Supporting Information

Single-atom transition metal supported on black phosphorene for electrochemical nitrogen reduction

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1. Computational details

The adsorption energies (E_{ads}) of the single-atom metals or the intermediate species were calculated by the following equation: $E_{ads} = E_{(sub+ads)} - E_{sub} - E_{ads}$, where $E_{(sub+ads)}$ is the total energy of an adsorbate on the substrate, E_{sub} is the energy of the substrate, and E_{ads} is the energy of the adsorbate species.

The Gibbs free energy of each elementary step was calculated as $\Delta G = \Delta E + \Delta ZPE - T*\Delta S + ne*U$, where ΔE is the reaction energy calculated by the DFT. ΔZPE and ΔS are the changes in zero-point energies and entropy during the reaction, respectively. T is a constant (298.15 K). ne and U are the number of electrons transferred and the applied electrode bias potential, respectively.

2. Results and discussion

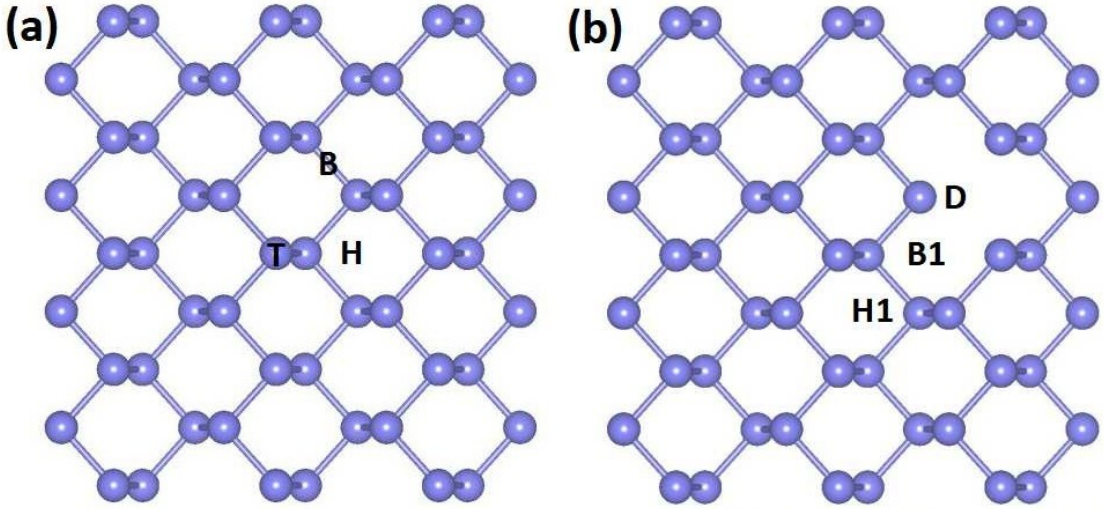

Fig. S1 (a) Top view of black phosphorene and three adsorption sites: hollow (H), bridge (B), and on-top (T). (b) Top view of defect black phosphorene and three adsorption sites: hollow 1 (H1), bridge 1 (B1), and defect (D).

Table S1 Adsorption energy of metal atoms for Top (T), Bridge (B), Hollow (H) sites for M@BP and Defect (D), Hollow 1 (H1), Bridge 1 (B1) sites for M-BP.

	H	B	T	D	H 1	B 1
Cu	-2.35 (eV)	-2.22	-1.26	-4.62	-3.64	-3.21
W	-4.66	-4.42	-0.96	-7.96	-5.32	-7.05

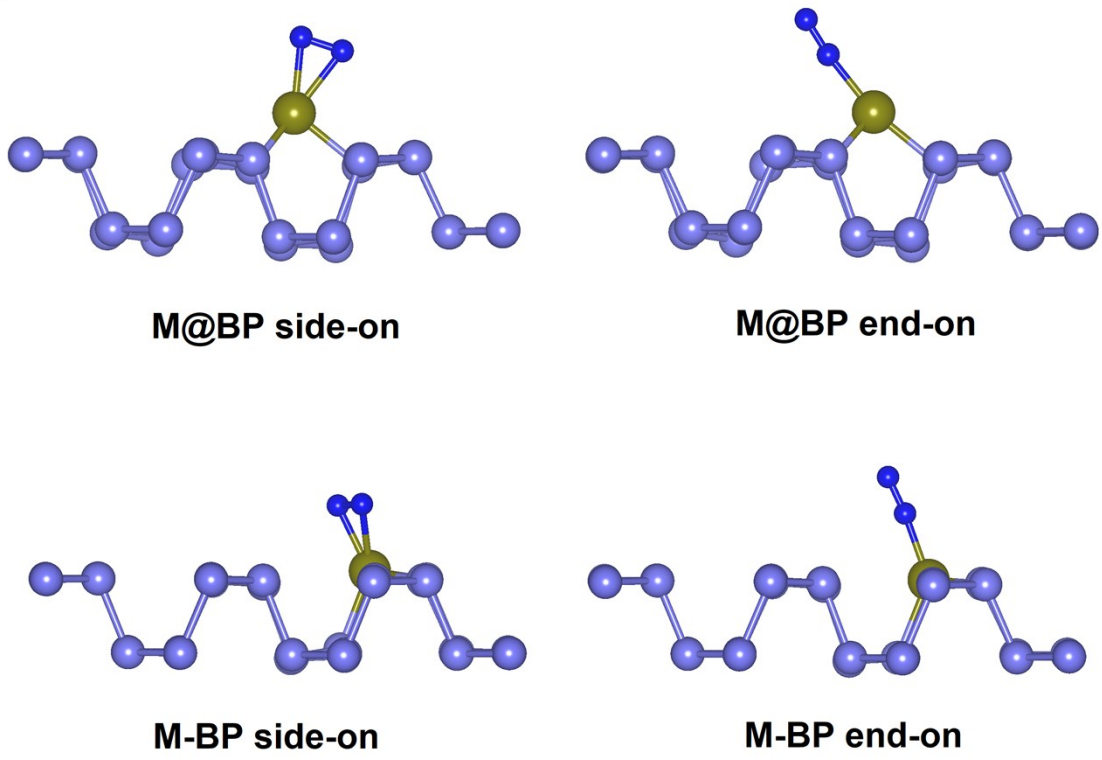

Fig. S2 The side view of N_2 adsorbed on the M@BP and M-BP through the side-on and end-on configurations.

