Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Theoretical Investigation of N and O Coordination Effects on the Bifunctional Oxygen Electrode Activity of Co-Based Single-Atom Catalysts

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Computational contents

(1) Formation Energy (E_f) and Dissolution Potential (U_{diss})

To evaluate the thermodynamic and electrochemical stability of the catalysts, the formation energy (E_f) and dissolution potential (U_{diss}) were calculated using equations (1) and (2):

$$E_f = E_{Co-N-C-gra} + y\mu_C - \left(E_{graphene} + x\mu_N + (4-x)\mu_O + \mu_{Co}\right) \quad (1)$$

$$U_{diss} = U_{diss}^{0}\,(metal,bulk) - E_f/n \quad (2)$$

Here, $E_{Co-N-C-gra}$ and $E_{graphene}$ represent the total energies of the optimized Co–N–C structure and the 4×4×1 graphene supercell, respectively. μ_C, μ_N, μ_O and μ_{Co} refer to the energies of a single C atom (from the 4×4×1 graphene supercell), half of an N_2 molecule, half of an O_2 molecule, and an isolated Co atom, respectively. The variables x and y denote the number of C and N atoms removed from pristine graphene. A more negative E_f indicates greater structural stability. $U_{diss}^{0}\,(metal,bulk)$ is the standard dissolution potential of bulk Co metal, and n is the number of electrons transferred per Co atom during dissolution.

(2) Adsorption Energy (ΔE_{ads})。

The adsorption energy ΔE_{ads} of an intermediate were defined by equation (3):

$$\Delta E_{ads} = E_{*m} - E_{Co-N-C-Gra} - E_m(\quad (3)$$

Here, E_{*m} represents the total energy of the Co–N–O–graphene system after adsorbing intermediate m, and E_m is the total energy of the isolated intermediate m. A negative ΔE_{ads} indicates that the catalyst can effectively adsorb and activate the reactant.

(3) Gibbs Free Energy Change（ΔG）。

The Gibbs free energy change ΔG for each reaction step is calculated using equation (4):

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{PH} \quad (4)$$

Where ΔE,ΔZPE and ΔS are the energy difference, zero-point energy correction, and entropy change at 298.15 K, respectively. $\Delta G_U = -neU$, where n is the number of transferred electrons and U is the electrode potential. $\Delta GpH = K_B T \times \ln 10 \times pH$, where K_B is the Boltzmann constant; in this work, the pH value was defined to be 0 for acidic medium.

Under acidic conditions, the four-electron ORR pathway can be described by equations (5)–(8), while the OER is the reverse of the ORR:

$$O_2 + * + H^+ + e^- \rightarrow *OOH \quad (5)$$

$$*OOH + H^+ + e^- \rightarrow *O + H_2O \quad (6)$$

$$*O + H^+ + e^- \rightarrow *OH \quad (7)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (8)$$

Here, * represents the adsorption site on the catalyst. Under acidic conditions, the overpotential (η) for ORR and OER can be calculated using equation (9):

$$\eta^{ORR(/OER)} = [\Delta G_1, \Delta G_1, \Delta G_1, \Delta G_1]^{max}/e \pm 1.23$$

(4) Adsorption Free Energy(ΔG_{ads})

The adsorption free energies of *OOH、*Oand *OH(ΔG_{ads})are calculated by equations (10)–(12):

$$\Delta G_{*OOH} = G_{*OOH} - G_{Co-N-C-gra} - (2G_{H_2O} - 3/2G_{H_2}) \quad (10)$$

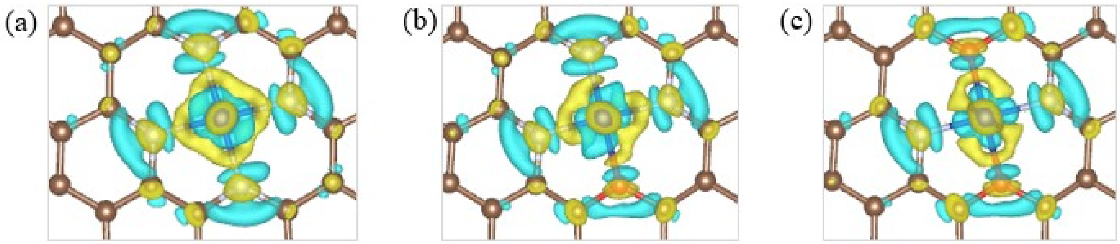
$$\Delta G_{*O} = G_{*O} - G_{Co-N-C-gra} - \left(G_{H_2O} - G_{H_2}\right) \quad (11)$$

$$\Delta G_{*OH} = G_{*OH} - G_{Co-N-C-gra} - (G_{H_2O} - 1/2G_{H_2}) \quad (12)$$

