ELECTRONIC SUPPLEMENTARY INFORMATION

High Performance Photocatalytic and Thermoelectric Two-Dimensional Asymmetrically Ordered Janus-like MXene Alloy

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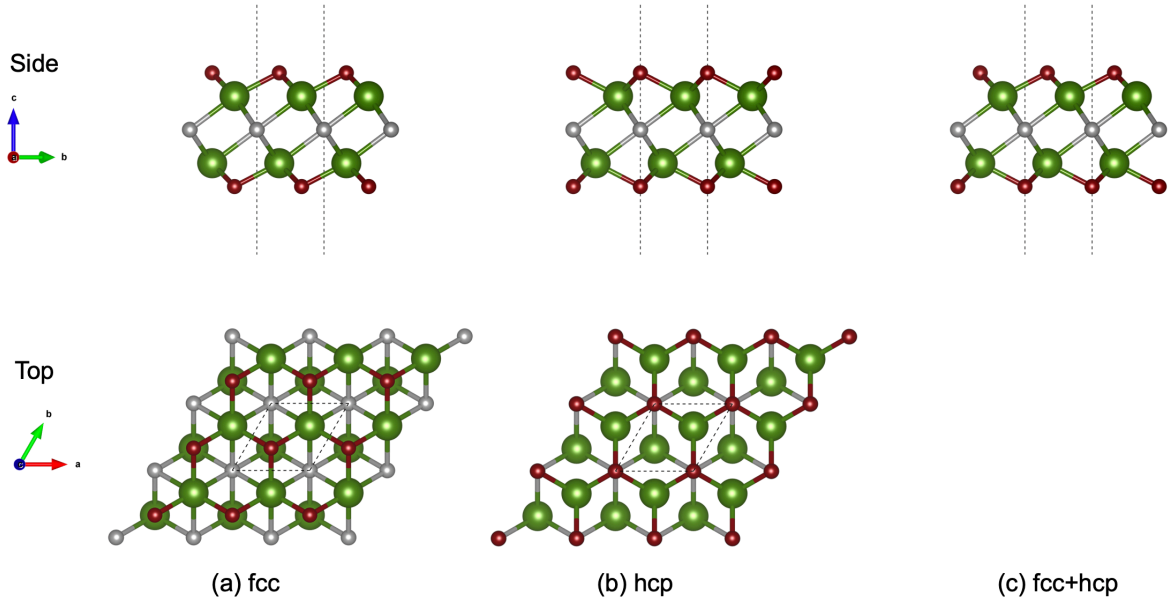


Figure S1. Depiction of the side and top views of the 3 different possible geometries of fully O-terminated MXenes with (a) fcc, (b) hcp, and (c) fcc+hcp O-sites occupied. The red, green, and grey spheres correspond to O, transition metal M, and C, respectively.

