Supporting Information for

Work Function Regulation of Surface-engineered Ti_2CT_2 MXene for Efficient Electrochemical Nitrogen Reduction Reaction

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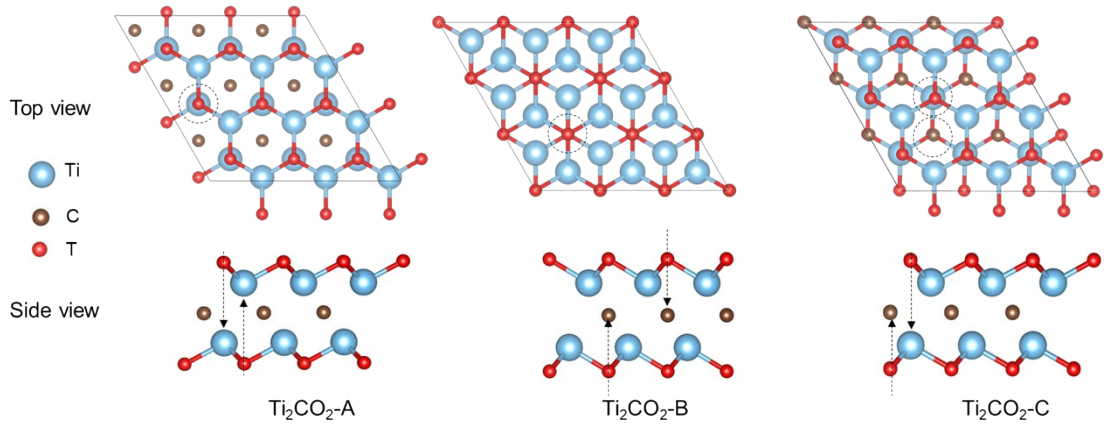

Fig. S1 Configurations of Ti_2CT_2 models

Table S1 Total electronic energy of supercell (E_0), unit cell (E_b), formation energy (E_f), and defect formation energy (E_{def}). Formation energy for Ti_2CT_2 MXene: $E_f = (E_0 - E_{Ti2C} - x \times E_T)/x$. Defect formation energy is only considered for the most stable one among the three configurations: $E_{def} = E_{Ti2CT2\text{-}V} - E_{Ti2CT2} + E_T$.

Ti_2CT_2	**E_0 (eV)**	**E_b (eV)**	**E_f (eV)**	**E_{def} (eV)**
Ti_2CF_2-A	**-354.42**	**-115.71**	**-6.81**	**6.60**
Ti_2CF_2-B	-349.92	-111.21	-6.54	NA
Ti_2CF_2-C	-352.57	-113.86	-6.70	NA
Ti_2CH_2-A	**-311.14**	**-63.92**	**-3.76**	**3.69**
Ti_2CH_2-B	-305.26	-58.04	-3.41	NA
Ti_2CH_2-C	-307.87	-60.65	-3.57	NA
Ti_2CO_2-A	**-402.17**	**-141.61**	**-8.33**	**7.59**
Ti_2CO_2-B	-388.23	-127.66	-7.51	NA
Ti_2CO_2-C	-395.76	-135.19	-7.95	NA
Ti_2COH_2-A	**-457.10**	**-101.90**	**-5.99**	**5.39**
Ti_2COH_2-B	-454.37	-99.17	-5.83	NA
Ti_2COH_2-C	-456.04	-100.84	-5.93	NA

