Supporting Information:

Coordination Engineering in Cobalt-Nitrogen Functionalized Materials for CO_2 Reduction

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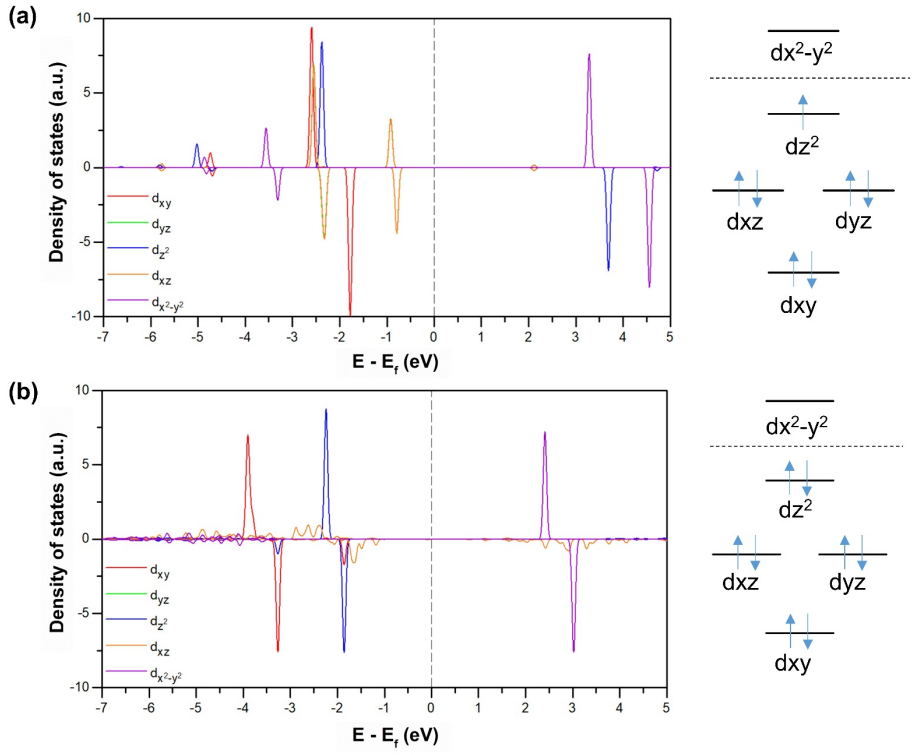

Figure S1. Projected density of states (PDOS) of Co in CoN_4 embedded (a) porphyrin and (b) graphene. The dashed line indicates the Fermi level.

