Supporting Information for

Layered FeCoNi double hydroxides with tailored surface electronic configuration induced by oxygen and unsaturated metal vacancies for boosting overall water splitting process

Zibo Zhai[a], Wei Yan[a,] *, Jiujun Zhang[a,]*

[a] Institute for Sustainable Energy/College of Sciences, Shanghai University, Shanghai, China 200444

1. Experimental section

1.1 Catalysts characterization

The nanostructures and morphologies of all as-prepared electrocatalysts were characterized by scanning electron microscopy (SEM, FEI Nova NanoSEM), transmission electron microscopy (TEM, JEM-3010), and X-ray diffraction (XRD, D/MAX2200V PC), X-ray photoelectron spectroscopy (XPS, 5600 Perkin-Elmer PHI). The element contents and their valance states were tested by the inductively coupled plasma optical emission spectra (ICP-OES, ICP plasma-2000) and X-ray photoelectron spectroscopy (XPS, 5600 Perkin-Elmer PHI).

1.2 The electrochemical measurements

The electrochemical measurements for hydrogen evolution (HER), oxygen evolution reaction (OER) and and overall water splitting process were carried out by a CHI 660D electrochemical workstation in a standard three-electrode system including the working electrode (the as-prepared electrocatalysts), the reference electrode (Hg/HgO electrode) and the counter electrode (Pt wire) in 1M KOH. The electrocatalytic performance was evaluated by linear sweep voltammetry (LSV) tests at a scan rate of 10 mV s^{-1} with iR-corrected. According to the Nernst equation ($E_{RHE} = E_{Hg/HgO} + 0.095 + 0.0591 \times pH$), all values of potential were converted to the reversible hydrogen electrode potential. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10^{-2} −10^{5} Hz. The electrochemical active surface area (ECSA) was evaluated from double-layer capacitance (C_{dl}) through cyclic voltammetry (CV) tests at the scan rates of 10 to 200 mV s^{-1}. Chronoamperometry measurements were adopted at 2.6 V (RHE) to characterize the OER stability for the catalysts.

Figure S1. Photographs of the precursor solution without (top) and with (bottom) NH_4F. Left to right are Fe-precursor, Co-precursor and Ni-precursor, respectively.

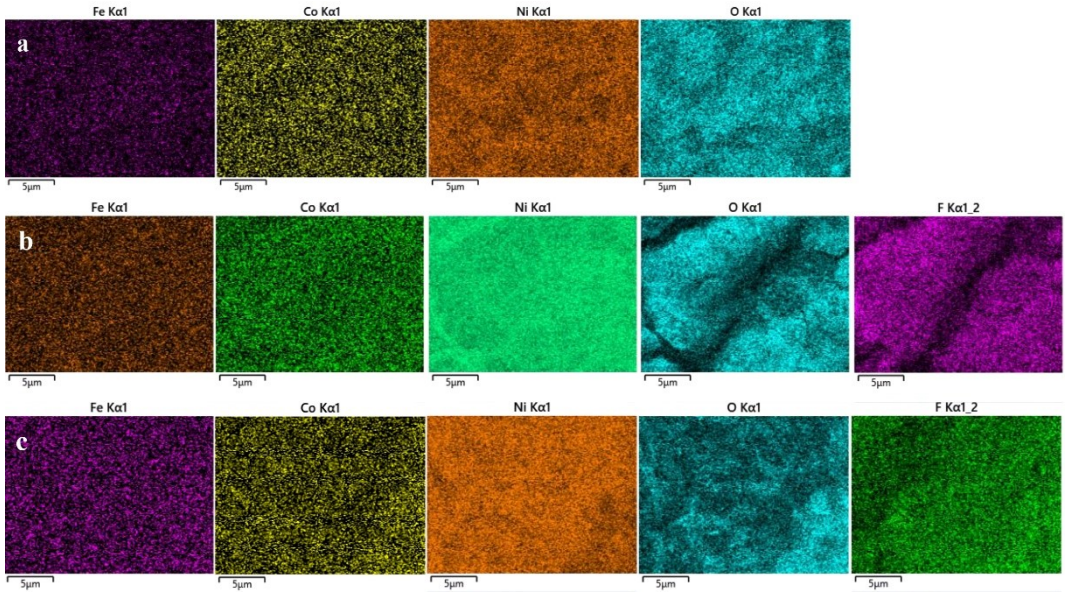

Figure S2. SEM mapping of (a) FeCoNi LDH/NF, (b) F-FeCoNi LDH/NF and (c) F-FeCoNi-Ov LDH/NF.