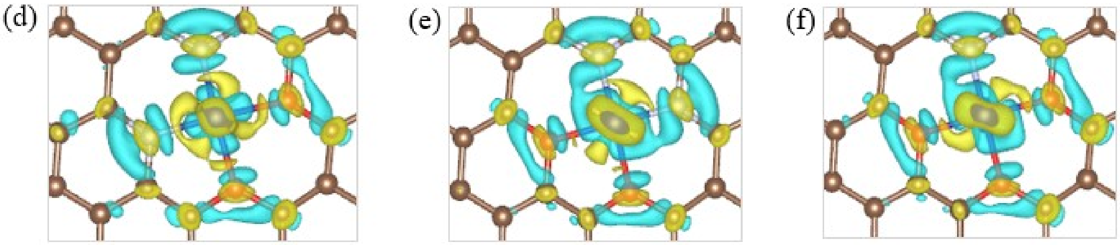
Here, G_{*OOH}, G_{*O}, and G_{*OH} are the Gibbs free energies of the systems with adsorbed OOH, O, and OH, respectively. G_{H_2O} and G_{H_2} represent the Gibbs free energies of isolated H_2O and H_2 molecules. $G_{Co-N-C-gra}$ denotes the Gibbs free energy of the graphene catalyst substrate with various N/O coordination doping concentrations.

Table S1 Formation energies (E_f, eV) and dissolution potentials (U_{diss},V) for Co–N–O-Gra.

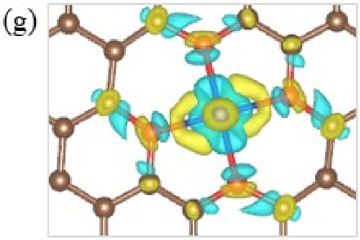
	CoN_4-Gra	**CoN_3O-Gra**	**CoN_2O_2-p-Gra**	**CoN_2O_2-h-Gra**	**CoN_2O_2-o-Gra**	**CoN_1O_3-Gra**	**CoO_4-Gra**
E_f	-3.90	-4.35	-3.91	-4.08	-4.00	-3.60	-3.25
U_{diss}	1.67	1.90	1.68	1.76	1.72	1.52	1.34



CoN$_4$ CoN$_3$O$_1$ CoN$_2$O$_2$-pen



CoN$_2$O$_2$-hex CoN$_2$O$_2$-oppo CoN$_1$O$_3$



CoN$_0$O$_4$

Figure S1 Charge density difference for Co–N–O-Gra.

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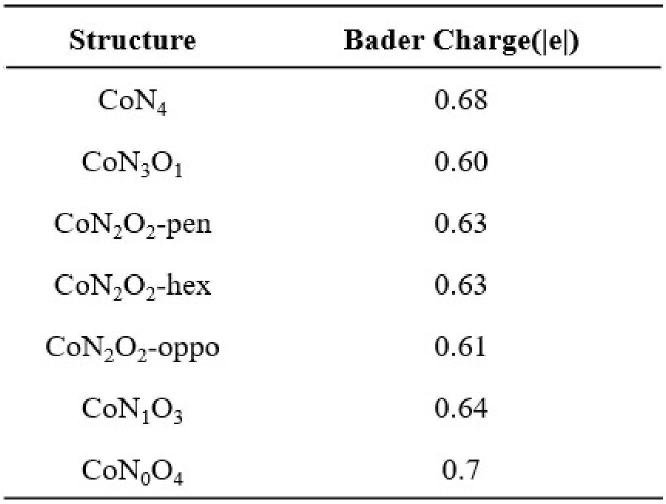
Table S2 The Bader charges of Co single atom in Co–N–O-Gra..



Structure	Bader Charge(|e|)
CoN_4	0.68
CoN_3O_1	0.60
CoN_2O_2-pen	0.63
CoN_2O_2-hex	0.63
CoN_2O_2-oppo	0.61
CoN_1O_3	0.64
CoN_0O_4	0.7

Table S3 The optimal adsorption configurations of O_2*, OOH*, O* and OH* on Co–N–O-Gra.