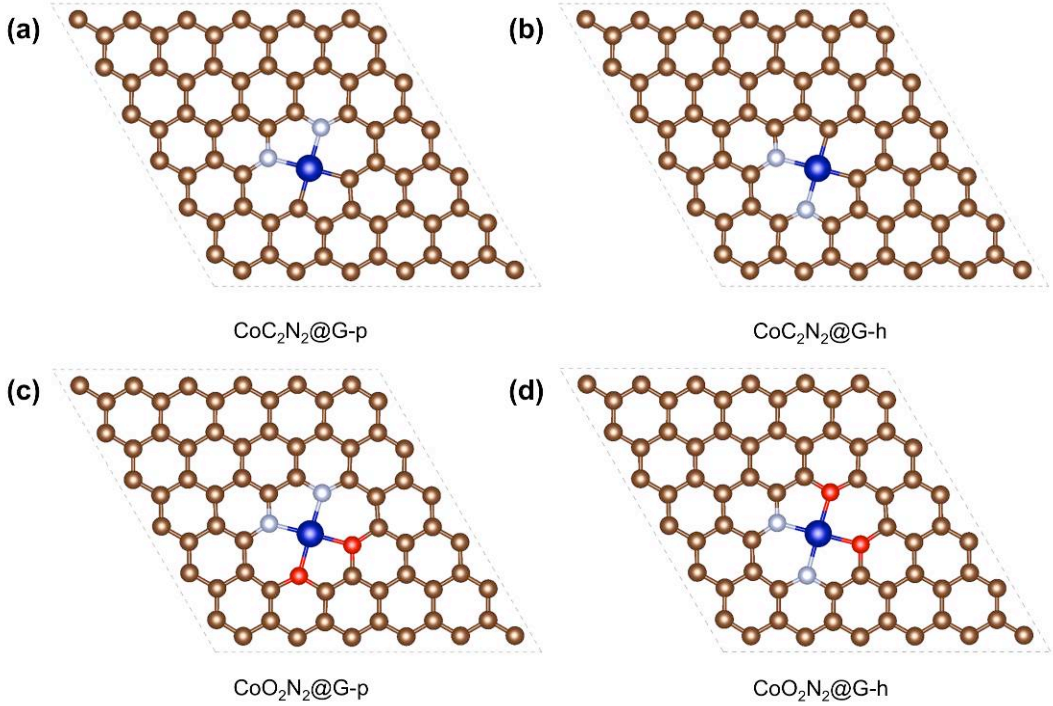

Figure S2. Atomic structures of (a) CoC_2N_2@G-p, (b) CoC_2N_2@G-h, (c) CoO_2N_2@G-p and (d) CoO_2N_2@G-h. The blue, brown, gray and red spheres represent for Co, C, N and O atoms, respectively.