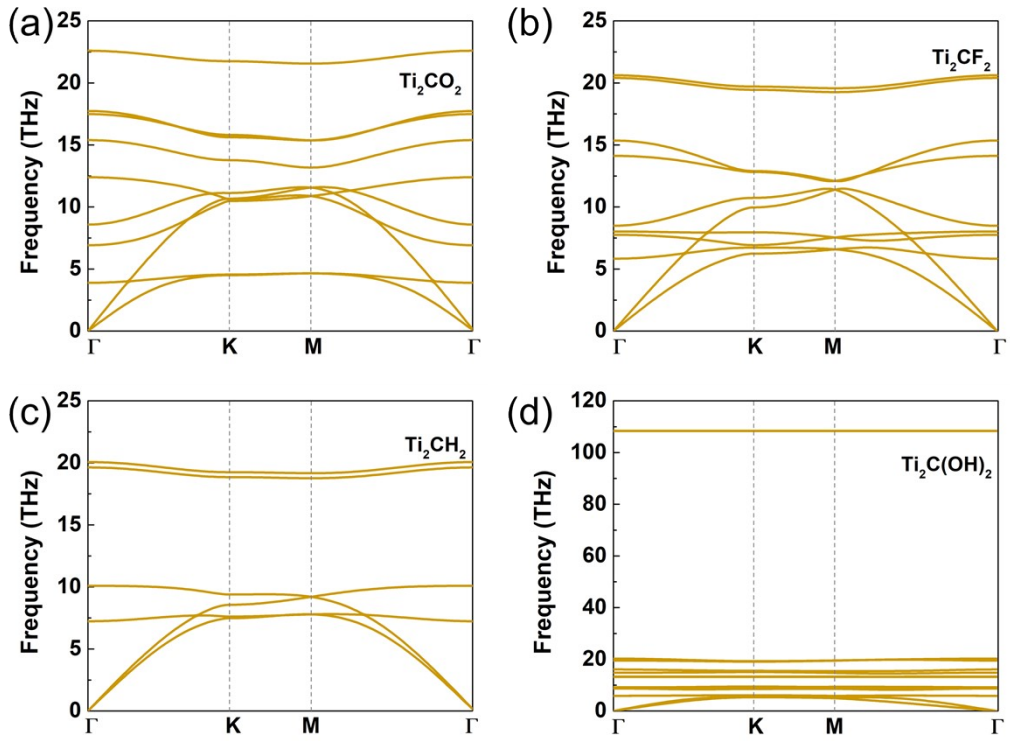

Fig. S2 Calculated phonon band structures of the Ti_2CT_2 unitcell.

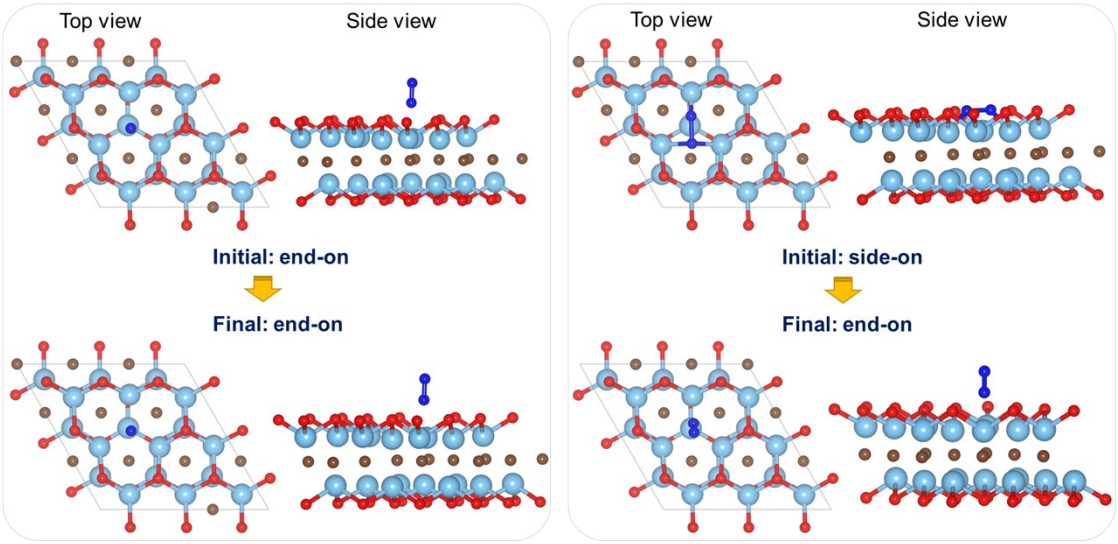

Fig. S3 The initial configurations of end-on and side-on adsorption and their optimized final states.

