Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

The Role of Nitrogen and Sulfur Dual Coordination of Cobalt in Co-$N_{4-x}S_x$/C Single Atom Catalysts in Oxygen Reduction Reaction

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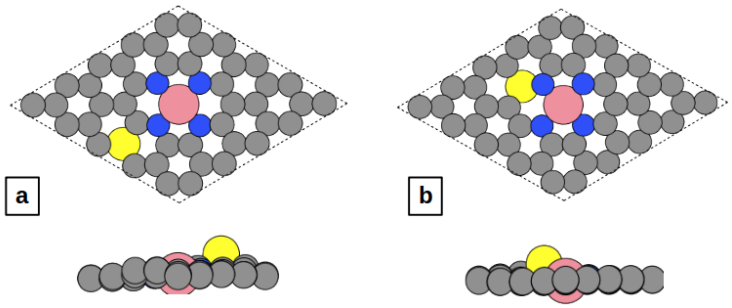

Figure S1: Top and side view of the structures of: a) Co-N_4S-1/C and b) Co-N_4S-2/C.

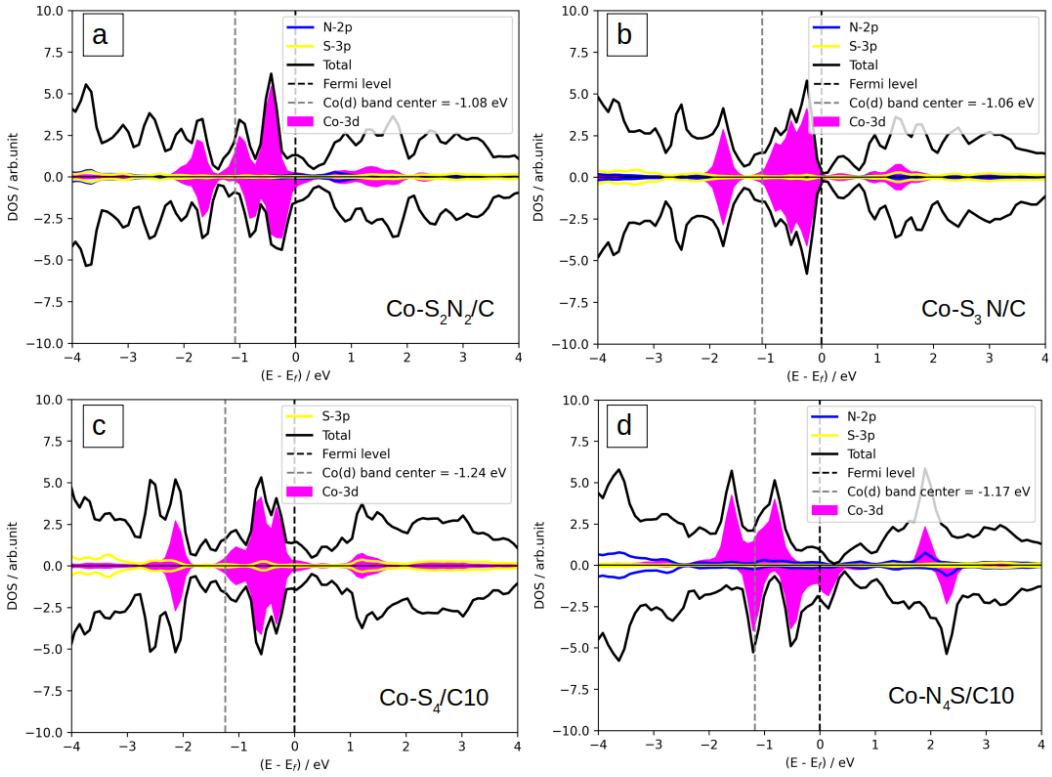

Figure S2: Partial density of states (PDOS) of Co, N, and S atom in: a) Co-N_2S_2/C, b) Co-NS_3/C, c) Co-S_4/C and d) CoN_4S/C systems.

