Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Oxygen evolution reaction on cobalt atoms embedded nitrogen doped graphene electrocatalysts: a density functional theory study

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Contents

Computational Details on adsorption Gibbs free energy ΔG_{OH^*}, ΔG_{O^*}, ΔG_{OOH^*}

The ΔG_{O^*}, ΔG_{OH^*} and ΔG_{OOH^*} are obtained by:

(1a) $OH^-(aq) + * \rightarrow OH^* + e^-$

$$\Delta G_1 = \Delta G_{OH^*} = G_{OH^*} - E_* - G[OH^-(aq) - e^-] = G_{OH^*} - E_* - G[H_2O(g)] - 0.8277\ eV$$

(1b) $OH^* + OH^-(aq) \rightarrow O^* + H_2O(l) + e^-$

$$\Delta G_2 = G_{O^*} + G[H_2O(l)] - G_{OH^*} - G[OH^-(aq) - e^-] =$$

$$G_{O^*} - G_{OH^*} + 1/2G[H_2(g)] - 0.8277\ eV$$

(1ab) $2OH^-(aq) + * \rightarrow O^* + H_2O(l) + 2e^-$

$$\Delta G_{O^*} = \Delta G_1 + \Delta G_2 = G_{O^*} + G[H_2O(l)] - E_* - 2 * G[OH^-(aq) - e^-] =$$

$$G_{O^*} - E_* - G[H_2O(l)] + G[H_2(g)] - 1.6554\ eV$$

(1c) $O^* + OH^-(aq) \rightarrow OOH^* + e^-$

$$\Delta G_3 = G_{OOH^*} - G_{O^*} - G[OH^-(aq) - e^-]$$

$$= G_{OOH^*} - G_{O^*} - G[H_2O(l)] + 1/2G[H_2(g)] - 0.8277\ eV$$

(1abc) $3OH^-(aq) + * \rightarrow OOH* + H_2O(l) + 3e^-$

$$\Delta G_{OOH^*} = \Delta G_1 + \Delta G_2 + \Delta G_3 = G_{OOH^*} + G[H_2O(l)] - E_* - 3 * G[OH^-(aq) - e^-] = G_{OO}$$
$$-E_* - 2G[H_2O(l)] + {}^3/_2 G[H_2(g)] - 2.4831\ eV$$

(1d) $OOH^* + OH^-(aq) \rightarrow O_2\,(g) + * + H_2O(l) + e^-$

$$\Delta G_4 = G[O2\ (g)] + G[H_2O(l)] + E_* - G_{OOH*} - G[OH^-(aq) - e^-] = 2G[H_2O(l)] -$$
$$H_2(g)] + 4.9148\ eV + G[H_2O(l)] + E_* - G_{OOH*} - G[H_2O(l)] + 1/2G[$$
$$H_2(g)] - 0.8277\ eV$$
$$= 2G[H_2O(l)] - {}^3/_2 G[H_2(g)] + E_* - G_{OOH*} + 4.0871\ eV$$

(1abcd) $4\mathrm{OH}^{-}(aq) \rightarrow O_2\,(\mathrm{g}) \;+\; 2H_2O(l) \;+\; 4e^{-}$

$\Delta G_{O_2} = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 = \; 1.604\; eV$

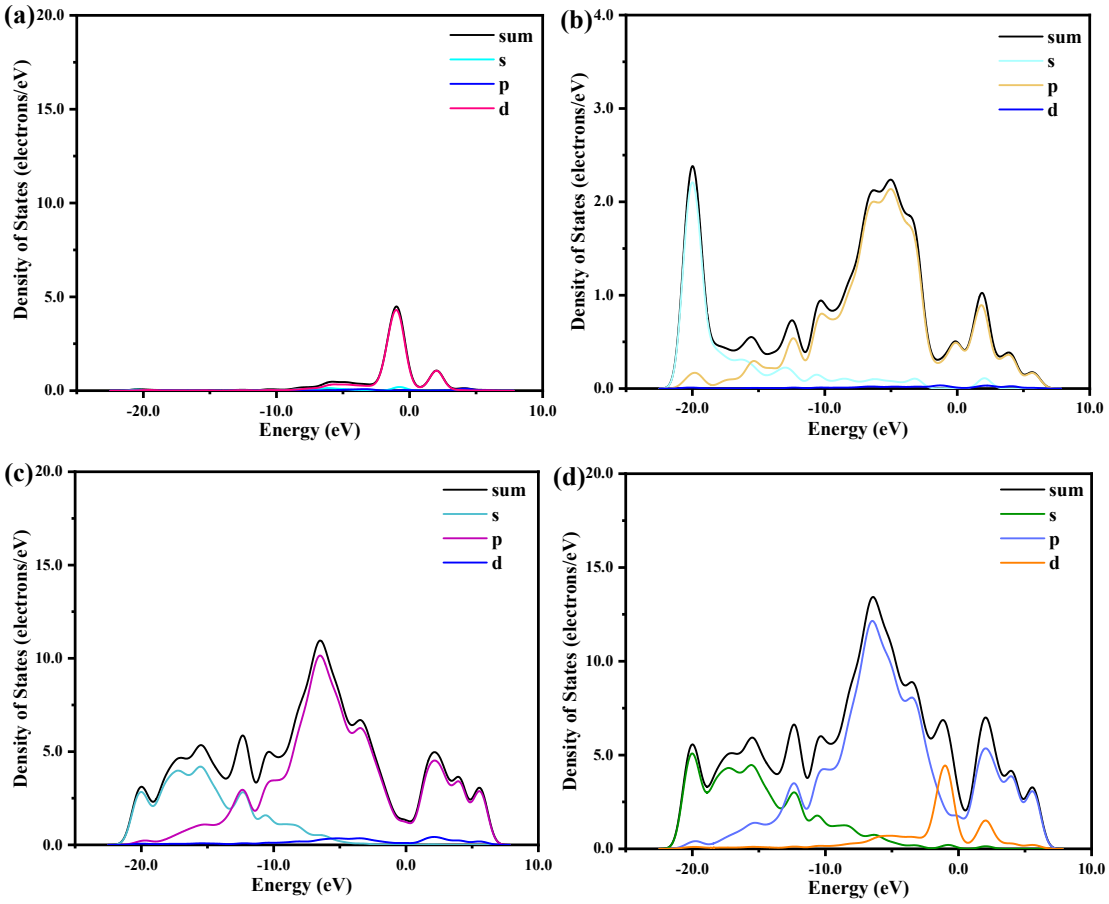
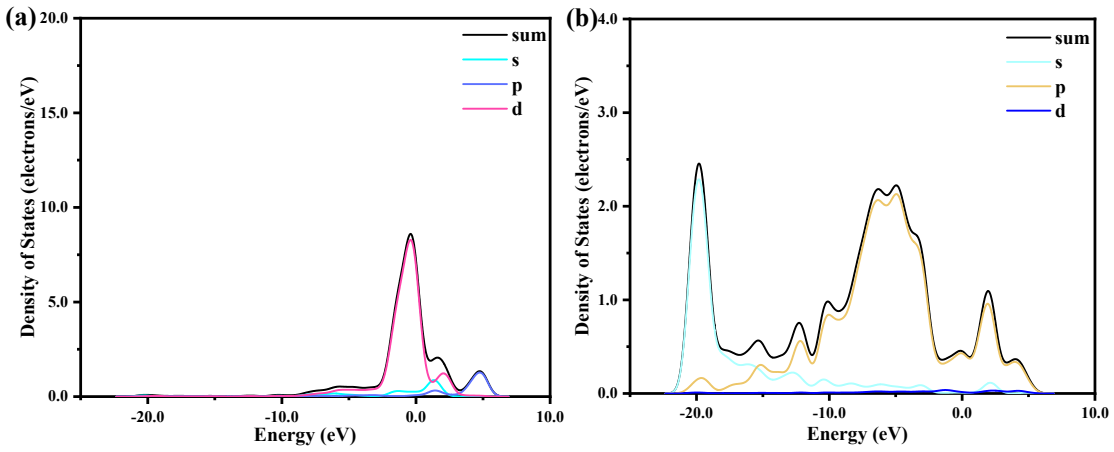


Figure S1. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co11-NG.



