Supporting Information

Oxygen Coordination Engineering in Fe–N–O–Graphene Single-Atom Catalysts for Enhanced Bifunctional Oxygen Electrocatalysis

Linlin Zhang[1]*, Yanning Wang[1], Kai Xiong[2]

[1]*Department of Physics, Mathematics and Computer Science, Kunming Medical University, Kunming, China.*

[2]*Materials Genome Institute, School of Materials and Energy, Yunnan University, Kunming 650091, China*

*Corresponding author email: ynuzll@163.com

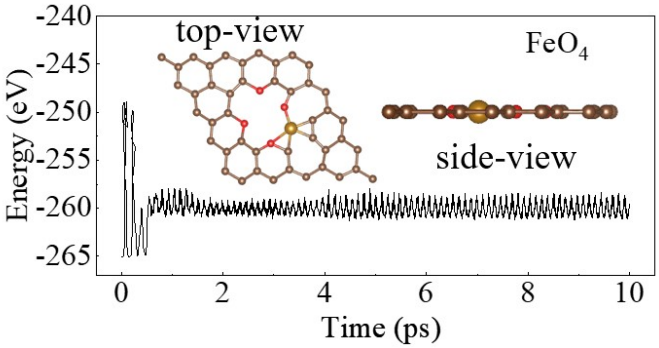

Figure S1. Ab initio molecular dynamics (AIMD) simulations of FeO_4–gra structures at 500 K for 10 ps in the NVT ensemble using the Nosé–Hoover thermostat. Inset in each panel shows the final atomic configuration obtained at the end of the simulation (t = 10 ps).

Table S1 Adsorption energy ΔE_{ads} (eV) of reactive species on Fe-N-O-gra.

Structure	ΔE_{*O_2} (side on)	ΔE_{*O_2} (end on)	ΔE_{*OOH}	ΔE_{*O}	ΔE_{*OH}
FeN_4	-0.56	-0.89	-1.41	-5.98	-2.83
FeN_3O	-1.01	-1.02	-1.54	-5.68	-2.48
FeN_2O_2-o	-1.54	-1.14	-1.41	-6.02	-2.70
FeN_2O_2-h	-1.66	-1.10	-1.32	-6.14	-2.75
FeN_2O_2-p	-1.77	-1.14	-1.46	-6.22	-3.45
$FeNO_3$	-2.29	-1.26	-1.75	-6.85	-4.19

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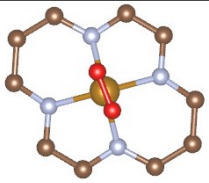
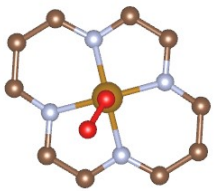
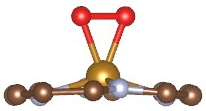
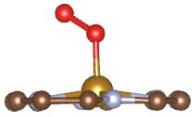
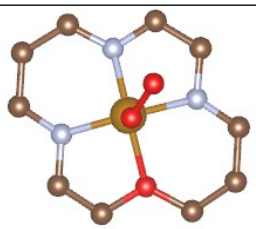
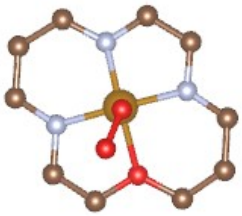
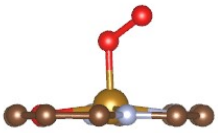
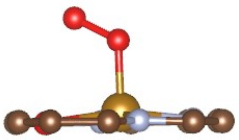
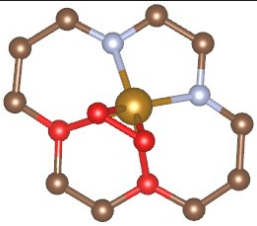
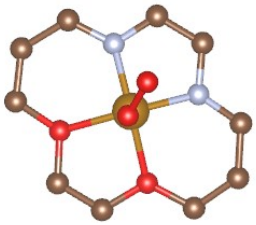
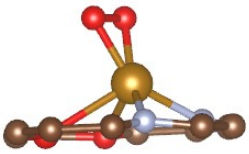
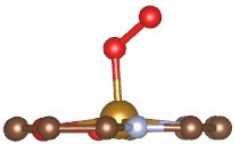
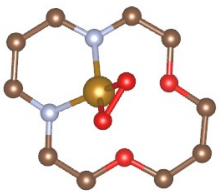
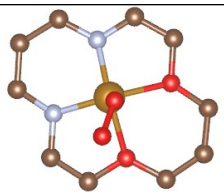
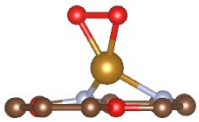
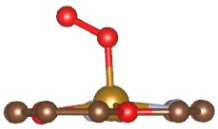
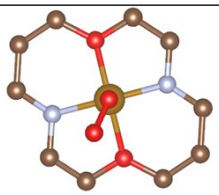
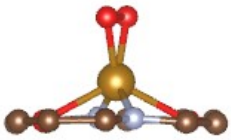
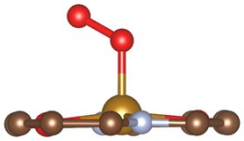
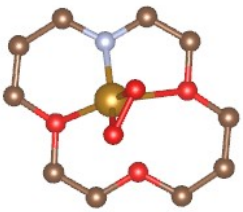
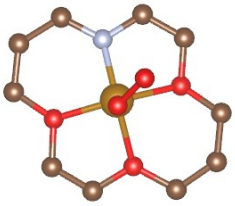
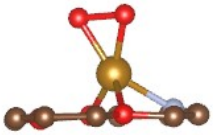
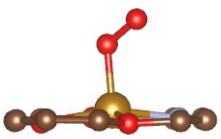
Table S2 The optimal adsorption configurations of O_2*on Fe–N–O-Gra.

