Supporting Information

Regulation of Electronic Structures to Boost Efficient Nitrogen Fixation: Synergistic Effects between Transition Metals and Boron Nanotube

Changhui Liu,[#a] Qingshan Bao,[#a] Xian Zhao,[b] and Yanlu Li[*a]

[a]State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, China

[b]Center for Optics Research and Engineering, Shandong University, Qingdao 266237, China

*Corresponding author: liyanlu@sdu.edu.cn

[#]Equal contribution to this work

Supplemental Note

The reaction free energy for each elementary step can be expressed as a function of the applied electrode potential U and the binding energy of *N_2H as follows:

$$* \boldsymbol{N_2} + \boldsymbol{6}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \rightarrow * \boldsymbol{N_2H} + \boldsymbol{5}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \#\#\#(1)$$

$$\Delta G_1 = \Delta G_{*N2H} - \Delta G_{*N2}$$

$$= \Delta E_{*N2H} + 0.82 - \Delta E_{*N2} - 0.53 + eU$$

$$= 0.54\Delta E_{*N2H} + 0.72 + eU$$

$$= 0.58\Delta E_{*N2H(sol)} + 0.71 + eU$$

$$* \boldsymbol{N_2H} + \boldsymbol{5}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \rightarrow * \boldsymbol{HN_2H} + \boldsymbol{4}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \#(2)$$

$$\Delta G_{2a} = \Delta G_{*HN2H} - \Delta G_{*N2H}$$

$$= \Delta E_{*HN2H} + 1.30 - \Delta E_{*N2H} - 0.8 + eU$$

$$= -0.34\Delta E_{*N2H} - 0.13 + eU$$

$$= -0.46\Delta E_{*N2H(sol)} - 0.42 + eU$$

$$* \boldsymbol{HN_2H} + \boldsymbol{4}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \rightarrow * \boldsymbol{HN_2H_2} + \boldsymbol{3}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \#(3)$$

$$\Delta G_{3a} = \Delta G_{*HN2H2} - \Delta G_{*HN2H}$$

$$= \Delta E_{*HN2H2} + 1.59 - \Delta E_{*HN2H} - 1.3 + eU$$

$$= 0.50\Delta E_{*N2H} - 0.88 + eU$$

$$= 0.39\Delta E_{*N2H(sol)} - 0.88 + eU$$

$$* \boldsymbol{HN_2H_2} + \boldsymbol{3}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \rightarrow * \boldsymbol{H_2N_2H_2} + \boldsymbol{2}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \#(4)$$

$$\Delta G_{4a} = \Delta G_{*H2N2H2} - \Delta G_{*HN2H2}$$

$$= \Delta E_{*HN2H2} + 2.07 - \Delta E_{*HN2H2} - 1.59 + eU$$

$$= -0.63\Delta E_{*N2H} + 0.28 + eU$$

$$= -0.34\Delta E_{*N2H(sol)} - 0.16 + eU$$

$$* \boldsymbol{H_2N_2H_2} + \boldsymbol{2}(\boldsymbol{H}^+ + \boldsymbol{e}^-) \rightarrow * \boldsymbol{NH_2} + (\boldsymbol{H}^+ + \boldsymbol{e}^-) + \boldsymbol{NH_3} \#(5)$$

$$\Delta G_{5a} = \Delta G_{*NH2} + \Delta G_{NH3} - \Delta G_{*H2N2H2}$$

$$= \Delta E_{*N2H} + 0.95 - 0.32 - \Delta E_{*H2N2H2} - 2.07 + eU$$

$$= 0.73\Delta E_{*N2H} - 1.96 + eU$$

$$= \Delta E_{*N2H(sol)} + 0.95 - 0.50 - \Delta E_{*H2N2H2(sol)} - 2.07 + eU$$

$$= 0.63\Delta E_{*N2H(sol)} - 1.39 + eU$$

$$* \boldsymbol{N_2H} + \boldsymbol{5}(\boldsymbol{H^+} + \boldsymbol{e^-}) \rightarrow * \boldsymbol{N_2H_2} + \boldsymbol{4}(\boldsymbol{H^+} + \boldsymbol{e^-}) \#(6)$$

$$\Delta G_{2d} = \Delta G_{*N2H2} - \Delta G_{*N2H}$$

$$= \Delta E_{*N2H2} + 1.27 - \Delta E_{*N2H} - 0.82 + eU$$

$$= -0.34\Delta E_{*N2H} - 0.33 + eU$$

$$= -0.38\Delta E_{*N2H(sol)} - 0.68 + eU$$

$$* \boldsymbol{N_2H_2} + \boldsymbol{4}(\boldsymbol{H^+} + \boldsymbol{e^-}) \rightarrow * \boldsymbol{N} + \boldsymbol{3}(\boldsymbol{H^+} + \boldsymbol{e^-}) + \boldsymbol{NH_3} \#(7)$$

$$\Delta G_{3d} = \Delta G_{*N} + \Delta G_{NH3} - \Delta G_{*N2H2}$$

$$= \Delta E_{*N} + 0.33 - 0.32 - \Delta E_{*N2H2} - 1.27 + eU$$

$$= 0.42\Delta E_{*N2H} - 1.53 + eU$$

$$= \Delta E_{*N(sol)} + 0.33 - 0.50 - \Delta E_{*N2H2(sol)} - 1.27 + eU$$

$$= 0.38\Delta E_{*N2H(sol)} - 0.99 + eU$$

$$* \mathbf{N} + \boldsymbol{3}(\boldsymbol{H^+} + \boldsymbol{e^-}) \rightarrow * \boldsymbol{NH} + \boldsymbol{2}(\boldsymbol{H^+} + \boldsymbol{e^-}) \#(8)$$

