Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Tuning the Electronic Structure of Transition Metal Embedded in Nitrogen-doped Graphene for Electrocatalytic Nitrogen Reduction: A first-principles Study

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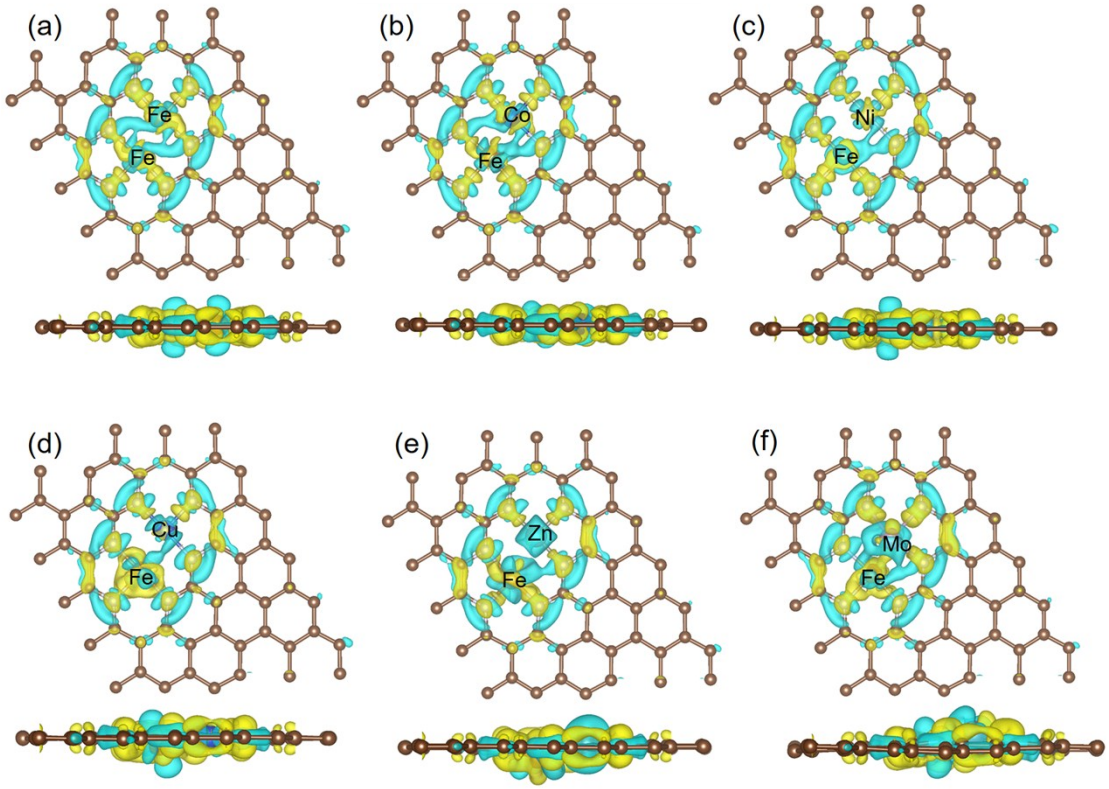

Fig.S1 Top-view and side-view of charge density differences for (a) Fe/Fe-N-C, (a) Fe/Co-N-C, (a) Fe/Ni-N-C, (a) Fe/Cu-N-C, (a) Fe/Zn-N-C and (a) Fe/Mo-N-C. The isosurface is set to be 0.03 e $Å^{-3}$. Cyan and yellow represents positive and negative region, respectively.