CoN_4O_0-Gra	*O_2		*OOH	*O	*OH
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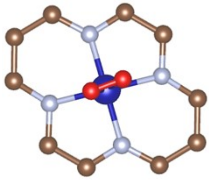
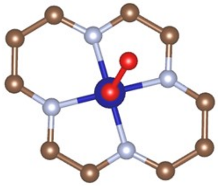
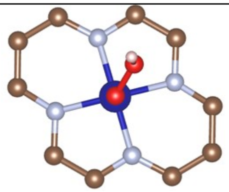
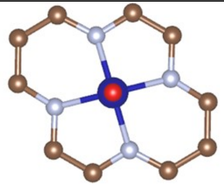
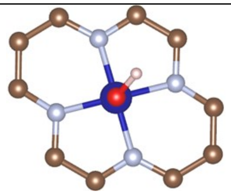
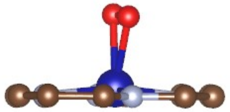
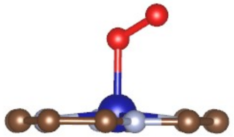
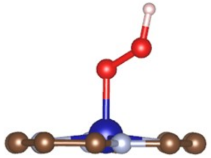
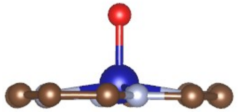
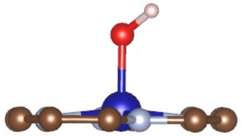
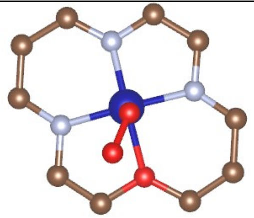
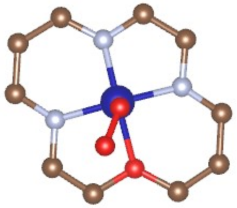
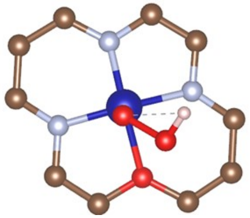
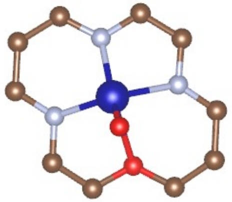
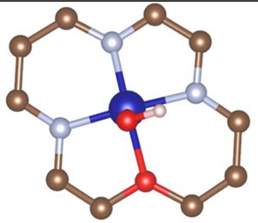
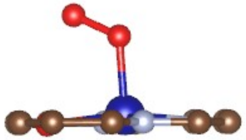
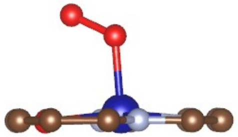
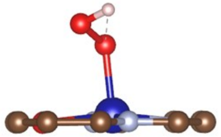
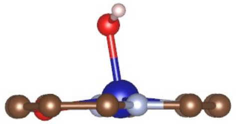
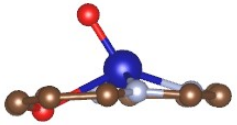
Top					
Side					
CoN_3O_1-Gra	*O_2		*OOH	*O	*OH
	End-on	Side-on			
Top					
Side					

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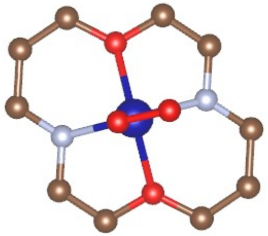
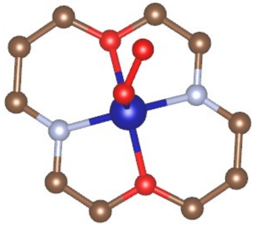
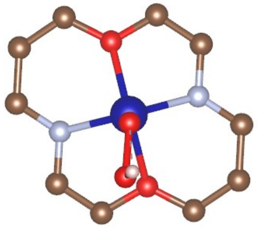
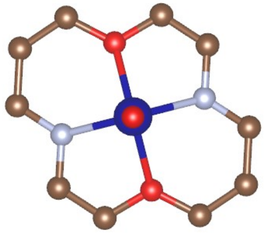
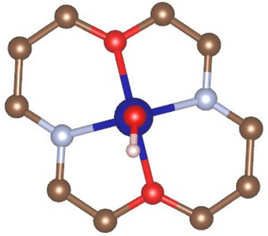
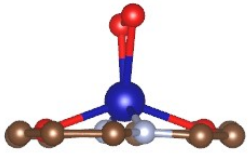
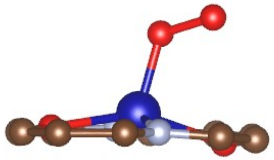
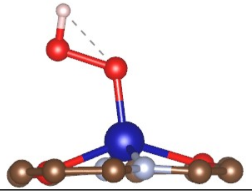
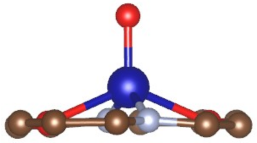
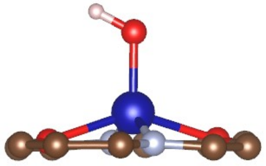
	End-on	Side-on			
Top					
Side					
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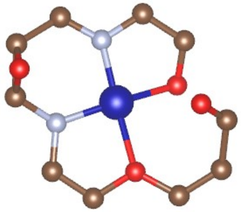
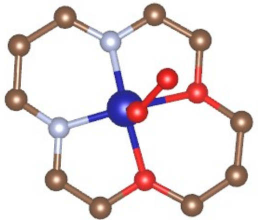
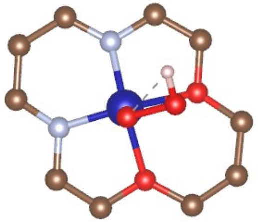
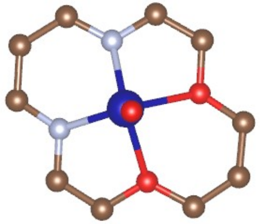
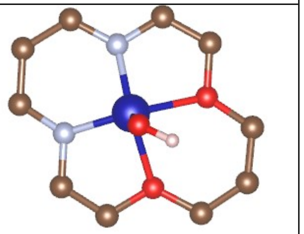
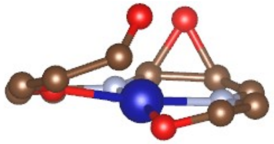
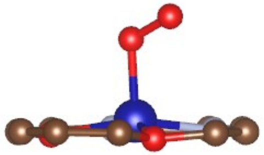
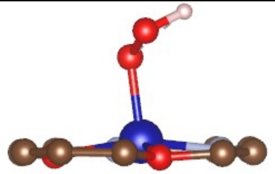
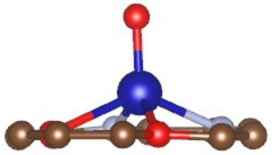
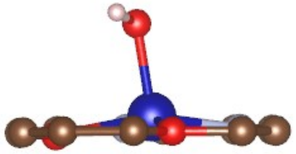
Top					
Side					