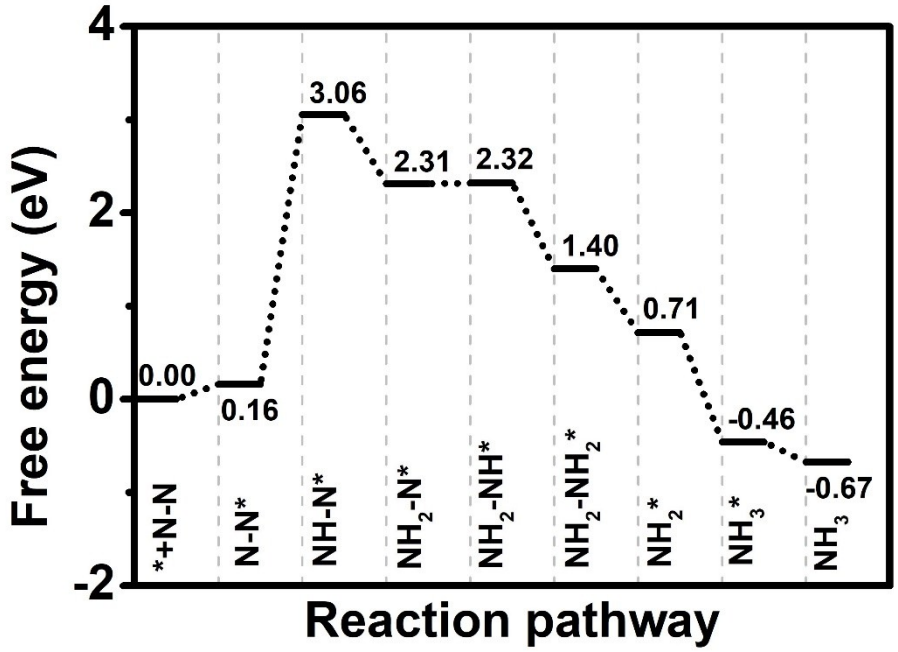

Fig. S3 Free energy diagrams for NRR on pristine BP.

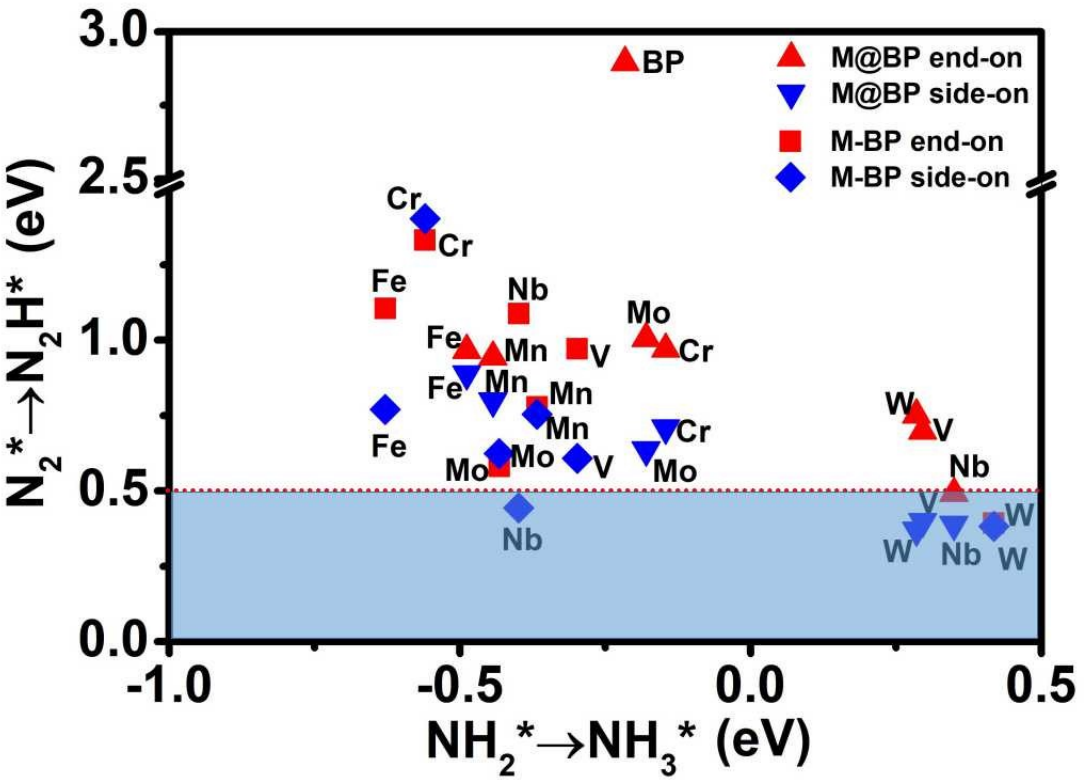

Fig. S4 The free energy barrier of potential determining steps for NRR on M@BP and M-BP without D2 correction.

