Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Modulating Electronic Structure of Ultrathin Layered Double Hydroxides Nanosheets with fluorine: an Effective Electrocatalyst for Oxygen Evolution Reaction

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Synthesis of pristine Co_3Fe LDHs: Pristine Co_3Fe LDHs were synthesized using a typical hydrothermal method. 0.9 M $Co(NO_3)_2{\cdot}6H_2O$ and 0.3 M $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 30 mL deionized water to form solution A. 1.92 m NaOH and 0.8 m Na_2CO_3 were dissolved in 30 mL deionized water to form solution B. Solution A and B were mixed together into a breaker under stirring. The obtained mixed solution was ransferred into a stainless-steel Teflon-lined autoclave suffered by 80 °C for 48 h. The production was collected by centrifugation, washed with water and dried at 60 °C overnight.

Synthesis of ultrathin F-Co_3Fe LDHs: 20 mg Co_3Fe LDHs was dispersed into 2 mL ethanol by ultrasound. Then 1.5 mL obtained ink was dropped into 4 cm*4 cm clean Ti foil followed by naturally drying. Put the dry Ti foil into MARCH plasma reactor. At last, the pristine Co_3Fe LDHs were treated by CHF_3 with the flowing of 5 sccm at power of 20 W for 1 min, 5 min, 15 min and 30 min. The ultrathin F-Co_3Fe LDHs was collated by stripped powder with blade.

Electrochemical Characterization: The OER capacity of obtained materials was test using a three-electrode system using CHI 600 electrochemical station. The catalyst ink was prepared by dispersing 4 mg materials into 500 μL deionized water and 500 μL ethanol containing 50 μL of 5 wt% Nafion under sonication for 30 min. Then 10 μL inks was dropped onto the surface of glass carbon electrode and worked as working electrode. Carbon rode and saturated calomel electrode (SCE) were used as counter electrode and the reference electrode, respectively. The electrolyte solution is 1.0 M KOH. Linear sweep voltammetry was recorded at a scan rate of 5 mVs^{-1} with iR compensation. All potentials were referenced to a reversible hydrogen electrode (RHE) according to the equal: $E_{RHE} = E_{SCE}+0.242 + 0.059*pH$. The impedance spectrum was measured at the frequency range from 0.01 Hz to 1000 kHz at 1.51 V (vs. RHE). To facilitate mass transfer, 1cm*1cm Ni foam with same catalyst loading (50 μL inks) was also used as working electrode.

Characterization

The morphology of LDHs nanosheets are investigated by scanning electron microscopy (SEM, JEOL 7600F). The bulk crystal structure of the obtained samples is characterized using powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, Cu Kα1). The phase structure of the samples was investigated using transmition electron microscopy (TEM, JEOL 2100F) and elements distribution was explored using FEI Talos 200x. The synchrotron EXAFS and XANES of Co K-edge were carried out at BL17C at National Synchrotron Radiation Research Center, Taiwan. X-ray photoelectron spectroscopy (XPS) with Al-Kα X-ray ($h\nu = 1486.6$ eV) radiation (Thermo Fisher Scientific, England) were used to explore the electronic structure. The fourier transform infrared spectroscopy (FTIR) was performed on Thermo Nicolet 6700 FT-IR. The size and thickness of electrocatalysts were determined by atomic force microscope (AFM, Brucker Bioscope system). BET analysis was performed on JW-BK200C.

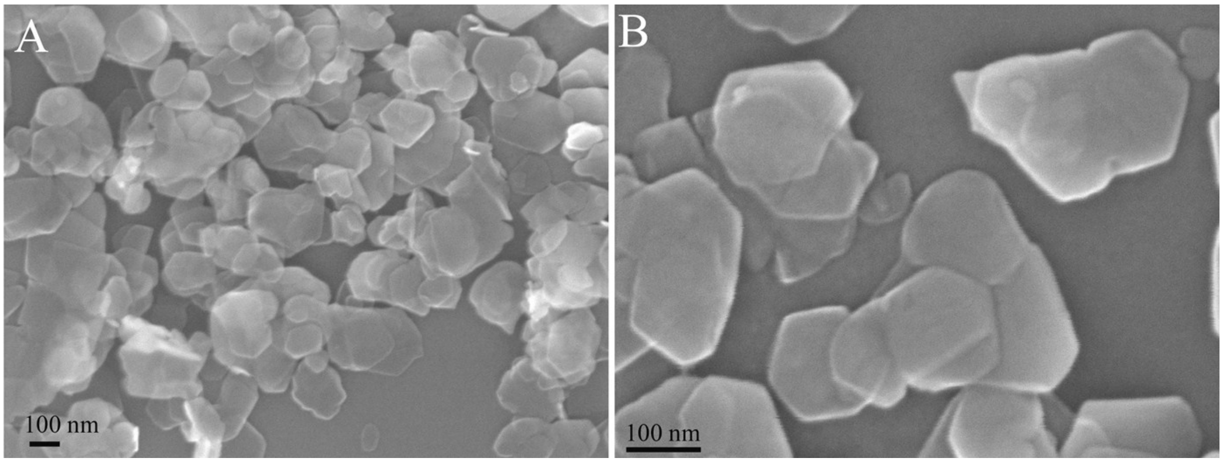

Figure S1. SEM images of pristine Co_3Fe LDHs.