Table S1. ICP-OES analysis of FeCoNi LDH/NF, F-FeCoNi LDH/NF and F-FeCoNi-Ov LDH/NF electrocatalysts.

Sample	Fe (wt%)	Co (wt%)	Ni (wt%)
FeCoNi LDH/NF	16.92	18.47	18.28
F-FeCoNi LDH/NF	17.50	18.40	17.29
F-FeCoNi-Ov LDH/NF	18.41	17.85	16.99

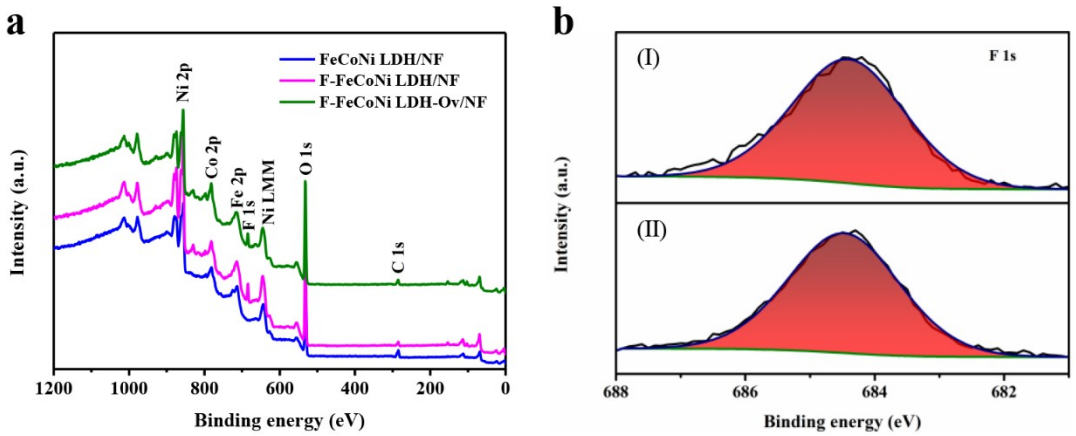

Figure S3. (a) XPS survey spectra of the as-prepared samples. (b) The comparison of fitted F 1s XPS spectrum of F-FeCoNi LDH/NF (I) and F-FeCoNi-Ov LDH/NF (II).

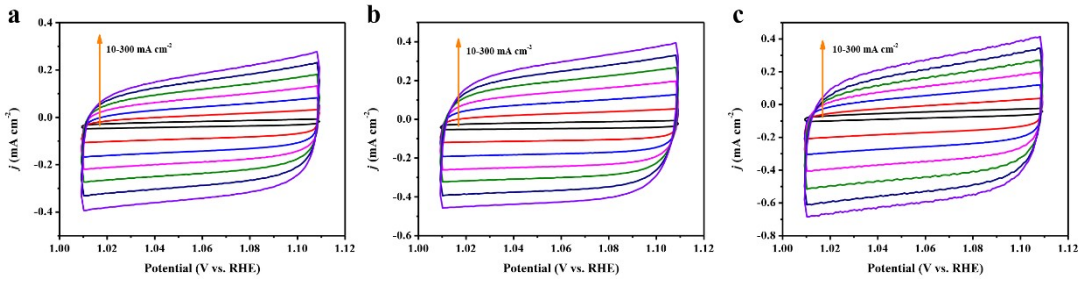

Figure S4. CV curves of (a) FeCoNi LDH/NF, (b) F-FeCoNi LDH/NF and (c) F-FeCoNi-Ov LDH/NF at different scan rates.

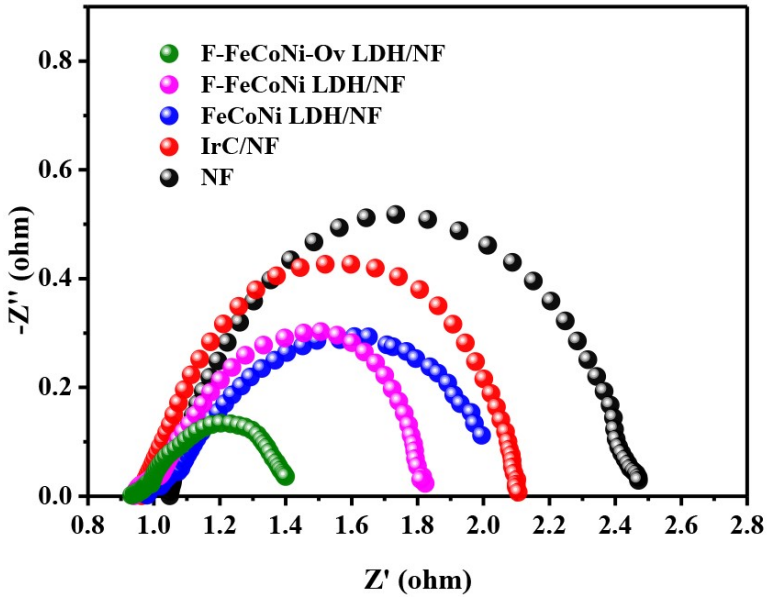

Figure S5. Nyquist plots of the as-prepared samples for OER electrocatalysis.

