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Supporting Information

Breaking scaling relations in nitric oxide reduction by surface functionalization on MXenes

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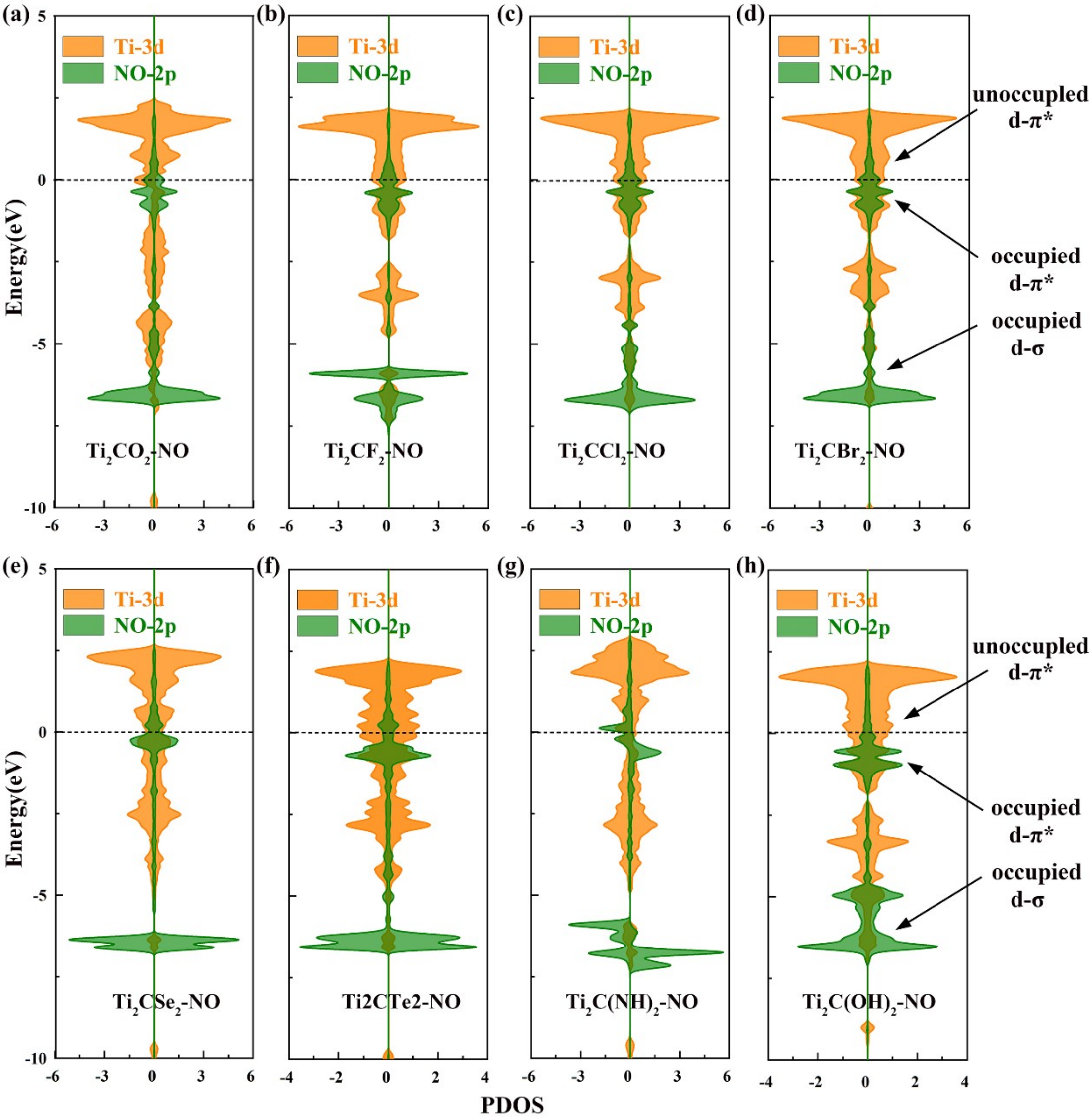

Fig. S1 Partial density of states (PDOS) of the interaction between Ti-3d and NO-2p orbitals on NO absorbed functionalized Ti_2CT_2 MXenes (T=O, F, Cl, Br, Se, Te, NH, OH). The Fermi level is set to be 0 eV.

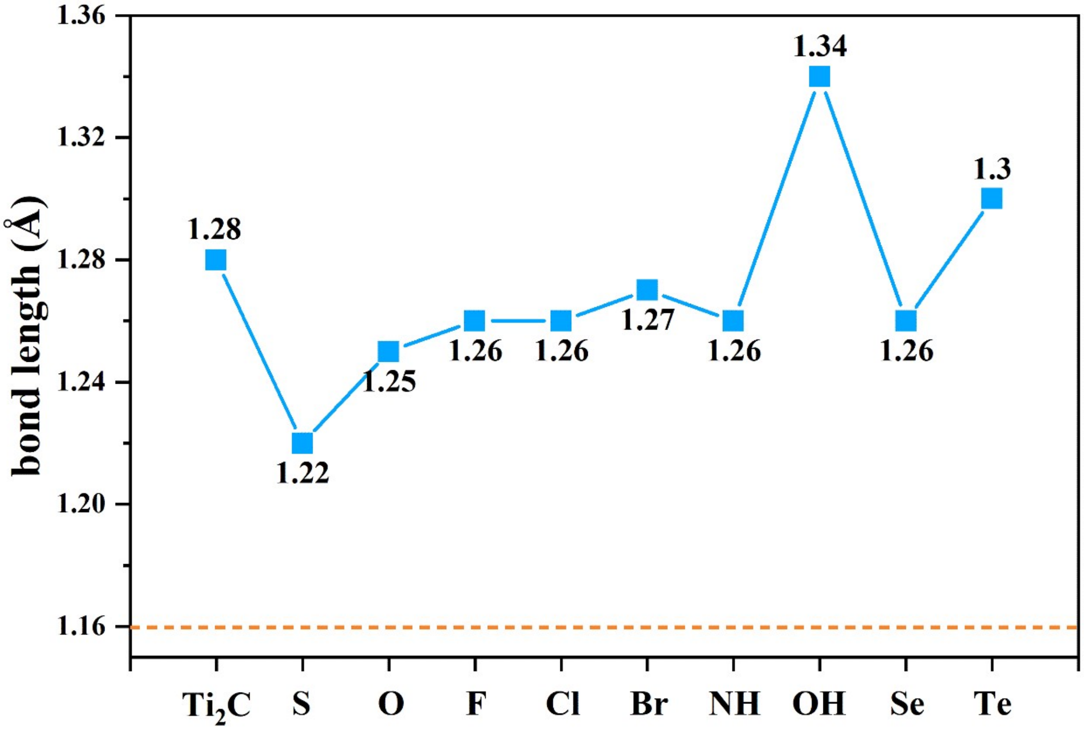

Fig. S2 N-O bond length (Å) for NO adsorbed on bare Ti_2C MXene and functionalized Ti_2CT_2 MXenes. The orange dashed line represents N-O bond length of free NO gas molecule.