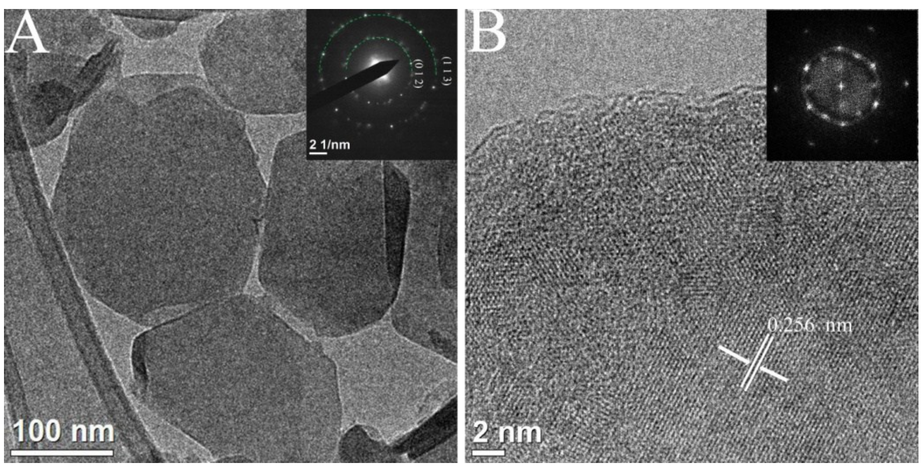

Figure S2: TEM (A) and HRTEM (B) image of pristine Co_3Fe LDHs. The insert image in A is its SAED images and the insert image in B is its corresponding FFT.

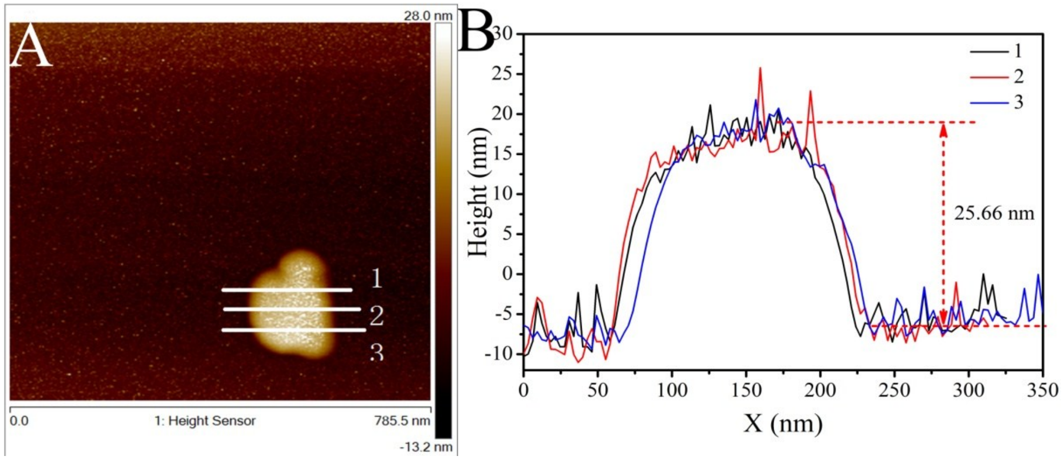

Figure S3. AFM image (A) and height carves (B) of pristine Co_3Fe LDHs.

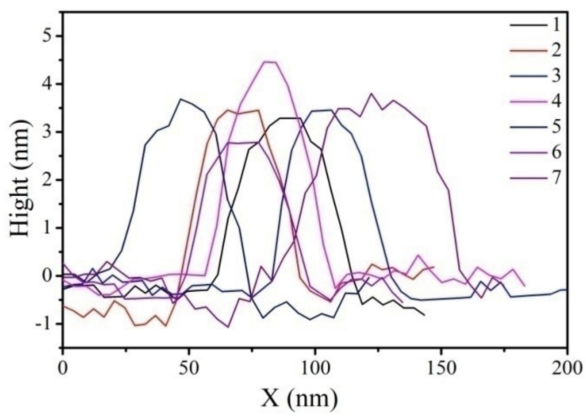

Figure S4. Height carves of F-Co_3Fe LDHs.