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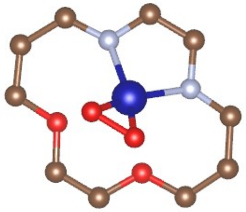
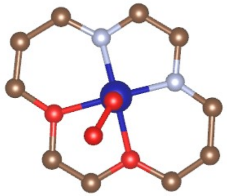
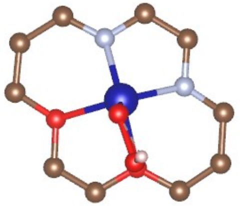
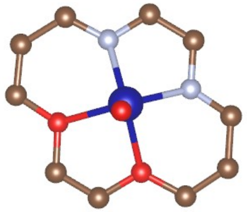
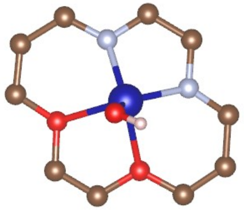
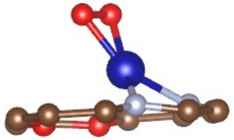
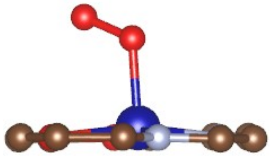
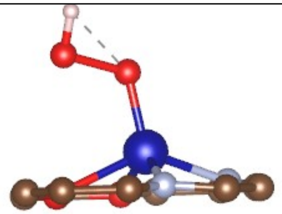
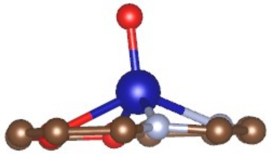
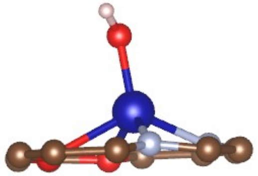
<tr><td>Top</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Side</td><td></td><td></td><td></td><td></td><td></td></tr>
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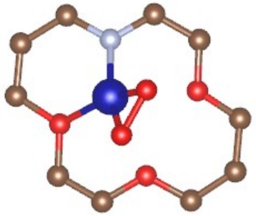
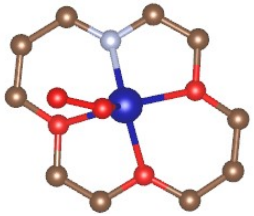
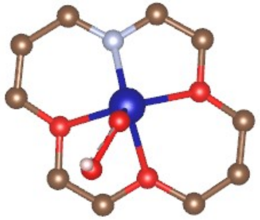
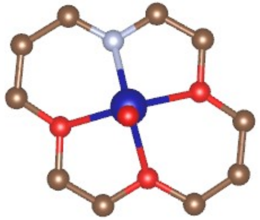
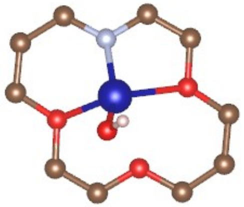
