Single-Metal Atom Sandwiched by Graphdiyne and BN-Doped Graphdiyne

Sheets as an Electrocatalyst for Nitrogen Reduction: A First-Principles Study

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Table S1. Calculated binding energies (in eV) of a TM atom sandwiched between graphdiyne and BN-doped graphdiyne.

TM atom	E_b^1 (eV)	E_b^2 (eV)
Sc	-8.27	-4.28
Ti	-8.92	-5.51
V	-7.81	-5.60
Cr	-4.69	-2.24
Mn	-5.24	-3.40
Fe	-6.41	-4.74
Co	-6.93	-5.57
Ni	-6.62	-5.59
Cu	-4.92	-3.37

E_b^1 is calculated as $E_b = E_{\text{BN-TM-G}} - E_G - E_{\text{BN}} - E_{\text{TM}}$ where the $E_{\text{BN-TM-G}}$, E_G, E_{BN} and E_{TM} are total energies of sandwich structures BN/TM/G, pure graphdiyne, BN-doped graphdiyne and single TM atoms, respectively.

E_b^2 is calculated as $E_b = E_{\text{TM-G}} - E_G - E_{\text{TM}}$ where $E_{\text{TM-G}}$, E_G and E_{TM} are total energies of graphdiyne with TM atom adsorption, pure graphdiyne and single TM atoms, respectively.

Table S2. Calculated results for the N_2 adsorption on the BN-TM-G, including the N_2 adsorption energies (E_{ads}), the N_2 adsorption free energy ($\Delta G(*N_2)$) and the N−N bond length (d_{N-N}).

BN-TM-G	E_{ads} (eV)	$\Delta G(*N_2)$ (eV)	d_{N-N} (Å)
BN-Sc-G	-0.45	-0.10	1.116
BN-Ti-G	-0.49	-0.12	1.115
BN-V-G	-0.53	-0.13	1.115
BN-Cr-G	-0.45	-0.05	1.116
BN-Mn-G	-0.47	-0.03	1.114
BN-Fe-G	-0.49	-0.16	1.116
BN-Co-G	-0.50	-0.13	1.115
BN-Ni-G	-0.43	-0.05	1.114
BN-Cu-G	-0.44	-0.06	1.115

Table S3. Total energy (E_{tot}), zero-potential correction energy (E_{zpe}), entropy contribution (TS, $T = 298.15$ K) of free molecules from NIST database.

Speciese	E_{tot} (eV)	E_{zpe} (eV)	TS (eV)
$H_2(g)$	-6.67	0.27	0.40
$N_2(g)$	-16.32	0.14	0.59
$NH_3(g)$	-19.73	0.60	0.89

Table S4. Total energy (E_{tot}), zero-potential correction energy (E_{zpe}) and entropy contribution (*TS*, $T = 298.15$ K) of the optimized intermediates for N_2 electroreduction to NH_3 on the BN-Sc-G.

BN-Sc-G	E_{tot} (eV)	E_{zpe} (eV)	*TS* (eV)
*N_2	-839.432	0.17	0.27
*NNH	-842.589	0.50	0.17
*NNH_2	-846.311	0.82	0.16
*NNH_3	-850.145	1.20	0.13
*NH	-834.485	0.37	0.07
*NH_2	-840.676	0.73	0.07
*NH_3	-843.606	1.07	0.07
*NHNH	-846.797	0.83	0.14
*$NHNH_2$	-851.332	1.17	0.19
*NH_2NH_2	-854.741	1.55	0.16
*NH_2NH_3	-860.310	1.67	0.28

Table S5. Total energy (E_{tot}), zero-potential correction energy (E_{zpe}) and entropy contribution (TS, T = 298.15 K) of the optimized intermediates for N_2 electroreduction to NH_3 on the BN-Ti-G.

BN-Ti-G	E_{tot} (eV)	E_{zpe} (eV)	TS (eV)
*N_2	-839.825	0.16	0.24
*NNH	-842.952	0.52	0.13
*NNH_2	-846.923	0.84	0.14
*NNH_3	-850.703	1.20	0.12
*NH	-834.866	0.37	0.07
*NH_2	-840.732	0.73	0.07
*NH_3	-844.197	1.08	0.07
*NHNH	-847.259	0.84	0.14
*$NHNH_2$	-851.496	1.20	0.16
*NH_2NH_2	-854.757	1.55	0.18
*NH_2NH_3	-860.424	1.68	0.20

Table S6. Total energy (E_{tot}), zero-potential correction energy (E_{zpe}) and entropy contribution (TS, T = 298.15 K) of the optimized intermediates for N_2 electroreduction to NH_3 on the BN-V-G.

