Electronic Supplementary Material (ESI)

Supporting Information

Molecular nitrogen induced structure evolution of single transition metal atom supported by B/N co-doped graphene for enhanced nitrogen electroreduction performance

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Table S1 The formation energies (eV) of B_2N_2/G, B_2N_2/G-1, B_2N_2/G-2 and N_3B_2/G.

Defect	B_2N_2/G	B_2N_2/G-1	B_2N_2/G-2	N_3B_2/G
Formation energy	-0.73	-0.51	-0.35	-0.83

*The formation energies of B_2N_2/G, B_2N_2/G-1 and B_2N_2/G-2 are calculated according to $E_{form\text{-}1} = E_{B2N2/G} + 4E_C - (E_{Gv\text{-}2C} + 2E_B + 2E_N)$, where $E_{B2N2/G}$, $E_{Gv\text{-}2C}$, E_C, E_B and E_N are the energies of B(N)-codoped graphene, divacancy graphene, atomic C, B and N, respectively. While the formation energies of N_3B_2/G is calculated according to $E_{form\text{-}2} = E_{N3B2/G} + 5E_C - (E_{Gv\text{-}1C} + 2E_B + 3E_N)$, where $E_{N3B2/G}$ and $E_{Gv\text{-}1C}$ are the energies of the N_3B_2/G structure and monovacancy graphene, respectively.

Table S2 The binding energies (E_b, eV) of TM and three substrates, including B_2N_2/G selected in the works, B_2N_2/G-1, B_2N_2/G-2.

TM	E_b (eV)		
	TM-B_2N_2/G in the work	TM-B_2N_2/G-1	TM-B_2N_2/G-2
Sc	-7.93	-5.05	-4.61
V	-7.04	-4.09	-5.04
Cr	-5.37	-3.68	-3.10
Mn	-5.38	-4.01	-3.99
Fe	-6.17	-4.73	-4.99
Co	-6.51	-5.29	-5.39
Ni	-6.70	-5.75	-5.64
Cu	-5.29	-4.19	-2.87
Zn	-3.53	-2.69	-0.71
Y	-7.79	-6.85	-4.38
Zr	-9.03	-8.34	-6.01
Nb	-8.46	-7.28	-6.76
Mo	-6.31	-5.00	-5.10
Tc	-7.22	-6.54	-5.94
Ru	-8.70	-8.12	-7.48
Rh	-6.85	-6.50	-6.45
Pd	-3.01	-2.82	-2.54
Ag	-2.97	-2.15	-1.47
Hf	-8.73	-6.61	-6.21
Ta	-11.14	-9.79	-9.65
W	-7.49	-6.39	-6.69
Re	-7.48	-6.90	-6.32
Os	-7.99	-7.49	-7.05
Ir	-7.70	-7.27	-7.38
Pt	-6.68	-6.11	-6.43
Au	-3.23	-3.17	-2.59

Table S3 Adsorption free energies (Δ*G*, eV) of atom hydrogen and molecular N_2 by end-on, side-on, side-on-1 and side-on-2 modes on fourteen TM-B_2N_2/G systems, which preferentially trap H atom. Here the "/" means that the corresponding optimized atomic structures are not obtained.

TM	ΔG^*H	$\Delta G^*N_{2\text{-end-on}}$	$\Delta G^*N_{2\text{-side-on}}$	$\Delta G^*N_{2\text{-side-on-1}}$	$\Delta G^*N_{2\text{-side-on-2}}$
Mn	-0.76	-0.40	0.11	0.02	-0.02
Co	-0.79	-0.32	/	0.99	0.22
Ni	-0.82	-0.26	/	1.33	0.38
Zn	1.17	/	/	1.88	1.61
Cu	-0.14	0.18	/	/	0.95
Y	-1.25	-1.02	-0.87	-1.19	-1.06
Tc	-0.62	-0.56	0.27	-0.17	0.93
Ru	-0.66	-0.30	1.33	-0.29	1.28
Rh	-1.27	-0.09	1.51	-0.86	1.60
Hf	-1.18	-0.98	-0.80	-0.82	-0.61
Re	-1.07	-0.76	0.77	-0.97	0.90
Os	-0.90	-0.43	1.79	-0.57	1.46
Ir	-1.38	-0.22	1.76	1.62	/
Pt	-1.22	0.12	1.28	/	2.04

Table S4 Adsorption free energies (Δ*G*, eV) of atomic hydrogen and molecular N_2 by end-on, side-on, side-on-1 and side-on-2 modes on remaining ten TM-B_2N_2/G systems, which preferentially trap N_2 molecule.