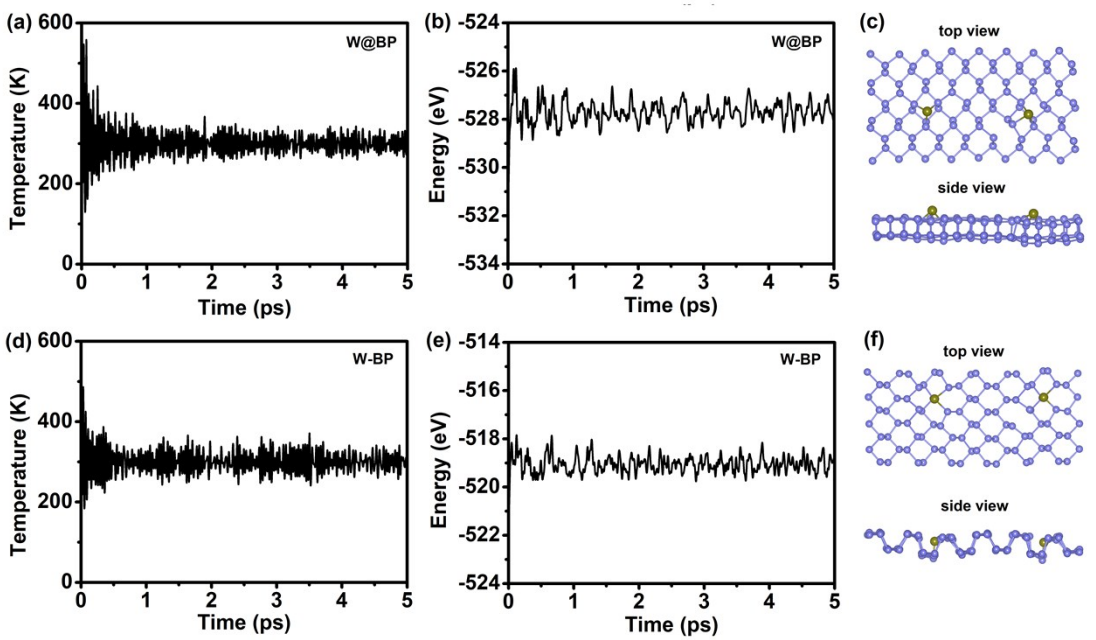

Fig. S5 The relationship between temperature and time for AIMD simulations of W@BP (a) and W-BP (d). The relationship between energy and time for AIMD simulations of W@BP (b) and W-BP (e). After run 5 ps with a time step of 1 fs, the top and side views of the structure of W@BP (c) and W-BP (f) under 300 K.

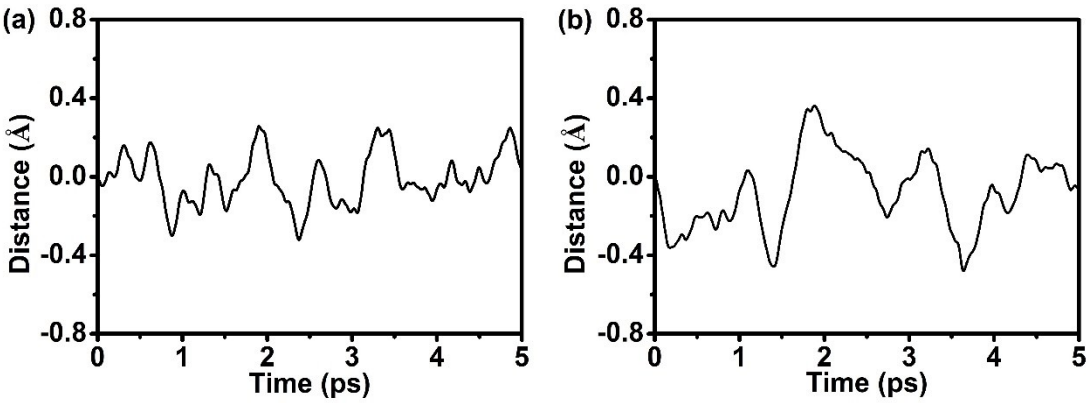

Fig. S6 The change of vertical height of metal atom on W@BP (a) and W-BP (b).

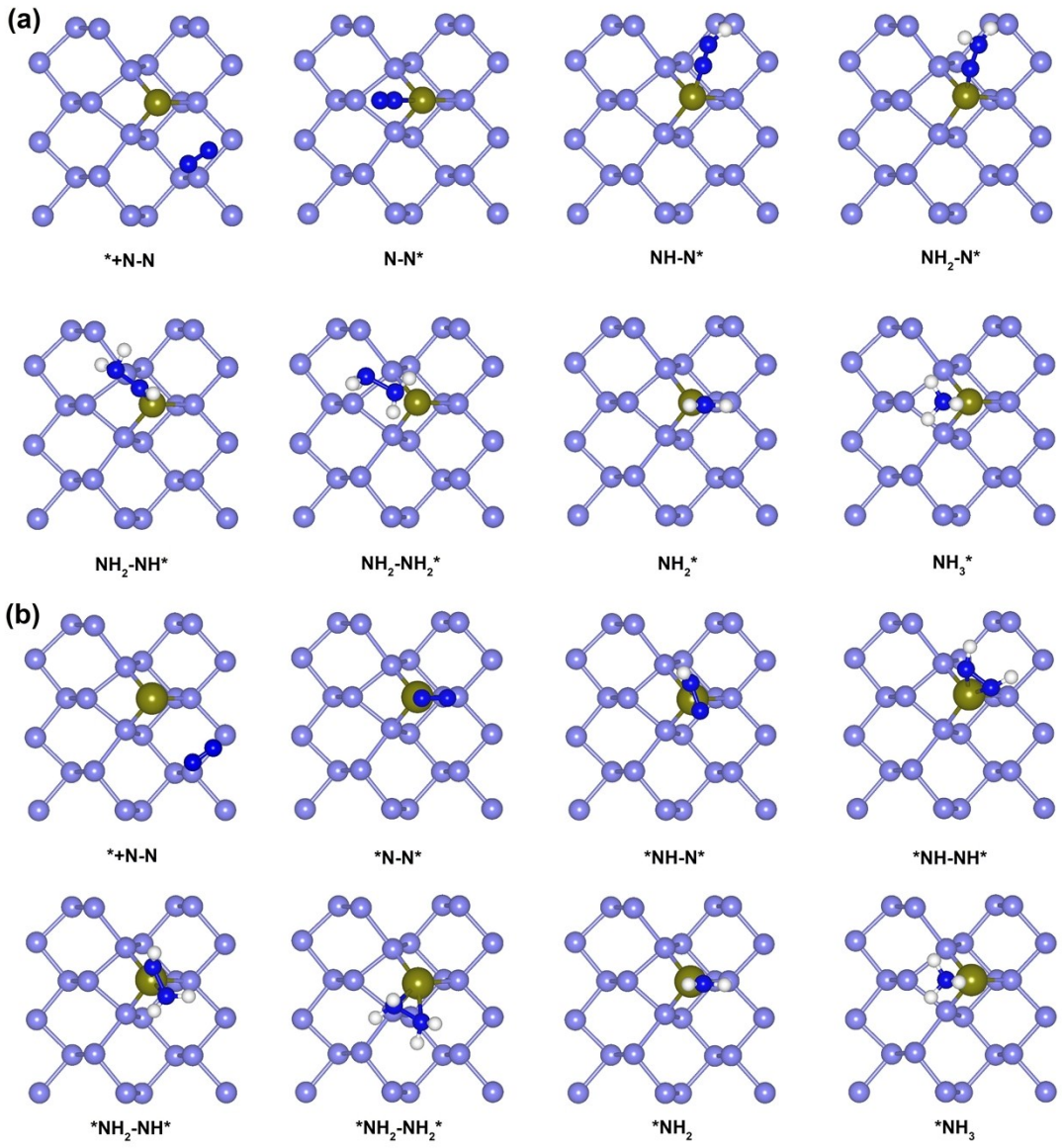

Fig. S7 The structures of intermediate species along the hybrid (a) and enzymatic (b) pathways of NRR on the W@BP (Baby blue–P; green–W; dark blue–N; white–H).

