Electronic Supplementary Material (ESI) for Energy Advances.

Supplementary Information

3D-Hierarchical Flower Architecture of Anion Induced Layered Double Hydroxides for Competing Anodic Reactions

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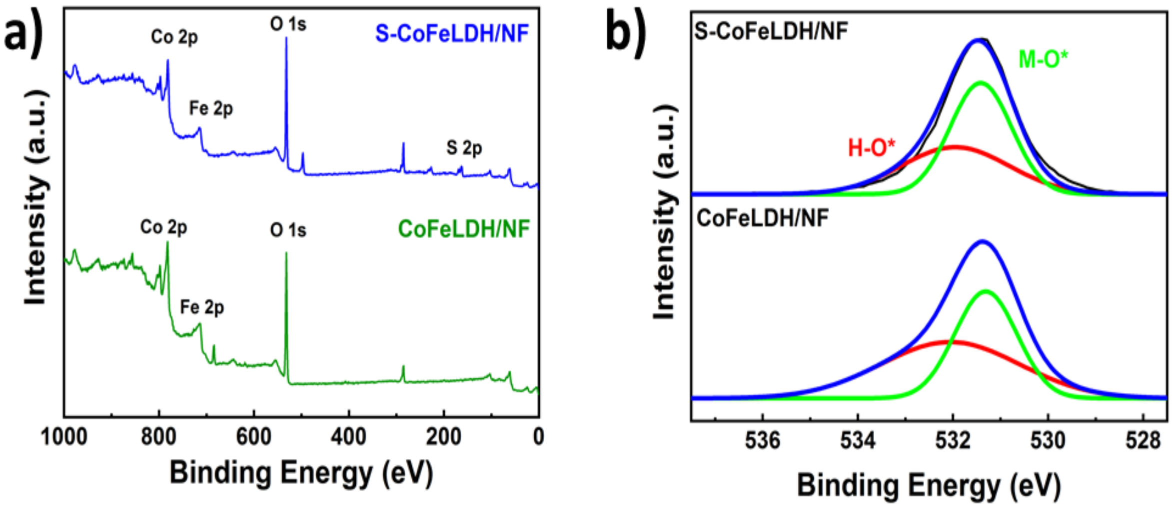


Figure S1 a) Wide scan survey spectrum of S-CoFeLDH/NF b) High resolution XPS of O 1s in S-CoFeLDH/NF