FeN_4-Gra	*O_2	
	End-on	Side-on
Top		
Side		
FeN_3O-Gra	*O_2	
	End-on	Side-on
Top		
Side		
FeN_2O_2-p-Gra	*O_2	
	End-on	Side-on
Top		
Side		

FeN_2O_2-h-Gra	$*O_2$	
	End-on	Side-on
Top		
Side		
FeN_2O_2-o-Gra	$*O_2$	
	End-on	Side-on
Top		
Side		
$FeNO_3$-Gra	$*O_2$	
	End-on	Side-on
Top		
Side		

The d-band center was computed with respect to the Fermi level using the expression:

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} E \cdot D_d(E) dE}{\int_{-\infty}^{+\infty} D_d(E) dE}$$

Where $D_d(E)$ is the density of states of Co 3d orbitals.

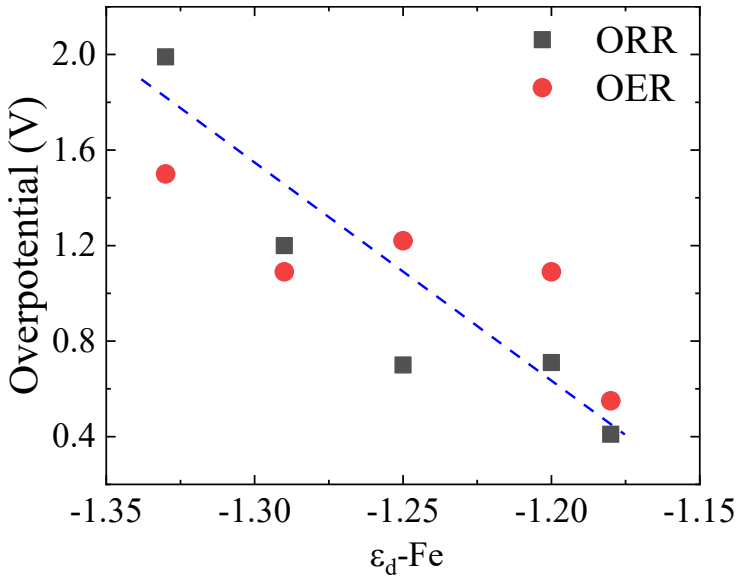


Figure S2 Correlation between the Fe d-band center (ε_d) after O_2 adsorption and the ORR/OER overpotentials for different Fe–N–O coordination structures.