Supplementary Information for

Curvature Effects on the Bifunctional Oxygen Catalytic Performance of Single Atom Metal-N-C

Xuyan Zhou,[a,c] Zeyu Jin,[a,c] Jingzi Zhang,[a,c] Kailong Hu,[a,c] Sida Liu,[b] Hua-Jun Qiu,[a,c*] and Xi Lin[a,c,d*]*

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen 518055, China

[b] Institute for Advanced Technology, Shandong University, Jinan 250061, China

[c] Blockchain Development and Research Institute, Harbin Institute of Technology, Shenzhen 518055, China

[d] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China

Supplementary computational details

The ORR and OER pathways were calculated in detail according to electrochemical framework developed by Nørskov and his co-workers[1]. As for ORR, in an alkaline electrolyte, H_2O rather than H_3O^+ may act as the proton donor, so overall reaction scheme of the ORR can be written as:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^- \quad (S1)$$

Usually, the ORR reaction is the four-electron reaction pathway:

$$* + O_2(g) + H_2O(l) + e^- \rightarrow OH^- + *OOH \quad (S2)$$

$$*OOH + e^- \rightarrow OH^- + *O \quad (S3)$$

$$*O + H_2O(l) + e^- \rightarrow OH^- + *OH \quad (S4)$$

$$*OH + e^- \rightarrow OH^- + * \quad (S5)$$

where * represents the catalyst surface and *OOH, *O and *OH species are oxygenated intermediates.

As the reverse process of ORR, OER is also consists of four elementary steps:

$$OH^- + * \rightarrow *OH + e^- \quad (S6)$$

$$OH^- + *OH \rightarrow *O + H_2O(l) + e^- \quad (S7)$$

$$OH^- + *O \rightarrow *OOH + e^- \quad (S8)$$

$$OH^- + *OOH \rightarrow * + O_2(g) + H_2O(l) + e^- \quad (S9)$$

The reaction free energy of each step can be calculated by

$$\Delta G = \Delta E_{DFT} + \Delta ZPE - T\Delta S - eU \quad (S10)$$

where ΔE_{DFT}, ΔZPE and ΔS are the energy changes in the DFT total energy, zero-point energy and entropy from the initial state to the final state, respectively. As shown in Table S9, ZPE is obtained from vibrational frequency calculation. As for H_2O and H_2 molecules, their entropy values are taken from the NIST-JANAF thermodynamics table[2], while the entropies of adsorbate and adsorption sites are negligible[3]. Besides, the differences between the calculated free energies in vacuum and aqueous solution (VASPsol) are shown in Table S10 and regular DFT is employed in this work.

The theoretical overpotential η is determined by the potential limiting step:

$$\eta^{ORR} = \Delta G_{max}/e + 1.23 \quad (S11)$$

$$\eta^{OER} = \Delta G_{max}/e - 1.23 \quad (S12)$$

In order to establish trends in reactivity, the overpotential is often related to binding energy differences. The binding energy of the intermediate species to the surface are defined as:

$$\Delta G_{*O} = E_{*O} - E_{*} - E_{H2O} + E_{H2} + \Delta ZPE - T\Delta S \quad (S13)$$

$$\Delta G_{*OH} = E_{*OH} - E_{*} - E_{H2O} + (1/2)E_{H2} + \Delta ZPE - T\Delta S \quad (S14)$$

$$\Delta G_{*OOH} = E_{*OOH} - E_{*} - 2E_{H2O} + (3/2)E_{H2} + \Delta ZPE - T\Delta S \quad (S15)$$

where E_{*}, E_{*O}, E_{*OH} and E_{*OOH} are the DFT total energies of a clean catalyst surface and that absorbed by a O, OH and OOH species, respectively; E_{H2O} and E_{H2} are the energies of a H_2O and H_2 molecule in a vacuum, respectively.

Then, the reaction free energy of equations (S2-S5) (ΔG_1, ΔG_2, ΔG_3, ΔG_4,) for ORR can be calculated by the following equations:

$$\Delta G_1 = \Delta G_{*OOH} - 4.92 \quad (S16)$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OOH} \quad (S17)$$

$$\Delta G_3 = \Delta G_{*OH} - \Delta G_{*O} \quad (S18)$$

$$\Delta G_4 = - \Delta G_{*OH} \quad (S19)$$

The reaction free energy of equations (S6-S9) (ΔG_1, ΔG_2, ΔG_3, ΔG_4,) for OER can be calculated by the following equations:

$$\Delta G_1 = \Delta G_{*OH} \quad (S20)$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OH} \quad (S21)$$

$$\Delta G_3 = \Delta G_{*OOH} - \Delta G_{*O} \quad (S22)$$

$$\Delta G_4 = 4.92 - \Delta G_{*OOH} \quad (S23)$$

We check for the stability of the SAC against metal atom aggregation by comparing the difference between the adsorption energies of the metal atom on the N-doped carbon substrates (E_{bind}) and the bulk cohesive energy (E_{coh}) .

$$E_{bind} = E_{all} - E_{substrate} - E_{metal\text{-}atom} \quad (S24)$$

$$E_{coh} = 1/n * E_{bulk} - E_{metal\text{-}atom} \quad (S25)$$

where n is the number of atoms in the bulk.