TM	ΔG^*_H	$\Delta G^*_{N_{2\text{-end-on}}}$	$\Delta G^*_{N_{2\text{-side-on}}}$	$\Delta G^*_{N_{2\text{-side-on-1}}}$	$\Delta G^*_{N_{2\text{-side-on-2}}}$
Sc	-0.07	-1.05	-0.38	-1.37	-1.26
Ti	-0.42	-0.86	-0.44	-1.84	-1.49
V	-0.59	-0.64	-0.27	-1.15	-0.51
Cr	-0.17	-0.26	-0.17	-0.79	-0.06
Fe	0.20	-0.35	0.74	-0.51	0.24
Zr	-0.98	-1.68	-0.48	-2.95	-2.72
Nb	-1.09	-1.39	-0.76	-2.12	-1.18
Mo	-0.44	-0.53	-0.41	-1.06	-0.09
Ta	-1.19	-1.56	-1.16	-2.54	-1.63
W	-1.03	-1.16	-1.35	-3.09	-0.59

Table S5 Hydrogenation free energies (Δ*G*, eV) of adsorbed side-on-1 N_2 on TM-B_2N_2/G.

	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Sc	-0.05	-1.29	-0.94	1.56
	*N*NH	*NH*NH		
	-0.05	0.51		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Ti	-1.08	-1.51	-0.32	1.29
	*N*NH	*NH*NH		
	-1.08	0.49		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
V	-1.91	-1.04	-0.51	1.08
	*N*NH	*NH*NH		
	-1.91	0.79		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Cr	-2.31	-1.15	-0.42	1.23
	*N*NH	*NH*NH		
	-2.31	0.72		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Fe	-1.17	-0.72	-0.33	0.99
	*N*NH	*NH*NH		
	-1.17	0.81		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Zr	-0.47	-1.33	0.13	1.15
	*N*NH	*NH*NH		
	-0.47	0.61		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Nb	-1.34	-0.89	0.22	1.36
	*N*NH	*NH*NH		
	-1.34	0.60		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Mo	-0.87	-0.63	-0.14	1.05
	*N*NH	*NH*NH		
	-0.87	0.55		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
Ta	-1.41	-0.44	0.08	1.54
	*N*NH	*NH*NH		
	-1.41	0.59		
	*N*NH	*N*NH_2	*N*NH_3	*NH*NH_3
W	-0.60	-0.13	-0.15	1.80
	*N*NH	*NH*NH		
	-0.60	0.74		

Table S6 Adsorption free energies (G_{*NH_3}, eV) of the first formed $*NH_3$ on N-TM-B_2N_2/G.

TM	Sc	Ti	V	Cr	Fe	Zr	Nb	Mo	Ta	W
G_{*NH_3}	-1.55	-2.09	-1.89	-1.49	-1.41	-1.75	-1.83	-1.61	-2.07	-1.74

Table S7 The comparison of binding energies (E_b, eV) of TM single atoms supported by B_2N_2/G and N_3B_2/G substrates.

TM	Sc	Ti	V	Cr	Fe	Zr	Nb	Mo	Ta	W
TM-B_2N_2/G	-7.93	-7.91	-7.04	-5.37	-6.17	-9.03	-8.46	-6.31	-11.14	-7.49
TM-N_3B_2/G	-8.99	-8.64	-7.83	-6.20	-6.19	-9.37	-8.83	-6.59	-11.46	-7.80

Table S8 The adsorption free energies (eV) of the 1st, 2nd, 3rd and even 4th N_2 molecule on TM-N_3B_2/G, accompanying with the corresponding free energies of competitive hydrogen adsorption. Here the "/" means that the corresponding optimized atomic structures are not obtained.

TM	Sc	Ti	V	Cr	Fe	Zr	Nb	Mo	Ta	W
Reactants	$*N_{2\text{-end-on}}$	$*N_{2\text{-end-on}}$	$*N_{2\text{-end-on}}$	$*N_{2\text{-end-on}}$	$*N_{2\text{-end-on}}$	*H	$*2N_{2\text{-end-on}}$	$*2N_{2\text{-end-on}}$	$*3N_{2\text{-end-on}}$	$*3N_{2\text{-end-on}}$
$\Delta G*_H$	0.55	-0.01	-0.34	-0.30	-0.48	-1.31	-0.79	-0.50	-1.26	-0.88
$\Delta G*_{N_{2\text{-end-on}}}$	-0.16	-1.01	-0.73	-0.40	-0.90	-1.03	-1.20	-0.64	-1.43	-1.00
$\Delta G*_{N_{2\text{-side-on}}}$	-0.02	-0.81	-0.42	-0.12	-0.63	-1.19	-1.05	-0.38	-1.28	-0.67
$\Delta G*_{N_{2\text{-end-on}}}*H$	0.68	0.54	0.45	0.38	0.48	/	0.34	0.08	0.02	0.24
$\Delta G*_{2N_{2\text{-end-on}}}$	0.13	0.14	0.10	0.05	0.07		-0.20	-0.65	-0.06	-0.65
$\Delta G*_{N_{2\text{-end-on}}}*N_{2\text{-side-on}}$	/	0.53	0.31	0.44	0.60		0.20	0.06	0.22	-0.31
$\Delta G*_{2N_{2\text{-end-on}}}*H$							0.59	0.63	0.07	0.08
$\Delta G*_{3N_{2\text{-end-on}}}$							0.30	0.16	-0.01	-0.18
$\Delta G*_{2N_{2\text{-end-on}}}*N_{2\text{-side-on}}$							0.62	0.36	0.25	0.05
$\Delta G*_{3N_{2\text{-end-on}}}*H$									0.40	0.58
$\Delta G*_{4N_{2\text{-end-on}}}$									0.43	0.73

Table S9 Hydrogenation free energies (ΔG_{*NNH}) of the 1st, 2nd, and 3rd adsorbed end-on N_2 molecule to *NNH on W(Nb, Ta, Mo)-N_3B_2/G, and their charge states (Q_{N_2}, e), bond lengths ($L_{N\text{-}N}$, Å) of N-N bond and distances ($D_{TM\text{-}N}$, Å) between TM single atom and near-end N atom of adsorbed N_2 molecules.