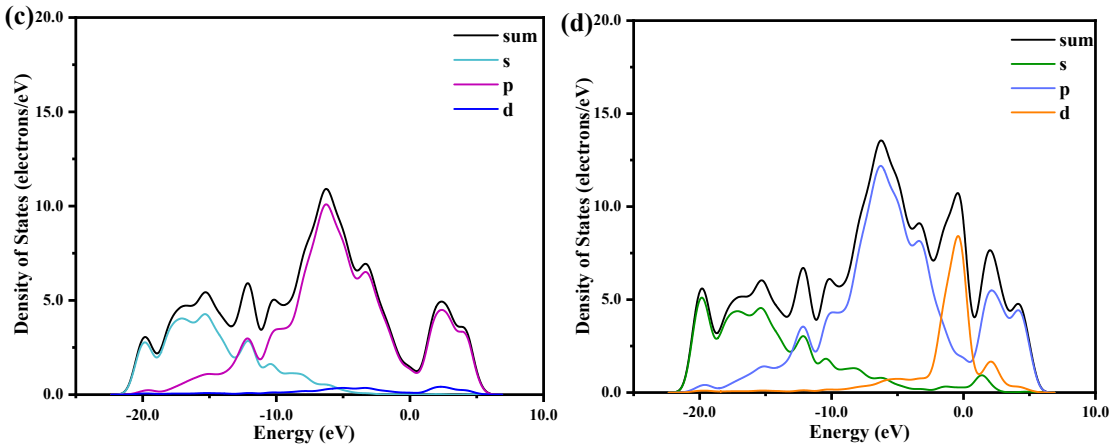


Figure S2. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co21-NG.

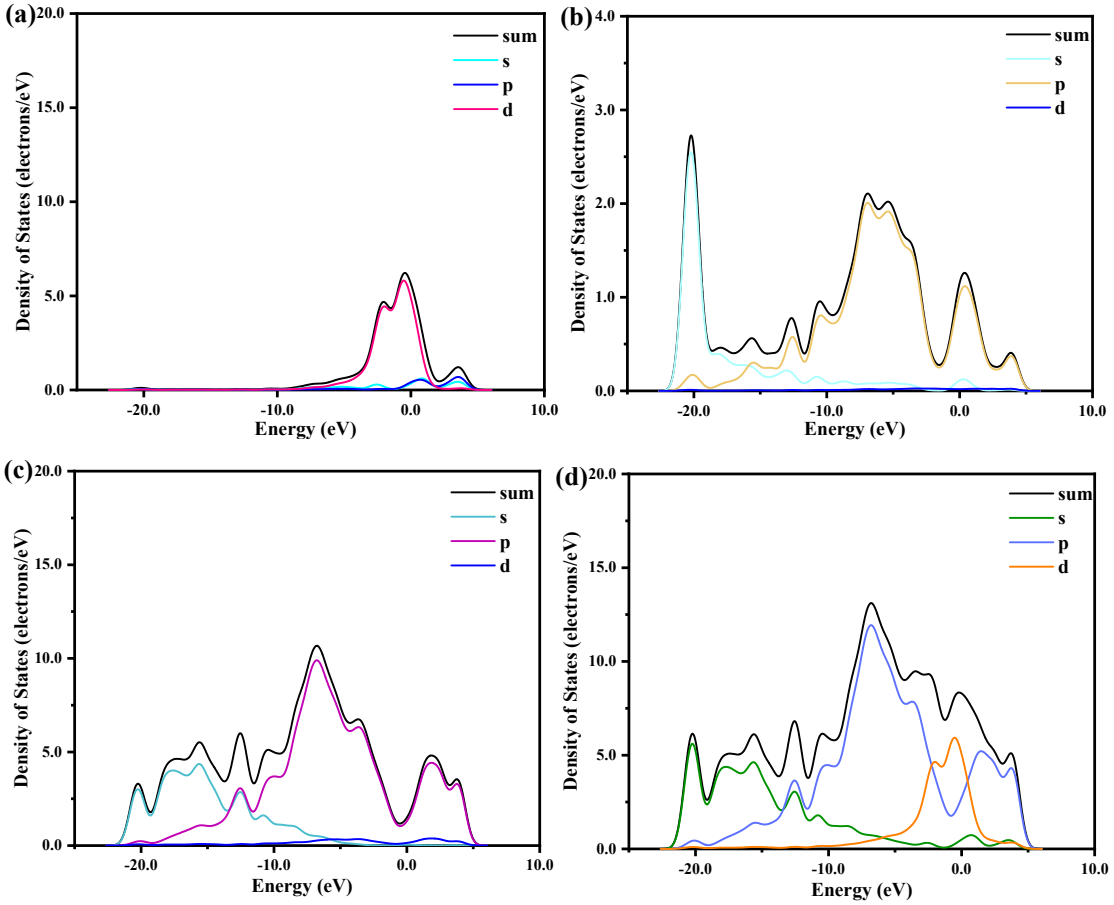


Figure S3. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms,

and (d) the total DOS in Co22-NG.

