

Systematic exploration of N, C coordination effects on the ORR performance of

Mn-N_x doped graphene catalysts based on DFT calculations

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Electronic Supplementary Information: Fig. S1-S3; Table S1-S7.

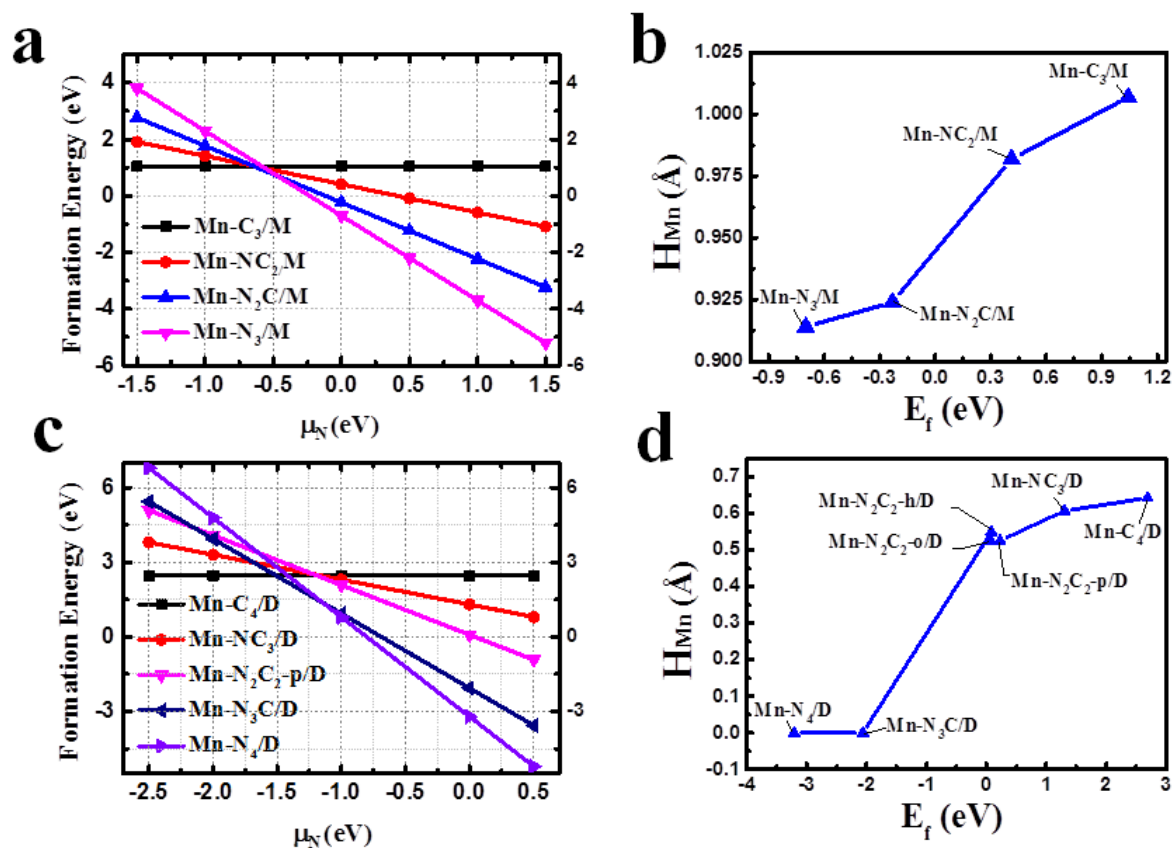


Fig. S1 The relations between (a, c) the ΔE_f of various Mn-N_x sites and the chemical potential of nitrogen (μ_N) respect to the one-half energy of the N₂ molecule, the μ_N varies with different nitrogen precursors defined; (b, d) the ΔE_f and the height of Mn atom respect to graphene basal plane (H_{Mn}).

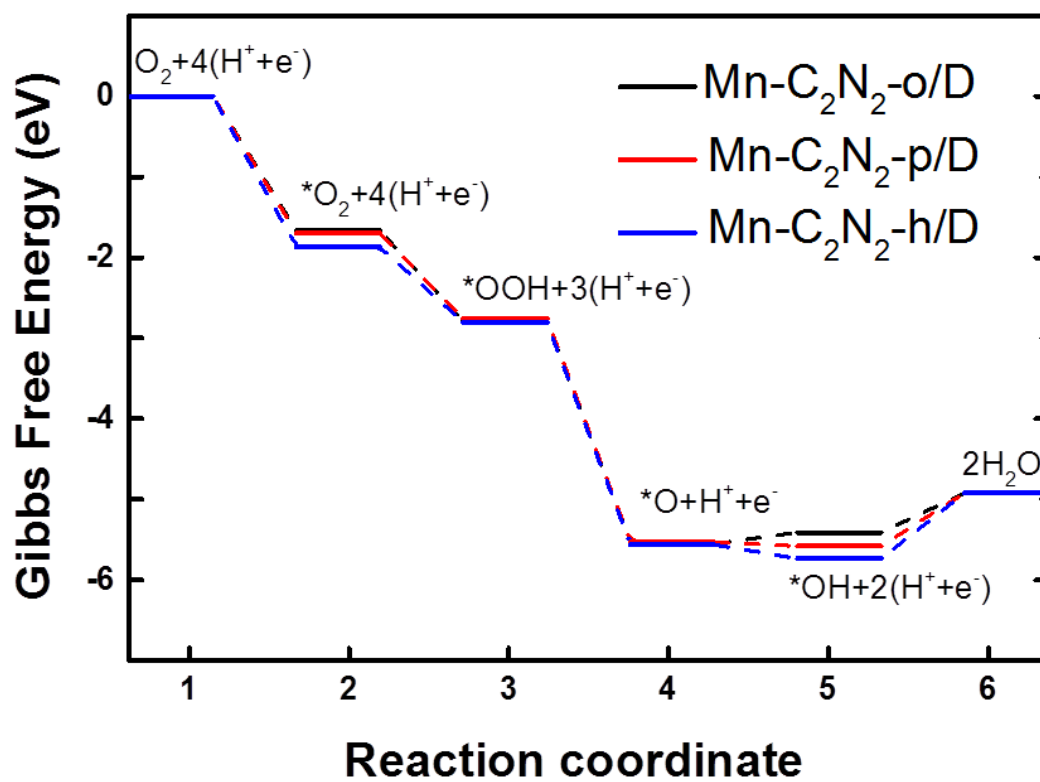


Fig. S2 The free energy diagrams of ORR pathways on the three types of Mn-N₂C₂/D structures.