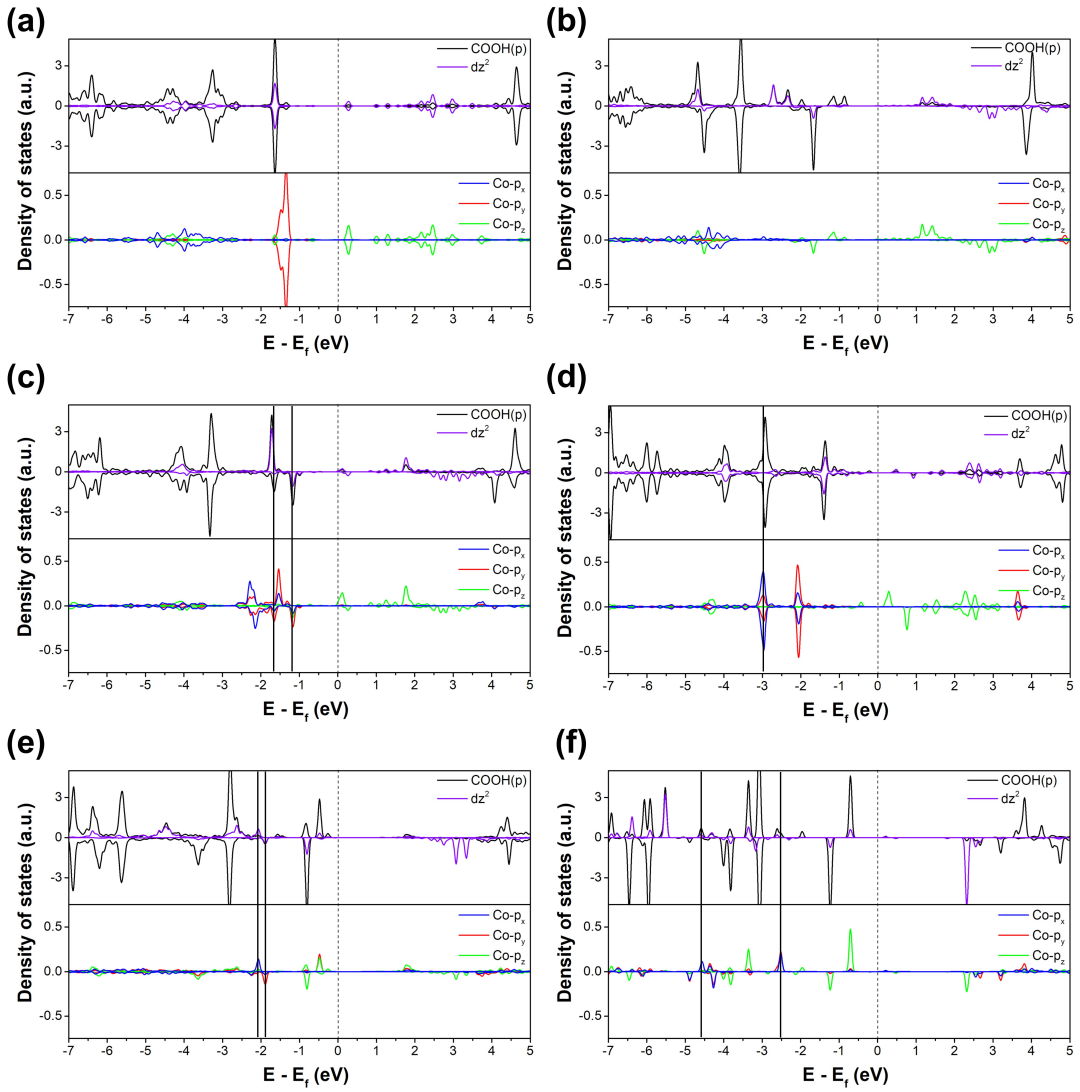

Figure S3. Projected density of states (PDOS) of Co and COOH in *COOH-adsorbed (a)CoC_2N_2@G-o, (b)CoO_2N_2@G-o, (c)CoC_2N_2@G-p, (d) CoC_2N_2@G-h, (e)CoO_2N_2@G-h and (f)CoO_2N_2@P-h. The dashed line indicates the Fermi level and the solid line indicates the bonding state between p_x/p_y from Co and p from *COOH.