Table S2 Gibbs free energy through distal and consecutive mechanism

Δ*G* (distal)	**Ti_2CO_2**	**Ti_2CF_2**	**Ti_2CH_2**	**$Ti_2C(OH)_2$**
Slab	0.00	0.00	0.00	0.00
*N_2	-0.03	-0.33	-0.39	-0.76
*NNH	0.50	-0.52	-0.65	-1.11
*NNH_2	-0.72	-1.21	-1.59	-1.14
*N	-0.97	-2.10	-2.10	-2.36
*NH	-2.06	-2.86	-2.90	-2.75
*NH_2	-2.02	-2.48	-2.56	-2.08
*NH_3	-1.90	-1.58	-1.36	-0.79
slab	-0.89	-0.89	-0.89	-0.89
Δ*G* (consecutive)	**Ti_2CO_2**	**Ti_2CF_2**	**Ti_2CH_2**	**$Ti_2C(OH)_2$**
Slab	0.00	0.00	0.00	0.00
*N_2	-0.03	-0.33	-0.39	-0.76
*NNH	0.50	-0.52	-0.65	-1.11
*NH-NH	0.00	-0.84	-1.11	-0.20
*NH-NH_2	-0.53	-0.99	-1.27	-0.09
*NH_2-NH_2	-0.12	0.15	0.27	1.33
*NH_2	-2.02	-2.48	-2.56	-2.08
*NH_3	-1.90	-1.58	-1.36	-0.79
slab	-0.89	-0.89	-0.89	-0.89

Table S3 Free energy barrier through distal and consecutive mechanism including electronic steps.

Δ*G* (distal)	**Ti_2CO_2**	**Ti_2CF_2**	**Ti_2CH_2**	**$Ti_2C(OH)_2$**
$*N_2$	NA	NA	NA	NA
*NNH	0.53	-0.19	-0.27	-0.35
$*NNH_2$	-1.22	-0.69	-0.94	-0.03
*N	-0.24	-0.90	-0.51	-1.21
*NH	-1.10	-0.75	-0.80	-0.40
$*NH_2$	0.04	0.38	0.34	0.67
$*NH_3$	0.12	0.90	1.21	1.29
Δ*G* (consecutive)	**Ti_2CO_2**	**Ti_2CF_2**	**Ti_2CH_2**	**$Ti_2C(OH)_2$**
$*N_2$	NA	NA	NA	NA
*NNH	0.53	-0.19	-0.27	-0.35
*NH-NH	-0.50	-0.32	-0.45	0.92
$*NH\text{-}NH_2$	-0.53	-0.15	-0.17	0.10
$*NH_2\text{-}NH_2$	0.41	1.15	1.54	1.42
$*NH_2$	-1.90	-2.63	-2.83	-3.41
$*NH_3$	0.12	0.90	1.21	1.29