<tr><td>Top</td><td></td><td></td><td></td><td></td><td></td></tr>
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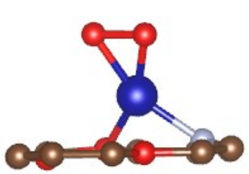
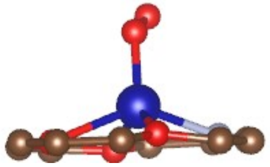
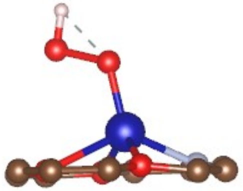
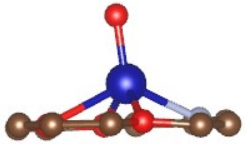
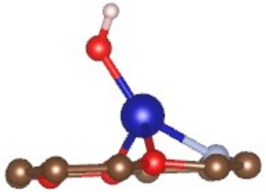
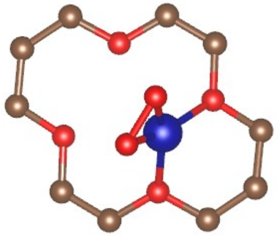
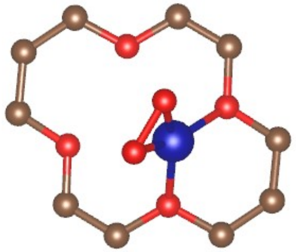
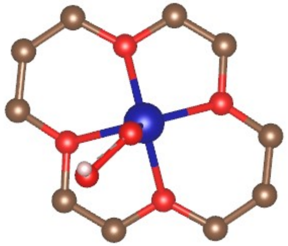
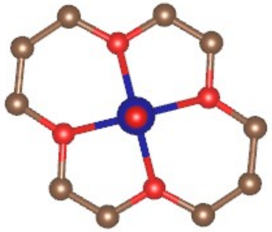
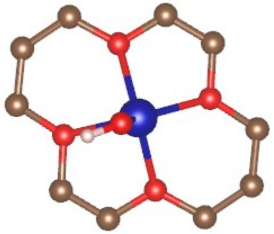
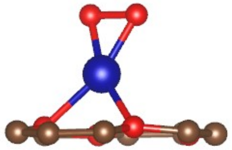
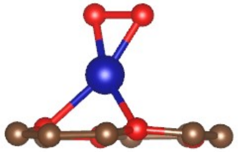
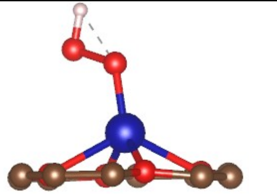
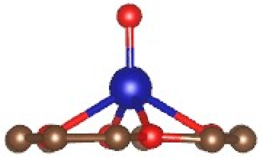
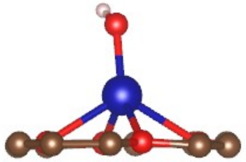
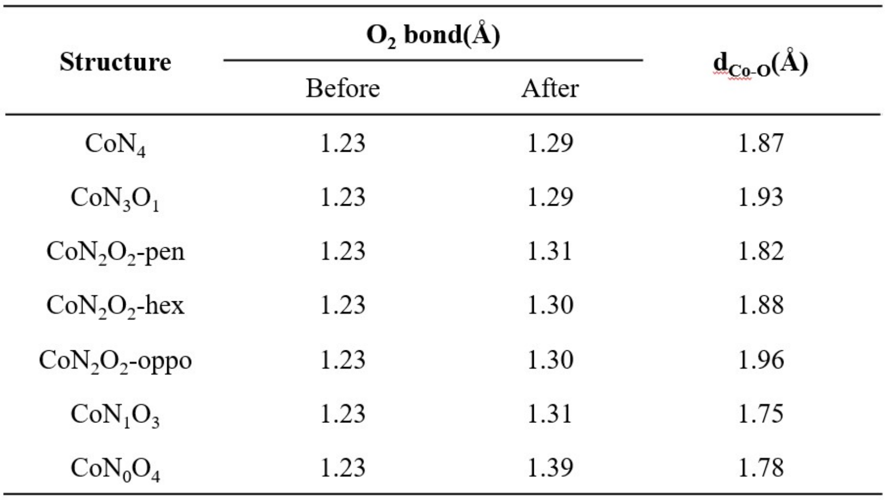
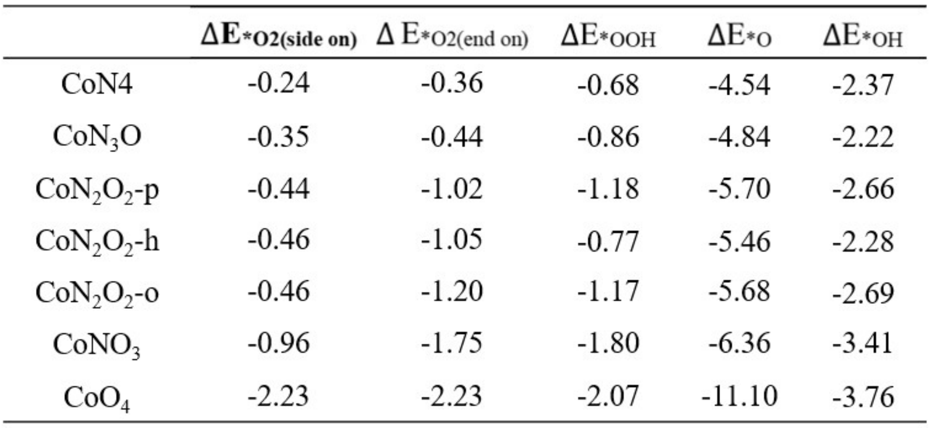
Side					
CoN$_0$O$_4$-Gra	*O$_2$		*OOH	*O	*OH
	End-on	Side-on			
Top					
Side					