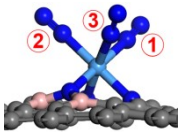
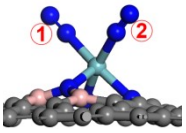
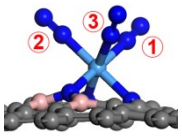
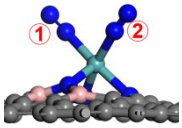
TM	Number	ΔG_{*NNH}/eV	Q_{N_2}/e	$L_{N\text{-}N}$/Å	$D_{TM\text{-}N}$/Å	
W	N_2-1	0.56	0.305	1.138	2.117	
	N_2-2	0.27	0.415	1.142	2.039	
	N_2-3	0.27	0.415	1.142	2.039	
Nb	N_2-1	0.77	0.412	1.140	2.143	
	N_2-2	0.77	0.412	1.140	2.143	
Ta	N_2-1	0.73	0.317	1.135	2.249	
	N_2-2	0.52	0.376	1.140	2.139	
	N_2-3	0.52	0.376	1.140	2.139	
Mo	N_2-1	0.74	0.363	1.139	2.058	
	N_2-2	0.74	0.363	1.139	2.058	

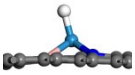
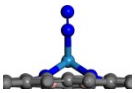
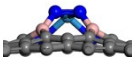
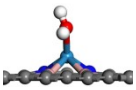
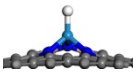
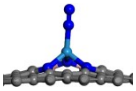
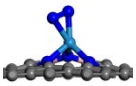
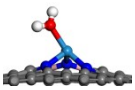
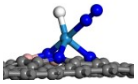
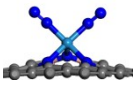
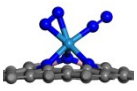
Table S10 Hydrogenation free energies (Δ*G*, eV) of the 3rd adsorbed end-on N_2 molecule along alternating and distal pathways on W-N_3B_2/G in the presence of other two adsorbed N_2 molecules. Where * represent $2N_2$-W-N_3B_2/G.

Alternating	*NNH	*NHNH	*$NHNH_2$	*NH_2NH_2	*NH_2	*NH_3
	0.27	0.72	-0.54	-0.02	-1.09	-0.39
Distal	*NNH	*NNH_2	*N	*NH	*NH_2	*NH_3
	0.27	-0.37	0.06	-0.51	-0.11	-0.39

Table S11 Free energies (Δ*G*, eV) of competitive H adsorption along energy-favorable distal pathway on W-N_3B_2/G in the presence of other two end-on adsorbed N_2 molecules and N_xH_y intermediates.

Distal pathway	$*N_2$	*NNH	$*NNH_2$	*N	*NH	$*NH_2$	$*NH_3$
	-0.18	0.27	-0.37	0.06	-0.51	-0.11	-0.39
H adsorption	*H	$*N_2*H$	*NNH*H	$*NNH_2*H$	*N*H	*NH*H	$*NH_2*H$
	-0.10	0.58	0.68	0.51	0.87	0.17	0.36

Table S12 The adsorption free energies (Δ*G*, eV) of *H, *H_2O, *N_2 on clean W-B_2N_2/G and reconstructed W-N_3B_2/G in the presence of no any reactant, one end-on N_2 molecule and two end-on N_2 molecules, respectively.

Reactants	TM	Configuration	W
Clean W-B_2N_2/G	ΔG_{*H}/eV		-1.03
	$\Delta G_{*N_2\text{-end-on}}$/eV		-1.16
	$\Delta G_{*N_2\text{-side-on}}$/eV		-1.35
	$\Delta G_{*N_2\text{-side-on-1}}$/eV		-3.09
	$\Delta G_{*N_2\text{-side-on-2}}$/eV		-0.59
	ΔG_{*H_2O}/eV		-1.17
Clean W-N_3B_2/G	ΔG_{*H}/eV		-0.88
	$\Delta G_{*N_2\text{-end-on}}$/eV		-1.00
	$\Delta G_{*N_2\text{-side-on}}$/eV		-0.67
	ΔG_{*H_2O}/eV		-0.92
$N_{2\text{-end-on}}$-W-N_3B_2/G	ΔG_{*H}/eV		0.24
	$\Delta G_{*N_2\text{-end-on}}$/eV		-0.65
	$\Delta G_{*N_2\text{-side-on}}$/eV		-0.41

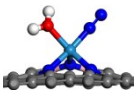
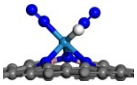
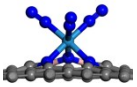
	ΔG_{*H_2O}/eV		-0.35
*$2N_{2\text{-end-on}}$-W-N_3B_2/G	ΔG_{*H}/eV		0.08
	$\Delta G_{*N_{2\text{-end-on}}}$/eV		-0.18
	ΔG_{*H_2O}/eV		0.13

Table S13 Hydrogenation free energies (Δ*G*, eV) along alternating and distal pathways on W-N_3B_2/G with only one end-on N_2 molecules. Where * represent W-N_3B_2/G.