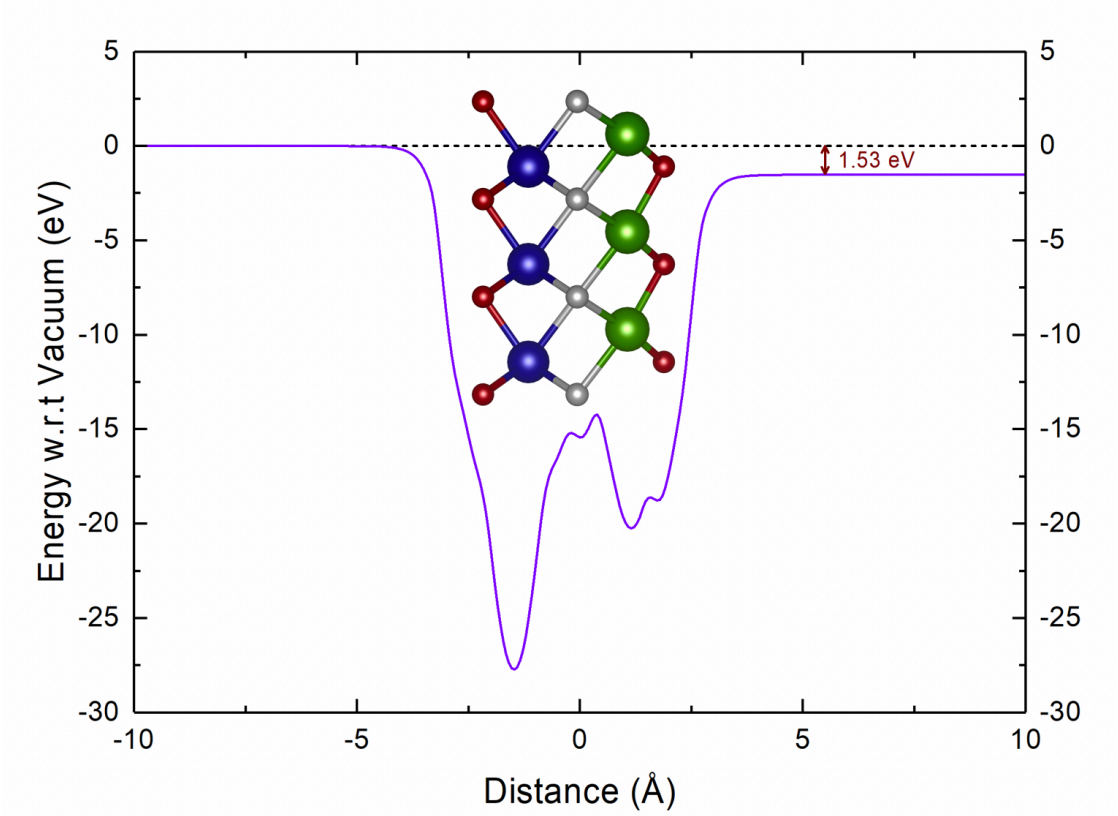


Figure S2. Schematic illustration of the electrostatic potential profile for the Janus-like ground-state $TiMoCO_2$ MXene alloy along the out-of-plane direction. The structure of the MXene is shown along the same direction with the positions of the atoms in relative to the electrostatic potential. The red, green, blue, and grey spheres correspond to O, Ti, Mo, and C, respectively. The value of the potential difference is indicated in red. The out-of-plane distance is referenced from the center of the MXene, i.e., the carbon layer.

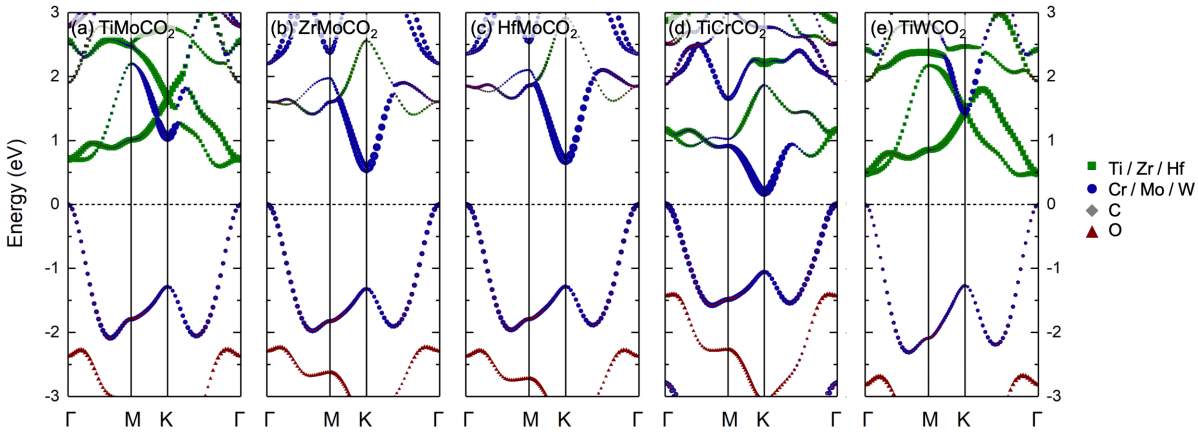
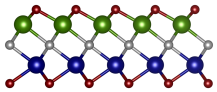
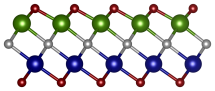
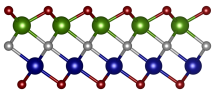
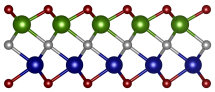
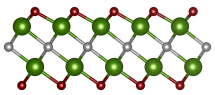
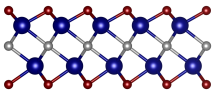


