Supporting Information

Interfacial interactions of doped-Ti_3C_2 MXene/$MAPbI_3$ heterostructures: Surfaces and theoretical approach

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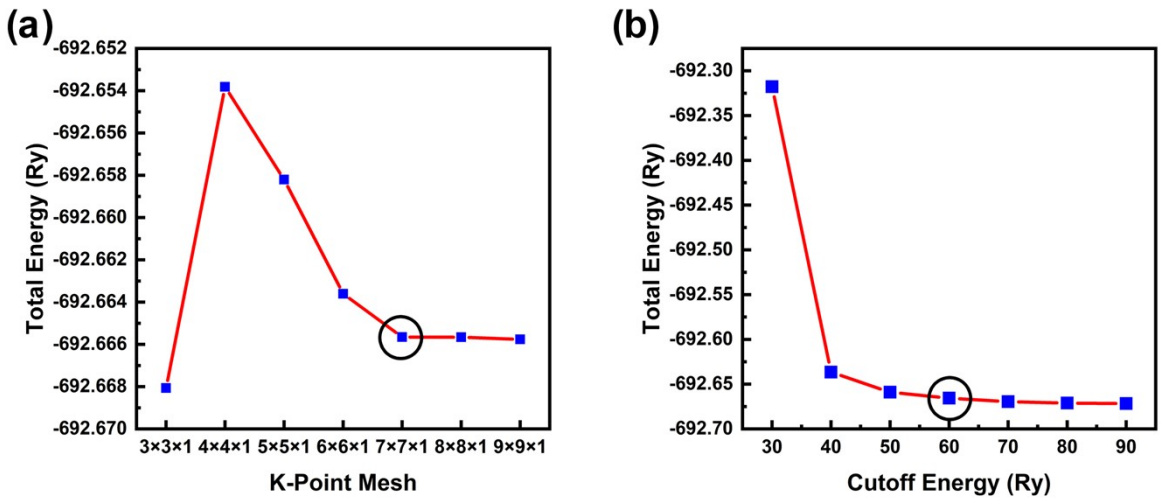

Figure S1. (a) K-Point mesh and (b) cutoff energy optimization.

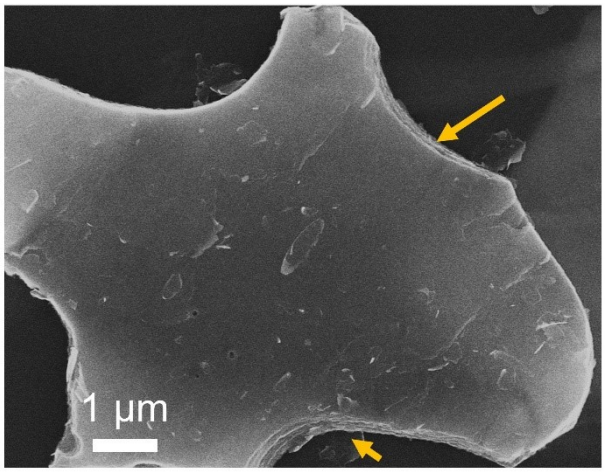

Figure S2. SEM image of F-MXene with yellow arrows marking the accordion-like structure.

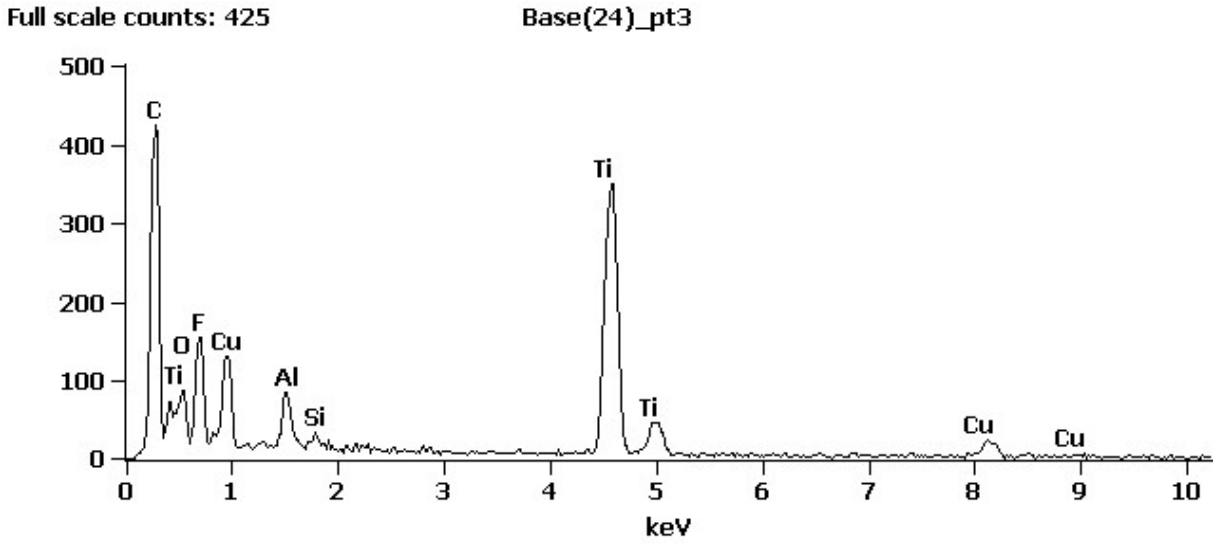

Figure S3. EDS spectra of as-synthesized F-MXene

Table S1. Weight and atomic percentage of chemical elements in as-synthesized Ti_3C_2.

Element	Wt.%	At.%
Titanium	17.51 ± 0.34	5.77 ± 0.11
Carbon*	57.54 ± 1.32	75.62 ± 1.74
Oxygen	7.77 ± 0.84	7.66 ± 0.83
Fluorine	10.83 ± 0.48	9.00 ± 0.40
Aluminium	0.93 ± 0.05	0.54 ± 0.03
Copper*	5.25 ± 0.74	1.30 ± 0.18

*: Cu and excessive C contributions come from carbon coated copper TEM grid.

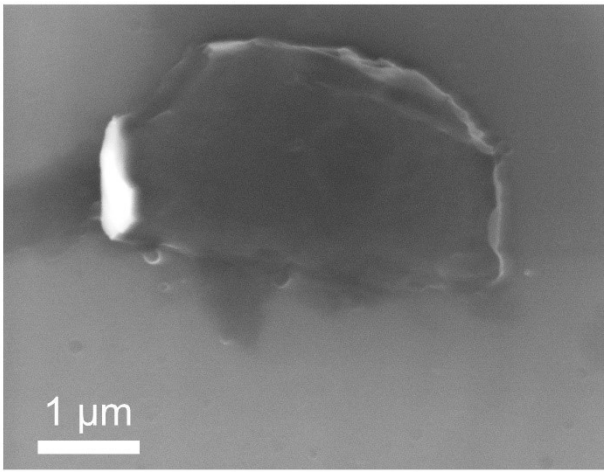

Figure S4. SEM image of N-MXene.