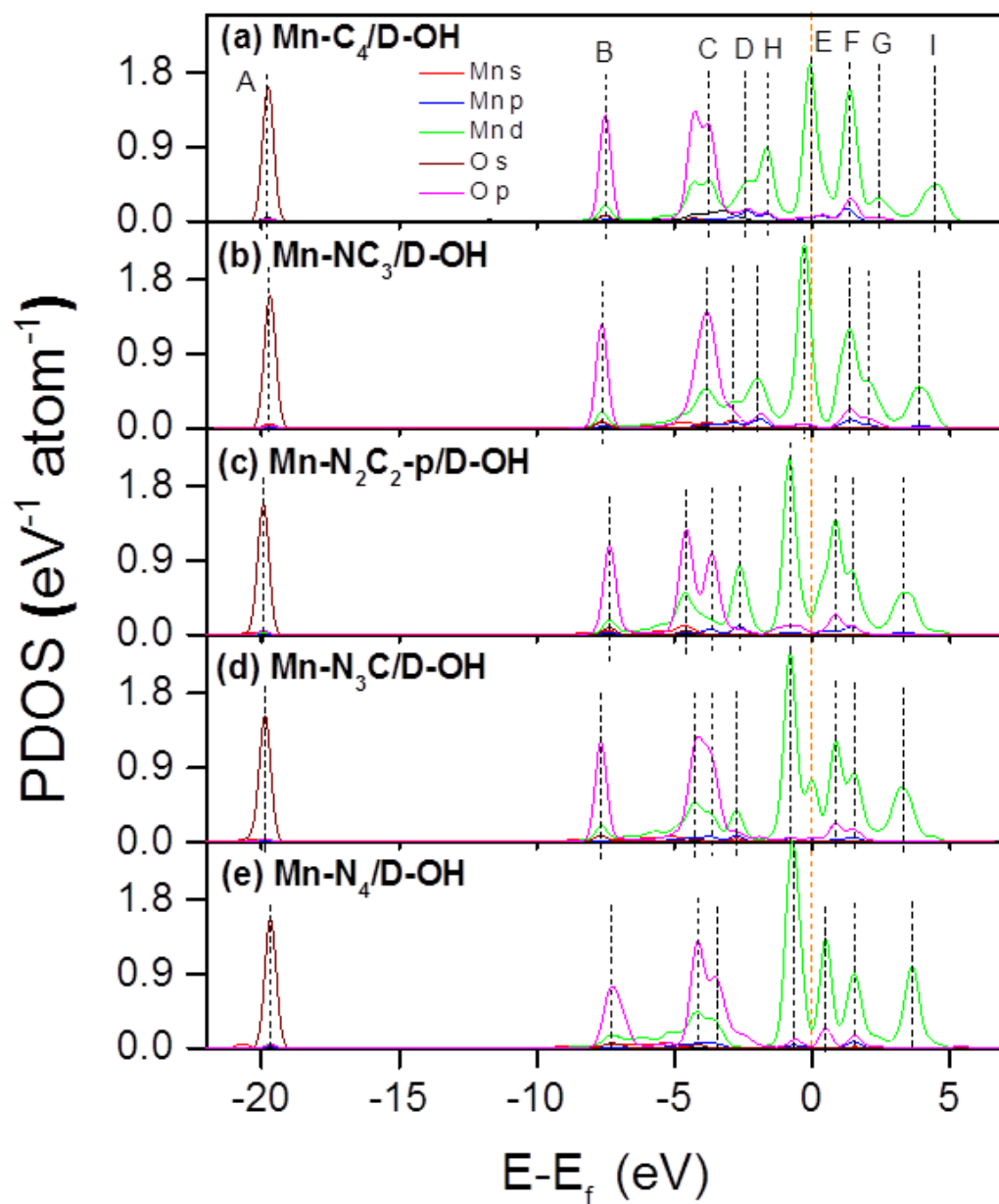
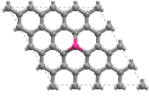
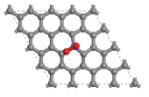
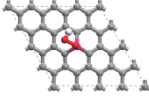
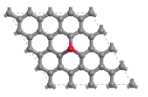
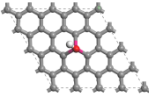

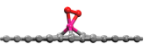
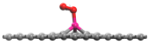
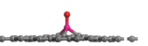
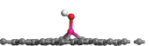
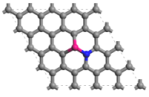
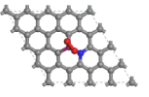
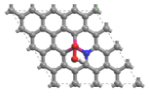
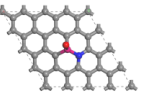
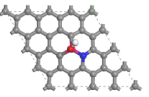
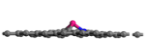
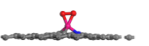
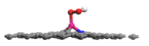
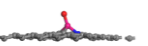
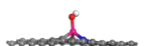
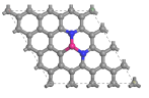
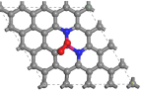
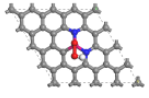
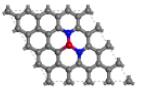
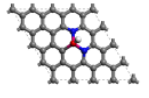
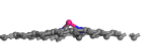
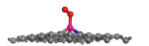