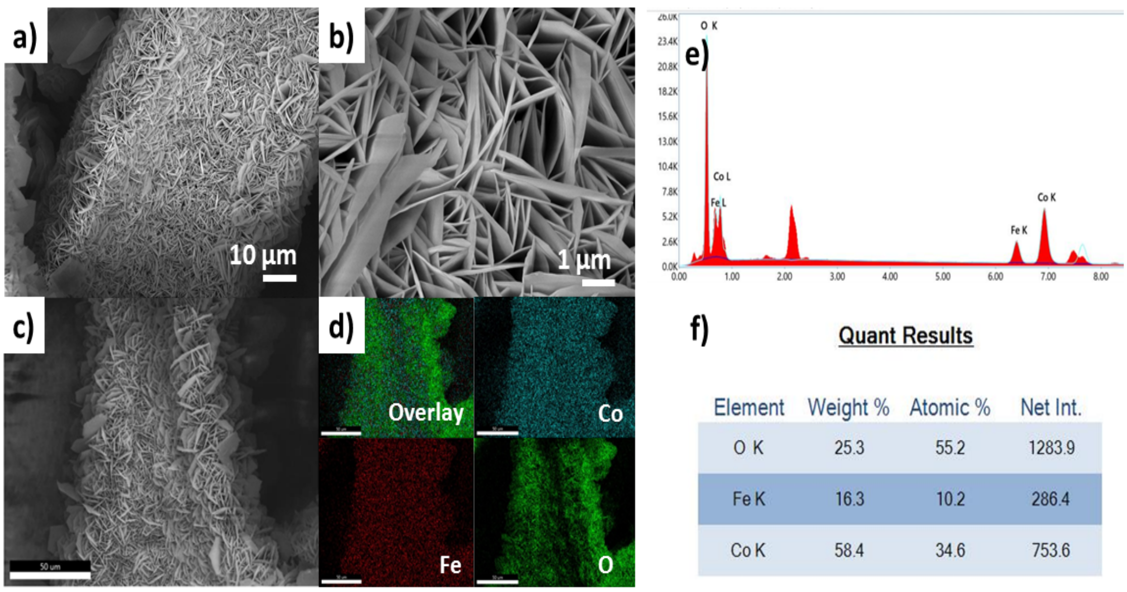
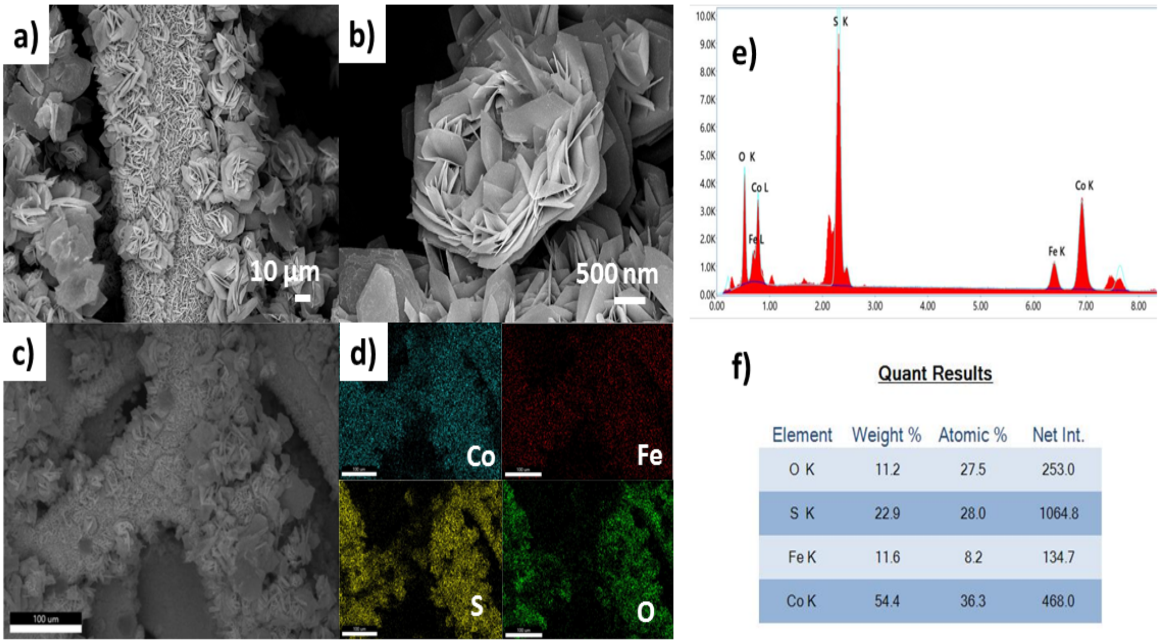


Figure S2a-c) FESEM micrographs of CoFeLDH/NF at different resolution. d) Corresponding elemental mapping of Co, Fe and O. e) EDAX f) Quantitative Results of elements



Element	Weight %	Atomic %	Net Int.
O K	11.2	27.5	253.0
S K	22.9	28.0	1064.8
Fe K	11.6	8.2	134.7
Co K	54.4	36.3	468.0

Figure S3 a-c) FESEM micrographs of S-CoFeLDH at different resolutions. d) Corresponding elemental mapping of Co, Fe, S and O. e-f) EDAX and corresponding quantitative results of elements

