Supporting Information for

Tailoring the coordination environment of double-atom catalyst to boost electrocatalytic nitrogen reduction: a first-principles study

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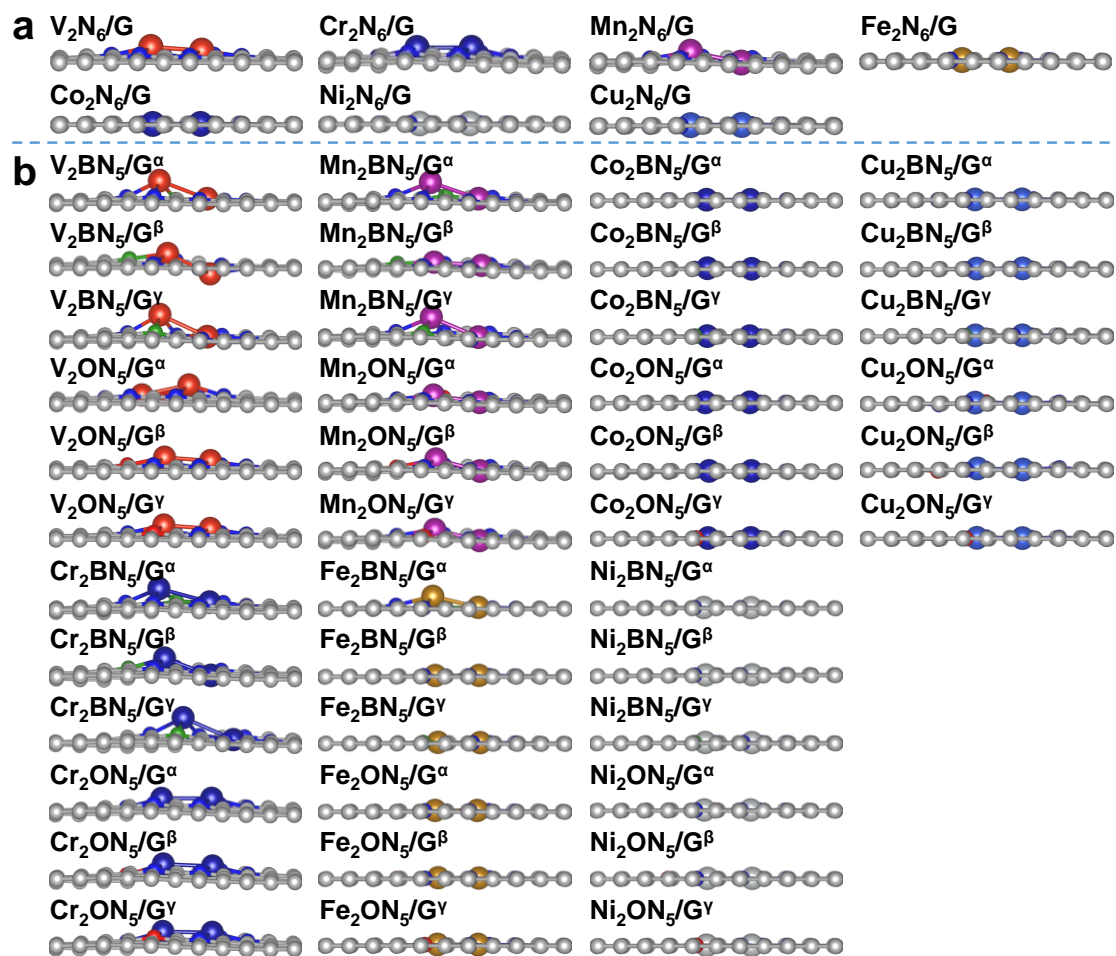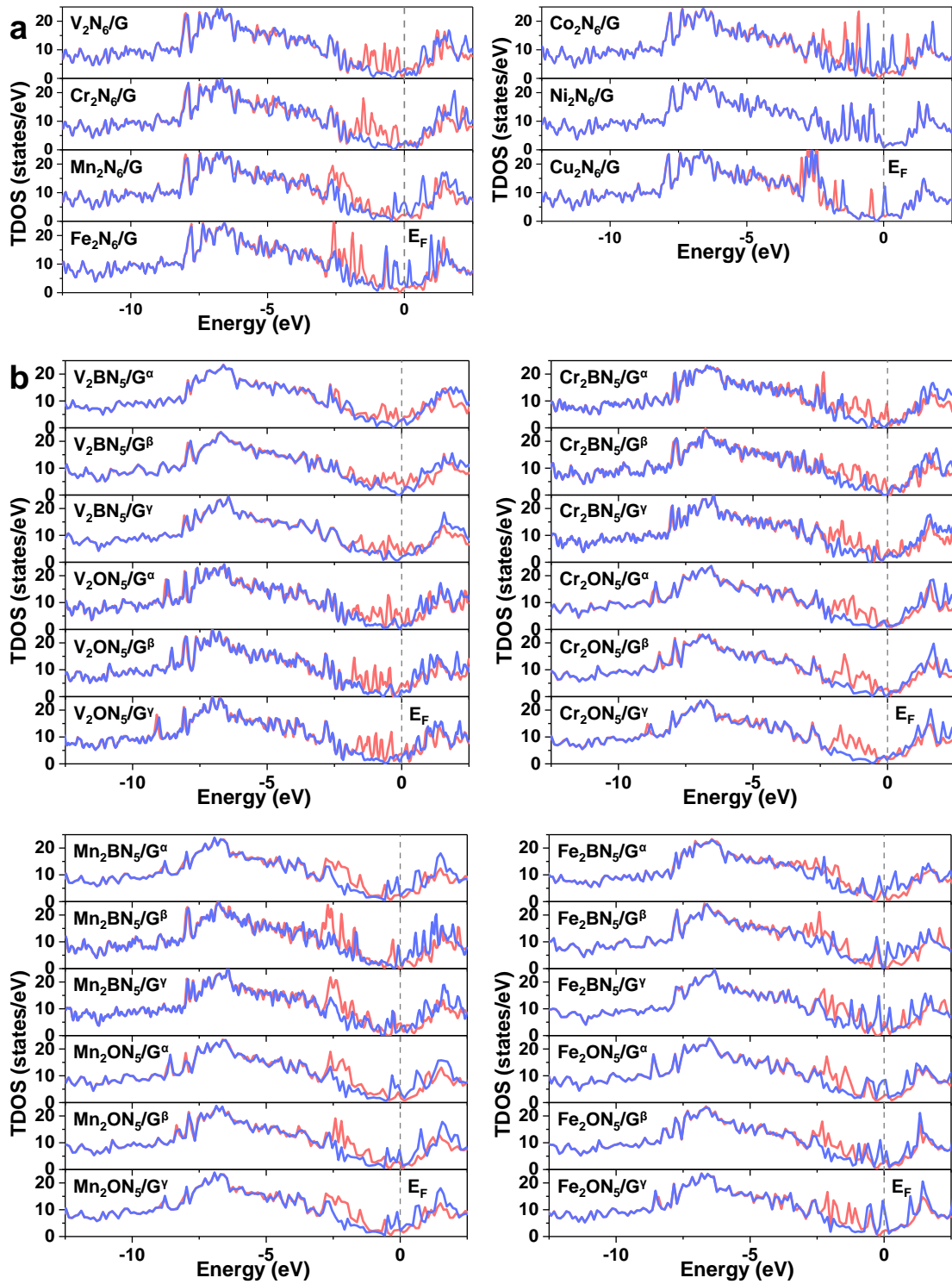
a

V$_2$N$_6$/G   Cr$_2$N$_6$/G   Mn$_2$N$_6$/G   Fe$_2$N$_6$/G

Co$_2$N$_6$/G   Ni$_2$N$_6$/G   Cu$_2$N$_6$/G

b

V$_2$BN$_5$/G$^\alpha$ Mn$_2$BN$_5$/G$^\alpha$ Co$_2$BN$_5$/G$^\alpha$ Cu$_2$BN$_5$/G$^\alpha$

V$_2$BN$_5$/G$^\beta$ Mn$_2$BN$_5$/G$^\beta$ Co$_2$BN$_5$/G$^\beta$ Cu$_2$BN$_5$/G$^\beta$

V$_2$BN$_5$/G$^\gamma$ Mn$_2$BN$_5$/G$^\gamma$ Co$_2$BN$_5$/G$^\gamma$ Cu$_2$BN$_5$/G$^\gamma$

V$_2$ON$_5$/G$^\alpha$ Mn$_2$ON$_5$/G$^\alpha$ Co$_2$ON$_5$/G$^\alpha$ Cu$_2$ON$_5$/G$^\alpha$

V$_2$ON$_5$/G$^\beta$ Mn$_2$ON$_5$/G$^\beta$ Co$_2$ON$_5$/G$^\beta$ Cu$_2$ON$_5$/G$^\beta$

V$_2$ON$_5$/G$^\gamma$ Mn$_2$ON$_5$/G$^\gamma$ Co$_2$ON$_5$/G$^\gamma$ Cu$_2$ON$_5$/G$^\gamma$