$$\Delta G_{4d} = \Delta G_{*NH} - \Delta G_{*N}$$

$$= \Delta E_{*NH} + 0.72 - \Delta E_{*N} - 0.33 + eU$$

$$= -0.56\Delta E_{*N2H} - 0.76 + eU$$

$$= -0.56\Delta E_{*N2H(sol)} - 0.95 + eU$$

$$* \boldsymbol{NH} + \boldsymbol{2}(\boldsymbol{H^+} + \boldsymbol{e^-}) \rightarrow * \boldsymbol{NH_2} + (\boldsymbol{H^+} + \boldsymbol{e^-}) \#(9)$$

$$\Delta G_{5d} = \Delta G_{*NH2} - \Delta G_{*NH}$$

$$= \Delta E_{*NH2} + 0.95 - \Delta E_{*NH} - 0.72 + eU$$

$$= 0.74\Delta E_{*N2H} - 0.07 + eU$$

$$= 0.78\Delta E_{*N2H(sol)} - 0.05 + eU$$

$$* \boldsymbol{NH_2} + (\boldsymbol{H^+} + \boldsymbol{e^-}) \rightarrow * \boldsymbol{NH_3} \#(10)$$

$$\Delta G_6 = \Delta G_{*NH3} - \Delta G_{*NH2}$$

$$= \Delta E_{*NH3} + 0.67 - \Delta E_{*NH2} - 0.95 + eU$$

$$= -0.67\Delta E_{*N2H} + 0.47 + eU$$

$$= -0.57\Delta E_{*N2H(sol)} - 0.15 + eU$$

Supplemental Tables

Table S1. Cutoff energy, k-mesh, supercell size, and magnetisation tests.

Test item	Range	Energy (eV)		
		E(W@BNT)	E(*N_2/W@BNT)	ΔE_{*N2}
Cutoff energy	400 eV	-838.641	-855.770	-0.489
	450 eV	-838.650	-855.792	-0.502
	500 eV	-838.696	-855.792	-0.456
K-mesh	1×1×3	-838.561	-855.652	-0.451
	1×1×4	-838.650	-855.792	-0.502
	1×1×5	-838.639	-855.766	-0.487
Supercell size	1×1×2	-560.677	-576.088	1.299
	1×1×3	-838.650	-855.792	-0.502
	1×1×4	-1121.275	-1138.358	-0.444
Magnetization	M=0	-838.650	-855.792	-0.502
	M=1	-838.643	-855.791	-0.508
	M=3	-838.643	-855.791	-0.508

Table S2. Comparison of the adsorption energies of reaction intermediates on the Mo@BNT surfaces computed using different functionals.

Reaction Intermediates	PBE (eV)	PBE+D3 (eV)	RPBE+D3 (eV)
*N_2	-0.06	-0.32	-0.19
*N_2H	0.32	0.14	0.28
*HN_2H	-0.14	-0.51	-0.23
*HN_2H_2	-1.42	-1.77	-1.37
*$H_2N_2H_2$	-1.38	-1.79	-1.43
*N_2H_2	-0.33	-0.65	-0.33
*N	-0.65	-0.82	-0.95
*NH	-1.78	-2.10	-1.75
*NH_2	-2.21	-2.49	-2.26

***NH_3**	-1.28	-1.58	-1.50

Table S3. Calculated formation ($E_{f(core/shell)}$) and insertion energies ($E_{i(core/shell)}$) in eV, core-shell structural diameter (D) and the shortest distance between TM and B (d_{TM-B}) in Å. Here (12,0) BNNT having a similar diameter with (0.6) BNT was chosen to encapsulate into the same fillers for comparison.

Systems	**TMs@BNT**				**TMs@BNNT**	
	$E_{f(core/shell)}$	$E_{i(core/shell)}$	**D**	d_{TM-B}	$E_{f(core/shell)}$	$E_{i(core/shell)}$
Sc	-1.60	-0.49	9.91	2.49	0.67	-0.06
Y	-0.80	-0.37	10.33	2.60	1.59	0.07
Ti	-1.41	-0.49	9.59	2.39	0.66	-0.09
Zr	-1.45	-0.50	10.02	2.50	0.92	-0.05
Hf	-1.37	-0.53	9.90	2.48	1.03	-0.07
Nb	-1.33	-0.50	9.77	2.43	0.84	-0.08
Ta	-1.14	-0.51	9.70	2.44	1.09	-0.08
Mo	-0.57	-0.37	9.55	2.42	1.03	-0.07
W	-0.24	-0.41	9.47	2.46	1.48	-0.08

Table S4. Computed vibrational frequencies (ν_i), zero-point energies (E_{ZPE}), and entropy (TS) of reaction intermediates on Mo@BNT. Energies are in the unit of eV.

Reaction Intermediates	**Mo@BNT**						**ZPE**	**TS**
	Vibrational Frequencies (ν_i, cm^{-1})							
***N_2**	2205.51	460.55	439.68	419.85	77.55	68.09	0.23	0.14
***N_2H**	2818.82	1641.09	1253.66	784.45	430.36	321.46	0.47	0.16
	216.49	103.37	51.98					
***HN_2H**	3322.90	3190.84	1513.29	1489.59	1320.00	1091.15	0.87	0.15
	686.47	621.45	368.82	256.77	108.72	59.90		
***HN_2H_2**	3500.39	3485.51	3362.30	1581.04	1459.91	1216.05	1.15	0.21
	1197.18	738.68	650.04	419.15	338.35	281.88		

	191.36	104.74	28.02					
$*H_2N_2H_2$	3407.17	3389.18	3324.95	3308.84	1624.55	1572.15	1.53	0.18
	1427.94	1285.33	1144.96	1126.72	894.64	780.25		
	548.88	287.52	280.54	163.60	113.03	62.36		
$*N_2H_2$	3498.89	3107.97	1578.73	1427.75	1235.53	701.00	0.84	0.15
	652.33	550.82	371.94	286.18	122.36	52.75		
*N	930.96	790.11	362.98				0.13	0.02
*NH	3423.01	1073.74	782.95	723.91	721.00	328.49	0.44	0.03
$*NH_2$	3624.94	3518.56	1558.95	900.03	729.35	351.58	0.70	0.11
	254.37	164.30	137.38					
$*NH_3$	3431.44	3400.02	3311.55	1600.00	1574.16	1342.33	1.08	0.10
	868.27	862.39	496.12	225.82	166.92	152.83		
*H	2381.60	639.37	554.30				0.22	0.01

Table S5. Computed vibrational frequencies (ν_i), zero-point energies (E_{ZPE}), and entropies (TS) of reaction intermediates on W@BNT. Energies are in the unit of eV.