Figures

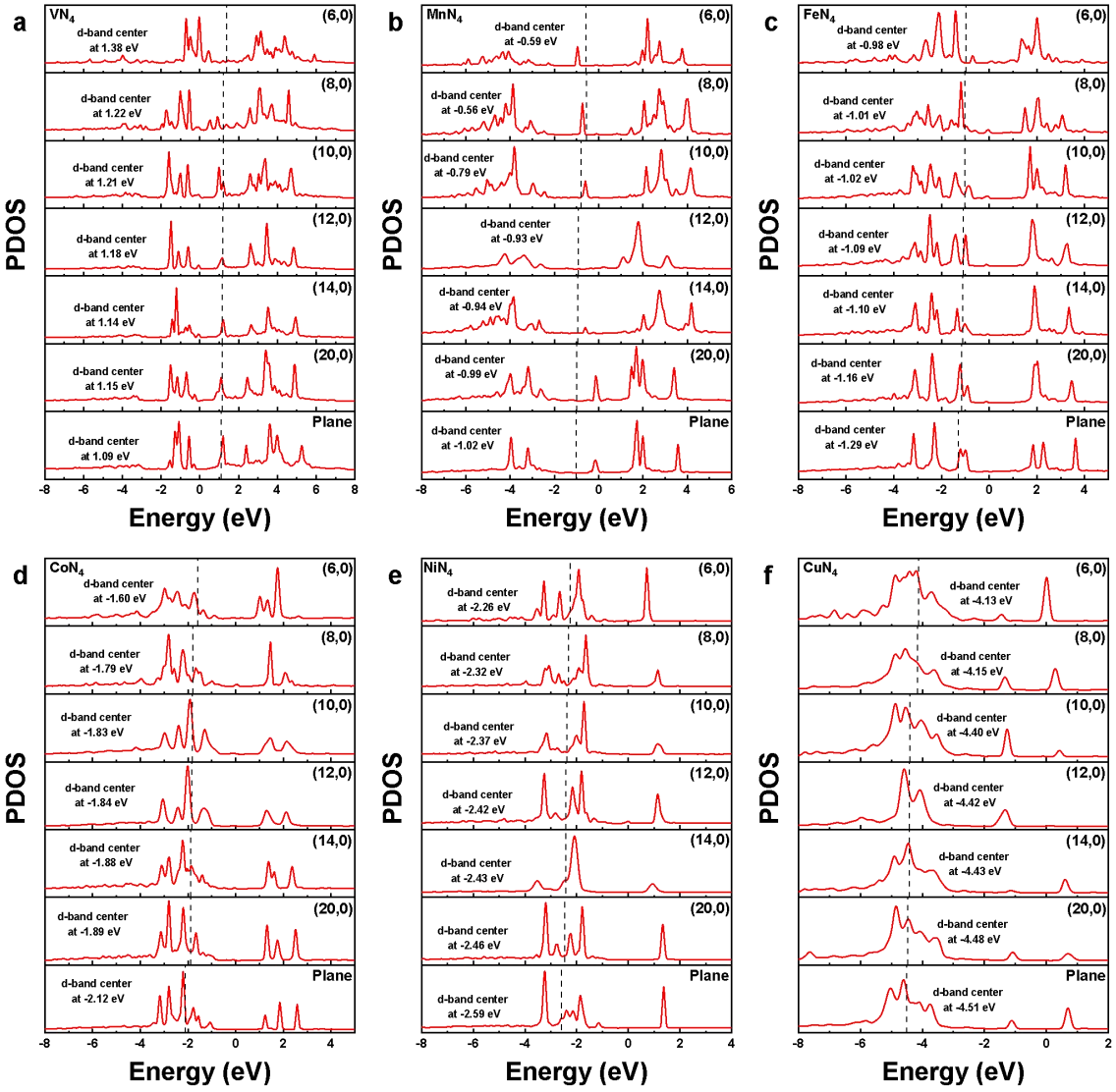

Fig. 1S. Projected density of states (pDOS) onto the d-orbital of metal atom: (a) VN_4, (b) MnN_4, (c) FeN_4, (d) CoN_4, (e) NiN_4 and (f) CuN_4. The black dashed lines indicate the d-band center.