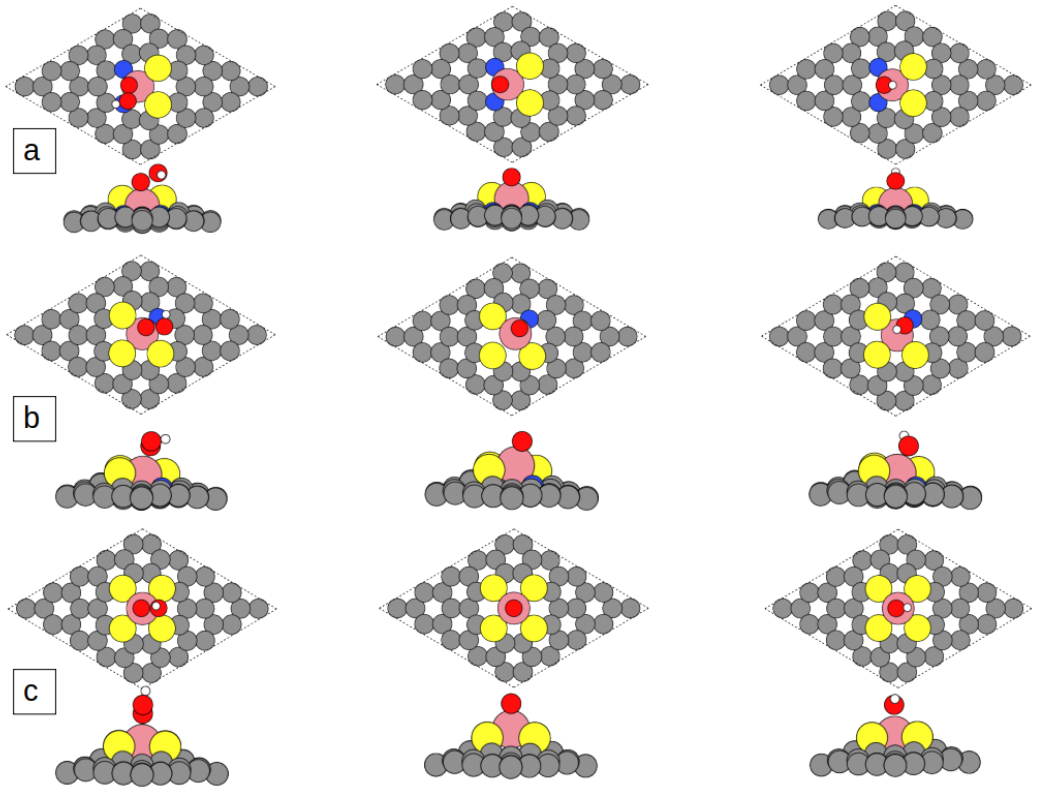

Figure S3: Optimized adsorption structures of ORR intermediates on: a) Co-N_2S_2/C, Co-NS_3/C, and Co-S_4/C. Pink, Cobalt (Co); blue, nitrogen (N); yellow, sulfur (S); gray, carbon (C); red, oxygen (O), and white, hydrogen (H).

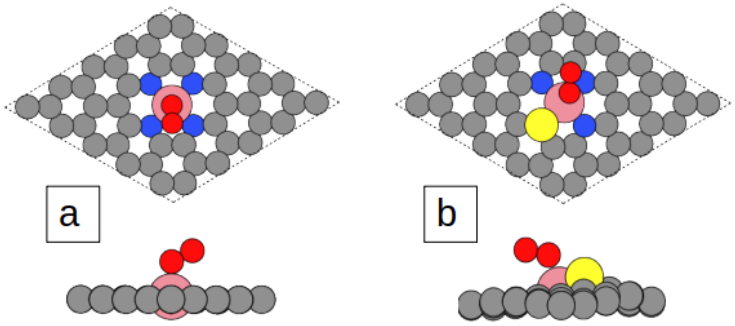

Figure S4: Optimized adsorption structures of O_2 adsorbed on: a) Co-N_4S/C and b) Co-N_3S/C

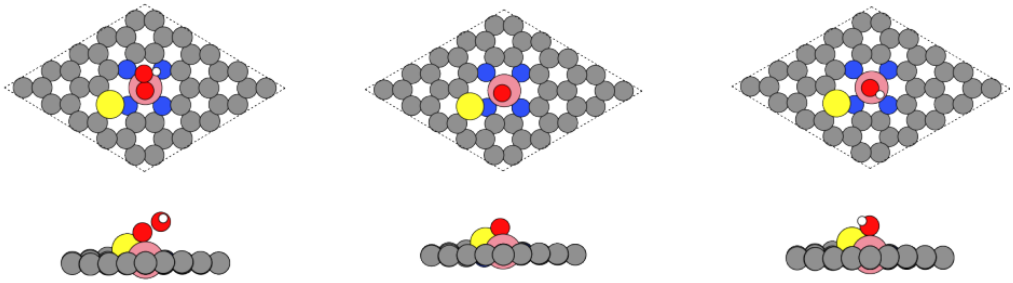

Figure S5: Optimized adsorption structures of ORR intermediates on Co-N_4S/C

Table S1: The Bader charge of the atoms at the active sites of (a) Co-N_4/C and (b) Co-N_3S/C. The charge of N is the average charge of the existing N atoms.