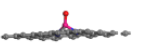
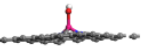
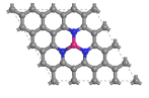
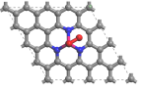
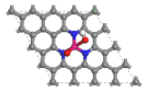
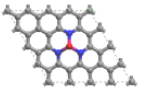
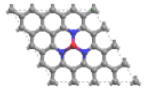

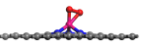

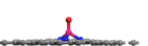
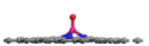
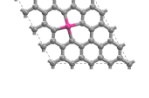
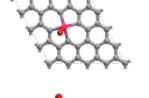
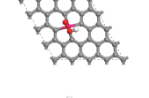
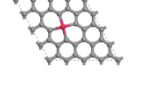
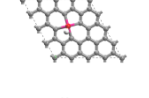





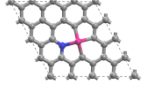
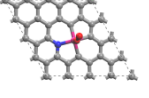
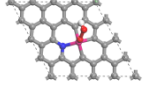
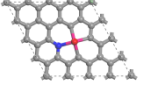
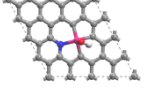

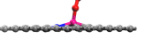
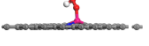
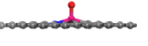
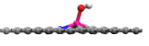
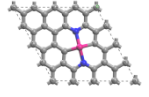
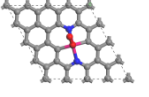
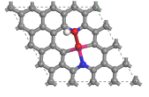
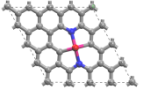
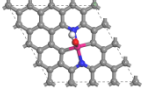
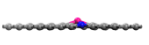
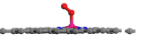
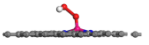
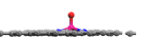
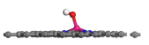
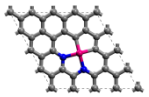
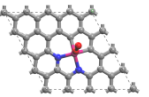
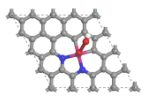
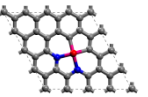
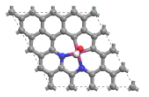
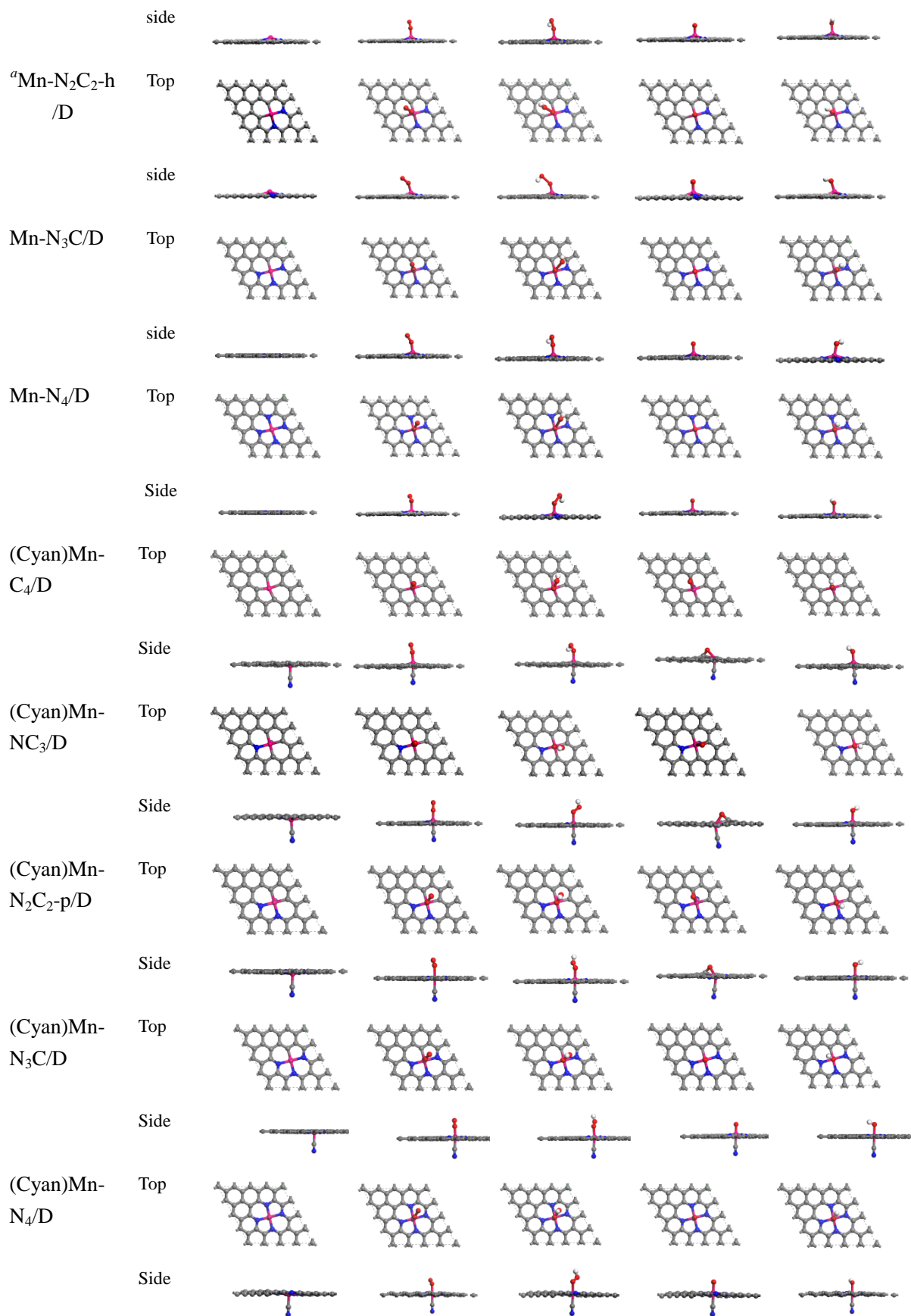
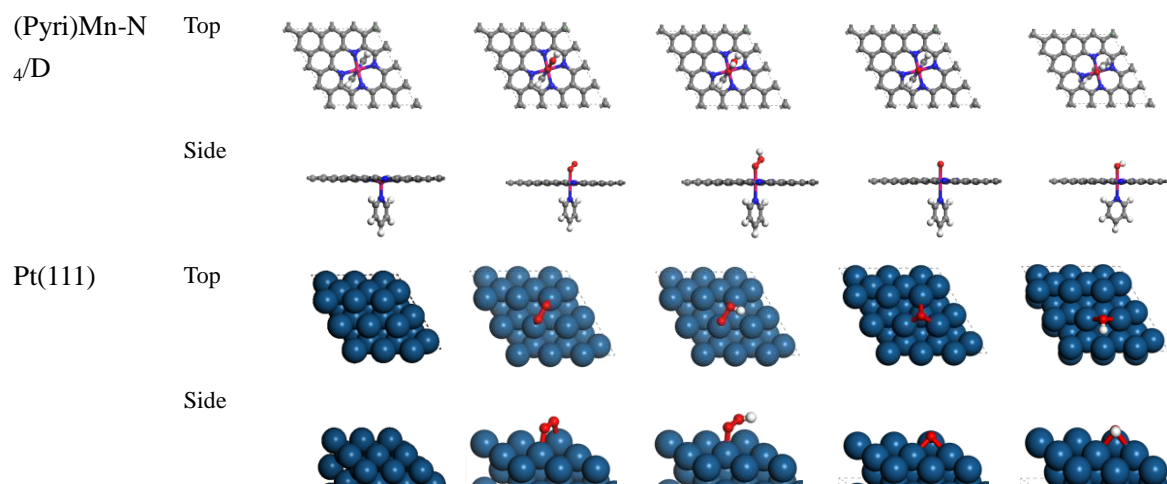