Cr$_2$BN$_5$/G$^\alpha$ Fe$_2$BN$_5$/G$^\alpha$ Ni$_2$BN$_5$/G$^\alpha$

Cr$_2$BN$_5$/G$^\beta$ Fe$_2$BN$_5$/G$^\beta$ Ni$_2$BN$_5$/G$^\beta$

Cr$_2$BN$_5$/G$^\gamma$ Fe$_2$BN$_5$/G$^\gamma$ Ni$_2$BN$_5$/G$^\gamma$

Cr$_2$ON$_5$/G$^\alpha$ Fe$_2$ON$_5$/G$^\alpha$ Ni$_2$ON$_5$/G$^\alpha$

Cr$_2$ON$_5$/G$^\beta$ Fe$_2$ON$_5$/G$^\beta$ Ni$_2$ON$_5$/G$^\beta$

Cr$_2$ON$_5$/G$^\gamma$ Fe$_2$ON$_5$/G$^\gamma$ Ni$_2$ON$_5$/G$^\gamma$

Fig. S1. Optimized configurations of the studied M$_2$N$_6$/G (a) and M$_2$B(O)N$_5$/G (b) DACs. The larger colorized balls denote TM atoms, and the small silver, blue, red, green balls represent C, N, O, and B atoms, respectively.
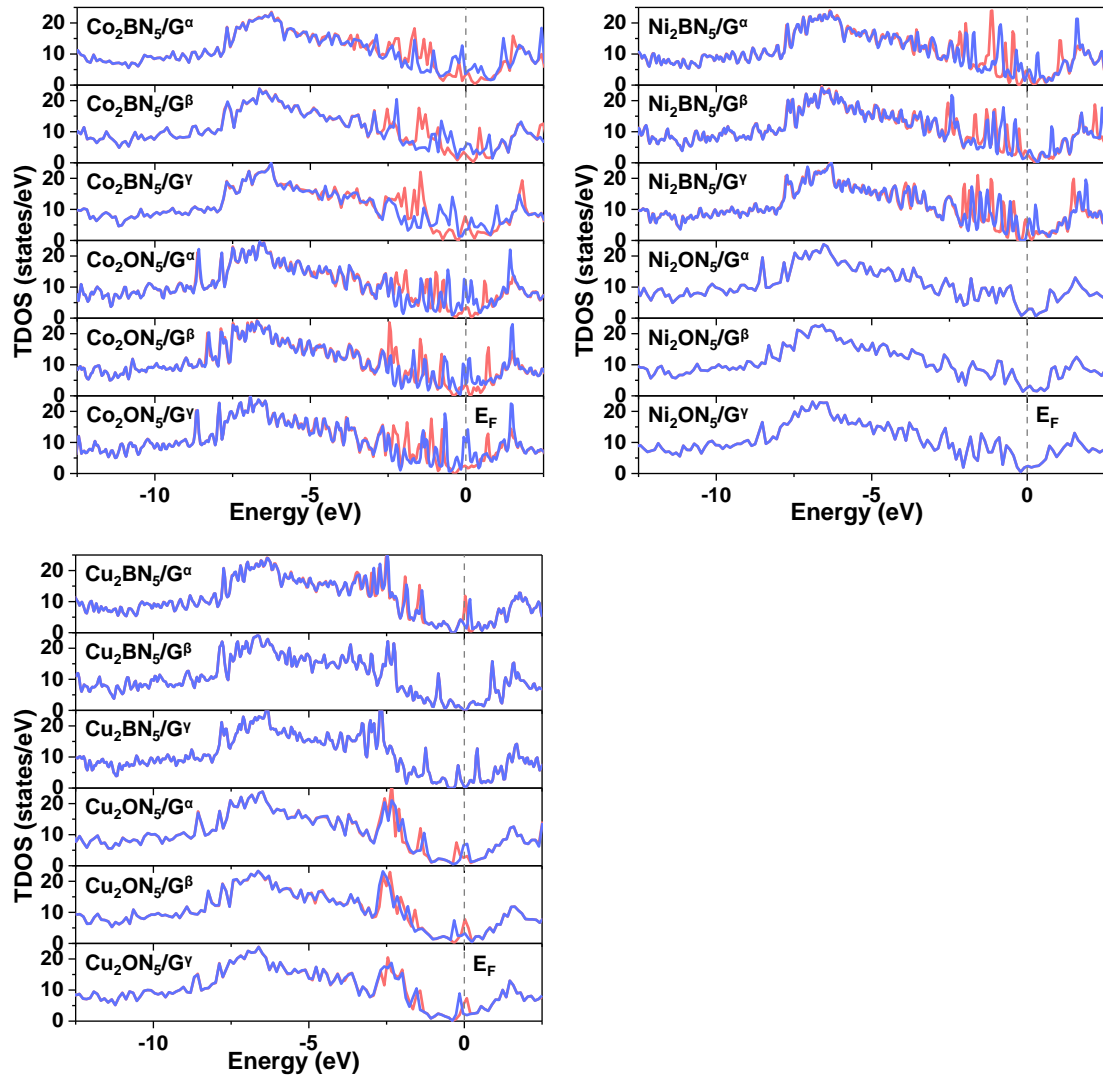
Fig. S2. The calculated total density of states (TDOS) of the studied M_2N_6/G (a) and $M_2B(O)N_5/G$ (b) DACs. The red and blue lines denote the spin-up and spin-down states, respectively. The vertical dashed lines represent Fermi level (E_F), which are set to 0 eV.
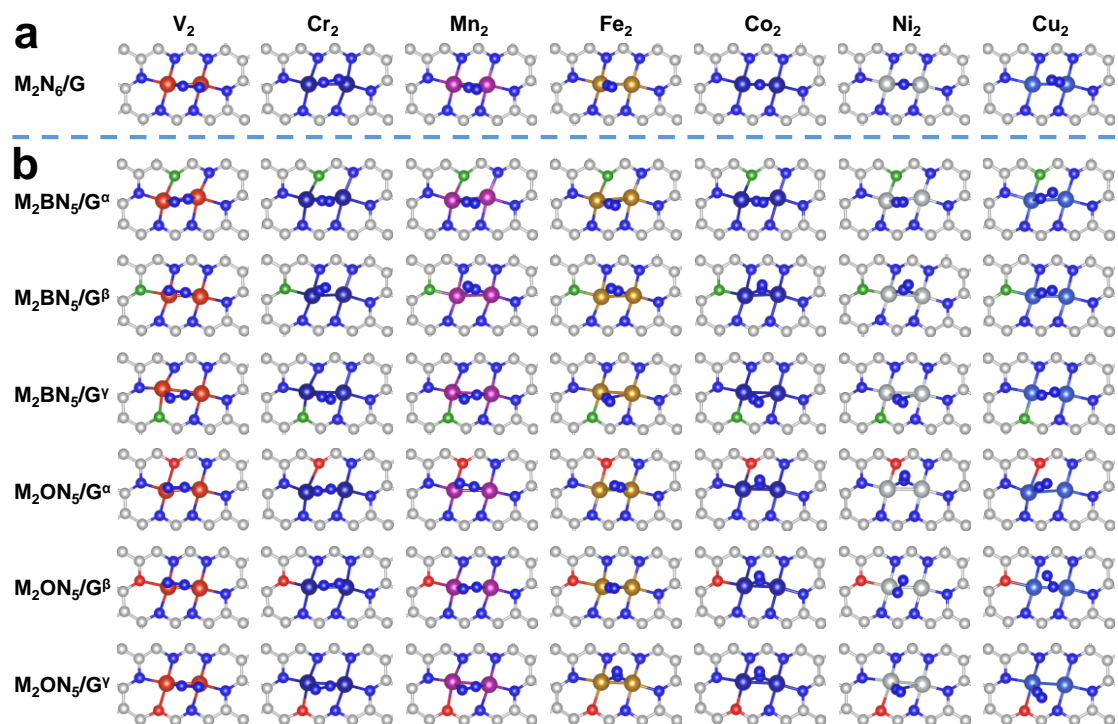
Fig. S3. Optimized configurations of the most favorable models for $*N_2$ adsorption on the studied M_2N_6/G (a) and $M_2B(O)N_5/G$ (b) DACs. The larger colorized balls denote TM atoms, and the small silver, blue, red, green balls represent C, N, O, and B atoms, respectively.
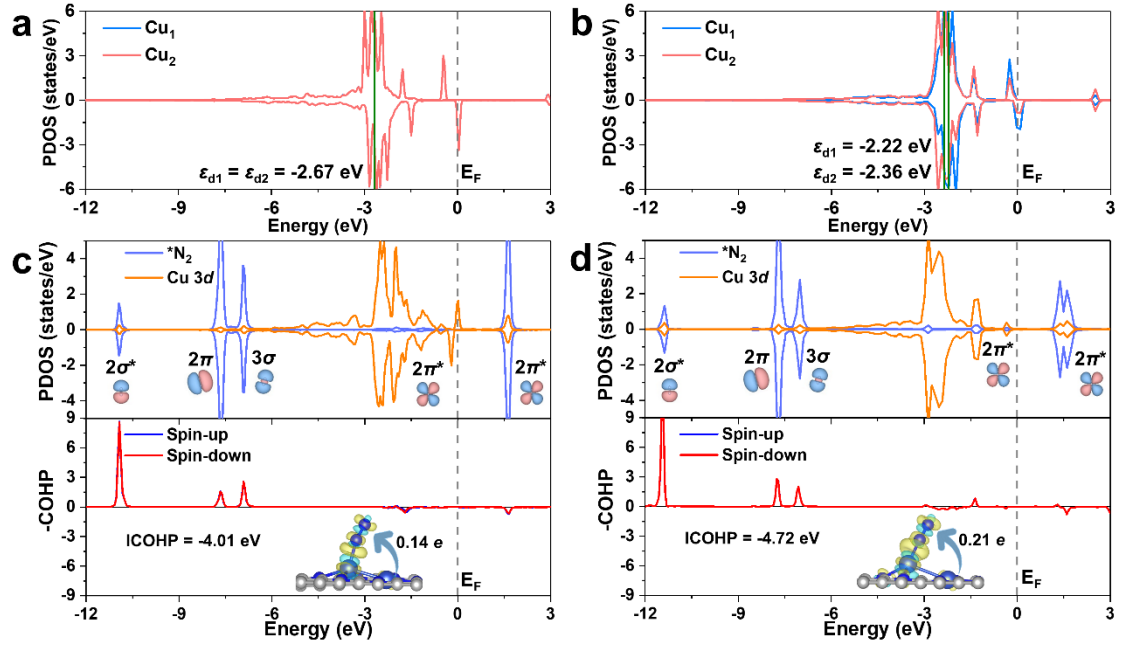
Fig. S4. Projected density of states (PDOS) and d-band center (ε_d) of the $3d$ orbitals of Cu atoms for Cu_2N_6/G (a) and Cu_2ON_5/G^α (b). In (b), Cu_1 denotes the Cu atom co-coordinated with O and N atoms, and Cu_2 is another Cu atom. The positive and negative PDOS denote the spin-up and spin-down states, respectively. PDOS for the molecular orbitals of $*N_2$ and the $3d$ orbitals of its bonded Cu atom (top panels) and the corresponding COHP (lower panels) for $*N_2$ adsorbed Cu_2N_6/G (c) and Cu_2ON_5/G^α (d). Insets in the lower panels are the charge density difference (CDD) plots, where the yellow and cyan regions denote electron accumulation and depletion, respectively, with an isosurface of 0.002 e/bohr^3. The vertical green and grey lines represent ε_d and E_F, respectively.
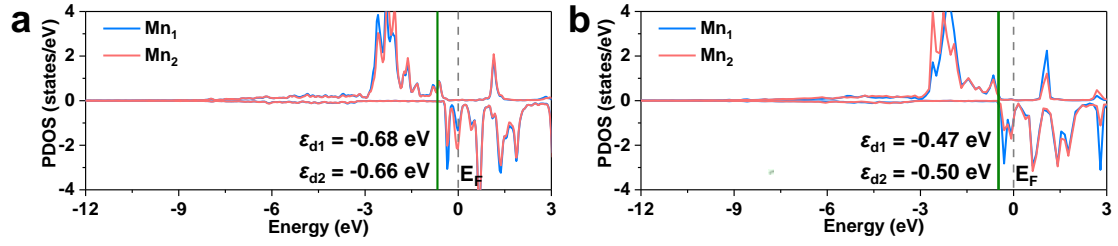
Fig. S5. PDOS and ε_d of $3d$ orbitals of the Mn atoms for Mn_2N_6/G (a) and Mn_2ON_5/G^{α} (b). In (b), Mn_1 denotes the Mn atom co-coordinated with O and N atoms, and Mn_2 is another Mn atom. The positive and negative PDOS denote the spin-up and spin-down states, respectively. The vertical green and grey lines represent ε_d and E_F, respectively.
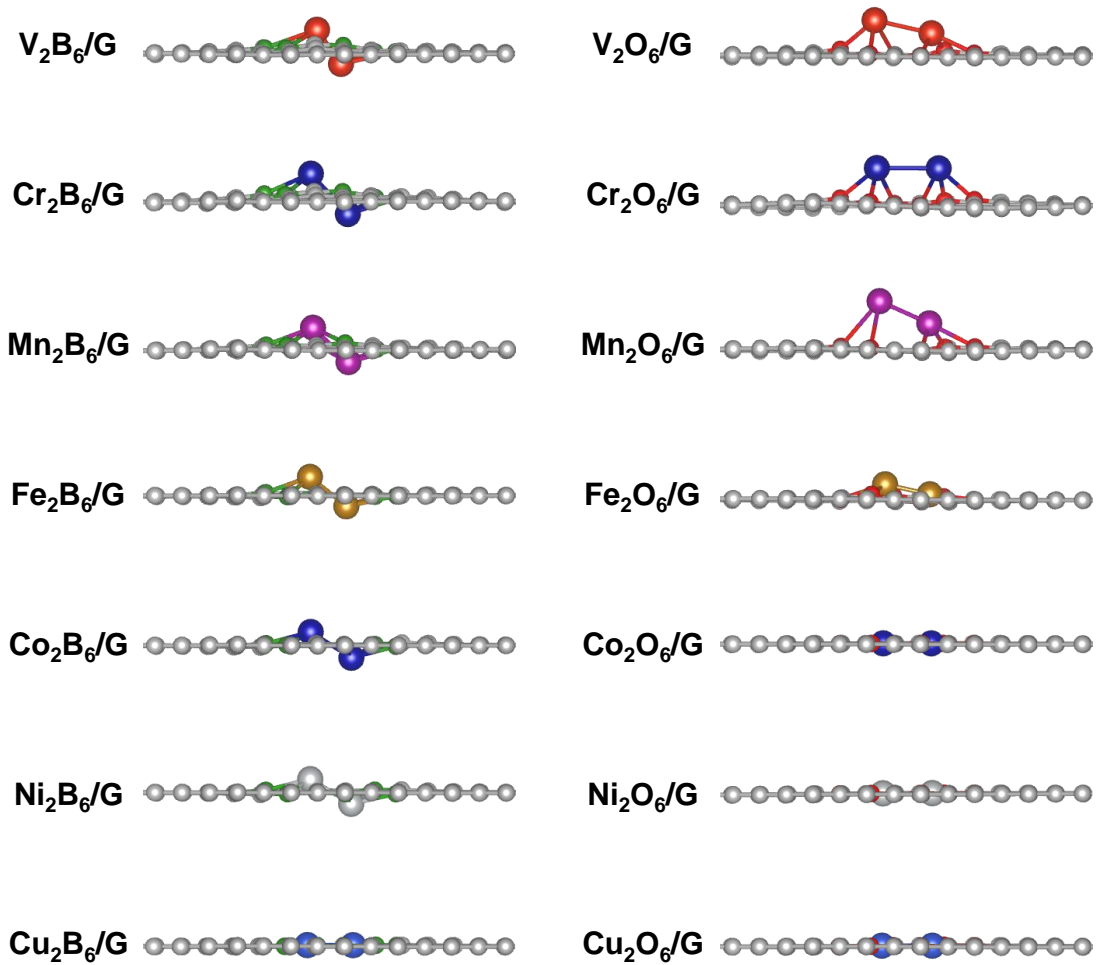
Fig. S6. Optimized configurations of the M_2B_6/G and M_2O_6/G DACs. The larger colorized balls denote TM atoms, and the small silver, red, and green balls represent C, O, and B atoms, respectively.