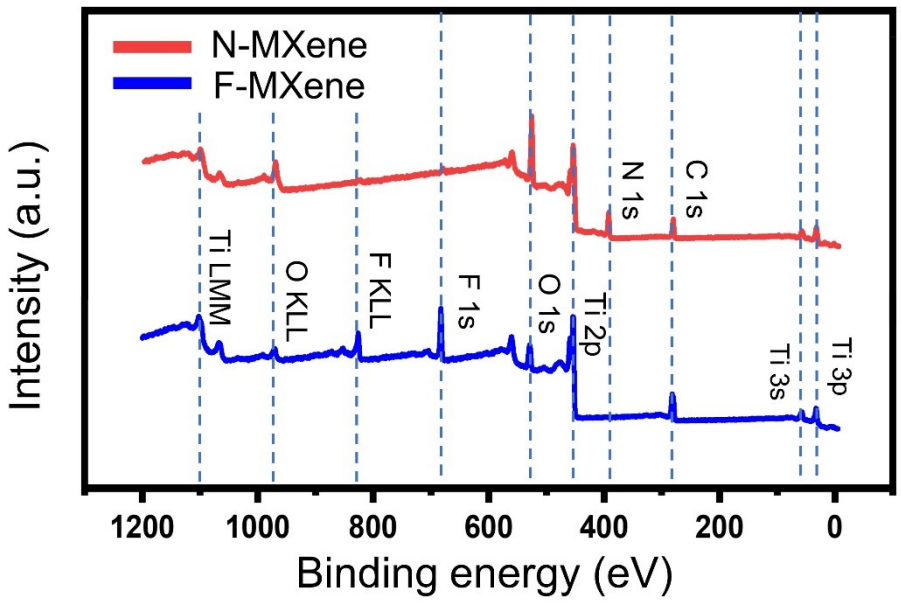

Figure S5. XPS survey spectra of F-MXene and N-MXene. Here, KLL and LMM peaks comes from Auger transition.

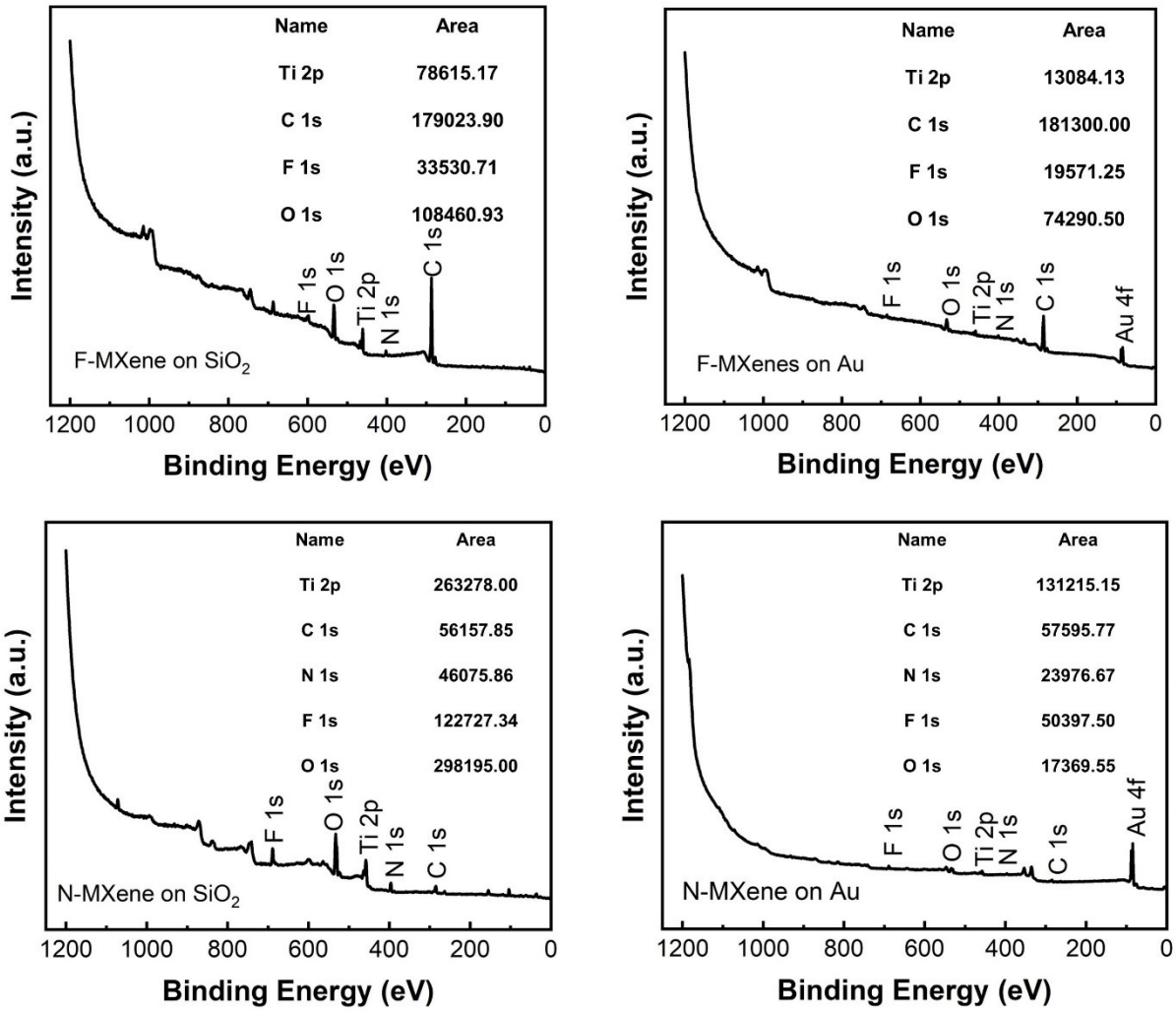

Figure S6. The elemental quantification of the F (N) to metal ratio of F-MXene, and N-MXene on SiO_2 and Au.