Fig. S3 The partial density of states (PDOS) plots calculated for various types of $\text{Mn-N}_y\text{C}_{4-y}$ ($y = 0-4$) configurations after the $^*\text{OH}$ adsorption.

Table S1 Optimized Models of different Mn-N_x configurations and their corresponding ideal *O₂, *OOH, *O and *OH adsorption configurations

Structure		Pristine	*O ₂	*OOH	*O	*OH
Mn-C ₃ /M	Top					
	side					
Mn-NC ₂ /M	Top					
	side					
Mn-N ₂ C/M	Top					
	side					
Mn-N ₃ /M	Top					
	side					
Mn-C ₄ /D	Top					
	side					
Mn-NC ₃ /D	Top					
	side					
^a Mn-N ₂ C ₂ -o /D	Top					
	side					
^a Mn-N ₂ C ₂ -p /D	Top					





^aFor Mn-N₂C₂/D, three configurations were considered: Mn center, two N atoms and two C atoms compose a pentatomic ring (Mn-N₂C₂-p/D); two N atoms are located at the opposite sides of Mn (Mn-N₂C₂-o/D); Mn center, two N atoms and three C atoms compose a hexatomic ring (Mn-N₂C₂-h/D).

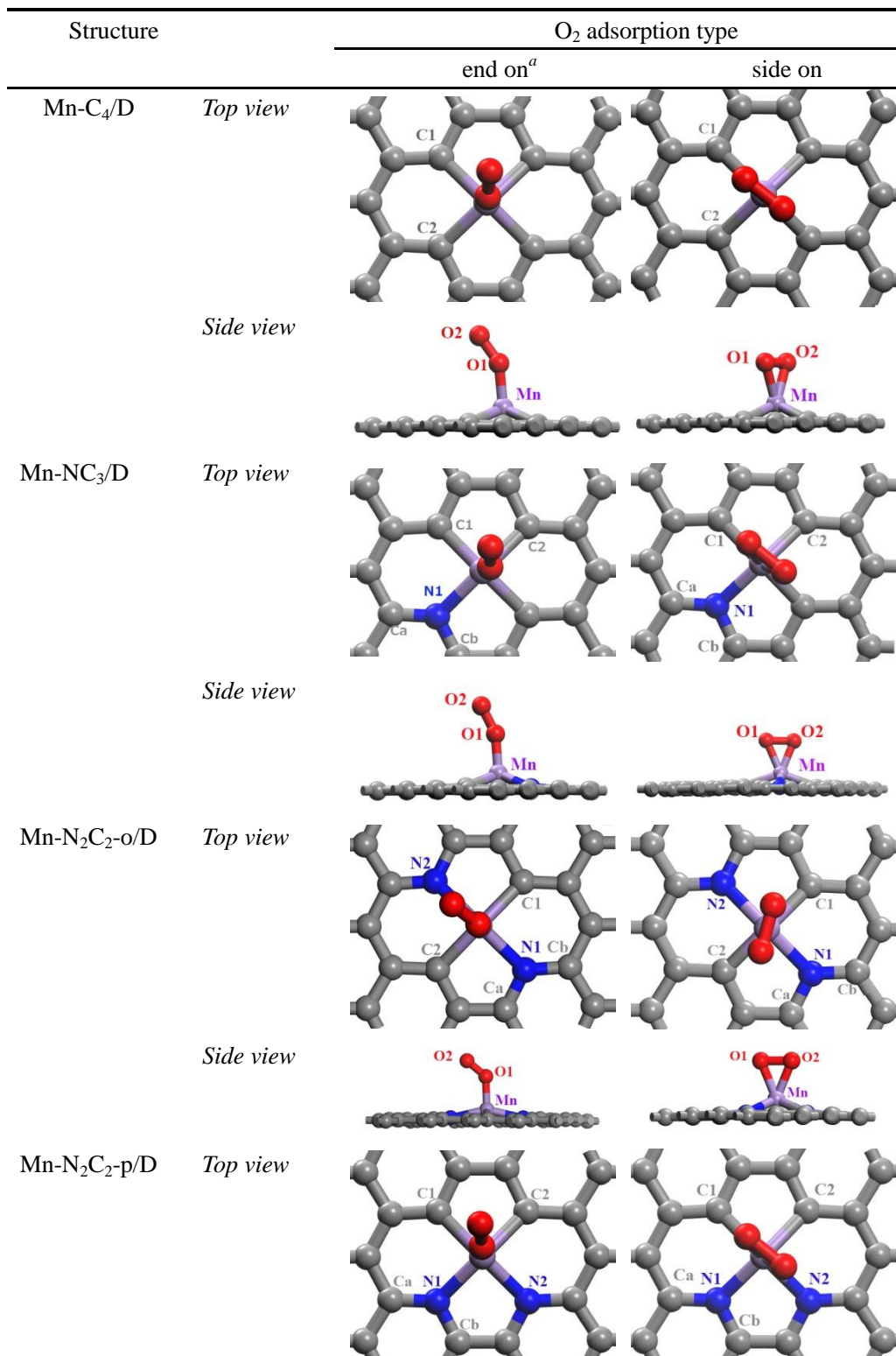
Table S2 Adsorption free energies (ΔG_{ads} , eV) of the key ORR intermediate species on the surface sites associated with various TM-N_x structures and Pt (111).