Fig. S7. Optimized intermediate configurations and corresponding free energy change (ΔG) for the first hydrogenation step (*N_2 + H^+ + e^- → *N_2H) and last hydrogenation step (*NH_2 + H^+ + e^- → *NH_3) during the NRR process on the M_2B_6/G DACs. The larger colorized balls denote TM atoms, and the small silver, blue, green, and pink balls represent C, N, B, and H atoms, respectively.
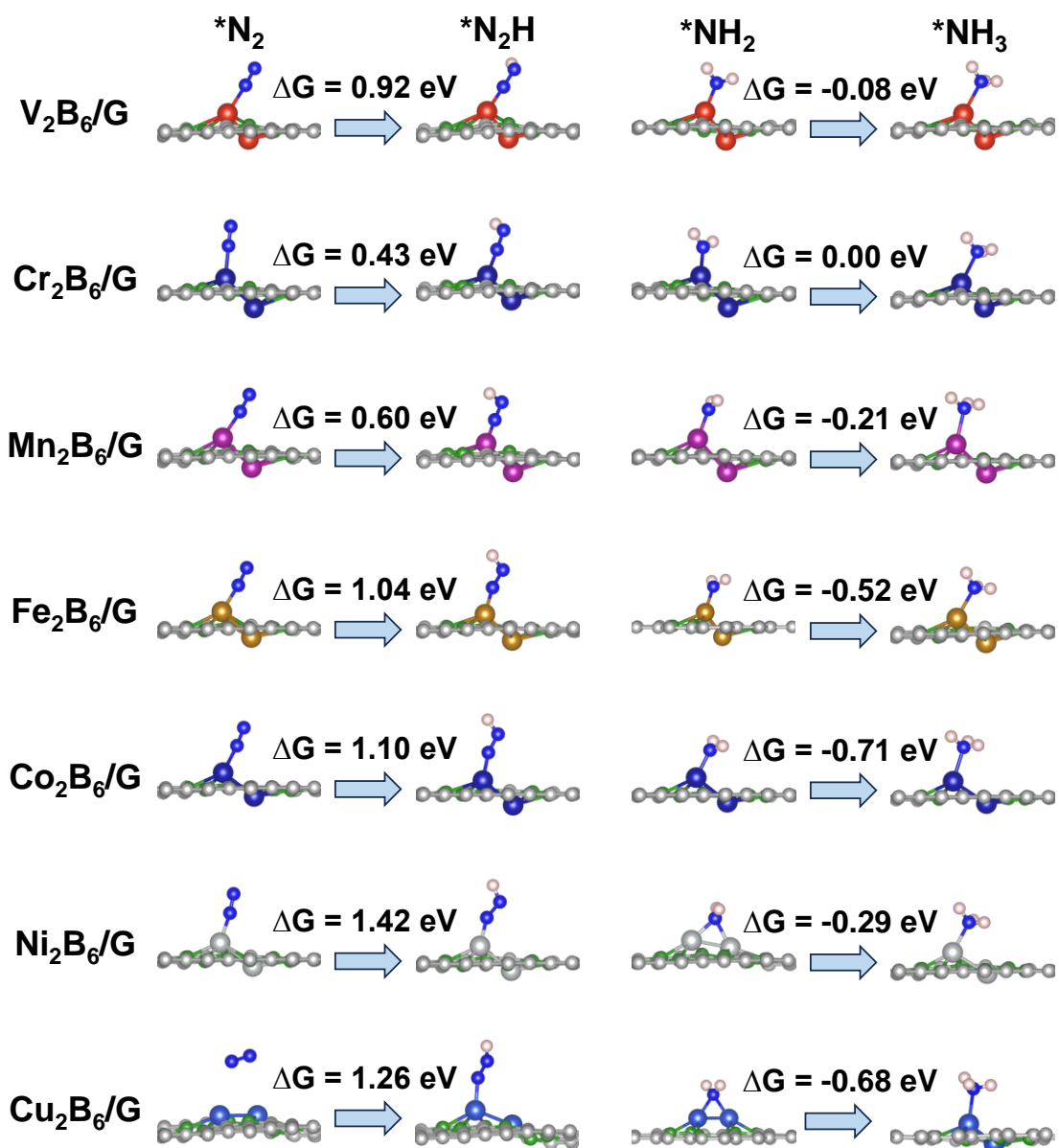
Fig. S8. Optimized intermediate configurations and corresponding free energy change (ΔG) for the first hydrogenation step (*N$_2$ + H$^+$ + e^- → *N$_2$H) and last hydrogenation step (*NH$_2$ + H$^+$ + e^- → *NH$_3$) during the NRR process on the M$_2$O$_6$/G DACs. The larger colorized balls denote TM atoms, and the small silver, blue, red, and pink balls represent C, N, O, and H atoms, respectively.