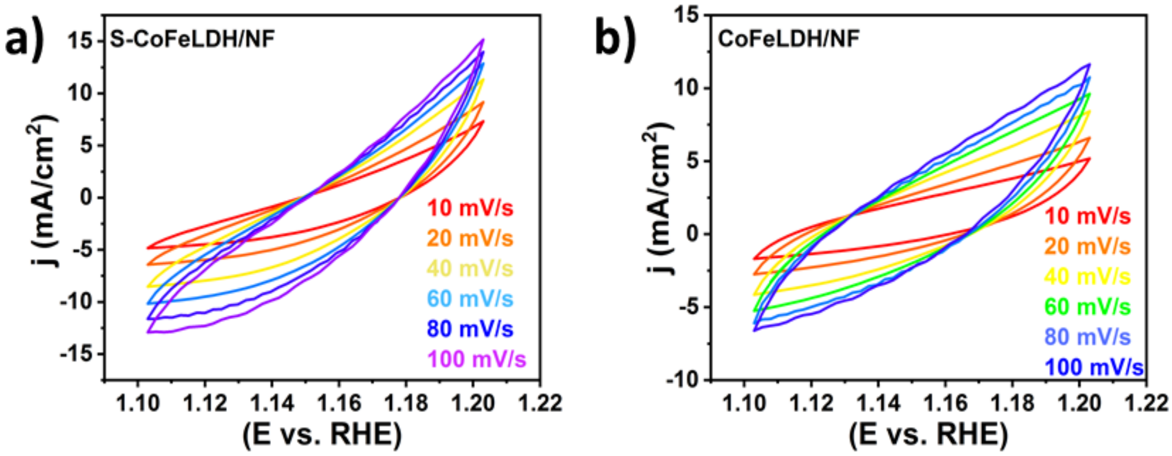


Figure S4 CV voltammogram of a) S-CoFeLDH/NF and b) CoFeLDH/NF

Table S1: Comparison of S-CoFeLDH with recently reported LDH based electrocatalyst for OER application

Material	Overpotential (mV) @ 10 mA/cm^2	Tafel slope (mV dec^{-1})	Stability (h)	year	Reference
S-CoFeLDH	268@40mA/cm^2	91	100	2023	This Work
Co-NC@Ni_2Fe-LDH	233	49.1	25	2022	[1]
NiFe-LDH/Ni_9S_8	233	38.1	60	2022	[2]
H-CoS_x@NiFe LDH	250	49	50	2021	[3]
NiFe LDH@NiCoP	220	48.6	100	2018	[4]
NiFe LDH@ITO	240	45	240	2021	[5]
NiFe LDH	217	45.1	20	2022	[6]
CoO–Co_4N@NiFe-LDH	231	39	24	2021	[7]
ReS_2/NiFe-LDH	266	43	30	2021	[8]
LDH-Bir	258	431	100	2021	[9]
NiFeV-LDH	280	53.7	32	2021	[10]
Pt/NiFe LDHs	190	53.5	45	2021	[11]
NiFe-CuCoLDH	212	48.31	100	2022	[12]
NiFe LDH	229	57	100	2020	[13]
Co9S8@NiFe LDH	220	52	20	2021	[14]
NiFe-60/Co_3O_4	190	34.6	24	2021	[15]
NiFe LDH@NiFe	201	48.5	25	2021	[16]
NiO@NiFe-LDH	265	72	1	2018	[17]
$Zn_{1-x}Fe_x$–LDH	221	53	30	2018	[18]
PM-LDH	230	47	50	2019	[19]
NiFeCo-LDH/CF	249	42	20	2020	[20]
Ni–Fe LDH@NiCu	218	56.9	6	2018	[21]
(Co,Ni)Se_2@NiFe LDH	277	74.8	6	2019	[22]
CoGa LDH/SSM	258	34.1	70	2018	[23]
Co@N-CS/N-HCP@CC	248	68	30	2019	[24]
3D NiFe LDH-POM	200	67	20	2020	[25]
NiCoFe-NC	250	31	24	2018	[26]
Co-LDH@Ti_3C_2T	330	82	20	2019	[27]
NiFeCo LDH	210	39	50	2019	[28]
NiCo LDH	290	31	30	2018	[29]
NiCoFe-LDH	277	68.83	50	2022	[30]

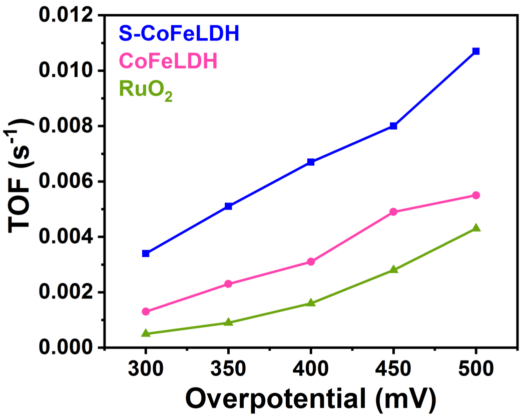


Figure S5 Apparent TOF of S-CoFeLDH/NF, CoFeLDH/NF and RuO_2

Table S2: Comparison of UOR activity of S-CoFeLDH with recently reported catalysts.