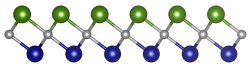
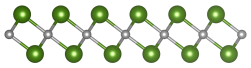
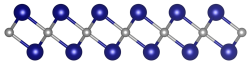
Figure S3. Projected electronic band structure of the (a) Janus-like ground-state $TiMoCO_2$, and its analogous conjectural (b) $ZrMoCO_2$, (c) $HfMoCO_2$, (d) $TiCrCO_2$, and (e) $TiWCO_2$ MXene alloys, via HSE06 functional plotted along high-symmetry path of the hexagonal Brillouin zone (see Figure 2f of main text). The size of each point corresponds to the relative magnitude of the respective elemental contribution to the band. The Fermi level is set to 0 eV.

Table S1. Structure of various $TiMoCO_2$ MXene alloys with different O-sites and their constituent MXenes Ti_2CO_2 and Mo_2CO_2, their relative energies with respect to the constituents obtained via density functional theory, and the Bader charges of the respective elements.

MXene	Configuration*	Relative Energy (meV/atom)	Bader Charge (*e*)				
			C	Ti	Mo	O_{Top}	O_{Bottom}
$TiMoCO_2$ Alloys							
fcc-hcp†		-19.0	-1.51	+1.92	+1.60	-1.08	-0.93
fcc-fcc		+74.9	-1.57	+1.92	+1.74	-1.00	-1.09
hcp-fcc		+204.3	-1.53	+1.82	+1.76	-0.98	-1.07
hcp-hcp		+118.3	-1.46	+1.82	+1.61	-0.93	-1.04
Constituents							
fcc Ti_2CO_2		0	-1.68	+1.93	N.A.	-1.09	-1.09
hcp Mo_2CO_2		0	-1.31	N.A.	+1.56	-0.91	-0.91

*: Red sphere: O; Green sphere: Ti; Blue sphere: Mo; Grey sphere: C.
†: Ground-state alloy.
N.B.: All mentions of $TiMoCO_2$ in the main text would correspond to the ground-state $TiMoCO_2$ alloy with fcc-hcp configuration for the O-sites.

Table S2. Calculated DFT and alloy formation energies of bare TiMoC MXene with respect to its constituent Ti_2C and Mo_2C MXenes.

MXene	Configuration*	DFT Energy, E (eV/atom)	Alloy Formation Energy, E_f (meV/atom) †
TiMoC		-9.0057	-81.8
Constituents			
Ti_2C		-8.3130	
Mo_2C		-9.5348	

*: Green sphere: Ti; Blue sphere: Mo; Grey sphere: C.
†: Determined via the equation, $E_f(\text{TiMoC}) = E(\text{TiMoC}) - 0.5\,E(\text{Ti}_2\text{C}) - 0.5\,E(\text{Mo}_2\text{C})$

Table S3. Band gap (calculated via HSE06 functional) and the respective contributions and directional effective hole and electron masses of the valence band maximum and conduction band minimum for Janus-like ground-state $TiMoCO_2$, and its analogous conjectural $ZrMoCO_2$, $HfMoCO_2$, $TiCrCO_2$, and $TiWCO_2$ MXene alloys.

MXene	Band Gap (eV)	Valence Band Maximum			Conduction Band Minimum		
		Contribution*	Effective Hole Mass (m_0)		Contribution	Effective Electron Mass (m_0)	
			x	y		x	y
$TiMoCO_2$	0.60	Mo-d_{z^2}, O-p_z	0.23	0.23	Ti-d_{xz}	0.81	1.31
$ZrMoCO_2$	0.56	Mo-d_{z^2}, O-p_z	0.29	0.29	Mo-d_{z^2}	0.27	0.27
$HfMoCO_2$	0.68	Mo-d_{z^2}, O-p_z	0.33	0.33	Mo-d_{z^2}	0.28	0.28
$TiCrCO_2$	0.19	Cr-d_{z^2}, O-p_z	0.38	0.38	Cr-d_{z^2}	0.34	0.34
$TiWCO_2$	0.46	W-d_{z^2}, O-p_z	0.18	0.18	Ti-d_{xz}	1.87	4.77

*: O-p_z orbitals are located on the Mo- / Cr- / W-side.