	Mn$_2$N$_6$/G	Mn$_2$ON$_5$/G	Mn$_2$O$_2$N$_4$/G	Mn$_2$O$_3$N$_3$/G	Mn$_2$O$_4$N$_2$/G	Mn$_2$O$_5$N/G	Mn$_2$O$_6$/G
a	▦	▦	▦	▦	▦	▦	▦
b		▦	▦	▦	▦	▦	
c		▦	▦	▦	▦	▦	
d			▦	▦	▦		
e			▦	▦	▦		
f			▦	▦	▦		
g			▦	▦	▦		
h			▦	▦	▦		
i			▦	▦	▦		
j				▦			

Fig. S9. Optimized configurations of the Mn$_2$O$_x$N$_{6-x}$/G (x=0-6) DACs. The larger colorized balls denote TM atoms, and the small silver, blue, and red balls represent C, N, and O atoms, respectively.

Fig. S10. Optimized intermediate configurations and corresponding free energy change (ΔG) for the first hydrogenation step (*N_2 + H^+ + e^- → *N_2H) and last hydrogenation step (*NH_2 + H^+ + e^- → *NH_3) during the NRR process on the $Mn_2O_2N_4$/G DACs. The larger colorized balls denote TM atoms, and the small silver, blue, red, and pink balls represent C, N, O, and H atoms, respectively.
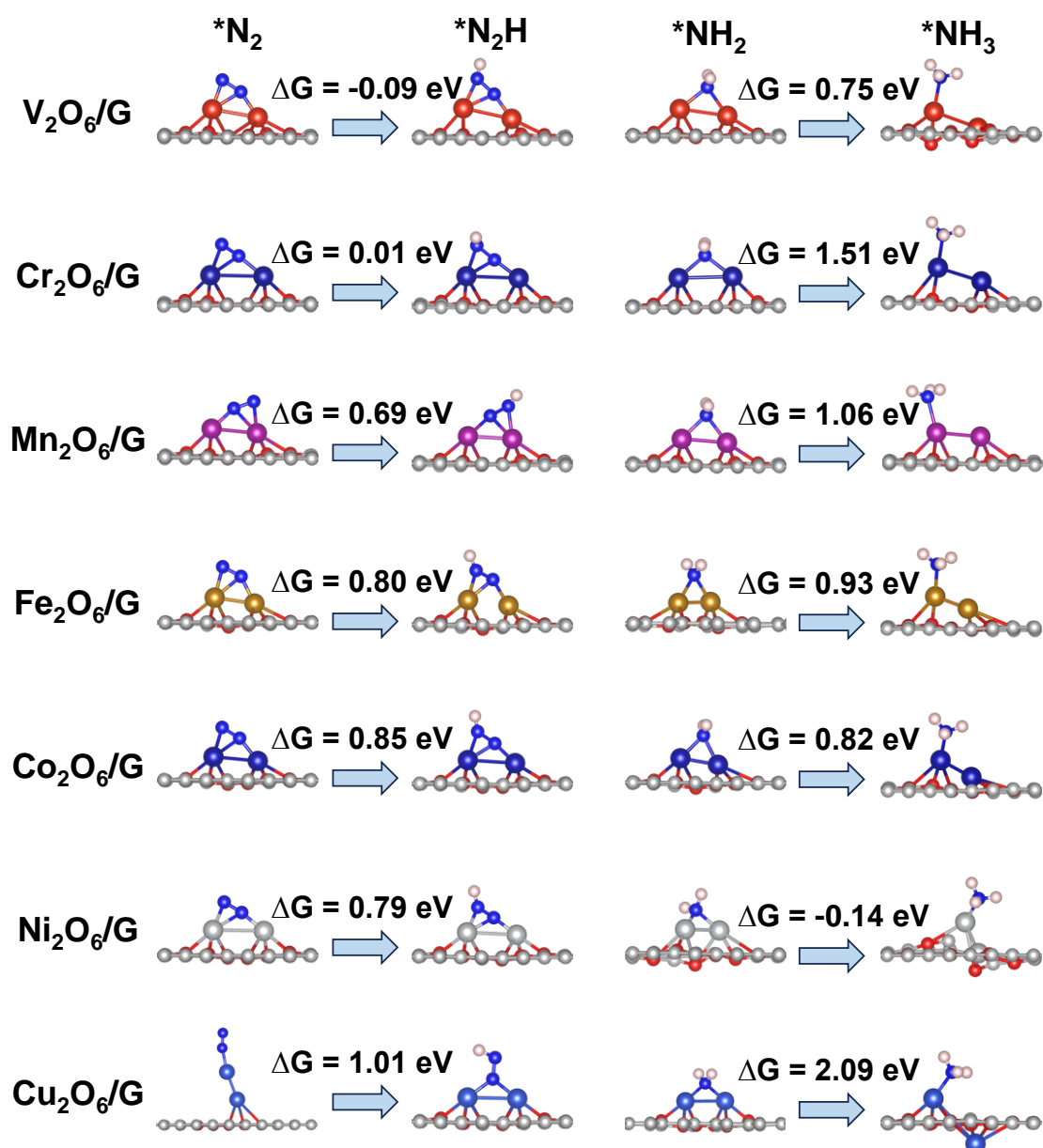
Fig. S11. Optimized intermediate configurations and corresponding free energy change (ΔG) for the first hydrogenation step (*N_2 + H^+ + e^- → *N_2H) and last hydrogenation step (*NH_2 + H^+ + e^- → *NH_3) during the NRR process on the $Mn_2O_3N_3$/G DACs. The larger colorized balls denote TM atoms, and the small silver, blue, red, and pink balls represent C, N, O, and H atoms, respectively.
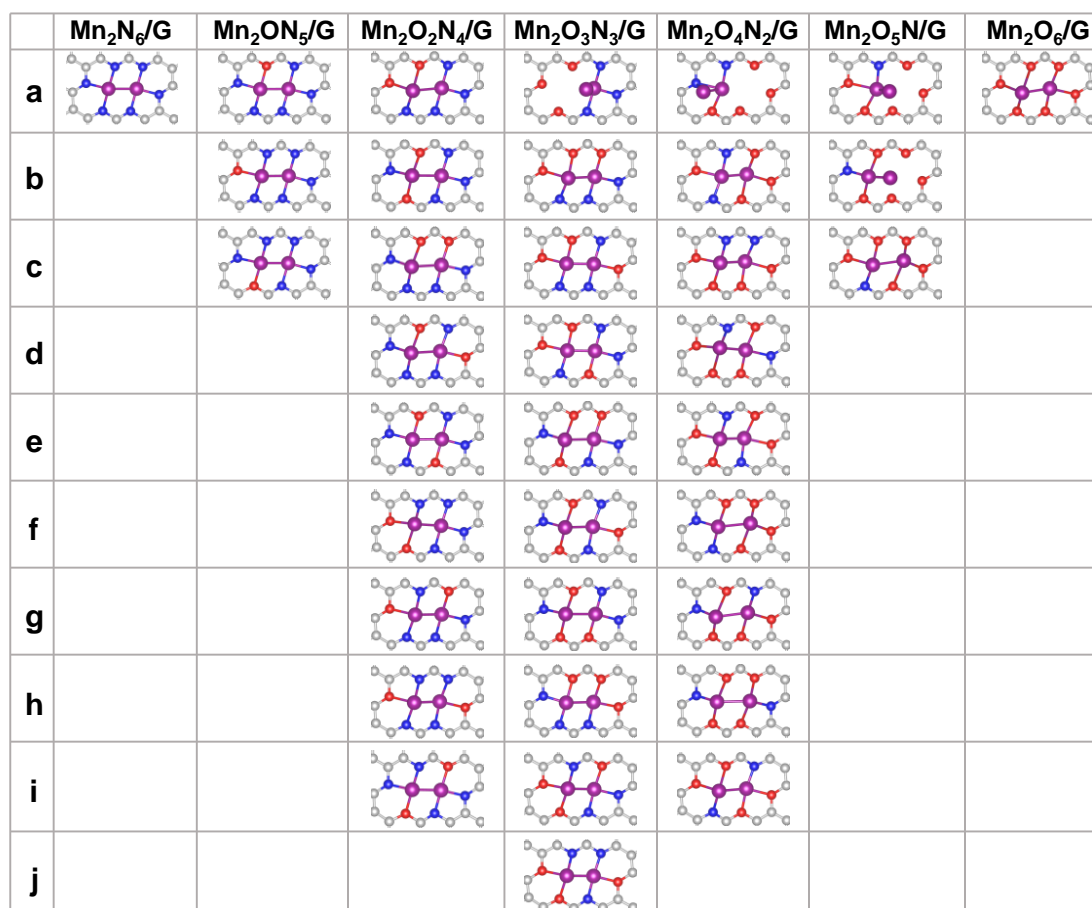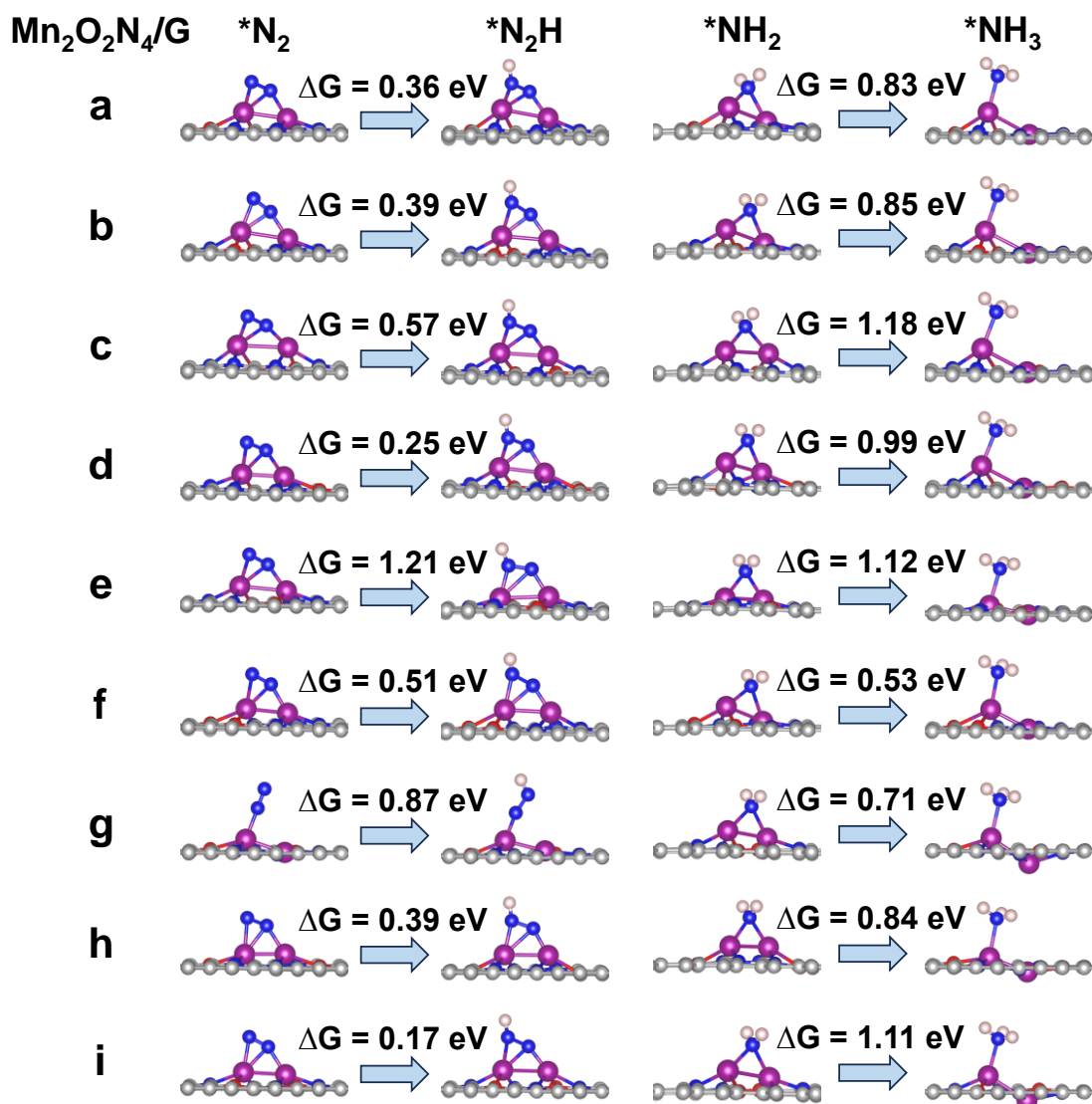
