Supporting Information

Asymmetric Electronic Structures of Transition Metals for Oxygen Evolution Reaction via Ligand-Metal Synergistic Strategy

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Fig. S1 | Schematic illustration of phen-Co@CoOOH orientation.

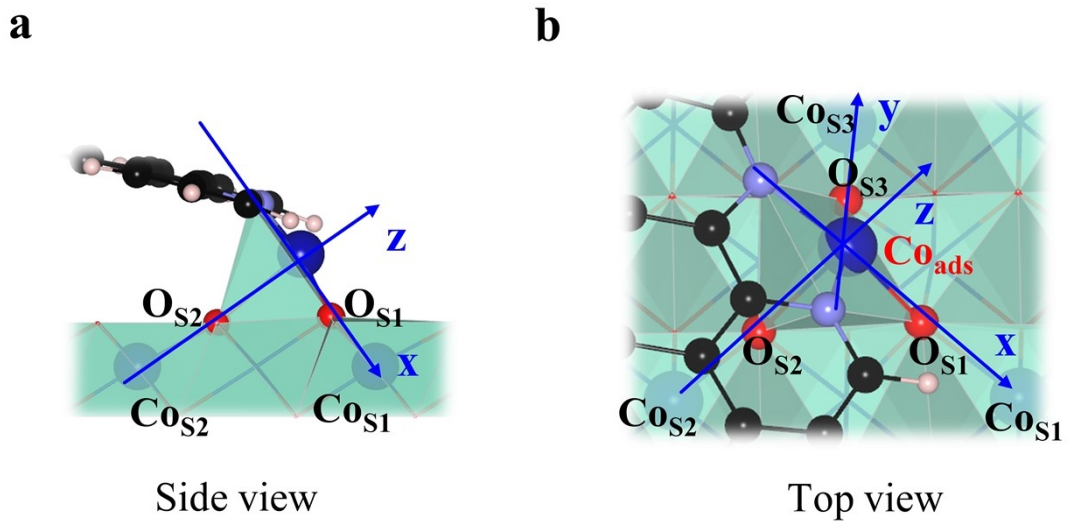

Fig. S2 | Transition state search by climbing image NEB (CI-NEB) for RDS of (a) Co@CoOOH (O_2 desorption) and (b) phen-Co@CoOOH (OOH* formation), showing the initial state (IS), transition state (TS), and final state (FS), respectively.

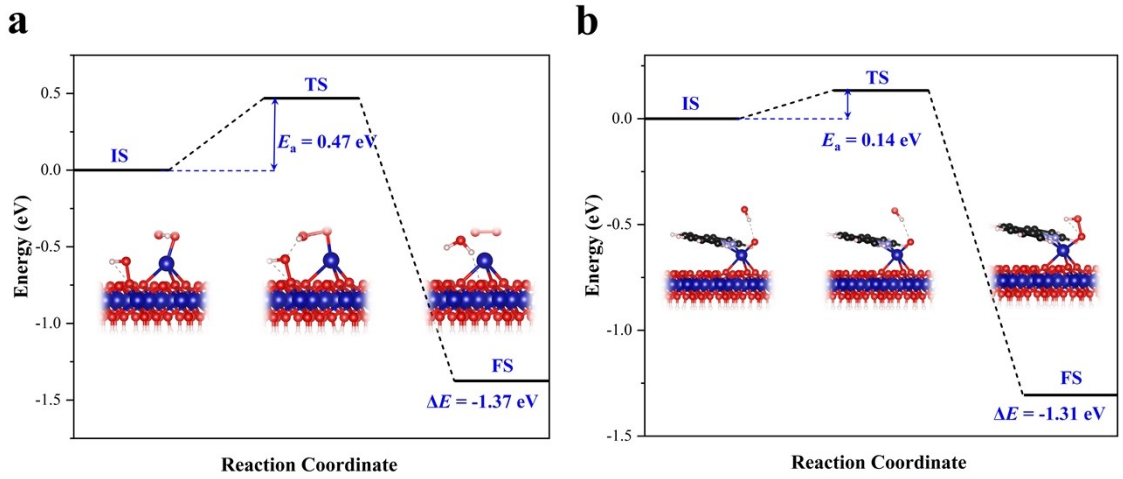

Fig. S3 | Structural identification diagram of Co_{ads} and Co_{S4} including (a) Co@CoOOH and (b) phen-Co@CoOOH.