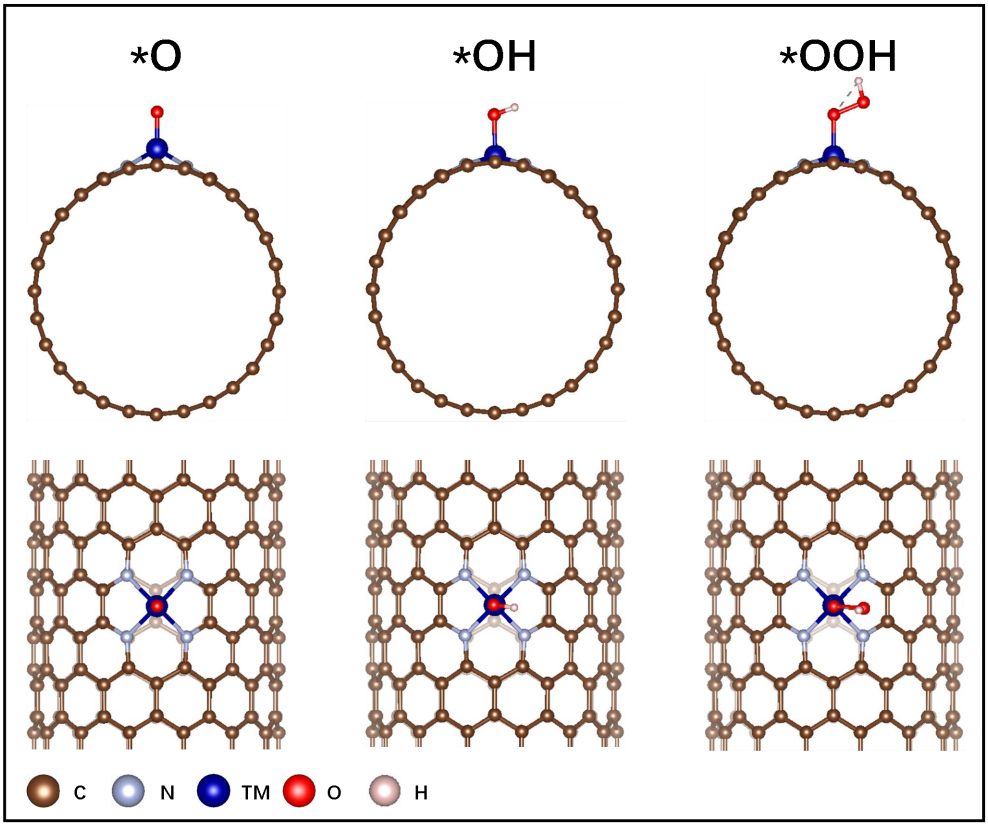

Fig. S2. The structures of reaction intermediates *OH, *O and *OOH.

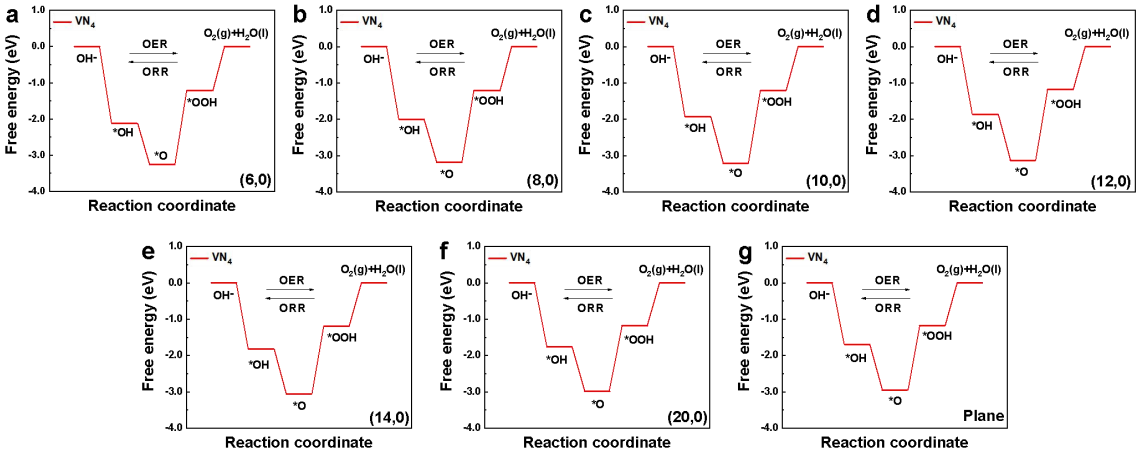

Fig. S3. Free energy diagrams of ORR and OER on VN_4 with different curvatures.

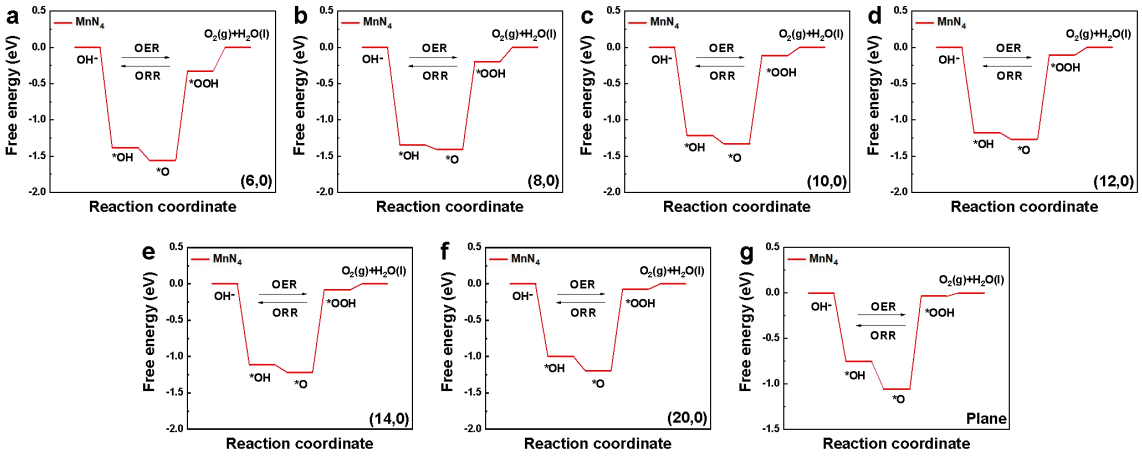

Fig. S4. Free energy diagrams of ORR and OER on MnN_4 with different curvatures.