Table S4 The O–O bond lengths before and after O_2 adsorption, and the Co−O bond lengths (d_{Co-O}, Å) after $*O_2$ adsorbed on Co-N-O-gra.



Structure	**O_2 bond(Å)**		**d_{Co-O}(Å)**
	Before	After	
CoN_4	1.23	1.29	1.87
CoN_3O_1	1.23	1.29	1.93
CoN_2O_2-pen	1.23	1.31	1.82
CoN_2O_2-hex	1.23	1.30	1.88
CoN_2O_2-oppo	1.23	1.30	1.96
CoN_1O_3	1.23	1.31	1.75
CoN_0O_4	1.23	1.39	1.78

Table S5 Adsorption energy ΔE_{ads} (eV) of reactive species on Co-N-O-gra.



	$\Delta E_{*O2(side\ on)}$	$\Delta E_{*O2(end\ on)}$	ΔE_{*OOH}	ΔE_{*O}	ΔE_{*OH}
CoN4	-0.24	-0.36	-0.68	-4.54	-2.37
CoN_3O	-0.35	-0.44	-0.86	-4.84	-2.22
CoN_2O_2-p	-0.44	-1.02	-1.18	-5.70	-2.66
CoN_2O_2-h	-0.46	-1.05	-0.77	-5.46	-2.28
CoN_2O_2-o	-0.46	-1.20	-1.17	-5.68	-2.69
$CoNO_3$	-0.96	-1.75	-1.80	-6.36	-3.41
CoO_4	-2.23	-2.23	-2.07	-11.10	-3.76

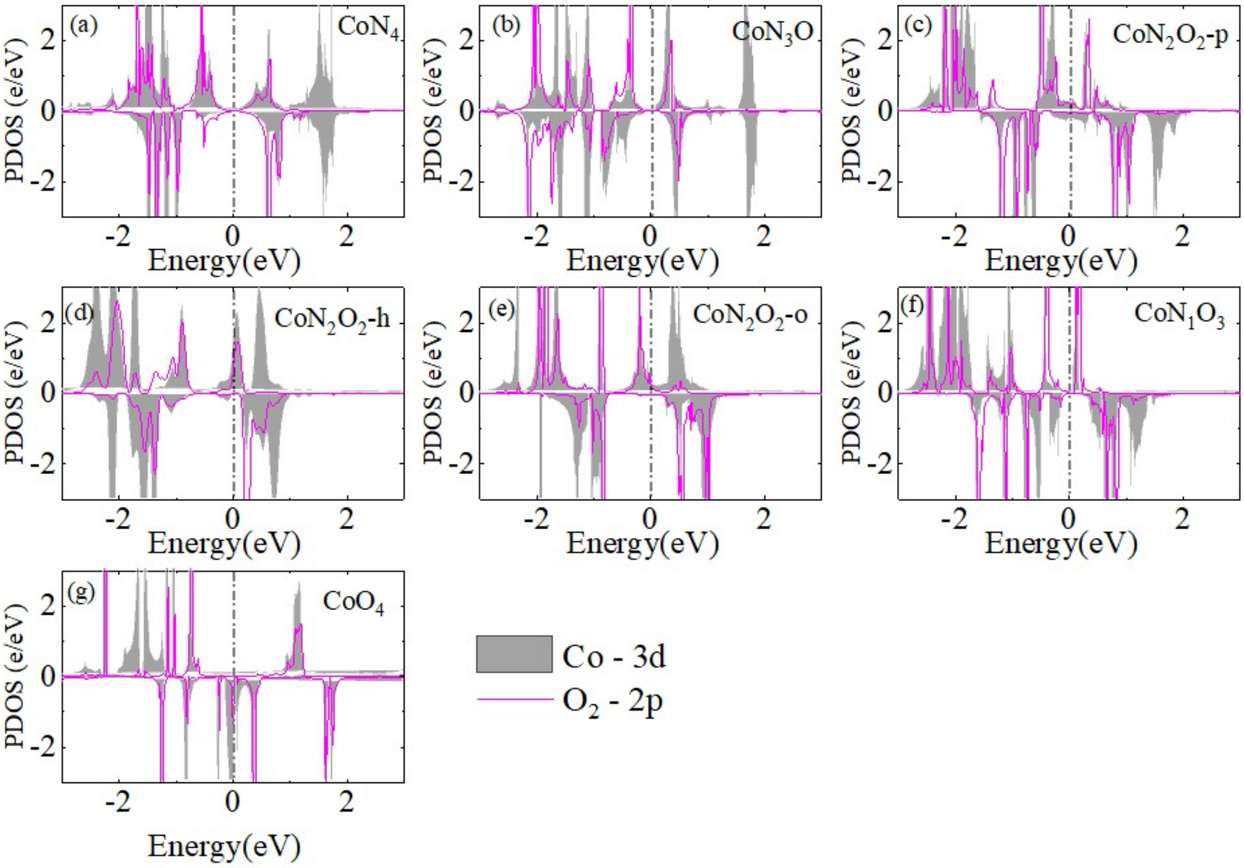
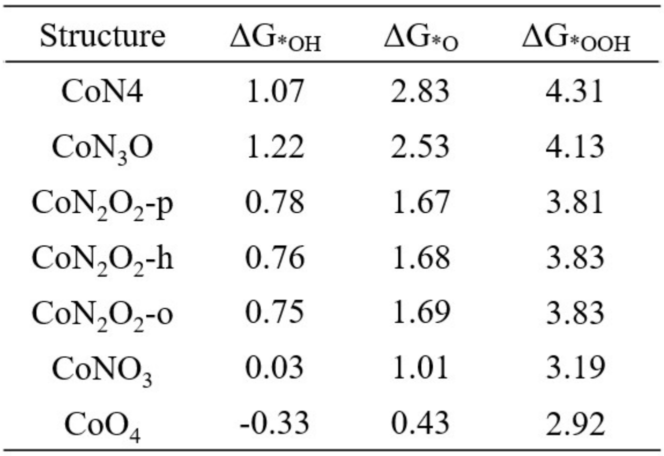


