Electronic Supplementary Information (ESI)

Theoretical study of atomically dispersed MN_4/C (M = Fe or Mn) as high-activity catalysts for oxygen reduction reaction

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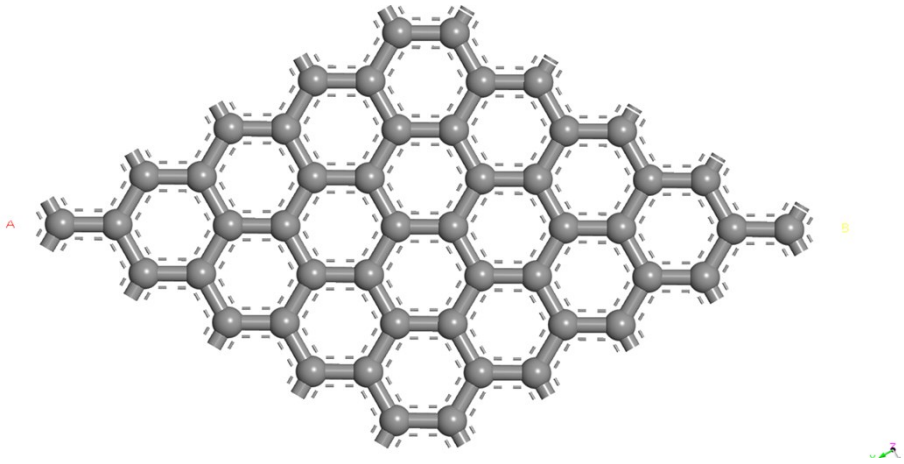

Fig. S1 Top view of the optimized geometry structure of pure graphene.

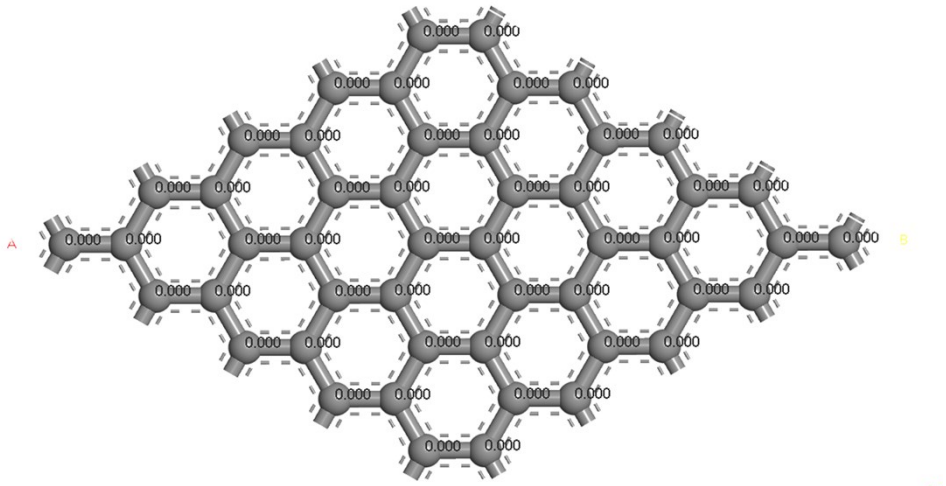

Fig. S2 Mulliken charge values of pure graphene.