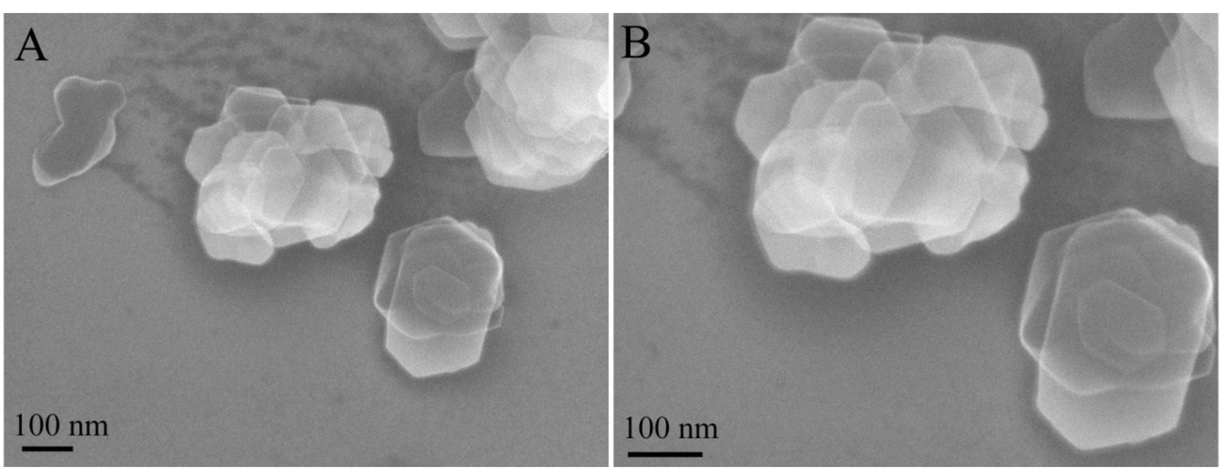

Figure S5. SEM images of Co_3Fe LDHs for CHF_3-plasma etching for 1 min.

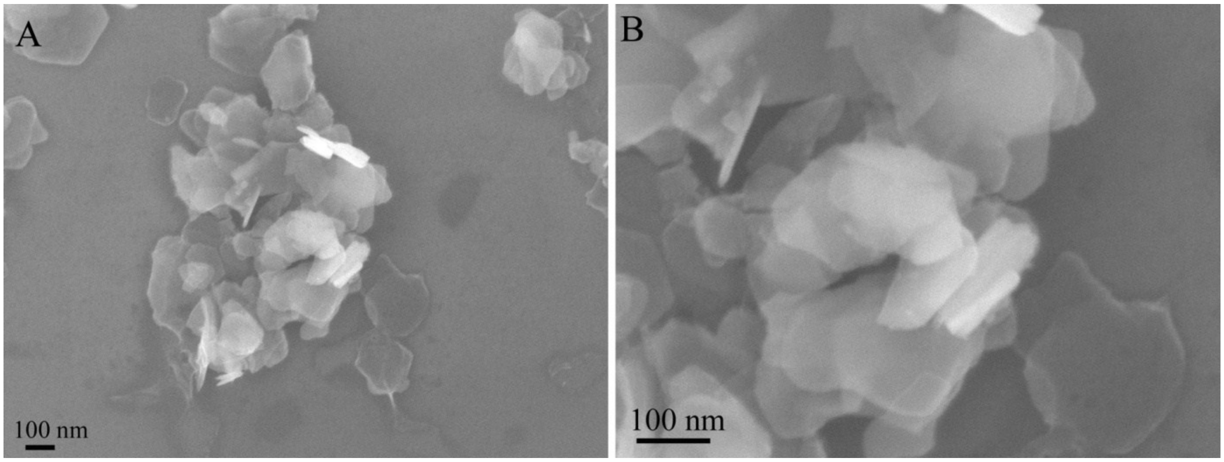

Figure S6. SEM images of Co_3Fe LDHs for CHF_3-plasma etching for 5 min.

