Electronic Supplementary Information (ESI)

Relating X-Ray Photoelectron Spectroscopy Data to Chemical Bonding in MXenes

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Table S1. Experimental results of XPS analysis in MXenes. Bold numbers are selected to compare and discuss our theoretical predictions.

MXene	Region	Binding energy (eV)	Asignation	Ref.
Nb_2CT_z	O (1s)	530.0 **531.8** 532.4	O in Nb_2O_5 **O/HO-Nb_2C** Water trapped between MXene layer	[1]
	C (1s)	**281.8** 282.0 283.6	**C in Nb_2C** Non-stoichiometric C in Nb_2C Adventitious contamination	
V_2CT_z	O (1s)	529.9 **531.3** 532.9	Mixed VO_x and surface oxide groups **Mixed VO_x and surface oxide groups** Water trapped between MXene layer	[1]
	C (1s)	**281.8** 286.1 284.5 288.3	**C in V_2C** Adventitious contamination Adventitious contamination Adsorbed methanol	
Ti_2CT_z before sputtering	O (1s)	**531.1** 532.0 533.1	**C-Ti-O_z** C-Ti-$(OH)_z$ Water trapped between MXene layer	[2]
	C (1s)	**281.9** 286.2 289.0	**C-Ti-T_z** C-O C-OO	
Ti_2CT_z after sputtering	O (1s)	**531.3** 532.2 533.5	**C-Ti-O_z** C-Ti-$(OH)_z$ Water trapped between MXene layer	
	C (1s)	**281.9** 286.2	**C-Ti-T_z** C-O	
Mo_2CT_z	O (1s)	**531.1** 532.2 533.4	**Mo_2CO_x (-O terminated)** $Mo_2C(OH)_x$ (-OH terminated) Water trapped between MXene layer	[3]
	C (1s)	**283.1**	**Mo-C species**	
MultiLayered Cr_2CT_z	O (1s)	530.2 531.2	**O-Cr-C (-O terminated)** HO-Cr-C	[4]
	C (1s)	283.2	**C-Cr-T_z**	
FewLayered Cr_2CT_z	O (1s)	**530.4** 531.6	**O-Cr-C (-O terminated)** HO-Cr-C	[4]
	C (1s)	**283.5**	**C-Cr-T_z**	

Table S2. Kohn-Sham orbital energy (ε_{1s}), Fermi energy (ε_F), initial state C(1s) CLBE relative to the Fermi energy of each system (see Eq. 2) and net charge on the C atom (Q_C) of partial relaxed O-terminated M_2CO_2 MXenes. The number of d electrons in the corresponding metal (d^n) is also provided. The units of energetic parameters (ε_{1s}, ε_F, and C(1s) CLBE) are in eV, whereas Q_C units are |e|. Note that the O layers are relaxed maintaining the M_2C fixed at the clean MXene.

MXene	**d^n**	**ε_{1s}**	**ε_F**	**CLBE**	**Q_C**
Ti_2CO_2	d^2	-267.8	-3.6	264.2	-1.9
Zr_2CO_2		-265.6	-2.0	263.6	-1.9
Hf_2CO_2		-265.2	-1.5	263.7	-1.9
V_2CO_2	d^3	-268.0	-2.7	265.3	-1.6
Nb_2CO_2		-267.6	-2.0	265.6	-1.8
Ta_2CO_2		-267.4	-1.6	265.8	-2.1
Cr_2CO_2	d^4	-267.7	-2.2	265.5	-1.3
Mo_2CO_2		-268.3	-1.7	266.6	-1.4
W_2CO_2		-267.3	-1.5	265.8	-1.5

Table S3. Kohn-Sham orbital energy (ε_{1s}), Fermi energy (ε_F), initial state O(1s) CLBE relative to the Fermi energy of each system (see Eq. 2) and net charge on the O atom (Q_O) of partial relaxed O-terminated M_2CO_2 MXenes. The number of d electrons in the corresponding metal (d^n) is also provided. The units of energetic parameters (ε_{1s}, ε_F, and O(1s) CLBE) are in eV, whereas Q_O units are |e|. Note that the O layers are relaxed maintaining the M_2C fixed at the clean MXene.

MXene	**d^n**	**ε_{1s}**	**ε_F**	**CLBE**	**Qo**
Ti_2CO_2	d^2	-508.8	-3.6	505.2	-1.0
Zr_2CO_2		-507.4	-2.0	505.4	-1.2
Hf_2CO_2		-507.0	-1.5	505.5	-1.3
V_2CO_2	d^3	-508.8	-2.7	506.1	-1.0
Nb_2CO_2		-508.3	-2.0	506.3	-1.1
Ta_2CO_2		-508.2	-1.6	506.6	-1.2
Cr_2CO_2	d^4	-508.7	-2.2	506.5	-0.9
Mo_2CO_2		-508.6	-1.7	506.9	-0.9
W_2CO_2		-508.2	-1.5	506.7	-1.0

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