Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Revealing a Power-Law Relationship Between Dopant-Metal Distance and Adsorption Free Energy Change for Precise Optimization of ORR on TM_1N_4 Single-Atom Catalysts

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Simulation Details

The structural, electronic and energetic performances of all TM_1N_4 active centers were simulated by density functional theory (DFT) as a branch of the first principle theory. DFT simulations were achieved by Vienna Ab-initio Simulation Package (VASP) [1]. All atomic structures involved were fully relaxed with the energy, force and displacement convergences of 1.0×10^{-6} eV/atom, 0.01 eV/Å and and 5.0×10^{-4} Å. The placewave cutoff energy and Monkhorst-Pack k-point meshes of 9×9×1 were tested to be converged under the Perdew-Burke-Ernzerh (PBE) functional of generalized gradient approximation (GGA) [2]. The empirical correction of Grimme′s scheme D3 was adopted to describe the *van der Waals* interactions between intermediates and substrates [3]. The solvent of water with the dielectric constant of 78.54 was also considered to obtain the effects of water molecule on the adsorption state and adsorption energy of all systems.

The electrochemical model of ORR in alkaline media could be divided for:

four-electron reactions:

$$* + O_2(g) + H_2O(l) + e^- \rightarrow OOH* + OH^- \qquad (S1)$$

$$OOH* + e^- \rightarrow O* + OH^- \qquad (S2)$$

$$O* + H_2O\ (l) + e^- \rightarrow OH* + OH^- \qquad (S3)$$

$$OH* + e^- \rightarrow * + OH^- \qquad (S4)$$

or two-electron reactions:

$$* + O_2(g) + H_2O(l) + e^- \rightarrow OOH* + OH^- \qquad (S1)$$

$$OOH* + + H_2O(l) + e^- \rightarrow H_2O_2* + OH^- \qquad (S5)$$

where the * denoted the TM_1N_4 active center. The adsorption energies of intermediates (OOH, O and OH groups) on substrates were calculated by following:

$$\Delta E_{*OOH} = E(\mathrm{sub/OOH}) - E(\mathrm{sub}) - [2\times E(H_2O) - 3\times E(H_2)/2] \qquad (S6)$$

$$\Delta E_{*OH} = E(\mathrm{sub/OH}) - E(\mathrm{sub}) - [E(H_2O) - E(H_2)/2] \qquad (S7)$$

$$\Delta E_{*O} = E(\mathrm{sub/O}) - E(\mathrm{sub}) - [E(H_2O) - E(H_2)] \qquad (S8)$$

where $E(\mathrm{sub}/H_2O)$, $E(\mathrm{sub/OOH})$, $E(\mathrm{sub/O})$ and $E(\mathrm{sub/OH})$ denoted the total energies of H_2O, OOH, O and OH groups on substrates. $E(\mathrm{sub})$, $E(H_2O)$ and $E(H_2)$ were the energies of bare substrate, water, and hydrogen gas, respectively.

Gibbs free energy changes of steps S1-S4 could be estimated by:

$$\Delta G_1 = 4.92\ \mathrm{eV} - \Delta G_{OOH*} \qquad (S9)$$

$$\Delta G_2 = \Delta G_{OOH*} - \Delta G_{O*} \qquad (S10)$$

$$\Delta G_3 = \Delta G_{O*} - \Delta G_{OH*} \qquad (S11)$$

$$\Delta G_4 = \Delta G_{OH*} \qquad (S12)$$

where the sum of $\Delta G_{1\text{-}4}$ was fixed to the negative of experimental Gibbs free energy of formation of two water molecules ($-2\Delta_{H2O} = 4.92$ eV). Gibbs free energy of ($H^+ + e^-$) in solution was estimated as the half energy of H_2 molecule at standard condition.

The correlations between the adsorption free energy ($\Delta G_{ads} = \Delta G_{OOH*}$, ΔG_{O*} or ΔG_{OH*}) and *d*-band center (ε_d) of d_{z2} orbitals for TM_1 monoatoms:

$$\Delta G_{OOH*} = -1.062\times\varepsilon_d + 2.274,\ R^2 = 0.830 \tag{S13}$$

$$\Delta G_{O*} = -2.651\times\varepsilon_d - 1.932,\ R^2 = 0.841 \tag{S14}$$

$$\Delta G_{OH*} = -1.202\times\varepsilon_d - 1.171,\ R^2 = 0.816 \tag{S15}$$

The correlations between the adsorption free energy change (ΔG_{doped} - $\Delta G_{pristine}$) and dopant nitrogen distance ($d_{TM\text{-}N}$) was regarded as the power functions:

$$\Delta G_{doped} - \Delta G_{pristine} = (d_{TM\text{-}N})^A \tag{S16}$$

where ΔG_{doped} and $\Delta G_{pristine}$ were the adsorption free energies for doped and pristine systems, the superscript A denoted the variable values related to the oxygenous intermediate and TM_1N_4 active centers (see **Tab. S4**).