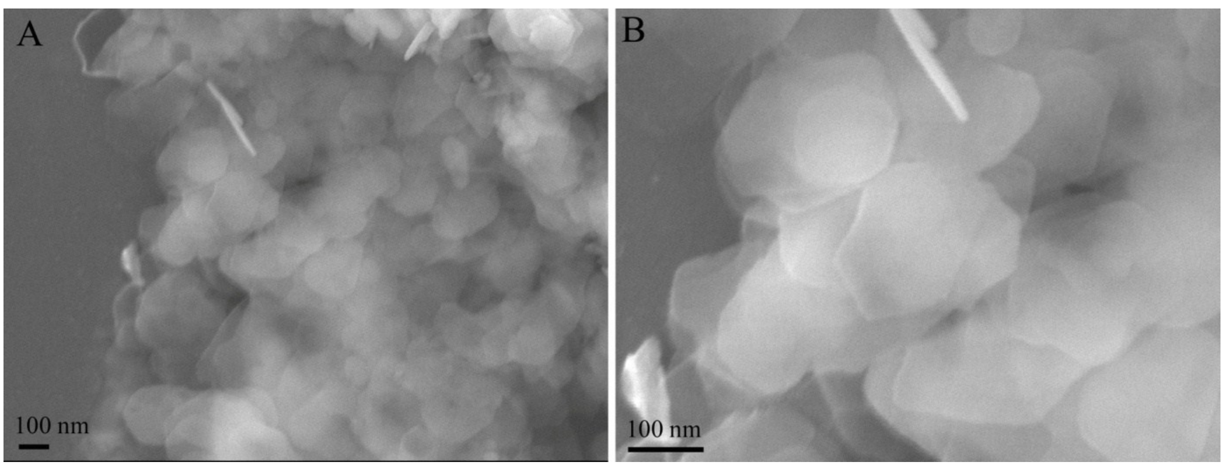

Figure S7. SEM images of Co_3Fe LDHs for CHF_3-plasma etching for 15 min (F-Co_3Fe LDHs).

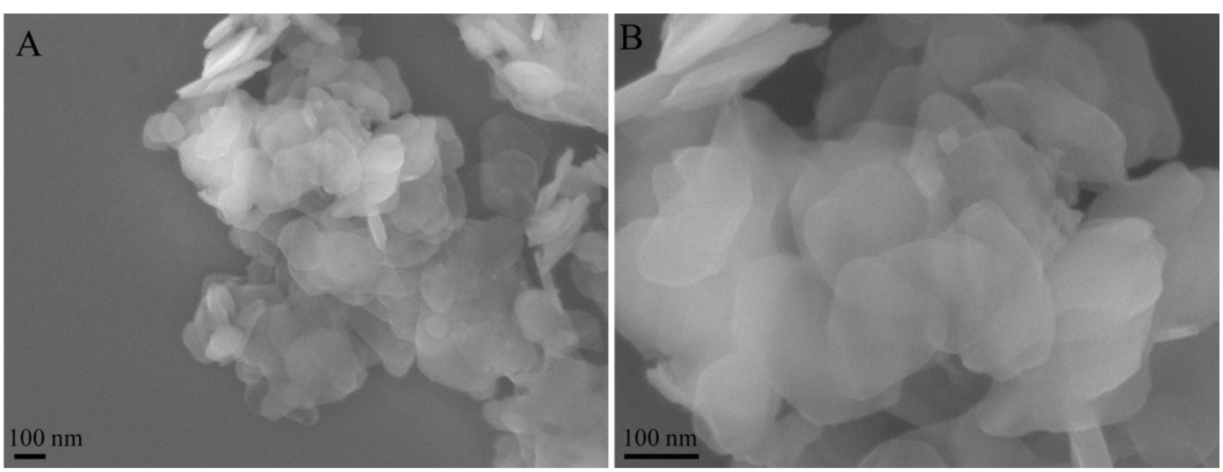

Figure S8. SEM images of Co_3Fe LDHs for CHF_3-plasma etching for 30 min.

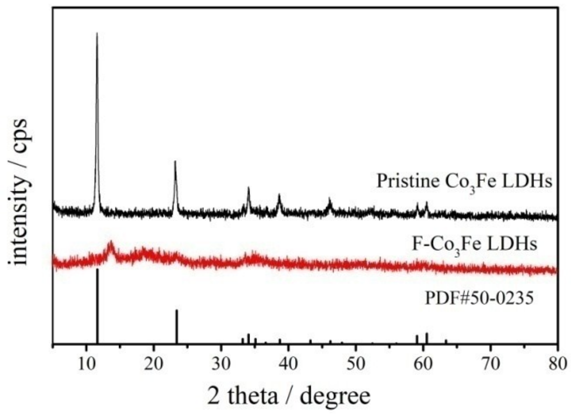

Figure S9. XRD patterns of pristine Co_3Fe LDHs and F-Co_3Fe LDHs.

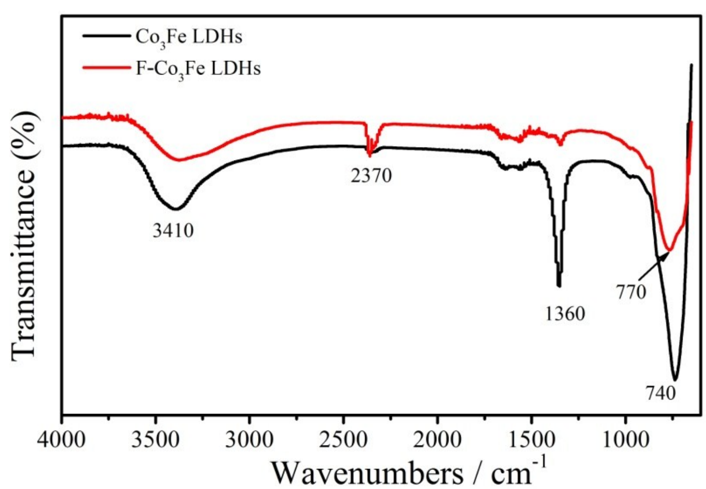

Figure S10. FT-IR image for pristine Co_3Fe LDHs and F-Co_3Fe LDHs.