Table S2. EIS calculation parameters of the as-prepared samples for OER electrocatalysis

Sample	Rs (Ω)	Rct (Ω)	CPE-T (Ω)	CPE-P (Ω)
F-FeCoNi-Ov LDH/NF	0.95585	0.47493	0.35968	0.6659
F-FeCoNi LDH/NF	0.97687	0.88588	0.21043	0.74517
FeCoNi LDH/NF	1.008	1.121	0.24851	0.61515
IrC/NF	0.97962	1.133	0.0051173	0.83342
NF	1.054	1.399	0.0030532	0.82638

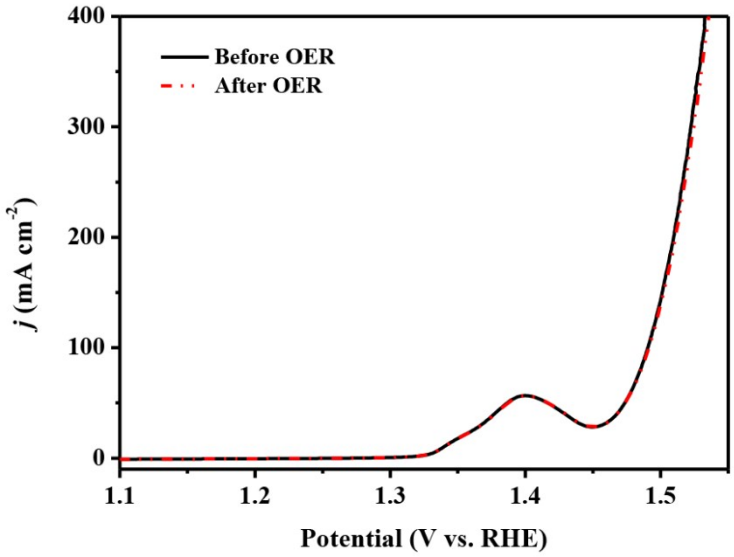

Figure S6. The LSV curves of F-FeCoNi-Ov LDH/NF before and after 50h OER cycling.

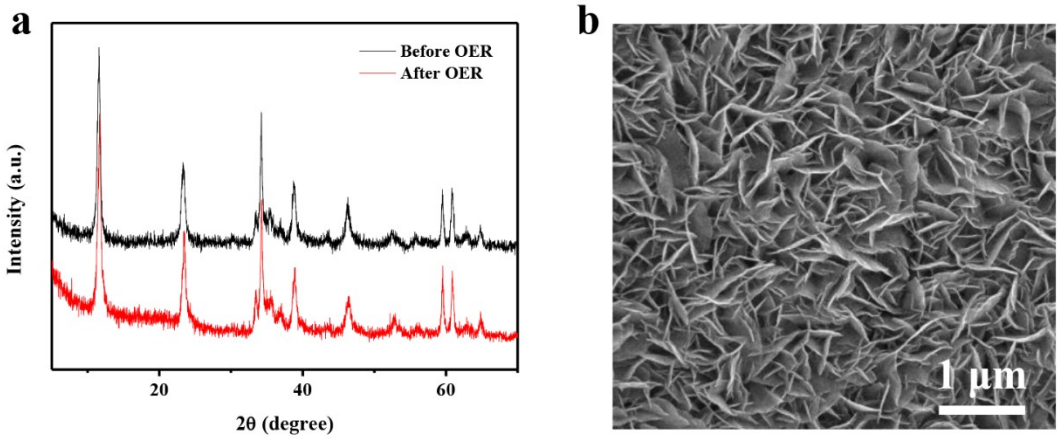

Figure S7. (a) XRD pattern of F-FeCoNi-Ov LDH/NF before and after 50 hours of OER cycling. (b) SEM image of F-FeCoNi-Ov LDH/NF after 50 hours of OER cycling.