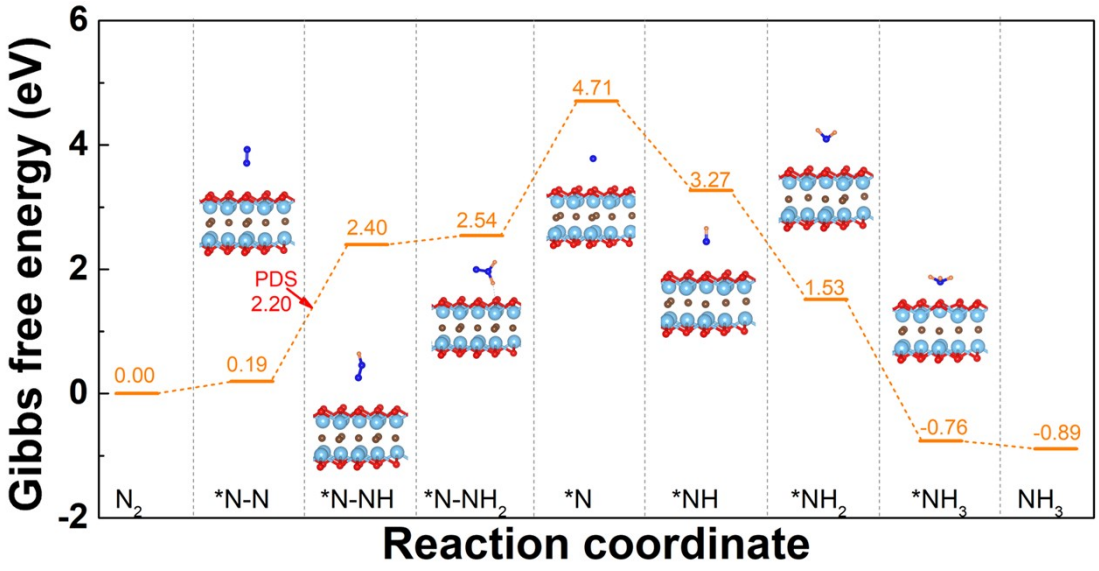

Fig. S4 Free energy profiles for nitrogen reduction on perfect Ti_2CO_2 through distal mechanisms, and the configuration for each reaction intermediate is shown as well.

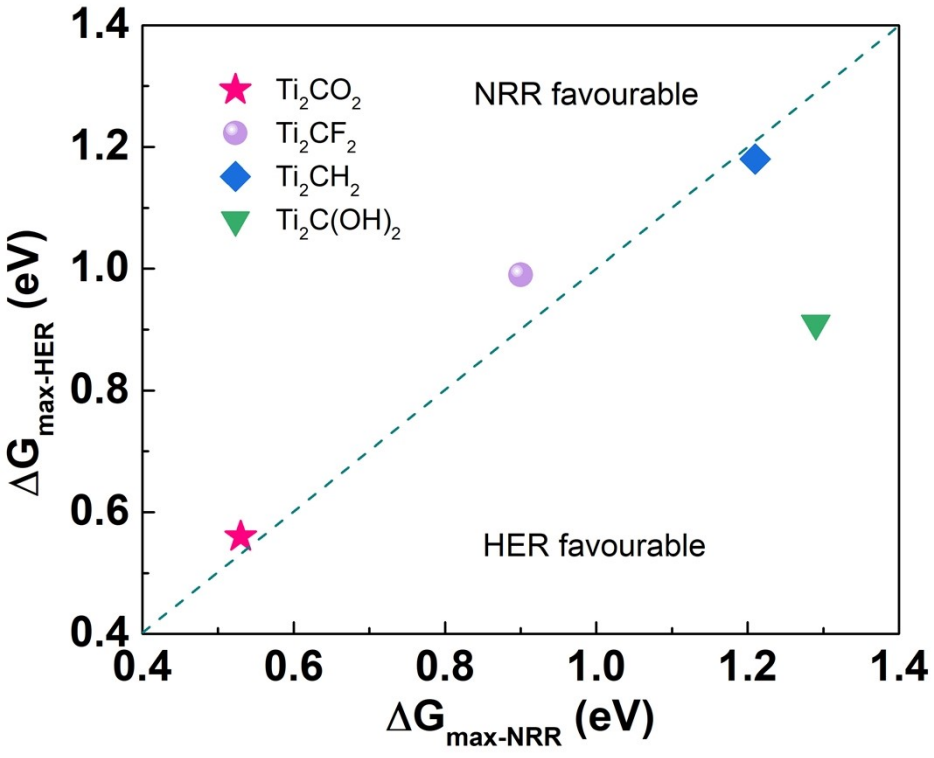

Fig. S5 Free energy potential of rate-determing steps for NRR and HER. The values of ΔG_{max} for HER are 0.56 eV (Ti_2CO_2), 0.99 eV (Ti_2CF_2), 1.18 eV (Ti_2CH_2), and 0.91 eV ($Ti_2C(OH)_2$). The dashed line represents $\Delta G_{max\text{-}HER} = \Delta G_{max\text{-}NRR}$.

