Supporting Information

Density functional theory study of transition metal single-atom anchored on graphyne as efficient electrocatalyst for nitrogen reduction reaction

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Table S1 The total energy (E_{total} in eV) of TM atoms (TM = Ti, V, Cr, Mn, Zr, Nb, Mo) adsorbed on the GY with the different adsorption sites.

E_{total} (eV)	Ti	V	Cr	Mn	Zr	Nb	Mo
H1	−421.31	−422.03	−422.30	−422.67	−421.81	−422.89	−423.02
H2	−419.68	−420.15	−420.38	−420.19	−420.24	−420.70	−420.58
B1	—	—	—	—	—	—	—
B2	—	—	—	—	—	−420.23	—
B3	—	—	—	—	—	−420.09	−420.38
C	−420.80	—	—	—	−421.51	—	—

Table S2 Binding energy (E_b in eV), distance from TM atoms to GY surface (d in Å), Bader charge for the TM atoms (Q_{TM} in e) and total magnetic moment (M in μ_B) (TM = Ti, V, Cr, Mn, Zr, Nb, Mo). The negative values represent loss of electrons, respectively.

	Ti	V	Cr	Mn	Zr	Nb	Mo
E_b (eV)	−4.96	−4.28	−2.64	−3.34	−5.59	−5.56	−4.50
d(Å)	1.36	1.20	0.99	0.76	1.61	1.42	1.28
$Q_{TM}(e)$	−2.01	−1.68	−1.39	−1.24	−1.61	−1.35	−1.07
$M(\mu_B)$	0.00	0.60	1.43	2.58	0.00	0.25	0.73

Table S3 Adsorption energy (E_{ads} in eV) of $*NH_2$ and $*NH_3$ adsorbed on TM@GY.

E_{ads}	Ti@GY	V@GY	Cr@GY	Mn@GY	Zr@GY	Nb@GY	Mo@GY
$*NH_2$	−3.75	−4.17	−3.83	−2.77	−3.98	−4.40	−4.45
$*NH_3$	−1.53	−1.68	−1.25	−0.80	−1.44	−1.67	−1.12

Table S4 Adsorption energy (E_{ads} in eV), bond length of Mn-N and N-N (d in Å), total magnetic moment (M in μ_B) and Bader charge (Q in e) of various reaction intermediates adsorbed on Mn@GY via the distal and alternating pathways, and the positive and negative values represent the acquisition and loss of electrons, respectively.

Distal	E_{ads} (eV)	$d_{Mn\text{-}N}$ (Å)	$d_{N\text{-}N}$ (Å)	M (μ_B)	Q (e)
*N-N	−0.33	1.82	1.14	1.02	0.34
*N-NH	−2.27	1.65	1.22	0.00	0.52
*N-NH_2	−2.79	1.62	1.30	0.00	0.34
*N	−5.45	1.54	—	0.00	0.72
*NH	−4.02	1.60	—	0.00	0.53
*NH_2	−2.83	1.77	—	0.58	0.32
*NH_3	−0.87	2.10	—	2.19	−0.11
Alternating	E_{ads} (eV)	$d_{Mn\text{-}N}$ (Å)	$d_{N\text{-}N}$ (Å)	M (μ_B)	Q (e)
*N-N	−0.33	1.82	1.14	1.02	0.34
*N-NH	−2.27	1.65	1.22	0.00	0.52
*NH-NH	−1.53	1.82	1.28	1.03	0.31
*NH-NH_2	−2.10	1.76	1.38	0.49	0.15
*NH_2-NH_2	−1.05	2.08	1.45	2.05	−0.10
*NH_2	−2.83	1.77	—	0.58	0.32
*NH_3	−0.87	2.10	—	2.19	−0.11

Table S5 Adsorption energy (E_{ads} in eV), bond length of V-N and N-N (d in Å), total magnetic moment (M in μ_B) and Bader charge (Q in e) of various reaction intermediates adsorbed on V@GY via the enzymatic pathways, and the positive and negative values represent the acquisition and loss of electrons, respectively.

Enzymatic	E_{ads} (eV)	$d_{V\text{-}N}$ (Å)	$d_{N\text{-}N}$ (Å)	M (μ_B)	Q (e)

*N-*N	−0.60	1.17	2.12/2.15	0.74	0.45
*N-*NH	−2.71	1.25	1.97/1.96	0.00	0.56
*NH-*NH	−2.45	1.33	1.98/2.01	0.58	0.52
NH-NH_2	−3.40	1.40	2.19/1.86	0.00	0.45
NH_2-NH_2	−1.93	1.45	2.18/2.16	0.00	−0.17
NH_2-NH_3	−4.44	1.87	—	0.00	0.46
*NH_3	−1.76	2.13	—	0.00	−0.10

Table S6 The Δ*ZPE* and Δ*S* values of various reaction intermediates adsorbed on Mn@GY via the distal and alternating pathways, and V@GY via the enzymatic pathways.

Distal	*N-N	*N-NH	*N-NH_2	*N	*NH	*NH_2	*NH_3
Δ*ZPE*	0.203154	0.478745	0.798123	0.096019	0.333621	0.675701	1.007576
Δ*S*	0.000568	0.000573	0.000511	0.000149	0.000334	0.000343	0.000527
Alternating	*N-N	*N-NH	*NH-NH	*NH-NH_2	*NH_2-NH_2	*NH_2	*NH_3
Δ*ZPE*	0.203154	0.478745	0.806456	1.141680	1.479819	0.675701	1.007576
Δ*S*	0.000568	0.000573	0.000631	0.000673	0.000892	0.000343	0.000527
Enzymatic	*N-*N	*N-*NH	*NH-*NH	*NH-*NH_2	*NH_2-*NH_2	*NH_2-*NH_3	*NH_3
Δ*ZPE*	0.171071	0.486798	0.759923	1.135869	1.462867	1.442786	1.007576
Δ*S*	0.000697	0.000550	0.000670	0.000627	0.000696	0.001319	0.000527

Table S7 Adsorption energy (E_{ads} in eV), Bader charge on Mn atom (Q in e) and bond length of N-N (d_{N-N} in Å) N_2 adsorbed on Mn@GY using DFT and DFT+U calculation, respectively.

*N-N	DFT	DFT+U (U=4)	DFT+U (U=6)
E_{ads} (eV)	-0.33	-0.54	-0.47
Q (e)	5.57	5.77	5.57
d_{N-N} (Å)	1.14	1.12	1.13