Fig. S12. Optimized intermediate configurations and corresponding free energy change (ΔG) for the first hydrogenation step (*N_2 + H^+ + e^- → *N_2H) and last hydrogenation step (*NH_2 + H^+ + e^- → *NH_3) during the NRR process on the $Mn_2O_4N_2$/G and Mn_2O_5N/G DACs. The larger colorized balls denote TM atoms, and the small silver, blue, red, and pink balls represent C, N, O, and H atoms, respectively.
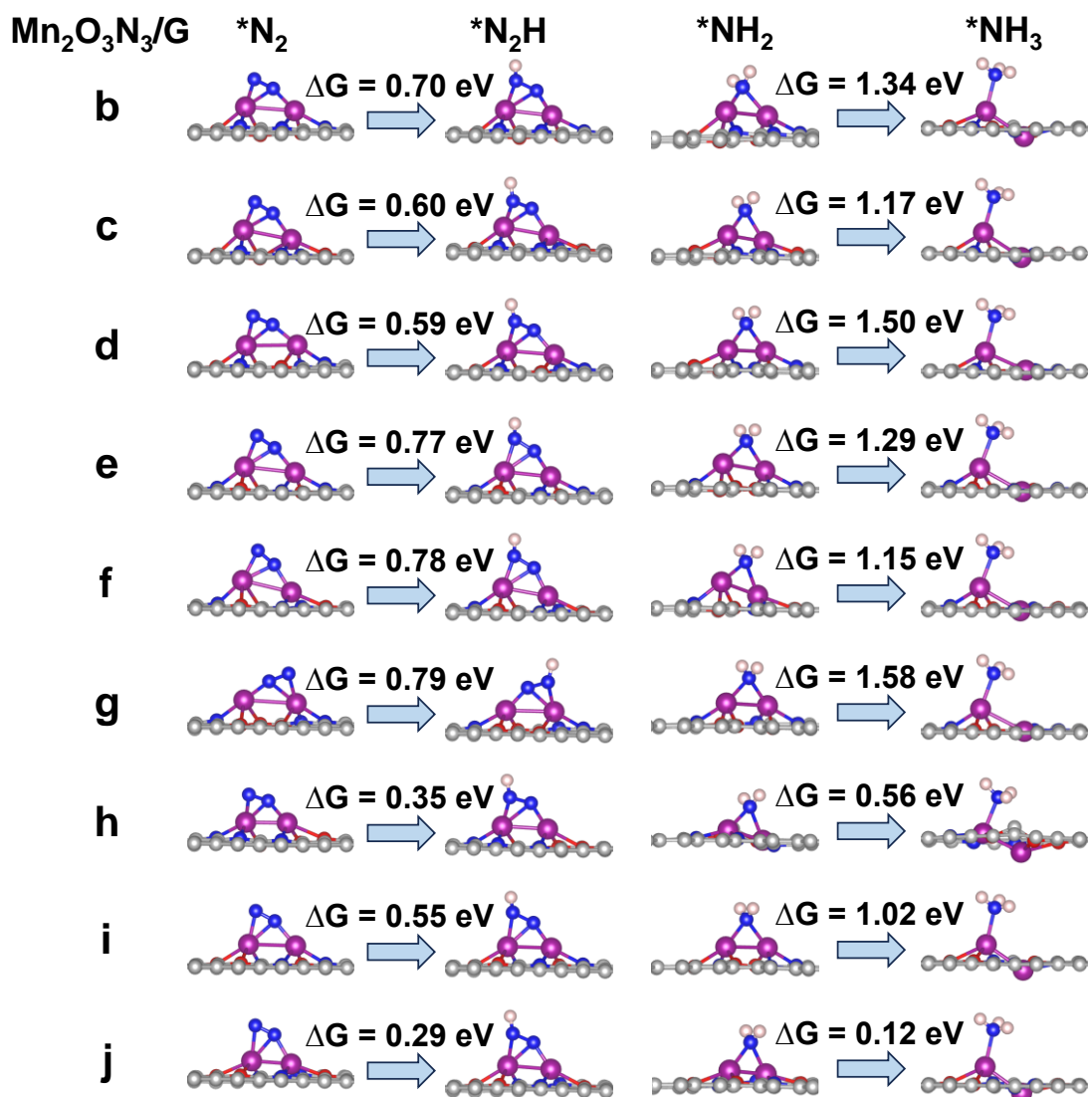
Table S1. The calculated zero-point energy (E_{ZPE} in eV) and the product (*TS* in eV) of the temperature (298.15 K) and entropy for the various intermediates during the NRR process.

Species	E_{ZPE}	*TS*
*N-*N	0.17	0.14
*N-*NH	0.47	0.08
*NH-*NH	0.79	0.11
*NH*NH$_2$	1.13	0.14
*NH$_2$*NH$_2$	1.50	0.15
*NH$_2$*NH$_3$	1.68	0.25
* NH$_2$	0.66	0.09
*N-N	0.22	0.16
*N-NH	0.47	0.10
*N-NH$_2$	0.85	0.13
*N-NH$_3$	1.03	0.12
*N	0.10	0.03
*NH	0.37	0.05

Table S2. The zero-point energy (E_{ZPE} in eV) and the product (TS in eV) of the temperature (298.15 K) and entropy for the free H_2, N_2, and NH_3 molecules.

Species	E_{ZPE}	TS
H_2	0.27	0.41
N_2	0.15	0.58
NH_3	0.89	0.60

Table S3. Key parameters of the studied M_2N_6/G and M_2BN_5/G DACs, including the bond length between two TM atoms ($d_{M1\text{-}M2}$, in Å); spin magnetic moment of the TM atom bonded with B atom (M_1, in μ_B) and another TM atom (M_2, in μ_B); the net charge of the TM atom bonded with B atom (Q_1, in e) and another TM atom (Q_2, in e), where the positive value means the electrons transfer from the metals to the supports; and the d-band center of the TM atom bonded with the B atom (ε_{d1}, in eV) and another TM atom (ε_{d2}, in eV).