Alternating	*NNH	*NHNH	*$NHNH_2$	*NH_2NH_2	*NH_2	*NH_3
	0.34	-0.78	-0.17	1.04	-1.70	-0.15
Distal	*NNH	*NNH_2	*N	*NH	*NH_2	*NH_3
	0.34	-0.84	-0.04	-0.60	-0.13	-0.15

Table S14 Adsorption free energies of atomic H and N_2 molecules on W-$N_{3\text{-pyridine}}$/G and W-$N_{3\text{-pyrrolic}}$/G during the adsorption saturation.

TM	W-$N_{3\text{-pyridine}}$/G	W-$N_{3\text{-pyrrolic}}$/G
Reactants	*$3N_{2\text{-end-on}}$	*$3N_{2\text{-end-on}}$
ΔG_{*H}/eV	-0.54	-0.47
$\Delta G_{*N_{2}\text{-end-on}}$/eV	-0.74	-0.63
$\Delta G_{*N_{2}\text{-side-on}}$/eV	-0.61	-0.58
$\Delta G_{*N_{2}\text{-end-on}*H}$/eV	-0.19	-0.21
$\Delta G_{*2N_{2}\text{-end-on}}$/eV	-0.46	-0.33
$\Delta G_{*2N_{2}\text{-end-on}*H}$/eV	0.02	0.26
$\Delta G_{*3N_{2}\text{-end-on}}$/eV	-0.09	-0.15
$\Delta G_{*3N_{2}\text{-end-on}*H}$/eV	0.55	0.59
$\Delta G_{*4N_{2}\text{-end-on}}$/eV	0.21	0.44
$\Delta G_{*2N_{2}\text{-end-on}*NNH}$/eV	0.36	0.34

Table S15 The adsorption free energies of N_2 molecule (ΔG_{*N2}, eV), the formation free energies of (ΔG_{*NNH}, eV), the charge states (Q_{*N_2}, e) of adsorbed N_2 molecule, the bond lengths ($L_{W\text{-}N}$, Å) of between W single atom and N atom of adsorbed N_2 molecule, and the bond lengths ($L_{N\text{-}N}$, Å) of adsorbed N_2 molecule on W-N_3B_2/G, W-$N_{3\text{-pyridine}}$/G and W-$N_{3\text{-pyrrolic}}$/G.

Catalyst	ΔG_{*N_2}	ΔG_{*NNH}	Q_{N_2}	$L_{W\text{-}N}$	$L_{N\text{-}N}$
W-N_3B_2/G	-0.18	0.27	0.427	2.034	1.142
W-$N_{3\text{-pyrrolic}}$/G	-0.15	0.34	0.414	2.054	1.140
W-$N_{3\text{-pyridine}}$/G	-0.09	0.36	0.410	2.059	1.139

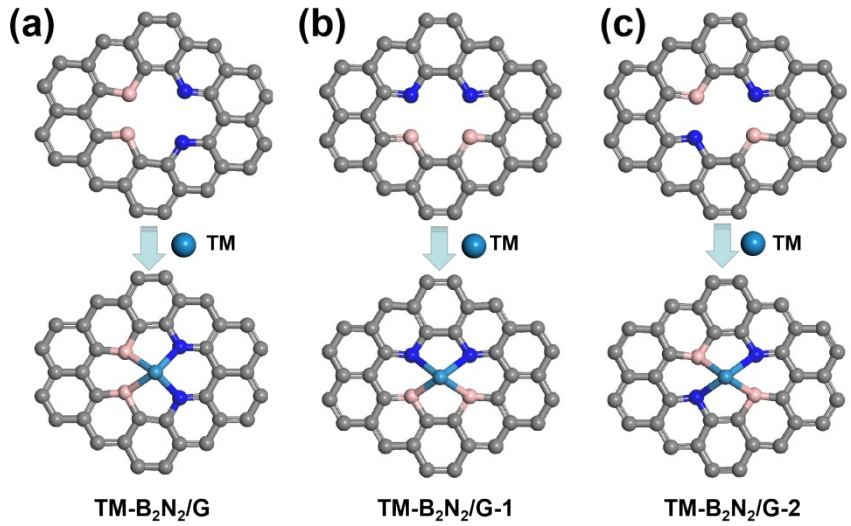


Fig. S1 Three possible arrangements of B and N dopants at B(N)-dual-doped graphene, including B_2N_2/G selected in this work (a), B_2N_2/G-1 (b) and B_2N_2/G-2 (c). Where the gray, blue, dark red, and green balls represent C, N, B and TM atoms, respectively.

