Supplementary Materials

for

Computational Insight into Defective Boron Nitride Supported Double-Atom Catalysts for Electrochemical Nitrogen Reduction

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Table S1. Computed cohesive energy (E_{coh}) and adsorption energy (E_a) of TM dimer (TM= Ti, Fe, Mo and Ru) anchored on the B-vacancy.

	$E_{coh/TM1}$	$E_{coh/TM2}$	E_{ads}	E_{coh}	E_{ads}-E_{coh}	E_f
Fe-Fe	-4.86	-4.86	-10.88	-4.86	-0.58	-1.18
Fe-Mo	-4.86	-6.29	-11.45	-5.58	-0.15	-1.15
Fe-Ru	-4.86	-6.76	-12.02	-5.81	-0.20	-1.15
Fe-Ti	-4.86	-5.45	-12.71	-5.16	-1.20	-1.20
Mo-Mo	-6.29	-6.29	-12.62	-6.29	-0.02	-1.10
Mo-Ru	-6.29	-6.76	-13.25	-6.53	-0.10	-1.12
Mo-Ti	-6.29	-5.45	-12.30	-5.87	-0.28	-1.16
Ru-Ru	-6.76	-6.76	-13.76	-6.76	-0.12	-1.12
Ru-Ti	-6.76	-5.45	-13.67	-6.11	-0.73	-1.18
Ti-Ti	-5.45	-5.45	-14.12	-5.45	-1.61	-1.22

Table S2. Calculated the amount of the transferred electrons from the anchored TM atoms to the V_B-BN (Q in e) of TM_1-TM_2@V_B-BN.

	Q
Fe-Fe	1.61
Fe-Mo	1.54
Fe-Ru	1.53
Fe-Ti	1.75
Mo-Mo	1.59
Mo-Ru	1.53
Mo-Ti	1.77
Ru-Ru	1.15
Ru-Ti	1.71
Ti-Ti	1.97

Table S3. Calculated bond lengths of adsorbed *N_2(d_{N-N} in Å) and the amount of charge that *N_2 gained from the TM_1-TM_2@V_B-BN catalysts (Q in e).

	Q/end-on	d_{N-N}/end-on	Q/side-on	d_{N-N} /side-on
Fe-Fe	0.35	1.143	0.48	1.180
Fe-Mo	0.43	1.145	0.55	1.189
Fe-Ru	0.41	1.143	0.51	1.184
Fe-Ti	0.41	1.146	0.56	1.190
Mo-Mo	0.48	1.150	0.86	1.263
Mo-Ru	0.52	1.154	0.84	1.255
Mo-Ti	0.52	1.153	0.72	1.230
Ru-Ru	0.39	1.141	0.52	1.195
Ru-Ti	0.41	1.145	0.48	1.179
Ti-Ti	0.53	1.153	0.82	1.220
Ti-Ru	0.48	1.149	0.63	1.210
Ti-Mo	0.50	1.151	0.74	1.230
Ti-Fe	0.51	1.152	0.72	1.220
Ru-Mo	0.39	1.145	0.52	1.194
Ru-Fe	0.39	1.144	0.46	1.180
Mo-Fe	0.52	1.154	0.84	1.253

Table S4: Calculated free energy changes of the first hydrogenation step ($\Delta G_{*N2\rightarrow *N2H}$) and the last hydrogenation step ($\Delta G_{*NH2\rightarrow *NH3}$) for 16 TM_1–TM_2@V_B-BN catalysts. "/ " indicates that TM atoms cannot adsorb intermediate $^*N_2H$.