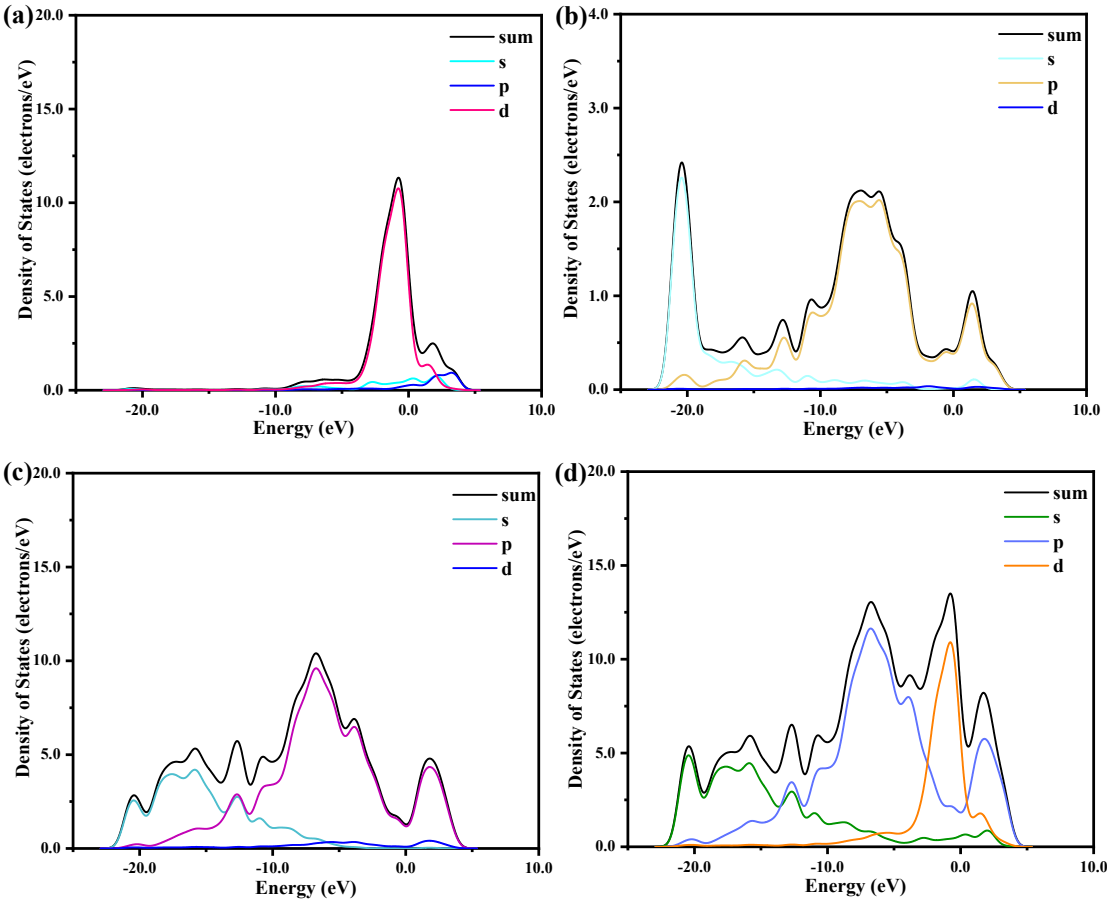


Figure S4. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co31-NG.

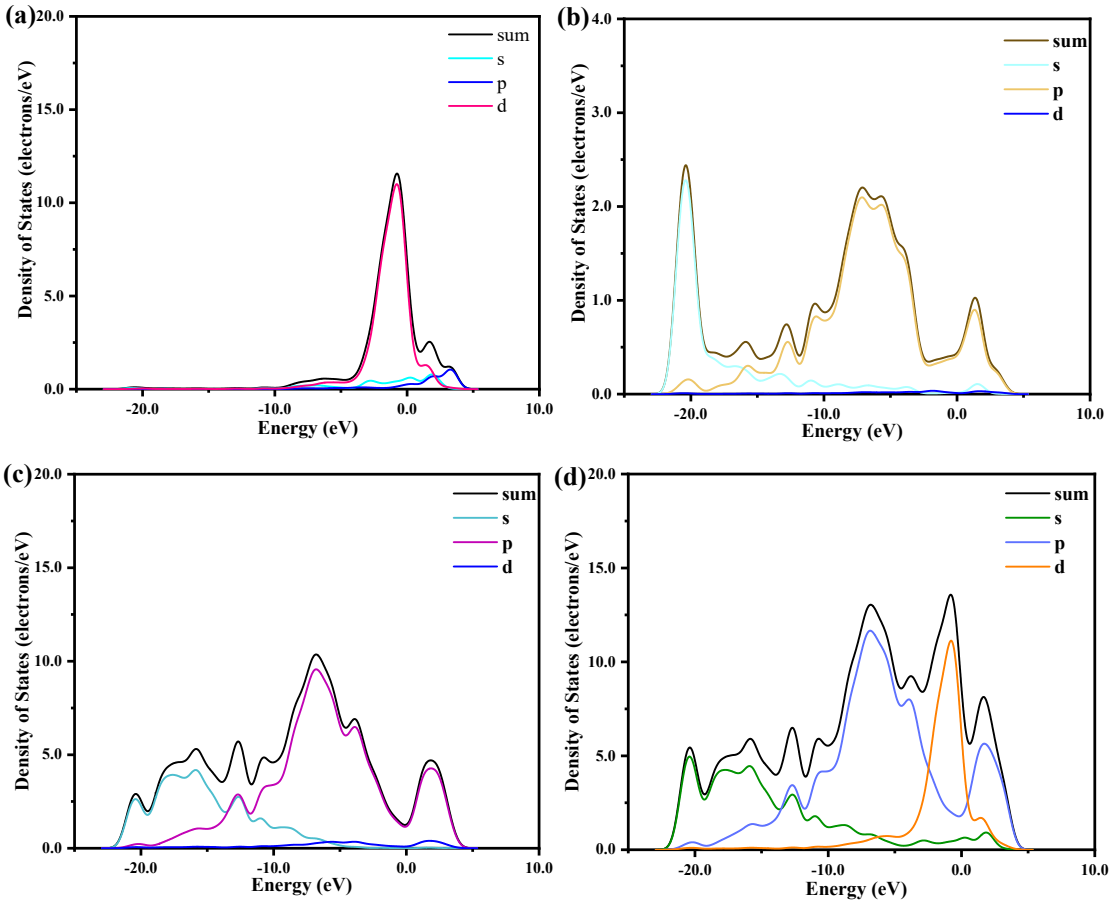
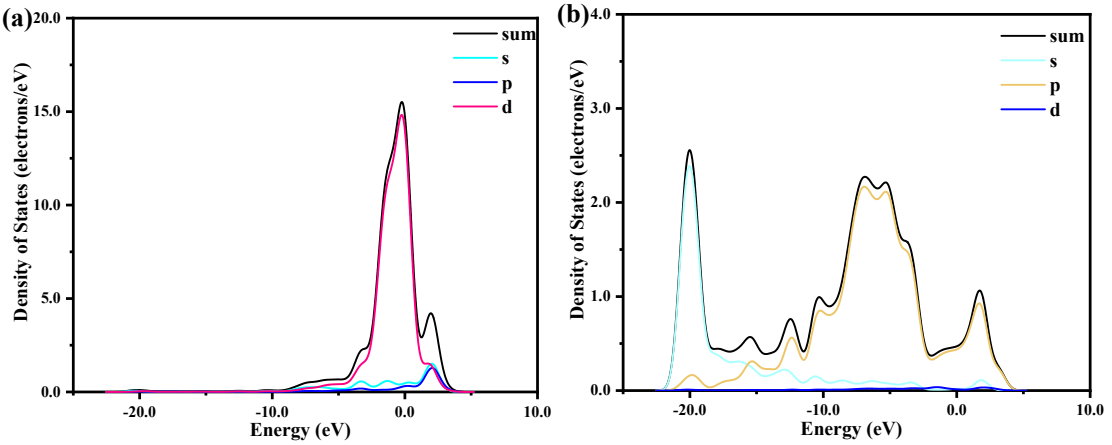


Figure S5. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co32-NG.