The ORR overpotential of two-electron steps was expressed as:

$$\eta^{2e} = |0.695 - \Delta G_1| \tag{S17}$$

The ORR overpotential of four-electron steps was expressed as:

$$\eta^{4e} = 1.23 - U_{ORR} \tag{S18}$$

$$U_{ORR} = \mathrm{Min}(\Delta G_1, \Delta G_2, \Delta G_3, G_4)/e \tag{S19}$$

Table S1. The d-band center (ε_d) values of d_{z2} orbitals in Fe_1 monoatom. The distance between TM atom and N dopant (d_{TM-N}) in Fe_1N_4@carbon. Adsorption energies of each intermediate (ΔG_{OOH*}, ΔG_{O*} or ΔG_{OH*}), the free energy change of each elemental step (ΔG_1, ΔG_2, ΔG_3 or ΔG_4) and the ORR overpotentials for four-electron (η^{4e}) and two-electron (η^{2e}) steps on pristine and nitrogen doped Fe_1N_4 active centers.

Positions	ε_d (eV)	d_{TM-N} (Å)	ΔG_{OOH*} (eV)	ΔG_{O*} (eV)	ΔG_{OH*} (eV)	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{2e} (V)	η^{4e} (V)
Pristine	-0.762	/	3.406	0.919	0.182	1.514	2.687	0.637	0.082	0.819	1.148
1 site	-1.296	2.639	3.786	1.334	0.461	1.134	2.452	0.873	0.461	0.439	0.769
2 site	-0.926	3.038	3.646	1.258	0.417	1.274	2.428	0.801	0.417	0.579	0.813
3 site	-1.038	3.421	3.629	1.236	0.393	1.291	2.393	0.843	0.393	0.596	0.837
4 site	-1.160	3.997	3.593	1.203	0.375	1.327	2.39	0.828	0.375	0.632	0.855
5 site	-1.312	4.286	3.523	1.176	0.358	1.397	2.347	0.818	0.358	0.702	0.872
6 site	-1.181	4.675	3.515	1.184	0.339	1.405	2.321	0.855	0.339	0.710	0.891
7 site	-1.561	4.894	3.499	1.146	0.327	1.421	2.373	0.799	0.327	0.726	0.903
8 site	-1.331	5.003	3.492	1.157	0.347	1.428	2.295	0.850	0.347	0.733	0.883
9 site	-1.342	5.517	3.489	1.163	0.333	1.431	2.276	0.880	0.333	0.736	0.897
10 site	-1.325	5.761	3.489	1.181	0.335	1.431	2.248	0.906	0.335	0.736	0.895
11 site	-1.352	6.083	3.475	1.172	0.343	1.445	2.303	0.829	0.343	0.750	0.887
12 site	-1.376	6.334	3.471	1.150	0.310	1.449	2.221	0.940	0.310	0.754	0.920
13 site	-1.446	6.771	3.474	1.141	0.319	1.446	2.283	0.872	0.319	0.751	0.911
14 site	-1.304	6.793	3.496	1.148	0.302	1.424	2.248	0.946	0.302	0.729	0.928
15 site	-1.397	7.016	3.488	1.138	0.300	1.432	2.290	0.898	0.300	0.737	0.930
16 site	-1.395	7.174	3.502	1.119	0.314	1.418	2.283	0.905	0.314	0.723	0.916
17 site	-1.279	7.417	3.477	1.122	0.288	1.443	2.255	0.934	0.288	0.748	0.942
18 site	-1.310	7.782	3.474	1.127	0.270	1.446	2.247	0.957	0.270	0.751	0.960
19 site	-1.289	8.202	3.431	1.121	0.264	1.489	2.210	0.957	0.264	0.794	0.966

Table S2. The *d*-band center (ε_d) values of d_{z2} orbitals in Co_1 monoatom. The distance between TM atom and N dopant ($d_{TM\text{-}N}$) in Co_1N_4@carbon. Adsorption energies of each intermediate (ΔG_{OOH*}, ΔG_{O*} or ΔG_{OH*}), the free energy change of each elemental step (ΔG_1, ΔG_2, ΔG_3 or ΔG_4) and the ORR overpotentials for four-electron (η^{4e}) and two-electron (η^{2e}) on pristine and nitrogen doped Co_1N_4 active centers.