Reaction Intermediates	**W@BNT**						**ZPE**	**TS**
	Vibrational Frequencies (ν_i, cm^{-1})							
$*N_2$	2240.53	472.74	454.98	443.76	89.09	71.67	0.23	0.13
$*N_2H$	3130.61	1806.37	1253.79	609.90	607.72	412.76	0.51	0.15
	288.45	76.63	57.84					
$*HN_2H$	3344.32	3210.28	1514.91	1456.06	1311.63	1094.77	0.87	0.19
	696.11	645.89	381.48	224.55	117.99	12.53		
$*HN_2H_2$	3509.22	3443.22	3347.23	1608.08	1448.45	1235.62	1.18	0.17
	1182.24	890.81	726.73	581.94	367.80	274.33		
	196.78	112.00	77.62					
$*H_2N_2H_2$	3410.03	3393.39	3343.95	3333.27	1631.54	1567.81	1.54	0.19
	1439.31	1285.40	1143.95	1139.23	900.76	774.56		

	566.59	286.98	262.01	164.13	92.94	65.55		
$*N_2H_2$	3498.89	3107.97	1578.73	1427.75	1235.53	701.00	0.84	0.15
	652.33	550.82	371.94	286.18	122.36	52.75		
*N	930.96	790.11	362.98				0.13	0.02
*NH	3423.01	1073.74	782.95	723.91	721.00	328.49	0.44	0.03
$*NH_2$	3606.13	3508.30	1551.80	874.34	831.23	517.42	0.72	0.09
	481.14	179.92	125.71					
$*NH_3$	3444.38	3411.83	3326.33	1596.48	1587.36	1331.68	1.08	0.12
	854.56	835.91	534.11	189.62	141.37	125.63		
*H	2381.60	639.37	554.30				0.22	0.01

Table S6. Computed vibrational frequencies (ν_i), zero-point energies (E_{ZPE}), and entropies (TS) of reaction intermediates on (0,6) BNT. Energies are in the unit of eV.

Reaction Intermediates	**(0,6) BNT**						**ZPE (eV)**	**TS (eV)**
	Vibrational Frequencies (ν_i, cm^{-1})							
$*N_2$	2221.92	453.21	447.33	421.55	100.12	70.67	0.23	0.13
$*N_2H$	3113.06	1609.97	1281.00	746.84	467.54	313.38	0.48	0.18
	194.60	96.73	22.04					
$*HN_2H$	3301.79	3243.65	1523.10	1390.09	1319.80	960.10	0.85	0.14
	643.64	615.43	365.43	234.63	104.67	67.02		
$*HN_2H_2$	3489.77	3476.09	3362.89	1577.76	1449.72	1213.38	1.14	0.19
	1179.63	742.76	633.66	408.34	339.95	259.32		
	179.97	108.32	55.65					
$*H_2N_2H_2$	3471.10	3383.70	3350.78	3309.92	1614.86	1581.58	1.52	0.19
	1361.70	1249.52	1206.33	1075.07	853.67	802.92		
	504.93	291.25	189.65	109.97	100.83	90.84		
$*N_2H_2$	3495.93	3220.54	1596.18	1363.09	1243.67	681.60	0.84	0.15
	612.92	585.02	368.96	272.53	126.18	55.44		

***N**	731.62	684.45	612.86				0.13	0.01
***NH**	3508.63	902.52	766.45	737.65	580.62	530.22		
***NH_2**	3609.55 261.06	3502.31 193.12	1556.97 107.76	889.49	680.76	307.85	0.44	0.02
***NH_3**	3441.61 835.03	3429.00 828.25	3330.77 456.94	1603.85 193.51	1583.04 160.51	1324.66 136.02	1.07	0.11
***H**	2338.48	780.67	707.73				0.23	0.01

Table S7. Calculated zero-point energies (ZPE) and entropies (TS) for the gas molecules H_2, N_2, and NH_3 (T = 298.15 K, P = 1 bar) and free H_2O (T = 298.15 K, P = 0.035 bar).

Species	ZPE	TS
H_2	0.27	0.41
N_2	0.15	0.59
NH_3	0.91	0.60
H_2O	0.55	0.67

Table S8. Computed boron (B) p band center (ε_{2p}), the position of lowest unoccupied states (ε_{LUS}), the net charge of B atom (δ_B), the electron numbers of p orbital (N_e), the boron average 2p-states energy ($\bar{\varepsilon}_{2p}$), the net charge of *N_2H (δ_{*N2H}), the bond populations between the active sites and *N_2H ($B_{B\text{-}N}$), and the metal d-band center ($\varepsilon_{TM\ d}$).

