Supplementary Information

Sodium hydroxide and vacuum annealing modifications of the surface terminations of a Ti_3C_2 (MXene) epitaxial thin film

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XPS details

XPS spectra were recorded for the following regions: Ti 2p, C 1s, O 1s, F 1s, Na 1s and Al 2p using a pass energy of 20 eV with a step size of 0.1 eV. The BE scale of all XPS spectra was referenced to the Fermi-edge (E_F), which was set to a BE of zero eV. Peak fitting for the high-resolution spectra was performed using CasaXPS Version 2.3.16 RP 1.6 in a similar manner as in Ref. [1]. Prior to peak fitting, the background contributions were subtracted using a Shirley function. For the Ti $2p_{3/2}$ and $2p_{1/2}$ components, the area ratios of the peaks were constrained to be 2:1, respectively.

The fitting for all peaks was done using a Gaussian-Lorentzian function except for the C-Ti-(O,OH) and C-Ti-T_x peaks in the Ti 2p and C 1s regions which were fitted using a Lorentzian asymmetric function similar as in Ref. [1, 2]. The BEs were allowed to shift ±0.3 eV from their initial values and the full width at half maximum (FWHM) values were allowed to shift ±0.2 eV from their initial values. The global atomic percentage of the various elements was calculated using the following equation:

$$X_i = 100\ x \frac{A_i}{\sum_{j=1}^{m} A_j}$$

where X_i, is the atomic concentration of the element i, A_i is the adjusted intensity of the element i, and A_j is the total adjusted intensity of all elements. The adjusted intensity is defined as follows:

$$A_i = \frac{I_i}{R_i}$$

where I_i, is the integrated peak area and R_i is the relative sensitivity factor. The atomic percentages of the various species were determined by multiplying the total atomic percentage of each element by the fraction of that element. The total atomic percentage of each element was obtained from the high-resolution spectra of that element.

The chemical formula of $Ti_3C_2T_x$ was calculated by multiplying the fraction of each MXene species from the high-resolution spectra of all the elements (found in Tables 1-6) by the atomic percentage of that element found in Table S1. The contribution of the organic compounds containing oxygen: “C-O” and “COO” species were subtracted from the species overlapping with them in the O 1s region. As an approximation, we kept the ratio between the peaks at this region of O termination, OH termination, $Al(OF)_x$, Al_2O_3 and H_2O_{ads} constant. The amounts of oxygen in the organic species, estimated from their carbon amounts, were calculated to be less than 1 at. % for $Ti_3C_2T_x$, 9.0 at. % for $Ti_3C_2T_x$-Na and less than 5 at. % for $Ti_3C_2T_x$-Na annealed. BE of C-Ti-O(I)$_x$ and TiO_2 in O 1s region are identical, in order to resolve this issue, the amount of Ti in TiO_2 was calculated from the Ti 2p region, then the O for that species was accounted for from the O 1s region to for a 1:2 ratio of Ti:O, the remaining O was identified to belong to C-Ti-O(I)$_x$. The margin of error in the elements presented in the chemical formulae is ± 10%.

XPS data

Table S1: XPS peak fitting results for Ti 2p region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV][a]	FWHM [eV][a]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	455.1 (461.3)	0.6 (1.1)	0.27	(OH, or O)-Ti-C	[1, 2]
	455.9 (461.6)	1.4 (2.8)	0.23	(OH, or O)-Ti^{2+}-C	[1, 2]
	456.9 (462.6)	2.0 (2.5)	0.34	(OH, or O)-Ti^{3+}-C	[1, 2]
	458.9 (464.5)	1.8 (3.0)	0.11	TiO_2	[1, 2]
	460.4 (466.4)	1.4 (3.0)	0.05	C-Ti-F_x	[1, 2]
MX-Na	455.1 (461.3)	0.6 (1.1)	0.08	(OH, or O)-Ti-C	[1, 2]
	455.8 (461.5)	1.4 (2.2)	0.19	(OH, or O)-Ti^{2+}-C	[1, 2]
	456.9 (462.5)	2.0 (2.4)	0.27	(OH, or O)-Ti^{3+}-C	[1, 2]
	459.1 (464.7)	1.5 (2.4)	0.37	TiO_2	[1, 2]
	459.3 (465.1)	1.1 (1.3)	0.04	O-Ti-F_x	[1, 2]
	460.2 (465.9)	1.7 (2.5)	0.05	C-Ti-F_x	[1, 2]
MX-Na-A	454.9 (461.1)	0.6 (1.2)	0.47	(OH, or O)-Ti-C	[1, 2]
	455.9 (461.6)	1.5 (2.4)	0.16	(OH, or O)-Ti^{2+}-C	[1, 2]
	457.1 (462.8)	2.1 (2.4)	0.24	(OH, or O)-Ti^{3+}-C	[1, 2]
	458.7 (464.3)	1.6 (2.3)	0.12	TiO_2	[1, 2]
	459.6 (465.3)	1.3 (2.0)	0.01	O-Ti-F_x	[1, 2]
	460.5 (466.5)	1.5 (2.6)	0.02	C-Ti-F_x	[1, 2]