	Fe-Fe	Fe-Mo	Fe-Ru	Fe-Ti	Mo-Mo	Mo-Ru	Mo-Ti	Ru-Ru
$*N_2\rightarrow *N_2H$/e	0.94	0.91	1.10	0.81	0.38	0.29	/	0.54
$*N_2\rightarrow *N_2H$/s	-	1.1	0.80	0.99	0.52	-0.25	0.15	0.58
$*NH_2\rightarrow *NH_3$	0.32	0.24	0.23	0.29	0.80	0.63	1.00	0.14
	Ru-Ti	**Ti-Ti**	**Ti-Ru**	**Ti-Mo**	**Ti-Fe**	**Ru-Mo**	**Ru-Fe**	**Mo-Fe**
$*N_2\rightarrow *N_2H$/e	0.53	0.45	-	-	-0.22	0.47	0.93	/
$*N_2\rightarrow *N_2H$/s	0.40	0.28	0.27	0.24	0.23	0.53	/	0.26
$*NH_2\rightarrow *NH_3$	-0.08	1.03	1.02	1.16	1.00	0.05	0.22	1.10

Table S5: The magnetic moments($M_{\mu B}$) of TMs in TM_1-TM_2@V_B-BN catalysts.

	M_1(Ru)	M_2(Mo/Ru/Ti)
Ru-Mo@V_B-BN	1.548	2.250
Ru-Ru@V_B-BN	1.079	1.044
Ru-Ti@V_B-BN	1.595	0.422

Table S6: The Gibbs free energies changes for each intermediate on Ru-Mo@V_B-BN via distal, alternating and enzymatic mechanisms at 298.15 K (in eV).

Ru-Mo (Distal)	Δ*G*(eV)
$*+ N_2\rightarrow *N_2$	-1.05
$*N_2+H^++e^-\rightarrow *N_2H$	0.47
$*N_2H+H^++e^-\rightarrow *N_2H_2$	-0.06
$*N_2H_2+H^++e^-\rightarrow *N+NH_3$	-0.48
$*N_2+H^++e^-\rightarrow *NH$	-0.26
$*NH+H^++e^-\rightarrow *NH_2$	-0.24
$*NH_2+H^++e^-\rightarrow *NH_3$	0.05

Ru-Mo (Alternating)	Δ*G*(eV)
$*+ N_2\rightarrow *N_2$	-1.05
$*N_2+H^++e^-\rightarrow *NNH$	0.47
$*NNH+H^++e^-\rightarrow *NHNH$	0.92
$*NHNH+H^++e^-\rightarrow *NHNH_2$	-0.43
$*NHNH_2+H^++e^-\rightarrow *NH_2NH_2$	-1.01
$*NH_2NH_2+H^++e^-\rightarrow *NH_2+NH_3$	-0.52
$*NH_2+H^++e^-\rightarrow *NH_3$	0.05

Ru-Mo (Enzymatic)	Δ*G*(eV)
$*+ N_2\rightarrow *N_2$	-0.70
$*N_2+H^++e^-\rightarrow *NNH$	0.53
$*NNH+H^++e^-\rightarrow *NHNH$	0.07
$*NHNH+H^++e^-\rightarrow *NHNH_2$	-0.32
$*NHNH_2+H^++e^-\rightarrow *NH_2NH_2$	-1.13
$*NH_2NH_2+H^++e^-\rightarrow *NH_2+NH_3$	-0.10
$*NH_2+H^++e^-\rightarrow *NH_3$	0.09

Table S7: Computed vibrational frequencies, zero-point energies and entropy of reaction intermediates on Ru-Mo@V_B-BN, where * denotes the adsorption site.

Reaction Intermediates	Vibrational Frequencies (cm^{-1})						ZPE (eV)	TS (eV)
*N_2	2107.12	417.67	406.77	398.43	62.59	47.39	0.21	0.15
*N_2H	3233.30	1685.80	1107.83	534.11	436.35	397.75	0.49	0.16
	390.32	45.58	27.81					
*N_2H_2	3512.72	3346.95	1552.70	1321.20	1180.83	608.77	0.81	0.17
	459.51	364.69	357.16	298.08	84.51	49.29		
*NHNH	3363.45	3241.89	1327.46	1118.70	1024.25	823.28	0.79	0.15
	667.11	454.15	388.08	207.47	99.80	89.12		
*N	1043.11	123.60	118.88				0.08	0.08
*NH	3277.22	859.21	672.44	626.26	112.18	105.81	0.35	0.10
*NH_2	3464.65	3380.44	1512.27	640.43	634.89	585.07	0.67	0.13
	460.58	118.53	44.05					
*NH_3	3491.58	3482.26	3389.81	1608.27	1601.25	1140.12	1.01	0.13
	546.92	509.10	336.12	99.85	60.85	36.32		
*$NHNH_2$	3450.19	3363.38	3353.46	1577.09	1339.37	1081.41	1.15	0.18
	1018.78	901.47	670.18	624.36	451.54	409.33		
	138.65	94.69	57.53					
*NH_2NH_2	3479.48	3477.35	3385.93	3383.53	1499.78	1493.69	1.31	0.20
	748.18	745.28	598.92	544.45	526.22	414.91		
	311.43	191.88	128.77	119.81	102.29	48.75		
*H	1999.04	610.06	570.74				0.20	0.02