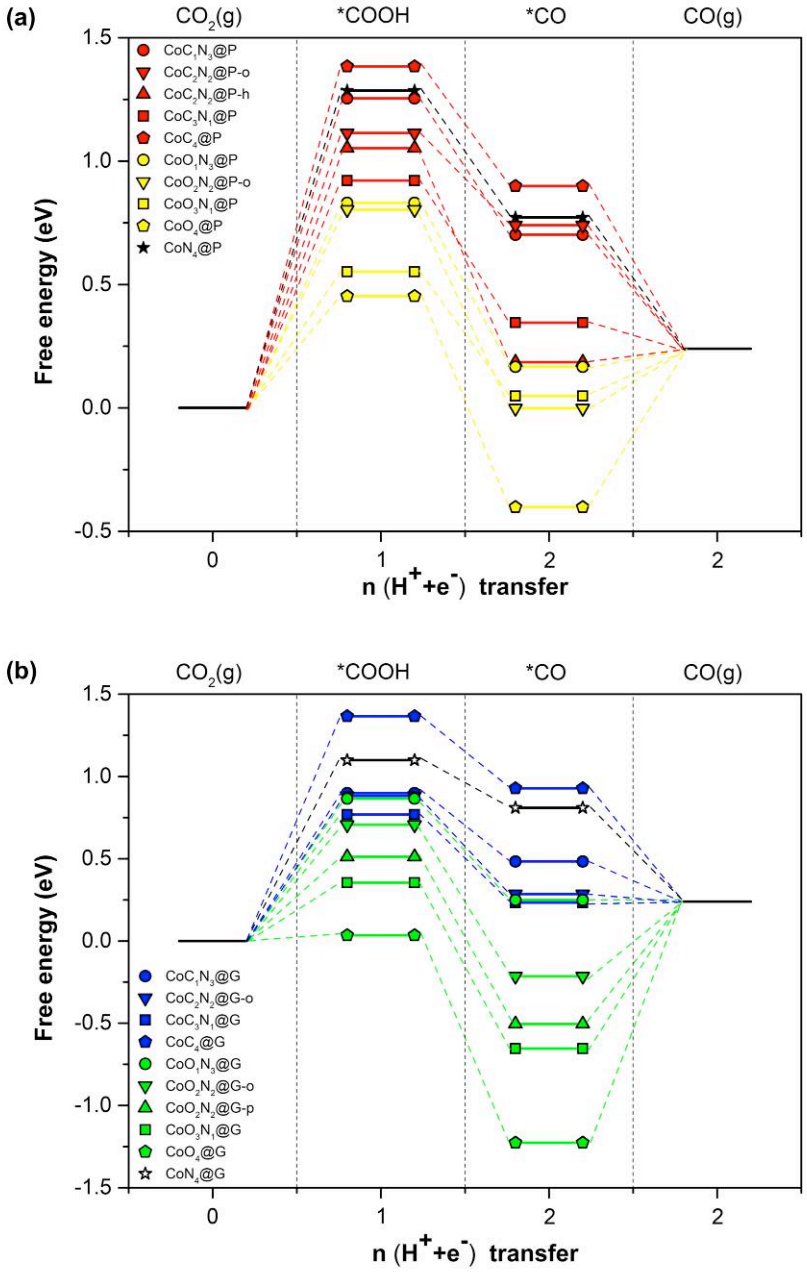

Figure S4. Free energy profiles of (a) CoX_nN_{4-n}@P and (b) CoX_nN_{4-n}@G, where X indicates substituted N atoms to C or O atoms and n=0, 1, 2, 3, 4.

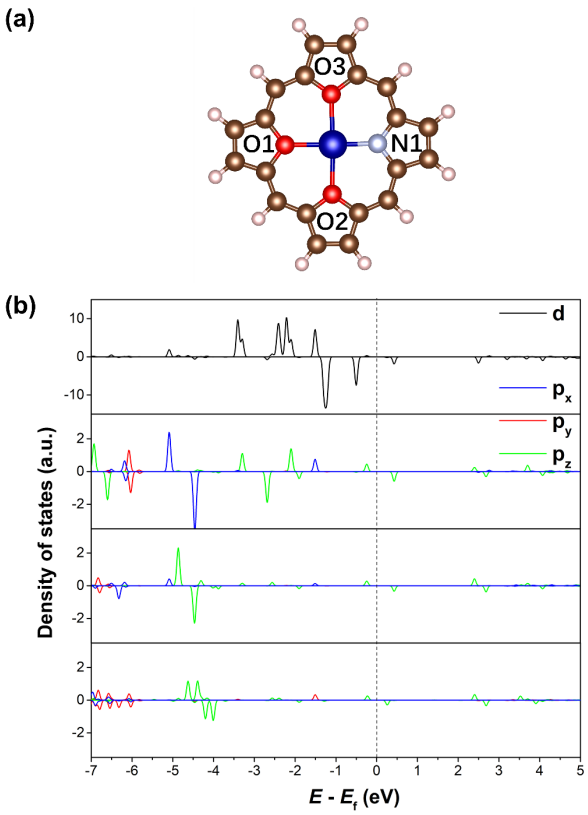

Figure S5. (a) Atomic structure of CoO_3N_1@P, and (b) projected density of states (PDOS) of Co and substituting O atoms in CoO_3N_1@P. The dashed line indicates the Fermi level.

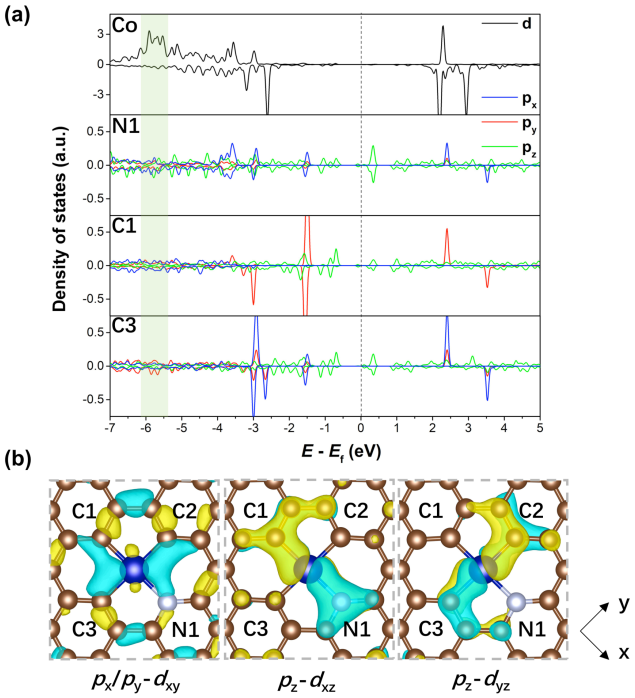

Figure S6. (a) Projected density of states (PDOS) of Co and substituting C atoms in CoC_3N_1@G. The dashed line indicates the Fermi level. The green-shaded area is marked to indicate the bonding states between Co atom and C atoms. (b) Isosurface (0.001 a.u.) of wavefunction of bonding states between Co and substituting C atoms in CoC_3N_1@G. It is noted that the green-shaded area represents bonding states of p_x/p_y-d_{xy}, p_z-d_{xz} and p_z-d_{yz} in real space, respectively.