Systems	ε_{2p}	ε_{LUS}	δ_B	N_e	$\bar{\varepsilon}_{2p}$	δ_{*N2H}	$B_{B\text{-}N}$	$\varepsilon_{TM\ d}$
Sc	-3.43	-3.84	0.16	1.299	-4.05	0.43	-7.90	-0.22
Y	-2.70	-3.60	0.26	1.283	-4.22	0.55	-7.47	-0.08
Ti	-3.91	-4.11	0.42	1.332	-4.22	0.45	-9.82	-0.11
Zr	-3.23	-3.92	0.19	1.297	-4.04	0.35	-7.91	-0.49
Hf	-3.33	-3.90	0.16	1.309	-4.16	0.46	-9.13	-0.19

Nb	-2.67	-4.08	0.09	1.293	-3.87	0.48	-10.80	-0.74
Ta	-2.91	-3.89	0.17	1.289	-3.92	0.50	-11.49	-1.03
Mo	-1.67	-3.97	-0.06	1.272	-3.68	0.50	-11.72	-1.19
W	-2.66	-3.97	-0.28	1.237	-3.56	0.33	-11.61	-1.25
(0.6)	-2.29	-3.97	0.33	1.352	-4.42	0.39	-7.82	-
β_{12}	-2.71	-3.51	0.54	1.350	-4.48	0.47	-7.80	-

Table S9. Adsorption free energies of H adatoms (ΔG_{*H}) on potential adsorption sites of the catalyst surfaces. Sites with the most negative energies are highlighted in red, and the values in parentheses are the energies obtained considering solvent effects.

Systems	**BR_{CN44}**	**BR_{CN45}**	**BR_{CN55}**	**T_{CN4}**	**T_{CN5}**
Sc	-0.10	-0.23	-0.36(-0.41)	-0.05	-0.27
Y	-0.25	-0.19	-0.23	-0.22	-0.28(-0.27)
Ti	-0.16	-0.25(-0.37)	-0.24	To CN45	-0.07
Zr	-0.63(-0.61)	-0.62	-0.56	-0.54	-0.46
Hf	-0.35	-0.38	-0.39(-0.45)	-0.21	-0.23
Nb	-0.37	-0.52(-0.61)	-0.21	-0.22	-0.34
Ta	-0.20	-0.38(-0.28)	-0.37	To CN45	-0.14
Mo	-0.02	-0.07(-0.09)	0.20	0.07	0.10
W	0.23	-0.26(-0.29)	-0.22	To CN45	0.02
(0.6)	0.08	0.11	0.83	-0.02(-0.05)	0.09
β_{12}	0.11	0.10	To CN5	0.02(0.05)	0.18

Supplemental Figures

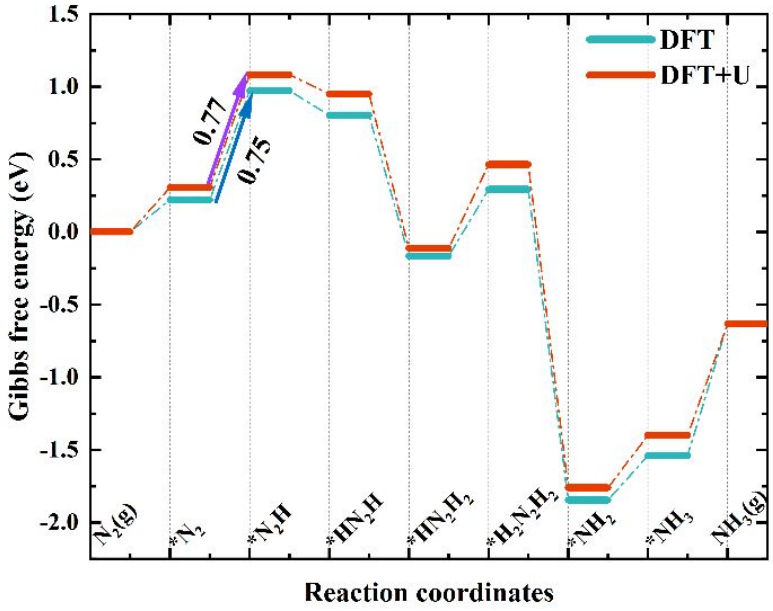

Figure S1. Comparison of NRR pathways on the Mo@BNT by using the DFT and DFT+U methods.