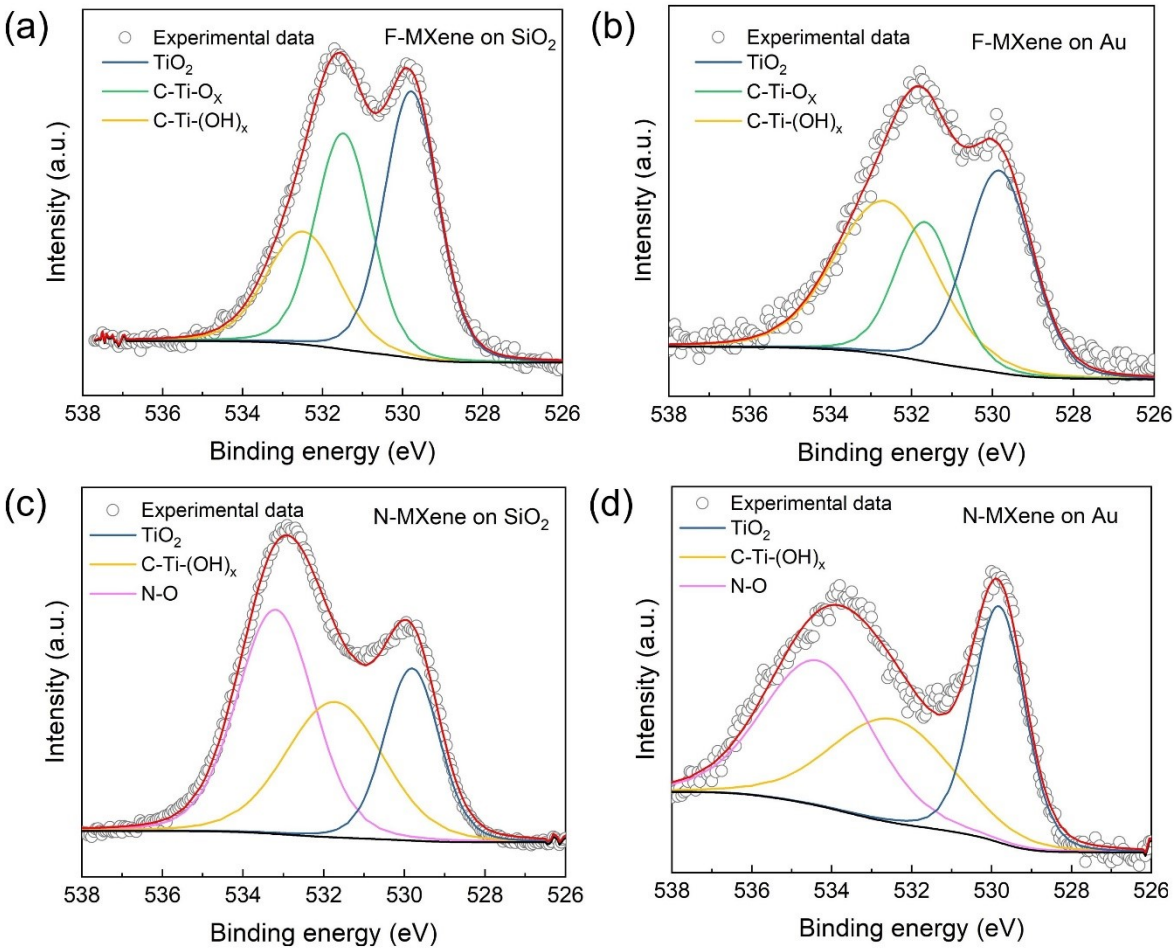

Figure S7. O 1s XPS spectra of (a) F-MXene on SiO_2, (b) F-MXene on Au, (c) N-MXene on SiO_2, and (d) N-MXene on Au.

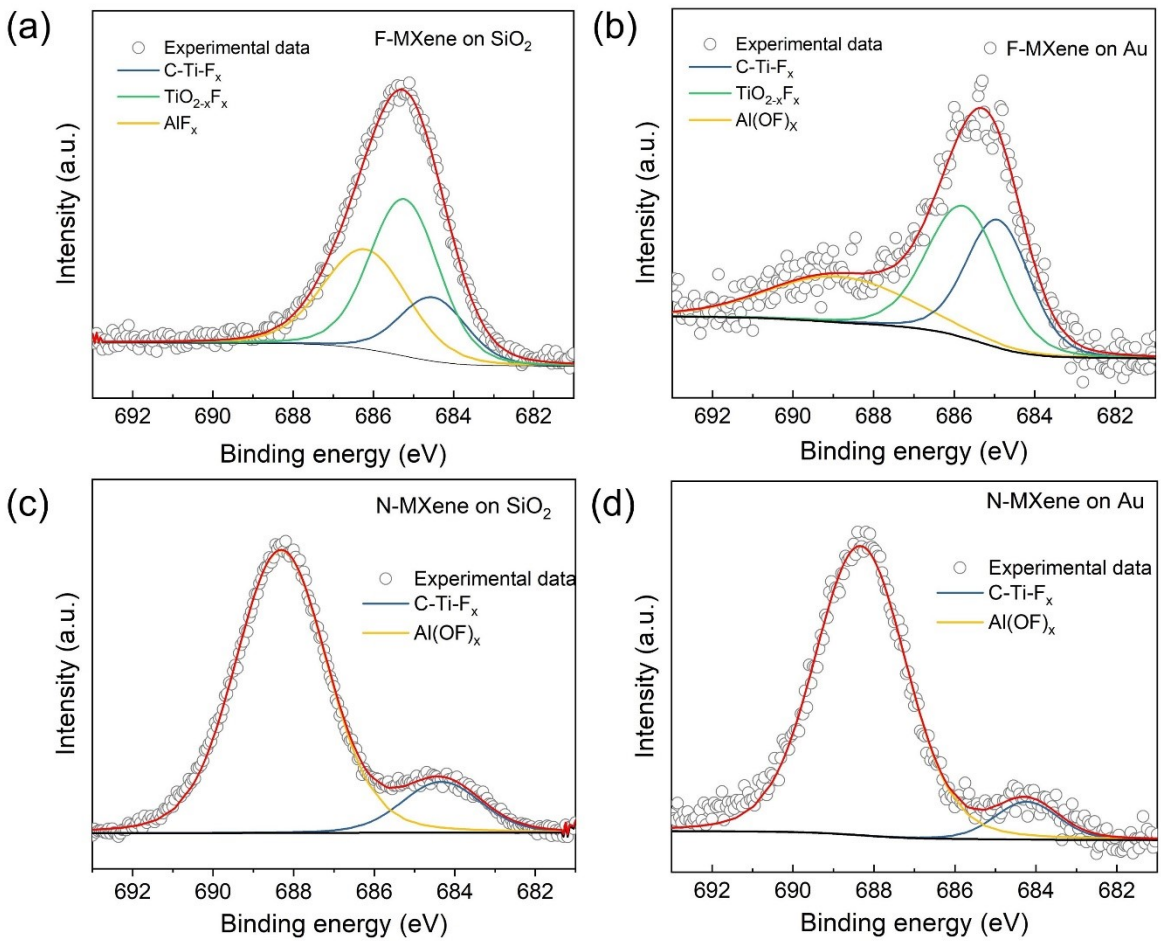

Figure S8. F 1s XPS spectra of (a) F-MXene on SiO_2, (b) F-MXene on Au, (c) N-MXene on SiO_2, and (d) N-MXene on Au.

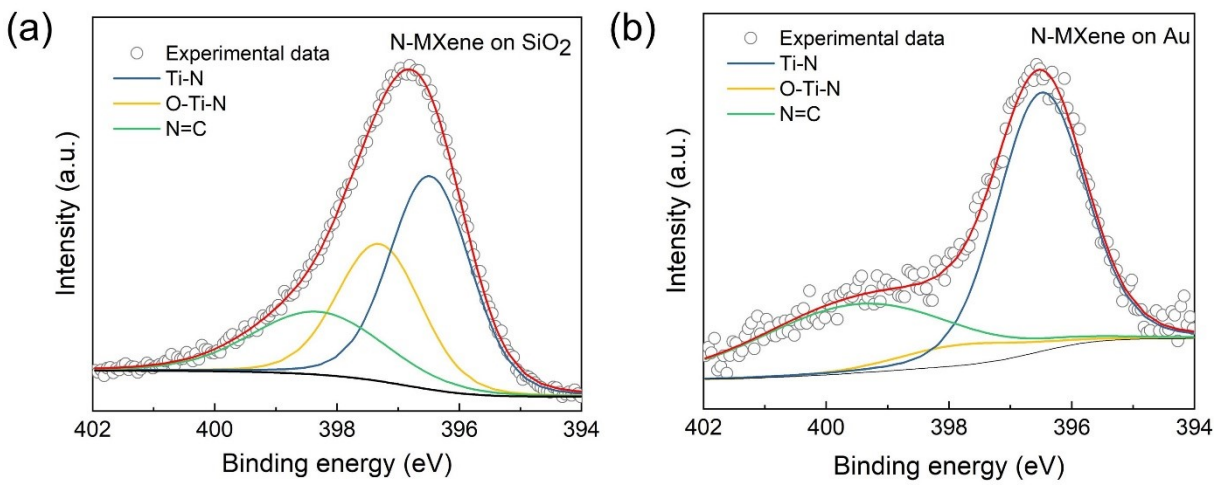

Figure S9. N 1s XPS spectra of (a) F-MXene on SiO_2 and (b) F-MXene on Au.

