Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

In Silico Design of Single Transition Metal Atom Anchored Defective Boron Carbide Monolayer as High−performance Electrocatalysts for the Nitrogen Reduction Reaction

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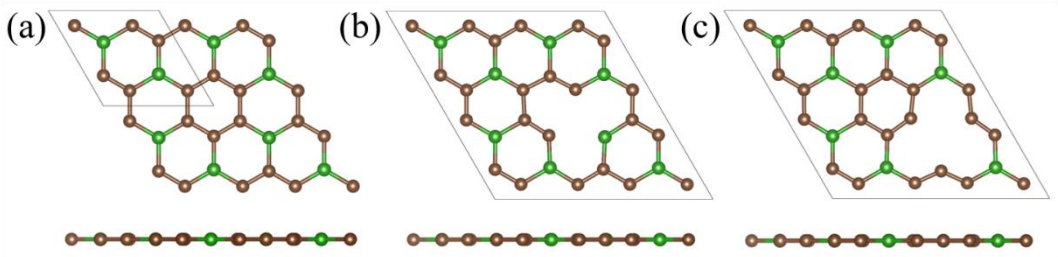

Fig. S1 Optimized structures of the (a) pristine, (b) C-atom-deficient and (c) B-atom-deficient BC_3 monolayers.

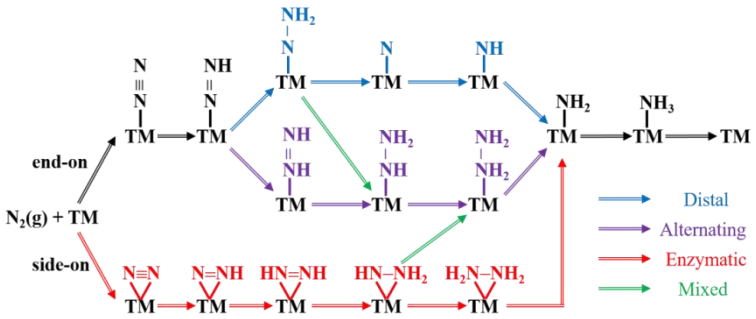

Fig. S2 Possible reaction mechanism of NRR occurring on TM doped on BC_3.