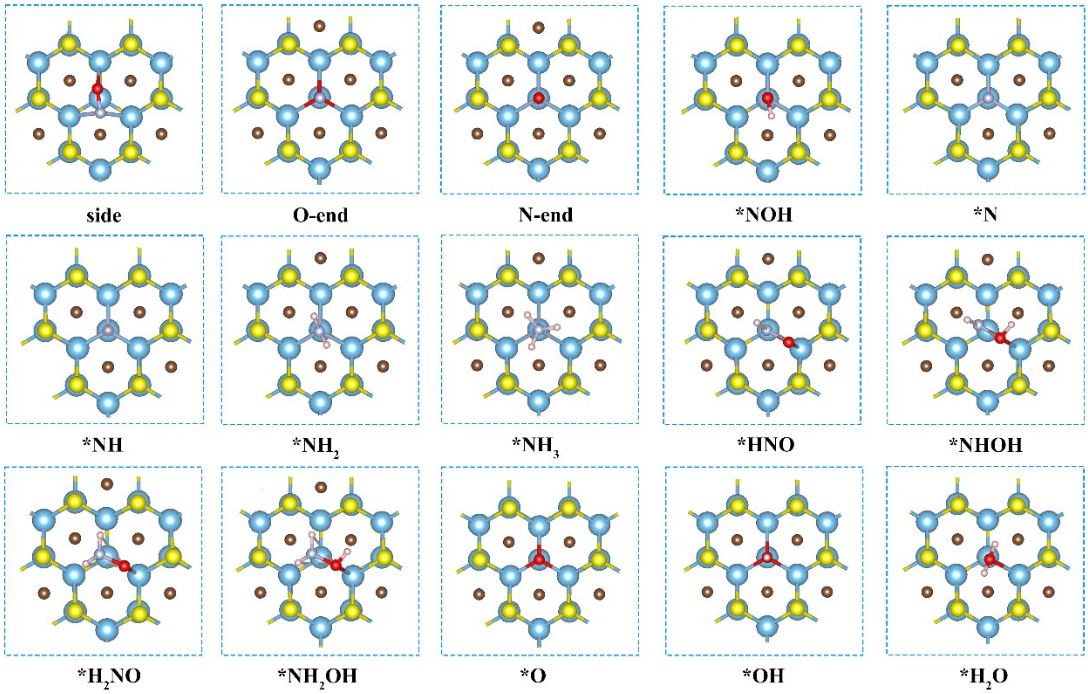

Fig. S3 The optimized configurations of all NORR intermediates on Ti_2CS_2 MXenes.

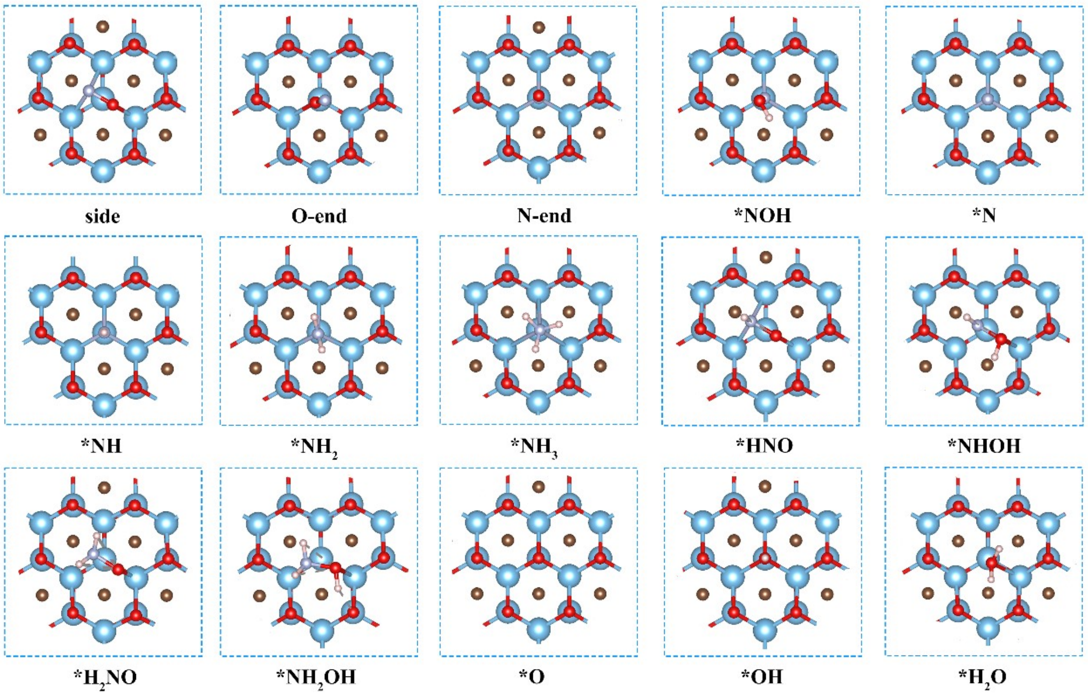

Fig. S4 The optimized configurations of all NORR intermediates on Ti_2CO_2 MXenes.

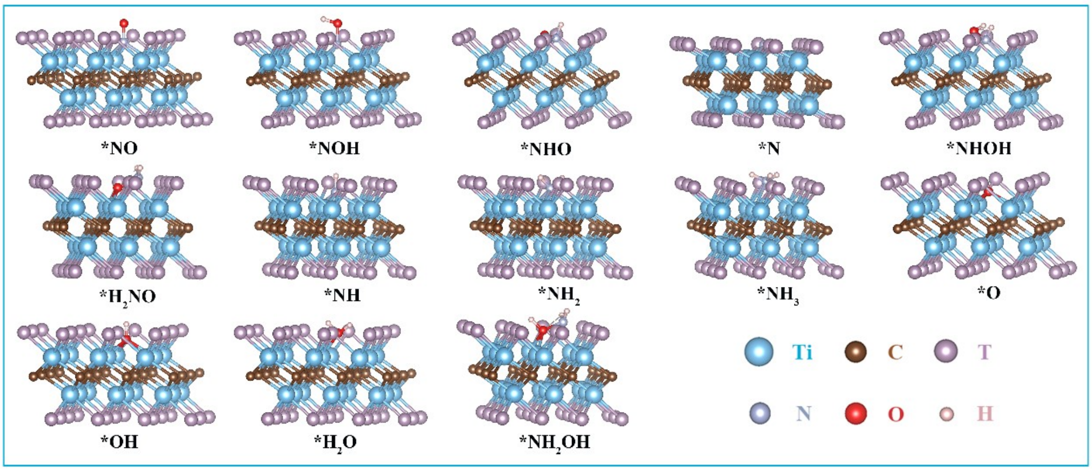

Fig. S5 The optimized configurations of all NORR intermediates on functionalized Ti_2CT_2 MXenes.

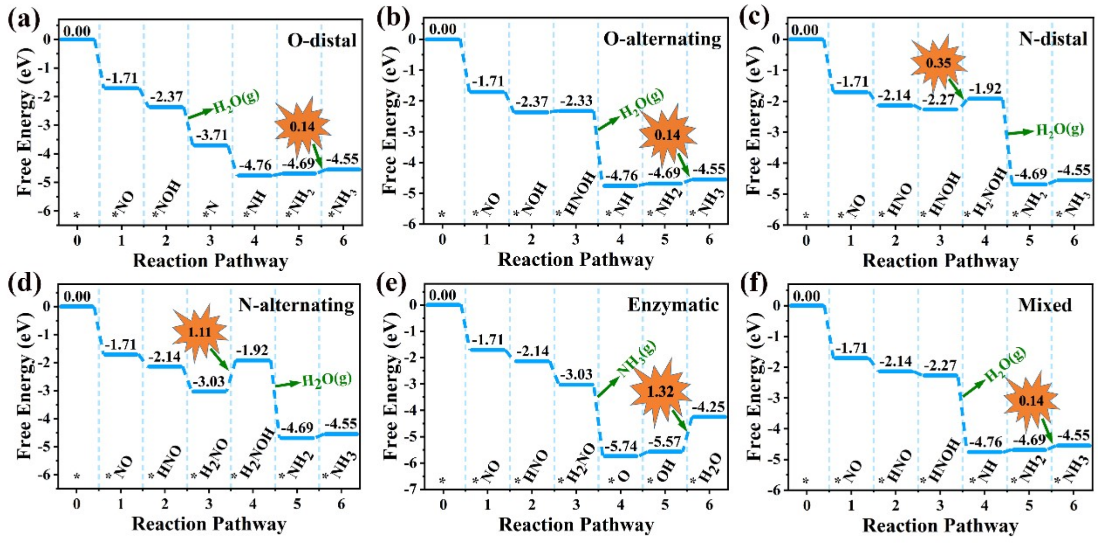

Fig. S6 NORR free energy diagrams of the considered pathways on Ti_2CO_2 MXene. The applied potential is zero.