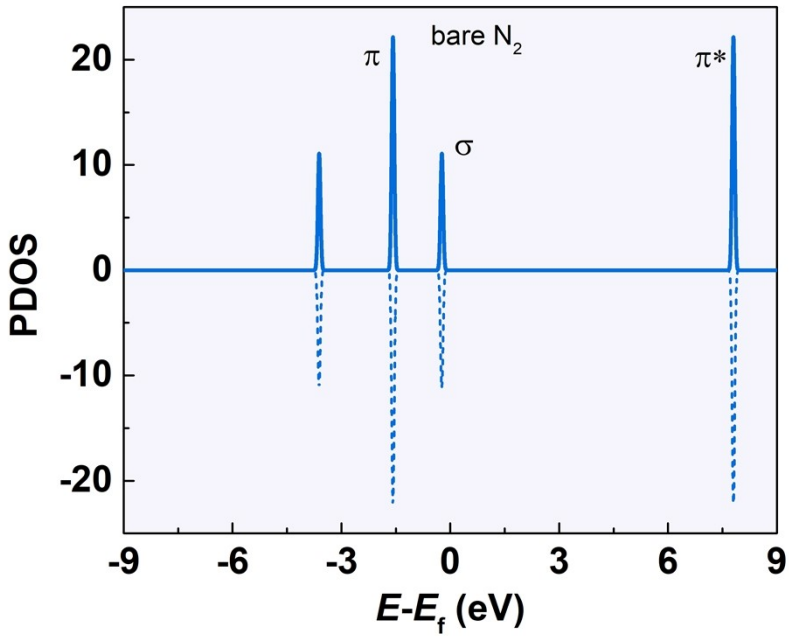

Fig. S6 Projected density of states of pure N_2 molecule.