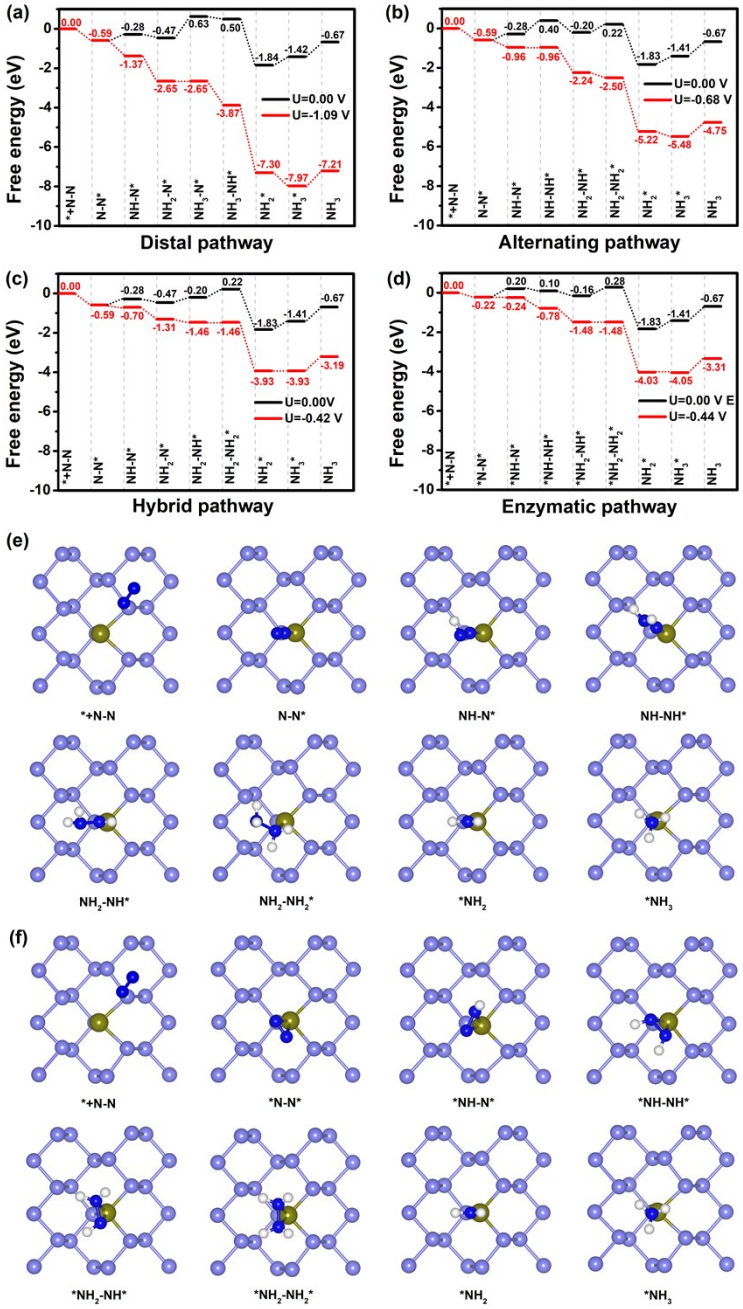

Fig. S8 Free energy diagrams for NRR on W-BP along (a) distal, (b) alternating, (c) hybrid and (d) enzymatic pathways at corresponding applied potentials. The structures of intermediate species along the hybrid (e) and enzymatic (f) pathways of NRR on the W-BP.