[a] Values in parentheses correspond to the $2p_{1/2}$ component

Table S2: XPS peak fitting results for O 1s region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV]	FWHM [eV]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	530.0	1.1	0.40	C-Ti-O(I)$_x$	[1, 2]
	531.1	1.5	0.20	C-Ti-O(II)$_x$/OR[a]	[1, 2]
	532.1	1.5	0.26	C-Ti- (OH)$_x$/OR[a]	[1, 2]
	533.0	1.3	0.06	Al(OF)$_x$ /OR[a]	[1, 2]
	533.8	2.0	0.08	H_2O_{ads}/OR[a]	[1, 2]
MX-Na	530.1	1.2	0.37	TiO_2	[1, 2]
	530.7	0.9	0.11	$TiO_{2-x}F_x$	[1, 2]
	531.2	1.3	0.26	C-Ti-O$_x$/OR[a]	[1, 2]
	532.2	1.3	0.14	C-Ti- (OH)$_x$/OR[a]	[1, 2]
	532.8	1.2	0.05	Al_2O_3 /OR[a]	[1, 2]
	533.5	1.8	0.07	H_2O_{ads}/OR[a]	[1, 2]
MX-Na-A	529.9	1.2	0.37	TiO_2	[1, 2]
	530.8	0.8	0.03	$TiO_{2-x}F_x$	[1, 2]
	531.2	1.2	0.34	C-Ti-O$_x$/OR[a]	[1, 2]
	532.1	1.4	0.15	C-Ti- (OH)$_x$/OR[a]	[1, 2]
	533.0	1.3	0.05	Al(OF)$_x$ /OR[a]	[1, 2]
	533.8	2.0	0.06	H_2O_{ads}/OR[a]	[1, 2]

[a] OR stands for organic compounds due to atmospheric surface contaminations.

Table S3: XPS peak fitting results for F 1s region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV][a]	FWHM [eV][a]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	685.4	1.4	0.93	C-Ti-(O,F)$_x$	[3]
	687.5	1.9	0.07	Al(OF)$_x$	[1, 2]
MX-Na	685.0	1.3	0.84	C-Ti-(O,F)$_x$	[3]
	685.7	1.4	0.16	TiO_2-F	[1, 2]
MX-Na-A	684.3	1.5	0.35	C-Ti-F$_x$	[3]
	685.7	2.0	0.25	$TiO_{2-x}F_x$	[1, 2]
	688.7	2.0	0.40	AlF_3	[1, 2]

C 1s region

The C 1s region (Figure 3b and Table 2) was fit by four peaks. The largest (~70% of the C 1s region) labelled "C-Ti-T_x" is assigned to C atoms bonded to Ti in $Ti_3C_2T_x$ compound. The rest of peaks labelled "C-C", "CH_x" and "C-O" are assigned to carbon and organic compounds surface contaminations resulting from the etching and washing processes. This peak assignment is consistent with Refs. [1, 2]. The same peaks are present in both MX-Na and MX-Na-A but with an additional peak to the far left of the BE assigned for COO species.

Table S4: XPS peak fitting results for C 1s region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV]	FWHM [eV]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	282.0	0.6	0.69	C-Ti-T_x	[1, 2]
	284.3	1.3	0.20	C-C	[1, 2]
	285.3	1.5	0.08	CH_x	[1, 2]
	286.6	1.0	0.03	C-O	[1, 2]
MX-Na	281.9	0.6	0.37	C-Ti-T_x	[1, 2]
	284.5	1.4	0.12	C-C	[1, 2]
	285.2	1.4	0.25	CH_x	[1, 2]
	286.7	1.6	0.19	C-O	[1, 2]
	288.9	1.6	0.07	COO	[1, 2]
MX-Na-A	281.9	0.6	0.63	C-Ti-T_x	[1, 2]
	284.7	1.5	0.25	C-C	[1, 2]
	286.4	1.5	0.08	CH_x/C-O	[1, 2]
	288.7	1.5	0.04	COO	[1, 2]

Table S5: XPS peak fitting results for O 1s region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV]	FWHM [eV]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	530.0	1.1	0.40	C-Ti-O(I)$_x$	[1, 2]
	531.1	1.5	0.20	C-Ti-O(II)$_x$/OR[a]	[1, 2]
	532.1	1.5	0.26	C-Ti- (OH)$_x$/OR[a]	[1, 2]
	533.0	1.3	0.06	Al(OF)$_x$ /OR[a]	[1, 2]
	533.8	2.0	0.08	H_2O_{ads}/OR[a]	[1, 2]
MX-Na	530.1	1.2	0.37	TiO_2	[1, 2]
	530.7	0.9	0.11	$TiO_{2-x}F_x$	[1, 2]
	531.2	1.3	0.26	C-Ti-O_x/OR[a]	[1, 2]
	532.2	1.3	0.14	C-Ti- (OH)$_x$/OR[a]	[1, 2]
	532.8	1.2	0.05	Al_2O_3 /OR[a]	[1, 2]
	533.5	1.8	0.07	H_2O_{ads}/OR[a]	[1, 2]
MX-Na-A	529.9	1.2	0.37	TiO_2	[1, 2]
	530.8	0.8	0.03	$TiO_{2-x}F_x$	[1, 2]
	531.2	1.2	0.34	C-Ti-O_x/OR[a]	[1, 2]
	532.1	1.4	0.15	C-Ti- (OH)$_x$/OR[a]	[1, 2]
	533.0	1.3	0.05	Al(OF)$_x$ /OR[a]	[1, 2]
	533.8	2.0	0.06	H_2O_{ads}/OR[a]	[1, 2]