Systems	$d_{M1\text{-}M2}$	M_1	M_2	Q_1	Q_2	ε_{d1}	ε_{d2}
V_2N_6/G	**2.42**	**3.04**	**3.04**	**1.06**	**1.06**	**0.43**	**0.43**
V_2BN_5/G^α	2.64	2.48	2.22	1.05	1.17	0.33	0.24
V_2BN_5/G^β	2.44	2.47	2.93	0.93	1.10	0.55	0.48
V_2BN_5/G^γ	2.69	2.33	2.94	0.89	1.14	0.38	0.53
Cr_2N_6/G	**2.57**	**4.17**	**4.17**	**1.00**	**1.00**	**0.33**	**0.33**
Cr_2BN_5/G^α	2.72	3.72	3.67	0.98	1.10	0.24	0.35
Cr_2BN_5/G^β	2.55	3.66	3.90	0.76	1.10	0.66	0.04
Cr_2BN_5/G^γ	2.83	3.52	3.80	0.79	1.15	0.39	-0.09
Mn_2N_6/G	**2.44**	**3.41**	**3.59**	**0.96**	**0.98**	**-0.68**	**-0.66**
Mn_2BN_5/G^α	2.62	4.25	3.32	0.92	1.05	-0.55	-0.77
Mn_2BN_5/G^β	2.45	3.61	4.14	0.74	1.04	-0.57	-0.74
Mn_2BN_5/G^γ	2.62	3.67	3.68	0.69	1.03	-0.30	-0.69
Fe_2N_6/G	**2.22**	**2.34**	**2.34**	**0.83**	**0.83**	**-0.89**	**-0.89**
Fe_2BN_5/G^α	2.42	3.28	2.24	0.79	0.86	-1.35	-1.07
Fe_2BN_5/G^β	2.25	2.57	2.99	0.60	0.88	-1.03	-1.08
Fe_2BN_5/G^γ	2.18	1.79	1.78	0.57	0.81	-0.67	-0.71
Co_2N_6/G	**2.25**	**1.24**	**1.24**	**0.69**	**0.69**	**-1.14**	**-1.14**
Co_2BN_5/G^α	2.27	1.83	1.18	0.53	0.71	-1.05	-1.02
Co_2BN_5/G^β	2.30	1.03	0.52	0.43	0.71	-1.02	-1.10
Co_2BN_5/G^γ	2.20	1.42	1.51	0.44	0.68	-1.03	-1.07
Ni_2N_6/G	**2.37**	**0.00**	**0.00**	**0.60**	**0.60**	**-1.01**	**-1.01**
Ni_2BN_5/G^α	2.45	0.61	0.36	0.46	0.67	-1.08	-1.45
Ni_2BN_5/G^β	2.41	0.14	0.84	0.33	0.64	-1.11	-1.12
Ni_2BN_5/G^γ	2.41	0.30	0.62	0.32	0.63	-1.18	-1.32
Cu_2N_6/G	**2.40**	**0.25**	**0.25**	**0.70**	**0.70**	**-2.67**	**-2.67**
Cu_2BN_5/G^α	2.43	0.04	0.09	0.45	0.77	-2.68	-3.23
Cu_2BN_5/G^β	2.37	0.00	0.00	0.52	0.64	-3.53	-2.42
Cu_2BN_5/G_γ	2.43	0.00	0.00	0.44	0.71	-3.22	-2.98

Table S4. Key parameters of the studied M_2N_6/G and M_2ON_5/G DACs, including the bond length between two TM atoms ($d_{M1\text{-}M2}$, in Å); spin magnetic moment of the TM atom bonded with O atom (M_1, in μ_B) and another TM atom (M_2, in μ_B); the net charge of the TM atom bonded with O atom (Q_1, in e) and another TM atom (Q_2, in e), where the positive value means the electrons transfer from the metals to the supports; and the d-band center of the TM atom bonded with the O atom (ε_{d1}, in eV) and another TM atom (ε_{d2}, in eV).

Systems	$d_{M1\text{-}M2}$	M_1	M_2	Q_1	Q_2	ε_{d1}	ε_{d2}
V_2N_6/G	**2.42**	**3.04**	**3.04**	**1.06**	**1.06**	**0.43**	**0.43**
V_2ON_5/G$^\alpha$	2.49	3.23	3.19	1.02	0.99	0.41	0.51
V_2ON_5/G$^\beta$	2.39	3.29	3.02	1.02	1.08	0.25	0.25
V_2ON_5/G$^\gamma$	2.42	3.26	3.10	1.00	1.05	0.34	0.31
Cr_2N_6/G	**2.57**	**4.17**	**4.17**	**1.00**	**1.00**	**0.33**	**0.33**
Cr_2ON_5/G$^\alpha$	2.59	4.23	4.28	0.98	0.94	0.11	0.29
Cr_2ON_5/G$^\beta$	2.55	4.41	4.11	0.95	1.03	0.28	0.25
Cr_2ON_5/G$^\gamma$	2.56	4.33	4.17	0.96	0.99	0.12	0.16
Mn_2N_6/G	**2.44**	**3.41**	**3.59**	**0.96**	**0.98**	**-0.68**	**-0.66**
Mn_2ON_5/G$^\alpha$	2.41	3.27	3.51	0.89	0.91	-0.47	-0.50
Mn_2ON_5/G$^\beta$	2.35	3.63	3.16	0.88	0.96	-0.43	-0.48
Mn_2ON_5/G$^\gamma$	2.38	3.57	3.25	0.91	0.93	-0.63	-0.62
Fe_2N_6/G	**2.22**	**2.34**	**2.34**	**0.83**	**0.83**	**-0.89**	**-0.89**
Fe_2ON_5/G$^\alpha$	2.18	2.08	2.23	0.74	0.74	-0.78	-0.72
Fe_2ON_5/G$^\beta$	2.10	2.40	2.03	0.73	0.78	-0.80	-0.76
Fe_2ON_5/G$^\gamma$	2.10	2.17	1.96	0.70	0.74	-0.66	-0.60
Co_2N_6/G	**2.25**	**1.24**	**1.24**	**0.69**	**0.69**	**-1.14**	**-1.14**
Co_2ON_5/G$^\alpha$	2.31	1.01	1.25	0.66	0.63	-1.14	-1.05
Co_2ON_5/G$^\beta$	2.18	1.49	0.93	0.68	0.69	-1.26	-1.18
Co_2ON_5/G$^\gamma$	2.21	1.25	0.98	0.63	0.66	-1.17	-1.13
Ni_2N_6/G	**2.37**	**0.00**	**0.00**	**0.60**	**0.60**	**-1.01**	**-1.01**
Ni_2ON_5/G$^\alpha$	2.39	0.00	0.00	0.60	0.56	-1.34	-1.17
Ni_2ON_5/G$^\beta$	2.32	0.00	0.00	0.55	0.64	-1.10	-1.36
Ni_2ON_5/G$^\gamma$	2.33	0.00	0.00	0.57	0.60	-1.27	-1.35
Cu_2N_6/G	**2.40**	**0.25**	**0.25**	**0.70**	**0.70**	**-2.67**	**-2.67**
Cu_2ON_5/G$^\alpha$	2.42	0.17	0.07	0.66	0.64	-2.22	-2.36
Cu_2ON_5/G$^\beta$	2.34	-0.12	-0.18	0.65	0.69	-2.36	-2.46
Cu_2ON_5/G$^\gamma$	2.35	-0.11	-0.11	0.64	0.65	-2.26	-2.34

Table S5. The calculated adsorption free energy ($\Delta G(*N_2)$, in eV), N-N bond length (d_{N-N}, in Å), charge transfer (Q, in e, the negative values denote the electron transfer from the DACs to $*N_2$), and corresponding adsorption patterns of $*N_2$ on M_2N_6/G and M_2BN_5/G DACs.

Systems	$\Delta G(*N_2)$	d_{N-N}	Q	patterns
V_2N_6/G	**-1.52**	**1.27**	**-0.95**	**side-on**
V_2BN_5/G^α	-1.42	1.24	-0.90	side-on
V_2BN_5/G^β	-1.21	1.24	-0.87	side-on
V_2BN_5/G^γ	-1.66	1.25	-0.97	side-on
Cr_2N_6/G	**-0.35**	**1.20**	**-0.71**	**side-on**
Cr_2BN_5/G^α	-0.40	1.14	-0.39	end-on
Cr_2BN_5/G^β	-0.22	1.13	-0.26	end-on
Cr_2BN_5/G^γ	-0.91	1.21	-0.81	side-on
Mn_2N_6/G	**-0.47**	**1.16**	**-0.51**	**end-on**
Mn_2BN_5/G^α	-0.27	1.14	-0.31	end-on
Mn_2BN_5/G^β	-0.53	1.15	-0.47	end-on
Mn_2BN_5/G^γ	-0.89	1.20	-0.74	side-on
Fe_2N_6/G	**-0.18**	**1.14**	**-0.30**	**end-on**
Fe_2BN_5/G^α	-0.42	1.14	-0.36	end-on
Fe_2BN_5/G^β	-0.52	1.14	-0.34	end-on
Fe_2BN_5/G^γ	-0.92	1.14	-0.34	end-on
Co_2N_6/G	**-0.17**	**1.16**	**-0.39**	**end-on**
Co_2BN_5/G^α	-0.49	1.14	-0.31	end-on
Co_2BN_5/G^β	-0.14	1.15	-0.36	end-on
Co_2BN_5/G^γ	-0.80	1.14	-0.32	end-on
Ni_2N_6/G	**0.40**	**1.13**	**-0.18**	**end-on**
Ni_2BN_5/G^α	-0.14	1.13	-0.26	end-on
Ni_2BN_5/G^β	0.19	1.13	-0.20	end-on
Ni_2BN_5/G^γ	-0.40	1.13	-0.22	end-on
Cu_2N_6/G	**0.41**	**1.13**	**-0.14**	**end-on**
Cu_2BN_5/G^α	0.25	1.12	-0.02	physisorption
Cu_2BN_5/G^β	0.25	1.12	-0.02	physisorption
Cu_2BN_5/G^γ	0.26	1.12	-0.02	physisorption

Table S6. The calculated adsorption free energy (ΔG(*N$_2$), in eV), N-N bond length (d_{N-N}, in Å), charge transfer (Q, in e, the negative values denote the electron transfer from the DACs to *N$_2$), and corresponding adsorption patterns of *N$_2$ on M$_2$N$_6$/G and M$_2$ON$_5$/G DACs.