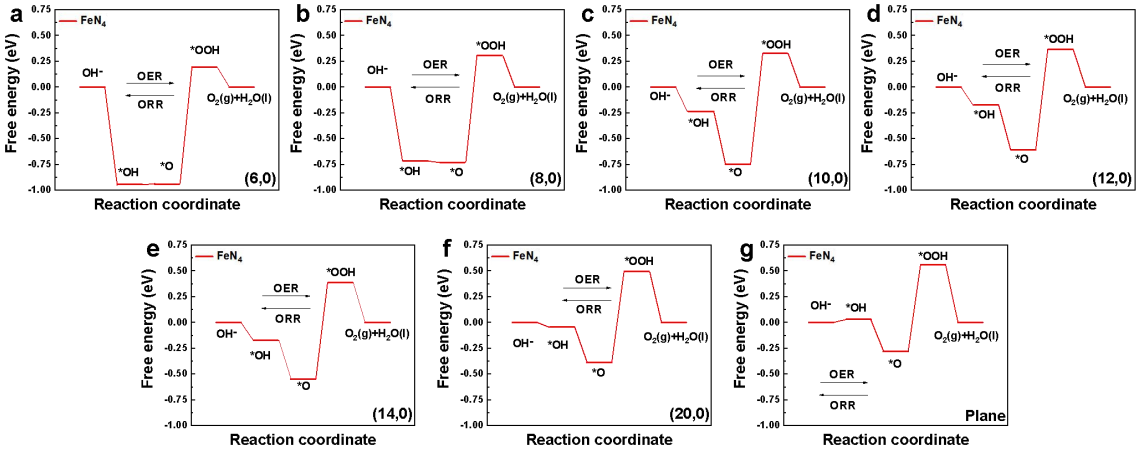

Fig. S5. Free energy diagrams of ORR and OER on FeN_4 with different curvatures.

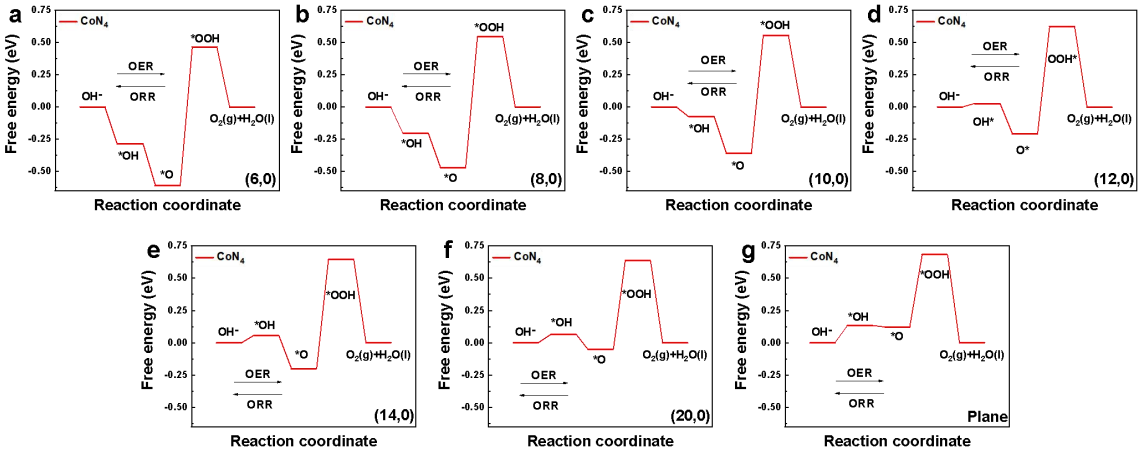

Fig. S6. Free energy diagrams of ORR and OER on CoN_4 with different curvatures.