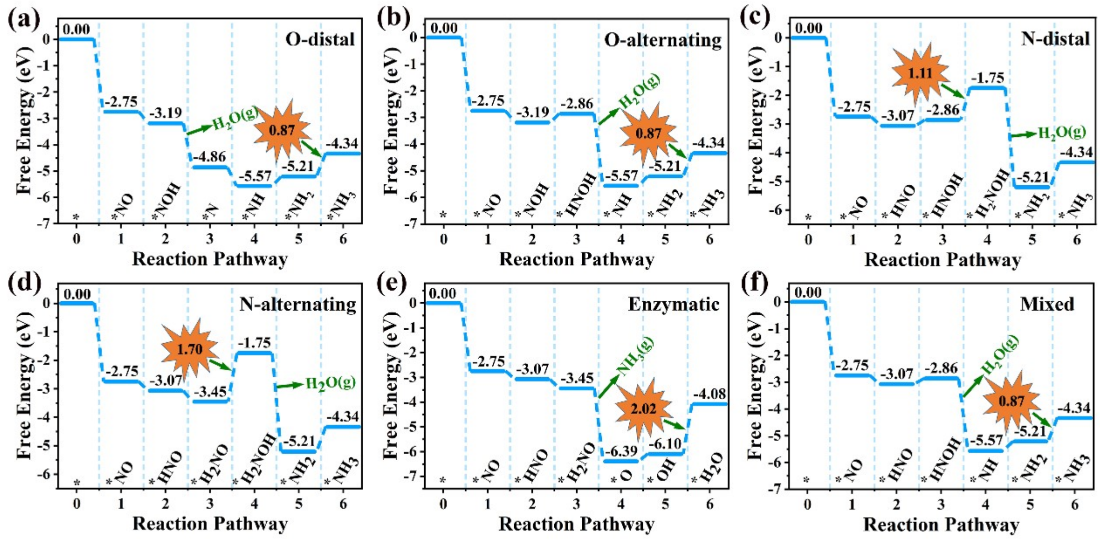

Fig. S7 NORR free energy diagrams of the considered pathways on Ti_2CF_2 MXene. The applied potential is zero.

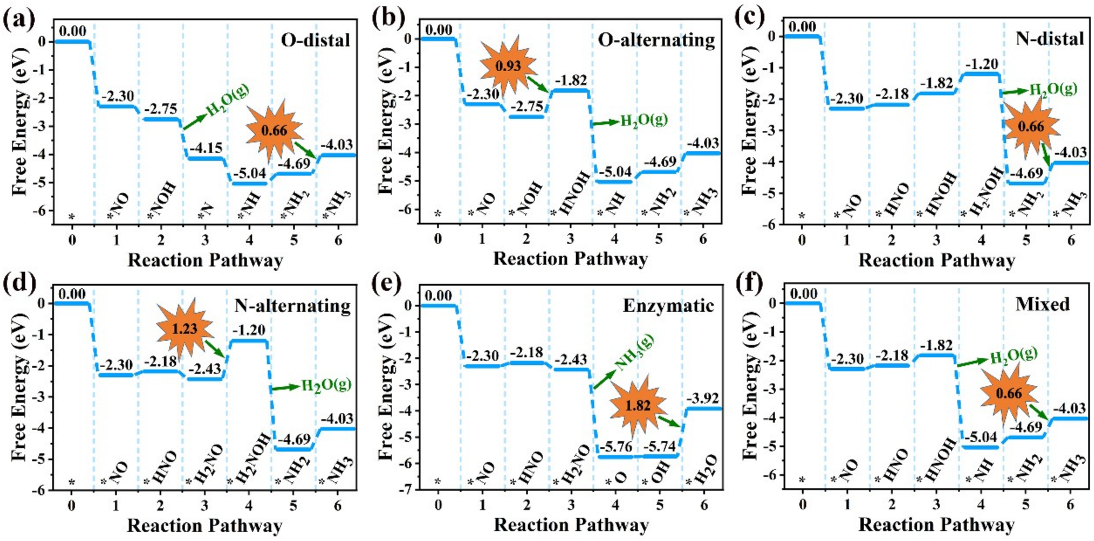

Fig. S8 NORR free energy diagrams of the considered pathways on Ti_2CCl_2 MXene. The applied potential is zero.

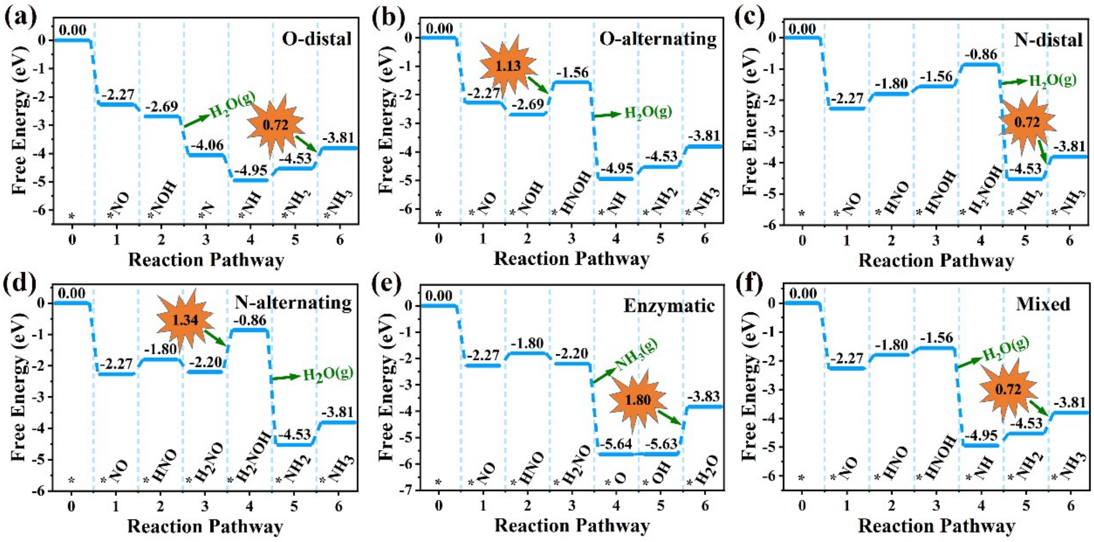

Fig. S9 NORR free energy diagrams of the considered pathways on Ti_2CBr_2 MXene. The applied potential is zero.

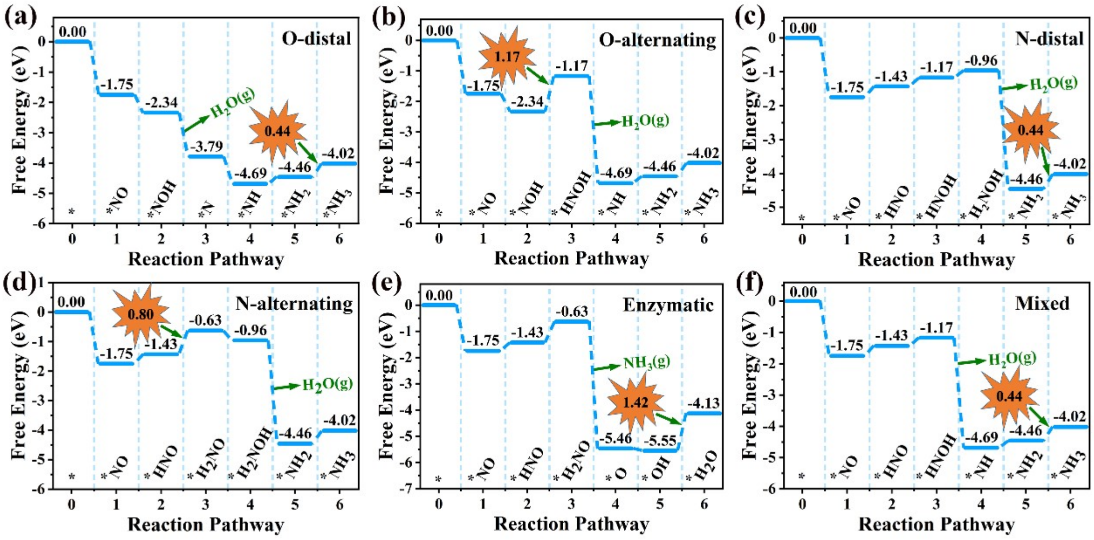

Fig. S10 NORR free energy diagrams of the considered pathways on Ti_2CSe_2 MXene. The applied potential is zero.