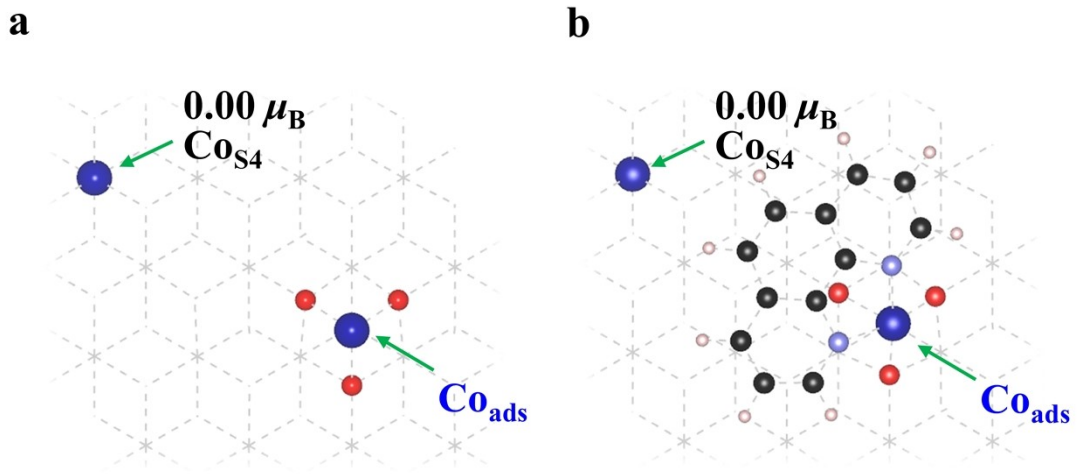

Table S1 | Summaries of the bonding information for Co@CoOOH and phen-Co@CoOOH two systems. The Co-$O_{\overline{S123}}$ represents the average bond length of Co_{ads}-$O_{S1\text{-}S3}$

Complex		Bond Length /Å						
		Co-O_{S1}	Co-O_{S2}	Co-O_{S3}	Co-$O_{\overline{S123}}$	Co-O*	Co-N_1	Co-N_2
Co@CoOOH	Slab	1.985	1.948	1.949	1.961	--	--	--
	OH*	1.984	2.376	2.083	2.148	1.778	--	--
	O*	2.183	2.183	1.996	2.121	1.627	--	--
	OOH*	2.131	1.989	2.220	2.113	1.816	--	--
phen-Co@CoOOH	Slab	1.954	2.279	1.931	2.055	--	1.944	1.934
	OH*	2.007	2.114	1.986	2.036	1.809	1.930	1.924
	O*	2.098	2.281	2.162	2.180	1.616	2.105	2.043
	OOH*	1.983	1.971	1.960	1.971	1.830	1.976	1.932

Table S2 | Summaries of local environments, occupation and Co-L bond information of Co_{ads} for phen-Co@CoOOH system.

Complex	Local environment	Occupation	Co-L (1) (z-axis ave) /Å	Co-L (2) (xy-axis ave) /Å	Difference (1)-(2) /Å	Jahn-Teller effect
Slab	square pyramid	$d_{xy}^2 d_{yz}^2 d_{xz}^2 d_{z2}^1 d_{x2-y2}^0$	2.279	1.941	0.34	z-in elongation
OH*	Octahedra	$d_{xy}^2 d_{yz}^2 d_{xz}^2 d_{z2}^0 d_{x2-y2}^0$	1.962	1.962	-0.00	no elongation
O*	Octahedra	$d_{xy}^2 d_{yz}^1 d_{xz}^1 d_{x2-y2}^1 d_{z2}^0$	1.949	2.102	-0.15	z-in compression
OOH*	Octahedra	$d_{xy}^2 d_{yz}^2 d_{xz}^2 d_{z2}^0 d_{x2-y2}^0$	1.901	1.963	-0.06	no elongation

Fig. S4 | The calculated partial density of states (PDOS) of the adsorption site Co_{ads}-3*d* orbitals for (a-c) its three OER intermediates in phen-Co@CoOOH system.