Positions	ε_d (eV)	$d_{TM\text{-}N}$ (Å)	ΔG_{OOH*} (eV)	ΔG_{O*} (eV)	ΔG_{OH*} (eV)	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{2e} (V)	η^{4e} (V)
Pristine	-1.218	/	3.963	2.506	0.650	0.957	1.487	1.926	0.55	0.262	0.680
1 site	-1.702	2.628	4.243	2.926	0.914	0.677	1.317	2.012	0.914	0.018	0.553
2 site	-1.637	3.010	4.199	2.788	0.791	0.721	1.479	1.929	0.791	0.026	0.509
3 site	-1.694	3.419	4.142	2.720	0.773	0.778	1.354	2.015	0.773	0.083	0.457
4 site	-1.736	3.983	4.114	2.713	0.751	0.806	1.401	1.962	0.751	0.111	0.479
5 site	-1.596	4.283	4.118	2.687	0.712	0.802	1.481	1.925	0.712	0.107	0.518
6 site	-1.753	4.672	4.156	2.677	0.733	0.764	1.479	1.944	0.733	0.069	0.497
7 site	-1.776	4.892	4.125	2.667	0.743	0.795	1.458	1.924	0.743	0.100	0.487
8 site	-1.731	5.004	4.099	2.685	0.732	0.821	1.374	1.993	0.732	0.126	0.498
9 site	-1.596	5.515	4.094	2.655	0.724	0.826	1.459	1.911	0.724	0.131	0.506
10 site	-1.607	5.759	4.111	2.697	0.716	0.809	1.414	1.981	0.716	0.114	0.514
11 site	-1.637	6.085	4.112	2.687	0.716	0.808	1.425	1.971	0.716	0.113	0.514
12 site	-1.803	6.330	4.093	2.692	0.720	0.827	1.401	1.972	0.720	0.132	0.510
13 site	-1.811	6.768	4.093	2.663	0.718	0.827	1.430	1.945	0.718	0.132	0.512
14 site	-1.758	6.792	4.117	2.674	0.732	0.803	1.373	2.012	0.732	0.108	0.498
15 site	-1.637	7.013	4.114	2.634	0.717	0.806	1.480	1.917	0.717	0.111	0.513
16 site	-1.859	7.171	4.096	2.648	0.701	0.824	1.448	1.947	0.701	0.129	0.529
17 site	-1.793	7.417	4.076	2.643	0.696	0.844	1.433	1.947	0.696	0.149	0.534
18 site	-1.769	7.784	4.112	2.661	0.710	0.808	1.421	1.981	0.710	0.113	0.520
19 site	-1.814	8.202	4.085	2.654	0.708	0.835	1.431	1.946	0.708	0.140	0.522

Table S3. The *d*-band center (ε_d) values of d_{z2} orbitals in Ni_1 monoatom. The distance between TM atom and N dopant ($d_{TM\text{-}N}$) in Ni_1N_4@carbon. Adsorption energies of each intermediate (ΔG_{OOH*}, ΔG_{O*} or ΔG_{OH*}), the free energy change of each elemental step (ΔG_1, ΔG_2, ΔG_3 or ΔG_4) and the ORR overpotentials for four-electron (η^{4e}) and two-electron (η^{2e}) on pristine and nitrogen doped Ni_1N_4 active centers.

Positions	ε_d (eV)	$d_{TM\text{-}N}$ (Å)	ΔG_{OOH*} (eV)	ΔG_{O*} (eV)	ΔG_{OH*} (eV)	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{2e} (V)	η^{4e} (V)
Pristine	-1.601	/	4.541	3.754	1.474	0.379	0.787	2.38	1.374	0.316	0.851
1 site	-2.413	2.631	4.774	4.083	1.694	0.146	0.691	2.389	1.694	0.549	1.084
2 site	-2.187	3.024	4.670	4.004	1.600	0.25	0.666	2.404	1.600	0.445	0.980
3 site	-2.403	3.423	4.647	3.903	1.585	0.273	0.744	2.318	1.585	0.422	0.957
4 site	-2.217	3.991	4.655	3.901	1.581	0.265	0.754	2.320	1.581	0.430	0.965
5 site	-2.105	4.282	4.640	3.907	1.573	0.280	0.733	2.334	1.573	0.415	0.950
6 site	-2.122	4.679	4.629	3.886	1.579	0.291	0.793	2.257	1.579	0.404	0.939
7 site	-2.167	4.897	4.623	3.893	1.578	0.297	0.730	2.315	1.578	0.398	0.933
8 site	-2.206	4.998	4.637	3.860	1.568	0.283	0.777	2.292	1.568	0.412	0.947
9 site	-2.135	5.514	4.581	3.897	1.555	0.339	0.684	2.342	1.555	0.356	0.891
10 site	-2.155	5.759	4.565	3.899	1.559	0.355	0.666	2.340	1.559	0.340	0.875
11 site	-2.164	6.082	4.566	3.897	1.573	0.354	0.669	2.324	1.573	0.341	0.876
12 site	-2.160	6.334	4.574	3.875	1.555	0.346	0.699	2.320	1.555	0.349	0.884
13 site	-2.105	6.769	4.576	3.850	1.527	0.344	0.726	2.323	1.527	0.351	0.886
14 site	-1.951	6.794	4.583	3.859	1.526	0.337	0.724	2.333	1.526	0.358	0.893
15 site	-2.059	7.018	4.582	3.852	1.519	0.338	0.730	2.333	1.519	0.357	0.892
16 site	-2.105	7.172	4.563	3.835	1.535	0.357	0.728	2.300	1.535	0.338	0.873
17 site	-2.125	7.418	4.583	3.820	1.534	0.337	0.763	2.286	1.534	0.358	0.893
18 site	-2.149	7.780	4.565	3.813	1.512	0.355	0.752	2.301	1.512	0.340	0.875
19 site	-2.148	8.202	4.571	3.820	1.514	0.349	0.751	2.306	1.514	0.346	0.881

Table S4. The variable values of A and R^2 for **Equation S16**.