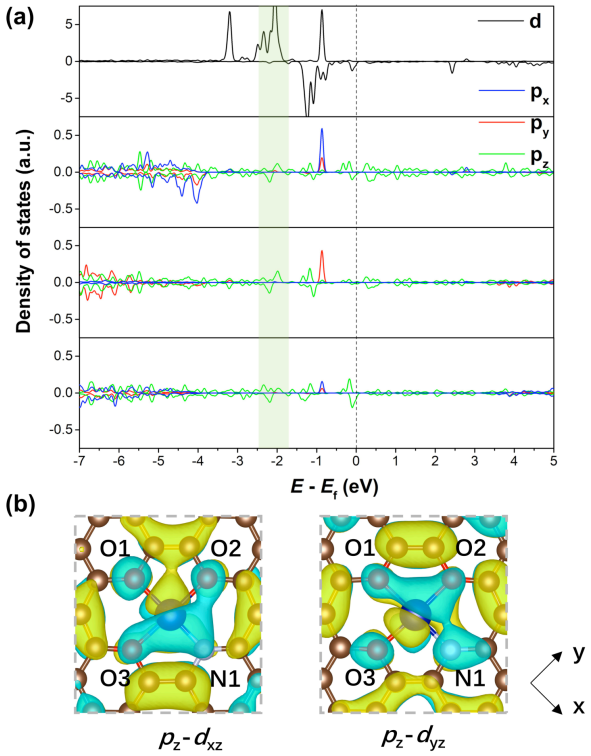

Figure S7. (a) Projected density of states (PDOS) of Co and substituting O atoms in CoO_3N_1@G. The dashed line indicates the Fermi level. The green-shaded area is marked to indicate the bonding states between Co atom and O atoms. (b) Isosurface (0.001 a.u.) of wavefunction of bonding states between Co and substituting O atoms in CoO_3N_1@G. It is noted that the green-shaded area represents bonding states of p_z-d_{xz} and p_z-d_{yz} in real space, respectively.

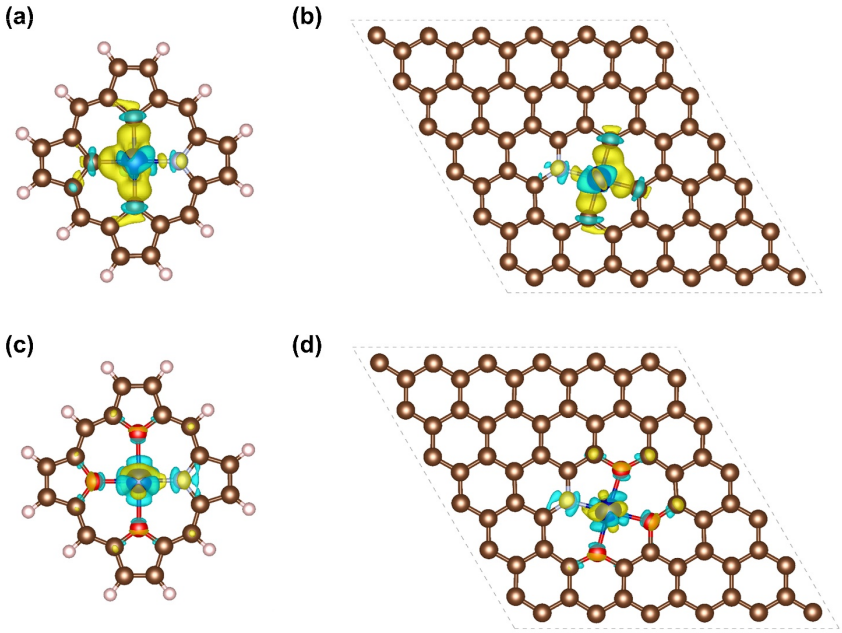

Figure S8. Charge density difference plots of (a) CoC_3N_1@P; (b) CoC_3N_1@G; (c) CoO_3N_1@P and (d) CoO_3N_1@G with isosurface level of ±0.05e/Å^3, where the yellow and blue represent the electron-rich and electron-deficient regions, respectively. The blue, gray, brown, red and white spheres represent for Co, N, C, O and H atoms, respectively.