Table S8: The Gibbs free energies changes for each intermediate on Ru-Ru@V_B-BN via distal, alternating and enzymatic mechanisms at 298.15 K (in eV).

Ru-Ru (Distal)	Δ*G*(eV)
+ N_2→N_2	-1.12
N_2+H^++e^-→N_2H	0.54
N_2H+H^++e^-→N_2H_2	0.31
*N_2H_2+H^++e^-→*N+NH_3	-1.26
*N_2+H^++e^-→*NH	0.31
NH+H^++e^-→NH_2	-0.56
NH_2+H^++e^-→NH_3	0.14

Ru-Ru (Alternating)	Δ*G*(eV)
+ N_2→N_2	-1.12
*N_2+H^++e^-→*NNH	0.54
*NNH+H^++e^-→*NHNH	0.59
NHNH+H^++e^-→$NHNH_2$	-0.08
$NHNH_2$+H^++e^-→NH_2NH_2	0.39
NH_2NH_2+H^++e^-→NH_2+NH_3	-2.10
NH_2+H^++e^-→NH_3	0.14

Ru-Ru (Enzymatic)	Δ*G*(eV)
+ N_2→N_2	-0.68
*N_2+H^++e^-→*NNH	0.58

$*NNH+H^++e^-\rightarrow *NHNH$	-0.04
$*NHNH+H^++e^-\rightarrow *NHNH_2$	-0.26
$*NHNH_2+H^++e^-\rightarrow *NH_2NH_2$	0.82
$*NH_2NH_2+H^++e^-\rightarrow *NH_2+NH_3$	-2.20
$*NH_2+H^++e^-\rightarrow *NH_3$	0.14

Table S9: Computed vibrational frequencies, zero-point energies and entropy of reaction intermediates on Ru-Ru@V_B-BN, where * denotes the adsorption site.

Reaction Intermediates	Vibrational Frequencies (cm^{-1})						ZPE (eV)	TS (eV)
$*N_2$	2120.32	381.68	316.86	314.88	41.68	29.24	0.20	0.18
$*N_2H$	3238.89	1396.32	1136.18	591.75	468.09	370.16	0.47	0.17
	208.62	79.32	52.73					
$*N_2H_2$	3490.15	3359.23	1567.99	1312.66	1170.58	553.60	0.79	0.21
	422.11	305.33	279.11	230.75	31.05	13.20		
*NHNH	3290.06	3250.63	1378.05	1147.33	1015.21	901.94	0.81	0.15
	732.07	534.86	433.14	194.44	98.44	91.07		
*N	1078.67	134.44	131.53				0.08	0.08
*NH	3341.41	840.12	441.65	296.04	105.60	103.52	0.32	0.12
$*NH_2$	3493.43	3398.43	1506.55	673.68	591.49	493.03	0.66	0.14
	332.02	103.50	44.74					
$*NH_3$	3477.26	3475.56	3383.58	1602.96	1601.68	1143.19	1.01	0.19
	535.45	534.07	354.81	132.27	48.39	42.53		
$*NHNH_2$	3448.34	3358.66	3351.79	1583.77	1332.65	1086.24	1.14	0.17
	1014.74	896.92	666.04	560.93	451.47	382.40		
	90.82	64.35						
$*NH_2NH_2$	3386.20	3383.03	3306.45	3304.82	1591.83	1571.85	1.47	0.20
	1334.03	1064.12	1051.77	1001.89	932.81	554.61		
	426.11	303.64	284.63	118.83	94.08	76.08		
*H	1822.17	430.87	360.30				0.16	0.03

Table S10: The Gibbs free energies changes for each intermediate on Ru-Ti@V_B-BN via distal, alternating and enzymatic mechanisms at 298.15 K (in eV).