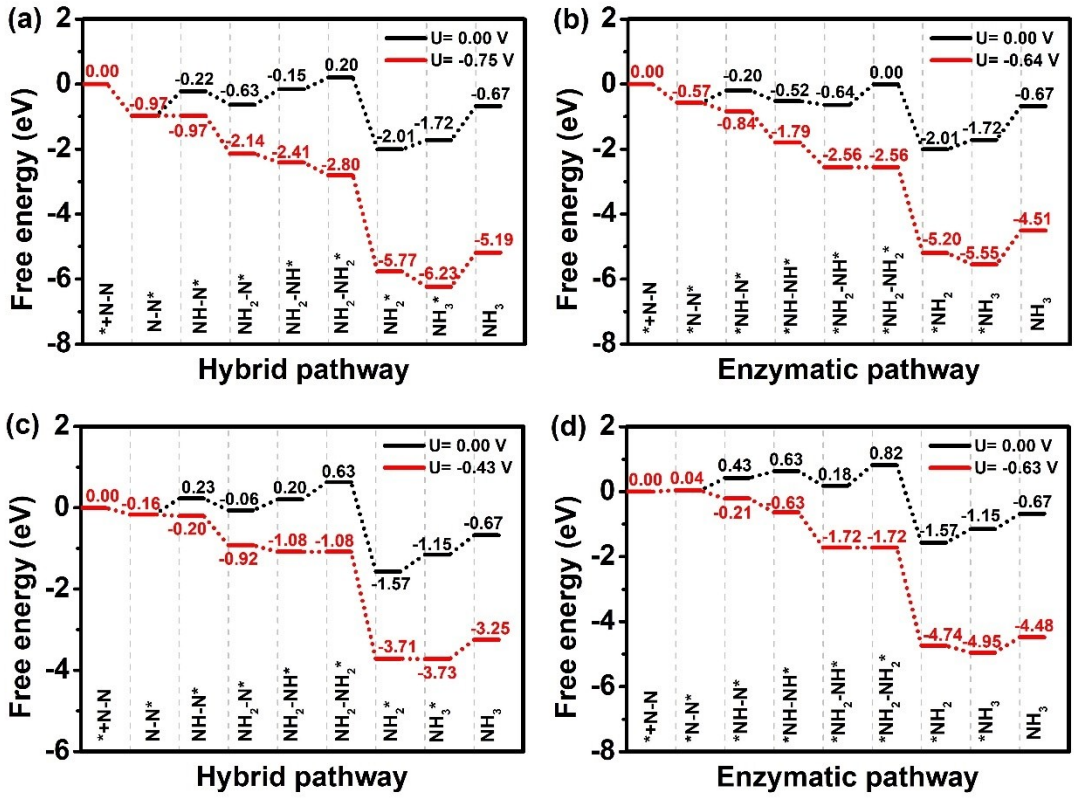

Fig. S9 Free energy diagrams for NRR on W@BP along hybrid (a) and enzymatic (b) pathways at applied potential of –0.75 and –0.64 V. W-BP along hybrid (c) and enzymatic (d) pathways at applied potential of –0.43 and –0.63 V.

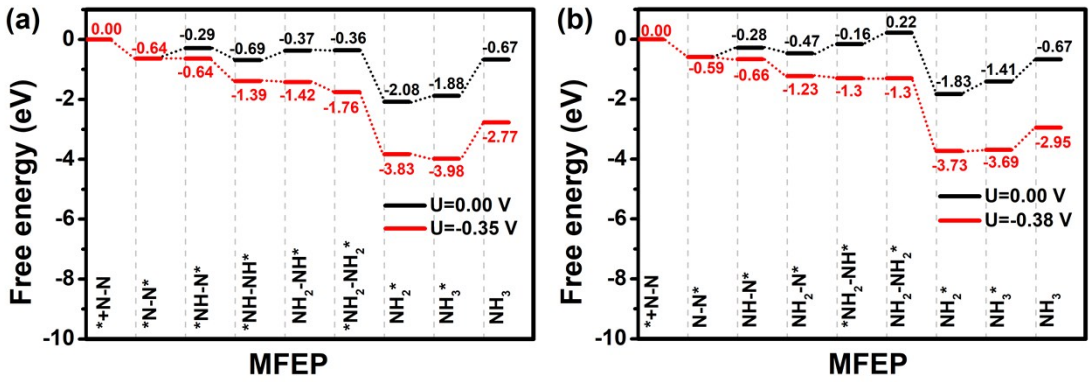

Fig. S10 The minimum free energy pathway (MFEP) on W@BP (a) and W-BP (b).

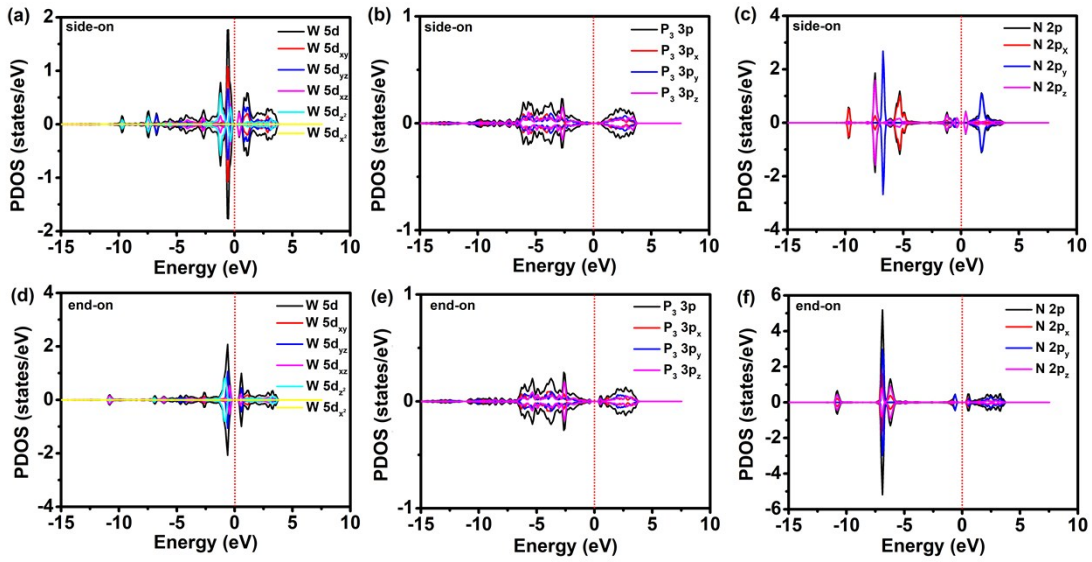

Fig. S11 The project density of states (PDOS) of W (a and d), P_3 (b and e), N (c and f) after N_2 adsorption on the W@BP with side-on and end-on configurations.