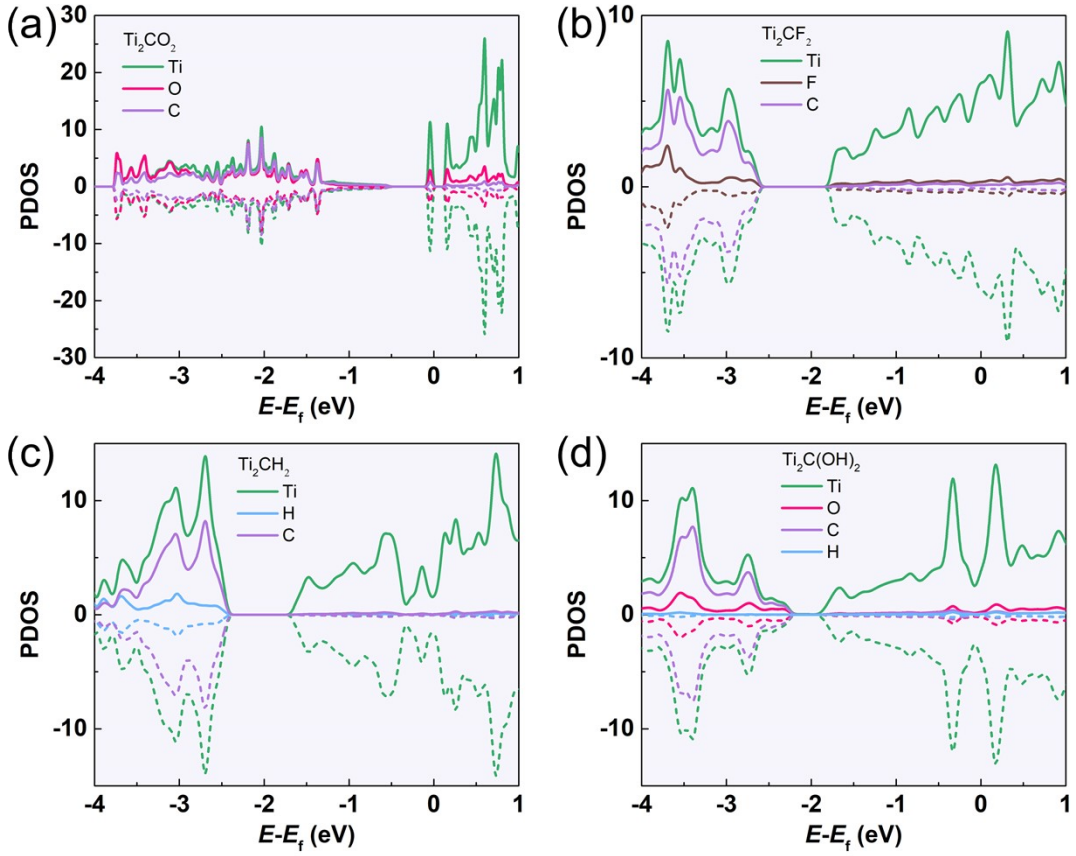

Fig. S7 Projected density of states of defective (a) Ti_2CO_2, (b) Ti_2CF_2, (c) Ti_2CH_2, and (d) $Ti_2C(OH)_2$.

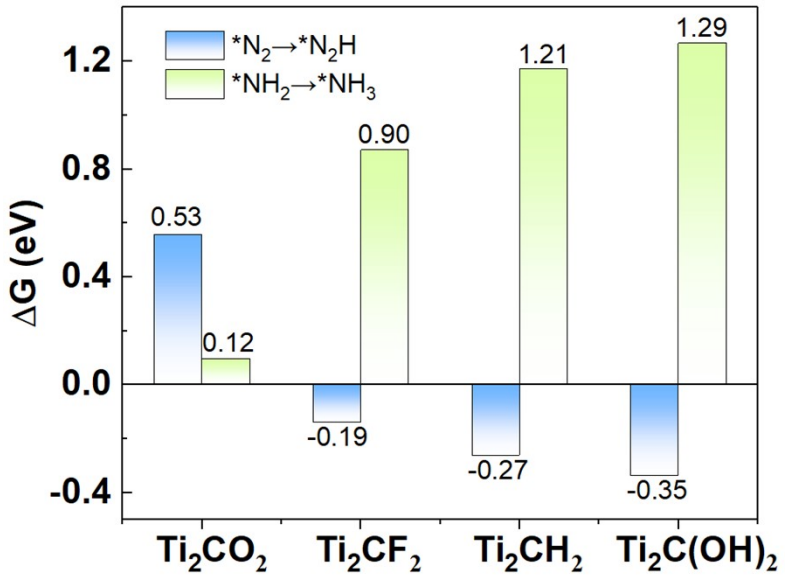

Fig. S8 Free energy barrier of potential-determining steps following distal path.