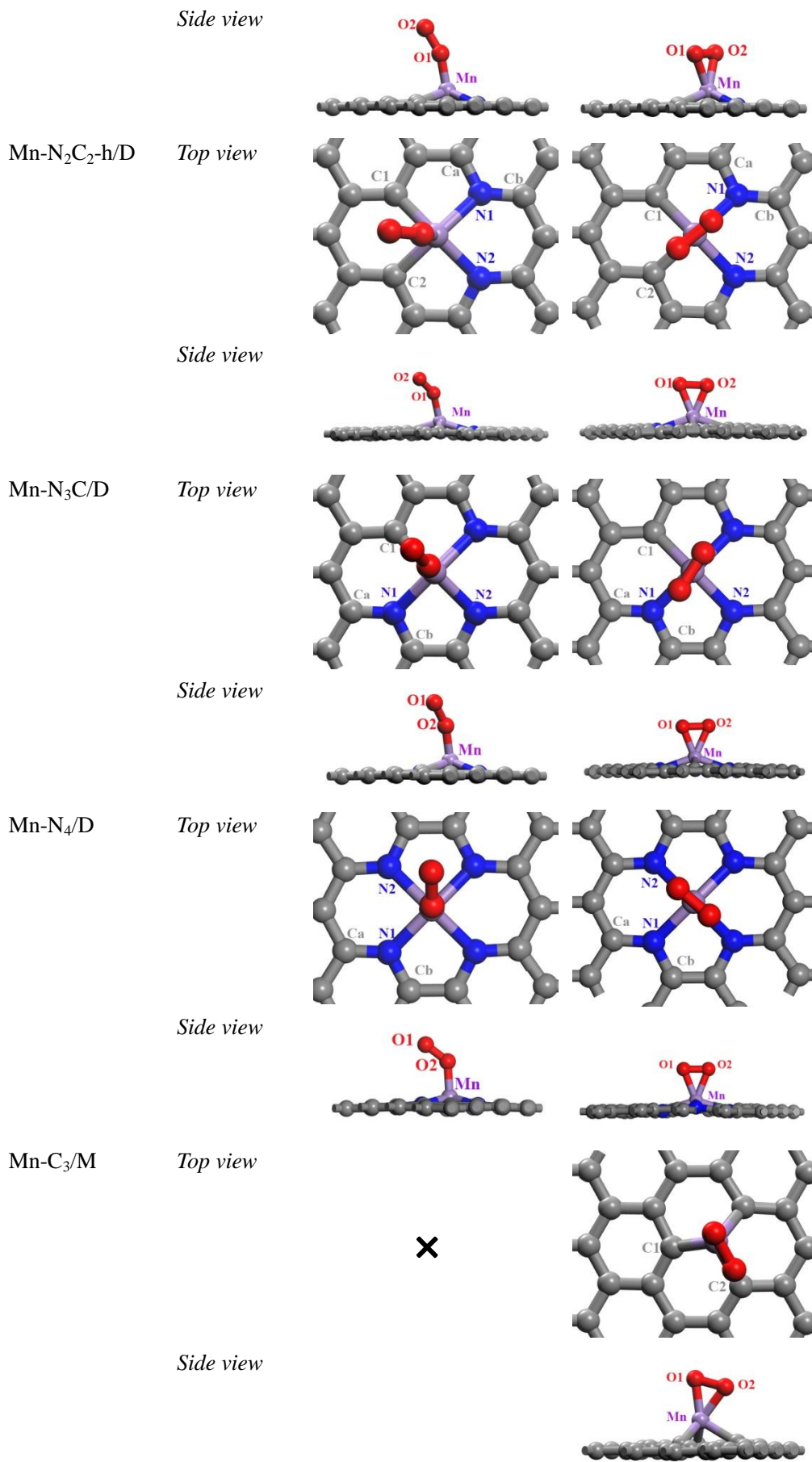
structures	ΔG_{*O_2}	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}
Fe-N ₄ /D	4.101	3.536	1.487	0.394
Ni-N ₄ /D	5.324	4.743	3.564	1.580
Zn-N ₄ /D	5.306	4.058	3.364	1.430
Cu-N ₄ /D	5.000	4.678	3.351	1.446
Pt-N ₄ /D	5.844	5.115	4.298	2.112
Pt (111)	5.100	4.030	2.218	0.905