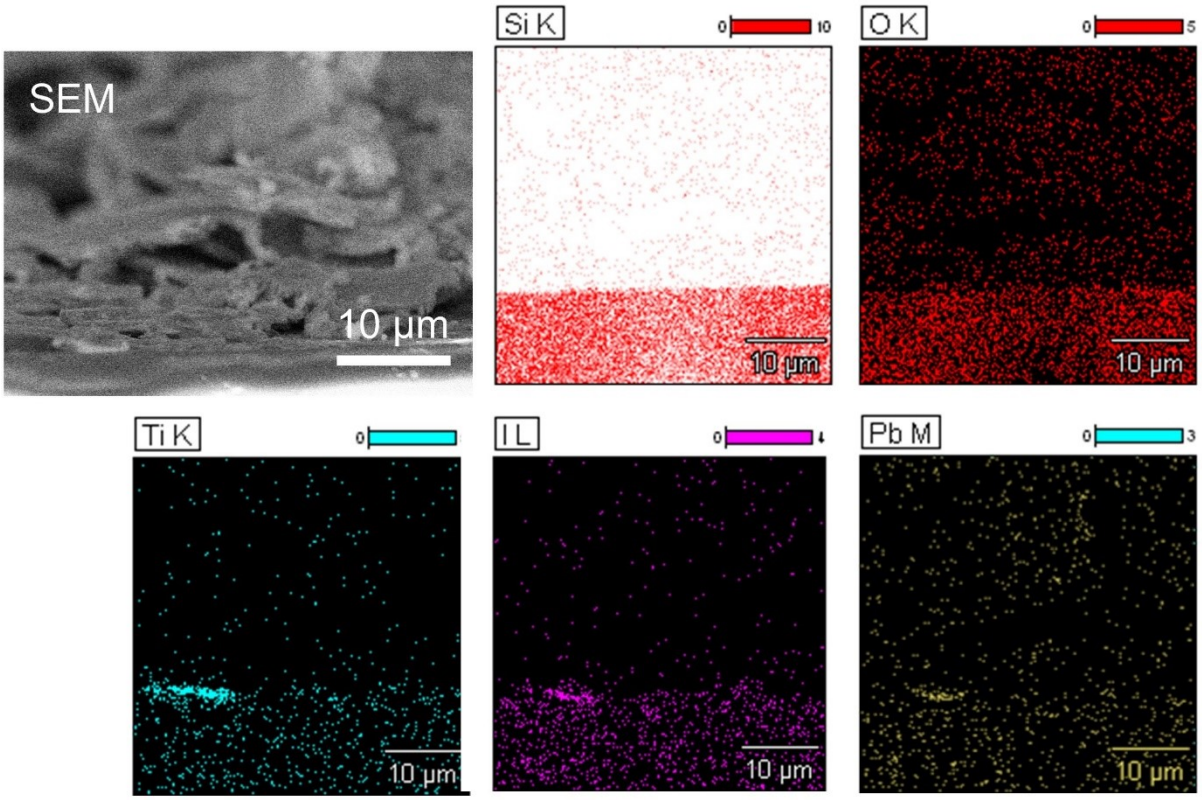

Figure S10. EDS mapping of F-MXene/$MAPbI_3$ thin film.

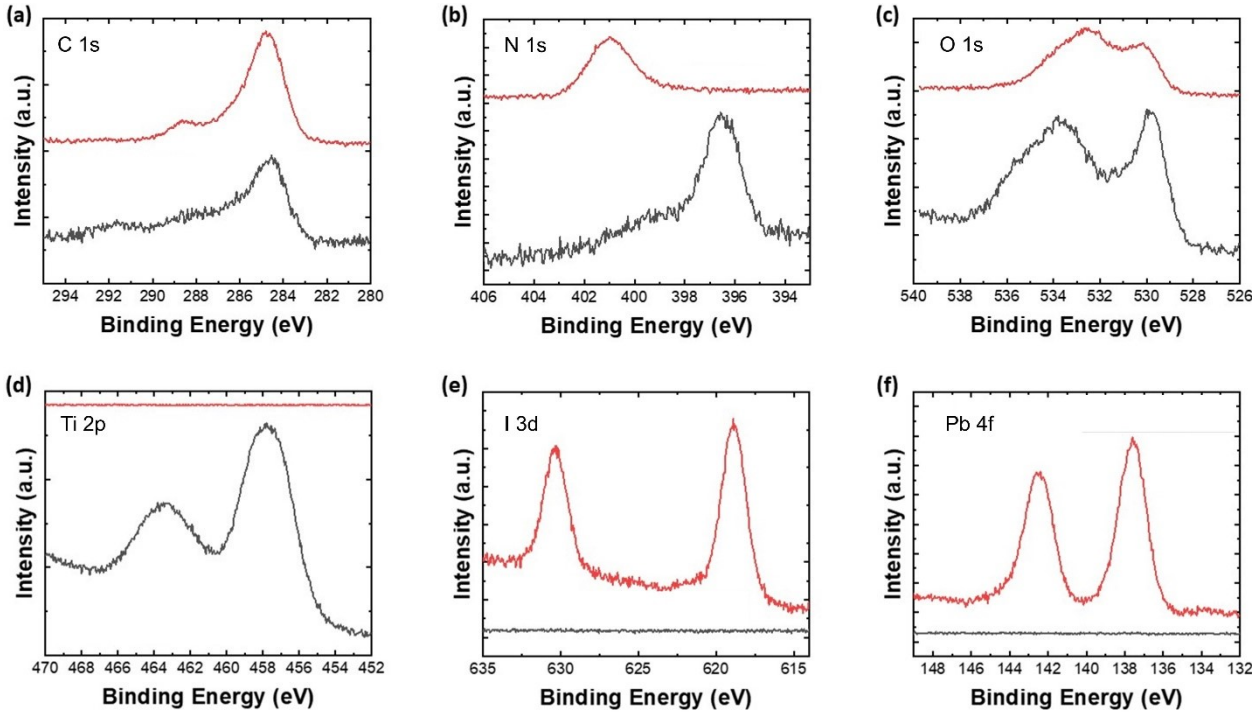

Figure S11. XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s, (d) Ti 2p, (e) I 3d, and (f) Pb 4f components of N-MXene/$MAPbI_3$ on Au substrate. Red line shows N-MXene/$MAPbI_3$ heterostructure and black line shows N-MXene.

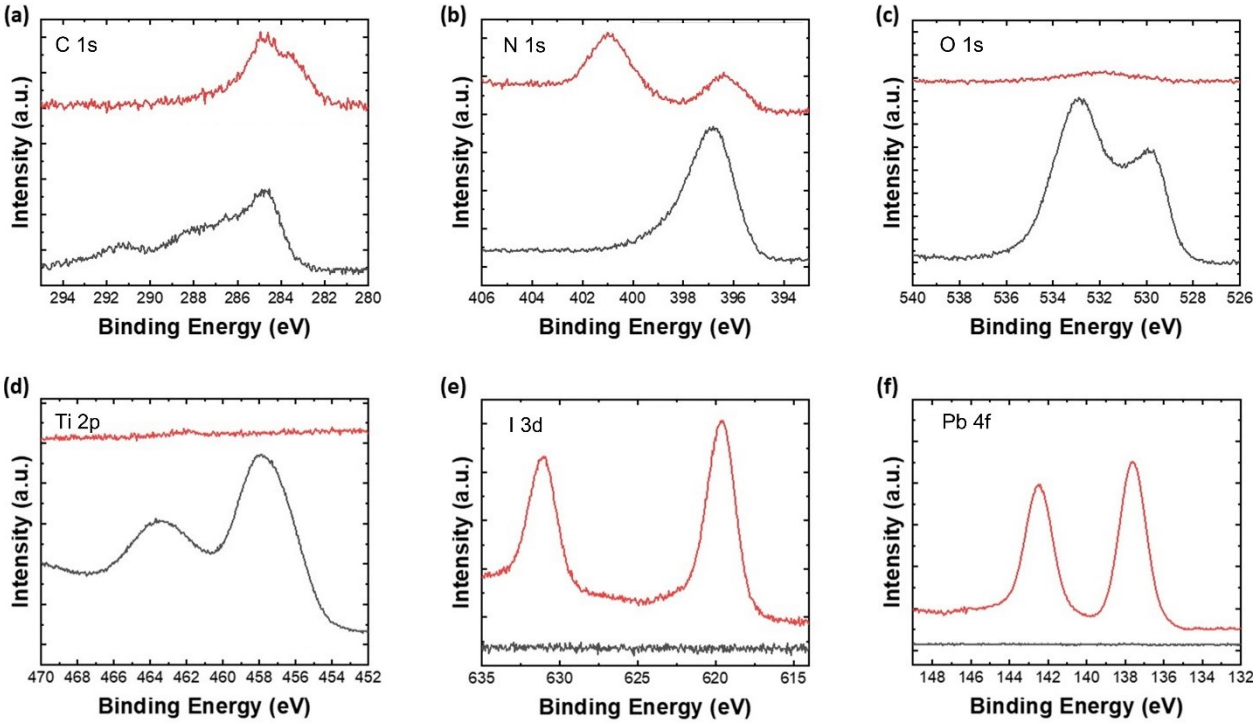

Figure S12. XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s, (d) Ti 2p, (e) I 3d, and (f) Pb 4f components of N-MXene/$MAPbI_3$ on SiO_2 substrate. Red line shows N-MXene/$MAPbI_3$ heterostructure and black line shows N-MXene.