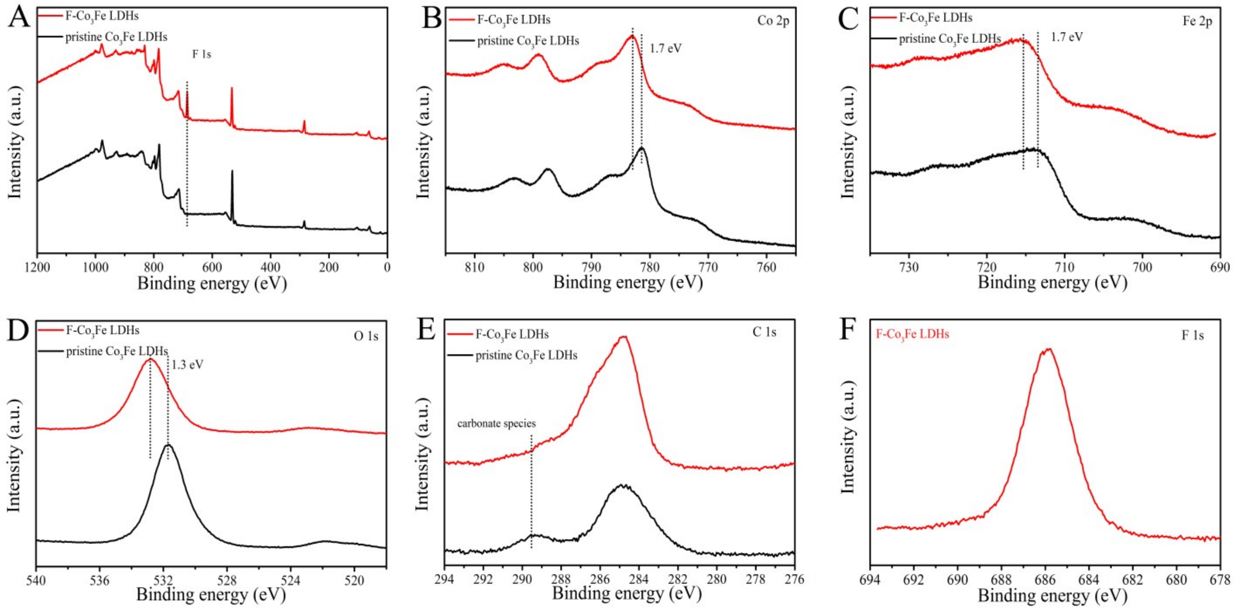

Figure S11. A) All XPS spectrum, B) Co2p XPS spectrum, C) Fe 2p XPS spectrum, D) O 1s XPS spectrum, E) C 1s XPS spectrum and F) F 1s XPS spectrum for pristine Co_3Fe LDHs and F-Co_3Fe LDHs.

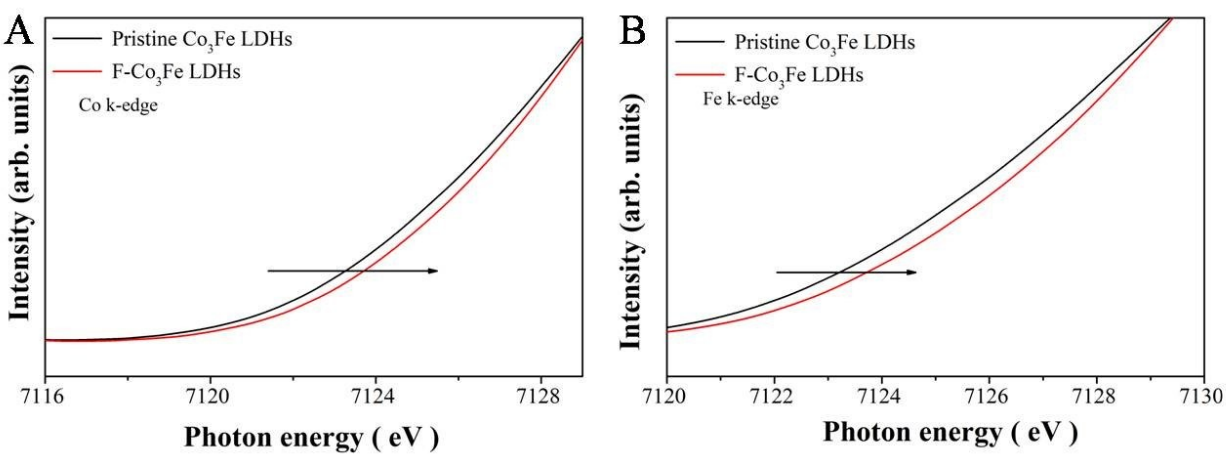

Figure S12. Magnified adsorption edge of Co k-edge (A) and Fe k-edge (B).