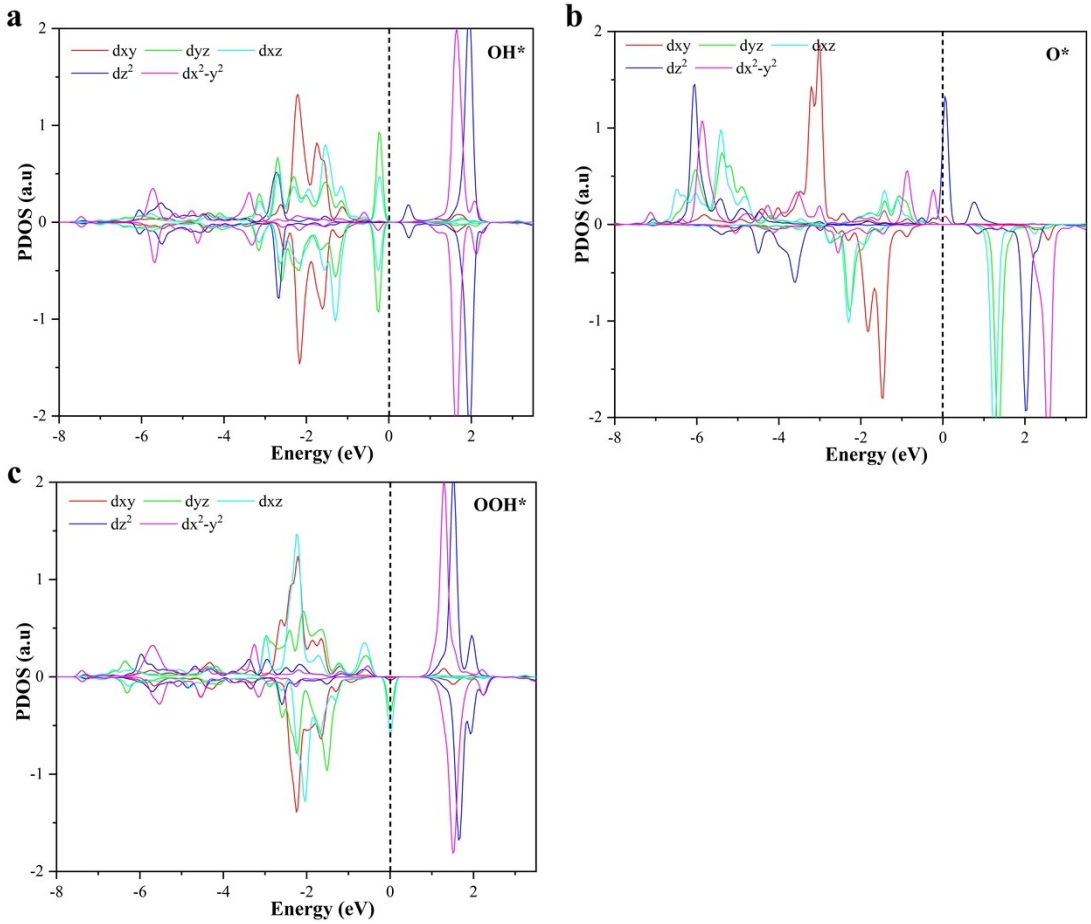

Fig. S5 | The calculated partial density of states (PDOS) and schematic diagrams of the adsorption site Co_{ads}-3*d* orbitals for (a-d) Co@CoOOH and its three OER intermediates. Spin electron occupations of *d*-orbitals are denoted as short arrows.