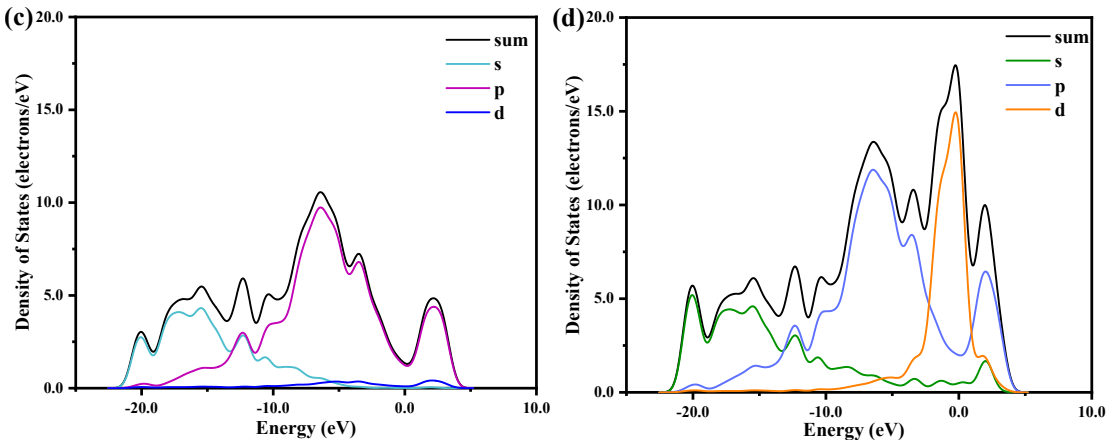


Figure S6. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co41-NG.

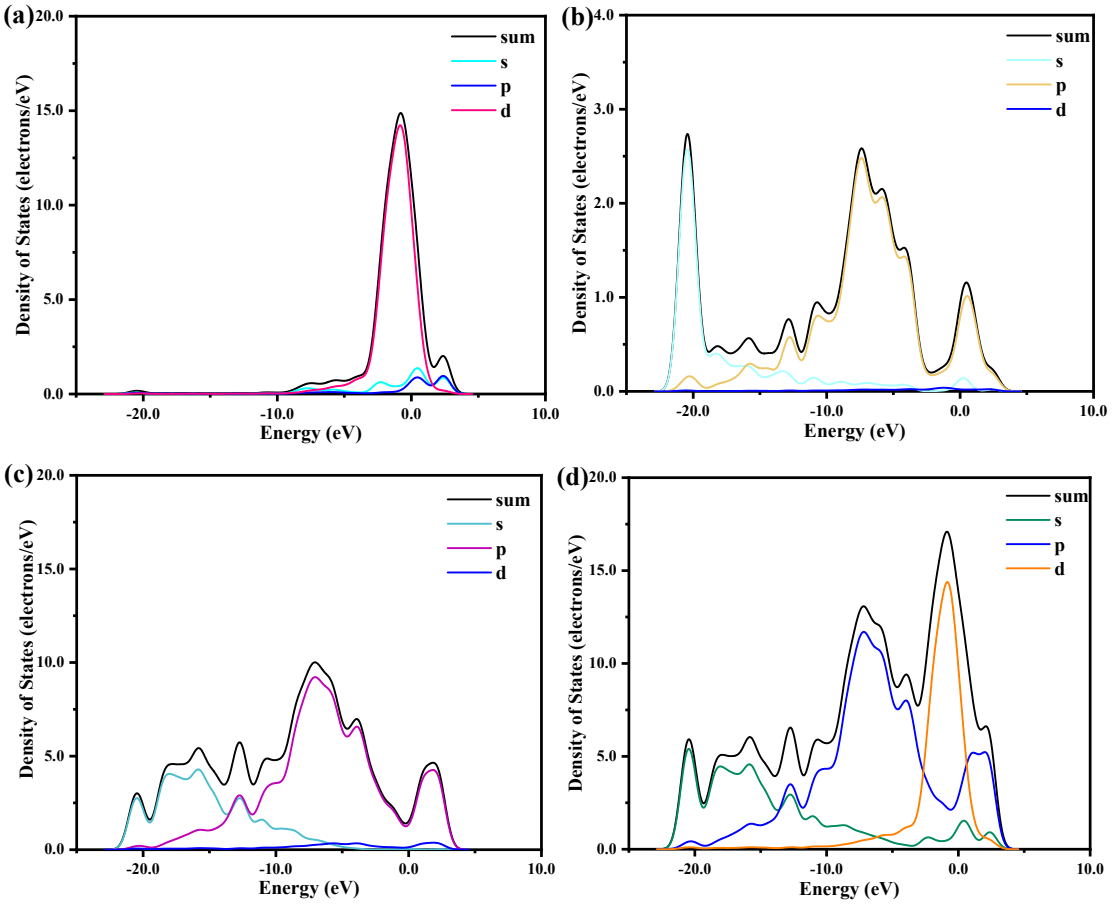


Figure S7. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co42-NG.