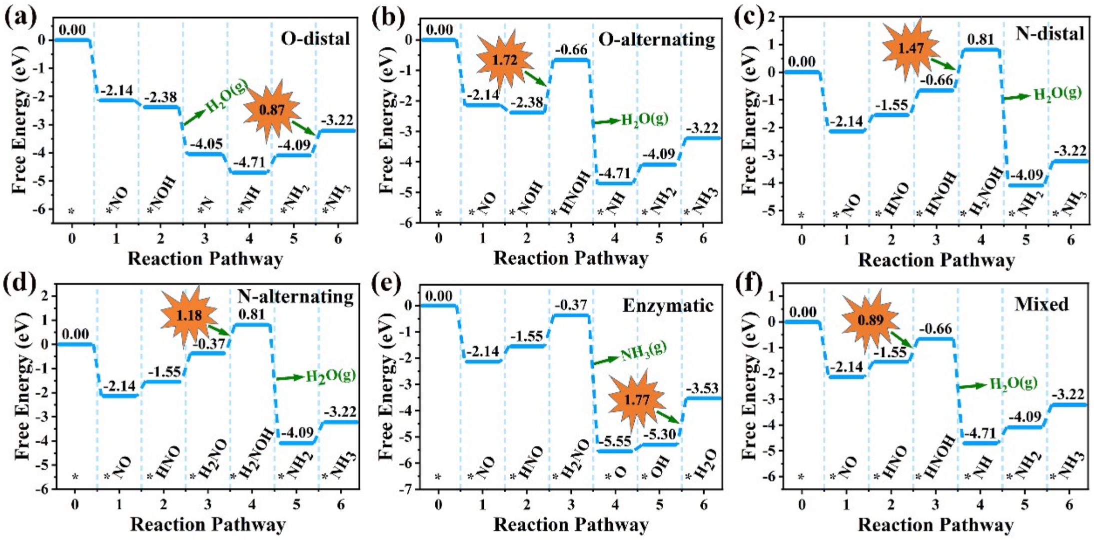

Fig. S11 NORR free energy diagrams of the considered pathways on Ti_2CTe_2 MXene. The applied potential is zero

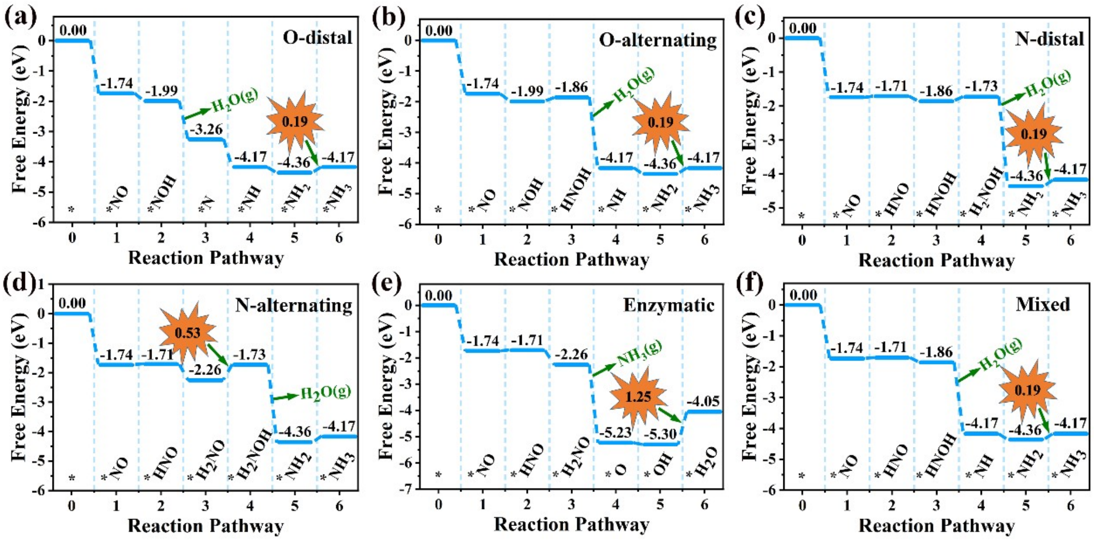

Fig. S12 NORR free energy diagrams of the considered pathways on $Ti_2C(NH)_2$ MXene. The applied potential is zero.

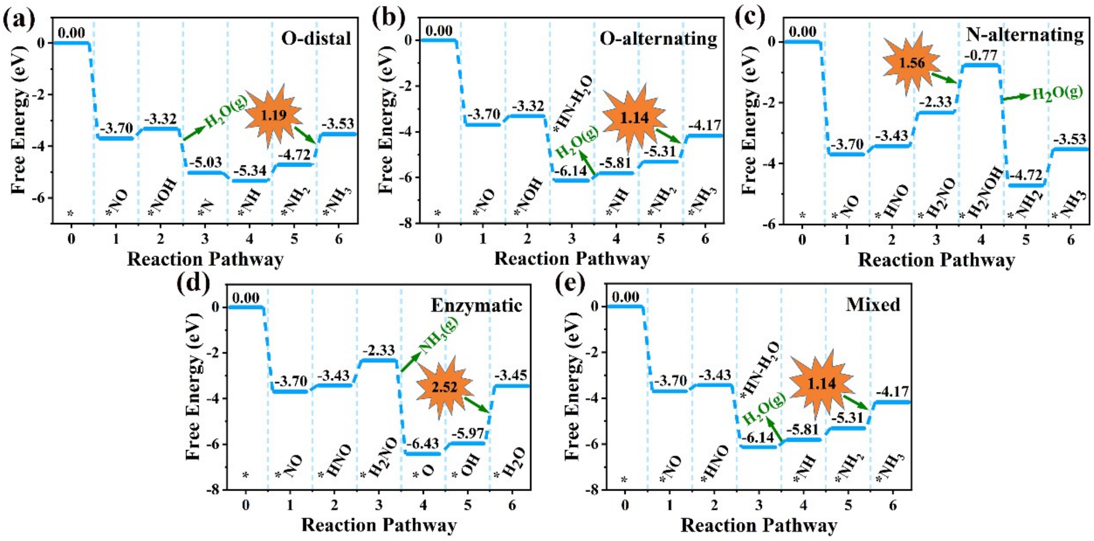

Fig. S13 NORR free energy diagrams of the considered pathways on $Ti_2C(OH)_2$ MXene. The applied potential is zero.

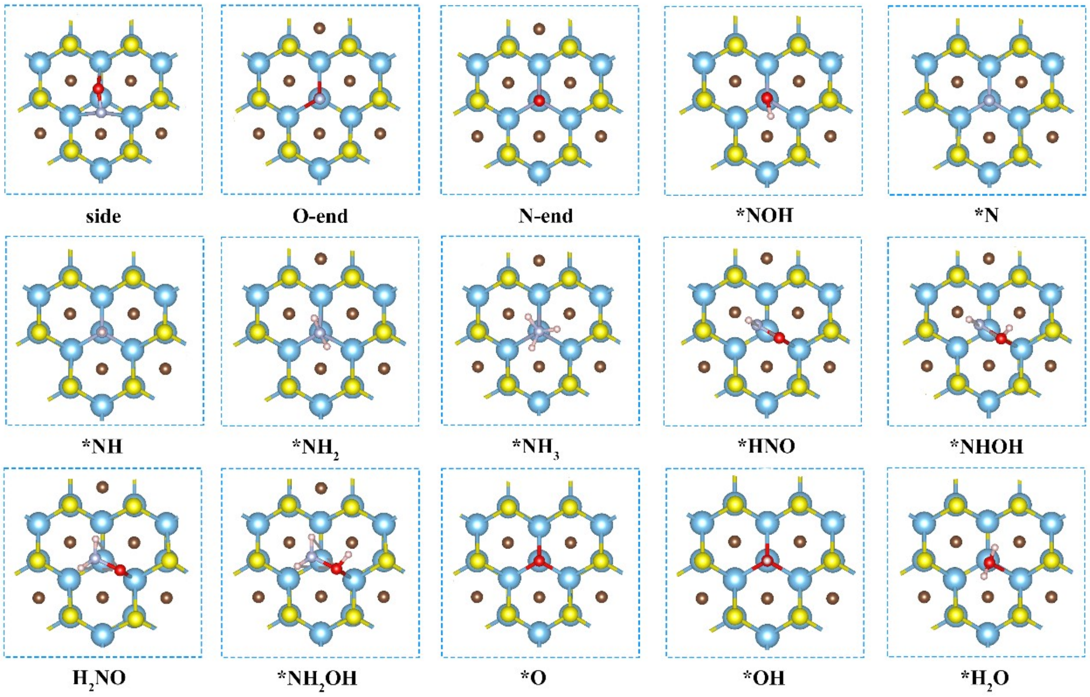

Fig. S14 The optimized configurations of all NORR intermediates on Ti_2CS_2 MXene with solvent effect.