Material	Potential (V) @10 mA/cm²	Tafel slope (mV dec⁻¹)	Stability (h)	year	Reference
S-CoFeLDH	1.401 @ 40 mA/cm²	39	100	2023	This work
NiOOH/(LDH/α-FeOOH)	1.35	34	200	2022	[31]
Rh/NiV-LDH	1.33	36	3000 Lsv cycles	2022	[32]
CoO–Co_4N@NiFe-LDH	1.393	43	32	2021	[33]
PBA/FeCoNi-LDH	1.383	45.76	20	2021	[34]
MoS_2-LDH	1.37	29	30	2019	[35]
NiFe-LDH/MWCNTs	1.335	75	20	2020	[36]
Ni9Fe1-LDH	1.41	39.8	2	2022	[37]
CoFe0.75Mn0.25-LDH	1.367	79.4	30	2022	[38]
NiTe@CoFe LDH	1.56	-	50	2022	[39]
NiCo-ZLDH	1.335	51.83	20	2022	[40]
NiAl-LDHs	1.42	59.8	14	2022	[41]

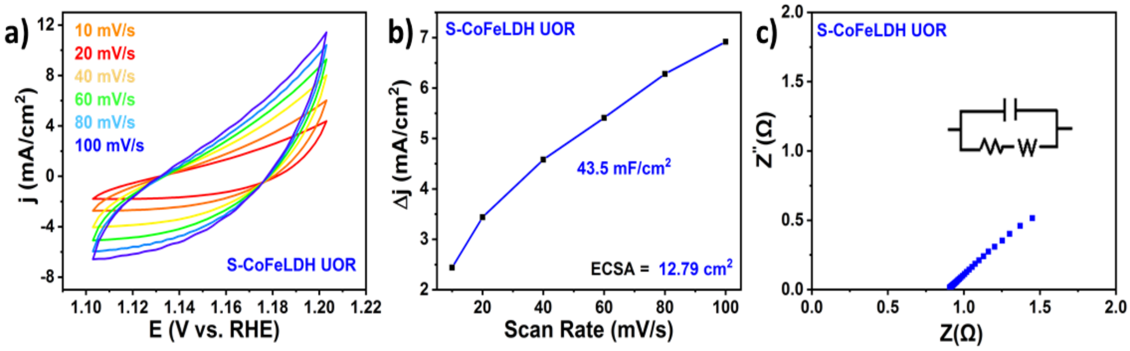


Figure S6 Electrochemical measurements for UOR a) CV at different scan rates, b) Cdl plot and c) EIS nyquist plot of S-CoFeLDH in 1 M KOH with 0.5 M Urea