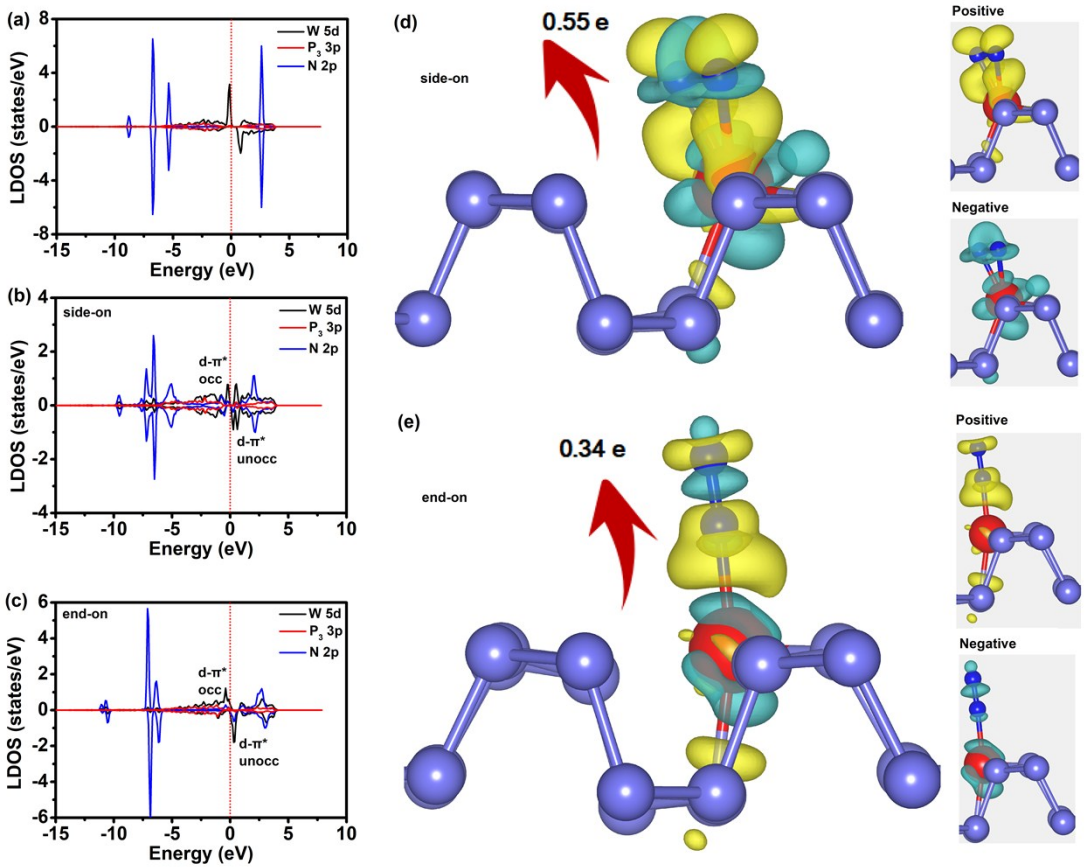

Fig. S12 LDOS of W 5d, P_3 3p and N 2p before N_2 adsorption (a), and after N_2 adsorption with side-on (b) and end-on (c) configurations on the W-BP. Charge density difference between the W-BP and N_2 with side-on (d) and end-on (e) configurations. Isosurface levels in (d) and (e) are 0.003 e • $bohr^{-3}$. The yellow and cyan represent positive and negative charges regions in (d) and (e).

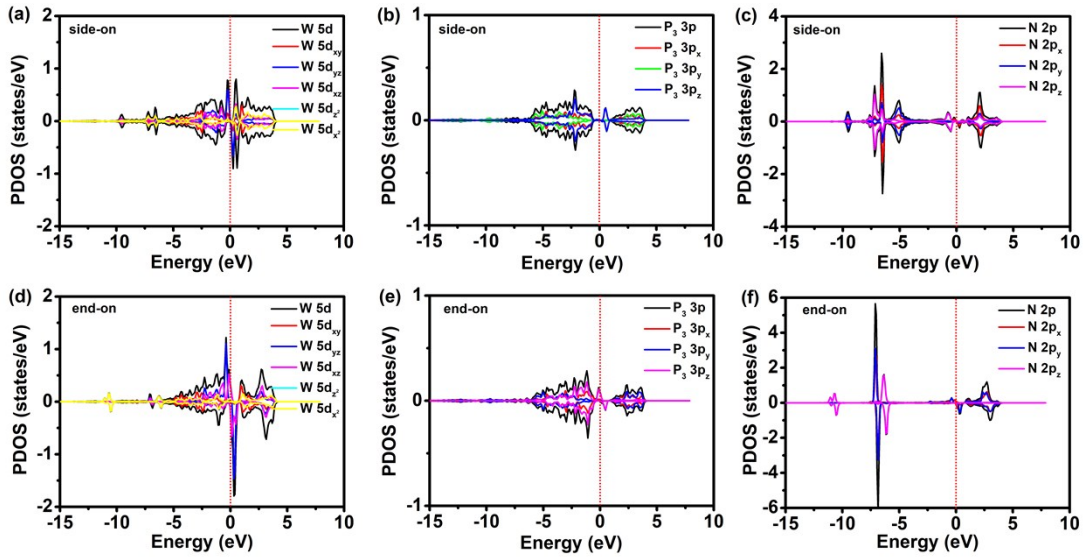

Fig. S13 The project density of states (PDOS) of W (a and d), P_3 (b and e), N (c and f) after N_2 adsorption on the W-BP with side-on and end-on configurations.