Active Centers	ΔG_{OOH*}		ΔG_{O*}		ΔG_{OH*}	
	A	R^2	A	R^2	A	R^2
Fe_1N_4	-1.314	0.852	-0.843	0.700	-1.167	0.784
Co_1N_4	-1.163	0.721	-1.040	0.738	-1.551	0.802
Ni_1N_4	-1.680	0.879	-1.257	0.842	-1.556	0.748

Table S5. Gibbs free energy change (ΔG_{dis}) and dissolution potential (E_{dis}) of dissolution reaction.

	TM	pristine	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
ΔG_{dis} (eV)	Fe	2.225	2.614	2.601	2.587	2.564	2.533	2.519	2.486	2.465	2.448
	Co	2.056	2.428	2.397	2.381	2.369	2.345	2.326	2.301	2.287	2.264
	Ni	1.859	2.195	2.173	2.156	2.133	2.119	2.095	2.064	2.048	2.037
E_{dis} (V)	Fe	-0.742	-0.871	-0.867	-0.862	-0.855	-0.844	-0.840	-0.829	-0.822	-0.816
	Co	-0.685	-0.809	-0.799	-0.794	-0.790	-0.782	-0.775	-0.767	-0.762	-0.755
	Ni	-0.620	-0.732	-0.724	-0.719	-0.711	-0.706	-0.698	-0.688	-0.683	-0.679
	TM	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15	Site 16	Site 17	Site 18	Site 19
ΔG_{dis} (eV)	Fe	2.423	2.416	2.395	2.374	2.342	2.318	2.289	2.271	2.259	2.247
	Co	2.244	2.230	2.208	2.189	2.176	2.152	2.128	2.107	2.085	2.071
	Ni	2.004	1.984	1.979	1.962	1.945	1.913	1.894	1.884	1.873	1.864
E_{dis} (V)	Fe	-0.808	-0.805	-0.798	-0.791	-0.781	-0.773	-0.763	-0.757	-0.753	-0.749
	Co	-0.748	-0.743	-0.736	-0.730	-0.725	-0.717	-0.709	-0.702	-0.695	-0.690
	Ni	-0.668	-0.661	-0.660	-0.654	-0.648	-0.638	-0.631	-0.628	-0.624	-0.621

Figure S1. Percentage change (%) of each TM-N bond length for (a) Fe_1N_4, (c) Co_1N_4, and (e) Ni_1N_4 active centers after one nitrogen doping. Averaged percentage changes in four TM-N bond lengths for (b) Fe_1N_4, (d) Co_1N_4, and (f) Ni_1N_4 active centers following nitrogen doping.