Ru-Ti (Distal)	ΔG(eV)
$*+ N_2\rightarrow *N_2$	-1.20
$*N_2+H^++e^-\rightarrow *N_2H$	0.53
$*N_2H+H^++e^-\rightarrow *N_2H_2$	0.33
$*N_2H_2+H^++e^-\rightarrow *N+NH_3$	-0.67
$*N_2+H^++e^-\rightarrow *NH$	-0.19
$*NH+H^++e^-\rightarrow *NH_2$	-0.43
$*NH_2+H^++e^-\rightarrow *NH_3$	-0.08

Ru-Ti (Alternating)	ΔG(eV)
$*+ N_2\rightarrow *N_2$	-1.20
$*N_2+H^++e^-\rightarrow *NNH$	0.53
$*NNH+H^++e^-\rightarrow *NHNH$	0.85
$*NHNH+H^++e^-\rightarrow *NHNH_2$	-0.37
$*NHNH_2+H^++e^-\rightarrow *NH_2NH_2$	-0.75
$*NH_2NH_2+H^++e^-\rightarrow *NH_2+NH_3$	1.45

$*NH_2+H^++e^-\rightarrow *NH_3$	-0.08

Ru-Ti (Enzymatic)	Δ*G*(eV)
$*+ N_2\rightarrow *N_2$	-0.89
$*N_2+H^++e^-\rightarrow *NNH$	0.40
$*NNH+H^++e^-\rightarrow *NHNH$	0.30
$*NHNH+H^++e^-\rightarrow *NHNH_2$	-0.58
$*NHNH_2+H^++e^-\rightarrow *NH_2NH_2$	-0.97
$*NH_2NH_2+H^++e^-\rightarrow *NH_2+NH_3$	0.11
$*NH_2+H^++e^-\rightarrow *NH_3$	-0.06

Table S11: Computed vibrational frequencies, zero-point energies and entropy of reaction intermediates on Ru-Ti@V_B-BN, where * denotes the adsorption site.

Reaction Intermediates	Vibrational Frequencies (cm^{-1})						ZPE (eV)	TS (eV)
$*N_2$	1866.94	456.23	346.86	182.48	69.03	64.36	0.19	0.16
$*N_2H$	3226.17	1693.91	1112.10	533.82	473.61	414.45	0.49	0.17
	386.53	50.50	41.79					
$*N_2H_2$	3474.90	3360.86	1556.31	1243.89	1161.16	586.85	0.79	0.15
	554.95	372.39	371.79	106.06	31.91	45.35		
*NHNH	3262.46	3234.06	1490.72	1368.86	1274.10	1046.76	0.82	0.20
	553.94	487.70	298.14	117.70	57.15	40.99		
*N	1036.61	149.83	137.31				0.08	0.07
*NH	3191.15	850.46	639.47	633.04	51.74	45.34	0.34	0.14
$*NH_2$	3457.87	3373.42	1517.11	663.21	649.58	578.04	0.68	0.13
	489.40	128.18	58.95					
$*NH_3$	3473.71	3455.43	3365.88	1613.83	1597.40	1156.67	1.02	0.16
	603.15	567.83	357.82	120.71	107.01	74.60		
$*NHNH_2$	3483.88	3355.74	3320.19	1588.52	1428.92	1165.03	1.14	0.20
	1090.56	783.59	683.60	534.50	337.48	294.68		
	184.80	68.32	21.86					
$*NH_2NH_2$	3514.43	3371.47	3331.33	1952.63	1582.64	1452.44	1.37	0.18
	1191.06	1113.59	803.51	782.77	745.19	669.31		
	572.87	367.52	318.96	232.44	91.35	71.56		
*H	1930.02	631.48	534.22				0.19	0.01

Table S12: Charge variations of Ru-Ti dimer, V_B-BN substrate and N_xH_y species on Ru-Ti@V_B-BN.