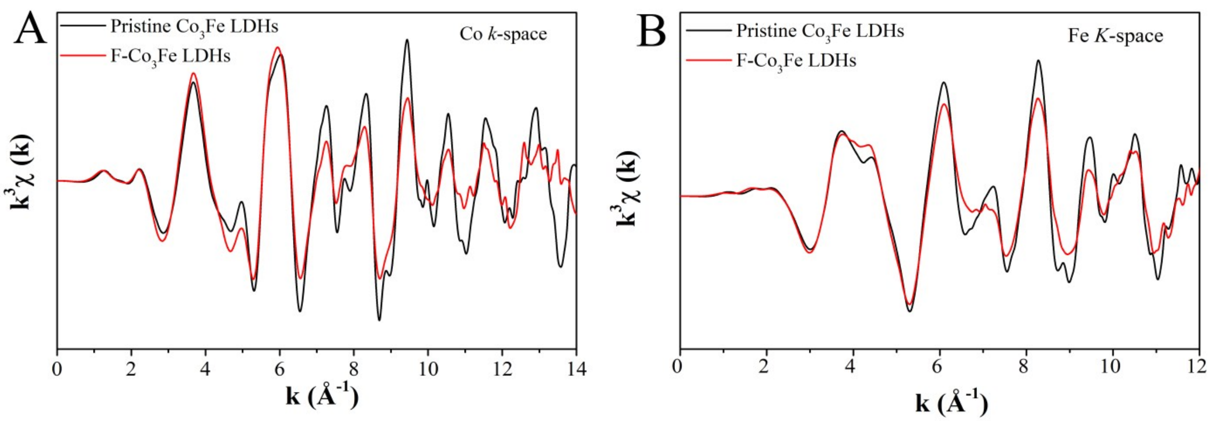

Figure S13: Co K-edge (A) and Fe K-edge (B) extended XANES oscillation functions k3x (k).

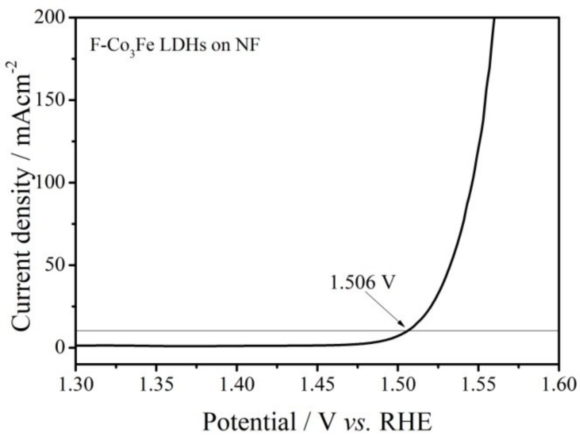

Figure S14. OER performance of F-Co_3Fe LDHs on Ni foam.

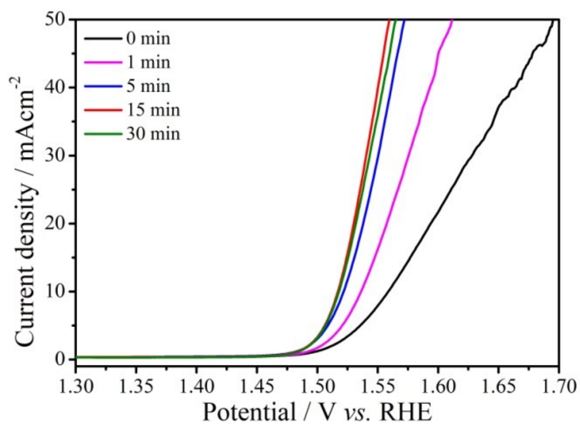

Figure S15. The OER performance of Co_3Fe LDHs that suffered from CHF_3-plasma for different time.