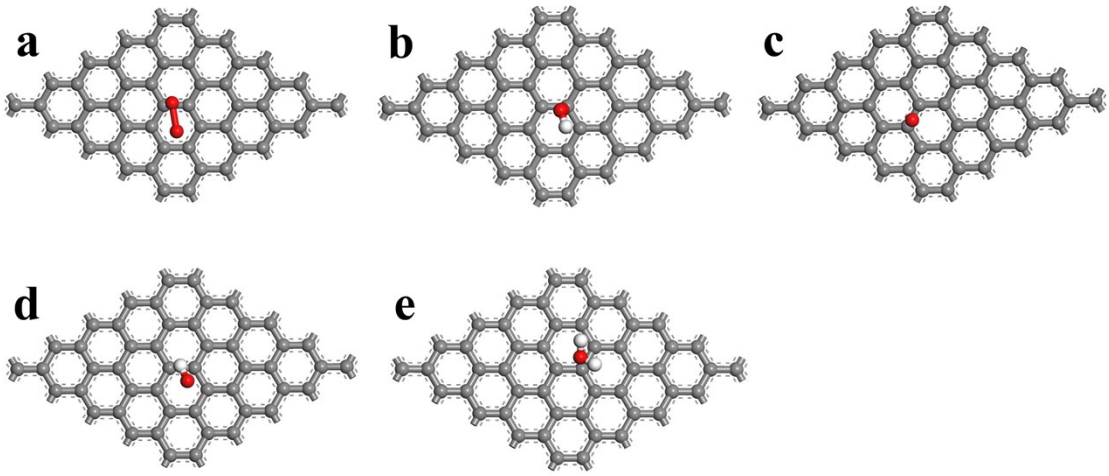

Fig. S3 Optimized configurations of the oxygen reduction reaction intermediates adsorbed on pure graphene: (a) O_2, (b) OOH, (c) O, (d) OH, and (e) H_2O.

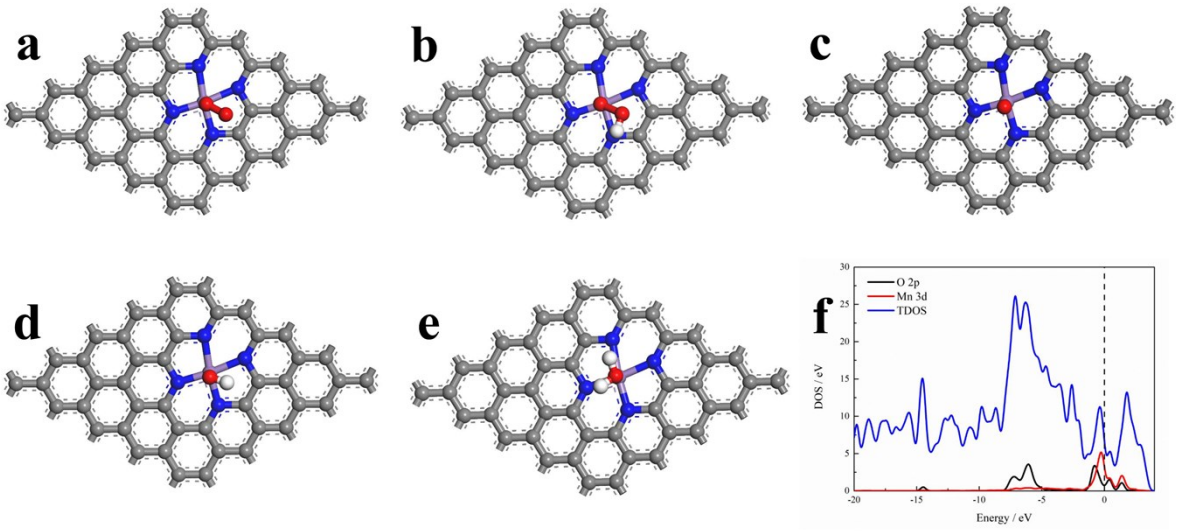

Fig. S4 Optimized configurations of the oxygen reduction reaction intermediates adsorbed on MnN_4/C: (a) O_2, (b) OOH, (c) O, (d) OH, and (e) H_2O. (f) Local density of state curves of O_2 adsorbed on MnN_4/C; the Fermi level is set to zero (dotted line).

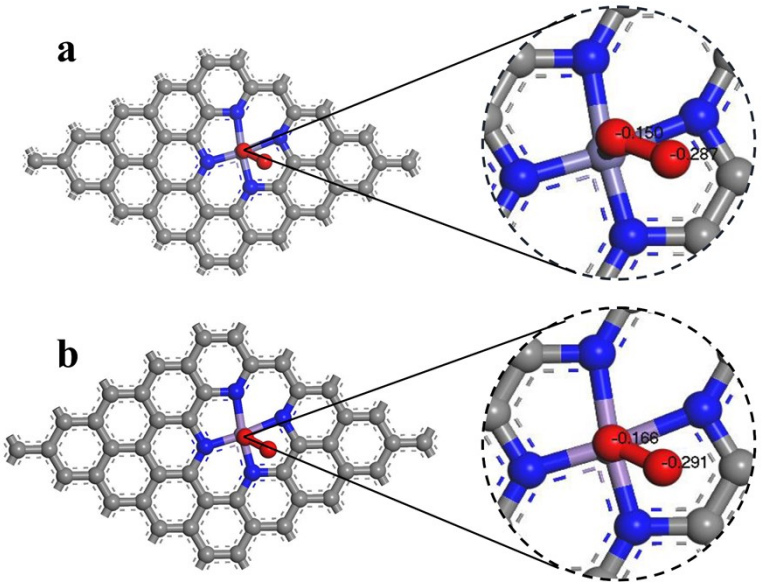

Fig. S5 Mulliken charge values on O_2 adsorbed on (a) FeN_4/C and (b) MnN_4/C.