BN-V-G	E_{tot} (eV)	E_{zpe} (eV)	TS (eV)
*N_2	-839.452	0.17	0.22
*NNH	-842.571	0.50	0.11
*NNH_2	-846.733	0.83	0.15
*NNH_3	-849.921	1.18	0.12
*NH	-834.696	0.36	0.08
*NH_2	-840.579	0.74	0.07
*NH_3	-843.342	1.08	0.09
*NHNH	-847.020	0.84	0.14
*$NHNH_2$	-851.759	1.19	0.14
*NH_2NH_2	-854.520	1.54	0.18
*NH_2NH_3	-860.393	1.67	0.20

Table S7. Total energy (E_{tot}), zero-potential correction energy (E_{zpe}) and entropy contribution (TS, T = 298.15 K) of the optimized intermediates for N_2 electroreduction to NH_3 on the BN-Cr-G.

BN-Cr-G	E_{tot} (eV)	E_{zpe} (eV)	TS (eV)
*N_2	-839.426	0.17	0.22
*NNH	-842.584	0.50	0.16
*NNH_2	-846.579	0.83	0.15
*NNH_3	-850.438	1.20	0.14
*NH	-834.878	0.37	0.07
*NH_2	-840.736	0.73	0.08
*NH_3	-843.873	1.08	0.08
*NHNH	-846.895	0.84	0.14
*$NHNH_2$	-851.459	1.17	0.14
*NH_2NH_2	-854.654	1.53	0.17
*NH_2NH_3	-860.483	1.68	0.25

Table S8. Total energy (E_{tot}), zero-potential correction energy (E_{zpe}) and entropy contribution (TS, T = 298.15 K) of the optimized intermediates for N_2 electroreduction to NH_3 on the BN-Mn-G.