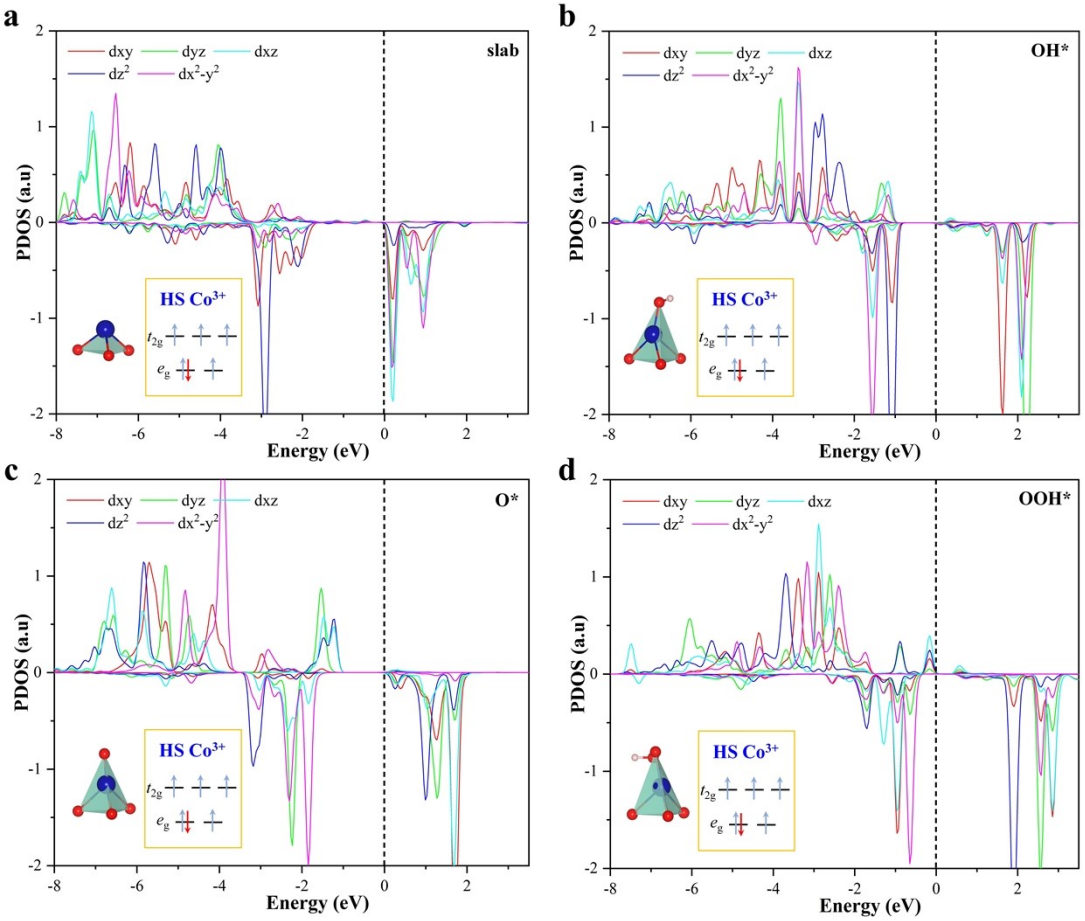

Fig. S6 | The calculated partial density of states (PDOS) and schematic diagrams of the adsorption site Co_{ads}-3*d* orbitals for (a-d) bpy-Co@CoOOH and its three OER intermediates. Spin electron occupations of *d*-orbitals are denoted as short arrows.