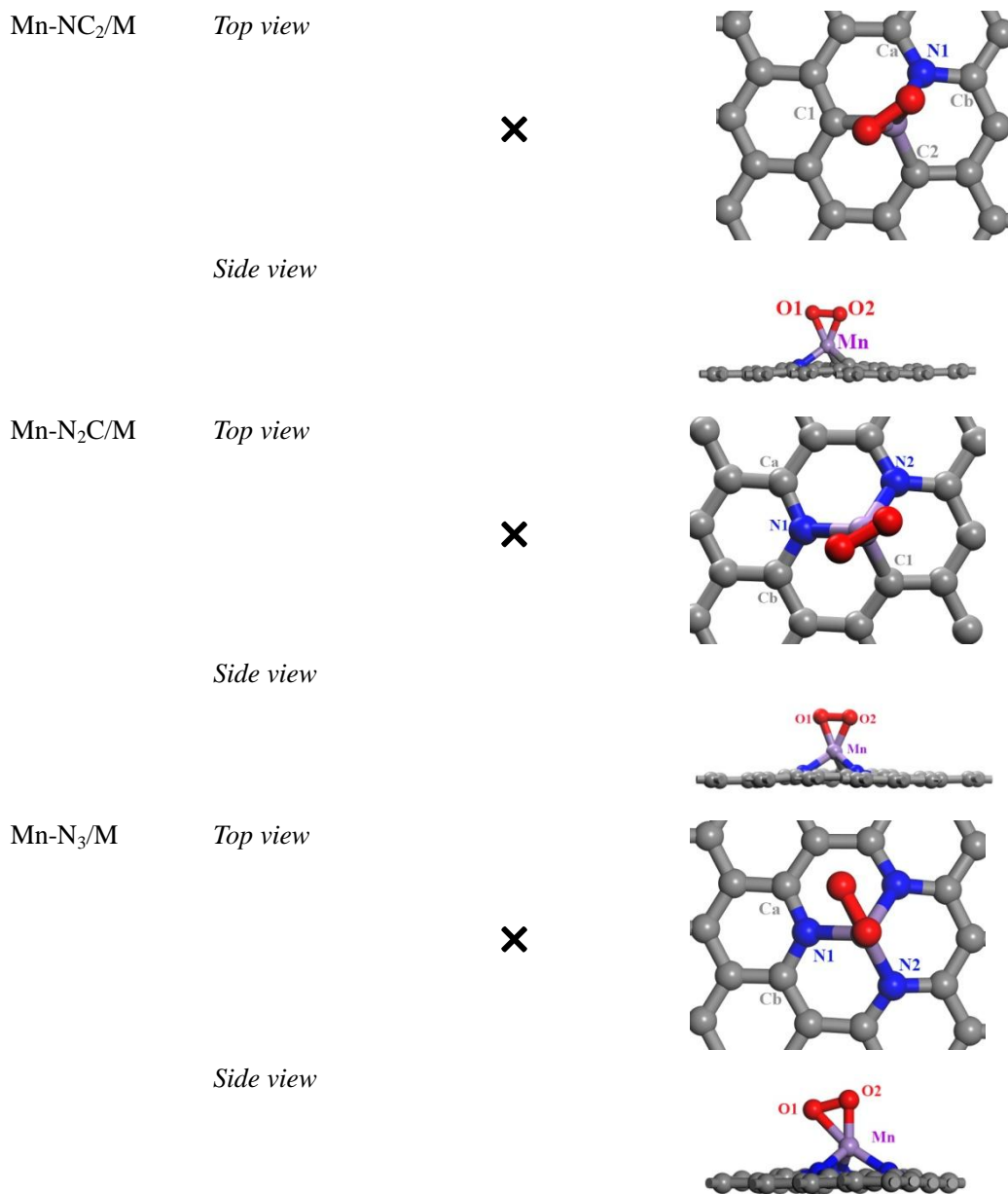
Table S3 Free energy variations of the ORR pathways for different TM-N_x structures and their corresponding theoretical overpotentials

Structures	Free energy variation (eV)					η_{SHE} (V)
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	
Mn-C ₃ /M	-1.864	-0.588	-2.225	-1.224	0.981	2.21
Mn-NC ₂ /M	-2.390	-0.484	-2.325	-0.875	1.154	2.38
Mn-N ₂ C/M	-2.532	-0.350	-2.684	-0.519	1.165	2.39
Mn-N ₃ /M	-2.897	-2.032	-1.014	-0.314	1.337	2.56
Mn-C ₄ /D	-1.266	-0.904	-2.890	-0.091	0.231	1.46
Mn-NC ₃ /D	-1.498	-0.791	-3.096	-0.085	0.550	1.78
Mn-N ₂ C ₂ -o/D	-1.669	-1.124	-2.759	0.140	0.492	1.72
Mn-N ₂ C ₂ -p/D	-1.703	-1.056	-2.772	-0.048	0.659	1.88
Mn-N ₂ C ₂ -h/D	-1.871	-0.934	-2.758	-0.172	0.815	2.04
Mn-N ₃ C/D	-0.860	-1.002	-2.63	0.015	-0.443	1.24
Mn-N ₄ /D	-0.808	-0.994	-2.384	-0.282	-0.452	0.94
(Cyan)Mn-C ₄ /D	-0.367	-0.762	-2.91	-0.614	-0.267	0.96
(Cyan)Mn-NC ₃ /D	-0.220	-0.527	-3.011	-0.283	-0.879	0.94
Cyan)Mn-N ₂ C ₂ -p/D	-0.063	-1.062	-2.782	-0.770	-0.243	0.98
(Cyan)Mn-N ₃ C/D	-0.042	-0.964	-2.257	-1.23	-0.427	0.80
(Cyan)Mn-N ₄ /D	-0.026	-0.895	-2.113	-0.897	-0.989	0.33
(Pyri)Mn-N ₄ /D	-0.766	-0.674	-2.369	-0.64	-0.471	0.75
Fe-N ₄ /D	-0.819	-0.565	-2.049	-1.093	-0.394	0.83
Ni-N ₄ /D	0.404	-0.581	-1.179	-1.984	-1.58	1.05
Zn-N ₄ /D	0.386	-1.248	-0.694	-1.934	-1.43	0.53
Cu-N ₄ /D	0.08	-0.322	-1.327	-1.905	-1.446	0.98
Pt-N ₄ /D	0.924	-0.729	-0.817	-2.186	-2.112	1.42
Pt(111)	0.18	-1.07	-1.812	-1.313	-0.905	0.34