BN-Mn-G	E_{tot} (eV)	E_{zpe} (eV)	TS (eV)
*N_2	-839.668	0.16	0.17
*NNH	-842.445	0.50	0.16
*NNH_2	-846.249	0.83	0.11
*NNH_3	-849.710	1.18	0.17
*NH	-834.086	0.34	0.09
*NH_2	-840.192	0.73	0.07
*NH_3	-843.658	1.06	0.08
*NHNH	-846.968	0.84	0.14
*$NHNH_2$	-851.510	1.19	0.14
*NH_2NH_2	-855.038	1.54	0.18
*NH_2NH_3	-860.156	1.67	0.26
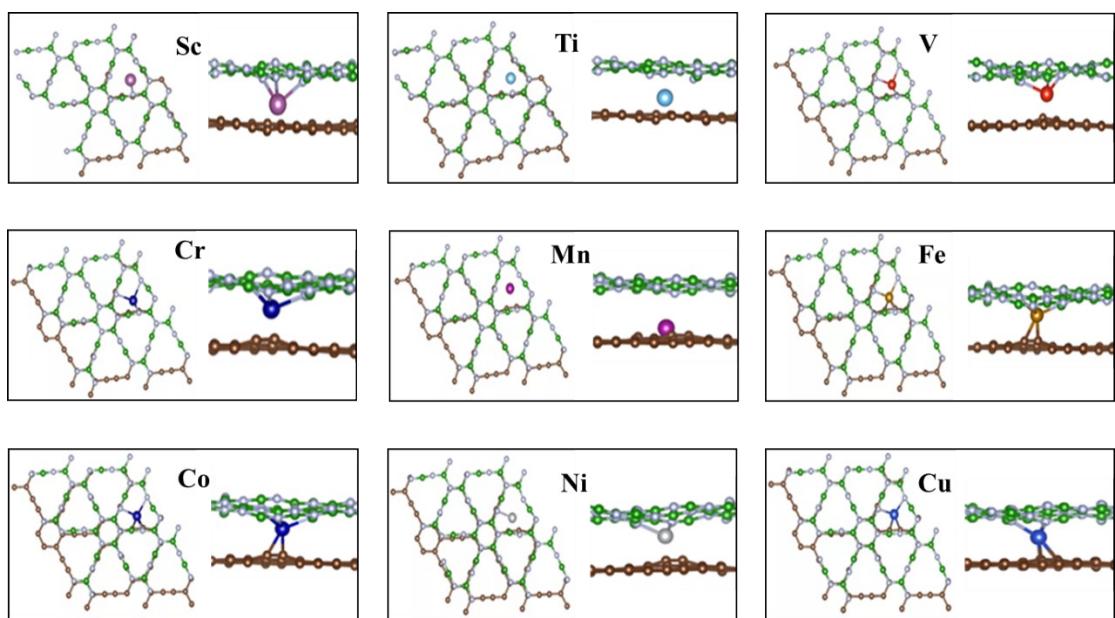
Figure S1. Top and side views of geometrical structures of BN-TM-G.
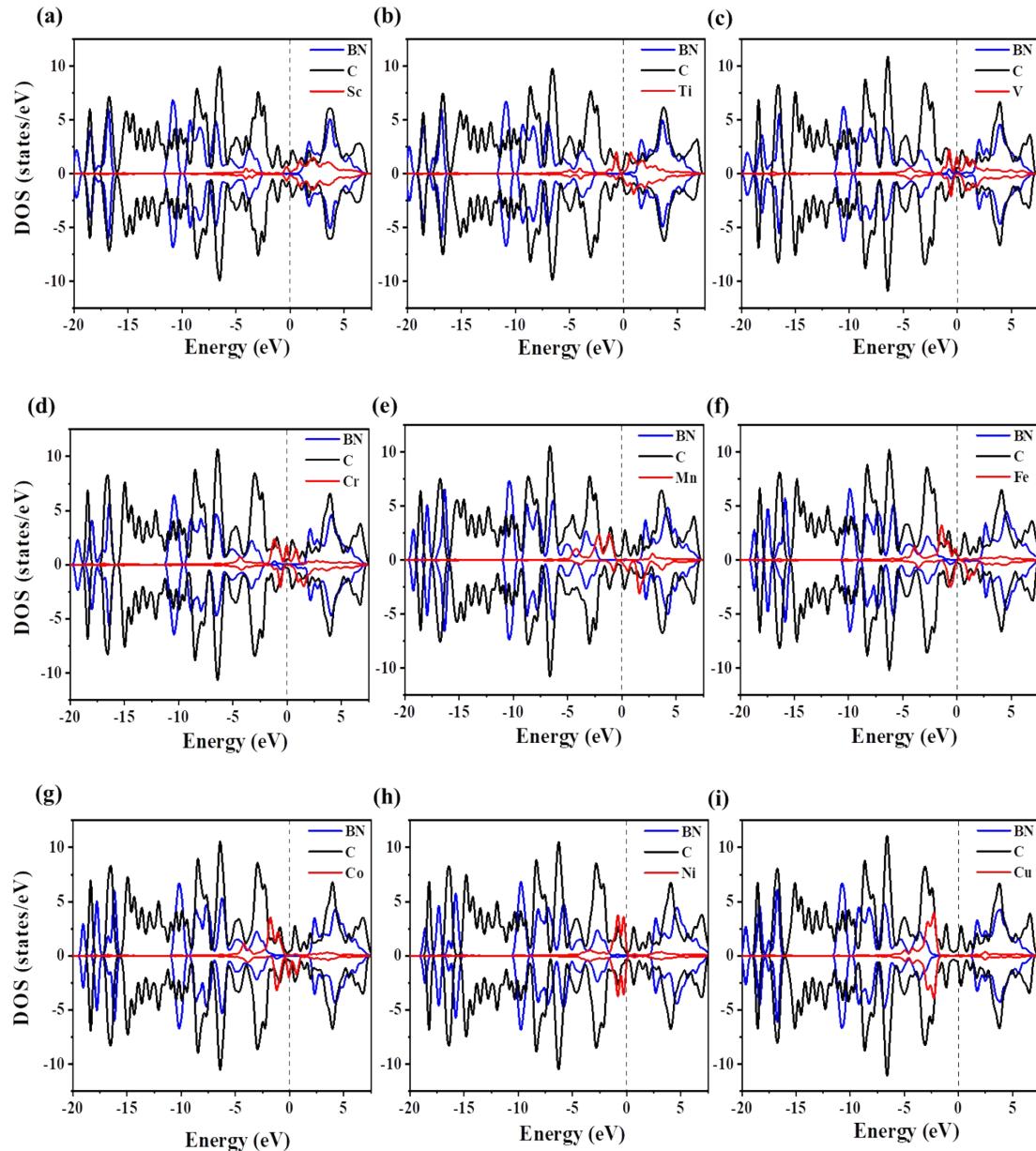