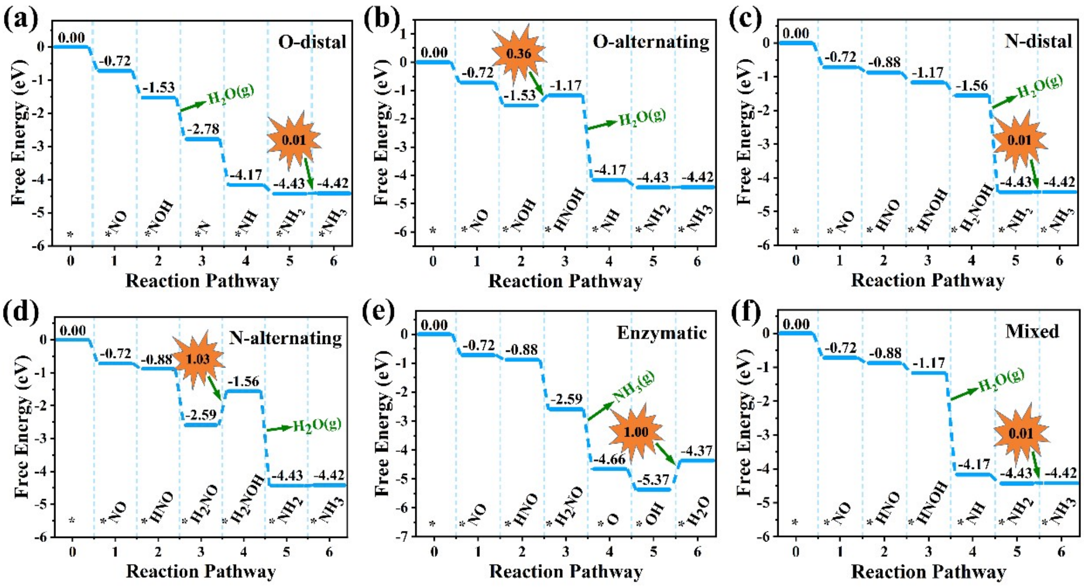

Fig. S15 NORR free energy diagrams of the considered pathways on Ti_2CS_2 MXene with solvent effect. The applied potential is zero.

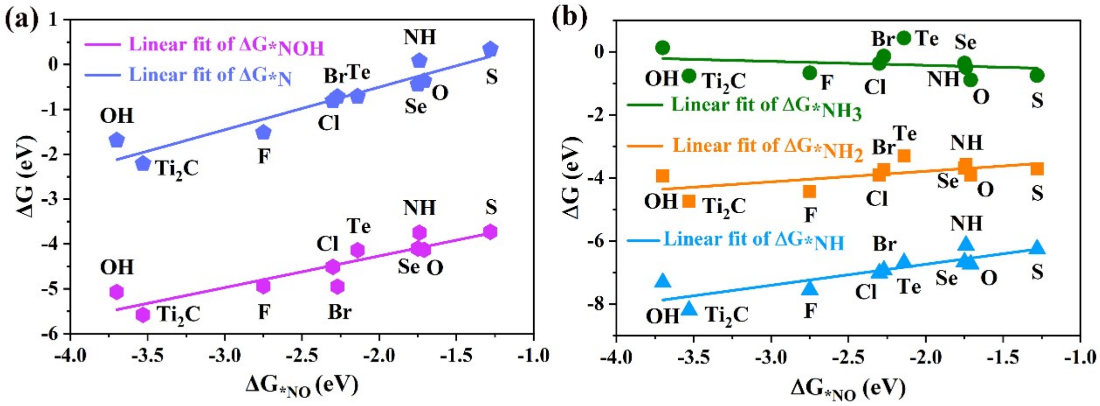

Fig. S16 Linear scaling relations between the adsorption energies of involved intermediates of the most favorable pathway and the adsorption energy of NO (ΔG_{*NO}).

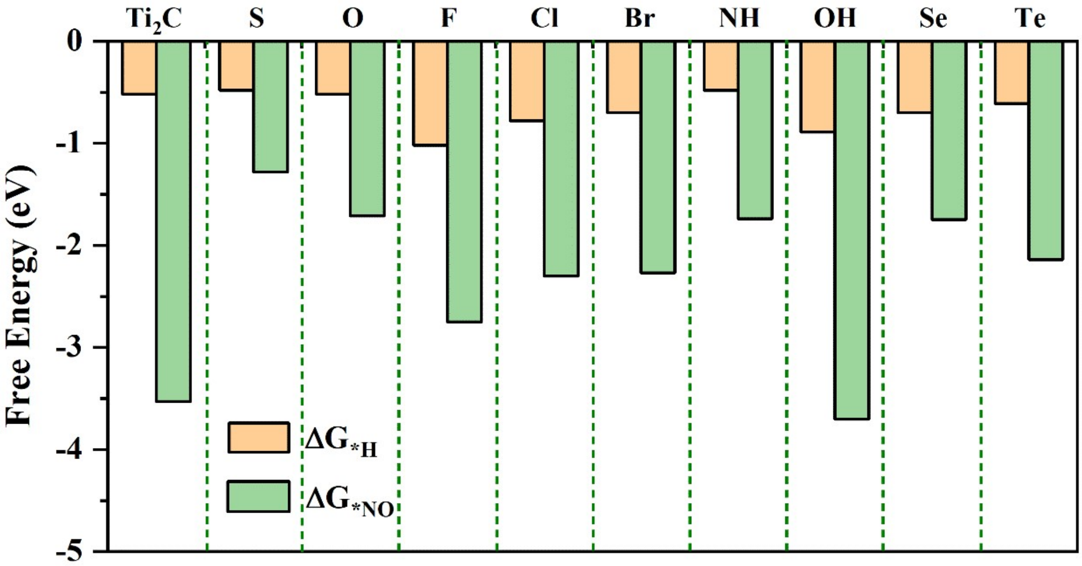

Fig. S17 Adsorption energies of *NO (ΔG_{*NO}) and *H (ΔG_{*H}) on bare Ti_2C and functionalized Ti_2CT_2 MXenes.

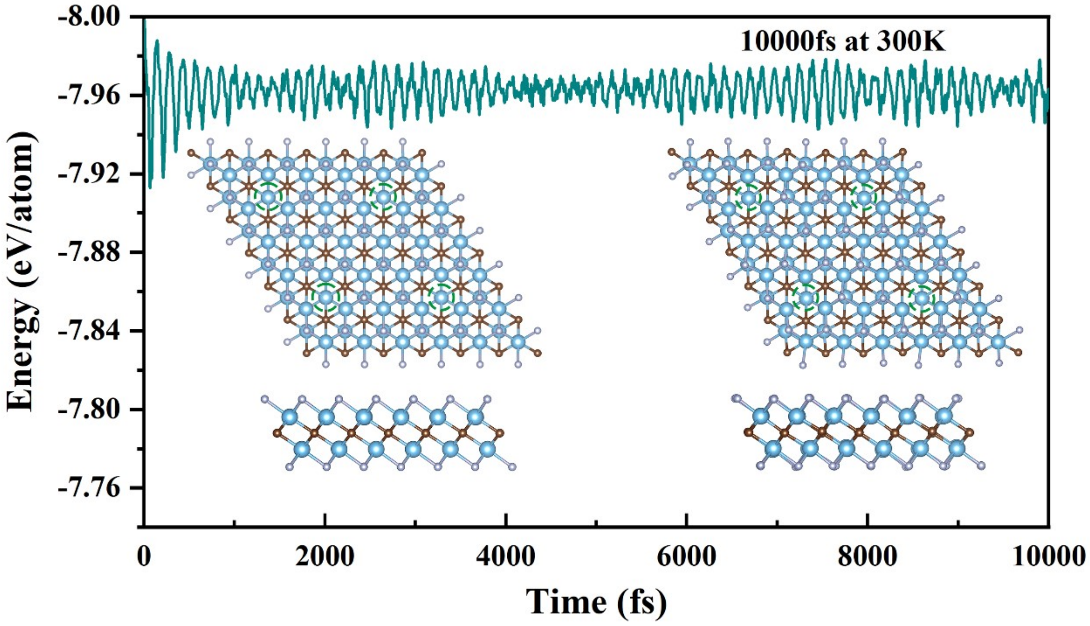

Fig. S18 AIMD simulation of Ti_2CF_2 MXene with F vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The green dotted circles represent the F vacancies.