	Ru-Ti	Substrate	N_xH_y
Slab	1.71	-1.71	0.00
$*N_2$	2.10	-1.62	-0.48
$*N_2H$	2.10	-1.68	-0.42
*NHNH	2.19	-1.64	-0.55
$*NH_2NH$	2.01	-1.79	-0.22
$*NH_2NH_2$	2.37	-1.61	-0.76
$*NH_2$	2.00	-1.66	-0.34
$*NH_3$	1.70	-1.83	0.12

Table S13: Bond lengths of Ru-Ti, N-N and Ru-N on Ru-Ti@V_B-BN.

	Ru-Ti	N-N	Ru-N
slab	2.66	-	-
***N_2**	2.54	1.17	2.04
***N_2H**	2.46	1.25	1.93
***NHNH**	2.53	1.38	2.00
***NH_2NH**	2.36	1.42	2.03
***NH_2NH_2**	2.54	3.03	1.96
***NH_2**	2.90	-	1.90
***NH_3**	2.82	-	2.17

Table S14: The calculated total energies (Energy-DFT), zero-points energy (ZPE) and entropy corrections (TS), in eV, for the gas phase N_2, H_2, NH_3 species of NRR (T = 298.15 K,P = 1 bar). In comparison, the experimental entropies (TS_{exp}) of the gas phase N_2, H_2, NH_3 species are also shown, which are from NIST standard reference database.

Species	Energy-DFT	ZPE	TS	Gibbs	TS_{exp}
H_2(g)	-6.77	0.27	0.40	-6.90	0.41
N_2(g)	-16.64	0.15	0.59	-17.08	0.59
NH_3(g)	-19.54	0.91	0.60	-19.23	0.60

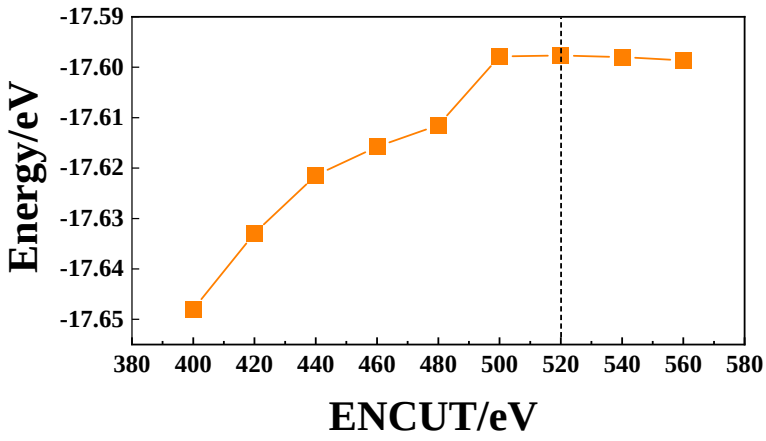

Figure S1. Convergence test on the ENCUT value for the BN primitive cell.