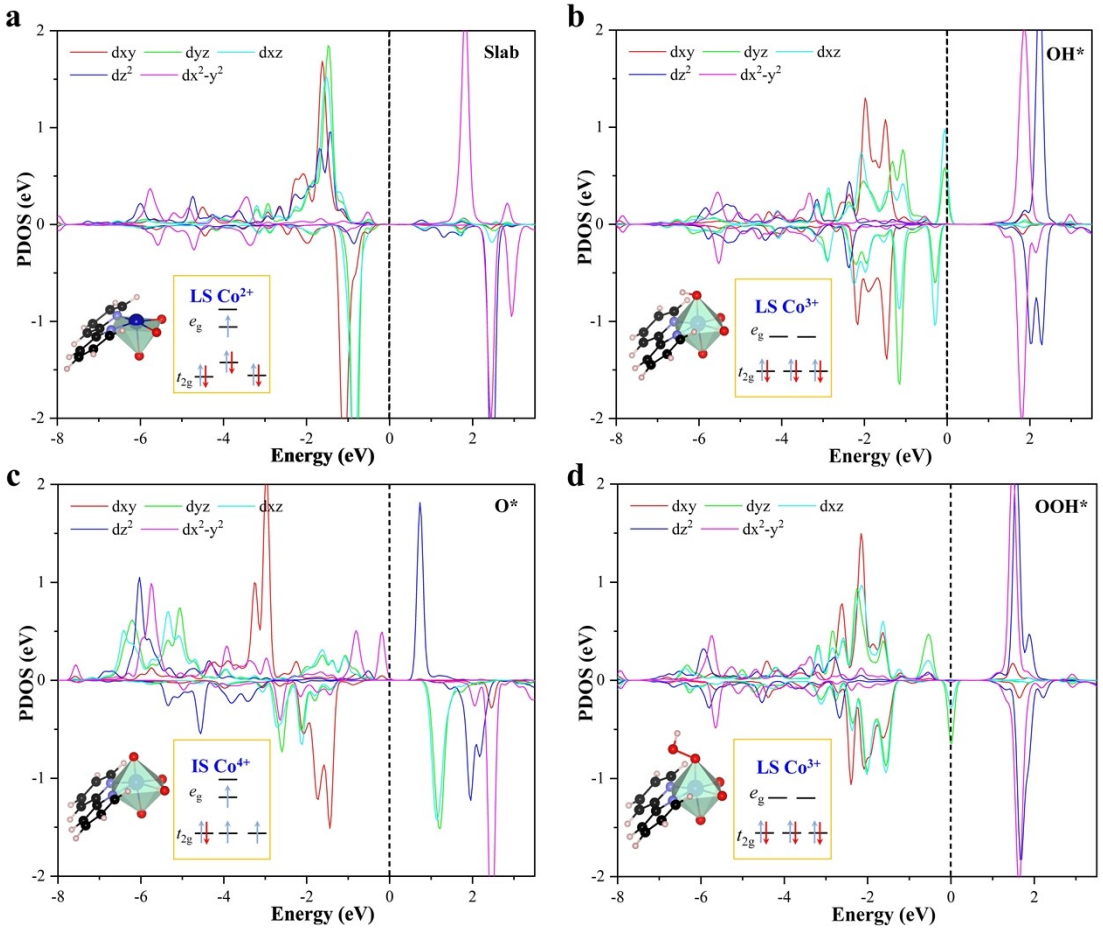

Fig. S7 | Differential charge density. The cyan and yellow colors indicate electron depletion and accumulation, respectively, with an iso-surface value of 0.006 e/Bohr^3 for (a) bpy-Ni@NiOOH; (e) phen-Ni@NiOOH. Sideview of three systems to present the bond and distance information between the ligand and substrate: (b) bpy-Ni@NiOOH; (f) phen-Ni@NiOOH; (i) phen-Co@CoOOH. The Spin density, the iso-surface value is 0.035 e/Bohr^3 for (c) bpy-Ni@NiOOH; (g) phen-Ni@NiOOH. The electronic arrangement of metal site for (d) bpy-Ni@NiOOH; (h) phen-Ni@NiOOH.