Adsorbate	Co-N_4/C		Co-N_3S/C		
	Co	N	Co	N	S
*	0.9	-1.21	0.72	-1.21	0.18
O_2	1.1	-1.2	0.94	-1.19	0.21
*OOH	1.1	-1.20	0.99	-1.20	0.24
*O	1.2	-1.20	1.18	-1.25	0.17
*OH	1.1	-1.20	1.02	-1.20	0.18
H_2O	1.0	-1.20	0.70	-1.16	0.17

Table S2: Zero point energy (E_{ZPE}), entropy (-TS) and enthalpy ($H_{0\to298}$) contributions to the free energy and corrections specific to the BEEF-vdW functional (BEEF) for different adsorbates. The differences are calculated with H_2O(g) in equilibrium with H_2O(l) as reference.

Adsorbate	ZPE	-TS	$H_{0\to289K}$	ΔE_{ZPE}	-TΔS	BEEF	ΔH	Total
H_2O	0.56	-0.67	0.103					
H_2	0.27	-0.40	0.088					
*O + H_2	0.33	-0.48	0.128	-0.23	0.19	0.12	0.03	0.11
*OOH + $\frac{3}{2}H_2$	0.82	-0.80	0.224	-0.29	0.55	0.395	0.02	0.67
*OH + $\frac{1}{2}H_2$	0.47	-0.32	0.104	-0.09	0.36	0.075	0.001	0.34

Table S3: ORR intermediates adsorption Gibbs free energies at $U = 0$ V_{RHE} and the calculated ORR overpotential (η_{ORR}) on the considered surfaces.

	$\Delta_{ads}G$/ eV			
Systems	OOH*	O*	OH*	η_{ORR} / V
Co-N_4/C	3.79	2.28	0.66	0.57
Co-N_3S/C	4.05	2.16	0.86	0.37
Co-N_2S_2/C	4.07	1.93	0.82	0.41
Co-NS_3/C10	4.09	2.05	0.91	0.40
Co-S_4/C10	4.16	2.28	0.97	0.47
Co-N_4S/C10	3.86	2.23	0.72	0.51

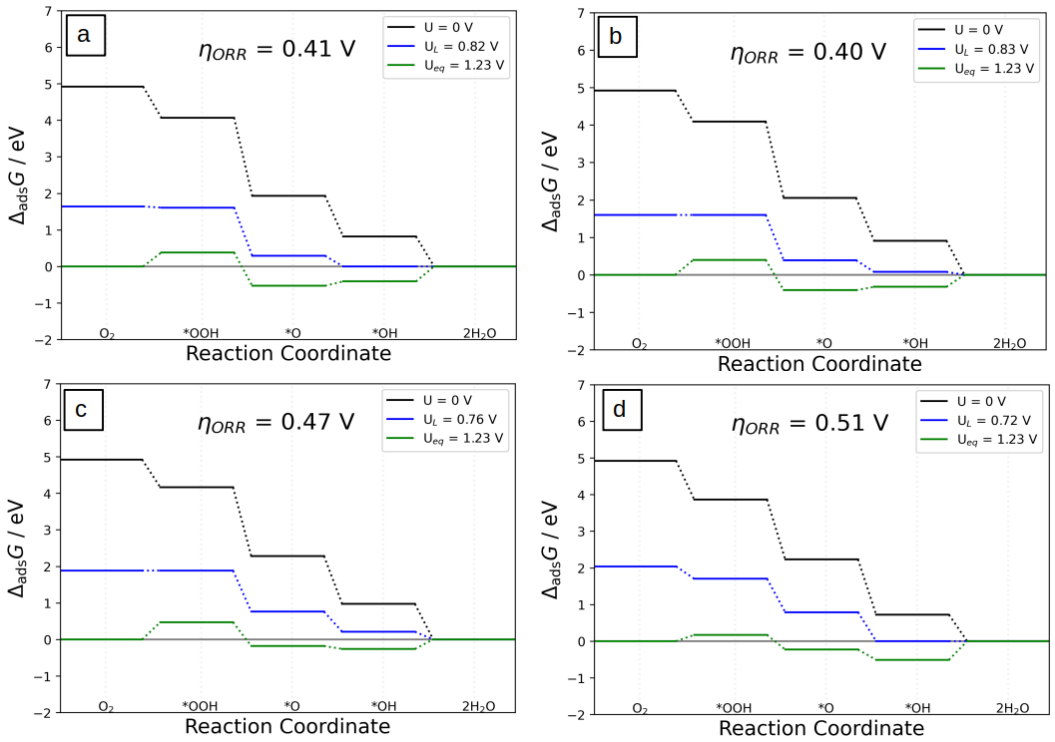

Figure S6: The free energy diagram of ORR on: a) Co-N_2S_2/C, b) Co-NS_3/C, c) Co-S_4/C, and d) Co-N_4S/C