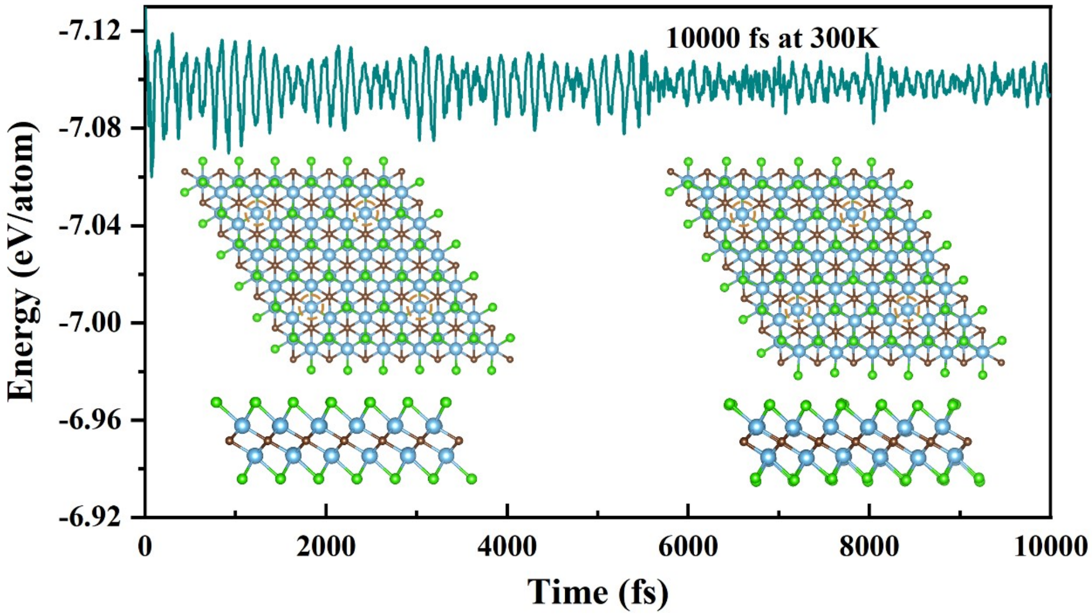

Fig. S19 AIMD simulation of Ti_2CCl_2 MXene with Cl vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The orange dotted circles represent the Cl vacancies.

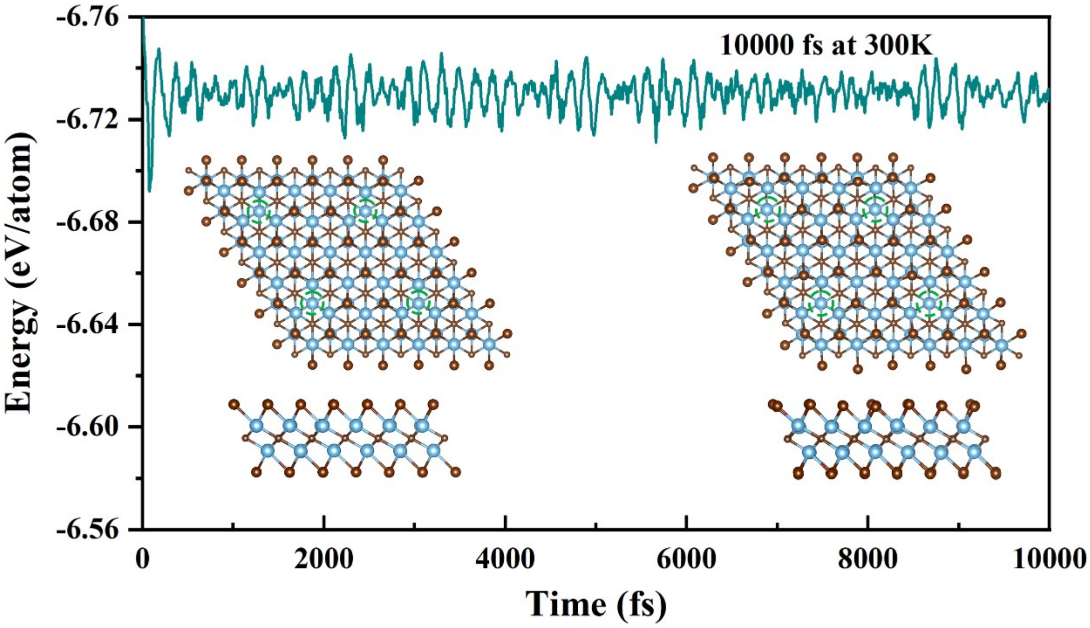

Fig. S20 AIMD simulation of Ti_2CBr_2 MXene with Br vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The green dotted circles represent the Br vacancies.

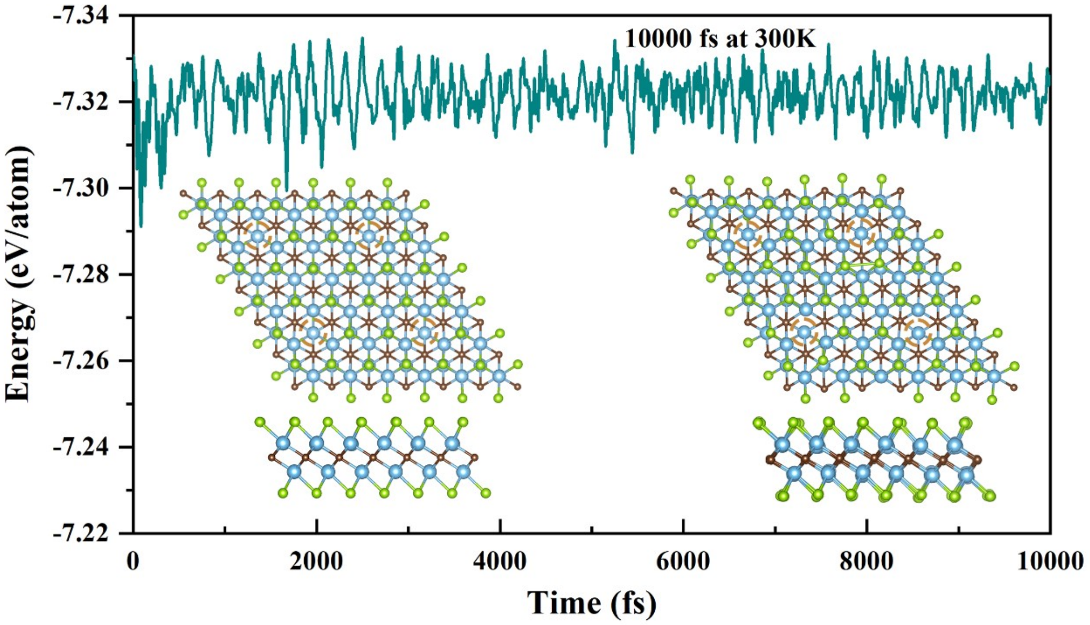

Fig. S21 AIMD simulation of Ti_2CSe_2 MXene with Se vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The orange dotted circles represent the Se vacancies.