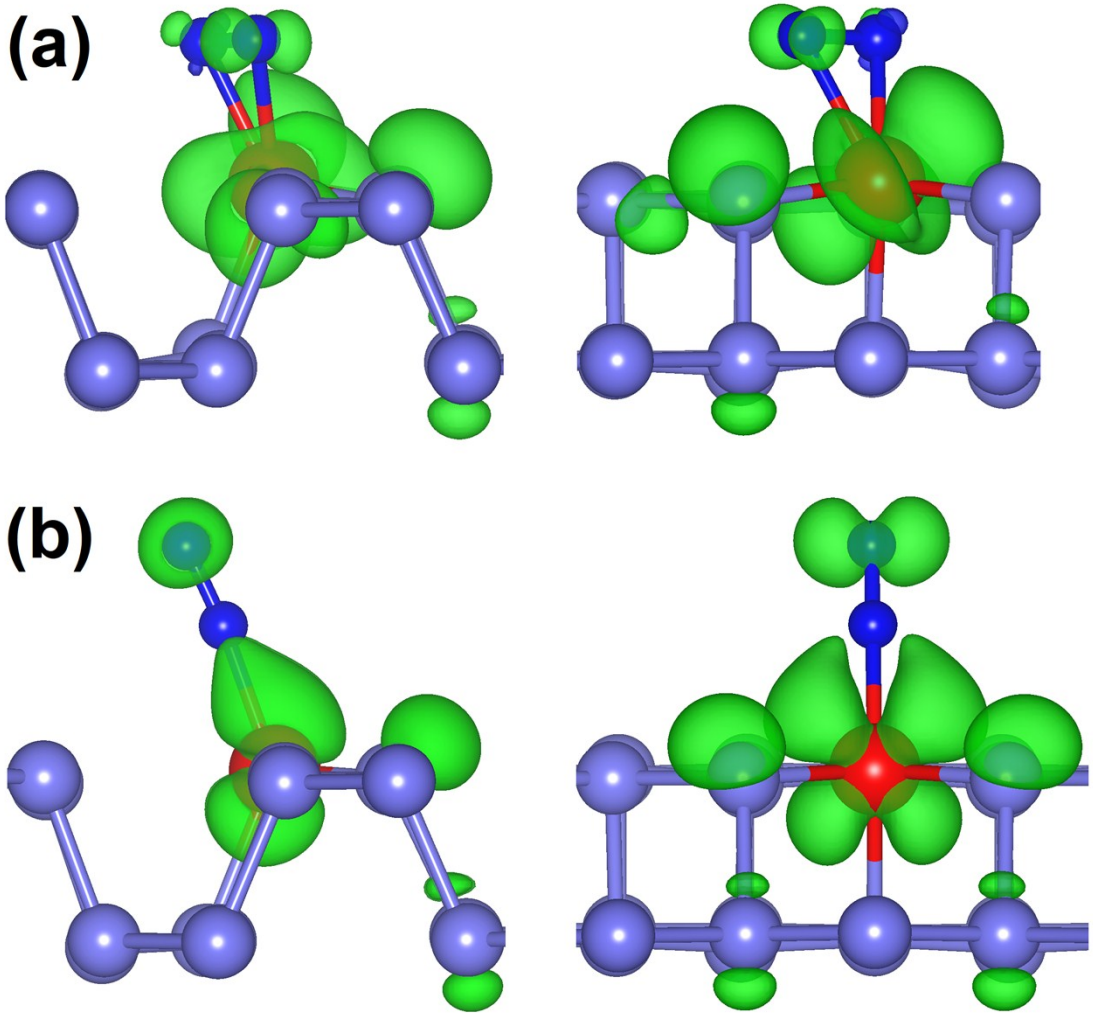

Fig. S14 The spin polarization density of N_2 adsorbed on the W-BP with side-on (a) and end-on (b) configurations.

Table S2 The calculated free energy barriers of elementary reaction steps along the distal pathway.

Distal	Fe@BP	Fe-BP	Mn@BP	Mn-BP	Cr@BP	Cr-BP	V@BP	V-BP	Mo@BP	Mo-BP	W@BP	W-BP	Nb@BP	Nb-BP
N_2	0 (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2*	-0.78	-0.34	-0.77	-0.16	-0.63	0.03	-0.72	-0.24	-0.89	-0.09	-1.10	-0.59	-0.83	0.04
NNH*	0.96	1.02	0.94	0.84	0.95	**1.24**	0.72	**0.90**	0.96	0.40	0.71	0.30	0.44	**1.03**
NNH_2*	0.11	-0.02	-0.05	-0.21	-0.16	-0.51	-0.24	-0.47	-0.26	-0.10	-0.41	-0.18	-0.14	-0.76
NNH_3*	**1.28**	**1.04**	**1.53**	**1.12**	**1.10**	0.70	**0.87**	0.82	**1.06**	**0.92**	**1.06**	**1.09**	**0.99**	0.72
$NHNH_3$*	-0.64	-0.87	-0.74	-0.49	-0.19	-0.42	0.00	-0.26	-0.34	-0.19	-0.14	-0.13	0.00	0.11
NH_2*	-2.04	-1.73	-2.13	-2.21	-2.45	-1.91	-2.53	-2.04	-1.95	-2.08	-2.19	-2.33	-2.23	-2.11
NH_3*	0.52	-0.71	-0.48	-0.43	0.31	-0.59	0.26	-0.34	-0.26	-0.14	0.20	0.42	0.31	-0.43
NH_3	0.95	0.92	1.02	0.83	0.39	0.76	0.95	0.94	1.02	0.59	1.20	0.72	0.80	0.70

Table S3 The calculated free energy barriers of elementary reaction steps along the alternating pathway.

Alternating	Fe@BP	Fe-BP	Mn@BP	Mn-BP	Cr@BP	Cr-BP	V@BP	V-BP	Mo@BP	Mo-BP	W@BP	W-BP	Nb@BP	Nb-BP
N_2	0 (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2*	-0.78	-0.34	-0.77	-0.16	-0.63	0.03	-0.71	-0.24	-0.89	-0.09	-1.10	-0.59	-0.83	0.04
NNH*	**0.96**	**1.02**	**0.94**	**0.84**	**0.95**	**1.24**	**0.72**	**0.90**	**0.96**	0.40	0.71	0.30	0.44	**1.03**
NHNH*	0.48	0.20	0.37	0.17	0.62	0.11	0.45	0.55	0.40	**0.51**	**0.96**	**0.68**	**0.81**	0.05
$NHNH_2$*	-0.40	-0.34	-0.26	-0.22	-0.75	-0.69	-0.67	-0.95	-0.33	-0.46	-0.94	-0.59	-0.51	-0.49
NH_2NH_2*	-0.10	-0.31	-0.06	-0.33	0.09	-0.30	0.44	0.01	-0.24	0.14	0.40	0.42	0.28	-0.20
NH_2*	-1.28	-1.14	-1.43	-1.40	-1.66	-1.26	-2.12	-1.57	-1.33	-1.65	-2.10	-2.05	-1.97	-1.39
NH_3*	-0.52	-0.71	-0.48	-0.43	0.31	-0.59	0.26	-0.34	-0.26	-0.14	0.20	0.42	0.31	-0.43
NH_3	0.95	0.92	1.02	0.83	0.39	0.76	0.95	0.94	1.02	0.59	1.20	0.72	0.80	0.70

Table S4 The calculated free energy barriers of elementary reaction steps along the hybrid pathway.