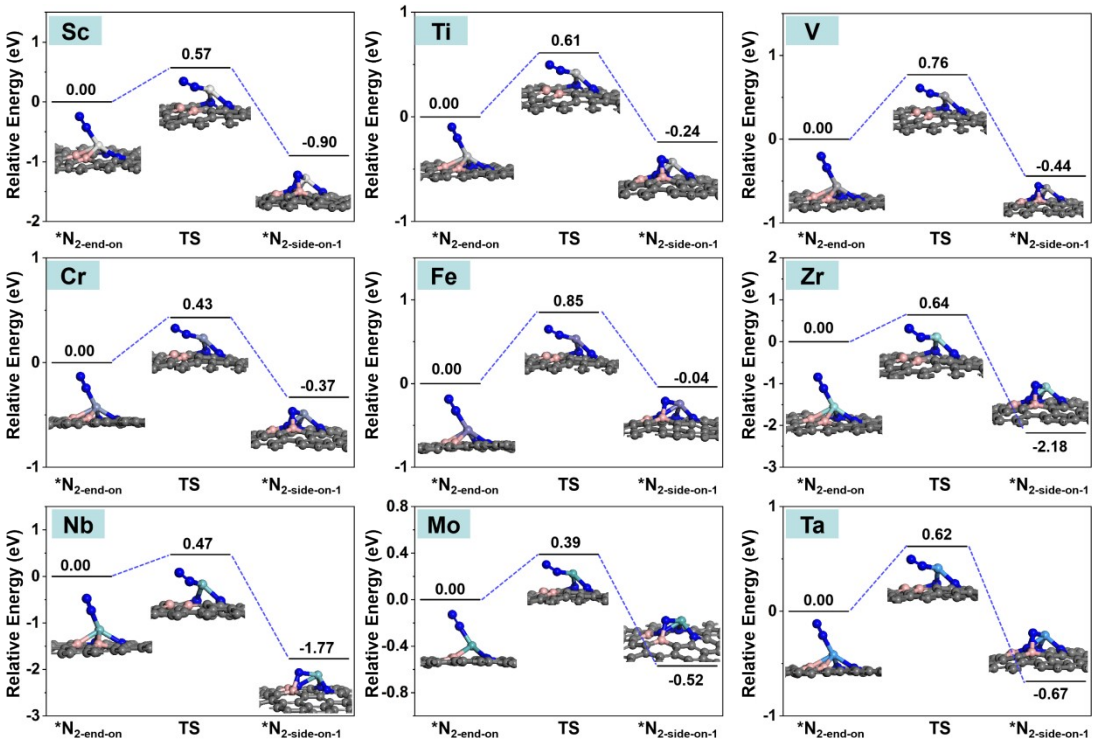


Fig. S2 The computed energy barriers for the pattern evolution of nitrogen adsorption from $*N_{2\text{-end-on}}$ (Fig. 2(a)) into novel $*N_{2\text{-side-on-1}}$ (Fig. 2(c)) on Sc(Ti, V, Cr, Fe, Zr, Nb, Mo, Ta)-B_2N_2/G, accompanying with the optimized configurations of transition state (TS). Where the gray, blue, dark red, white and green balls represent C, N, B, H and TM atoms, respectively.

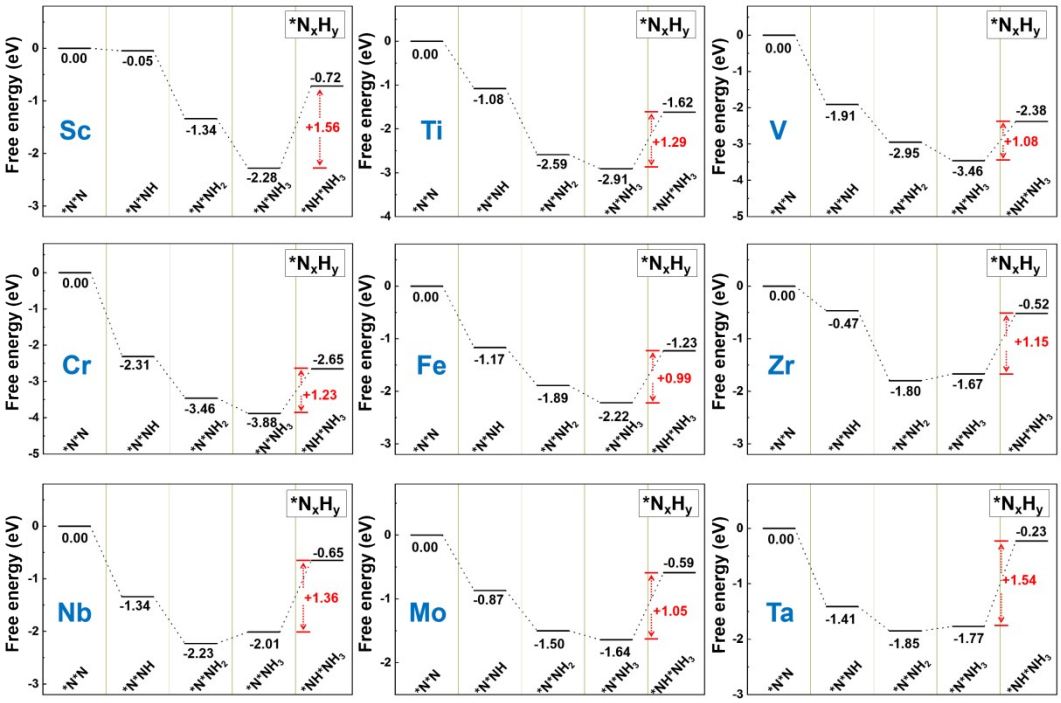


Fig. S3 Hydrogenation free energies of adsorbed side-on-1 N_2 molecule on TM-B_2N_2/G.