Table S4 The O₂ adsorption configurations in different binding types associated with the Mn-N_yC_{4-y}/D (y = 0-4) and Mn-N_xC_{3-x}/M (x = 0-3) structures.







^a(×) No stable O₂-end on adsorption configuration was obtained after geometric optimization for Mn-N_xC_{3-x}/M(x = 0-3) structures.

Table S5. Binding energy (E_b) of O_2 in different binding types, the atomic distance between Mn, C, N, O atoms (d , Å) and the height of Mn atom (H_{Mn} , Å) respect to the graphene basal plane of each Mn- N_x site after $*O_2$ adsorption. The positive and negative values in the brackets represent the increase and reduction in d or H_{Mn} after $*O_2$ adsorption, respectively. The Mn, N1, C1, O1 and O2 atoms correspond to Table S4.

Structure	$*O_2$ type	${}^a E_b$ /eV	Distance / Å					
			d_{O1-O2}	d_{Mn-O1}	d_{Mn-O2}	d_{Mn-C1}	d_{Mn-N1}	H_{Mn}
Mn-C ₄ /D	<i>end-on</i>	-1.72	1.298	1.723	-	2.008(0.011)	-	0.596(-0.047)
	<i>side-on</i>	-2.28	1.416	1.825	1.825	2.015(0.018)	-	0.696(0.053)
Mn-C ₃ N/D	<i>end-on</i>	-1.73	1.298	1.665	-	1.986(0.006)	2.028(0.013)	0.578(-0.03)
	<i>side-on</i>	-2.24	1.423	1.822	1.855	1.986(0.006)	2.056(0.041)	0.682(0.074)
Mn-C ₂ N ₂ -o/D	<i>end-on</i>	-2.11	1.302	1.657	-	1.952(0.002)	2.009(0.03)	0.58(0.056)
	<i>side-on</i>	-2.34	1.441	1.857	1.856	1.966(0.016)	2.029(0.05)	0.666(0.142)
Mn-C ₂ N ₂ -p/D	<i>end-on</i>	-2.17	1.302	1.658	-	1.96(-0.004)	2.011(0.036)	0.589(0.063)
	<i>side-on</i>	-2.42	1.417	1.873	1.839	1.984(0.022)	2.028(0.053)	0.604(0.078)
Mn-C ₂ N ₂ -h/D	<i>end-on</i>	-2.39	1.304	1.706	-	2.045(0.102)	1.96(-0.04)	0.598(0.048)
	<i>side-on</i>	-2.69	1.431	1.87	1.825	2.04(0.097)	1.97(-0.028)	0.697(0.147)
Mn-CN ₃ /D	<i>end-on</i>	-1.41	1.309	1.665	-	1.917(0.013)	1.998(0.054)	0.580(0.580)
	<i>side-on</i>	-1.68	1.454	1.882	1.811	1.944(0.04)	2.203(0.259)	0.680(0.680)
Mn-N ₄ /D	<i>end-on</i>	-1.32	1.328	1.712	-	--	1.945(0.029)	0.385(0.385)
	<i>side-on</i>	-1.45	1.394	1.877	1.884	-	1.959(0.043)	0.479(0.479)
Mn-C ₃ /M	<i>side-on</i>	-2.26	1.417	1.842	1.838	1.855(0.026)	-	1.062(0.055)
Mn-C ₂ N/M	<i>side-on</i>	-2.74	1.43	1.872	1.787	1.835(0.015)	1.875(0.046)	1.039(0.057)
Mn-CN ₂ /M	<i>side-on</i>	-3.05	1.442	1.838	1.828	1.80(-0.001)	1.864(0.054)	1.018(0.094)
Mn-N ₃ /M	<i>side-on</i>	-3.32	1.448	1.992	1.759		1.847(0.034)	0.988(0.074)

^a E_b is calculated according to equation $E_b = E_{*O_2} - (E_{Mn-N_x} + E_{O_2})$, where E_{*O_2} , E_{Mn-N_x} and E_{O_2} represent the total DFT energy of the Mn- N_x adsorption model, the pristine Mn- N_x model and the O_2 molecule.

Table S6. Mulliken charge population (q, e/atom) on Mn, N, C and O atoms of each Mn-N_x site with an adsorbed O₂. The positive and negative values in the brackets represent the loss and accumulation of electrons after *O₂ adsorption, respectively. The Mn, N1, N2, Ca, Cb, C1, C2, O1 and O2 atoms correspond to Table S4.