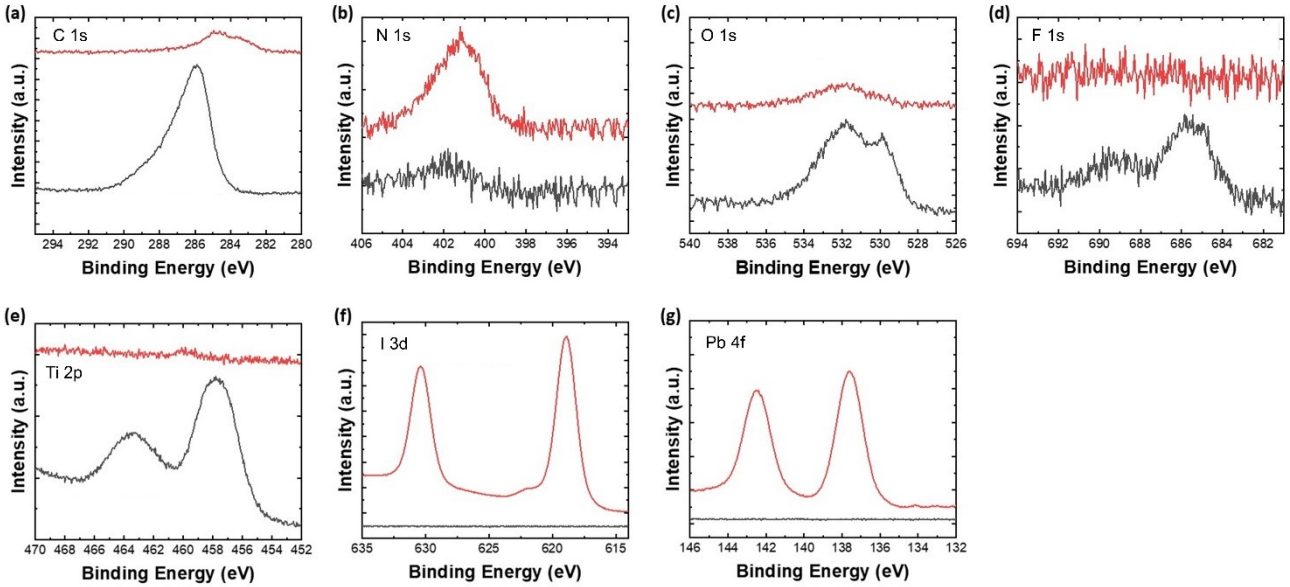

Figure S13. XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s, (d) F 1s, (e) Ti 2p, (f) I 3d, and (g) Pb 4f components of F-MXene/$MAPbI_3$ on Au substrate. Red line shows F-MXene/$MAPbI_3$ heterostructure and black line shows F-MXene.

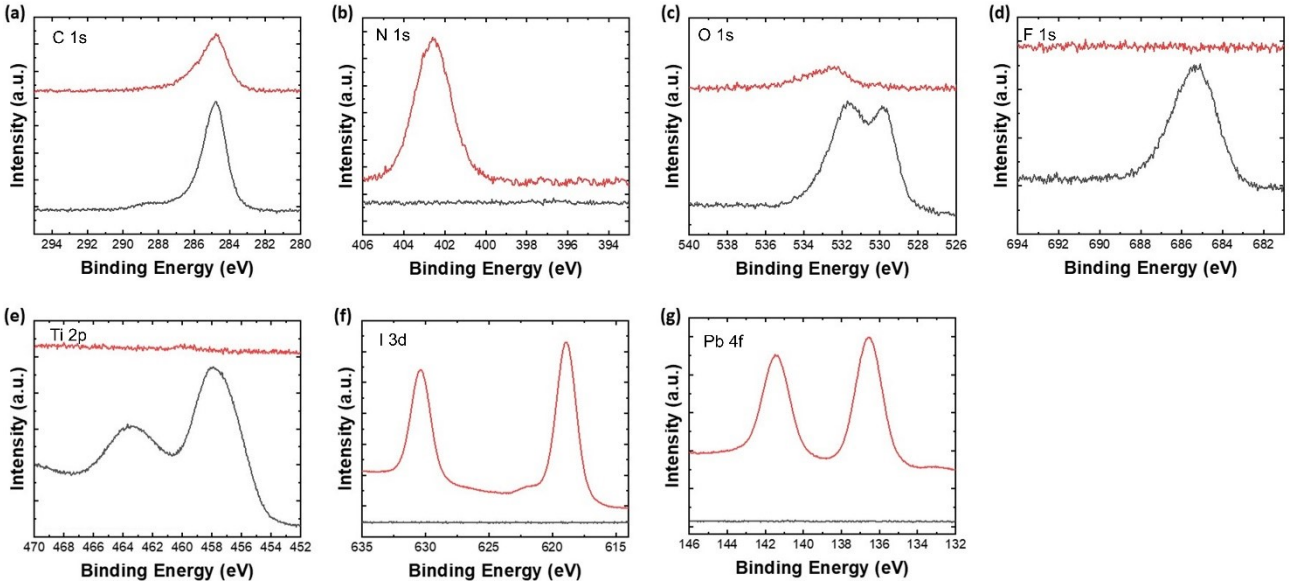

Figure S14. XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s, (d) F 1s, (e) Ti 2p, (f) I 3d, and (g) Pb 4f components of F-MXene/$MAPbI_3$ on SiO_2 substrate. Red line shows F-MXene/$MAPbI_3$ heterostructure and black line shows F-MXene.

Table S2. Relative formation energy for every adsorption site of F-MXene

Adsorption site for F-MXene	Relative energy (eV)
Bridge	0.0002
FCC	0
HCP	1.9587
Top	6.0143

Table S3. Relative formation energy for every adsorption site of N-MXene

Adsorption site for N-MXene	Relative energy (eV)
Bridge	1.4664
FCC	1.4655
HCP	0
Top	8.2451

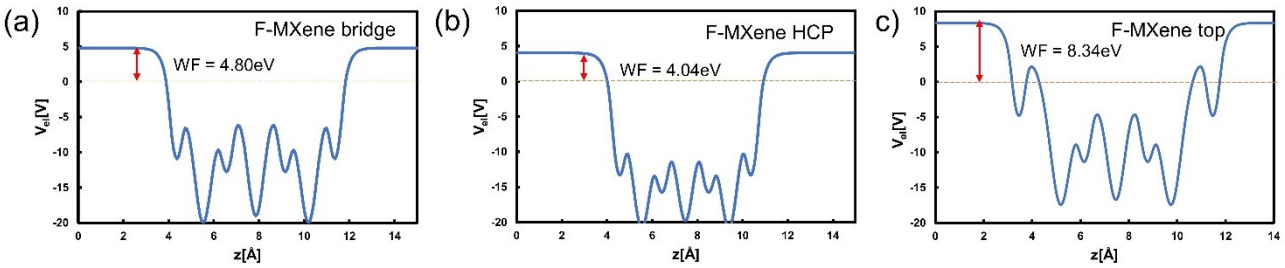

Figure S15. Plane averaged electronic potential vs z for MXenes with F termination, zero referenced as the Fermi energy (a) Bridge (b) HCP (c) Top.