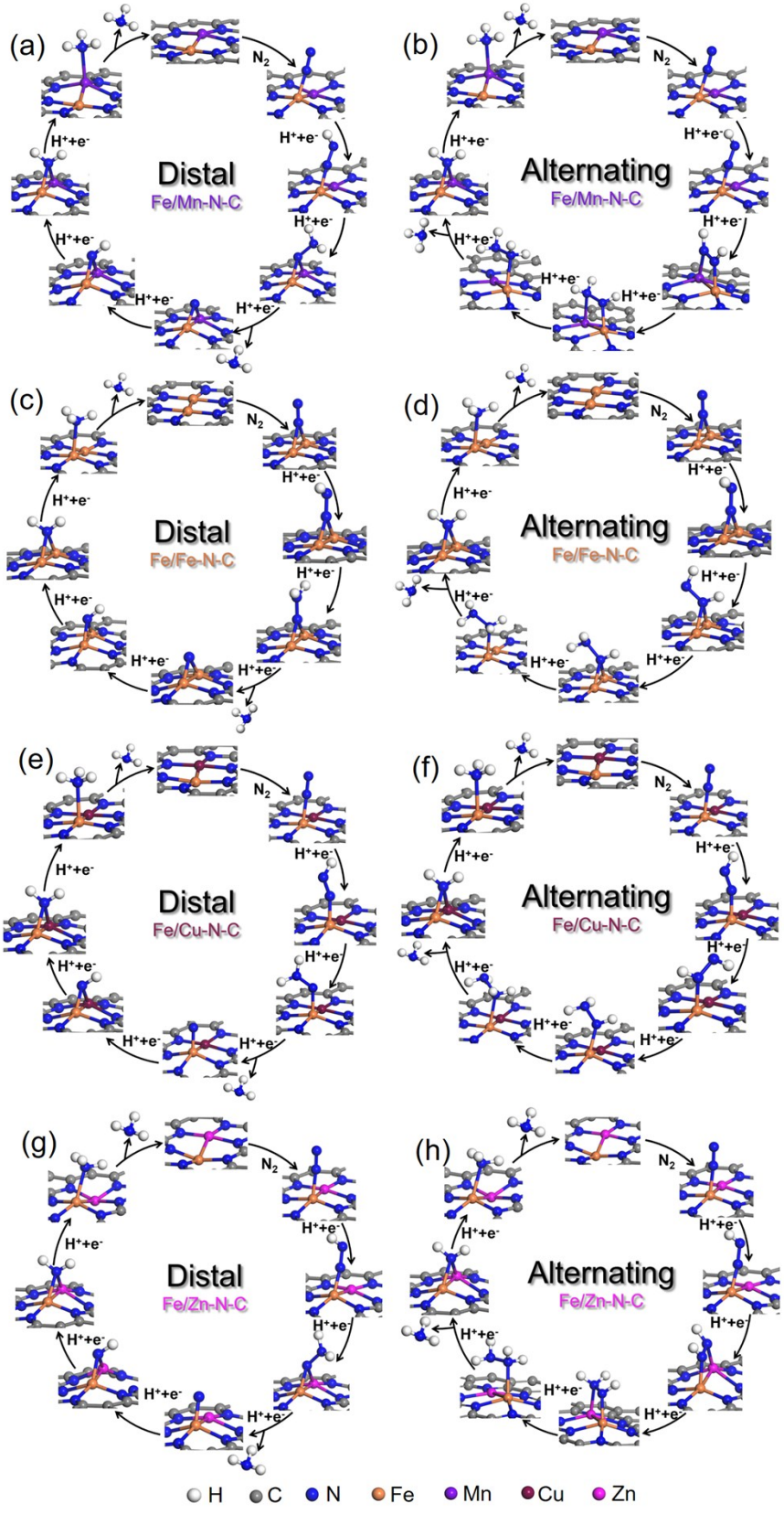

Fig.S2 The optimized configurations of the intermediates of each step for NRR catalyzed by Fe/M-N-C (M=Mn, Fe, Cu, Zn) starting with Fe-end adsorption configuration.