Structure	*O ₂ type	Mulliken charge population (e/atom)									
		qMn	Spin Mn	qN1	qN2	qCa	qCb	qC1	qC2	qO1	qO2
Mn-C ₄ /D	<i>end-on</i>	0.105(0.013)	2.355(0.568)	-	-	-	-	-0.12(0.012)	-0.082(0.05)	-0.173	-0.250
	<i>side-on</i>	0.149(0.057)	1.735(-0.052)	-	-	-	-	-0.087(0.045)	-0.062(0.07)	-0.289	-0.289
Mn-C ₃ N/D	<i>end-on</i>	0.092(0.002)	0(0)	-0.333(0.019)	-	0.199(0.008)	0.125(0.008)	-0.058(0.057)	-0.04(0.051)	-0.161	-0.275
	<i>side-on</i>	0.184(0.094)	0(0)	-0.346(0.006)	-	0.194(0.003)	0.119(0.002)	-0.053(0.062)	-0.043(0.048)	-0.27	-0.278
Mn-C ₂ N ₂ -o/D	<i>end-on</i>	0.193(0.054)	1.696(1.696)	-0.365(-0.002)	-0.362(0.001)	0.2(0.01)	0.136(0.005)	-0.009(0.081)	0.005(0.095)	-0.147	-0.282
	<i>side-on</i>	0.265(0.126)	0(0)	-0.334(0.029)	-0.301(0.062)	0.189(-0.001)	0.136(0.005)	-0.029(0.061)	-0.012(0.078)	-0.317	-0.287
Mn-C ₂ N ₂ -p/D	<i>end-on</i>	0.137(-0.019)	0(0)	-0.327(0.036)	-0.33(0.033)	0.166(0.005)	0.116(0.003)	-0.032(0.079)	-0.023(0.088)	-0.154	-0.302
	<i>side-on</i>	0.26(0.104)	0(0)	-0.3(0.063)	-0.301(0.062)	0.165(0.004)	0.112(-0.001)	-0.05(0.061)	-0.032(0.079)	-0.305	-0.285
Mn-C ₂ N ₂ -h/D	<i>end-on</i>	0.159(0.011)	0(0)	-0.311(0.049)	-0.32(0.04)	0.195(0.002)	0.121(0.005)	-0.064(0.037)	-0.034(0.067)	-0.173	-0.300
	<i>side-on</i>	0.262(0.114)	0(0)	-0.314(0.046)	-0.313(0.047)	0.194(0.001)	0.119(0.003)	-0.025(0.076)	-0.026(0.075)	-0.328	-0.321
Mn-CN ₃ /D	<i>end-on</i>	0.229(-0.133)	0(-3.601)	-0.315(0.076)	-0.329(0.033)	0.196(0.025)	0.138(0.03)	0.044(0.141)	-	-0.161	-0.321
	<i>side-on</i>	0.361(-0.001)	0(-3.601)	-0.29(0.101)	-0.318(0.044)	0.171(0)	0.125(0.017)	0.008(0.105)	-	-0.358	-0.332
Mn-N ₄ /D	<i>end-on</i>	0.342(-0.061)	0(-3.264)	-0.281(-0.115)	-0.31(-0.141)	0.175(0.126)	0.129(0.091)	-	-	-0.175	-0.342
	<i>side-on</i>	0.408(0.005)	0(-3.264)	-0.27(-0.104)	-0.31(-0.145)	0.163(0.114)	0.127(0.089)	-	-	-0.292	-0.280
Mn-C ₃ /M	<i>side-on</i>	0.047(0.043)	1.011(-1.492)	-	-	-	-	0.018(0.021)	-0.058(0.015)	-0.321	-0.264
Mn-C ₂ N/M	<i>side-on</i>	0.139(0.118)	0(-0.001)	-0.301(0.025)	-	0.152(0.02)	0.147(0.015)	0.021(0.029)	0.007(0.015)	-0.346	-0.305
Mn-CN ₂ /M	<i>side-on</i>	0.248(0.093)	0(-1.173)	-0.304(0.033)	-0.302(0.035)	0.16(0.007)	0.153(0.026)	0.086(0.094)	-	-0.358	-0.344
Mn-N ₃ /M	<i>side-on</i>	0.379(0.119)	0(0)	-0.266(0.025)	-0.276(0.015)	0.183(0.032)	0.172(0.033)	-	-	-0.385	-0.396

Table S7. The energy level (eV) of each peak respect to the Fermi energy level (E_f) in the PDOS plots of *OH adsorbed on the three-coordination (Figure 8) and four-coordination (Figure S3) Mn-N_x sites.

structure	Energy level (eV) of each peak respect to the E_f								
	A	B	C	D	E	F	G	H	I
Mn-C ₃ /M	-19.27	-6.94	-3.26	-2.42	0.40	1.63	2.89	– ^a	–
Mn-NC ₂ /M	-19.28	-7.00	-3.42	-2.49	-0.2	1.42	2.67	–	–
Mn-N ₂ C/M	-19.45	-7.05	-3.95	-3.02	-0.38	1.19	2.53	–	–
Mn-N ₃ /M	-20.16	-7.83	-4.54	-3.66	-1.22	0.46	1.63	–	–
Mn-C ₄ /D	-19.77	-7.51	-3.77	-2.44	-0.04	1.37	2.44	-1.64	4.45
Mn-NC ₃ /D	-19.72	-7.64	-3.82	-2.86	-0.31	1.34	2.07	-1.99	3.89
Mn-N ₂ C ₂ -p/D	-19.92	-7.34	-4.57	-3.66	-0.82	0.84	1.47	-2.59	3.34
Mn-N ₃ C/D	-19.87	-7.65	-4.15	-3.6	-0.79	0.84	1.54	-2.75	3.31
Mn-N ₄ /D	-19.65	-7.28	-4.13	-3.45	-0.71	0.47	1.53	–	3.63

^a(–) No peaks were found in the corresponding PDOS plots.