Hybrid	Fe@BP	Fe-BP	Mn@BP	Mn-BP	Cr@BP	Cr-BP	V@BP	V-BP	Mo@BP	Mo-BP	W@BP	W-BP	Nb@BP	Nb-BP
N_2	0 (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2*	-0.78	-0.34	-0.77	-0.16	-0.63	0.03	-0.72	-0.24	-0.89	-0.09	-1.10	-0.59	-0.83	0.04
NNH*	**0.96**	**1.02**	**0.94**	**0.84**	**0.95**	**1.24**	**0.72**	**0.90**	**0.96**	**0.40**	**0.71**	0.30	**0.44**	**1.03**
NNH_2*	0.11	-0.02	-0.05	-0.21	-0.16	-0.51	-0.24	-0.47	-0.26	-0.10	-0.41	-0.18	-0.14	-0.76
$NHNH_2$*	-0.02	-0.11	0.15	0.15	0.03	-0.07	0.02	0.07	0.33	0.15	0.42	0.26	0.44	0.31
NH_2NH_2*	-0.09	-0.31	-0.06	-0.33	0.09	-0.30	0.44	0.01	-0.24	0.14	0.40	**0.42**	0.28	-0.20
NH_2*	-1.28	-1.14	-1.43	-1.40	-1.66	-1.26	-2.12	-1.57	-1.33	-1.65	-2.10	-2.05	-1.97	-1.39
NH_3*	-0.52	-0.71	-0.48	-0.43	0.31	-0.59	0.26	-0.34	-0.26	-0.14	0.20	0.42	0.31	-0.43
NH_3	0.95	0.92	1.02	0.83	0.39	0.76	0.95	0.94	1.02	0.59	1.20	0.72	0.80	0.70

Table S5 The calculated free energy barriers of elementary reaction steps along the enzymatic pathway.

Enzymatic	Fe@BP	Fe-BP	Mn@BP	Mn-BP	Cr@BP	Cr-BP	V@BP	V-BP	Mo@BP	Mo-BP	W@BP	W-BP	Nb@BP	Nb-BP
N_2	0 (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2*	-0.37	0.26	-0.40	0.17	-0.31	0.00	-0.43	0.23	-0.48	0.11	-0.64	-0.22	-0.54	**0.43**
NNH*	**0.84**	**0.75**	**0.79**	**0.65**	**0.70**	**1.31**	0.38	**0.56**	**0.72**	**0.62**	0.35	0.42	0.17	0.39
NHNH*	0.05	-0.10	0.14	0.31	0.04	-0.09	-0.26	0.05	-0.38	-0.02	-0.40	-0.11	-0.01	-0.04
$NHNH_2$*	-0.46	-0.59	-0.61	-0.99	-0.43	-0.66	-0.44	-0.75	-0.14	-0.44	-0.13	-0.25	-0.25	-0.52
NH_2NH_2*	0.52	-0.13	0.43	0.02	0.51	-0.31	**0.78**	0.18	0.15	0.28	**0.46**	**0.44**	**0.63**	0.26
NH_2*	-1.69	-1.10	-1.56	-1.25	-1.88	-1.11	-1.92	-1.56	-1.31	-1.70	-1.72	-2.12	-1.78	-1.50
NH_3*	-0.52	-0.71	-0.48	-0.43	0.31	-0.59	0.26	-0.34	-0.26	-0.14	0.20	0.42	0.31	-0.43
NH_3	0.95	0.92	1.02	0.83	0.39	0.76	0.95	0.94	1.02	0.59	1.20	0.72	0.80	0.70

Table S6 The calculated free energy barriers of elementary reaction steps along the hybrid pathway (without D2 correction).

hybrid	Fe@BP	Fe-BP	Mn@BP	Mn-BP	Cr@BP	Cr-BP	V@BP	V-BP	Mo@BP	Mo-BP	W@BP	W-BP	Nb@BP	Nb-BP
N_2	0 (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2*	-0.69	-0.20	-0.68	0.17	-0.56	0.20	-0.60	0.03	-0.73	-0.06	-0.97	-0.16	-0.70	0.21
NNH*	**0.97**	**1.11**	**0.94**	**0.78**	**0.97**	**1.33**	**0.70**	**0.97**	**1.01**	**0.58**	**0.75**	0.39	**0.49**	**1.09**
NHNH*	0.11	-0.03	0.04	-0.10	-0.10	-0.46	-0.23	-0.44	-0.25	-0.10	-0.42	-0.29	-0.07	-0.73
$NHNH_2$*	0.07	-0.003	0.14	0.17	0.04	-0.03	0.04	0.01	0.36	0.21	0.48	0.26	0.41	0.41
NH_2NH_2*	-0.05	-0.22	0.01	-0.24	0.16	-0.25	0.50	0.07	0.00	0.12	0.36	**0.43**	0.21	-0.17
NH_2*	-1.43	-1.38	-1.59	-1.57	-1.81	-1.41	-2.25	-1.71	-1.73	-1.48	-2.21	-2.20	-2.07	-1.53
NH_3*	-0.49	-0.63	-0.44	-0.37	-0.15	-0.56	0.30	-0.30	-0.18	-0.43	0.29	0.42	0.35	-0.40
NH_3	0.83	0.68	0.92	0.49	0.77	0.51	0.87	0.61	0.84	0.39	1.05	0.48	0.71	0.46

Table S7 The calculated free energy barriers of elementary reaction steps along the enzymatic pathway (without D2 correction).

Enzymatic	Fe@BP	Fe-BP	Mn@BP	Mn-BP	Cr@BP	Cr-BP	V@BP	V-BP	Mo@BP	Mo-BP	W@BP	W-BP	Nb@BP	Nb-BP
N_2	0 (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2*	-0.32	0.44	-0.30	0.40	-0.23	0.17	-0.38	0.50	-0.27	0.33	-0.57	0.04	-0.	**0.67**
NNH*	**0.89**	**0.77**	**0.80**	**0.75**	**0.71**	**1.40**	0.40	**0.61**	**0.64**	**0.62**	0.37	0.38	0.17	0.44
NHNH*	0.09	-0.04	0.19	0.07	0.09	-0.03	-0.20	0.10	-0.26	0.12	-0.32	0.21	-0.01	0.01
$NHNH_2$*	-0.41	-0.60	-0.59	-0.63	-0.41	-0.63	-0.45	-0.66	-0.15	-0.40	-0.12	-0.45	-0.25	-0.41
NH_2NH_2*	0.59	-0.06	0.51	0.03	0.58	-0.27	**0.86**	0.25	0.27	0.37	**0.64**	**0.63**	**0.63**	0.23
NH_2*	-1.85	-1.24	-1.76	-1.43	-2.04	-1.27	-2.06	-1.77	-1.57	-1.67	-2.00	-2.39	-1.78	-1.67
NH_3*	-0.49	-0.63	-0.44	-0.37	-0.15	-0.56	0.30	-0.30	-0.18	-0.43	0.29	0.42	0.31	-0.40
NH_3	0.83	0.68	0.92	0.49	0.77	0.51	0.87	0.61	0.84	0.38	1.04	0.48	0.80	0.46