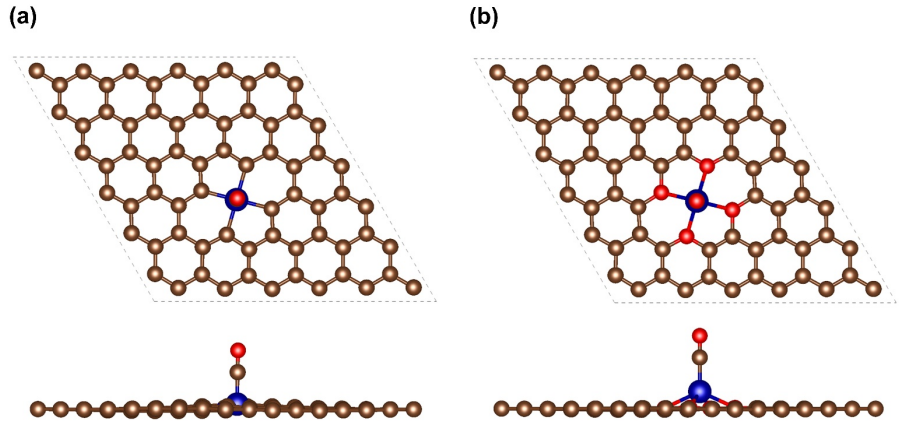

Figure S9. Atomic configuration of *CO adsorption on (a) CoC_4@G and (b) CoO_4@G. The blue, brown and red spheres represent for Co, C and O atoms, respectively.

Table S1. Calculated zero point energy (E_{ZPE}), entropy ($T\Delta S$), adsorption free energy of hydrogen (ΔG_H) and $U_L(CO_2)$-$U_L(H_2)$ on CoX_nN_{4-n}@P and CoX_nN_{4-n}@G (n=0, 1, 2, 3, 4, X indicates substituting C or O atoms)

Structure	E_{ZPE}(eV)	TS(eV)	ΔG_H(eV)	$U_L(CO_2)$-$U_L(H_2)$(V)
CoC_1N_3@P	0.160	0.120	0.904	0.350
CoC_2N_2@P-o	0.132	0.016	0.584	0.529
CoC_2N_2@P-h	0.180	0.020	1.397	-0.344
CoC_3N_1@P	0.150	0.010	1.800	-0.879
CoC_4@P	0.113	0.000	1.038	0.346
CoO_1N_3@P	0.161	0.017	0.489	0.342
CoO_2N_2@P-o	0.185	0.014	0.984	-0.181
CoO_3N_1@P	0.145	0.007	0.555	-0.003
CoO_4@P	0.204	0.010	1.034	-0.581
CoN_4@P	0.224	0.007	1.236	0.049
CoC_1N_3@G	0.200	0.010	0.918	-0.020
CoC_2N_2@G-o	0.133	0.008	0.927	-0.045
CoC_3N_1@G	0.129	0.011	2.698	-1.930
CoC_4@G	0.149	0.034	1.515	-0.150
CoO_1N_3@G	0.166	0.017	0.329	0.536
CoO_2N_2@G-o	0.169	0.018	0.246	0.461
CoO_2N_2@G-p	0.164	0.022	0.291	0.220
CoO_3N_1@G	0.155	0.028	0.178	0.176
CoO_4@G	0.167	0.020	0.237	-0.202
CoN_4@G	0.006	0.223	0.597	0.502

Table S2. Calculated values for the zero-point energy (E_{ZPE}) and entropy ($T\Delta S$) of *CO and *COOH adsorbed CoX_nN_{4-n}@P and CoX_nN_{4-n}@G (n=0, 1, 2, 3, 4, X indicates substituting C or O atoms).