[a] OR stands for organic compounds due to atmospheric surface contaminations.

Table S6: XPS peak fitting results for F 1s region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV][a]	FWHM [eV][a]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	685.4	1.4	0.93	C-Ti-(O,F)$_x$	[3]
	687.5	1.9	0.07	Al(OF)$_x$	[1, 2]
MX-Na	685.0	1.3	0.84	C-Ti-(O,F)$_x$	[3]
	685.7	1.4	0.16	TiO_2-F	[1, 2]
MX-Na-A	684.3	1.5	0.35	C-Ti-F_x	[3]
	685.7	2.0	0.25	$TiO_{2-x}F_x$	[1, 2]
	688.7	2.0	0.40	AlF_3	[1, 2]

Al 2p region

The Al 2p region of $Ti_3C_2T_x$, MX-Na and MX-Na-A (Figure 4c bottom, middle, and top, respectively) was fit by the corresponding components listed in column 5 in Table 6. For $Ti_3C_2T_x$ and MX-Na, the Al 2p region was fit by one component belonging to Al-oxyfluoride an etching byproduct. After vacuum annealing, the Al 2 p region was fit by one component belonging to AlF_3 which might be due to the conversion of the $Al(OF)_x$ to AlF_3 upon annealing. It is worth noting that the total atomic percentage of Al in the three cases is less than 3 at. %.

Table S5: XPS peak fitting results for Al 2p region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV][a]	FWHM [eV][a]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	75.6	1.6	1.0	$Al(OF)_x$	[1, 2]
MX-Na	75.6	1.5	1.0	$Al(OF)_x$	[1, 2]
MX-Na-A	75.1	1.4	1.0	AlF_3	[1, 2]

Na 1s region

The Na 1s region of $Ti_3C_2T_x$, MX-Na and MX-Na-A (Figure 4b bottom, middle, and top, respectively) was fit by the corresponding components listed in column 5 in Table 5. Because this region overlaps with the Ti Auger LMM lines, peak fitting of $Ti_3C_2T_x$ was first performed to locate the Ti Auger LMM lines. The region was then fit by two components assigned to titanium surface oxide at BE of 1066.4 eV labelled as "TiO_2" and Ti in the MXene compound at BE of 1069.2 eV labeled as "Ti-C" similar to Ref. [1]. After NaOH treatment, a third peak appears at a BE of 1072.2 eV assigned to Na^+ cations intercalated in $Ti_3C_2T_x$ in agreement with Ref. [1]. After vacuum annealing the intensity of the peak assigned to Na^+ intercalated has significantly reduced as shown in Figure 5a, top curve.

Table S6: XPS peak fitting results for Na 1s region of various $Ti_3C_2T_x$ MXenes thin films.

Sample	BE [eV]	FWHM [eV]	Fraction	Assigned to	Reference
$Ti_3C_2T_x$	1066.4	2.3		TiO_2 (Auger LMM line)	[1]
	1069.2	5.3		Ti-C (Auger LMM line)	[1]
MX-Na	1066.3	2.3		TiO_2 (Auger LMM line)	[1]
	1068.9	5.3		Ti-C (Auger LMM line)	[1]
	1072.2	1.8	1.0	Na^+ (Na 1s)	[1]
MX-Na-A	1066.1	2.1		TiO_2 (Auger LMM line)	[1]
	1069.3	5.3		Ti-C (Auger LMM line)	[1]
	1072.2	1.9	1.0	Na^+ (Na 1s)	[1]

Table S7. Summary of global atomic percentages obtained from the high resolution XPS spectra of the following regions: Ti 2p, C 1s, O 1s, F 1s, Al 2p, and Na 1s of $Ti_3C_2T_x$ thin films.

	Ti at%	C at.%	O at.%	F at.%	Al at.%	Na at.%
$Ti_3C_2T_x$	37.2±0.2	33.3±0.1	17.9±0.3	9.9±0.3	1.7±0.1	
MX-Na	24.1±0.2	28.4±0.5	37.1±0.2	4.2±0.1	2.8±0.1	3.4±0.1
MX-Na-A	36.0±0.2	30.2±0.2	29.7±0.2	2.0±0.2	1.7±0.1	0.4±0.1

References:

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