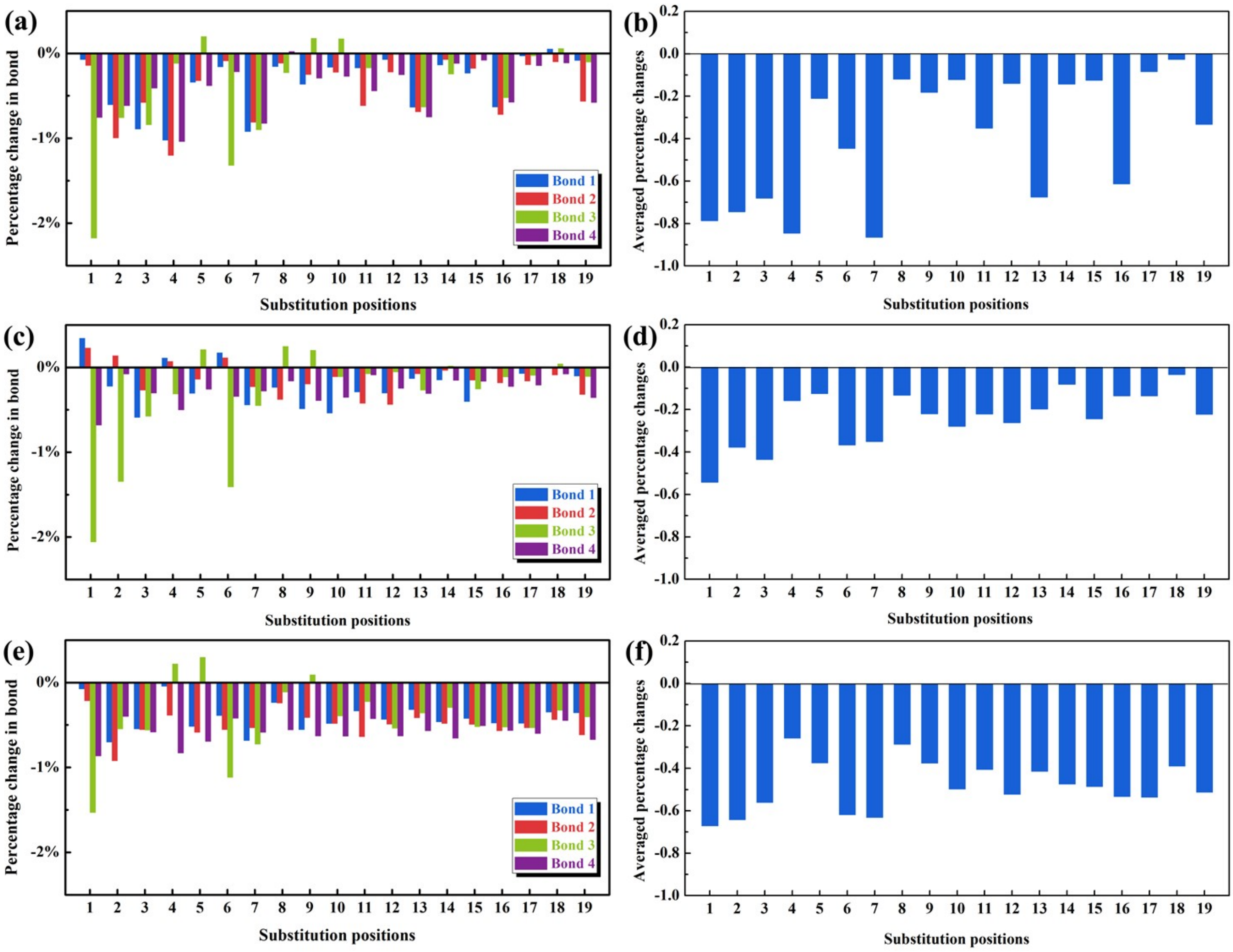


Figure S2. The d_{z2} orbitals of TM cations in (a)-(c) Fe_1N_4@carbon, (d)-(f) Co_1N_4@carbon, and (g)-(i) Ni_1N_4@carbon systems.