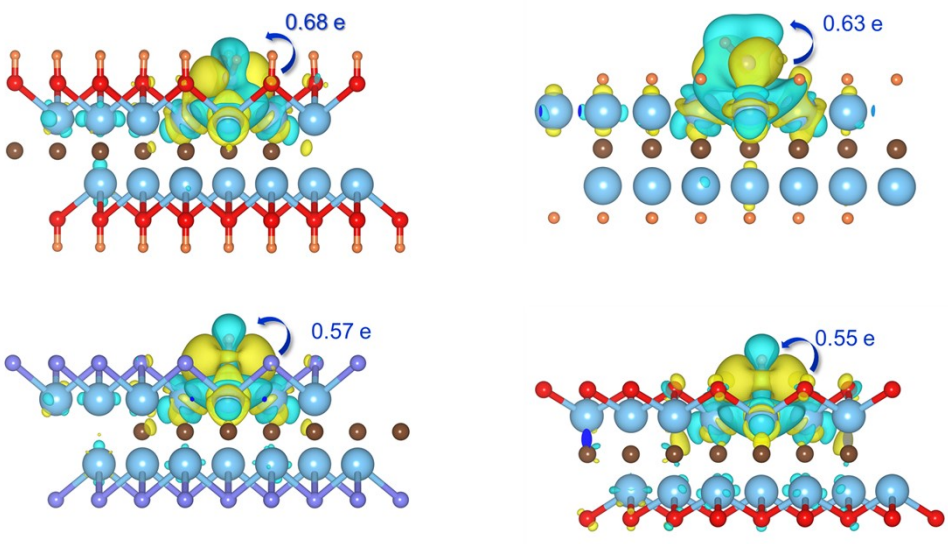

Fig. S9 Charge transfer and electron density difference between defective (a) $Ti_2C(OH)_2$, (b) Ti_2CH_2, (c) Ti_2CF_2, and (d) Ti_2CO_2 and intermediate $*NH_2$.

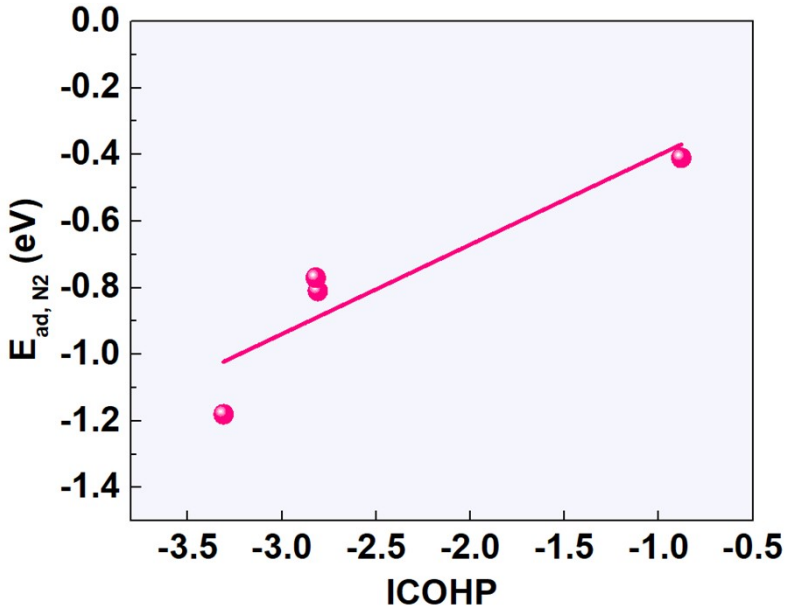

Fig. S10 Linear fitting between ICOHP and adsorption energy of N_2.

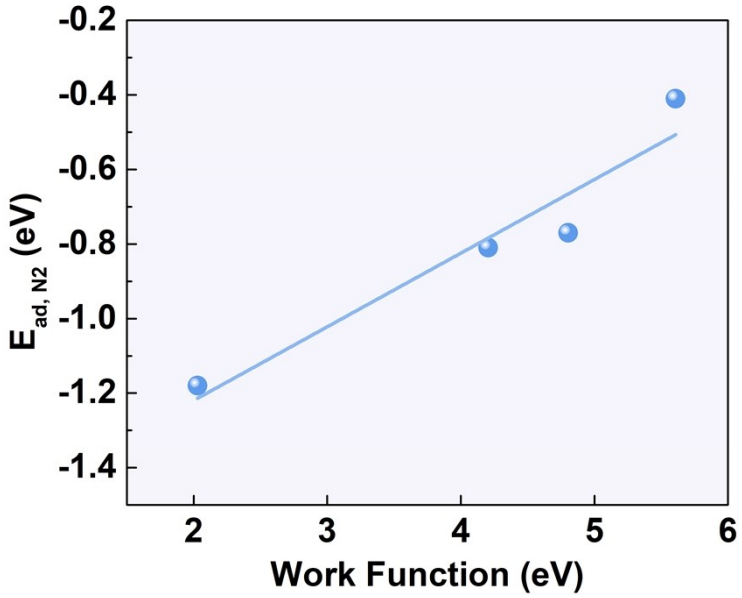

Fig. S11 Linear fitting between work function and adsorption energy of N_2.