Figure S2. The calculated density of states of : (a) BN-Sc-G, (b) BN-Ti-G, (c) BN-V-G, (d) BN-Cr-G, (e) BN-Mn-G, (f) BN-Fe-G, (g) BN-Co-G, (h) BN-Ni-G and (i) BN-Cu-G. The Fermi level is set as zero in dotted lines.
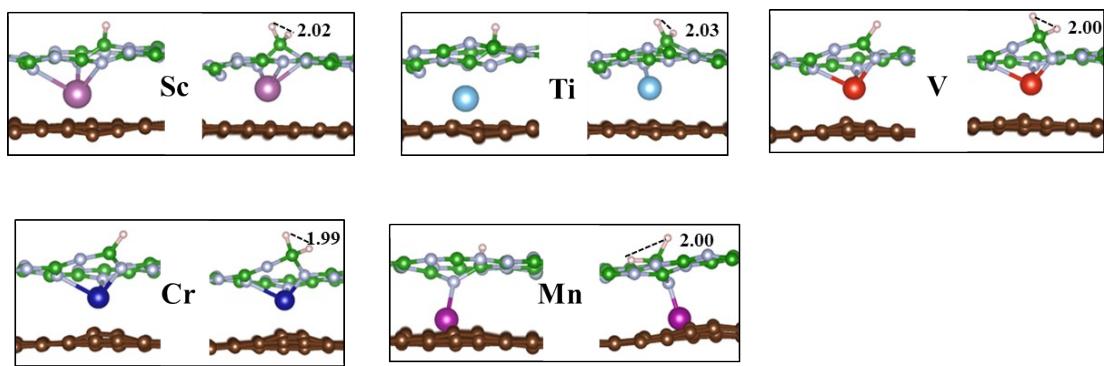
Figure S3. Optimized structures for the adsorption of one H atom and two H atoms on BN-TM-G.
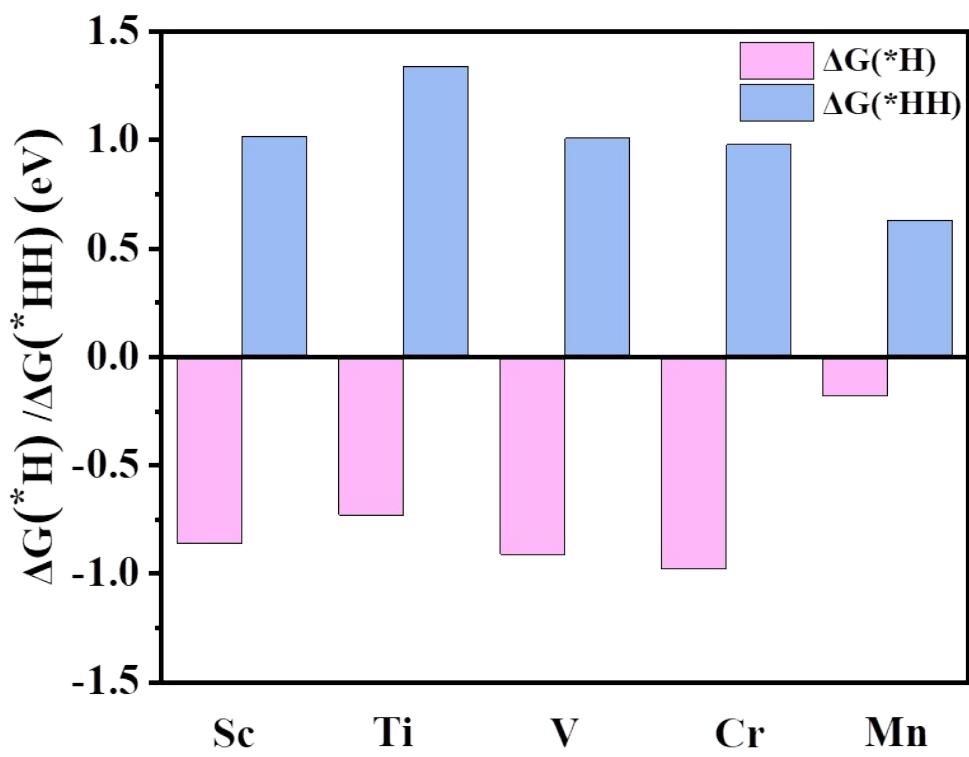

Figure S4. Calculated adsorption free energies for the first H atoms (ΔG(*H) in eV) and the second H atoms (ΔG(*HH) in eV) on the BN/Sc/G, BN/Ti/G, BN/V/G, BN/Cr/G and BN/Mn/G catalysts.