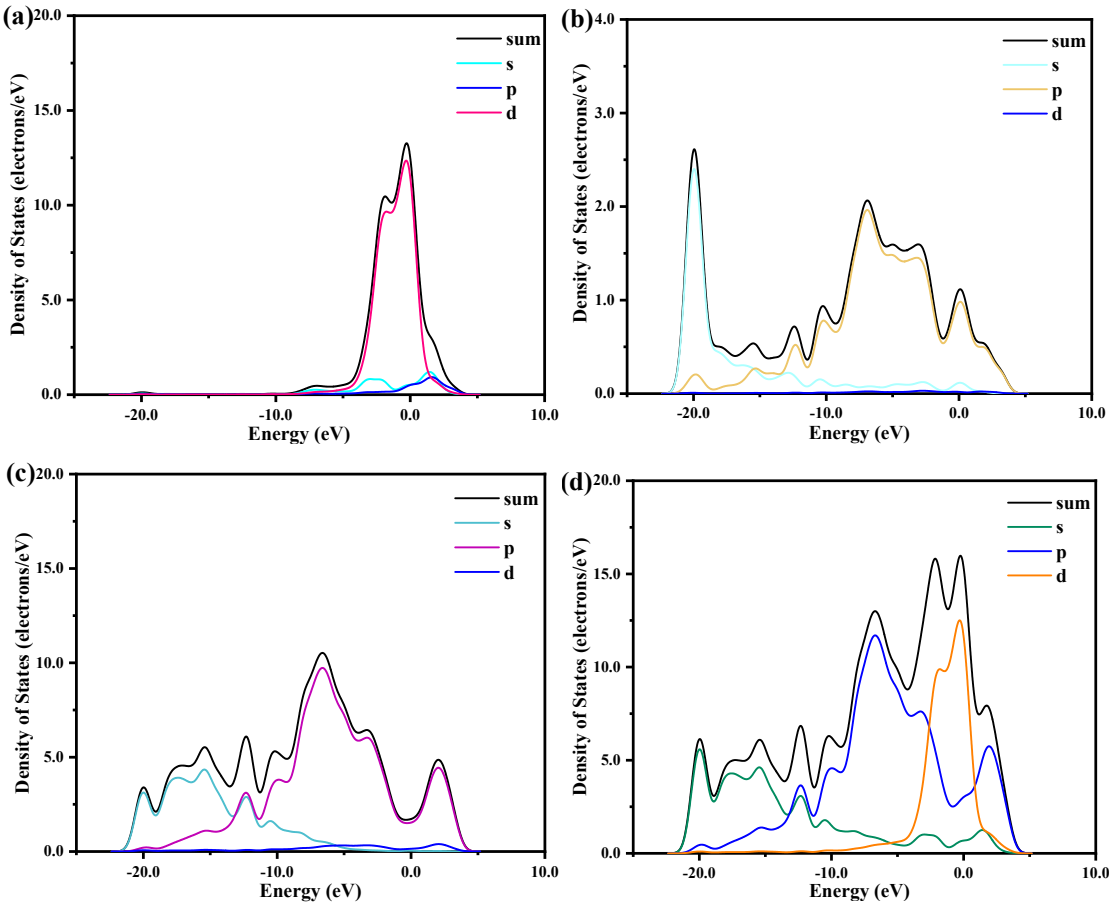


Figure S8. PDOS (partial density of state) of (a) Co atoms, (b) N atoms, (c) C atoms, and (d) the total DOS in Co43-NG.

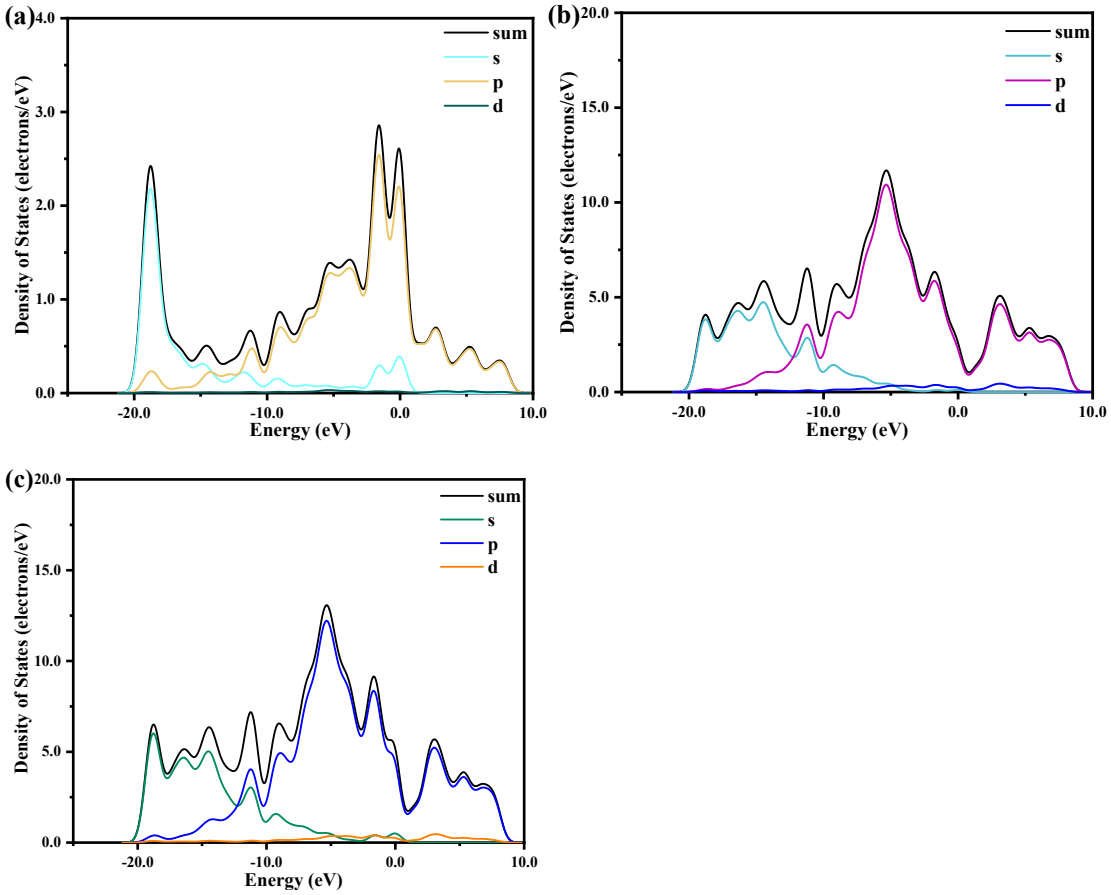
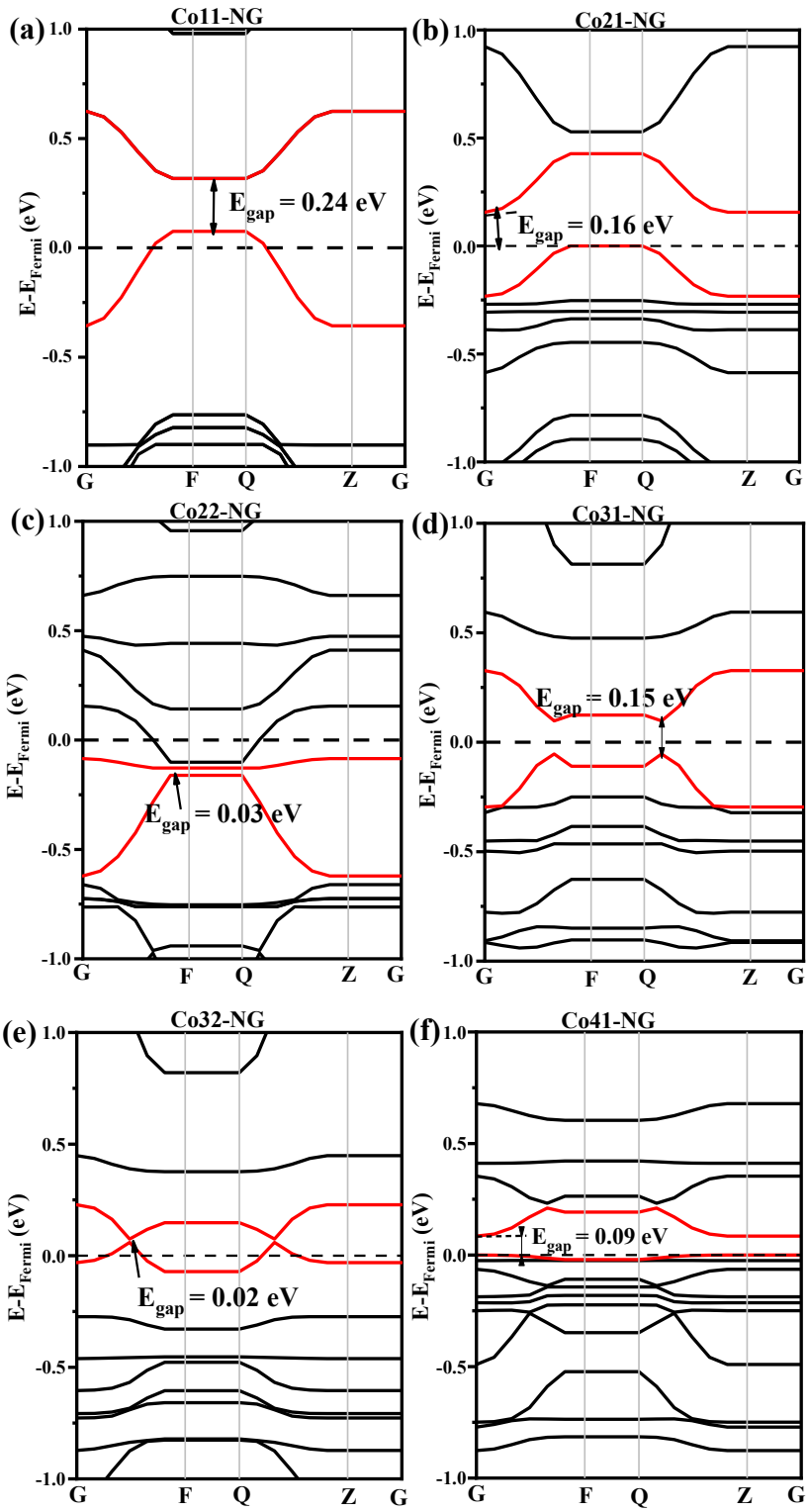