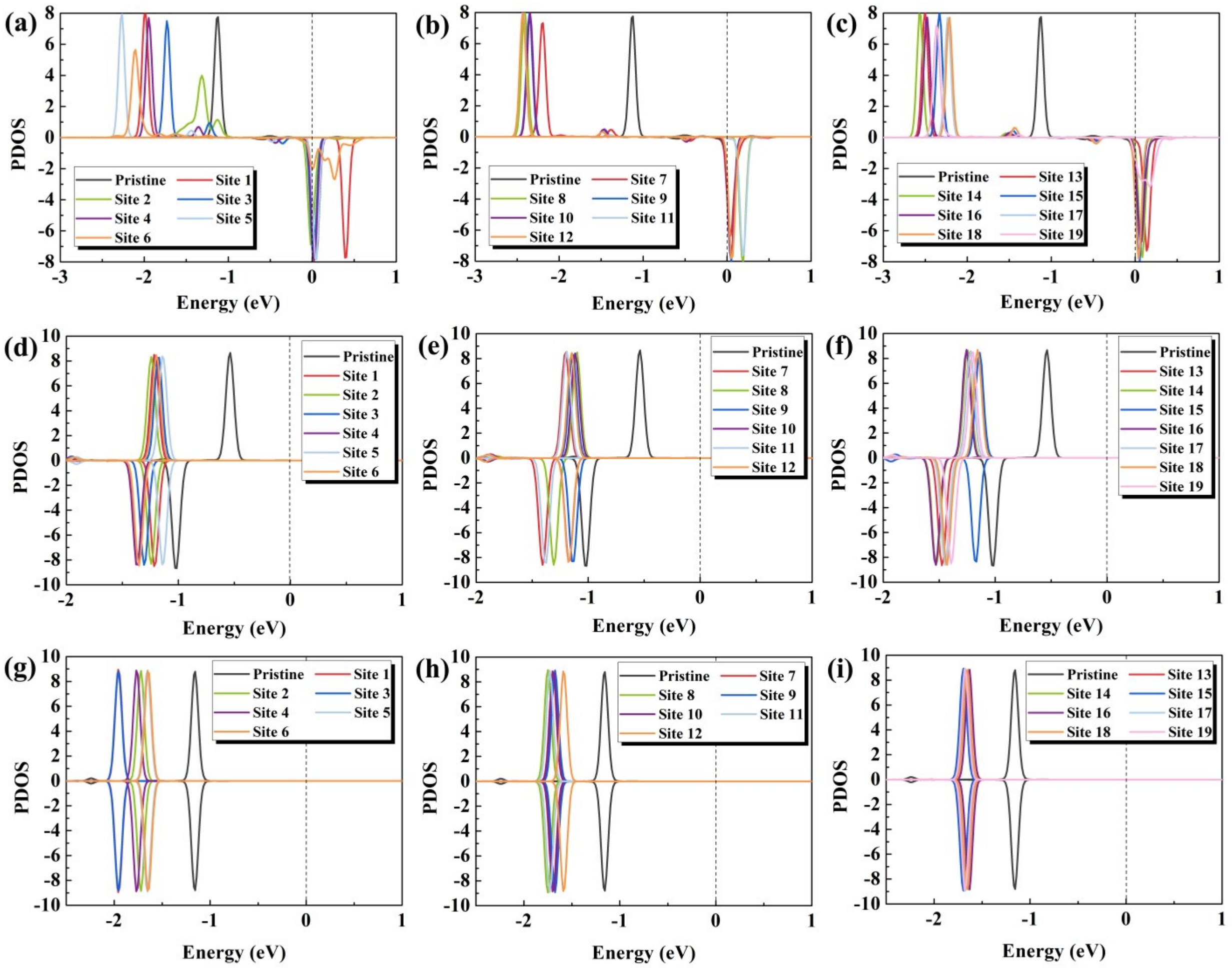


Figure S3. The top and side views of stable configurations for (a) *, (b) OOH*, (c) O*, and (d) O*, where the white, red, gray, blue and yellow balls denoting the H, O, C, N and TM atoms.