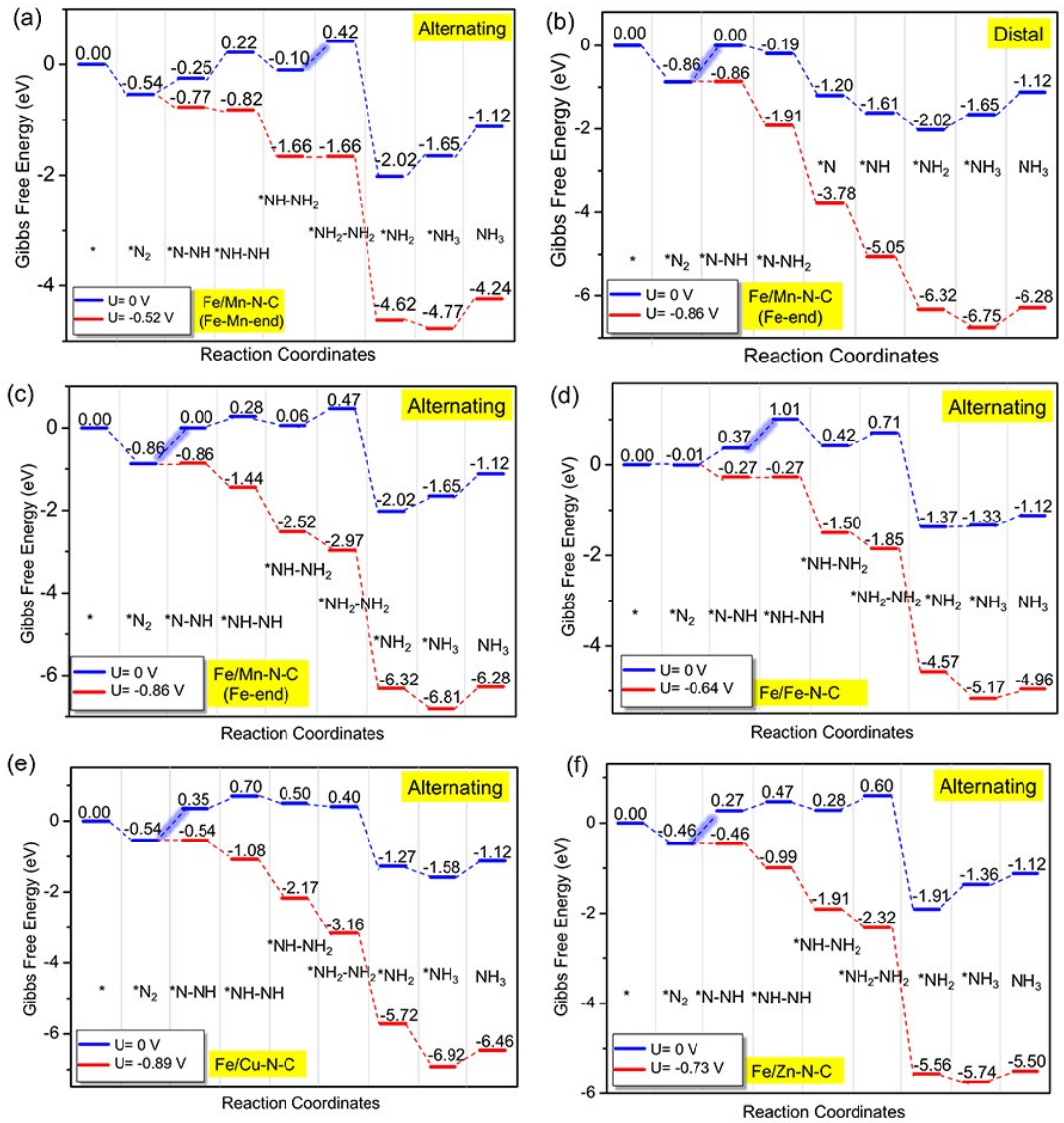

Fig.S3 Gibbs free energy diagrams for NRR along (a) alternating pathway on Fe-Mn-N-C in Fe-Mn-end configuration, distal (b) and (c) alternating on Fe/Mn-N-C in Fe-end configuration, alternating pathway on (d) Fe/Fe-N-C, (e) Fe/Cu-N-C and (f) Fe/Zn-N-C, respectively. The blue and red line represents the free energy for NRR at zero and applied potential (limiting potential).

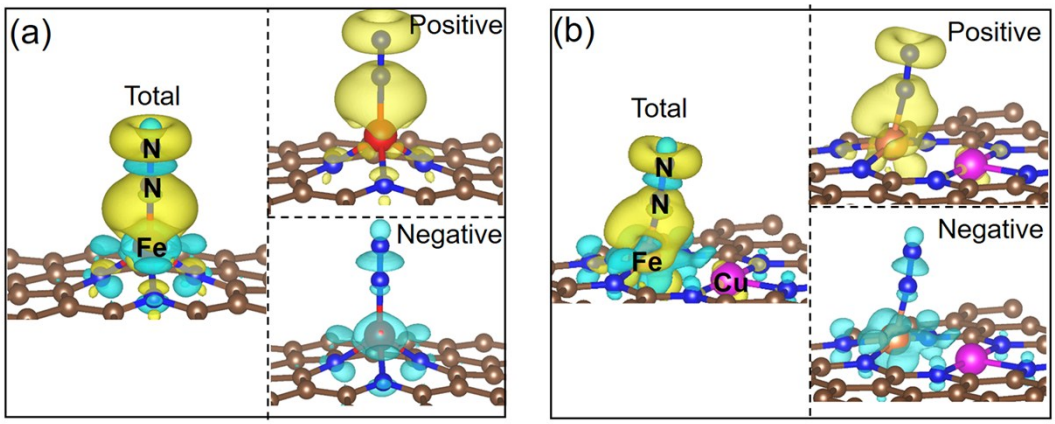

Fig.S4 Charge difference density of N_2 adsorbed on (a) Fe-N-C and (b) Fe/Cu-N-C catalysts. The positive and negative charges are shown in yellow and cyan, respectively.

