of $Ti_3C_2T_x$-10HF samples: pristine (black curve), heating to 1000 ºC (blue curve) and 1500 ºC (pink curve).

Raman spectrum of pristine $Ti_3C_2T_x$-10HF showed peaks at 213, 280, 618 and 700 cm^{-1}, which are typical signatures for titanium carbide MXene.[1, 2] Thermal treatment of $Ti_3C_2T_x$ MXene at 1000 ºC in the inert atmosphere converted it into rutile (TiO_2), TiC and disordered carbon, as evidenced from the Raman spectrum (blue profile). The peaks at 441 and 610 cm^{-1} correspond to rutile TiO_2 phase. The broad D and G bands at 1335 and 1605 cm^{-1} are due to presence of disordered carbon in the samples treated at 1000 ºC. Probably, this structural transformation of $Ti_3C_2T_x$ MXene can be explained by the disproportionation reaction, based on the following reaction.[3]

At 1000 ºC: $Ti_3C_2O_x = 2TiO_2 + TiC + C$ (disproportionation reaction) (I)

Interestingly, after increasing the annealing temperature to 1500 ºC, the oxide phase is reduced by the free carbon, leading to the formation of cubic titanium carbide phase with the liberation of CO_x

species. Raman signatures of MXene sample annealed at 1500 ºC are similar to that of the pristine sample, signifying that bonding changes are being reverted. More interestingly, the peak at 700 cm^{-1} corresponds out-of-plane of vibrations of carbon atoms in $Ti_3C_2O(OH)$ and the absence of this peak in the sample annealed at 1500 ºC can be attributed to the reduction of oxy/hydroxy functionalities significantly.

At 1500 ºC: $TiO_y + zC = TiC + CO_2$, CO (carbothermal reduction) (II)