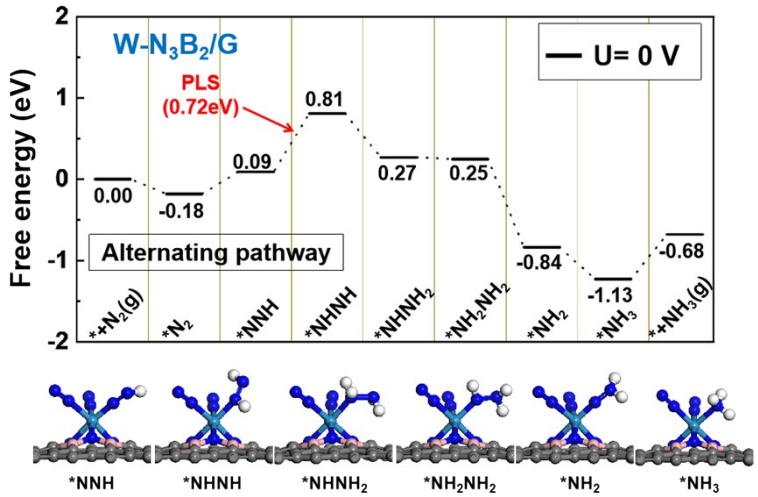


Fig. S4 Free energy diagram of hydrogenation toward ammonia of the third adsorbed end-on N_2 molecule on W-N_3B_2/G along alternating pathway in the presence of other two end-on N_2 molecules, accompanying with the optimized intermediates. Where * represents $2N_2$-W-N_3B_2/G, and the gray, blue, dark red, white and green balls represent C, N, B, H and W atoms, respectively.

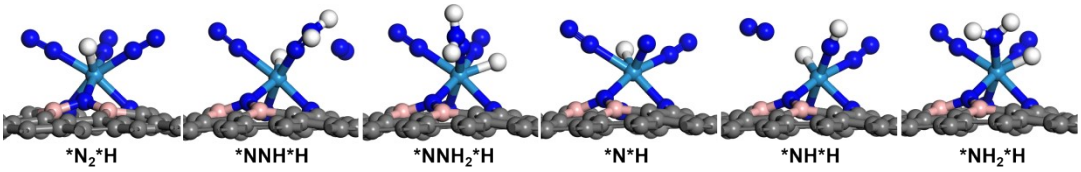


Fig. S5 The configurations of competitive H adsorption on W-N_3B_2/G along distal pathway in the presence of other two adsorbed end-on N_2 molecules and N_xH_y intermediates. Where * represents $2N_2$-W-N_3B_2/G. The gray, blue, dark red, white and green balls represent C, N, B, H and W atoms, respectively.