Structure	*CO		*COOH	
	E_{ZPE}(eV)	$T\Delta S$(eV)	E_{ZPE}(eV)	$T\Delta S$(eV)
CoC_1N_3@P	0.199	0.096	0.657	0.190
CoC_2N_2@P-o	0.259	0.205	0.623	0.173
CoC_2N_2@P-h	0.170	0.218	0.652	0.168
CoC_3N_1@P	0.218	0.148	0.624	0.170
CoC_4@P	0.237	0.095	0.641	0.191
CoO_1N_3@P	0.213	0.076	0.642	0.179
CoO_2N_2@P-o	0.214	0.150	0.647	0.186
CoO_3N_1@P	0.229	0.102	0.726	0.107
CoO_4@P	0.225	0.140	0.623	0.172
CoN_4@P	0.189	0.119	0.652	0.213
CoC_1N_3@G	0.205	0.090	0.650	0.195
CoC_2N_2@G-o	0.210	0.086	0.658	0.190
CoC_3N_1@G	0.224	0.077	0.646	0.208
CoC_4@G	0.238	0.127	0.630	0.228
CoO_1N_3@G	0.201	0.151	0.627	0.227
CoO_2N_2@G-o	0.207	0.099	0.622	0.224
CoO_2N_2@G-p	0.215	0.081	0.618	0.188
CoO_3N_1@G	0.213	0.157	0.630	0.225
CoO_4@G	0.217	0.083	0.610	0.123
CoN_4@G	0.197	0.105	0.652	0.144

Table S3. Co vacancy formation energy (E_{vac}) for CoX_nN_{4-n}@P and CoX_nN_{4-n}@G (n=0, 1, 2, 3, 4, X indicates substituting C or O atoms).

Structure	E_{vac}(eV)	Structure	E_{vac}(eV)
CoC_1N_3@P	7.638	CoC_1N_3@G	5.103
CoC_2N_2@P-o	7.020	CoC_2N_2@G-o	5.307
CoC_2N_2@P-h	7.430	CoC_3N_1@G	6.184
CoC_3N_1@P	7.593	CoC_4@G	4.199
CoC_4@P	8.656	CoO_1N_3@G	3.012
CoO_1N_3@P	5.108	CoO_2N_2@G-o	2.342
CoO_2N_2@P-o	3.059	CoO_2N_2@G-p	1.972
CoO_3N_1@P	1.810	CoO_3N_1@G	0.326
CoO_4@P	0.831	CoO_4@G	-0.571
CoN_4@P	7.777	CoN_4@G	5.236

Table S4. Formation energy (ΔE) for CoX_nN_{4-n}@P and CoX_nN_{4-n}@G (n=1, 2, 3, 4, X indicates substituting C or O atoms). This formation energy is defined as: $\Delta E = E(CoX_nN_{4-n}@P/G) + E(N) - E(CoN_4@P/G) - E(X)$ (n = 1, 2, 3, 4), where $E(CoX_nN_{4-n}@P/G)$, $E(CoN_4@P/G)$, $E(N)$ and $E(X)$ are the total energy of CoX_nN_{4-n}@P/G and CoN_4@P/G, chemical potential of N atom and X atom (X indicates to substituting C or O atoms).

Structure	ΔE(eV)	Structure	ΔE(eV)
CoC_1N_3@P	2.378	CoC_1N_3@G	0.907
CoC_2N_2@P-o	4.834	CoC_2N_2@G-o	2.688
CoC_2N_2@P-h	4.672	CoC_3N_1@G	3.411
CoC_3N_1@P	6.844	CoC_4@G	5.058
CoC_4@P	8.549	CoO_1N_3@G	0.081
CoO_1N_3@P	-0.093	CoO_2N_2@G-o	-0.071
CoO_2N_2@P-o	-1.173	CoO_2N_2@G-p	0.298
CoO_3N_1@P	-1.712	CoO_3N_1@G	-0.219
CoO_4@P	-2.659	CoO_4@G	-0.050
CoN_4@P	0.000	CoN_4@G	0.000