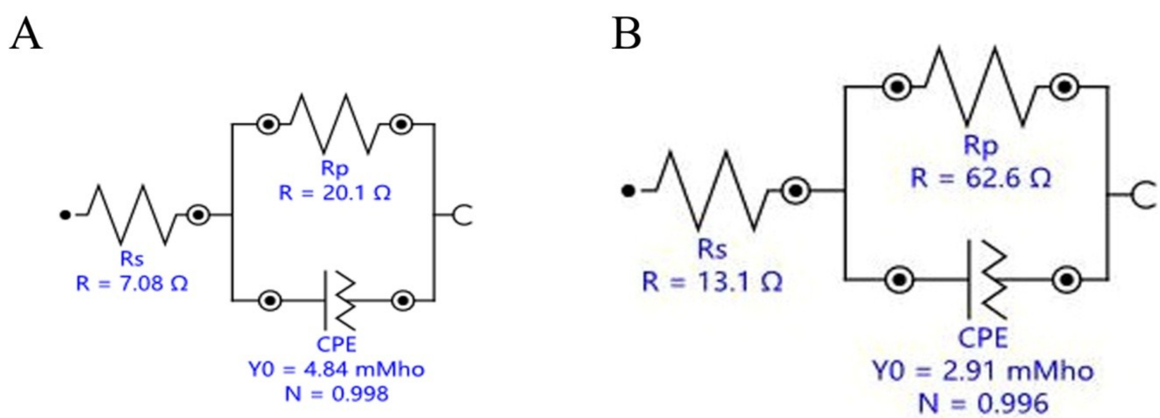

Figure S16.The equivalent circuit of pristine Co_3Fe LDHs and F-Co_3Fe LDHs.

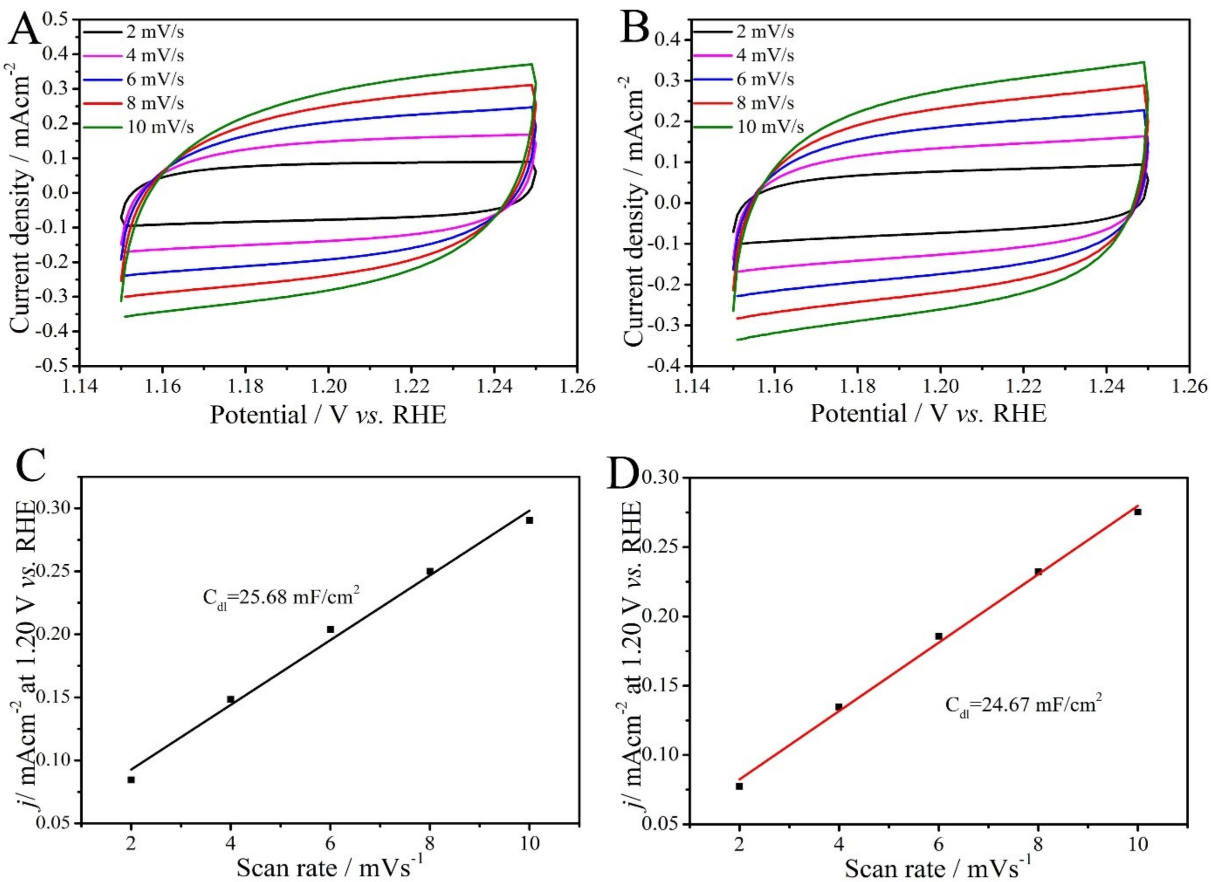

Figure S17. CV carves (A, B) and C_{dl} (C, D) for pristine Co_3Fe LDHs and F-Co_3Fe LDHs, respectively.