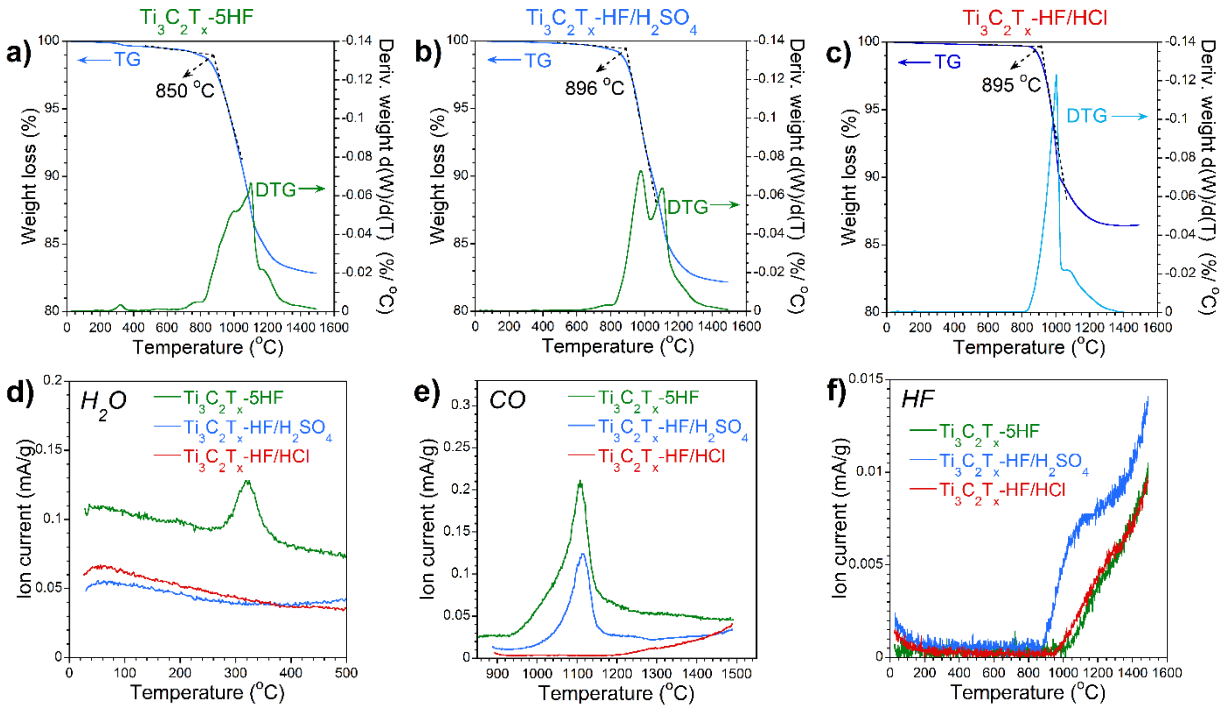

Figure S5. Thermal gravimetric (TG) curves with derivatives of the weight losses (DTG) for $Ti_3C_2T_x$ MXene (a); etched with an acid mixture of HF/H_2SO_4 (5 wt % HF, 25 wt % H_2SO_4, 70 wt % H_2O) (b) HF/HCl (5 wt % HF, 25 wt % HCl, 70 wt % H_2O) (c), and mass spectrometry analysis for the atomic mass unit (amu) of 18/H_2O (d), 28/CO (e) and 20/HF (f).

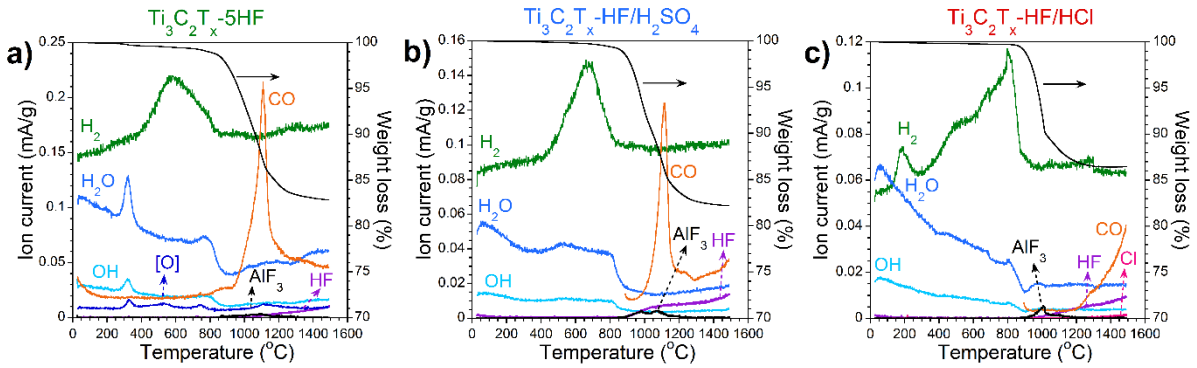

Figure S6. Thermal gravimetric (TG) curves with mass spectrometry analysis for $Ti_3C_2T_x$ MXene obtained by etching (a); with an acid mixture of HF/H_2SO_4 (5 wt % HF, 25 wt % H_2SO_4, 70 wt % H_2O) (b), and HF/HCl (5 wt % HF, 25 wt % HCl, 70 wt % H_2O) (c).