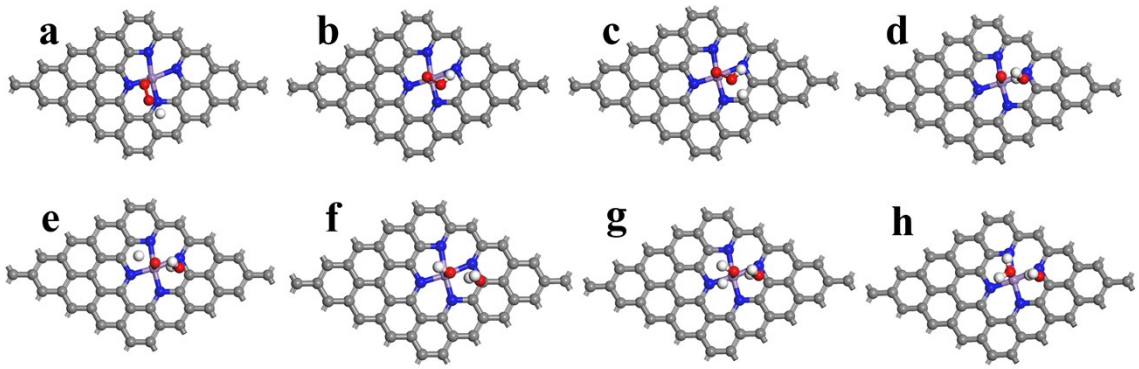

Fig. S6 Optimized four-electron pathway of the OOH dissociation on MnN_4/C: (a) $O_2^* + H^+ + e^-$, (b) OOH*, (c) $OOH^* + H^+ + e^-$, (d) $H_2O + O^*$, (e) $O+ H^+ + e^- + H_2O$, (f) $OH^* + H_2O$, (g) $OH^* + H^+ + e^- + H_2O$, and (h) $2H_2O$.

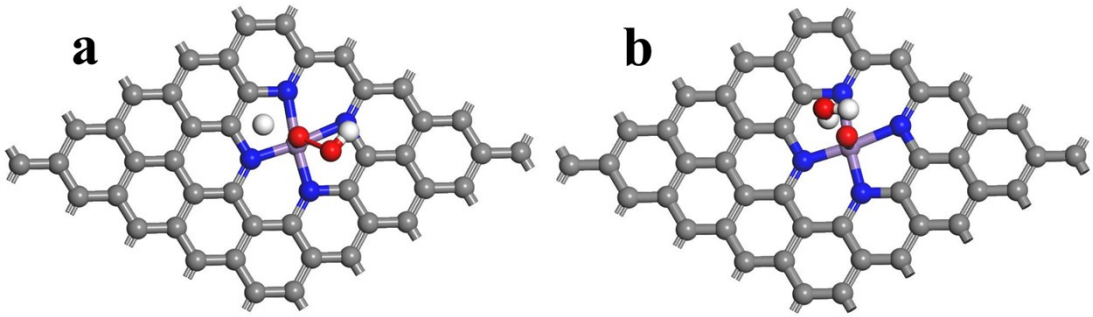

Fig. S7 Optimized two-electron pathway of the OOH hydrogenation into HOOH on MnN_4/C: (a) $OOH^* + H^+ + e^-$ and (b) $O^* + H_2O$.