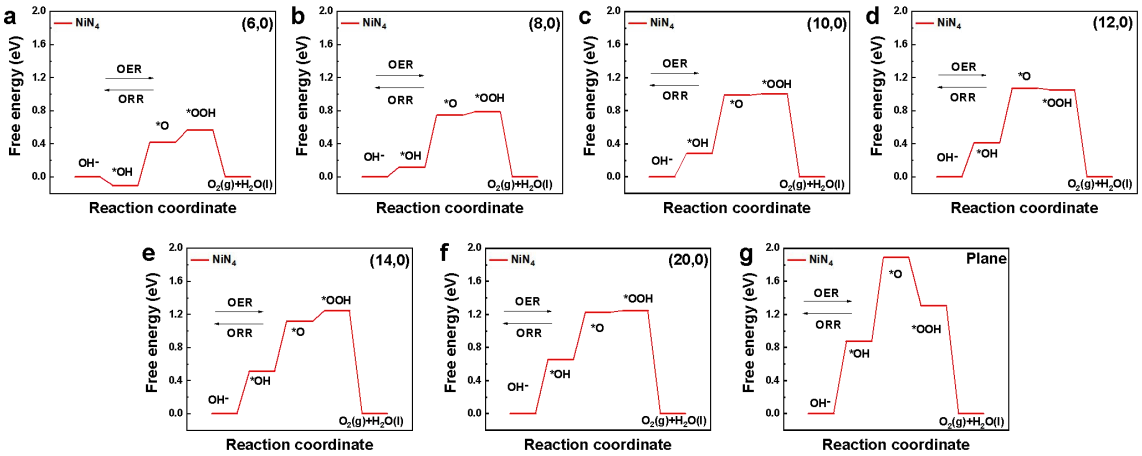

Fig. S7. Free energy diagrams of ORR and OER on NiN_4 with different curvatures.

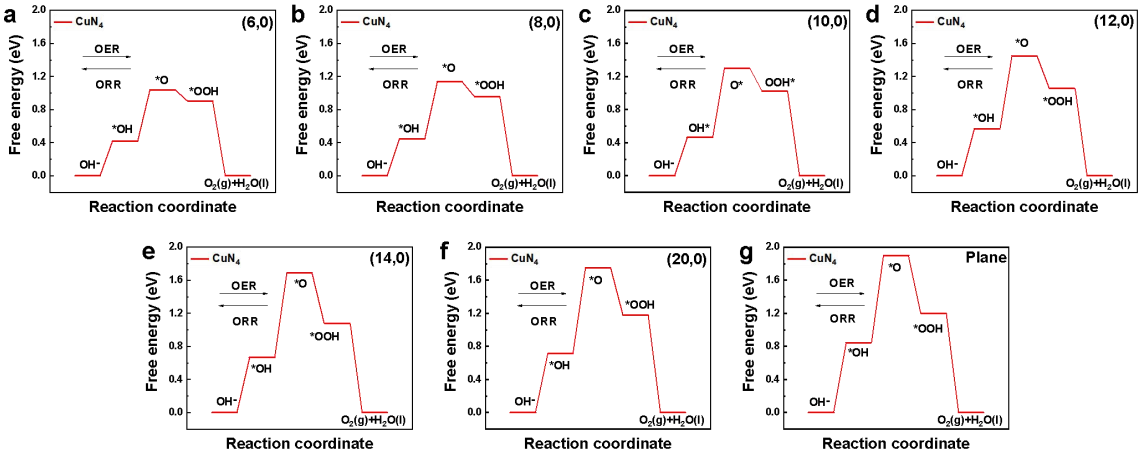

Fig. S8. Free energy diagrams of ORR and OER on CuN_4 with different curvatures.

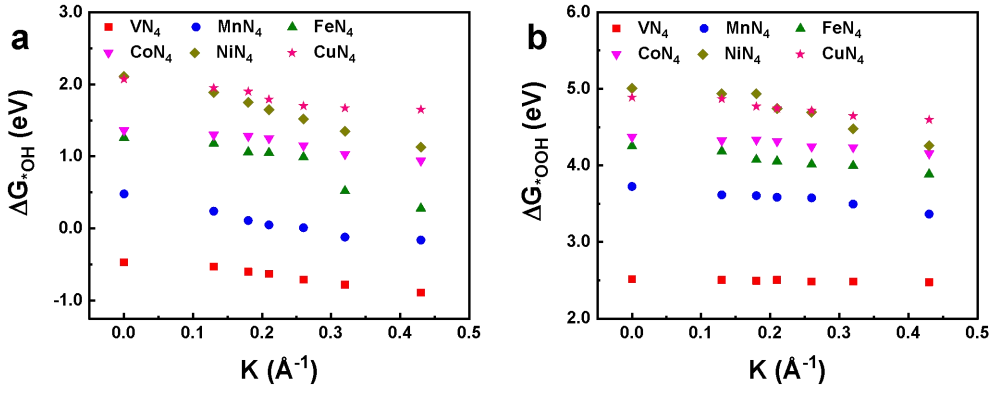

Fig. S9. ΔG_{*OH} (a) and ΔG_{*OOH} (b) versus K.

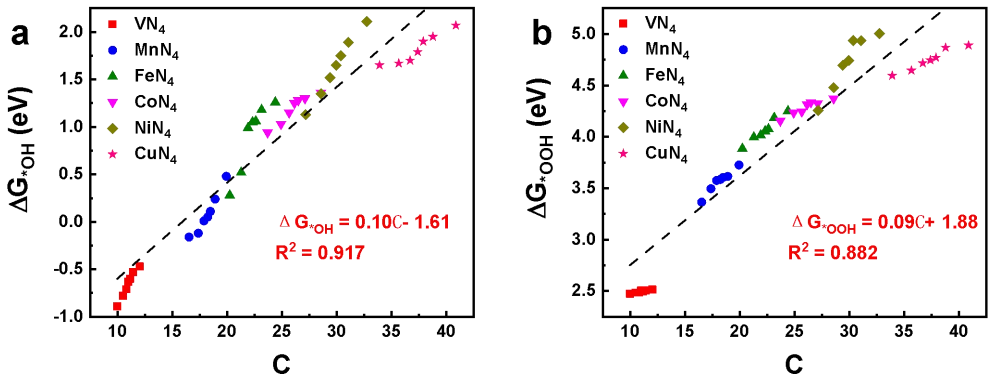

Fig. S10. ΔG_{*OH} (a) and ΔG_{*OOH} (b) versus the descriptor C.