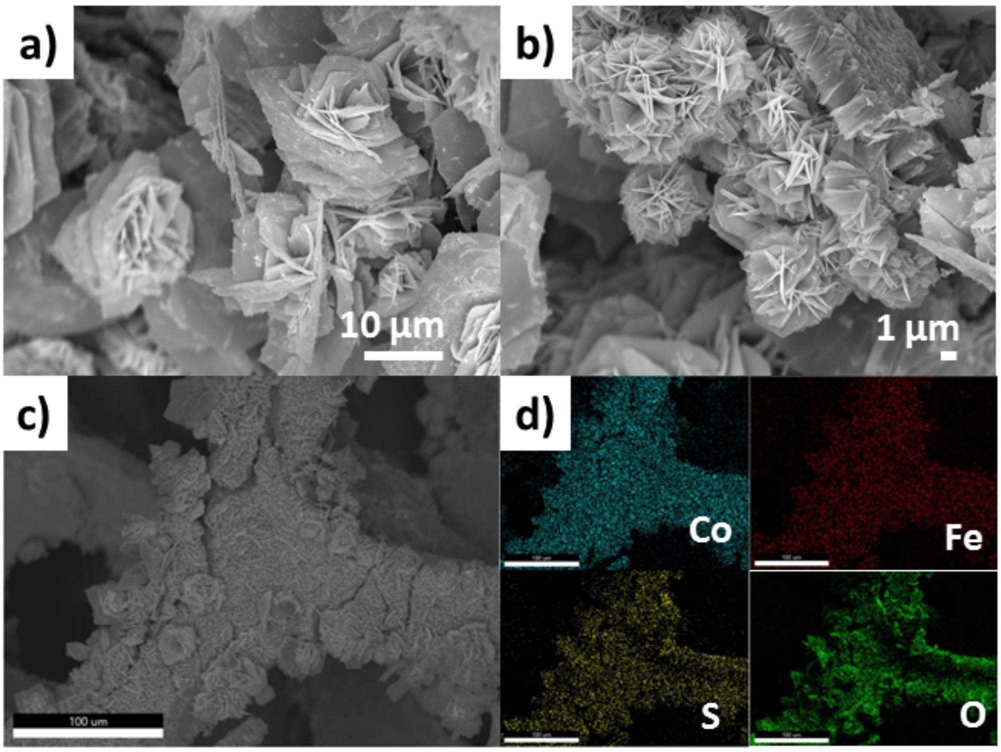


Figure S7 a-c) FESEM micrographs of S-CoFeLDH/NF after electrochemical stability. d) elemental mapping corresponding to Co, Fe, S and O.

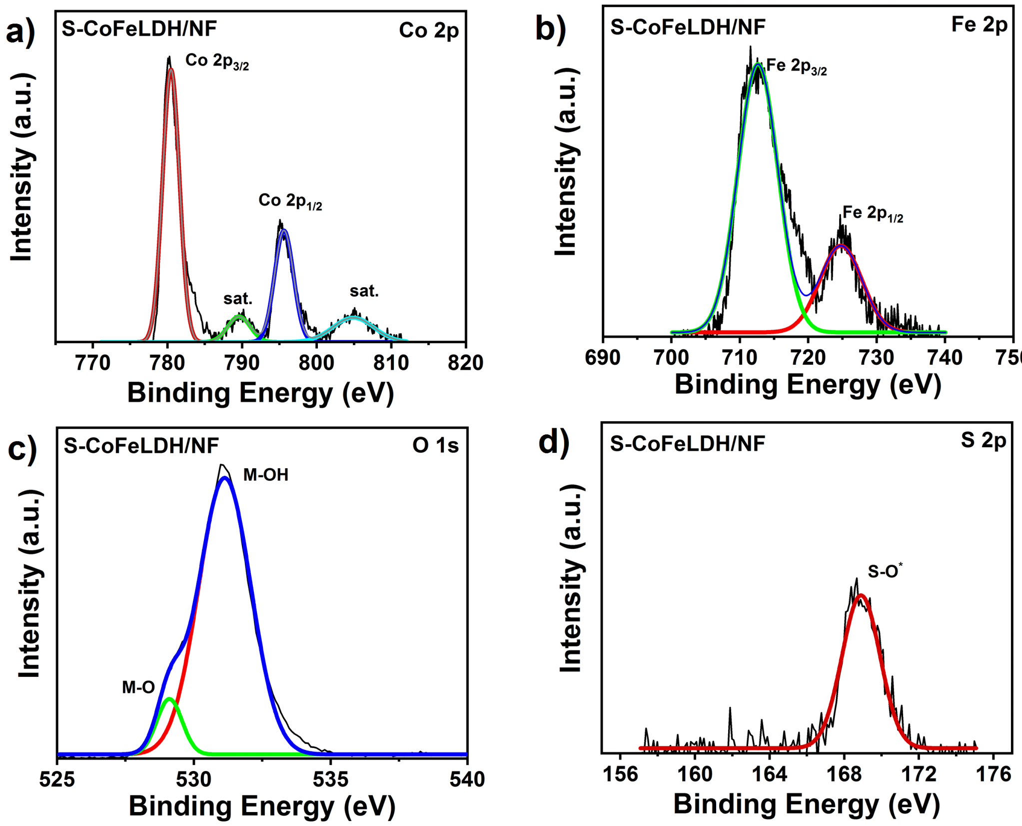


Figure S8 XPS analysis after electrochemical stability. High resolution XPS of a) Co2p b) Fe2p c) O1s and d) S2p

S1. DFT Calculation

The adsorption energies of oxygen-containing intermediates over assumed electrochemical active sites were calculated by the following equations: -