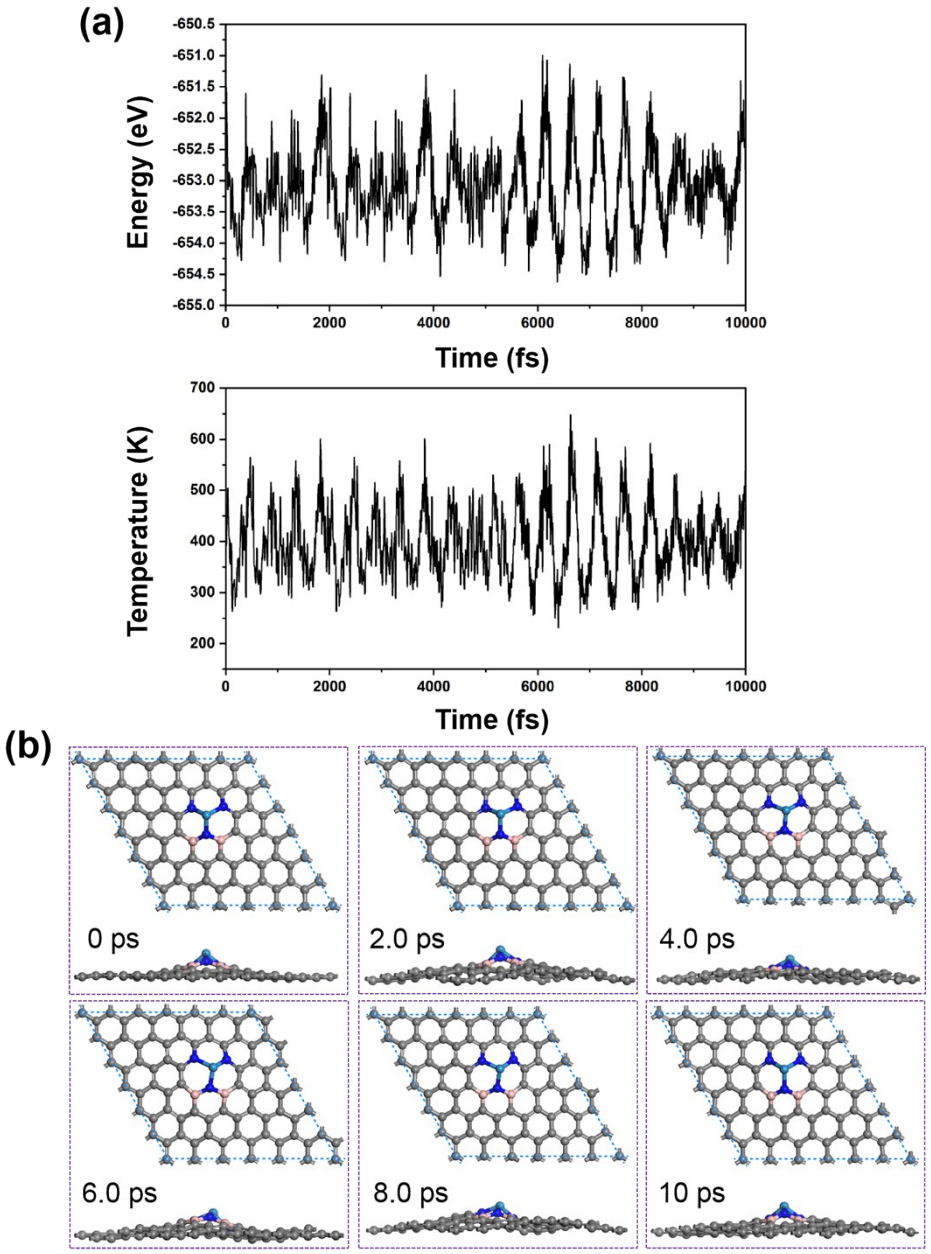


Fig. S6 (a) The molecule dynamic (MD) simulations for variation of total energy and temperature of W-N_3B_2/G at 400 K lasting 10 ps with each step of 1 fs, in which the Nosé-Hoover method is employed with controlling temperature. (b) Atomic configurations of W-N_3B_2/G at 2 ps, 4 ps, 6 ps, 8 ps and 10 ps. Where the gray, blue, dark red and green balls represent C, N, B and W atoms, respectively.

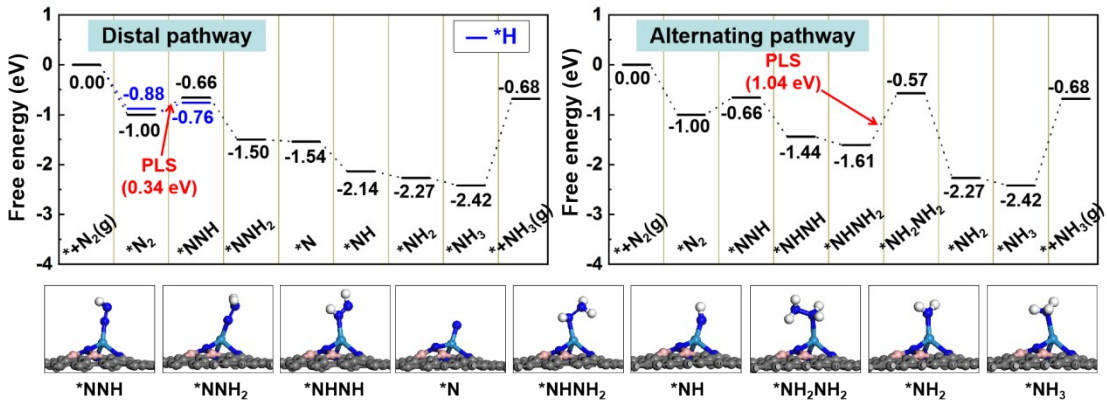


Fig. S7 Hydrogenation free energies of N_2 molecule along alternating and distal pathways on W-N_3B_2/G with only one adsorbed end-on N_2 molecule, accompanying with adsorption free energies of H atom in the presence of no any species and only one end-on $*N_2$. Where * represent W-N_3B_2/G. The gray, blue, dark red, white and green balls represent C, N, B, H and TM atoms, respectively.

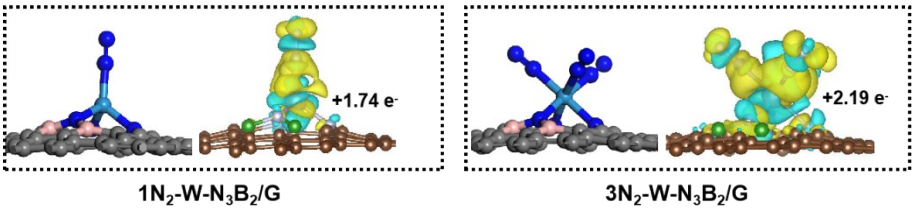


Fig. S8 Differential charge density on W-N_3B_2/G in the presence of one and three adsorbed end-on N_2 molecules, respectively. Where the isosurface levels are set to 0.002 e/Å^3. Yellow and cyan represent the accumulation and depletion of electrons, respectively.