Tables

Table S1 Values of U-J parameters for each metal element.

	V	Mn	Fe	Co	Ni	Cu
U-J	2.72	3.06	3.29	3.42	3.40	3.87

Table S2 Diameter (D), radius (R) and curvature (K) of each model.

Models	D (Å)	R (Å)	K ($Å^{-1}$)
(6,0)	4.70	2.35	0.43
(8,0)	6.26	3.13	0.32
(10,0)	7.83	3.92	0.26
(12,0)	9.39	4.70	0.21
(14,0)	10.96	5.48	0.18
(20,0)	15.66	7.83	0.13
Plane	∞	∞	0

Table S3 Reaction free energies of each step for ORR and overpotentials for VN_4, MnN_4, FeN_4, CoN_4, NiN_4, and CuN_4. The rate-limiting steps are highlighted in bold font.

Models		ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{ORR} (V)
VN_4	(6,0)	-2.45	-3.27	-0.09	**0.89**	2.12
	(8,0)	-2.44	-3.21	-0.05	**0.78**	2.01
	(10,0)	-2.44	-3.23	0.04	**0.71**	1.94
	(12,0)	-2.41	-3.17	0.03	**0.63**	1.86
	(14,0)	-2.43	-3.09	0.00	**0.60**	1.83
	(20,0)	-2.41	-3.03	-0.01	**0.53**	1.76
	Plane	-2.40	-3.02	0.03	**0.47**	1.70
MnN_4	(6,0)	-1.56	-2.46	-1.06	**0.16**	1.39
	(8,0)	-1.43	-2.45	-1.16	**0.12**	1.35
	(10,0)	-1.35	-2.44	-1.12	**-0.01**	1.22
	(12,0)	-1.34	-2.40	-1.13	**-0.05**	1.18
	(14,0)	-1.32	-2.37	-1.12	**-0.11**	1.12
	(20,0)	-1.30	-2.35	-1.03	**-0.24**	0.99
	Plane	-1.19	-2.33	-0.93	**-0.47**	0.75
FeN_4	(6,0)	-1.03	-2.37	-1.23	**-0.29**	0.95
	(8,0)	-0.93	-2.26	-1.21	**-0.52**	0.71

	(10,0)	-0.91	-2.31	**-0.71**	-0.99	0.52
	(12,0)	-0.87	-2.2	**-0.80**	-1.05	0.43
	(14,0)	**-0.84**	-2.17	-0.85	-1.06	0.39
	(20,0)	**-0.74**	-2.11	-0.89	-1.18	0.49
	Plane	**-0.67**	-2.07	-0.92	-1.26	0.56
	(6,0)	**-0.77**	-2.31	-0.90	-0.94	0.46
	(8,0)	**-0.68**	-2.25	-0.96	-1.03	0.55
	(10,0)	**-0.67**	-2.15	-0.95	-1.15	0.56
CoN_4	(12,0)	**-0.61**	-2.06	-1.00	-1.25	0.62
	(14,0)	**-0.59**	-2.07	-0.98	-1.28	0.64
	(20,0)	**-0.59**	-1.91	-1.12	-1.30	0.64
	Plane	**-0.55**	-1.79	-1.22	-1.36	0.68
	(6,0)	**-0.66**	-1.38	-1.75	-1.13	0.57
	(8,0)	**-0.44**	-1.27	-1.86	-1.35	0.79
	(10,0)	**-0.23**	-1.24	-1.93	-1.52	1.00
NiN_4	(12,0)	**-0.18**	-1.20	-1.89	-1.65	1.05
	(14,0)	**0.02**	-1.36	-1.83	-1.75	1.25
	(20,0)	**0.01**	-1.24	-1.8	-1.89	1.24
	Plane	**0.08**	-0.65	-2.24	-2.11	1.31
	(6,0)	**-0.32**	-1.10	-1.85	-1.65	0.91
	(8,0)	**-0.27**	-1.05	-1.93	-1.67	0.96
	(10,0)	**-0.21**	-0.95	-2.06	-1.70	1.03
CuN_4	(12,0)	**-0.18**	-0.84	-2.11	-1.79	1.05
	(14,0)	**-0.14**	-0.62	-2.26	-1.90	1.08
	(20,0)	**-0.04**	-0.66	-2.27	-1.95	1.18
	Plane	**-0.03**	-0.53	-2.29	-2.07	1.20

Table S4 Reaction free energies of each step for OER and overpotentials for VN_4, MnN_4, FeN_4, CoN_4, NiN_4, and CuN_4. The rate-limiting steps are highlighted in bold font.