$\Delta E_{O*} = E_{o*} - E_{*} - [E_{H2O} - E_{H2}]$

$\Delta E_{OH*} = E_{OH*} - E_{*} - [E_{H2O} - 1/2E_{H2}]$

$\Delta E_{OOH*} = E_{OOH*} - E_{*} - [2\ E_{H2O} - 3/2\ E_{H2}]$

Where, E^*, E^*_{OH}, E^*_{OOH} and E^*_{O} are the total energies of the catalytic substrate without and with the adsorption of the intermediates of OOH, OH and O respectively. E_{H2O} and E_{H2} are the energy of water and hydrogen molecules in gas phase respectively. In alkaline medium the overall OER could be expressed as:

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

The elementary reaction steps would be:

- $OH^- + * \rightarrow OH^- + e^-$
- $OH^- + OH^* \rightarrow O^* + H_2O(l) + e^-$
- $OH^- + O^* \rightarrow OOH^* + e^-$
- $OH^- + OOH^* \rightarrow O_2(g) + H_2O(l) + e^-$

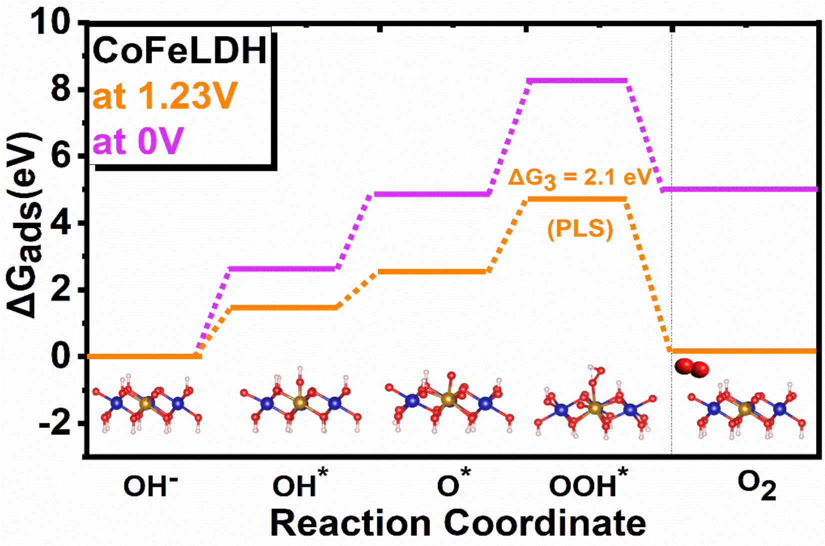


Figure S9 Gibbs free energy plot for CoFeLDH/NF

Table S3: Gibbs free energy of structural intermediates after calculation at 0 V and 1.23 V.

Structure	ΔG at 0V	ΔG at 1.23V
CoFeLDH-OH*	2.65187	1.45187
CoFeLDH-O*	4.84458	2.41458
CoFeLDH-OOH*	8.24452	4.58452
CoFeLDH + O_2	4.92	0.03
S-CoFeLDH-OH*	2.91247	1.68247
S-CoFeLDH-O*	3.88538	1.42538
S-CoFeLDH-OOH*	6.44542	2.75542
S-CoFeLDH + O_2	4.92	0
S-CoFeLDH-OH*	0.92751	-0.78591
S-CoFeLDH-O*	2.58372	-0.48631
S-CoFeLDH-OOH*	4.59381	0.53371
S-CoFeLDH + O_2	4.92	0

Where, * stands for an adsorption site on catalysts. The change in free energy ΔG for each reaction step is given by the equation: - $\Delta G = \Delta E + \Delta ZPE - T\,\Delta S + \Delta G_u$

Here, the overpotential can be calculate to evaluate the performance for OER by [1].