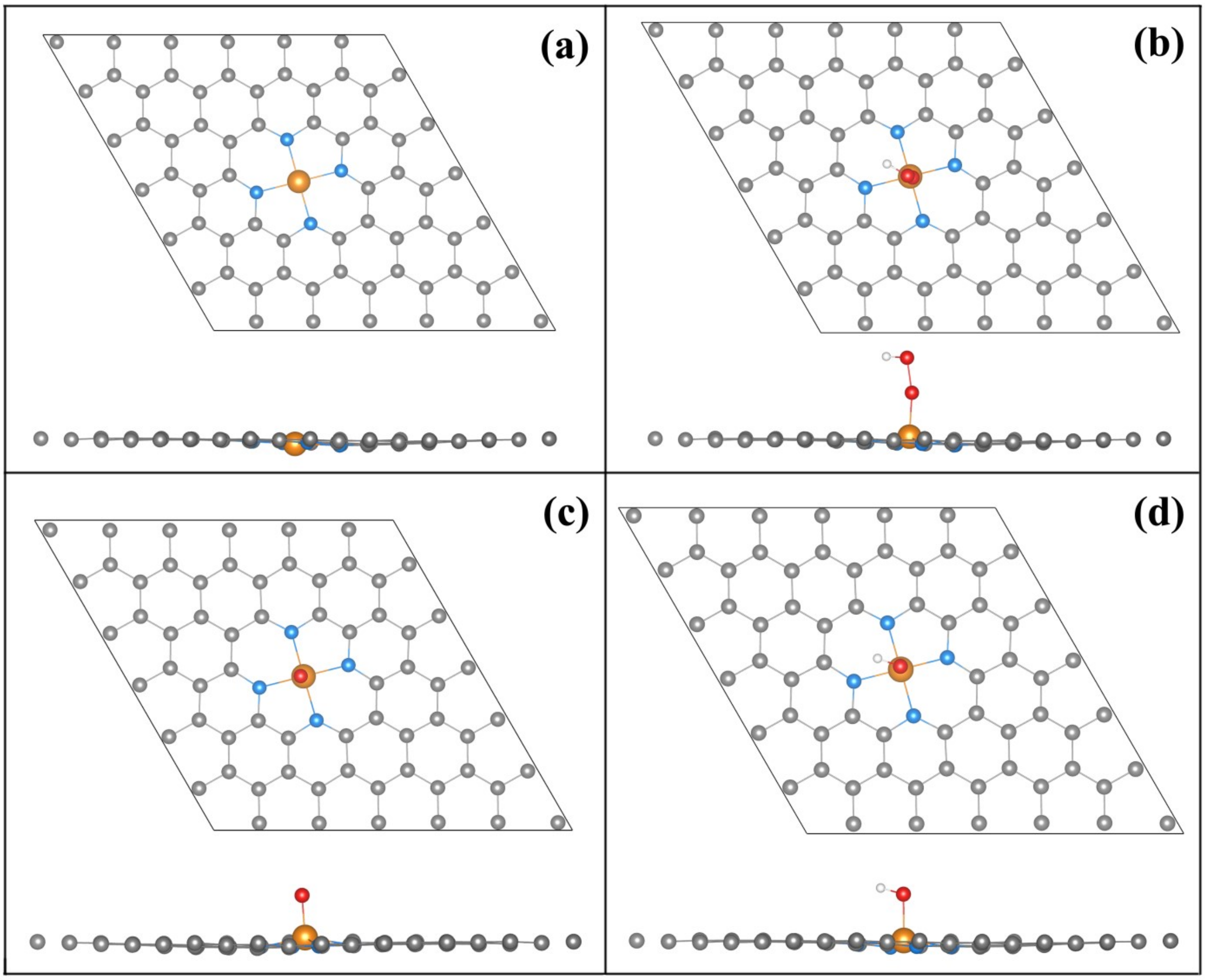


Figure S4. The correlation between the spin magnetic moments of TMN_4 centers and adsorption free energy of (a) ΔG_{OH*}, (b) ΔG_{O*} and (c) ΔG_{OOH*}.

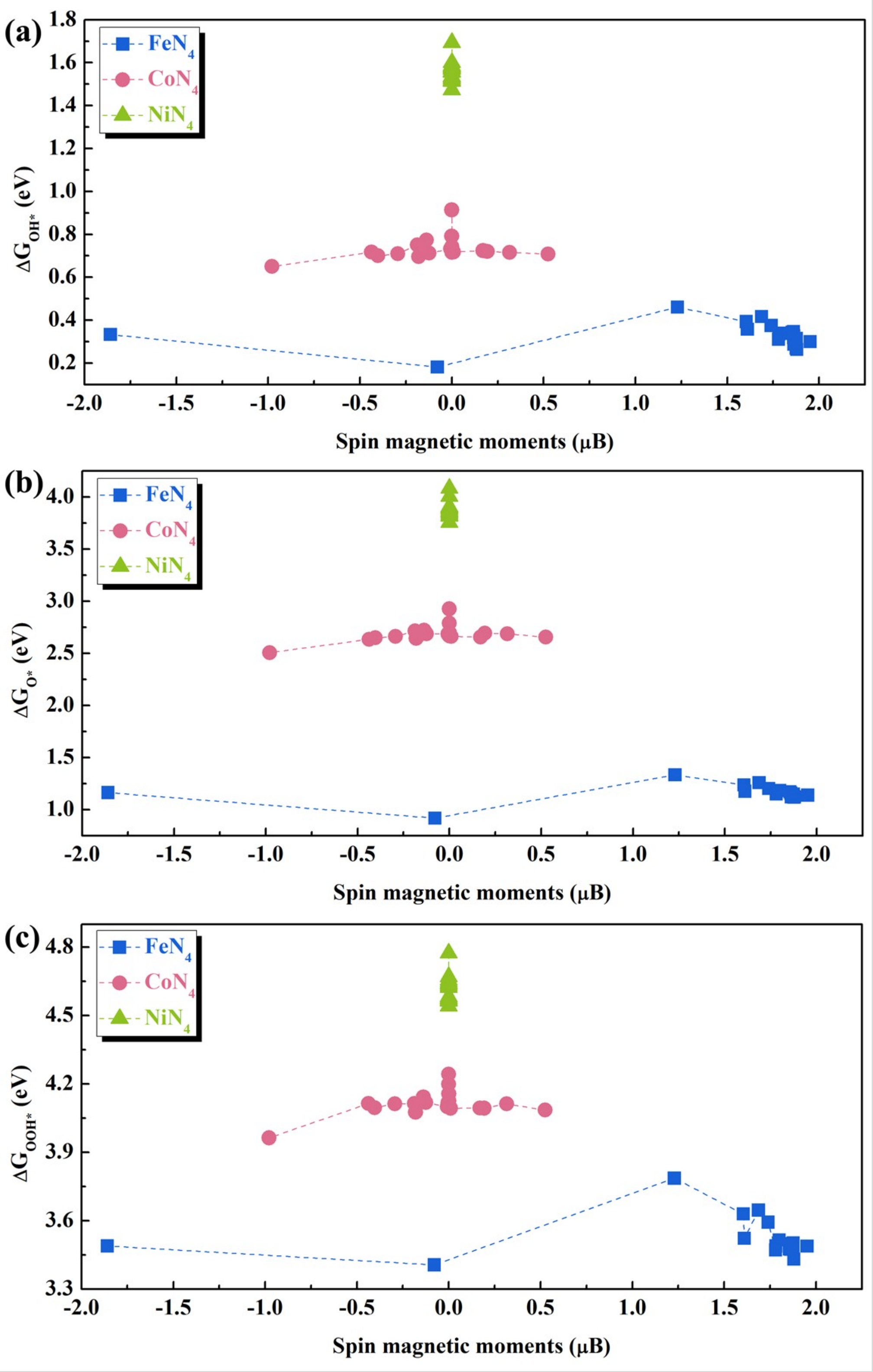


Figure S5. Variations in theoretical overpotential for (a) two-electron pathway and (b) four-electron pathway as the functions of average percentage changes in TM-N bond lengths.