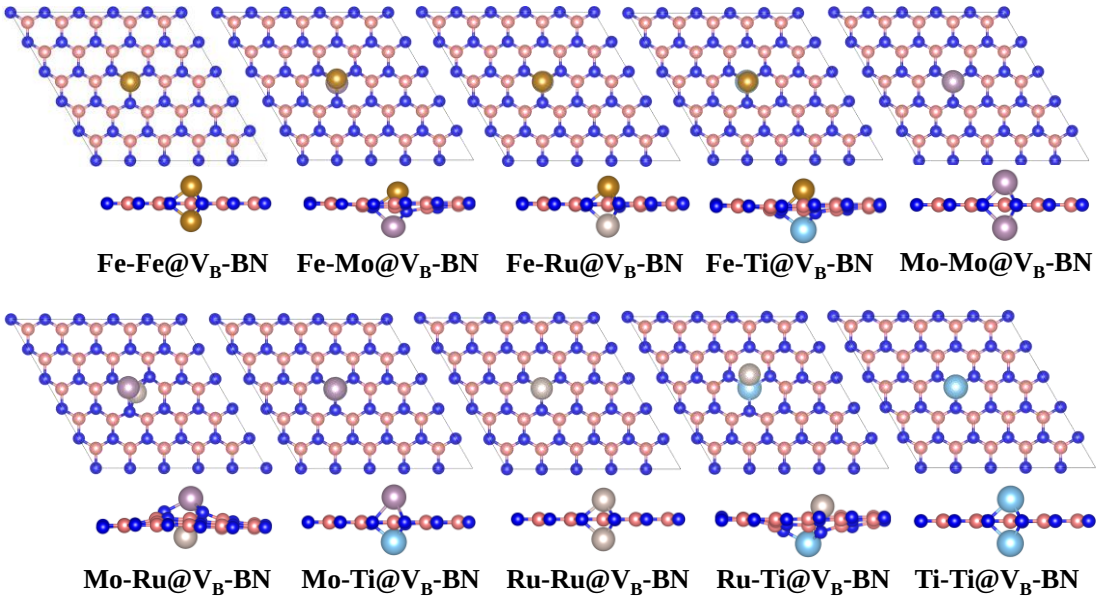

Figure S2. Schematic diagrams of the fully relaxed structures of TM_1-TM_2 @V_B-BN (TM=Fe, Mo, Ru and Ti).

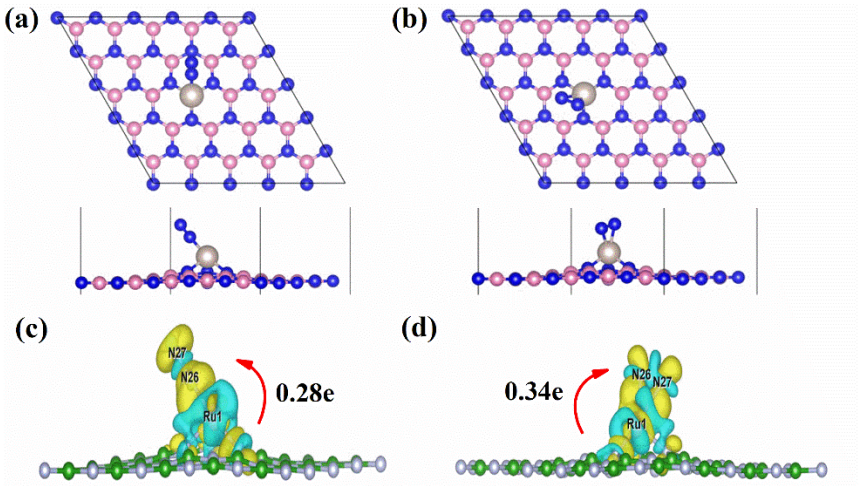

Figure S3. Top and side views of N_2 molecule adsorbed on a single Ru atom in (a)end-on and (b) side-on configuration, respectively. Change density differences of N_2 adsorption on Ru@V_B-BN monolayer for (c)end-on and (d) side-on configurations.