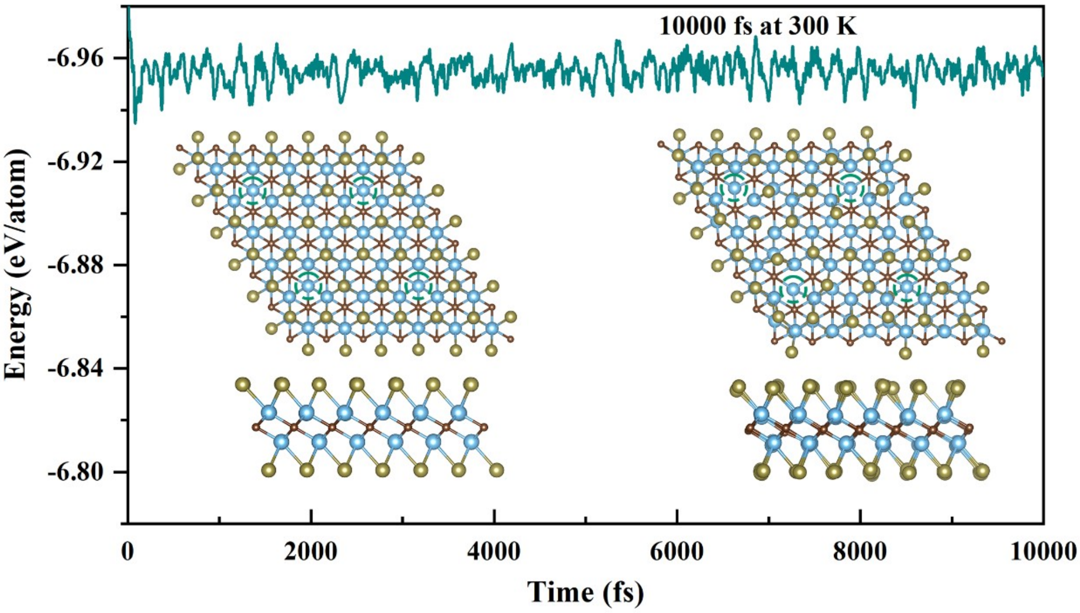

Fig. S22 AIMD simulation of Ti_2CTe_2 MXene with Te vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The green dotted circles represent the Te vacancies.

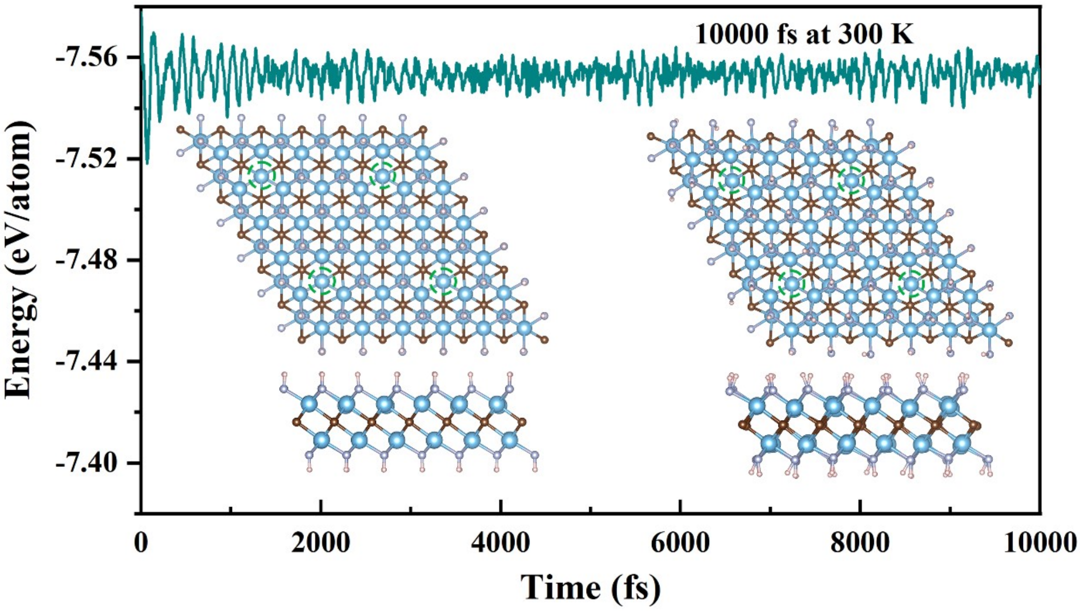

Fig. S23 AIMD simulation of $Ti_2C(NH)_2$ MXene with NH vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The green dotted circles represent the NH vacancies.

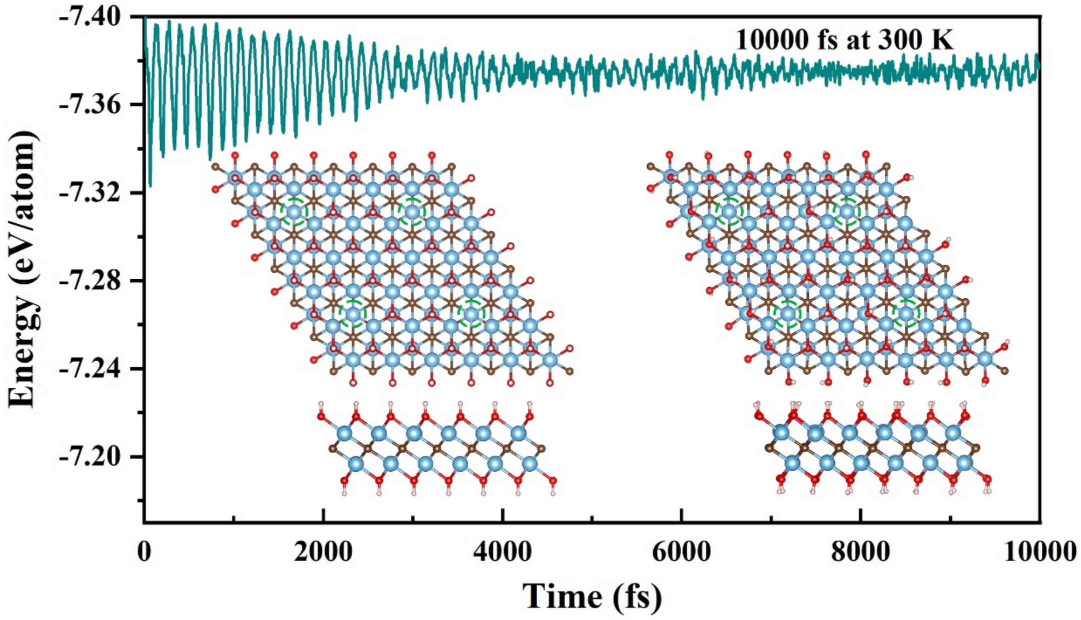

Fig. S24 AIMD simulation of $Ti_2C(OH)_2$ MXene with OH vacancies. The inserts illustrate the initial and final (10000 fs) atomic structures shown in the top and side view. The green dotted circles represent the OH vacancies.

Table S1. Comparison of adsorption energy of Mode 1 and Mode 2 for functionalized Ti_2CT_2 MXenes unit cells (units in eV). "/" represents structural instability.