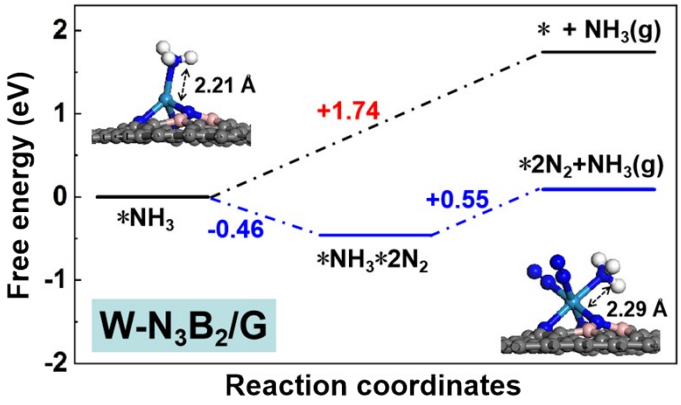


Fig. S9 Ammonia desorption on W-N_3B_2/G in the presence of no any adsorbate and three adsorbed end-on N_2 molecules, respectively. Where * represent the clean W-N_3B_2/G.

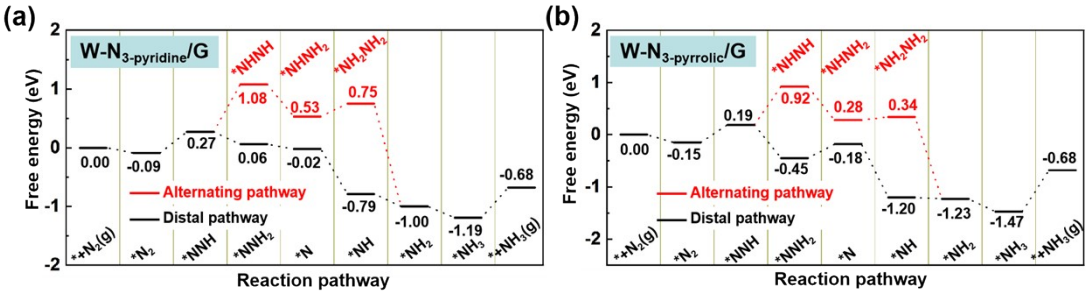


Fig. S10 Hydrogenation free energies of the 3rd N_2 molecule along alternating and distal pathways on (a) W-$N_{3\text{-pyridine}}$/G and (b) W-$N_{3\text{-pyrrolic}}$/G in the presence of other two adsorbed end-on *N_2.

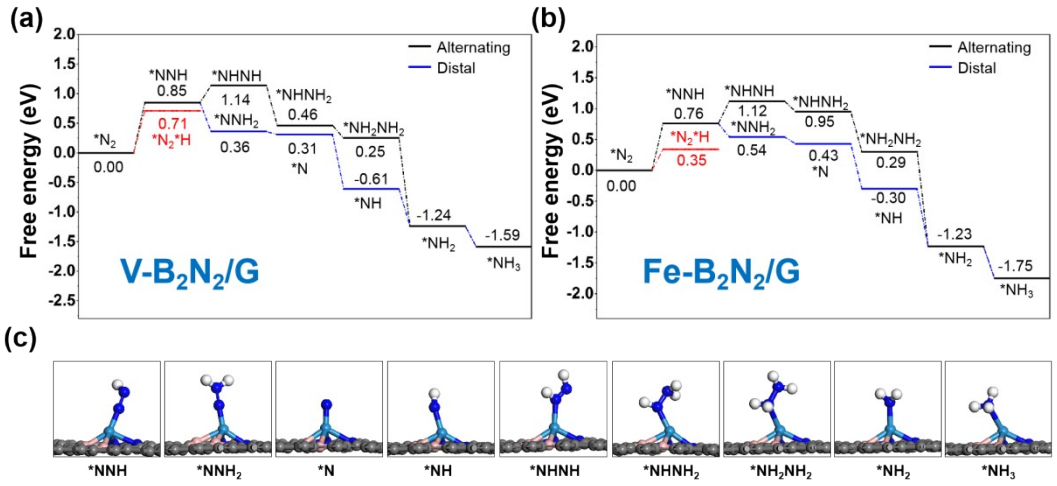


Fig. S11 Hydrogenation free energy changes of adsorbed end-on $*N_2$ along alternating and distal pathways on (a) V-B_2N_2/G and (b) Fe-B_2N_2/G, accompanying with competitive H adsorption in the presence of one end-on $*N_2$. (c) Atomic configurations of $*N_xH_y$ intermediates. Where * represents V(Fe)-B_2N_2/G, and the gray, blue, dark red, white, and green balls represent C, N, B, H and V(Fe) atoms, respectively.