Figure S2 Projected density of states (PDOS) for O2 adsorption on Co–N–O-Gra.

Table S6 Adsorption free energies of intermediates *OH, *O, and *OOH on various Co–N–O–gra structures (eV).



Structure	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}
CoN4	1.07	2.83	4.31
CoN_3O	1.22	2.53	4.13
CoN_2O_2-p	0.78	1.67	3.81
CoN_2O_2-h	0.76	1.68	3.83
CoN_2O_2-o	0.75	1.69	3.83
$CoNO_3$	0.03	1.01	3.19
CoO_4	-0.33	0.43	2.92

Table S7 Free energy changes of ΔG_x (x=1-4, eV) and overpotential (η, V) of ORR/OER on Co-N-

O-gra.

Structure		ΔG_1	ΔG_2	ΔG_3	ΔG_4	$\boldsymbol{\eta}$
CoN4	OER	1.07	1.76	1.48	0.61	0.52
	ORR	-0.61	-1.48	-1.76	-1.07	0.62
CoN_3O	OER	1.22	1.31	1.60	0.79	0.37
	ORR	-0.79	-1.60	-1.31	-1.22	0.44
CoN_2O_2-p	OER	0.78	0.89	2.14	1.11	0.91
	ORR	-1.11	-2.14	-0.89	-0.78	0.45
CoN_2O_2-h	OER	0.76	0.92	2.15	1.09	0.92
	ORR	-1.09	-2.15	-0.92	-0.76	0.47
CoN_2O_2-o	OER	0.75	0.94	2.14	1.09	0.90
	ORR	-1.09	-2.14	-0.94	-0.75	0.48
$CoNO_3$	OER	0.03	0.98	2.18	1.73	0.95
	ORR	-1.73	-2.18	-0.98	-0.03	1.20
CoO_4	OER	-0.33	0.76	2.49	2	1.25
	ORR	-2	-2.49	-0.76	0.33	1.56