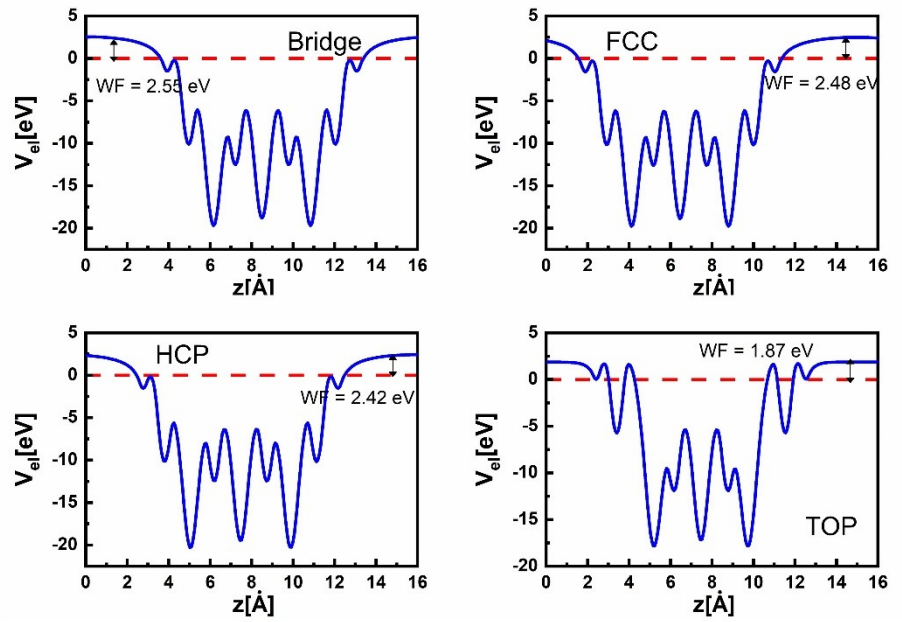

Figure S16. Plane averaged electronic potential vs z for MXenes with -OH termination, zero referenced as the Fermi energy (a) Bridge (b) FCC (c) HCP, and (d) top.

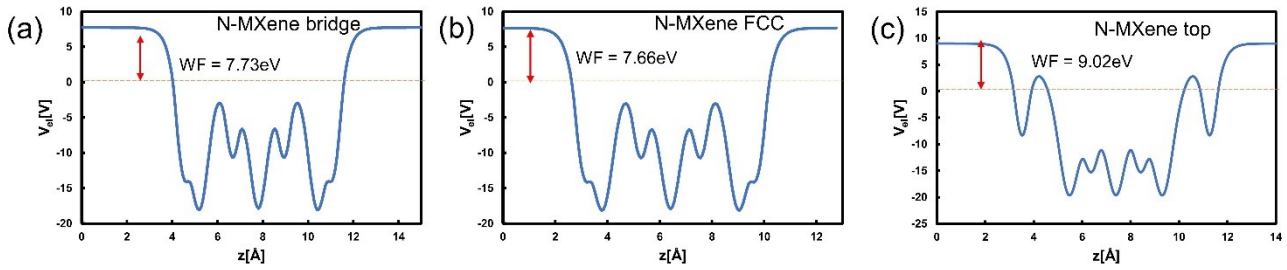

Figure S17. Plane averaged electronic potential vs z for MXenes with N termination, zero referenced as the Fermi energy (a) Bridge (b) FCC (c) Top.

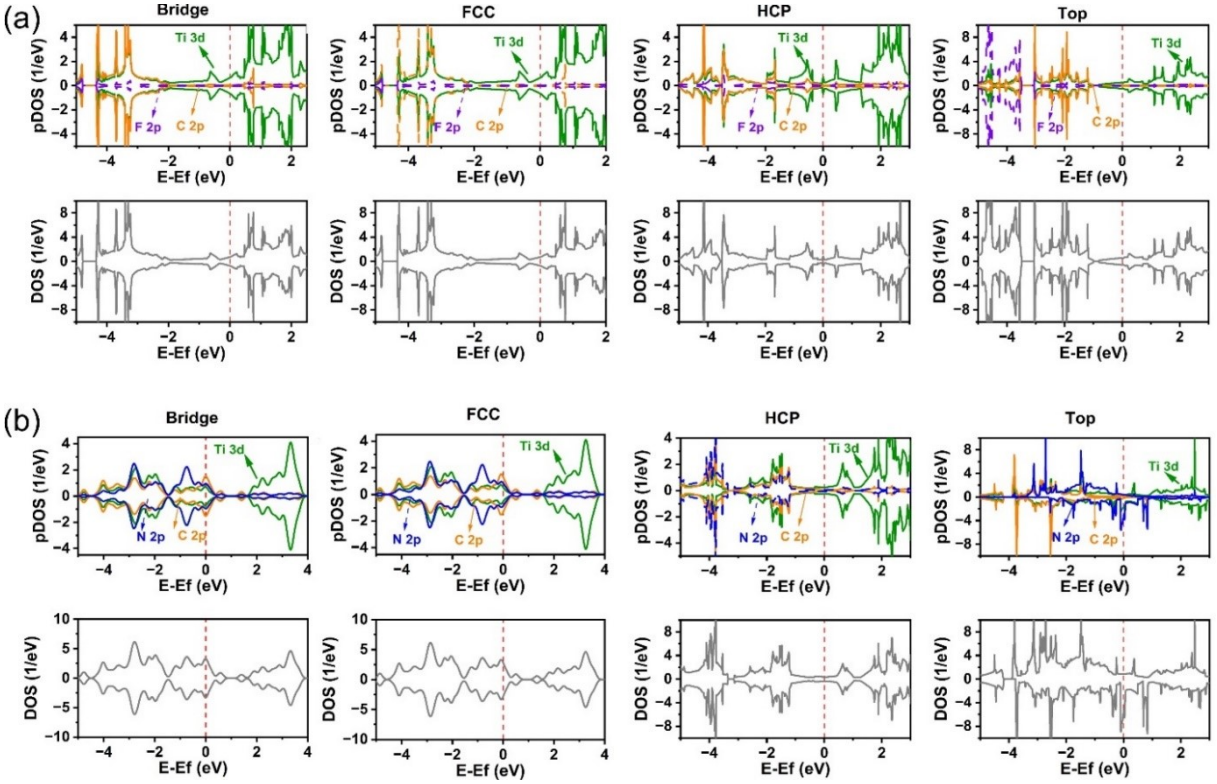

Figure S18. Partial (PDOS) and total density of states (DOS) of (a) F-MXene and (b) N-MXene with different adsorption sites for the respective terminated/dopant atoms, i.e., bridge, face-centred cubic (FCC), HCP, and top.