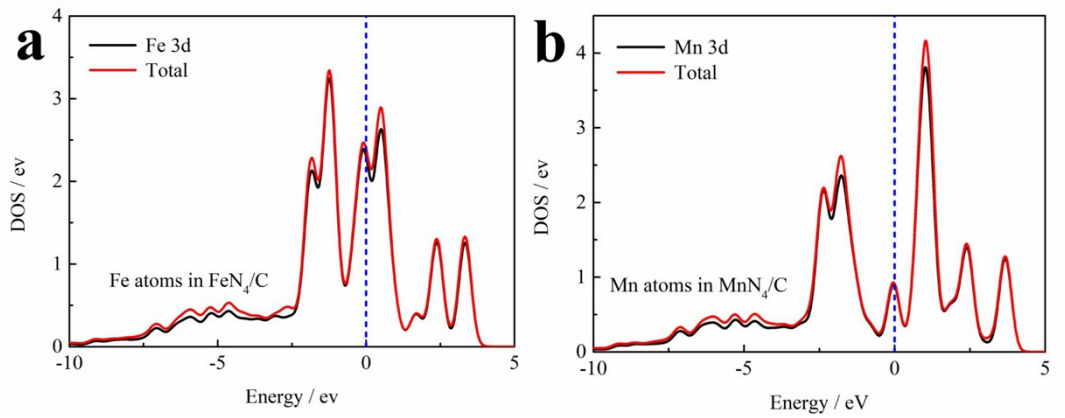

Fig. S8 The calculated PDOS of metal atoms in FeN_4/C and MnN_4/C, with the aligned Fermi level. (a) The PDOS of Fe atom in FeN_4/C, (b) The PDOS of Mn atom in MnN_4/C.

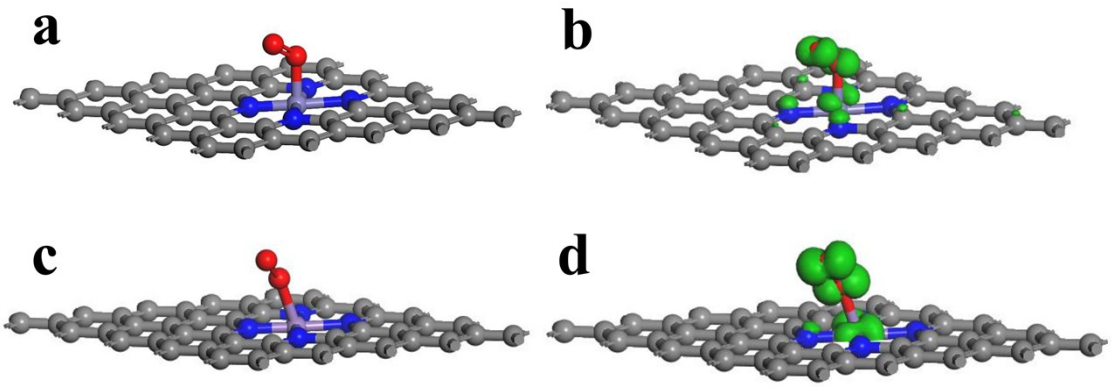

Fig. S9 The geometry structure and corresponding orbitals isosurface for the (a, b) $FeN_4/C@O_2$ and (c, d) $MnN_4/C@O_2$.

Table S1 The calculation process for free energy on FeN_4/C at different electrode potentials

U= 0 V			
	$\Delta E+\Delta ZPE+T\Delta S$ (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	3.95833	0	3.95833
O*	2.35386	0	2.35386
OH*	0.7998	0	0.7998
H_2O*	0	0	0

U= 1.23 V			
	$\Delta E+\Delta ZPE+T\Delta S$ (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	-1.23*4	0
OOH*	3.95833	-1.23*3	0.26833
O*	2.35386	-1.23*2	-0.10614
OH*	0.7998	-1.23*1	-0.4302
H_2O*	0	-1.23*0	0

U= 0.79 V			
	$\Delta E+\Delta ZPE+T\Delta S$ (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	-0.79*4	1.76
OOH*	3.95833	-0.79*3	1.58833
O*	2.35386	-0.79*2	0.77386
OH*	0.7998	-0.79*1	0.0098
H_2O*	0	-0.79*0	0

Table S2 The calculation process for free energy on MnN_4/C at different electrode potentials

U= 0 V			
	$\Delta E+\Delta ZPE+T\Delta S$ (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	4.39162	0	4.39162
O*	2.38258	0	2.38258
OH*	0.73089	0	0.73089
H_2O*	0	0	0

U= 1.23 V			
	$\Delta E+\Delta ZPE+T\Delta S$ (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	-1.23*4	0
OOH*	4.39162	-1.23*3	0.70162
O*	2.38258	-1.23*2	-0.07742
OH*	0.73089	-1.23*1	-0.49911

H_2O*	0	-1.23*0	0

U= 0.52 V			
	$\Delta E+\Delta ZPE+T\Delta S$ (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	-0.52*4	2.84
OOH*	4.39162	-0.52*3	2.83162
O*	2.38258	-0.52*2	1.34258
OH*	0.73089	-0.52*1	0.21089
H_2O*	0	-0.52*0	0