Figure S9. PDOS (partial density of state) of (a) N atoms, (b) C atoms, and (c) the total DOS in NG.


(a)
Co11-NG
E_{gap} = 0.24 eV
(b)
Co21-NG
E_{gap} = 0.16 eV
(c)
Co22-NG
E_{gap} = 0.03 eV
(d)
Co31-NG
E_{gap} = 0.15 eV
(e)
Co32-NG
E_{gap} = 0.02 eV
(f)
Co41-NG
E_{gap} = 0.09 eV
$E-E_{Fermi}$ (eV)
1.0
0.5
0.0
-0.5
-1.0
G
F
Q
Z
G

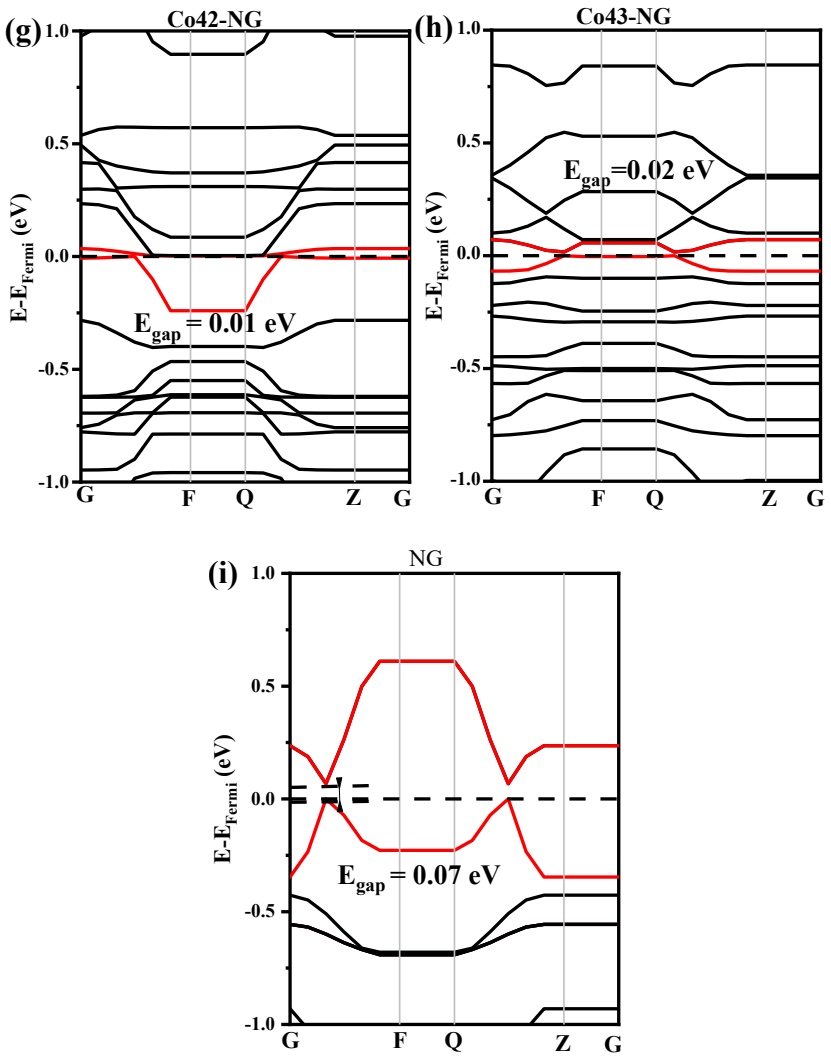
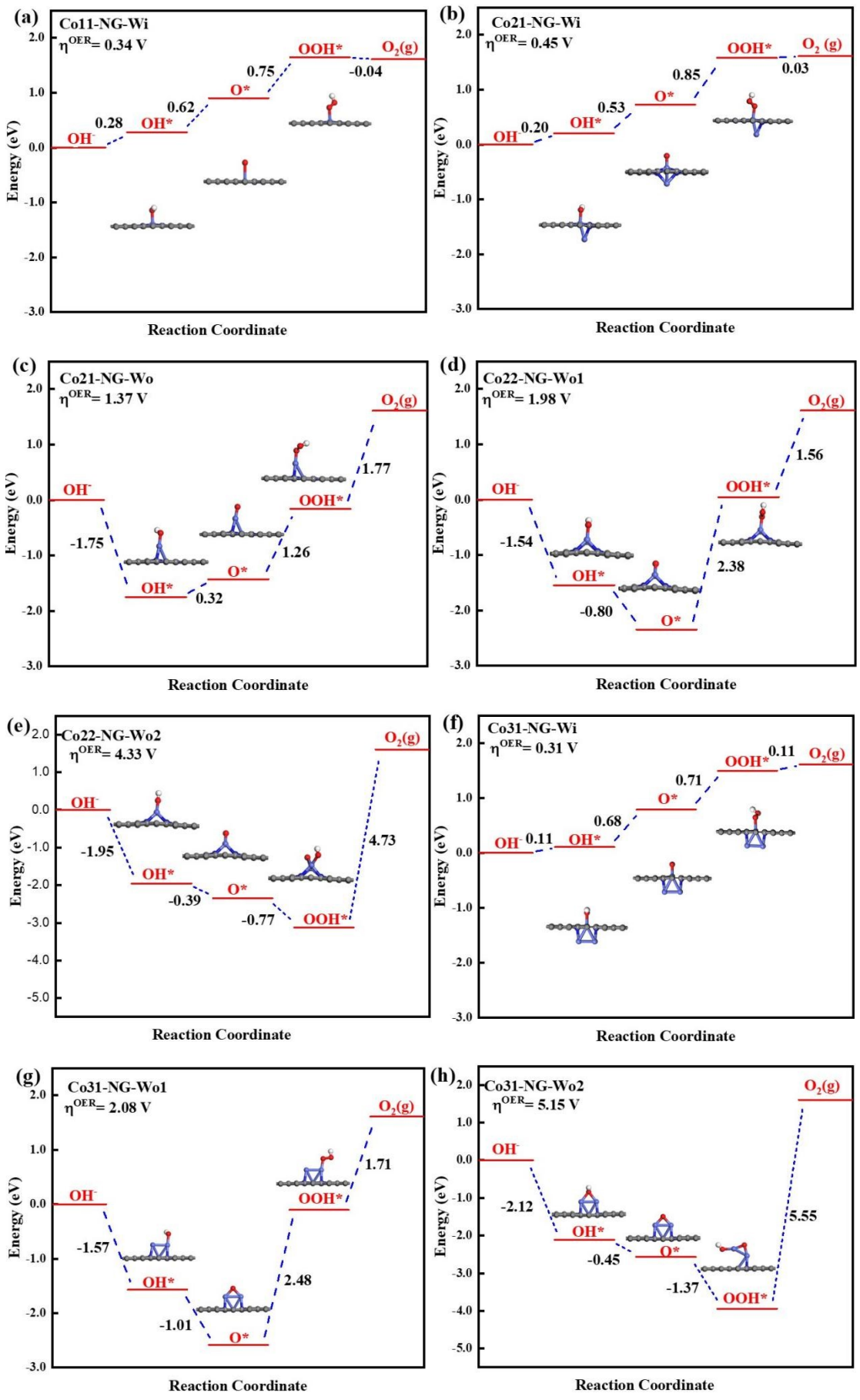
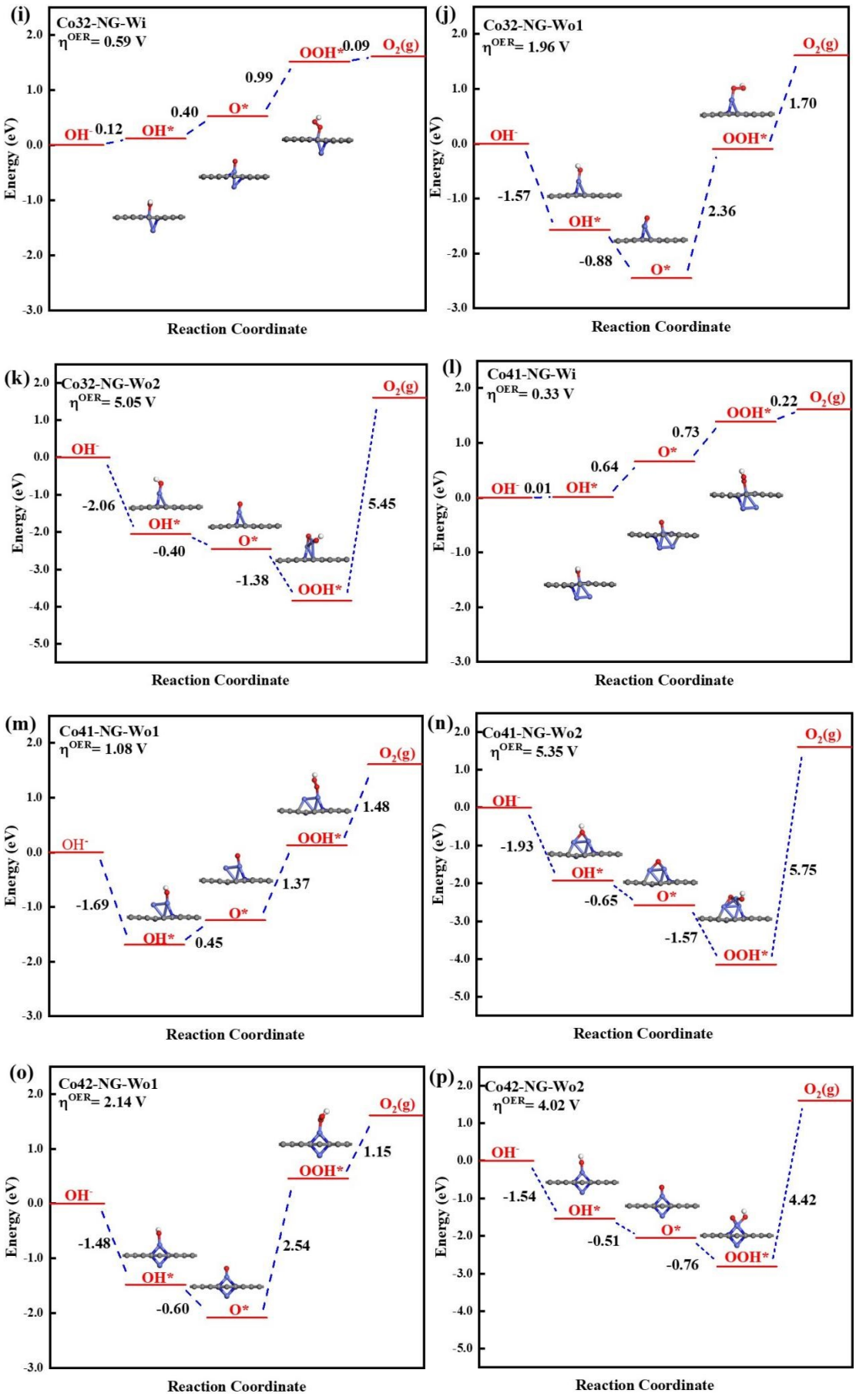