Systems	ΔG(*N$_2$)	d_{N-N}	Q	patterns
V$_2$N$_6$/G	**-1.52**	**1.27**	**-0.95**	**side-on**
V$_2$ON$_5$/G$^\alpha$	-1.90	1.28	-1.04	side-on
V$_2$ON$_5$/G$^\beta$	-1.93	1.28	-0.98	side-on
V$_2$ON$_5$/G$^\gamma$	-1.82	1.28	-1.00	side-on
Cr$_2$N$_6$/G	**-0.35**	**1.20**	**-0.71**	**side-on**
Cr$_2$ON$_5$/G$^\alpha$	-0.70	1.25	-0.99	side-on
Cr$_2$ON$_5$/G$^\beta$	-0.27	1.20	-0.72	side-on
Cr$_2$ON$_5$/G$^\gamma$	-0.48	1.20	-0.76	side-on
Mn$_2$N$_6$/G	**-0.47**	**1.16**	**-0.51**	**end-on**
Mn$_2$ON$_5$/G$^\alpha$	-0.64	1.20	-0.76	side-on
Mn$_2$ON$_5$/G$^\beta$	-0.32	1.20	-0.75	side-on
Mn$_2$ON$_5$/G$^\gamma$	-0.79	1.21	-0.82	side-on
Fe$_2$N$_6$/G	**-0.18**	**1.14**	**-0.30**	**end-on**
Fe$_2$ON$_5$/G$^\alpha$	-0.25	1.15	-0.37	end-on
Fe$_2$ON$_5$/G$^\beta$	-0.07	1.14	-0.29	end-on
Fe$_2$ON$_5$/G$^\gamma$	0.01	1.16	-0.47	end-on
Co$_2$N$_6$/G	**-0.17**	**1.16**	**-0.39**	**end-on**
Co$_2$ON$_5$/G$^\alpha$	-0.47	1.16	-0.42	end-on
Co$_2$ON$_5$/G$^\beta$	0.02	1.16	-0.40	end-on
Co$_2$ON$_5$/G$^\gamma$	-0.29	1.16	-0.41	end-on
Ni$_2$N$_6$/G	**0.40**	**1.13**	**-0.18**	**end-on**
Ni$_2$ON$_5$/G$^\alpha$	0.51	1.14	-0.32	end-on
Ni$_2$ON$_5$/G$^\beta$	0.26	1.12	-0.04	physisorption
Ni$_2$ON$_5$/G$^\gamma$	0.15	1.14	-0.27	end-on
Cu$_2$N$_6$/G	**0.41**	**1.13**	**-0.14**	**end-on**
Cu$_2$ON$_5$/G$^\alpha$	-0.24	1.13	-0.21	end-on
Cu$_2$ON$_5$/G$^\beta$	0.27	1.12	-0.02	physisorption
Cu$_2$ON$_5$/G$^\gamma$	-0.11	1.13	-0.18	end-on

Table S7. The calculated limiting potential (U_L, in V), potential-determining step (PDS), and reaction free energy of the first hydrogenation step (*N$_2$ + H$^+$ + e$^-$ → *N$_2$H) (ΔG_1, in eV) and last hydrogenation step (*NH$_2$ + H$^+$ + e$^-$ → *NH$_3$) (ΔG_6, in eV) for NRR on M$_2$N$_6$/G and M$_2$BN$_5$/G DACs.

Systems	U_L	PDS	ΔG_1	ΔG_6
V$_2$N$_6$/G	**-1.01**	***NH$_2$→*NH$_3$**	**-0.04**	**1.01**
V$_2$BN$_5$/G$^\alpha$	-0.85	*NH$_2$→*NH$_3$	0.29	0.85
V$_2$BN$_5$/G$^\beta$	-0.96	*NH$_2$→*NH$_3$	0.13	0.96
V$_2$BN$_5$/G$^\gamma$	-1.02	*NH$_2$→*NH$_3$	0.23	1.02
Cr$_2$N$_6$/G	**-0.84**	***NH$_2$→*NH$_3$**	**0.26**	**0.84**
Cr$_2$BN$_5$/G$^\alpha$	-0.69	*NH$_2$→*NH$_3$	0.60	0.69
Cr$_2$BN$_5$/G$^\beta$	-0.70	*N$_2$→*N$_2$H	0.70	0.66
Cr$_2$BN$_5$/G$^\gamma$	-0.78	*NH$_2$→*NH$_3$	0.11	0.78
Mn$_2$N$_6$/G	**-0.48**	***NH$_2$→*NH$_3$**	**0.47**	**0.48**
Mn$_2$BN$_5$/G$^\alpha$	-0.76	*N$_2$→*N$_2$H	0.76	0.18
Mn$_2$BN$_5$/G$^\beta$	-0.61	*N$_2$→*N$_2$H	0.61	0.57
Mn$_2$BN$_5$/G$^\gamma$	-0.80	*NH$_2$→*NH$_3$	0.62	0.80
Fe$_2$N$_6$/G	**-0.62**	***N$_2$→*N$_2$H**	**0.62**	**0.02**
Fe$_2$BN$_5$/G$^\alpha$	-0.76	*N$_2$→*N$_2$H	0.76	0.08
Fe$_2$BN$_5$/G$^\beta$	-0.59	*N$_2$→*N$_2$H	0.59	0.33
Fe$_2$BN$_5$/G$^\gamma$	-0.63	*N$_2$→*N$_2$H	0.63	0.63
Co$_2$N$_6$/G	**-0.48**	***N$_2$→*N$_2$H**	**0.48**	**0.43**
Co$_2$BN$_5$/G$^\alpha$	-0.51	*NH$_2$→*NH$_3$	0.50	0.51
Co$_2$BN$_5$/G$^\beta$	-0.52	*N$_2$→*N$_2$H	0.52	0.28
Co$_2$BN$_5$/G$^\gamma$	-0.71	*NH$_2$→*NH$_3$	0.44	0.71
Ni$_2$N$_6$/G	**-1.36**	***N$_2$→*N$_2$H**	**1.36**	**-0.62**
Ni$_2$BN$_5$/G$^\alpha$	-1.26	*N$_2$→*N$_2$H	1.26	-0.02
Ni$_2$BN$_5$/G$^\beta$	-1.07	*N$_2$→*N$_2$H	1.07	-0.01
Ni$_2$BN$_5$/G$^\gamma$	-1.03	*N$_2$→*N$_2$H	1.03	0.23
Cu$_2$N$_6$/G	**-1.86**	***N$_2$→*N$_2$H**	**1.86**	**-0.91**
Cu$_2$BN$_5$/G$^\alpha$	-1.62	*N$_2$→*N$_2$H	1.62	-0.56
Cu$_2$BN$_5$/G$^\beta$	-2.02	*N$_2$→*N$_2$H	2.02	-0.59
Cu$_2$BN$_5$/G$^\gamma$	-1.65	*N$_2$→*N$_2$H	1.65	-0.21

Table S8. The calculated limiting potential (U_L, in V), potential-determining step (PDS), and reaction free energy of the first hydrogenation step (*N$_2$ + H$^+$ + e^- → *N$_2$H) (ΔG_1, in eV) and last hydrogenation step (*NH$_2$ + H$^+$ + e^- → *NH$_3$) (ΔG_6, in eV) for NRR on M$_2$N$_6$/G and M$_2$ON$_5$/G DACs.