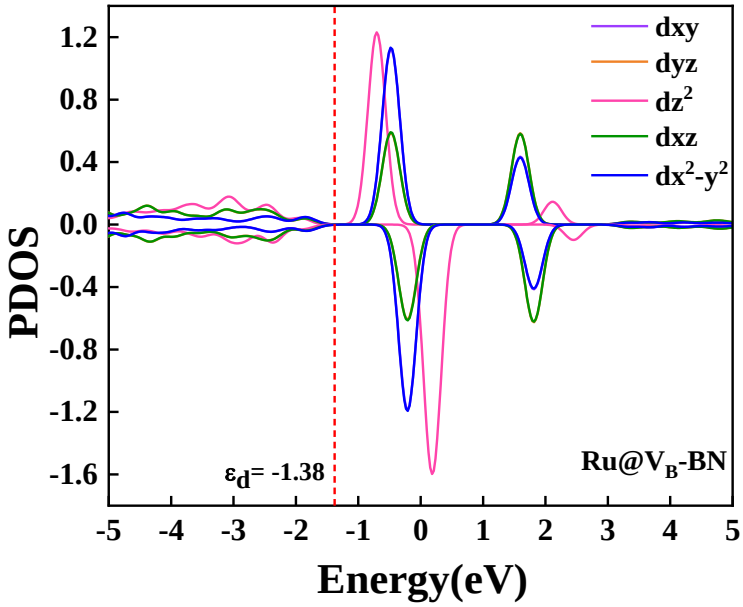

Figure S4. Projected density of states(PDOS) of Ru *d* orbitals in Ru@V_B-BN. The red dotted line represents the position of the *d*-band center.

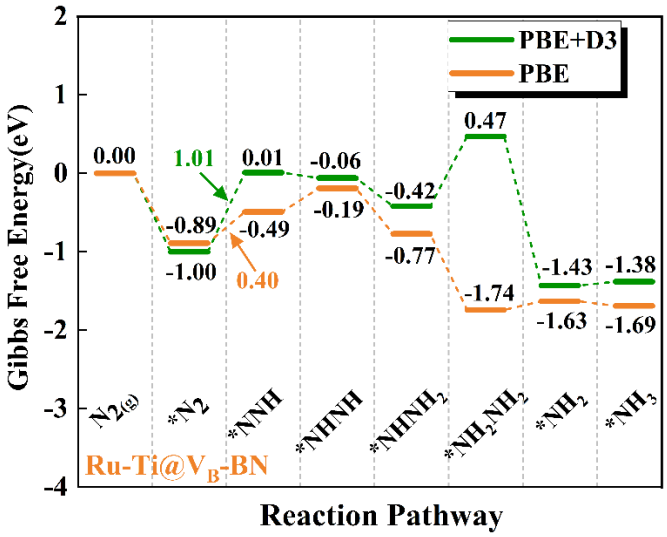

Figure S5. Gibbs free energy diagram for N_2 electroreduction on Ru-Ti@V_B-BN with and without consideration of vdW interaction.

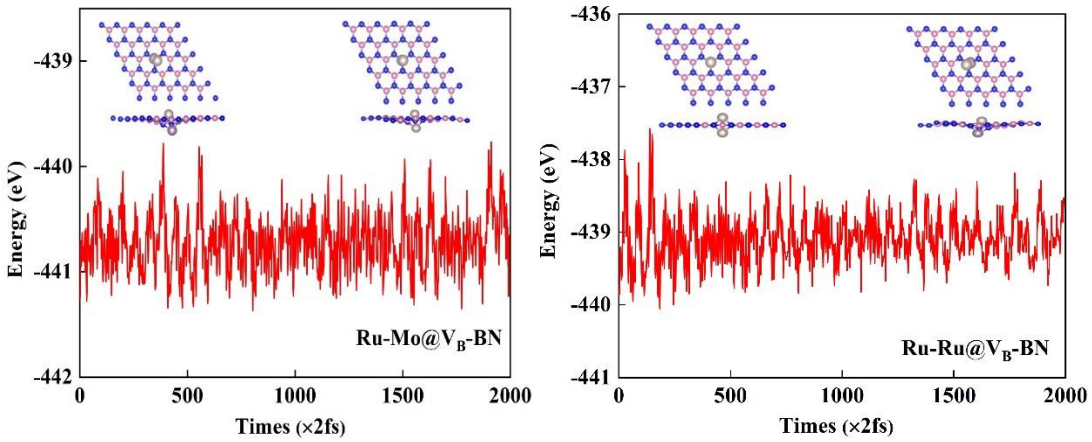

Figure S6. Variations of the total energy against the time for the AIMD simulation for Ru-Mo @V_B-BN and Ru-Ru @V_B-BN under 400K.