Figure S10. Energy band structure profile of (a) Co11-NG, (b) Co21-NG, (c) Co22-NG, (d) Co31-NG, (e) Co32-NG, (f) Co41-NG, (g) Co42-NG, (h) Co43-NG, and (i) NG.


(a)
Co11-NG-Wi
η^{OER}= 0.34 V
OH⁻
0.28
OH*
0.62
O*
0.75
OOH*
-0.04
O₂(g)
Energy (eV)
Reaction Coordinate
(b)
Co21-NG-Wi
η^{OER}= 0.45 V
OH⁻
0.20
OH*
0.53
O*
0.85
OOH*
0.03
O₂ (g)
Energy (eV)
Reaction Coordinate
(c)
Co21-NG-Wo
η^{OER}= 1.37 V
OH⁻
-1.75
OH*
0.32
O*
1.26
OOH*
1.77
O₂(g)
Energy (eV)
Reaction Coordinate
(d)
Co22-NG-Wo1
η^{OER}= 1.98 V
OH⁻
-1.54
OH*
-0.80
O*
2.38
OOH*
1.56
O₂(g)
Energy (eV)
Reaction Coordinate
(e)
Co22-NG-Wo2
η^{OER}= 4.33 V
OH⁻
-1.95
OH*
-0.39
O*
-0.77
OOH*
4.73
O₂(g)
Energy (eV)
Reaction Coordinate
(f)
Co31-NG-Wi
η^{OER}= 0.31 V
OH⁻
0.11
OH*
0.68
O*
0.71
OOH*
0.11
O₂(g)
Energy (eV)
Reaction Coordinate
(g)
Co31-NG-Wo1
η^{OER}= 2.08 V
OH⁻
-1.57
OH*
-1.01
O*
2.48
OOH*
1.71
O₂(g)
Energy (eV)
Reaction Coordinate
(h)
Co31-NG-Wo2
η^{OER}= 5.15 V
OH⁻
-2.12
OH*
-0.45
O*
-1.37
OOH*
5.55
O₂(g)
Energy (eV)
Reaction Coordinate