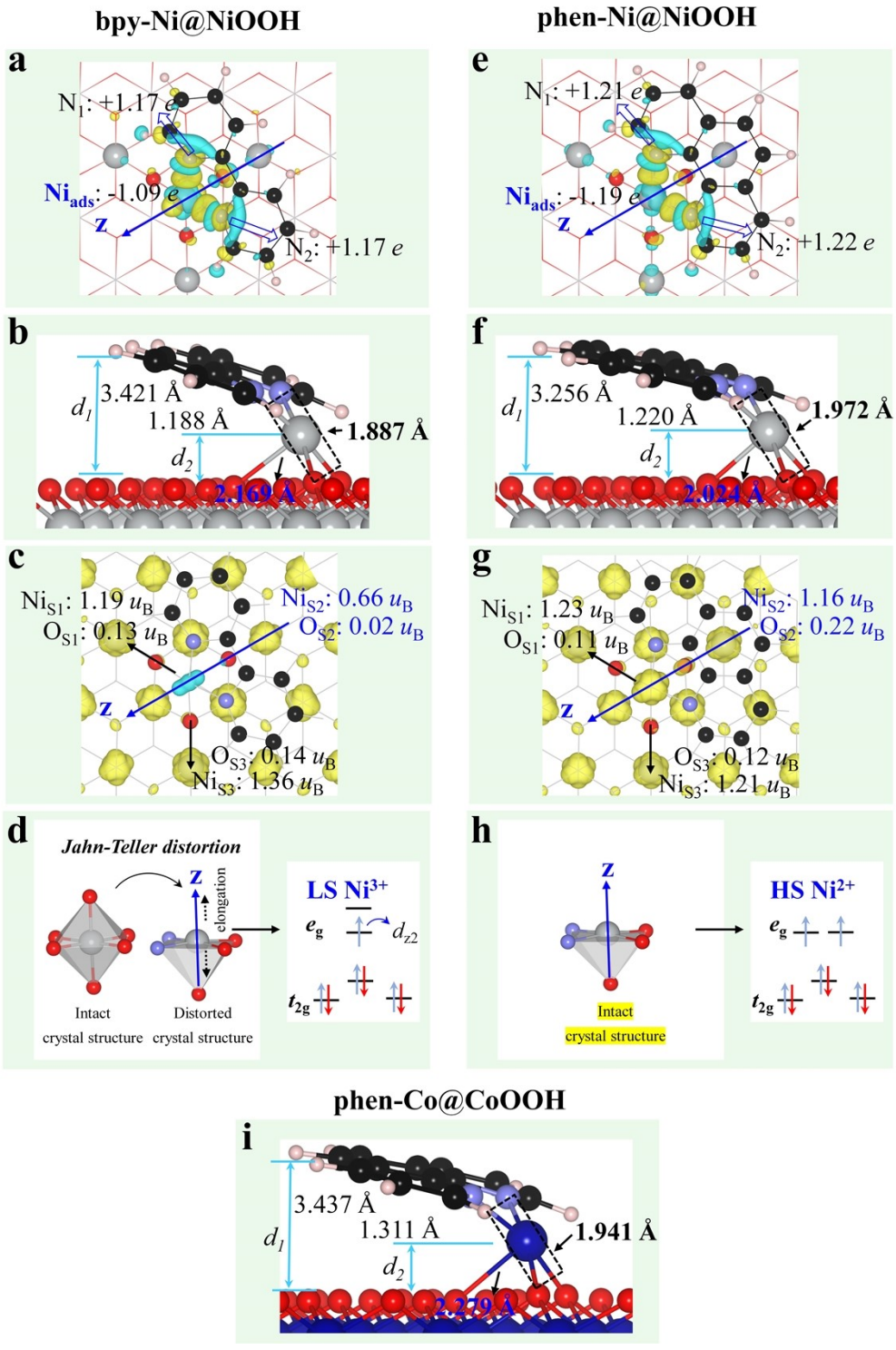

Fig. S8 | The calculated partial density of states (PDOS) and schematic diagrams of the adsorption site 3*d* orbitals for (a) CoOOH; (b) Co@CoOOH; (c) phen-Co@CoOOH; (d) bpy-Co@CoOOH; (e) bpy-Ni@NiOOH; (f) phen-Ni@NiOOH. Spin electron occupations of *d*-orbitals are denoted as short arrows.