Systems	U_L	PDS	ΔG_1	ΔG_6
V$_2$N$_6$/G	**-1.01**	***NH$_2$→*NH$_3$**	**-0.04**	**1.01**
V$_2$ON$_5$/G$^\alpha$	-1.24	*NH$_2$→*NH$_3$	0.44	1.24
V$_2$ON$_5$/G$^\beta$	-1.31	*NH$_2$→*NH$_3$	0.27	1.31
V$_2$ON$_5$/G$^\gamma$	-1.10	*NH$_2$→*NH$_3$	0.24	1.10
Cr$_2$N$_6$/G	**-0.84**	***NH$_2$→*NH$_3$**	**0.26**	**0.84**
Cr$_2$ON$_5$/G$^\alpha$	-1.25	*NH$_2$→*NH$_3$	0.22	1.25
Cr$_2$ON$_5$/G$^\beta$	-1.00	*NH$_2$→*NH$_3$	0.34	1.00
Cr$_2$ON$_5$/G$^\gamma$	-0.96	*NH$_2$→*NH$_3$	0.09	0.96
Mn$_2$N$_6$/G	**-0.48**	***NH$_2$→*NH$_3$**	**0.47**	**0.48**
Mn$_2$ON$_5$/G$^\alpha$	-0.27	*N$_2$→*N$_2$H	0.27	0.26
Mn$_2$ON$_5$/G$^\beta$	-0.62	*N$_2$→*N$_2$H	0.62	0.30
Mn$_2$ON$_5$/G$^\gamma$	-0.59	*NH$_2$→*NH$_3$	0.50	0.59
Fe$_2$N$_6$/G	**-0.62**	***N$_2$→*N$_2$H**	**0.62**	**0.02**
Fe$_2$ON$_5$/G$^\alpha$	-0.46	*N$_2$→*N$_2$H	0.46	0.39
Fe$_2$ON$_5$/G$^\beta$	-0.76	*N$_2$→*N$_2$H	0.76	0.10
Fe$_2$ON$_5$/G$^\gamma$	-0.52	*N$_2$→*N$_2$H	0.52	0.21
Co$_2$N$_6$/G	**-0.48**	***N$_2$→*N$_2$H**	**0.48**	**0.43**
Co$_2$ON$_5$/G$^\alpha$	-0.69	*NH$_2$→*NH$_3$	0.58	0.69
Co$_2$ON$_5$/G$^\beta$	-0.61	*N$_2$→*N$_2$H	0.61	0.20
Co$_2$ON$_5$/G$^\gamma$	-0.66	*N$_2$→*N$_2$H	0.66	0.37
Ni$_2$N$_6$/G	**-1.36**	***N$_2$→*N$_2$H**	**1.36**	**-0.62**
Ni$_2$ON$_5$/G$^\alpha$	-1.15	*N$_2$→*N$_2$H	1.15	0.09
Ni$_2$ON$_5$/G$^\beta$	-1.85	*N$_2$→*N$_2$H	1.85	-0.46
Ni$_2$ON$_5$/G$^\gamma$	-1.65	*N$_2$→*N$_2$H	1.65	-0.33
Cu$_2$N$_6$/G	**-1.86**	***N$_2$→*N$_2$H**	**1.86**	**-0.91**
Cu$_2$ON$_5$/G$^\alpha$	-1.67	*N$_2$→*N$_2$H	1.67	-0.25
Cu$_2$ON$_5$/G$^\beta$	-1.86	*N$_2$→*N$_2$H	1.86	-0.65
Cu$_2$ON$_5$/G$^\gamma$	-1.80	*N$_2$→*N$_2$H	1.80	-0.05

Table S9. The calculated formation energy (E_f, in eV) of M_2N_6/G, M_2B_6/G, and M_2O_6/G DACs.

Metal	M_2N_6/G	M_2B_6/G	M_2O_6/G
V	4.34	12.64	6.89
Cr	4.07	13.22	5.87
Mn	3.65	12.04	5.01
Fe	4.03	12.36	6.39
Co	3.85	11.30	6.68
Ni	3.06	11.25	5.56
Cu	3.78	11.65	5.76

Table S10. The calculated limiting potential (U_L, in V), potential-determining step (PDS), and reaction free energy of the first hydrogenation step (*N_2 + H^+ + e^- → *N_2H) (ΔG_1, in eV) and last hydrogenation step (*NH_2 + H^+ + e^- → *NH_3) (ΔG_6, in eV) for NRR on M_2N_6/G, M_2B_6/G, and M_2O_6/G DACs.

Systems	U_L	PDS	ΔG_1	ΔG_6
V_2N_6/G	**-1.01**	***NH_2→*NH_3**	**-0.04**	**1.01**
V_2B_6/G	-0.92	*N_2→*N_2H	0.92	-0.08
V_2O_6/G	-0.75	*NH_2→*NH_3	-0.09	0.75
Cr_2N_6/G	**-0.84**	***NH_2→*NH_3**	**0.26**	**0.84**
Cr_2B_6/G	-0.43	*N_2→*N_2H	0.43	-0.01
Cr_2O_6/G	-1.51	*NH_2→*NH_3	0.00	1.51
Mn_2N_6/G	**-0.48**	***NH_2→*NH_3**	**0.47**	**0.48**
Mn_2B_6/G	-0.60	*N_2→*N_2H	0.60	-0.21
Mn_2O_6/G	-1.06	*NH_2→*NH_3	0.69	1.06
Fe_2N_6/G	**-0.62**	***N_2→*N_2H**	**0.62**	**0.02**
Fe_2B_6/G	-1.04	*N_2→*N_2H	1.04	-0.52
Fe_2O_6/G	-0.93	*NH_2→*NH_3	0.80	0.93
Co_2N_6/G	**-0.48**	***N_2→*N_2H**	**0.48**	**0.43**
Co_2B_6/G	-1.10	*N_2→*N_2H	1.10	-0.71
Co_2O_6/G	-0.85	*N_2→*N_2H	0.85	0.82
Ni_2N_6/G	**-1.36**	***N_2→*N_2H**	**1.36**	**-0.62**
Ni_2B_6/G	-1.42	*N_2→*N_2H	1.42	-0.29
Ni_2O_6/G	-0.79	*N_2→*N_2H	0.79	-0.14
Cu_2N_6/G	**-1.86**	***N_2→*N_2H**	**1.86**	**-0.91**
Cu_2B_6/G	-1.26	*N_2→*N_2H	1.26	-0.68
Cu_2O_6/G	-2.09	*NH_2→*NH_3	1.01	2.09

Table S11. The calculated E_f (eV) of $Mn_2O_xN_{6-x}$/G (x=0-6) DACs.

No.	Mn_2N_6/G	Mn_2ON_5/G	$Mn_2O_2N_4$/G	$Mn_2O_3N_3$/G	$Mn_2O_4N_2$/G	Mn_2O_5N/G	Mn_2O_6/G
a	3.65	3.86	4.30	3.51	4.68	3.61	5.01
b	/	3.33	4.45	4.56	4.43	4.38	/
c	/	3.90	5.05	3.89	4.86	3.96	/
d	/	/	4.25	4.26	5.00	/	/
e	/	/	4.65	4.64	4.30	/	/
f	/	/	4.12	3.82	4.66	/	/
g	/	/	4.31	4.62	4.80	/	/
h	/	/	3.95	4.12	5.30	/	/
i	/	/	4.20	3.94	4.36	/	/
j	/	/	/	3.52	/	/	/

Table S12. The calculated U_L (V), PDS, and reaction free energy of ΔG_1 and ΔG_6 (eV) for NRR on $Mn_2O_xN_{6-x}/G$ (x=0-6) DACs.

Systems	U_L	PDS	ΔG_1	ΔG_6
Mn_2N_6/G	**-0.48**	***NH$_2$→*NH$_3$**	**0.47**	**0.48**
Mn_2ON_5/G$^\alpha$	**-0.27**	***N$_2$→*N$_2$H**	**0.27**	**0.26**
Mn_2ON_5/G$^\beta$	**-0.62**	***N$_2$→*N$_2$H**	**0.62**	**0.30**
Mn_2ON_5/G$^\gamma$	**-0.59**	***NH$_2$→*NH$_3$**	**0.50**	**0.59**
$Mn_2O_2N_4$/G^a	-0.83	*NH$_2$→*NH$_3$	0.36	0.83
$Mn_2O_2N_4$/G^b	-0.85	*NH$_2$→*NH$_3$	0.39	0.85
$Mn_2O_2N_4$/G^c	-1.18	*NH$_2$→*NH$_3$	0.57	1.18
$Mn_2O_2N_4$/G^d	-0.99	*NH$_2$→*NH$_3$	0.25	0.99
$Mn_2O_2N_4$/G^e	-1.21	*N$_2$→*N$_2$H	1.21	1.12
$Mn_2O_2N_4$/G^f	-0.53	*NH$_2$→*NH$_3$	0.51	0.53
$Mn_2O_2N_4$/G^g	-0.87	*N$_2$→*N$_2$H	0.87	0.71
$Mn_2O_2N_4$/G^h	-0.84	*NH$_2$→*NH$_3$	0.39	0.84
$Mn_2O_2N_4$/G^i	-1.11	*NH$_2$→*NH$_3$	0.17	1.11
$Mn_2O_3N_3$/G^b	-1.34	*NH$_2$→*NH$_3$	0.70	1.34
$Mn_2O_3N_3$/G^c	-1.17	*NH$_2$→*NH$_3$	0.60	1.17
$Mn_2O_3N_3$/G^d	-1.50	*NH$_2$→*NH$_3$	0.59	1.50
$Mn_2O_3N_3$/G^e	-1.29	*NH$_2$→*NH$_3$	0.77	1.29
$Mn_2O_3N_3$/G^f	-1.15	*NH$_2$→*NH$_3$	0.78	1.15
$Mn_2O_3N_3$/G^g	-1.58	*NH$_2$→*NH$_3$	0.79	1.58
$Mn_2O_3N_3$/G^h	-0.56	*NH$_2$→*NH$_3$	0.35	0.56
$Mn_2O_3N_3$/G^i	-1.02	*NH$_2$→*NH$_3$	0.55	1.02
$Mn_2O_3N_3$/G^j	-0.29	*N$_2$→*N$_2$H	0.29	0.12
$Mn_2O_4N_2$/G^b	-1.30	*NH$_2$→*NH$_3$	0.69	1.30
$Mn_2O_4N_2$/G^c	-1.39	*NH$_2$→*NH$_3$	0.55	1.39
$Mn_2O_4N_2$/G^d	-1.51	*NH$_2$→*NH$_3$	0.66	1.51
$Mn_2O_4N_2$/G^e	-0.92	*NH$_2$→*NH$_3$	0.78	0.92
$Mn_2O_4N_2$/G^f	-1.18	*NH$_2$→*NH$_3$	0.63	1.18
$Mn_2O_4N_2$/G^g	-1.31	*NH$_2$→*NH$_3$	0.74	1.31
$Mn_2O_4N_2$/G^h	-1.44	*NH$_2$→*NH$_3$	0.91	1.44
$Mn_2O_4N_2$/G^i	-1.48	*NH$_2$→*NH$_3$	0.60	1.48
Mn_2O_5N/G^c	-1.06	*NH$_2$→*NH$_3$	0.73	1.06
Mn_2O_6/G	-1.06	*NH$_2$→*NH$_3$	0.69	1.06