Models		ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{OER} (V)
VN_4	(6,0)	-0.89	0.09	**3.27**	2.45	2.04
	(8,0)	-0.78	0.05	**3.21**	2.44	1.98
	(10,0)	-0.71	-0.04	**3.23**	2.44	2.00
	(12,0)	-0.63	-0.03	**3.17**	2.41	1.94
	(14,0)	-0.6	0.00	**3.09**	2.43	1.86
	(20,0)	-0.53	0.01	**3.03**	2.41	1.80
	Plane	-0.47	-0.03	**3.02**	2.4	1.79
MnN_4	(6,0)	-0.16	1.06	**2.46**	1.56	1.23
	(8,0)	-0.12	1.16	**2.45**	1.43	1.22
	(10,0)	0.01	1.12	**2.44**	1.35	1.21
	(12,0)	0.05	1.13	**2.4**	1.34	1.17
	(14,0)	0.11	1.12	**2.37**	1.32	1.14
	(20,0)	0.24	1.03	**2.35**	1.3	1.12
	Plane	0.47	0.93	**2.33**	1.19	1.10
FeN_4	(6,0)	0.29	1.23	**2.37**	1.03	1.14
	(8,0)	0.52	1.21	**2.26**	0.93	1.03
	(10,0)	0.99	0.71	**2.31**	0.91	1.08
	(12,0)	1.05	0.80	**2.20**	0.87	0.97
	(14,0)	1.06	0.85	**2.17**	0.84	0.94
	(20,0)	1.18	0.89	**2.11**	0.74	0.88
	Plane	1.26	0.92	**2.07**	0.67	0.84
CoN_4	(6,0)	0.94	0.90	**2.31**	0.77	1.08
	(8,0)	1.03	0.96	**2.25**	0.68	1.02
	(10,0)	1.15	0.95	**2.15**	0.67	0.92
	(12,0)	1.25	1.00	**2.06**	0.61	0.83
	(14,0)	1.28	0.98	**2.07**	0.59	0.84
	(20,0)	1.3	1.12	**1.91**	0.59	0.68
	Plane	1.36	1.22	**1.79**	0.55	0.56
NiN_4	(6,0)	1.13	**1.75**	1.38	0.66	0.52
	(8,0)	1.35	**1.86**	1.27	0.44	0.63
	(10,0)	1.52	**1.93**	1.24	0.23	0.70

	(12,0)	1.65	**1.89**	1.20	0.18	0.66
	(14,0)	1.75	**1.83**	1.36	-0.02	0.60
	(20,0)	**1.89**	1.80	1.24	-0.01	0.66
	Plane	2.11	**2.24**	0.65	-0.08	1.01
	(6,0)	1.65	**1.85**	1.10	0.32	0.62
	(8,0)	1.67	**1.93**	1.05	0.27	0.70
	(10,0)	1.70	**2.06**	0.95	0.21	0.83
CuN_4	(12,0)	1.79	**2.11**	0.84	0.18	0.88
	(14,0)	1.90	**2.26**	0.62	0.14	1.03
	(20,0)	1.95	**2.27**	0.66	0.04	1.04
	Plane	2.07	**2.29**	0.53	0.03	1.06

Table S5 Adsorption free energies of *O, *OH and *OOH for each model.

Models		ΔG_{*O} (eV)	ΔG_{*OH} (eV)	ΔG_{*OOH} (eV)
	(6,0)	-0.80	-0.89	2.47
	(8,0)	-0.73	-0.78	2.48
	(10,0)	-0.75	-0.71	2.48
VN_4	(12,0)	-0.67	-0.63	2.51
	(14,0)	-0.60	-0.60	2.49
	(20,0)	-0.53	-0.53	2.50
	Plane	-0.49	-0.47	2.52
	(6,0)	0.90	-0.16	3.36
	(8,0)	1.05	-0.12	3.49
	(10,0)	1.13	0.01	3.57
MnN_4	(12,0)	1.19	0.05	3.58
	(14,0)	1.24	0.11	3.60
	(20,0)	1.26	0.24	3.61
	Plane	1.40	0.48	3.73
	(6,0)	1.52	0.28	3.89
FeN_4	(8,0)	1.73	0.52	3.99
	(10,0)	1.71	0.99	4.01
	(12,0)	1.85	1.05	4.05

	(14,0)	1.91	1.06	4.08
	(20,0)	2.07	1.18	4.18
	Plane	2.18	1.26	4.25
	(6,0)	1.84	0.94	4.15
	(8,0)	1.99	1.03	4.24
	(10,0)	2.10	1.15	4.25
CoN_4	(12,0)	2.25	1.25	4.31
	(14,0)	2.26	1.28	4.33
	(20,0)	2.41	1.30	4.33
	Plane	2.58	1.36	4.37
	(6,0)	2.88	1.13	4.26
	(8,0)	3.21	1.35	4.48
	(10,0)	3.45	1.52	4.69
NiN_4	(12,0)	3.53	1.65	4.74
	(14,0)	3.58	1.75	4.94
	(20,0)	3.69	1.89	4.93
	Plane	4.35	2.11	5.00
	(6,0)	3.50	1.65	4.60
	(8,0)	3.60	1.67	4.65
	(10,0)	3.76	1.70	4.72
CuN_4	(12,0)	3.91	1.79	4.74
	(14,0)	4.15	1.90	4.77
	(20,0)	4.21	1.95	4.87
	Plane	4.36	2.07	4.89

Table S6 The valence electrons in the d-orbital (N_d) and electronegativity (χ) for each element.