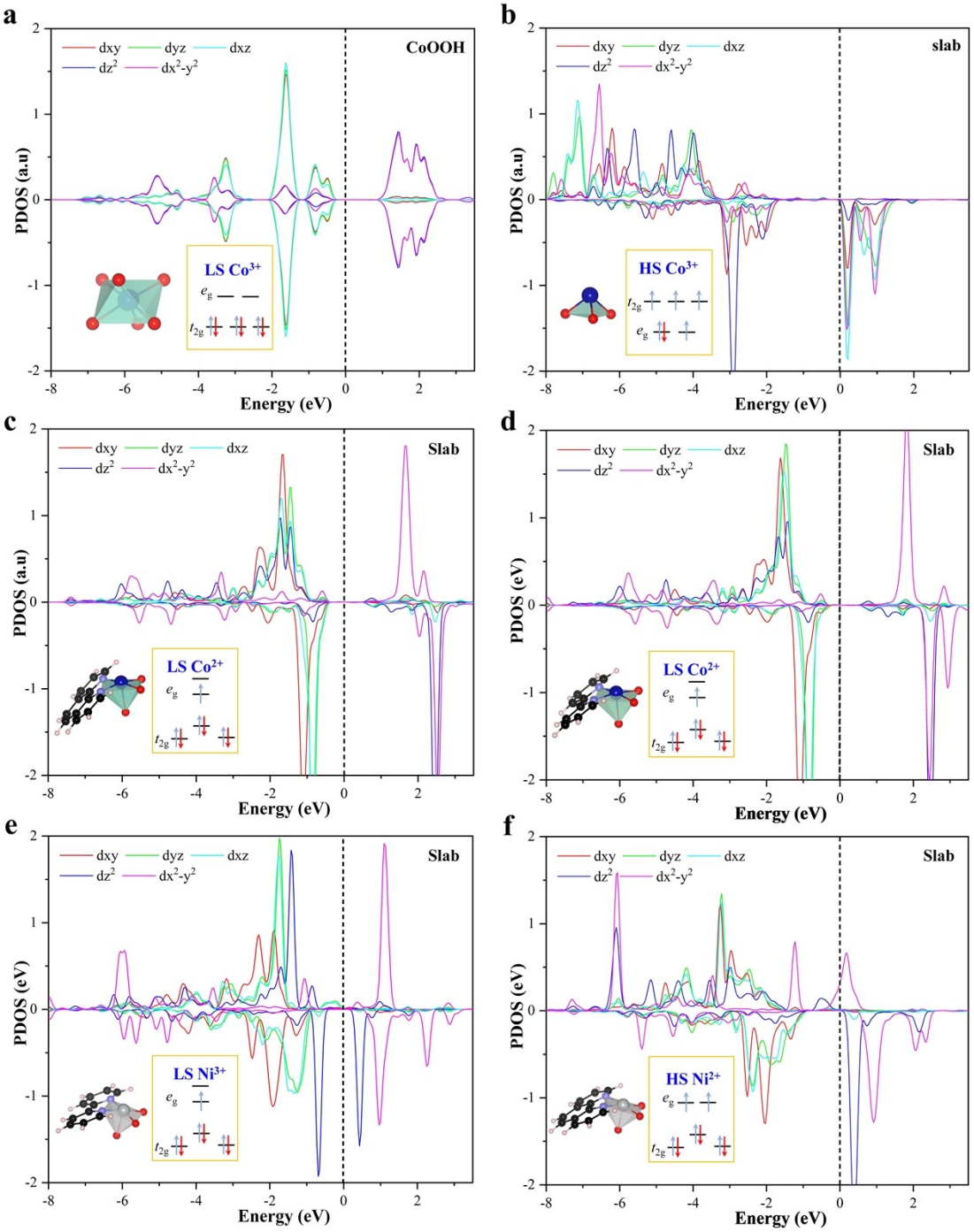

Fig. S9 | Calculated surface charge transfer (q) and work function (Φ) at IS, TS and FS for studied electrochemical steps RDS of (a) Co@CoOOH (O_2 desorption) and (b) phen-Co@CoOOH (OOH* formation), respectively.

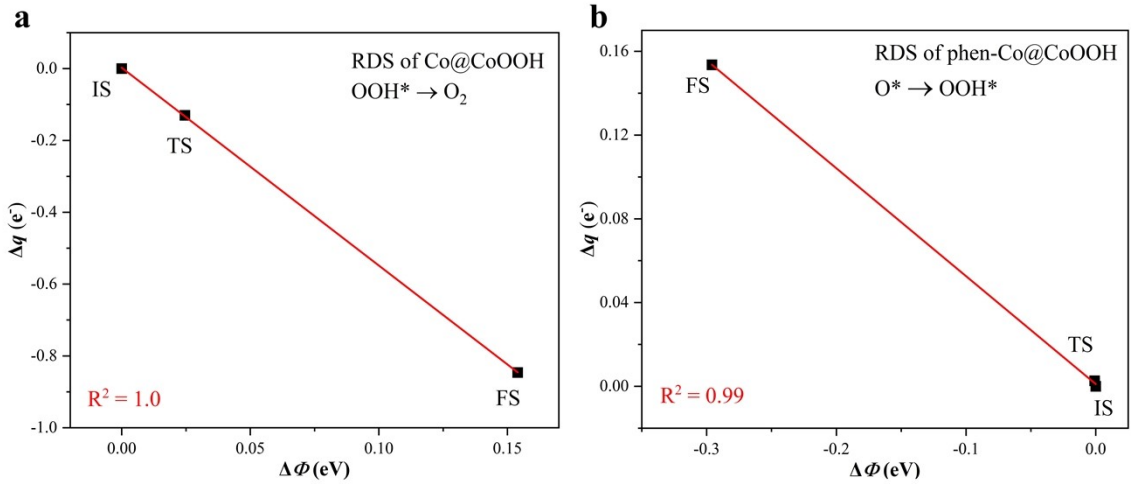

Fig. S10 | RDS Structure diagram for phen-Co@CoOOH using an explicit solvent model.