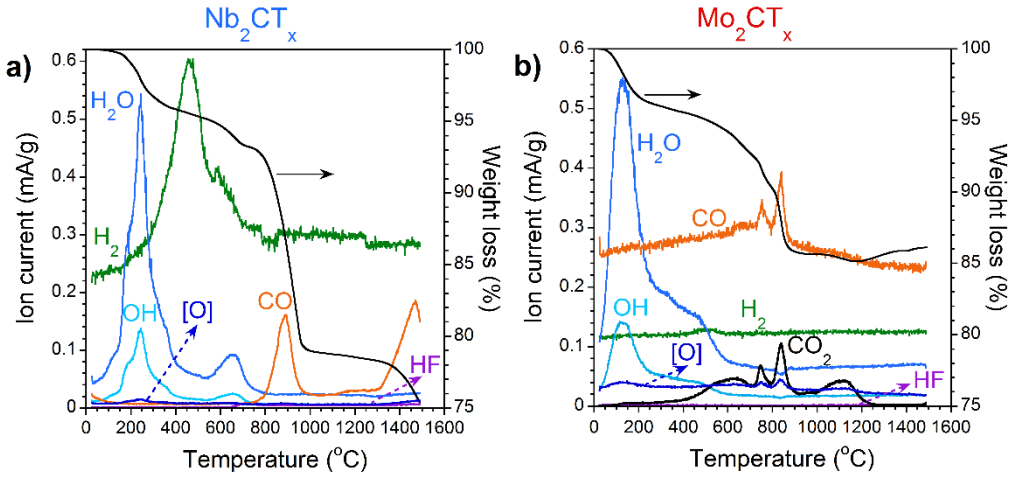

Figure S7. Thermal gravimetric (TG) curves with mass spectrometry analysis for multilayer Nb_2CT_x (a) and Mo_2CT_x (b) powders obtained by etching Nb_2AlC and Mo_2Ga_2C in 50 wt % HF for 48, and 120 h at 50 °C, respectively.

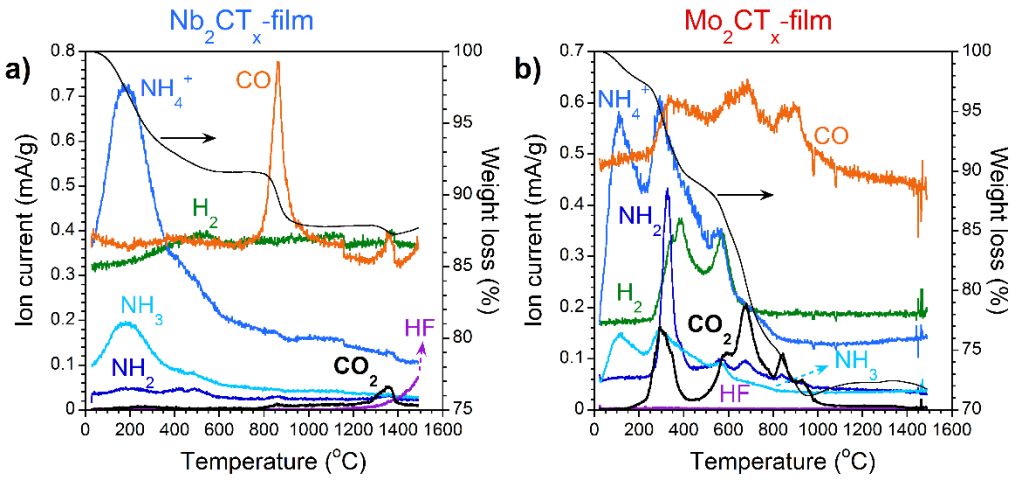

Figure S8. Thermal gravimetric (TG) curves with mass spectrometry analysis for Nb_2CT_x (a) and Mo_2CT_x (b) films produced by vacuum assisted filtration of colloidal solution of MXenes delaminated with tetramethylammonium hydroxide (TMAOH).

REFERENCES

1. Jiang, Q.; Kurra, N.; Alhabeb, M.; Gogotsi, Y.; Alshareef, H. N., All Pseudocapacitive MXene-RuO_2 Asymmetric Supercapacitors. *Adv. Energy Mater.* **2018**, *8*, 1703043.
2. Hu, M.; Li, Z.; Hu, T.; Zhu, S.; Zhang, C.; Wang, X., High-Capacitance Mechanism for $Ti_3C_2T_x$ MXene by in situ Electrochemical Raman Spectroscopy Investigation. *ACS Nano* **2016**, *10*, 11344-11350.
3. Naguib, M.; Mashtalir, O.; Lukatskaya, M. R.; Dyatkin, B.; Zhang, C.; Presser, V.; Gogotsi, Y.; Barsoum, M. W., One-step Synthesis of Nanocrystalline Transition Metal Oxides on Thin Sheets of Disordered Graphitic Carbon by Oxidation of MXenes. *Chem. Commun.* **2014**, *50*, 7420-7423.