MXenes	Model 1	Model 2
Ti_2CS_2	-38.10	-39.17
Ti_2CO_2	-43.76	-45.57
Ti_2CF_2	-39.55	-40.08
Ti_2CCl_2	-35.81	-36.29
Ti_2CBr_2	-34.21	-34.60
Ti_2CSe_2	-36.65	-37.47
Ti_2CTe_2	-35.06	-35.52
$Ti_2C(NH)_2$	/	-54.15
$Ti_2C(OH)_2$	/	-52.15

Table S2. Comparison of the free energy change of ΔG (*NO - *NOH) and ΔG (*NO - *HNO) on functionalized Ti_2CT_2 MXenes (ΔG, units in eV)

MXenes	**ΔG(*NO - *NOH)**	**ΔG(*NO - *HNO)**
Ti_2CS_2	-0.69	-0.05
Ti_2CO_2	-0.66	-0.43
Ti_2CF_2	-0.44	-0.32
Ti_2CCl_2	-0.45	0.12
Ti_2CBr_2	-0.42	0.47
Ti_2CSe_2	-0.59	0.32
Ti_2CTe_2	-0.24	0.59
$Ti_2C(NH)_2$	-0.25	0.03
$Ti_2C(OH)_2$	0.38	0.27

Table S3. Comparison of the adsorption energy of ΔG_{*NOH} and ΔG_{*NHO} on functionalized Ti_2CT_2 MXenes (ΔG, units in eV)

MXenes	**ΔG_{*NOH}**	**ΔG_{*NHO}**
Ti_2CS_2	-3.73	-1.30
Ti_2CO_2	-4.13	-2.11
Ti_2CF_2	-4.94	-3.03
Ti_2CCl_2	-4.51	-2.15
Ti_2CBr_2	-4.45	-1.77
Ti_2CSe_2	-4.10	-1.40

Ti_2CTe_2	-4.14	-1.52
$Ti_2C(NH)_2$	-3.75	-1.68
$Ti_2C(OH)_2$	-5.07	-3.40

Table S4. Computed Gibbs free energy of each elementary step on the Ti_2CS_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CS_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$*+NO \rightarrow *NO$	-1.28	-0.72
$*NO+H^++e^- \rightarrow *NOH$	-0.69	-0.81
$*NO+H^++e^- \rightarrow *HNO$	-0.05	-0.16
$*NOH+H^++e^- \rightarrow *N+H_2O$	-1.02	-1.25
$*N+ H^++e^- \rightarrow *NH$	-1.29	-1.39
$*NH+ H^++e^- \rightarrow *NH_2$	-0.21	-0.26
$*NH_2+ H^++e^- \rightarrow *NH_3$	0.08	0.01
$*NOH+H^++e^- \rightarrow *NHOH$	0.49	0.36
$*HNO+H^++e^- \rightarrow *NHOH$	-0.15	-0.29
$*HNO+H^++e^- \rightarrow *H_2NO$	-1.62	-1.71
$*NHOH+H^++e^- \rightarrow *NH_2OH$	-0.07	-0.39
$*H_2NO+H^++e^- \rightarrow *NH_2OH$	1.40	1.03
$*O+H^++e^- \rightarrow *OH$	-0.50	-0.71
$*OH+H^++e^- \rightarrow *H_2O$	1.17	1.00

Table S5. Computed Gibbs free energy of the optimal pathway for ammonia formation on the Ti_2CO_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CO_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$* + NO \rightarrow *NO$	-1.71	-1.00
$*NO + H^+ + e^- \rightarrow *NOH$	-0.67	-0.84
$*NOH + H^+ + e^- \rightarrow *N + H_2O$	-1.34	-1.49
$*N + H^+ + e^- \rightarrow *NH$	-1.05	-1.16
$*NH + H^+ + e^- \rightarrow *NH_2$	0.06	-0.01
$*NH_2 + H^+ + e^- \rightarrow *NH_3$	**0.14**	-0.10

Table S6. Computed Gibbs free energy of the optimal pathway for ammonia formation on the Ti_2CF_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CF_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$* + NO \rightarrow *NO$	-2.75	-2.19
$*NO + H^+ + e^- \rightarrow *NOH$	-0.44	-0.49
$*NOH + H^+ + e^- \rightarrow *N + H_2O$	-1.67	-1.88
$*N + H^+ + e^- \rightarrow *NH$	-0.71	-0.73
$*NH + H^+ + e^- \rightarrow *NH_2$	0.36	0.26
$*NH_2 + H^+ + e^- \rightarrow *NH_3$	**0.87**	**0.60**

Table S7. Computed Gibbs free energy of the optimal pathway for ammonia formation on the Ti_2CCl_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CCl_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$* + NO \rightarrow *NO$	-2.30	-2.14
$*NO + H^+ + e^- \rightarrow *NOH$	-0.45	-0.49
$*NOH + H^+ + e^- \rightarrow *N + H_2O$	-1.40	-1.66
$*N + H^+ + e^- \rightarrow *NH$	-0.89	-0.92
$*NH + H^+ + e^- \rightarrow *NH_2$	0.35	0.30
$*NH_2 + H^+ + e^- \rightarrow *NH_3$	**0.66**	**0.56**

Table S8. Computed Gibbs free energy of the optimal pathway for ammonia formation on the Ti_2CBr_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CBr_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$* + NO \rightarrow *NO$	-2.27	-2.29
$*NO + H^+ + e^- \rightarrow *NOH$	-0.42	-0.49
$*NOH + H^+ + e^- \rightarrow *N + H_2O$	-1.37	-1.67
$*N + H^+ + e^- \rightarrow *NH$	-0.89	-0.89
$*NH + H^+ + e^- \rightarrow *NH_2$	0.42	0.39
$*NH_2 + H^+ + e^- \rightarrow *NH_3$	**0.72**	**0.69**

Table S9. Computed Gibbs free energy of the optimal pathway for ammonia formation on the Ti_2CSe_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CSe_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$*+NO \rightarrow *NO$	-1.75	-1.53
$*NO+H^++e^- \rightarrow *NOH$	-0.59	-0.64
$*NOH+H^++e^- \rightarrow *N+H_2O$	-1.45	-1.73
$*N+ H^++e^- \rightarrow *NH$	-0.90	-0.96
$*NH+ H^++e^- \rightarrow *NH_2$	0.23	0.20
$*NH_2+ H^++e^- \rightarrow *NH_3$	**0.44**	**0.39**

Table S10. Computed Gibbs free energy of the optimal pathway for ammonia formation on the Ti_2CTe_2 MXene without and with solvation effects. (ΔG, units in eV)

Ti_2CTe_2	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$*+NO \rightarrow *NO$	-2.14	-2.22
$*NO+H^++e^- \rightarrow *NOH$	-0.24	-0.23
$*NOH+H^++e^- \rightarrow *N+H_2O$	-1.67	-1.99
$*N+ H^++e^- \rightarrow *NH$	-0.66	-0.68
$*NH+ H^++e^- \rightarrow *NH_2$	0.62	0.61
$*NH_2+ H^++e^- \rightarrow *NH_3$	**0.87**	**0.85**

Table S11. Computed Gibbs free energy of the optimal pathway for ammonia formation on the $Ti_2C(NH)_2$ MXene without and with solvation effects. (ΔG, units in eV)

$Ti_2C(NH)_2$	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$*+NO \rightarrow *NO$	-1.74	-1.83
$*NO+H^++e^- \rightarrow *NOH$	-0.25	-0.23
$*NOH+H^++e^- \rightarrow *N+H_2O$	-1.27	-1.61
$*N+ H^++e^- \rightarrow *NH$	-0.91	-0.83
$*NH+ H^++e^- \rightarrow *NH_2$	-0.19	-0.20
$*NH_2+ H^++e^- \rightarrow *NH_3$	**0.19**	**0.16**

Table S12. Computed Gibbs free energy of the optimal pathway for ammonia formation on the $Ti_2C(OH)_2$ MXene without and with solvation effects. (ΔG, units in eV)

$Ti_2C(OH)_2$	**ΔG (without solvation effects)**	**ΔG (with solvation effects)**
$*+NO \rightarrow *NO$	-3.70	-3.95
$*NO+H^++e^- \rightarrow *HNO$	0.27	0.40
$*HNO+H^++e^-\rightarrow *NH\text{-}H_2O$	-2.71	-2.67
$*NH\text{-}H_2O\rightarrow *NH+H_2O(g)$	0.33	-0.004
$*NH+ H^++e^- \rightarrow *NH_2$	0.50	0.57

$*NH_2 + H^+ + e^- \rightarrow *NH_3$	**1.14**	**1.20**

Table S13. Bader charge variation of three "active" Ti atoms upon NO adsorption

MXenes	**charge transfer (e^-)**
bare Ti_2C	0.911
Ti_2CS_2	0.102
Ti_2CO_2	0.480
Ti_2CF_2	0.490
Ti_2CCl_2	0.280
Ti_2CBr_2	0.309
Ti_2CSe_2	0.208
Ti_2CTe_2	0.311
$Ti_2C(NH)_2$	0.205
$Ti_2C(OH)_2$	0.541