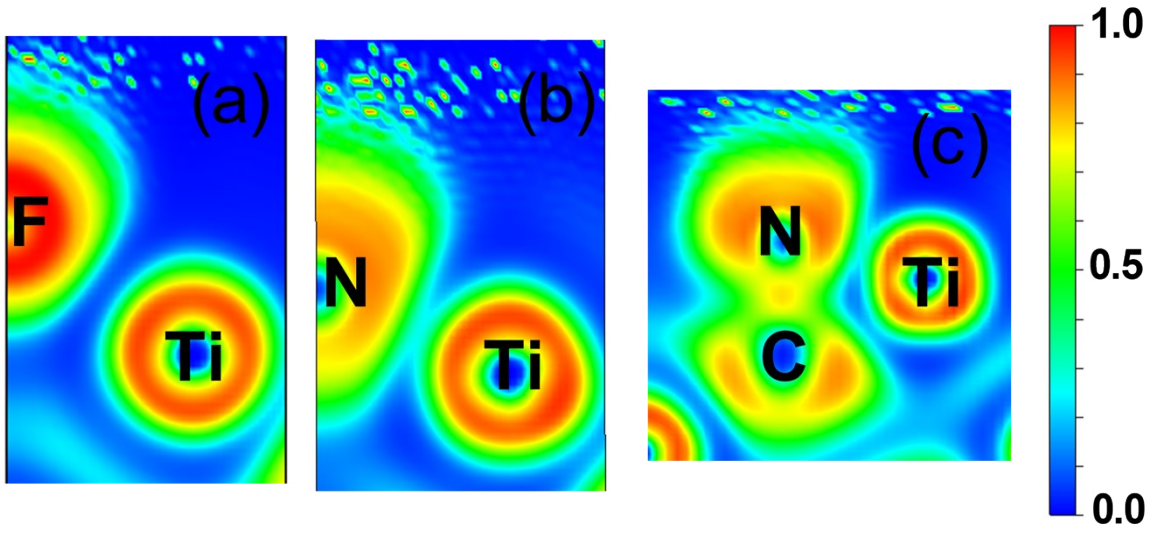

Figure S19. Electron localization function (ELF) of (a) F-MXene FCC, (b) N-MXene FCC, (c) N-MXene HCP

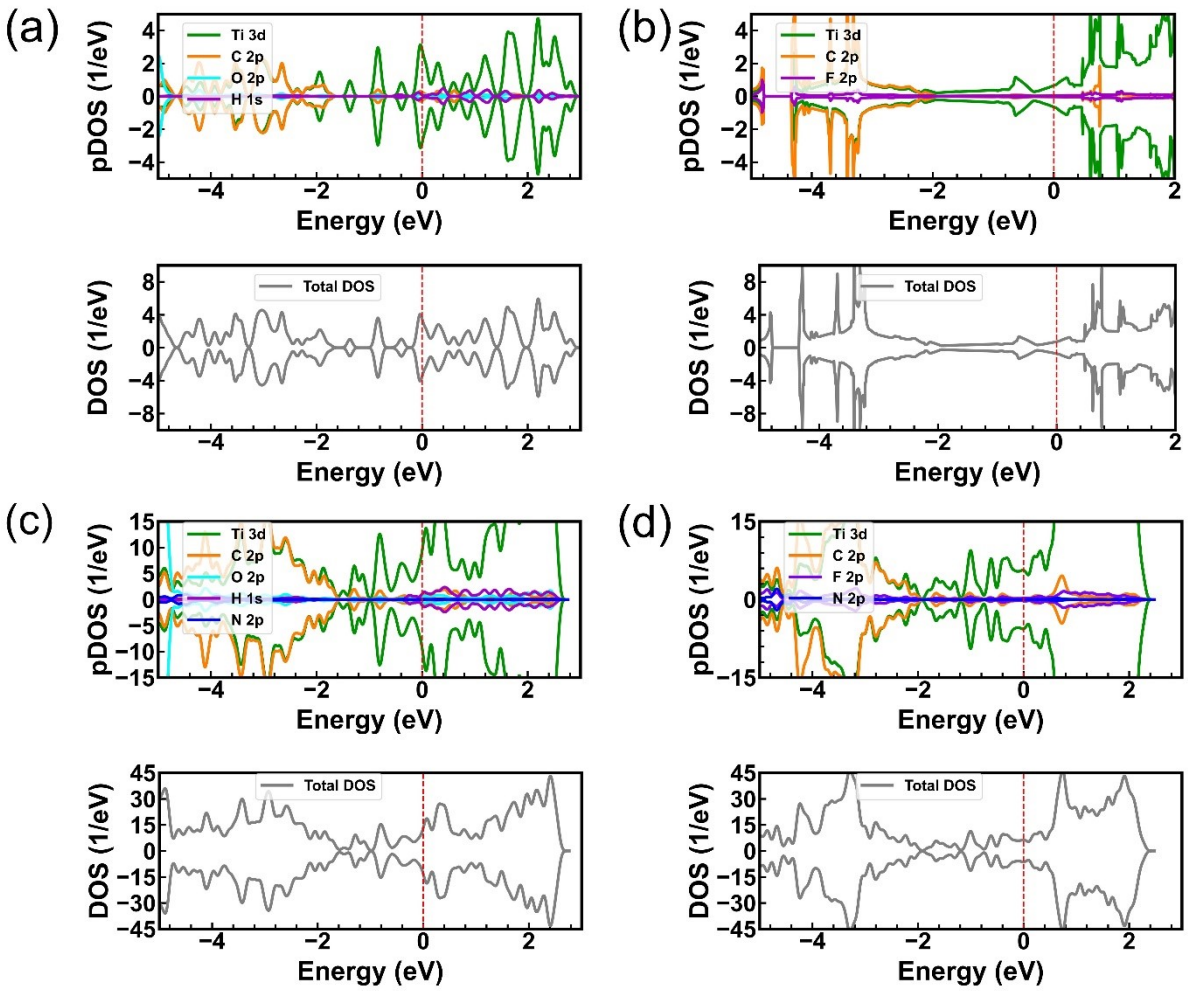

Figure S20. PDOS and DOS of (a) -OH terminated MXene at HCP sites. (b) -F terminated MXene at FCC sites. (c) N-doped -OH HCP terminated MXene. (d) N-doped -F terminated FCC MXene.

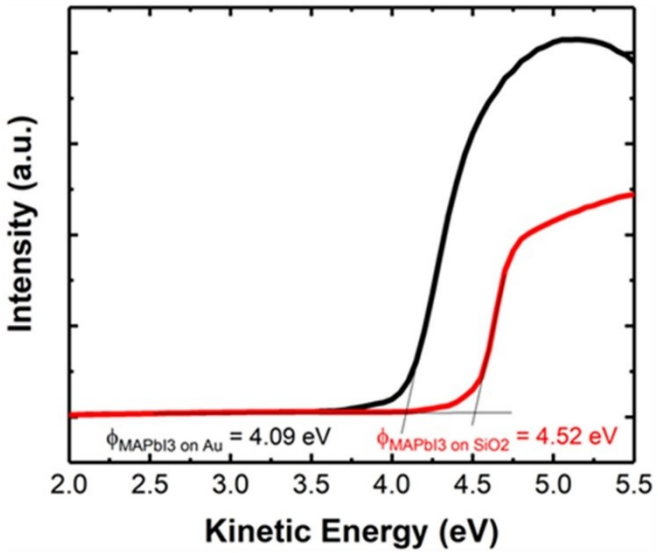

Figure S21. SECO signals of $MAPbI_3$ on Au (black) and SiO_2 (red).

Table S4. Summary of MXene WF value obtained from experiment and DFT prediction.