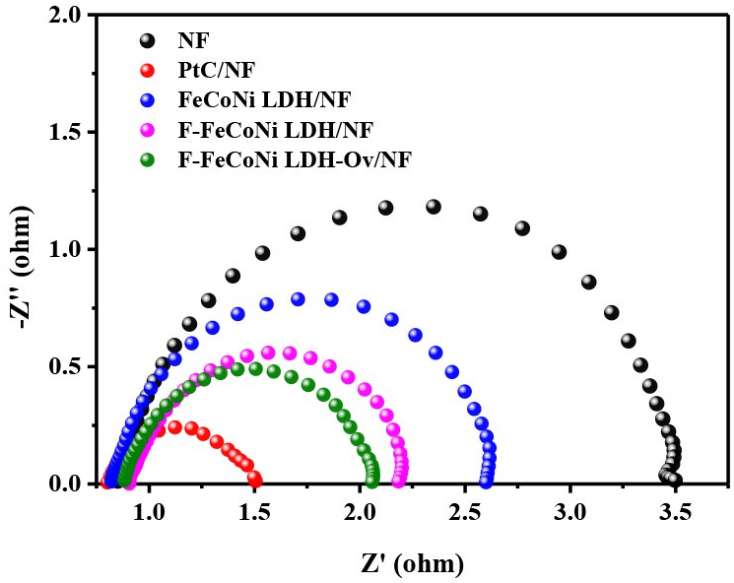

Figure S8. Nyquist plots of the as-prepared samples for HER electrocatalysis.

Table S3. EIS calculation parameters of the as-prepared samples for HER electrocatalysis

Sample	Rs (Ω)	Rct (Ω)	CPE-T (Ω)	CPE-P (Ω)
F-FeCoNi-Ov LDH/NF	0.89736	1.152	0.0005062	0.92253
F-FeCoNi LDH/NF	0.94956	1.304	0.00055028	0.90449
FeCoNi LDH/NF	0.84081	1.78	0.00046778	0.93772
PtC/NF	0.80837	0.65433	0.0032331	0.65433
NF	0.91592	2.185	0.00038211	0.94059

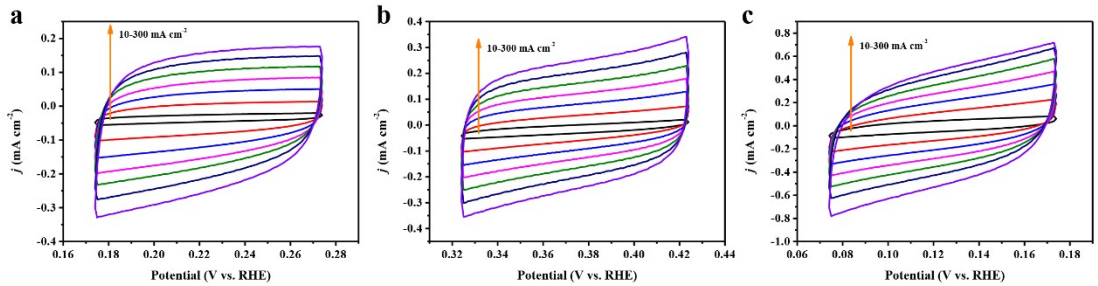

Figure S9. CV curves of (a) FeCoNi LDH/NF, (b) F-FeCoNi LDH/NF and (c) F-FeCoNi-Ov LDH/NF at different scan rates.

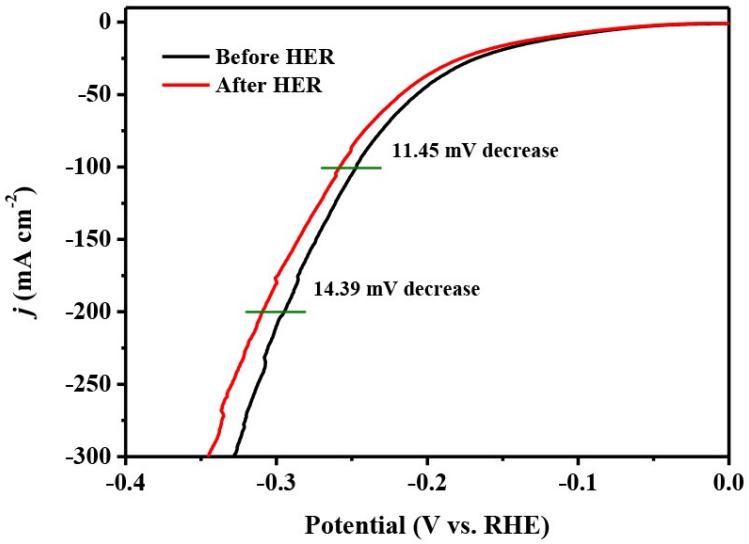

Figure S10. The LSV curves of F-FeCoNi-Ov LDH/NF before and after 50 hours of HER cycling.