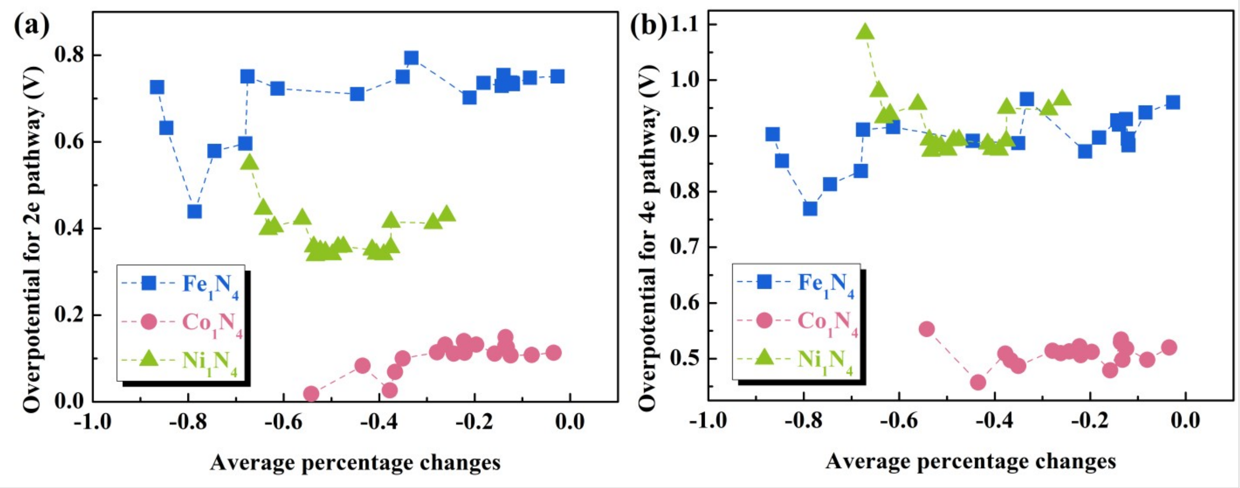
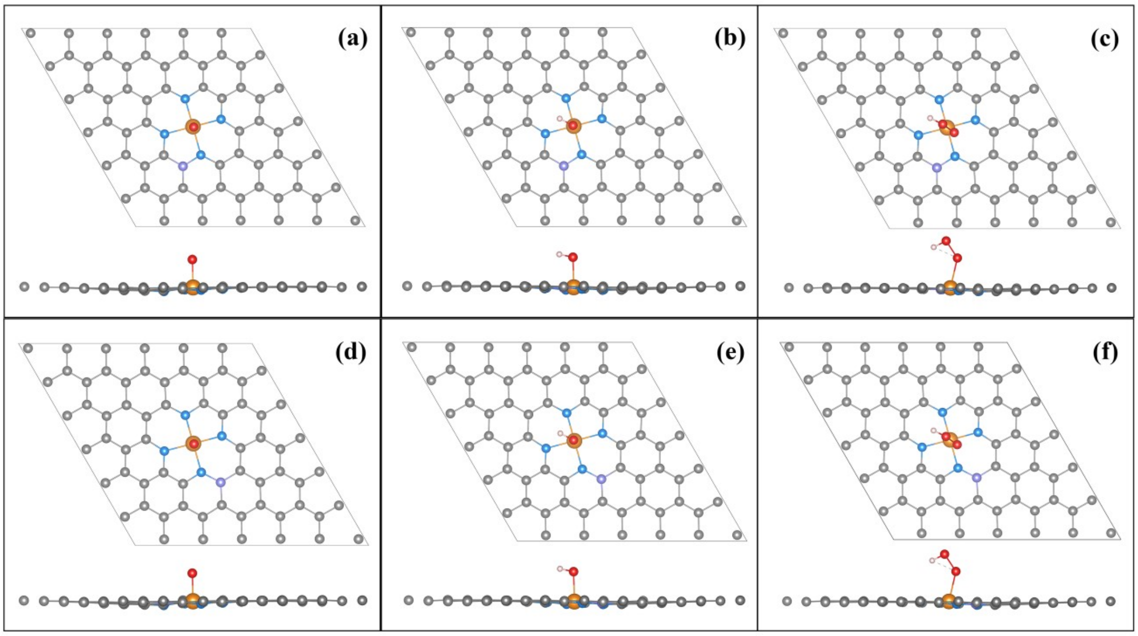


Figure S6. Top and side views of the most stable molecular configurations: (a) O*, (b) OH*, and (c) OOH* for N dopant at position 1 and (d) O*, (e) OH*, and (f) OOH* for N dopant at position 2.



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