Elements	N_d	χ_M
N	-	3.04
O	-	3.44
Sc	1	1.36
Ti	2	1.54
V	3	1.63
Cr	5	1.66
Mn	5	1.55
Fe	6	1.83
Co	7	1.88
Ni	8	1.92
Cu	10	1.90
Zn	10	1.65
Y	1	1.22
Zr	2	1.33
Nb	4	1.59
Mo	5	2.16
Tc	5	1.91
Ru	7	2.20
Rh	8	2.28
Pd	10	2.20
Ag	10	1.93
Cd	10	1.69
Hf	2	1.32
Ta	3	1.51
W	4	2.36
Re	5	1.93
Os	6	2.18
Ir	7	2.20
Pt	9	2.28
Au	10	2.54

Table S7 The corresponding descriptor (C) for VN_4, MnN_4, FeN_4, CoN_4, NiN_4, and CuN_4.

Models	C						
	(6,0)	(8,0)	(10,0)	(12,0)	(14,0)	(20,0)	Plane
VN_4	9.98	10.49	10.80	11.00	11.15	11.41	12.03
MnN_4	16.53	17.38	17.89	18.23	18.48	18.91	19.93
FeN_4	20.24	21.29	21.91	22.32	22.62	23.15	24.40
CoN_4	23.70	24.92	25.66	26.14	26.49	27.11	28.57
NiN_4	27.16	28.57	29.40	29.95	30.36	31.07	32.74
CuN_4	33.91	35.66	36.70	37.39	37.90	38.78	40.87

Table S8 The corresponding descriptor (C) for other models.

Models	C						
	(6,0)	(8,0)	(10,0)	(12,0)	(14,0)	(20,0)	Plane
ScN_4	3.26	3.43	3.53	3.60	3.64	3.73	3.93
TiN_4	6.61	6.95	7.15	7.29	7.39	7.56	7.97
CrN_4	16.66	17.52	18.04	18.38	18.62	19.06	20.09
ZnN_4	33.30	35.02	36.05	36.72	37.22	38.09	40.15
YN_4	3.23	3.39	3.49	3.56	3.61	3.69	3.89
ZrN_4	6.51	6.84	7.04	7.17	7.27	7.44	7.84
NbN_4	13.26	13.95	14.36	14.63	14.82	15.17	15.99
MoN_4	17.27	18.16	18.69	19.04	19.30	19.75	20.81
TcN_4	16.97	17.84	18.36	18.71	18.96	19.40	20.45
RuN_4	24.24	25.49	26.24	26.73	27.09	27.72	29.22
RhN_4	27.86	29.30	30.16	30.72	31.14	31.86	33.58
PdN_4	34.63	36.42	37.49	38.19	38.71	39.61	41.74
AgN_4	33.98	35.73	36.78	37.47	37.98	38.86	40.96
CdN_4	33.40	35.12	36.15	36.83	37.33	38.20	40.26
HfN_4	6.50	6.84	7.04	7.17	7.27	7.44	7.84
TaN_4	9.89	10.40	10.71	10.91	11.05	11.31	11.92
WN_4	14.01	14.73	15.16	15.45	15.65	16.02	16.88
ReN_4	16.99	17.87	18.39	18.73	18.99	19.43	20.48
OsN_4	20.75	21.82	22.46	22.88	23.19	23.73	25.01
IrN_4	24.24	25.49	26.24	26.73	27.09	27.72	29.22
PtN_4	31.34	32.96	33.93	34.56	35.03	35.84	37.78
AuN_4	35.45	37.28	38.37	39.09	39.62	40.54	42.73

Table S9 Zero-point energy (ZPE) and entropy correction (TS) at T = 298 K for relevant species.

Species	ZPE (eV)	TS (eV)
H_2O	0.56	0.67
H_2	0.27	0.41
*OOH	0.35	0
*OH	0.30	0
*O	0.05	0

Table S10 Adsorption free energies of *O, *OH and *OOH in vacuum and aqueous solution.

Models		VASP			VASPsol		
		ΔG_{*O} (eV)	ΔG_{*OH} (eV)	ΔG_{*OOH} (eV)	ΔG_{*O} (eV)	ΔG_{*OH} (eV)	ΔG_{*OOH} (eV)
CoN_4	(6,0)	1.84	0.94	4.15	1.84	0.91	4.10
	(8,0)	1.99	1.03	4.24	1.98	1.03	4.20
	(10,0)	2.10	1.15	4.25	2.07	1.15	4.24
	(12,0)	2.25	1.25	4.31	2.22	1.25	4.31
	(14,0)	2.26	1.28	4.33	2.22	1.27	4.32
	(20,0)	2.41	1.30	4.33	2.41	1.30	4.33
	Plane	2.58	1.36	4.37	2.58	1.35	4.35

References

1 J. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvistt, *J. Phys. Chem. B,* 2004, **108**, 17886 – 17892.

2 M. Chase Jr, NIST JANAF Thermochemical Tables; American Institute of Physics: New York, 1998.

3 H. Xu, D. Cheng, D. Cao, X. C. Zeng, *Nat. Catal.,* 2018, **1**, 339-348.