Table S1 Calculated total energy (E_{DFT}), ZPE, TS for N_2, H_2 and NH_3 (T = 298.15 K, P = 1 bar). In comparison, the experimental entropies (TS_{exp}) of the gas phase N_2, H_2 and NH_3 are also listed, which are from NIST standard reference database (https://doi.org/10.18434/T4D303).

Species	**E_{DFT}/eV**	**E_{ZPE}/eV**	**TS/eV**	**TS_{exp}/eV**
N_2	−16.65	0.15	0.59	0.59
H_2	−6.77	0.27	0.40	0.41
NH_3	−19.56	0.91	0.59	0.60

Table S2 Calculated zero point energies (E_{ZPE}) and entropy of different adsorption species, where the * denotes the adsorption site. Therefore, *N-*N and *N-N represent the side-on and end-on adsorption configurations, respectively. The "Fe/M" represents corresponding Fe/M-N-C catalysts.

Adsorption species	**E_{ZPE}/eV**						**TS/eV**					
	Fe/Mn (Fe-Mn-end)	Fe/Mn (Fe-end)	Fe/Fe	Fe/Cu	Fe/Zn	Fe/Mo	Fe/Mn (Fe-Mn-end)	Fe/Mn (Fe-end)	Fe/Fe	Fe/Cu	Fe/Zn	Fe/Mo
*N-N(*N-*N)	0.22	0.22	0.20	0.20	0.21	0.18	0.12	0.14	0.13	0.16	0.15	0.11
*N-NH(*N-NH)	0.51	0.48	0.51	0.48	0.49	0.47	0.12	0.17	0.13	0.17	0.15	0.12
*N-NH_2(*N-*NH_2)	0.80	0.80	0.83	0.80	0.81	0.86	0.16	0.16	0.15	0.19	0.15	0.11
*NH-NH(*NH-*NH)	0.83	0.80	0.82	0.83	0.81	0.82	0.12	0.13	0.14	0.18	0.13	0.12
*NH-NH_2(*NH-*NH_2)	1.15	1.17	1.17	1.13	1.14	1.16	0.16	0.14	0.15	0.20	0.17	0.13
NH_2-NH_2(NH_2-*NH_2)	1.47	1.48	1.49	1.49	1.49	1.48	0.22	0.22	0.18	0.25	0.21	0.18
*N	0.09	0.09	0.09	0.08	0.08	0.09	0.04	0.04	0.03	0.06	0.06	0.04
*NH	0.37	0.37	0.37	0.36	0.37	0.37	0.05	0.05	0.05	0.06	0.05	0.06
*NH_2	0.71	0.71	0.72	0.70	0.71	0.71	0.07	0.07	0.06	0.08	0.07	0.08
*NH_3	1.00	1.00	1.01	1.01	1.02	1.02	0.22	0.22	0.19	0.13	0.16	0.13

Table S3 The distance of two metal atoms (d_{Fe-M}, Å), Fe atom and N atom (d_{Fe-N}, Å), M atom and N (d_{M-N}, Å) of Fe/M-N-C catalyst.

Catalyst	**d_{Fe-M}/ Å**	**d_{Fe-N}/ Å**	**d_{M-N}/ Å**
Fe/Mn-N-C	2.25	1.87	1.93
		1.95	1.96
		1.98	2.06
Fe/Fe-N-C	2.22	1.91	1.91
		1.91	1.91
		2.02	2.02
Fe/Co-N-C	2.18	1.90	1.89
		1.92	1.90
		2.06	2.00
Fe/Ni-N-C	2.30	1.90	1.88
		1.92	1.90
		2.01	1.95
Fe/Cu-N-C	2.38	1.94	1.91
		1.95	1.93
		2.00	1.96
Fe/Zn-N-C	2.50	1.93	1.93
		1.95	1.96
		1.96	1.97
Fe/Mo-N-C	2.04	1.90	2.03
		1.94	2.04
		2.04	2.24

Table S4 Calculated binding energies (E_b) of Fe/M-N-C catalysts and experimental cohesive energies (E_c) of metals

Catalyst	E_b(eV)	Metal	E_c(eV/atom)
Fe/Mn-N-C	−10.58	Mn	−2.92
Fe/Fe-N-C	−11.68	Fe	−4.28
Fe/Co-N-C	−12.61	Co	−4.39
Fe/Ni-N-C	−12.52	Ni	−4.44
Fe/Cu-N-C	−10.23	Cu	−3.49
Fe/Zn-N-C	−6.88	Zn	−1.35
Fe/Mo-N-C	−12.05	Mo	−6.82

a) Experimental values are taken from reference[1].