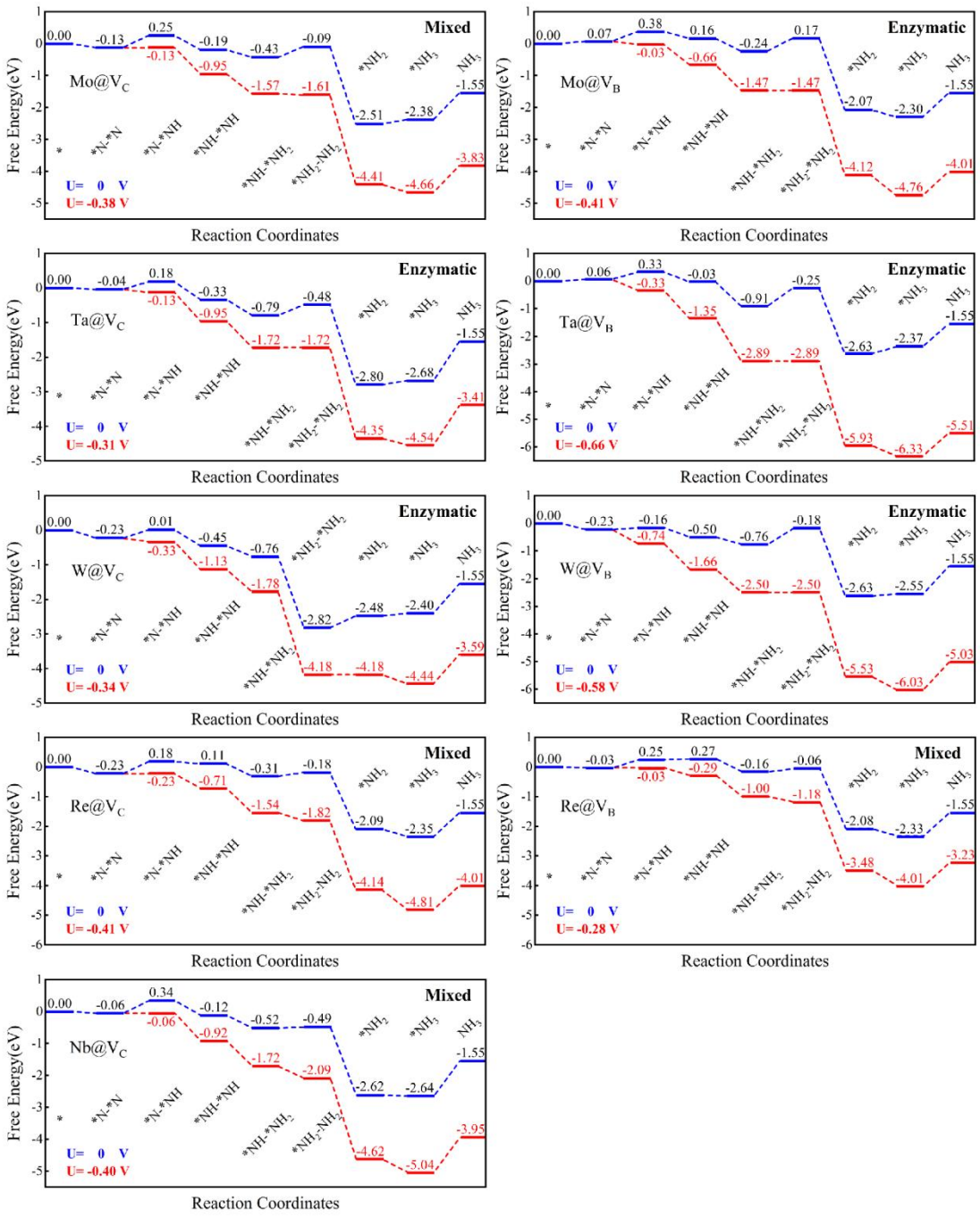

Fig. S3 Free-energy diagram along enzymatic or mixed path at zero and limiting potential for NRR on 9 candidate SACs.

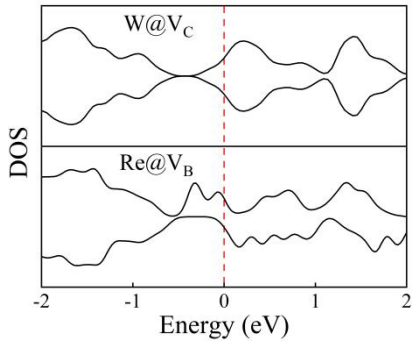

Fig. S4 DOS of W@V_C and Re@V_B.

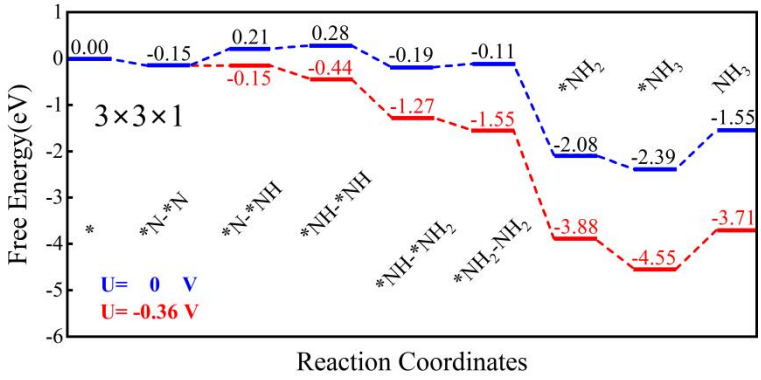

Fig. S5 Free-energy diagram along mixed path at zero and limiting potential for NRR on Re@V_B of 3×3.

Table S1. Gibbs free energy changes for the first and last protonation steps on 13 candidates capable of adsorbing N_2 in side-on mode

	ΔG_{*N-*NH} (eV)	ΔG_{*NH_3} (eV)
Y@V_C	0.73	-0.18
Nb@V_C	0.40	-0.02
Mo@V_C	0.38	0.13
Mo@V_B	0.31	-0.23
Ru@V_C	1.39	-1.96
Hf@V_C	0.62	0.14
Ta@V_C	0.22	0.12
Ta@V_B	0.27	0.26
W@V_C	0.24	0.08
W@V_B	0.07	0.08
Re@V_C	0.41	-0.26
Re@V_B	0.28	-0.25
Os@V_C	1.29	-0.84

Table S2. Gibbs free energy changes for the first protonation step on TM@V_C and TM@V_B capable of adsorbing N_2 in end-on mode

TM@V_C	ΔG (eV)	TM@V_B	ΔG (eV)
Y@V_C	1.15	Y@V_B	1.16
Hf@V_C	1.19	Hf@V_B	1.18
Zr@V_C	0.92	Zr@V_B	1.30
Ta@V_C	0.53	Ta@V_B	0.74
Nb@V_C	0.69	Nb@V_B	0.89
W@V_C	0.58	W@V_B	0.70
Mo@V_C	0.62	Mo@V_B	0.84
Re@V_C	0.85	Re@V_B	0.71
Ru@V_C	1.52	Ru@V_B	0.84
Os@V_C	1.35	Os@V_B	1.46
Rh@V_C	1.33	Rh@V_B	1.79
Ir@V_C	1.06	Ir@V_B	1.55
Pd@V_C	1.68	Pd@V_B	1.75
Pt@V_C	1.56	Pt@V_B	-
Ag@V_C	1.60	Ag@V_B	1.66
Au@V_C	-	Au@V_B	-

Table S3. The calculated energy (E), zero point energies (ZPE) and entropy of H_2, N_2 amd NH_3 in eV

	E	ZEP	TS
H_2	-6.77	0.27	0.13
N_2	-16.63	0.15	0.59
NH_3	-19.55	0.89	0.60