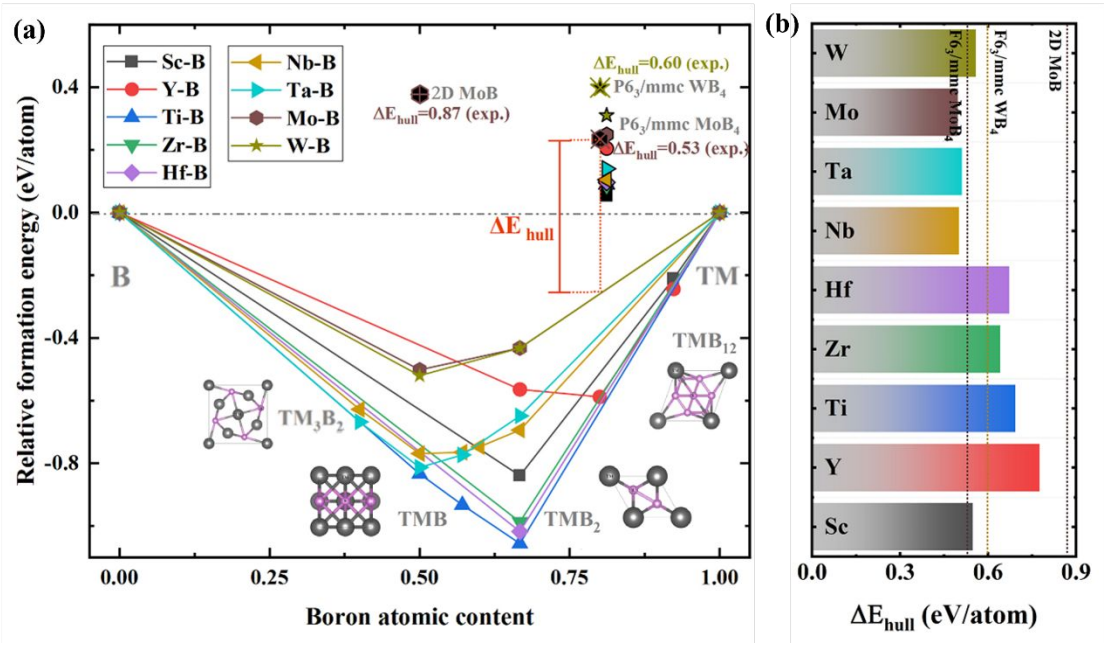

Figure S2. (a) Formation energies of TM@BNT and the stable TM_3B_2, TMB, TMB_2 and TMB_{12} compounds fall on the convex hull in the binary B-TM system. The energy above the hull ΔE_{hull} is indicated by the red. (b) Computed ΔE_{hull} of TM@BNT as compared with those of TMBs (2D MoB, P63/mmc MoB_4 and P63/mmc WB_4) that are experimentally available.

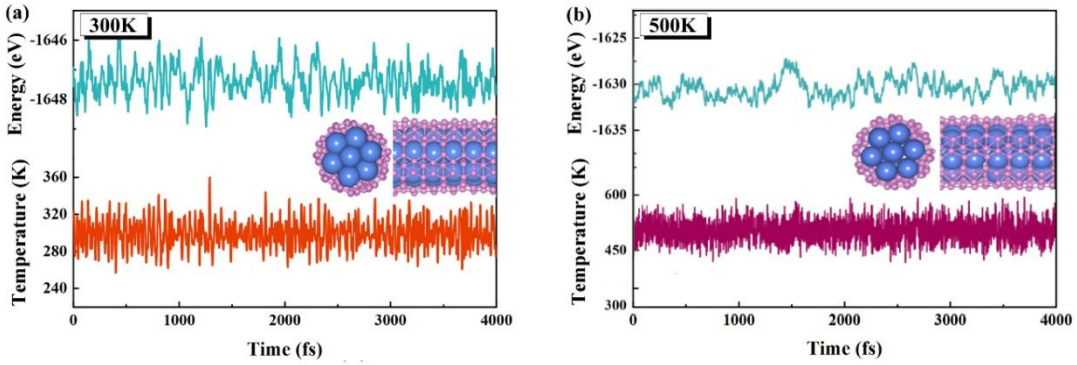

Figure S3. (a) Temperature and energy evolution of W@BNT by ab initio molecular dynamics simulations at 300 K and (b) 500k for 4 ps.

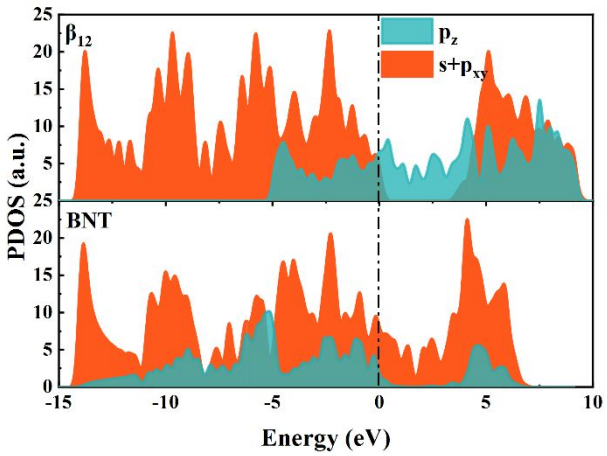

Figure S4. Computed partial densities of state (PDOS) of borophene and (0,6) BNT.

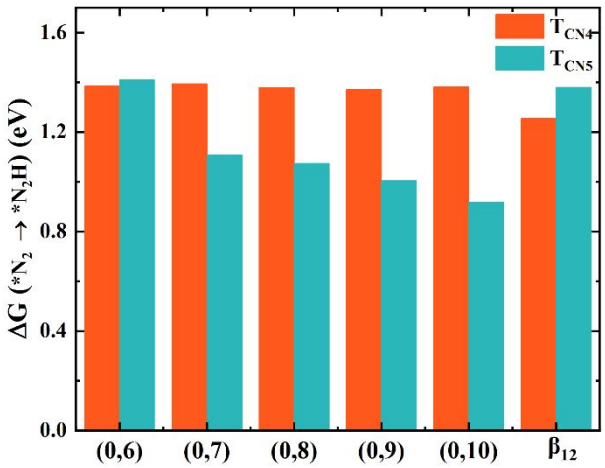

Figure S5. Changes in the reactive free energy of the first hydrogenation step of primitive BNT with different diameters.