Sample	Experimental by UPS (eV)		DFT prediction (eV)			
	On Au	On SiO_2	HCP	Bridge	FCC	Top
F-MXene	3.68	3.62	4.04	4.80	4.80	8.34
N-MXene	4.30	4.22	4.25	7.73	7.66	9.02

Table S5. Summary of WF and VB changes in MXene/$MAPbI_3$ heterostructure on SiO_2 and Au substrate

Sample	WF (eV)		VBM (eV)	
	On Au	On SiO_2	On Au	On SiO_2
$MAPbI_3$/F-MXene	3.00	3.45	3.00	7.62
$MAPbI_3$/N-MXene	4.45	4.35	5.12	3.45

Section S1. Optimized cartesian coordinates of F-MXene and N-MXene, and N-doped MXene with -F and -OH terminations

The most stable F-MXene (FCC)

Lattice Parameters:

a = 3.0159399509 Å

Atom	x	y	z
Ti	0.666667223	0.333332807	0.31959793
Ti	0.333333164	0.666666627	0.68040216
Ti	0	0	0.50000006
F	0	0	0.225402802
F	0	0	0.774597287
C	0.333333164	0.666666627	0.402085185
C	0.666667223	0.333332807	0.597914934

The most stable N-MXene (HCP)

Lattice Parameters:

a = 3.22864 Å

Atom	x (Å)	y (Å)	z (Å)
Ti	1.614323	0.932028	5.343353
Ti	-0.000002	1.864058	9.903636
Ti	0	0	7.623495
N	-0.000002	1.864058	4.828737
N	1.614323	0.932028	10.418252
C	-0.000002	1.864058	6.372128
C	1.614323	0.932028	8.874861

N-doped MXenes with -F termination

a = 9.04736 Å

Atom	x (Å)	y (Å)	z (Å)
F	0.015973	0.009222	17.078411
F	2.99981	0.009222	17.078411
F	6.031567	0.000031	17.097134
F	-1.483694	2.597775	17.084453
F	1.507887	2.593309	17.078411
F	4.499478	2.597775	17.084453
F	-3.015783	5.25143	17.084453
F	-0.000027	5.223474	17.097134
F	3.01581	5.223474	17.097134
Ti	-0.013775	1.749116	15.857957
Ti	3.029549	1.749116	15.857957
Ti	6.031567	1.737622	15.873564
Ti	-1.504829	4.354687	15.873564
Ti	1.507883	4.353472	15.87901
Ti	4.520603	4.354687	15.873564
Ti	-3.015788	6.948756	15.857957

Atom	x (Å)	y (Å)	z (Å)
Ti	0.000475	6.964379	15.87901
Ti	3.015299	6.964379	15.87901
N	1.507892	0.870582	14.837169
C	4.521947	0.869391	14.807418
C	7.541204	0.869391	14.807418
C	0.0019	3.481418	14.807418
C	3.013892	3.481418	14.807418
C	6.031576	3.482327	14.813704
C	-1.507729	6.096171	14.807418
C	1.507887	6.094079	14.815466
C	4.523512	6.096171	14.807418
Ti	0.005686	0.003283	13.552852
Ti	3.010097	0.003283	13.552852
Ti	6.031567	0.000878	13.551497
Ti	7.538431	2.612348	13.546295
Ti	1.507892	2.605179	13.552852
Ti	4.524711	2.612348	13.546295
Ti	6.031567	5.222299	13.546295
Ti	-0.000765	5.223059	13.551497
Ti	3.016539	5.223059	13.551497
C	0.001778	1.740137	12.287799
C	3.013996	1.740137	12.287799
C	6.031567	1.740427	12.283112
C	-1.507258	4.353284	12.283112
C	1.507892	4.350746	12.288585
C	4.523033	4.353284	12.283112
C	-3.015792	6.966722	12.287799
C	-0.001877	6.965742	12.288585
C	3.017652	6.965742	12.288585
Ti	1.507892	0.870582	11.218348
Ti	4.522567	0.870731	11.222548
Ti	7.540576	0.870731	11.222548
Ti	0.000434	3.481292	11.222548
Ti	3.015358	3.481292	11.222548
Ti	6.031576	3.482327	11.217671
Ti	-1.508579	6.094965	11.222548
Ti	1.507887	6.094079	11.227967
Ti	4.524354	6.094965	11.222548
F	0.000005	0.000008	10.00391
F	3.015779	0.000008	10.00391
F	1.507887	7.834616	10.008597
F	-1.505435	2.610327	10.003639
F	1.507896	2.611737	10.00391
F	4.521219	2.610327	10.003639
F	-3.015783	5.226326	10.003639
F	0.000538	5.223811	10.008597

N-doped MXenes with -OH termination

a = 8.93018

Atom	x (Å)	y (Å)	z (Å)
Ti	1.489058	0.859863	5.05731

Atom	x (Å)	y (Å)	z (Å)
Ti	0	3.437224	5.050997
Ti	-1.48754	6.015466	5.05731
Ti	4.465085	0.859306	5.064301
Ti	2.976589	3.436342	5.05731
Ti	1.487531	6.015466	5.05731
Ti	7.441111	0.859863	5.05731
Ti	5.95358	3.436342	5.05731
Ti	4.465085	6.015141	5.054709
Ti	0	1.730491	9.867078
Ti	-1.478069	4.290582	9.867078
Ti	-2.978286	6.87355	9.875451
Ti	2.973307	1.720584	9.881357
Ti	1.478069	4.290582	9.867078
Ti	-0.000004	6.870495	9.881357
Ti	5.956862	1.720584	9.881357
Ti	4.465085	4.298324	9.875451
Ti	2.978277	6.87355	9.875451
Ti	4.465089	7.733699	7.466137
Ti	-1.485535	2.57955	7.468738
Ti	5.953401	5.155866	7.466137
Ti	2.976924	0.000116	7.47161
Ti	1.485535	2.57955	7.468738
Ti	0	5.152572	7.468738
Ti	5.953245	0.000116	7.47161
Ti	4.465085	2.577686	7.47161
Ti	2.976777	5.155866	7.466137
O	-0.000004	1.718078	3.770013
O	-1.488826	4.296793	3.770013
O	-2.975022	6.87543	3.769417
O	2.97671	1.71862	3.773102
O	1.488817	4.296793	3.770013
O	-0.000009	6.874432	3.773102
O	5.953459	1.71862	3.773102
O	4.465085	4.294565	3.769417
O	2.975013	6.87543	3.769417
O	1.473908	0.862454	11.157492
O	0	3.437224	11.143158
O	-1.492862	6.001051	11.157492
O	4.465085	0.859306	11.167219
O	2.966761	3.448167	11.157492
O	1.492853	6.001051	11.157492
O	7.456261	0.862454	11.157492
O	5.963399	3.448167	11.157492
O	4.465085	6.015141	11.160825
C	-0.000004	1.721852	6.210947
C	-1.485557	4.294906	6.210947
C	-2.974933	6.875476	6.208536
C	2.976259	1.718875	6.215634
C	1.485557	4.294906	6.210947
C	0	6.873906	6.215634
C	5.95391	1.718875	6.215634
C	4.46508	4.294465	6.208536
C	2.974933	6.875476	6.208536
C	1.484825	0.864209	8.723332

Atom	x (Å)	y (Å)	z (Å)
N	0	3.437224	8.72325
C	-1.485883	6.009627	8.723332
C	4.465085	0.859306	8.73062
C	2.9707	3.437835	8.723332
C	1.485874	6.009627	8.723332
C	7.445344	0.864209	8.723332
C	5.959461	3.437835	8.723332
C	4.465085	6.015141	8.722708
H	0	1.715735	2.790572
H	-1.490853	4.297968	2.790572
H	-2.976518	6.874571	2.789813
H	2.977339	1.718256	2.793634
H	1.490853	4.297968	2.790572
H	-0.000009	6.875159	2.793634
H	5.95283	1.718256	2.793634
H	4.465085	4.296282	2.789813
H	2.976509	6.874571	2.789813
H	1.475797	0.858919	12.137312
H	0	3.437224	12.119998
H	-1.494974	6.004446	12.137312
H	4.465085	0.859306	12.146741
H	2.970767	3.448298	12.137312
H	1.494974	6.004446	12.137312
H	7.454372	0.858919	12.137312
H	5.959394	3.448298	12.137312
H	4.465085	6.015141	12.140591