Table S5 Bader charge (q, in |e|) of the two metal atoms and N-C of Fe/M-N-C catalyst.

Catalyst	q(M)	q(Fe)	q(N-C)
Fe/Mn-N-C	0.99	0.72	−1.63
Fe/Fe-N-C	0.83	0.83	−1.59
Fe/Co-N-C	0.62	0.89	−1.43
Fe/Ni-N-C	0.57	0.96	−1.45
Fe/Cu-N-C	0.66	0.92	−1.50
Fe/Zn-N-C	0.99	0.87	−1.78
Fe/Mo-N-C	1.10	0.67	−1.69

Table S6 The ΔG value for each step of the Fe/M-N-C catalysts. The step corresponds to each reaction step in NRR of free energy diagrams. The ΔG_L was highlighted by red color.

Step	ΔG/eV											
	Fe/Mn-N-C				Fe/Fe-N-C		Fe/Cu-N-C		Fe/Zn-N-C		Fe/Mo-N-C	
	Fe-Mn-end		Fe-end		Fe-Fe-end		Fe-end		Fe-end		Fe-Mo-side	
	Distal	Alternating	Distal	Alternating	Distal	Alternating	Distal	Alternating	Distal	Alternating	Consecutive	Enzymatic
1	−0.54	−0.54	−0.87	−0.86	−0.01	−0.01	−0.54	−0.54	−0.46	−0.46	−0.19	−0.19
2	0.29	0.29	0.86	0.86	0.38	0.38	0.89	0.89	0.73	0.73	0.37	0.37
3	0.07	0.47	−0.18	0.28	0.31	0.64	0.35	0.35	0.20	0.19	−0.16	−0.28
4	−1.01	−0.32	−1.01	−0.22	−1.17	−0.59	−0.43	−0.19	−0.51	−0.18	−1.37	0.27
5	−0.42	0.52	−0.42	0.41	−0.27	0.29	−0.41	−0.10	−0.86	0.31	−0.35	0.10
6	−0.40	−2.44	−0.40	−2.49	−0.60	−2.08	−1.12	−1.68	−1.01	−2.51	−0.18	−2.16
7	0.37	0.37	0.37	0.37	0.03	0.03	−0.30	−0.30	0.55	0.55	0.19	0.19
8	0.53	0.53	0.47	0.47	0.21	0.21	0.46	0.46	0.24	0.24	0.56	0.56

Table S7 Comparison of the N_2 electrochemical reduction activity for Fe/Mn-N-C with other catalysts.

Catalyst	ΔG_{max} (eV)	PDS	Ref.
Fe/Mn-N-C	0.37	$*NH_2+H^++e^-\rightarrow *NH_3$	This work
$Mo@N_1C_2$	0.47	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	2
$Ru@N_3$-G	0.73	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	3
$Ru@N_4$-G	0.77	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	3
Ru(101)	0.91	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	3
Ru/B_α	0.42	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	4
Ru/B_β	0.44	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	4
$Fe/Ti_3C_2O_2$	0.75	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	5
Mn@MoP	0.95	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	6
W@N-doped graphyne	0.38	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	7
Fe-N_3-G	0.84	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	8
FeOOH (110)	0.52	$*N\text{-}NH+H^++e^-\rightarrow *N\text{-}NH_2$	9
BP	0.56	$*NH\text{-}NH_2+H^++e^-\rightarrow *NH_2\text{-}NH_2$	10
$Ti@N_4$-G	0.69	$*NH_2+H^++e^-\rightarrow *NH_3$	11
$V@N_4$-G	0.87	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	11
Nb_2O_5 (181)	0.56	$*N\text{-}NH + H^++e^- \rightarrow *NN\text{-}H_2$	12
CoO (200)	0.75	$*N_2+H^++e^-\rightarrow *N\text{-}NH$	13

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