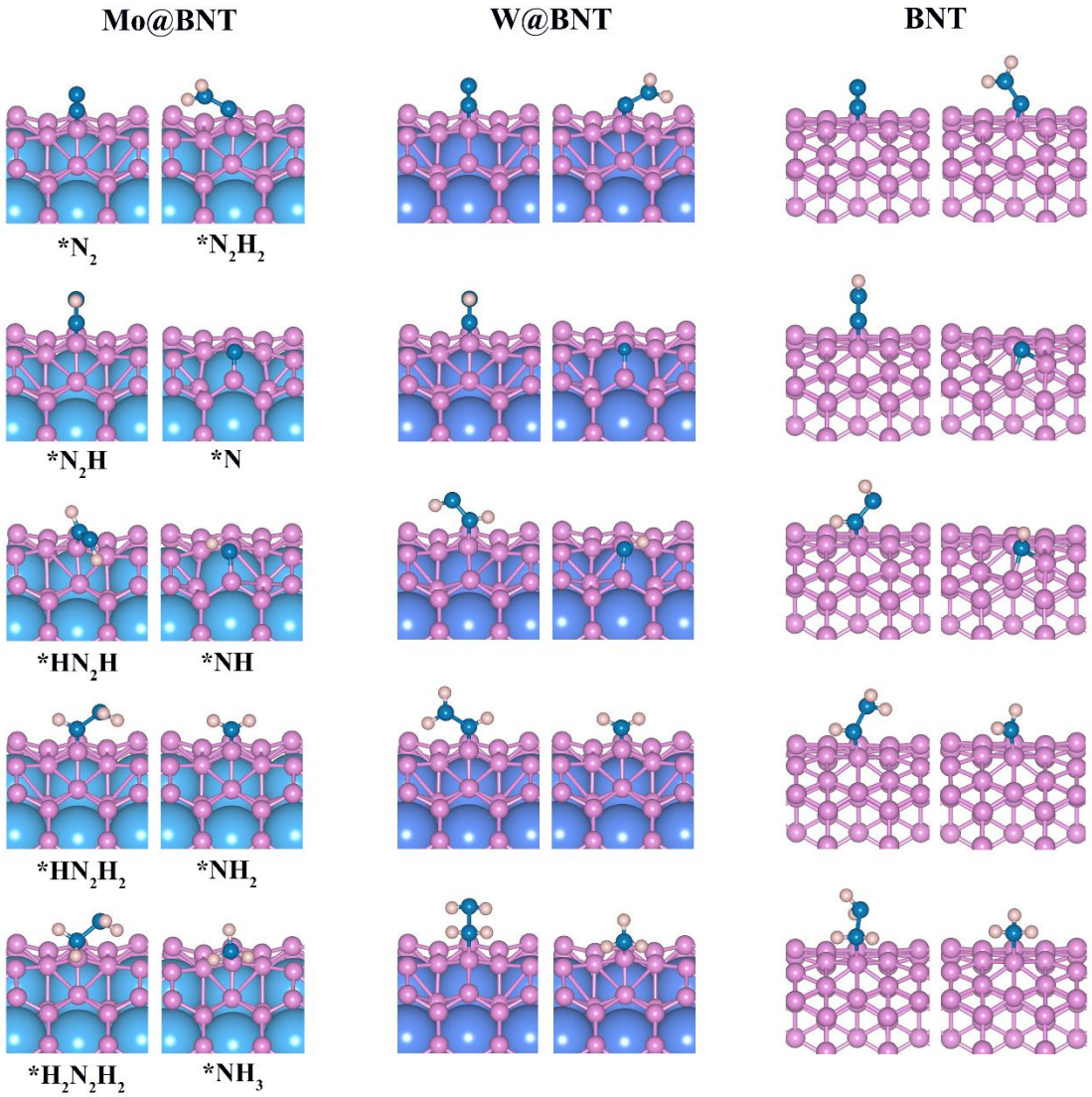

Figure S6. Optimised structures of the reaction intermediates on the Mo@BNT,

W@BNT, and (0,6) BNT surfaces.

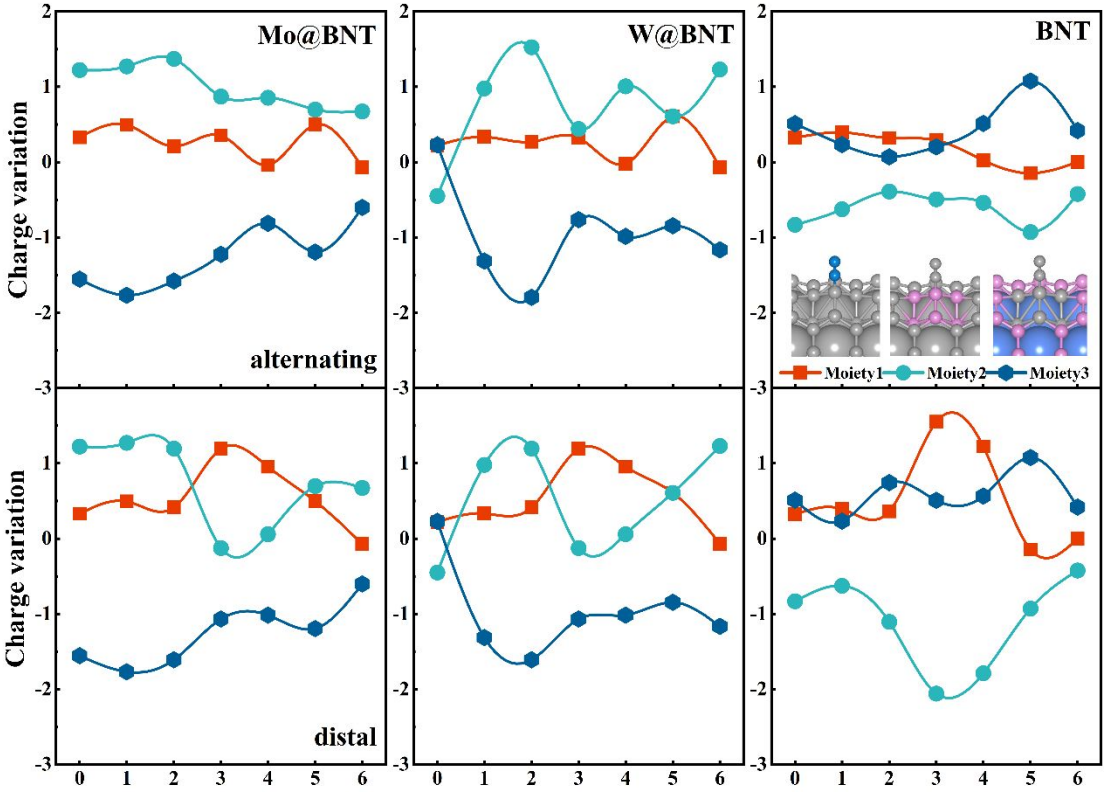

Figure S7. Variations in the charge of N_2 chemisorbed on Mo@BNT, W@BNT, and (0,6) BNT in the alternating and distal pathways. Moieties 1, 2, and 3 represent the adsorbed N_xH_y species, the B_6 unit, and the rest of the substrates, respectively.