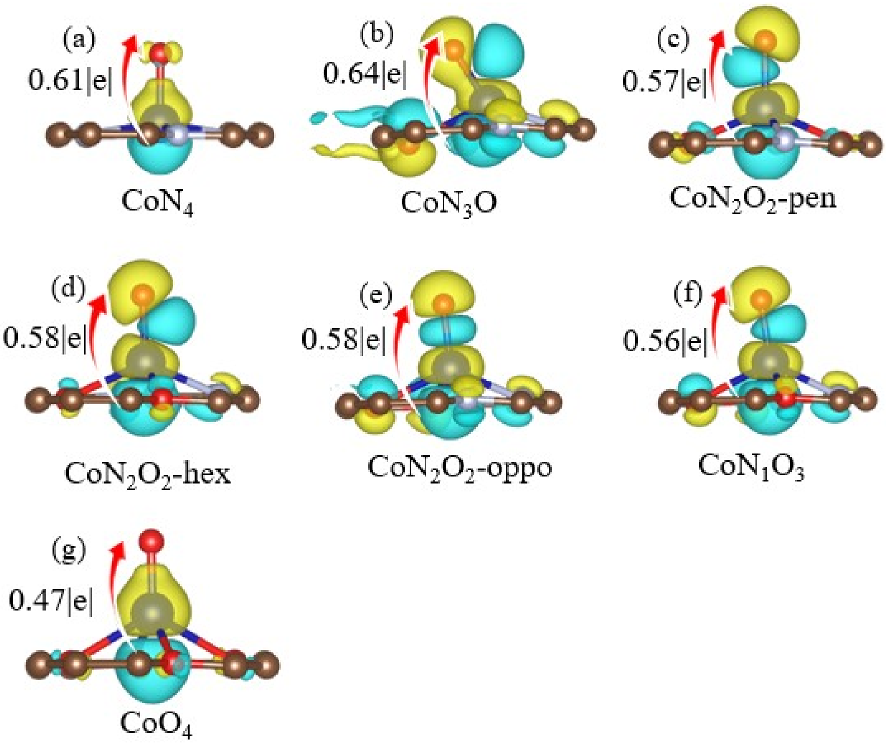


Figure S3 Bader charge, Charge density difference for O adsorption on Co–N–O-Gra.

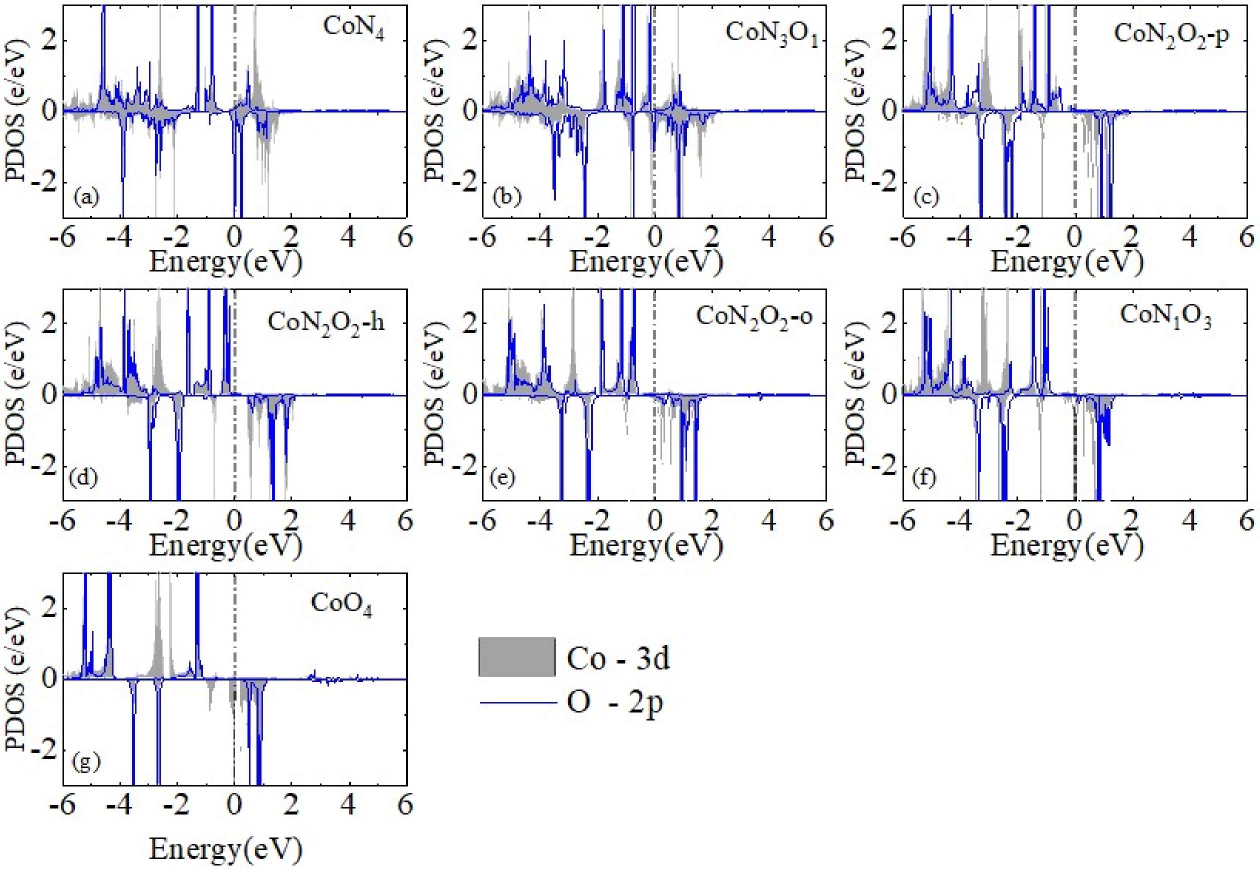


Figure S4 Projected density of states (PDOS) for O adsorption on Co–N–O-Gra.