$\eta = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e - 1.23$

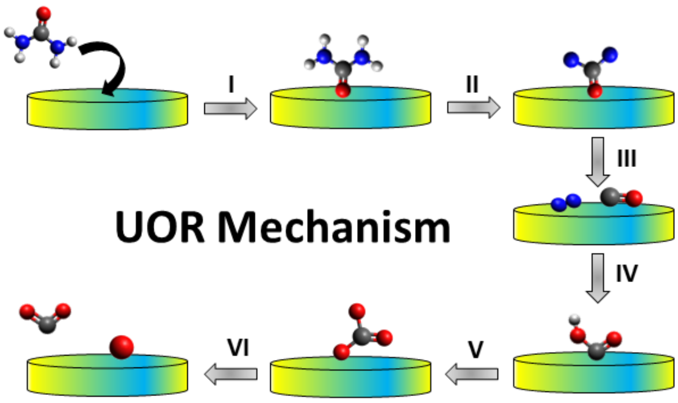


Figure S10: Detailed UOR mechanism.

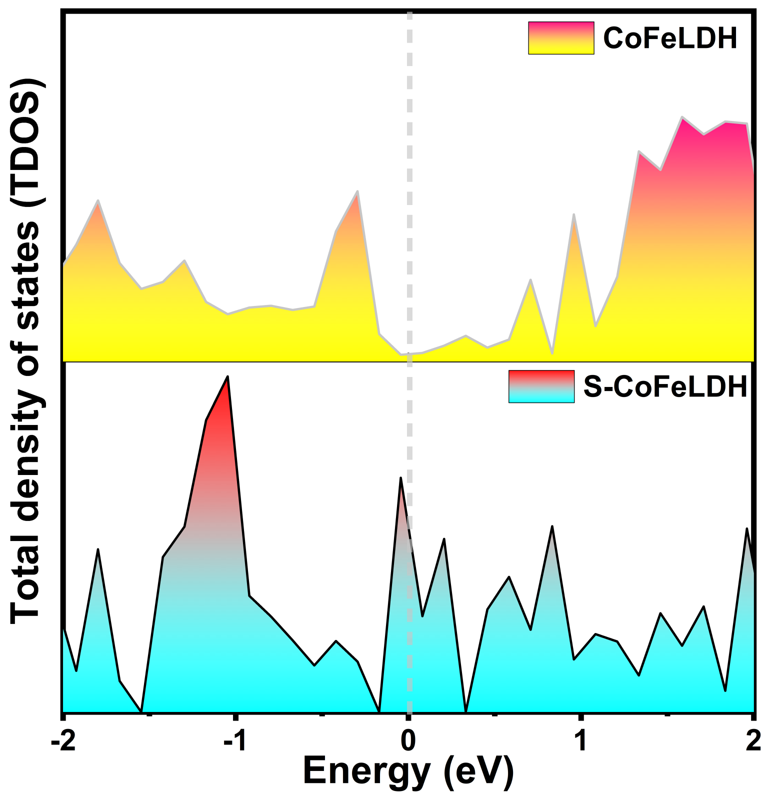


Figure S11: TDOS plot for S-CoFeLDH (bottom) and CoFeLDH (top)

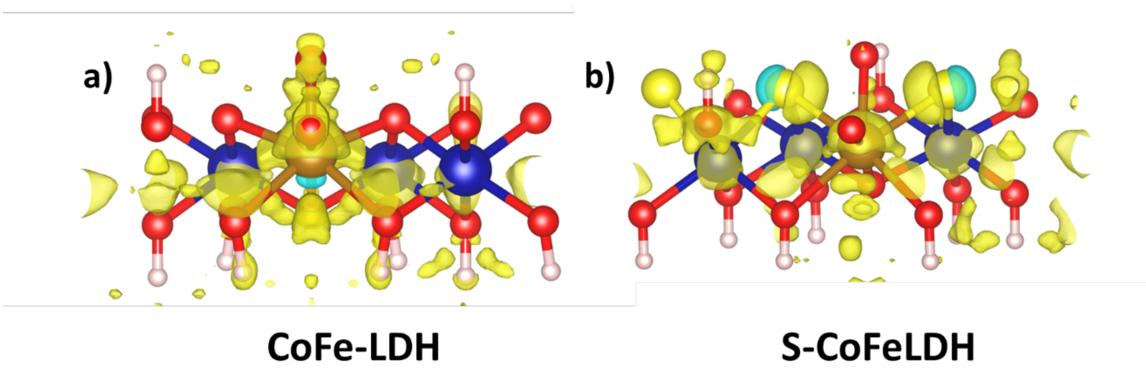


Figure S12: Differential charge density curve a) CoFe-LDH and b) S-CoFeLDH.

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