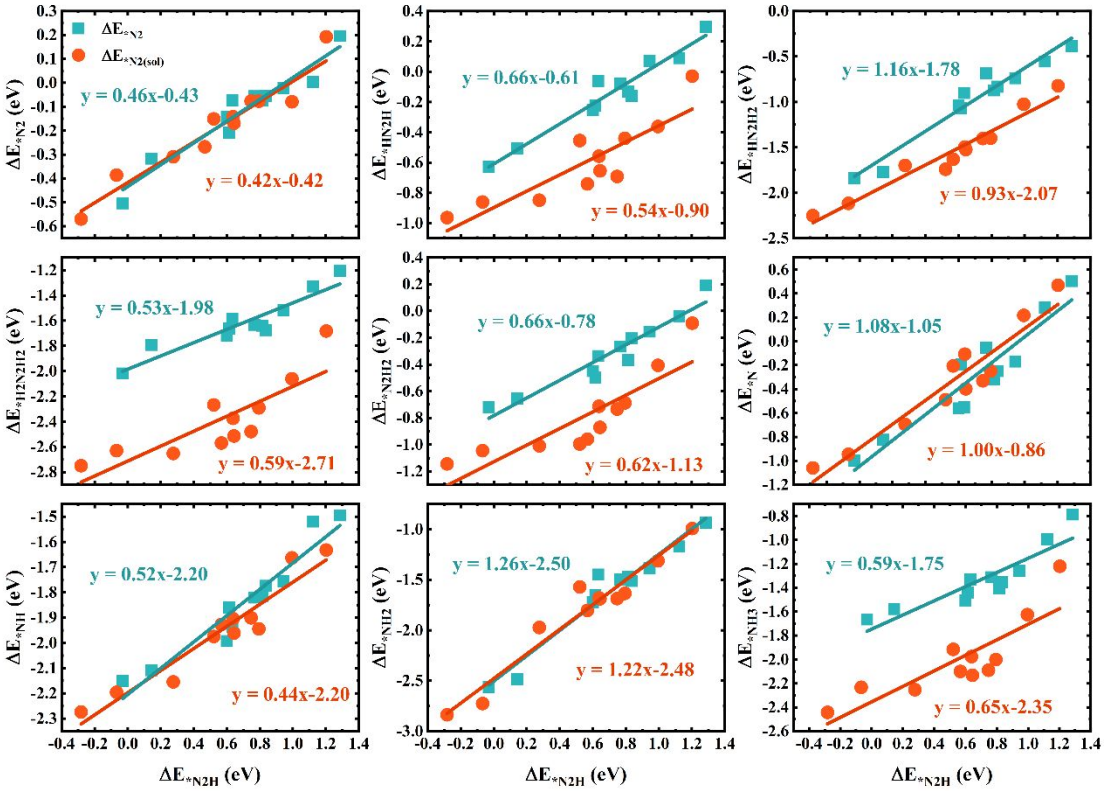

Figure S8. Scaling relations between the adsorption energy of *N_2H (ΔE_{*N2H}) and other intermediates on studied catalysts. The solvation effect (orange circles) is provided for comparison.