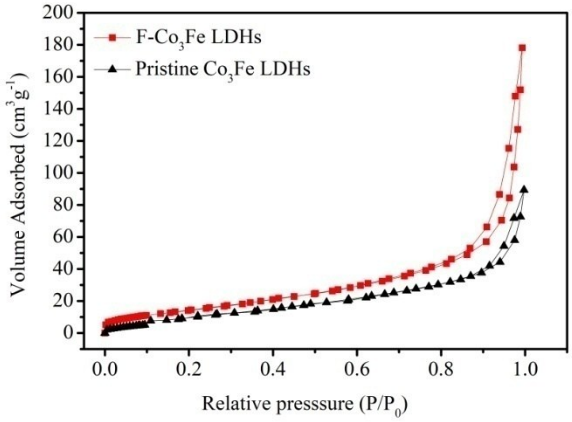

Figure S18. N_2 adsorption-desorption isotherms of pristine Co_3Fe LDHs and F-Co_3Fe LDHs.

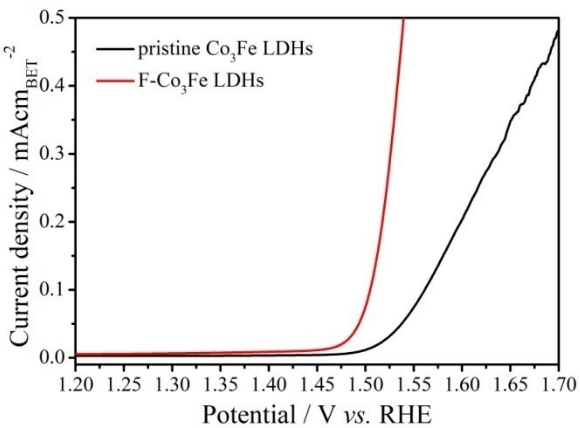

Figure S19. The LSV curves of pristine Co_3Fe LDHs and F-Co_3Fe LDHs after BET normalization in 1M KOH.

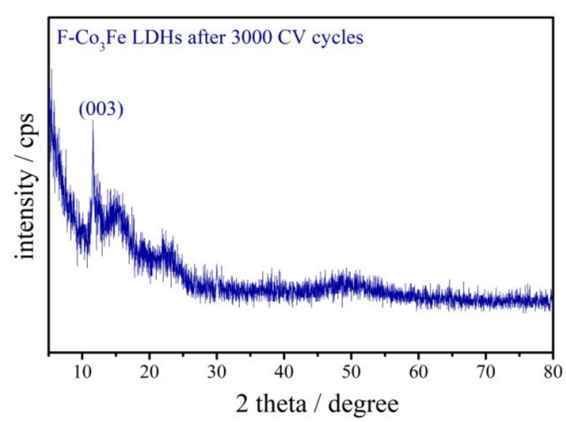

Figure S20. XRD patterns of F-Co_3Fe LDHs after 3000 CV cycles.

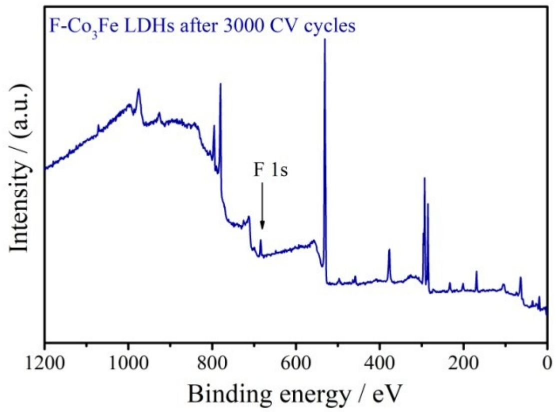

Figure S21. All XPS spectrum of F-Co_3Fe LDHs after 3000 CV cycles.

Table S1. Content of Co, Fe, C, O and F element in pristine Co_3Fe LDHs and F-Co_3Fe LDHs.

Content of element (atom %)	Pristine Co_3Fe LDHs	F-Co_3Fe LDHs
Co	54.60	51.50
Fe	18.37	17.81
O	21.79	15.01
C	5.24	6.46
F	0	9.21

Table 2. Comparison of OER performance F-Co_3Fe LDHs ultrathin nanosheets with other non-noble-metal OER electrocatalysts on glass carbon electrode in 1.0 M KOH.

Electrocatalyst	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV/dec)	Reference
F-Co_3Fe LDHs	287	39.17	This work
Co-LDHs-1	312	68.4	[1]
Mono-NiTi-MMO	320	52	[2]

F-doped $\alpha Ni(OH)_2$	325 ±5	31.89 ± 2	[3]
Co(OH)F	313	52.8	[4]
CoNi-NS/rGO	330	62	[5]
CoCo-LDH 2D nanomesh	319	42	[6]
$Ni_{0.75}Fe_{0.25}(OH)_x$	310	68	[7]
$Ni_{0.75}Fe_{0.125}V_{0.125}$-LDHs	361	39.4	[8]

Table S3. Content of Co, Fe, C, O and F element in F-Co_3Fe LDHs after 3000 CV cycles.

Content of element (atom %)	F-Co_3Fe LDHs after 3000 CV cycles
Co	8.60
Fe	5.04
O	52.44
C	30.63
F	3.29

Reference:

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