(i)
Co32-NG-Wi
η^{OER}= 0.59 V
OH⁻
0.12
OH*
0.40
O*
0.99
OOH*
0.09
O2(g)
(j)
Co32-NG-Wo1
η^{OER}= 1.96 V
OH⁻
-1.57
OH*
-0.88
O*
2.36
OOH*
1.70
O2(g)
(k)
Co32-NG-Wo2
η^{OER}= 5.05 V
OH⁻
-2.06
OH*
-0.40
O*
-1.38
OOH*
5.45
O2(g)
(l)
Co41-NG-Wi
η^{OER}= 0.33 V
OH⁻
0.01
OH*
0.64
O*
0.73
OOH*
0.22
O2(g)
(m)
Co41-NG-Wo1
η^{OER}= 1.08 V
OH⁻
-1.69
OH*
0.45
O*
1.37
OOH*
1.48
O2(g)
(n)
Co41-NG-Wo2
η^{OER}= 5.35 V
OH⁻
-1.93
OH*
-0.65
O*
-1.57
OOH*
5.75
O2(g)
(o)
Co42-NG-Wo1
η^{OER}= 2.14 V
OH⁻
-1.48
OH*
-0.60
O*
2.54
OOH*
1.15
O2(g)
(p)
Co42-NG-Wo2
η^{OER}= 4.02 V
OH⁻
-1.54
OH*
-0.51
O*
-0.76
OOH*
4.42
O2(g)
Energy (eV)
Reaction Coordinate

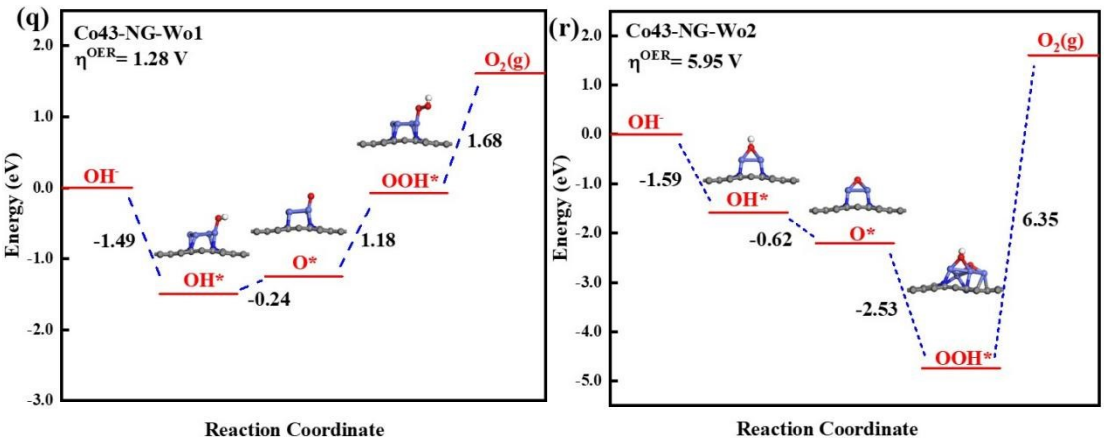


Figure S11. The computed free energy profiles and optimized intermediate structure for OER on Coxy-NG (x=1-4,y=1-3).

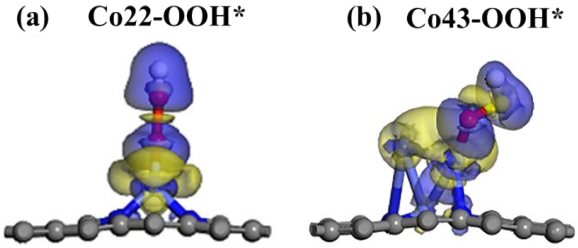


Figure S12. Charge differential density (CDD) of the rate determining step (RDS) of Co22-NG and Co43-NG.

Table S1. The Millikan charges (in e) for each Co atom and all N atoms (total charge) of Coxy-NG (x=1-4, y=1-3).

Catalyst	Charge Population		
	In-plane Co	Out-plane Co	N
Co11-NG	0.147	\	-1.426
Co21-NG	0.161	0.134	-1.498
Co22-NG	\	0.052(Co1), 0.067(Co2)	-1.320
Co31-NG	0.283	0.079(Co1), 0.078(Co2)	-1.562
Co32-NG	0.273	0.069(Co1), 0.069(Co2)	-1.611
Co41-NG	0.256	0.076(Co1), 0.121(Co2), 0.119(Co3)	-1.617
Co42-NG	\	0.124(Co1),0.124(Co2),0.124(Co3), 0.123(Co4)	-1.836
Co43-NG	\	0.051(Co1), 0.051(Co2), 0.052(Co3), 0.052(Co4)	-1.327

Table S2. The computed binding energies (E_b, eV), cohesive energies (E_c, eV), shortest distances between Co and N atoms ($d_{Co-N,}$ Å), corresponding descriptor (ΔG_{OH*}, ΔG_{O*},ΔG_{OOH*}, all in eV) , the RDS barrier (E_{RDS}, eV), and overpotential (η^{OER}, V) for Coxy-NG (x=1-4; y=1-3).

Catalyst	E_b	E_c	d_{Co-N}	ΔG_{OH*}	ΔG_{O*}	ΔG_{OOH*}	E_{RDS}	η^{OER}
Co11-NG	-11.25	-7.67	1.90	0.28	0.90	1.65	0.75	0.34
Co21-NG(Wi)	-13.17	-7.49	2.03	0.20	0.73	1.58	0.85	0.45
Co21-NG(Wo)	-13.17	-7.49	2.03	-1.75	-1.43	-0.16	1.77	1.37
Co22-NG(Wo1)	-11.32	-7.43	1.88	-1.54	-2.34	0.04	2.38	1.98
Co22-NG(Wo2)				-1.95	-2.35	-3.12	4.73	4.33
Co31-NG(wi)	-16.13	-7.35	1.90	0.11	0.79	1.50	0.71	0.31
Co31-NG(wo1)	-16.13	-7.35	1.90	-2.12	-2.59	0.05	2.64	2.24
Co31-NG(wo2)				-2.12	-2.57	-3.94	5.55	5.15
Co32-NG(wi)	-16.10	-7.36	2.02	0.12	0.52	1.52	0.99	0.59
Co32-NG(wo1)	-16.10	-7.36	2.02	-2.06	-2.47	-0.97	2.58	2.18
Co32-NG(wo2)				-2.06	-2.46	-3.84	5.45	5.05
Co41-NG(wi)	-19.78	-7.25	2.15	0.01	0.66	1.39	0.73	0.33
Co41-NG(wo1)	-19.78	-7.25	2.15	-1.29	-0.73	0.28	1.33	0.93
Co41-NG(wo2)				-1.93	-2.58	-4.14	5.75	5.35
Co42-NG(Wo1)	-17.40	-7.18	2.02	-1.48	-2.08	0.46	2.54	2.14
Co42-NG(Wo2)				-1.54	-2.05	-2.81	4.42	4.02
Co43-NG(Wo1)	-16.48	-7.15	1.91	-1.49	-1.25	-0.07	1.68	1.28
Co43-NG(Wo2)				-1.59	-2.21	-4.74	6.35	5.95