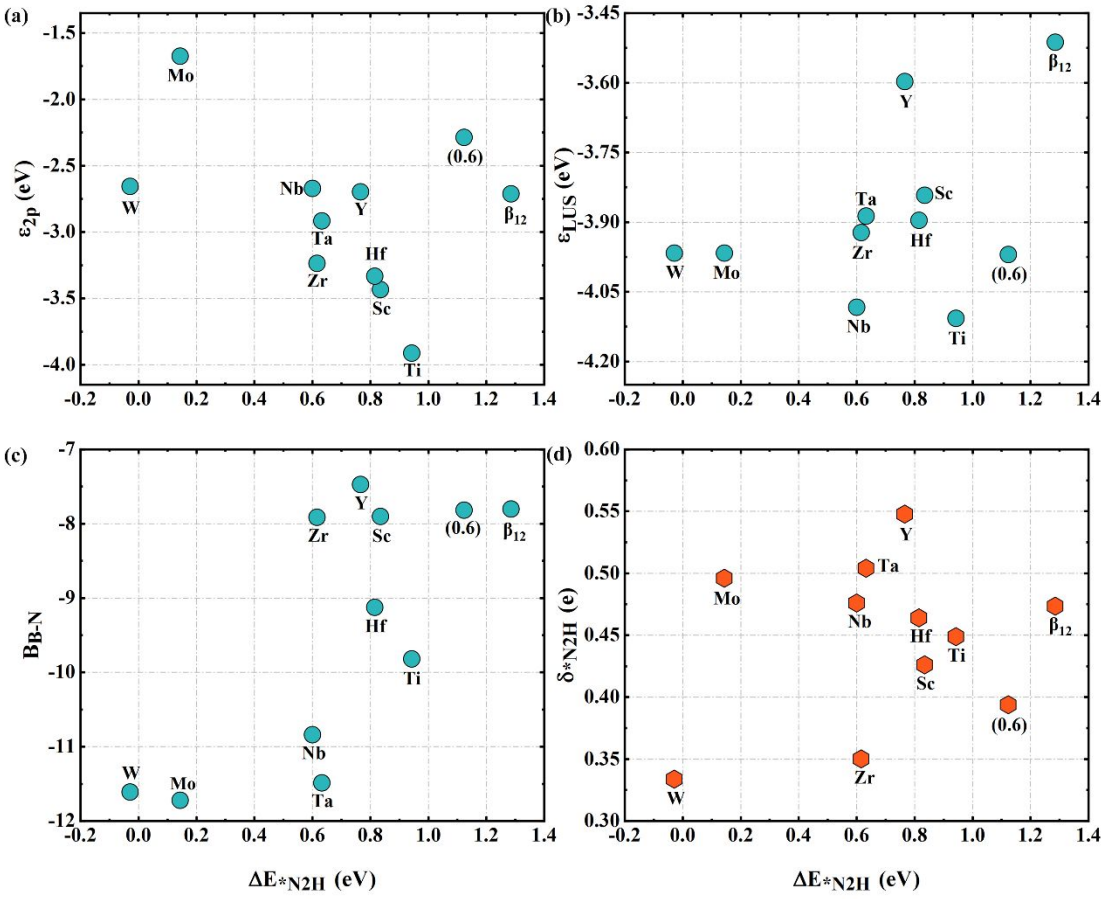

Figure S9. Relationships between the adsorption energy of $*N_2H$ (ΔE_{*N2H}) and (a) the boron (B) p-band centre (ε_{2p}), (b) the position of the lowest unoccupied state (ε_{LUS}), (c) the bond populations between the active sites and $*N_2H$ (B_{B-N}), and (d) the net charge of $*N_2H$ (δ_{*N2H}).

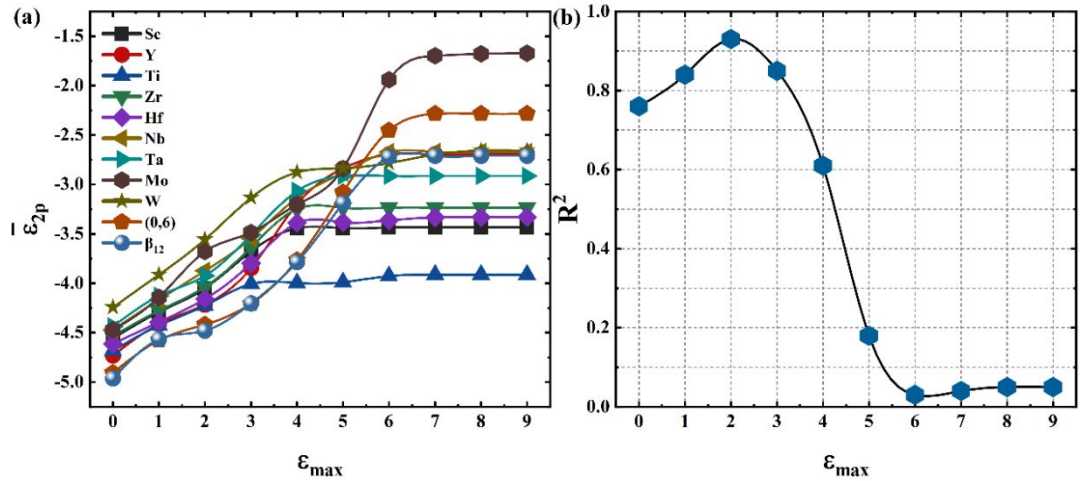

Figure S10. (a) Sensitivity of the correlation of the boron average 2p-state energy ($\bar{\varepsilon}_{2p}$) with the integrated upper boundary (ε_{max}). (b) Changes in the evaluation index (R^2) of

the model fitting as a function of ε_{max}.

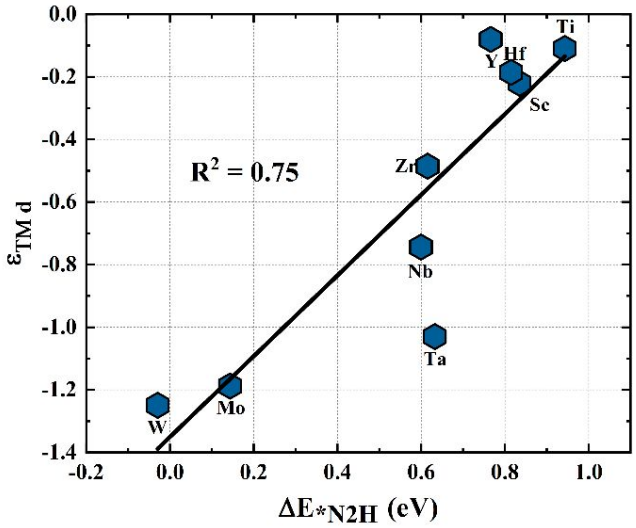

Figure S11. Relationship between the adsorption energy of $*N_2H$ (ΔE_{*N2H}) and the metal d-band centre ($\varepsilon_{TM\ d}$).

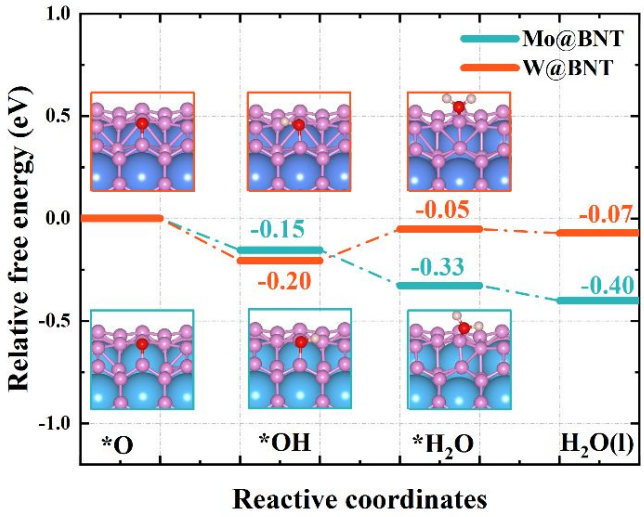

Figure S12. Relative free energy changes along the deoxidation/dehydroxylation process on the Mo@BNT and W@BNT surfaces at the relative potential of U_L.