## Supporting Information

# Promoting Hydrogen Evolution Reaction through Oxygen Vacancies and Phase Transformation Engineering on Layered Double Hydroxide

### Nanosheets

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#### **Experimental Section**

#### 1. Material Synthesis

*Preparation of CoFe LDH and Ce/CoFe LDH.* To prepare CoFe LDH, 0.5 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.5 mmol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (with Co/Fe molar ratios of 1:1 were dissolved in 30 mL of deionized water. Then 0.8 mmol Na<sub>2</sub>CO<sub>3</sub> and 1.92 mmol NaOH were dissolved in 30 mL deionized water. Equal volumes of two solutions were mixed and added into a beaker under vigorous stirring 30 min. At last, 60 mL mixed solution was transferred to 100 mL stainless-steel Teflon-lined autoclave with a piece of nickel foam (NF, thickness:1.5 mm, 2.5 cm×2.5 cm) and heated at 80 °C for 48 h. For comparison, the NiCo- and NiFe LDHs were prepared by the similar approach. In order to fabricate the anode for the water splitting, the relatively thick CoFe LDH was fabricated according to the literature.<sup>1</sup> The Ce/CoFe LDH were prepared by the same method as the CoFe LDH except for adding different concentrations of cerium source. The molar ratio for Ce:(Co+Fe) is 1%, 2% and 5%, and the corresponding samples were denoted as 1%Ce/CoFe LDH, 2%Ce/CoFe LDH, and 5%Ce/CoFe LDH, respectively.

*Preparation of V-CoFe LDH and V-Ce/CoFe LDH*. The CoFe LDH and 2%Ce/CoFe LDH was put on the quartz boat in a plasma reactor, and treated using  $N_2$  plasma with different power densities (100, 200, 300, 400, and 500 W) and times.

#### 2. Electrochemical measurements

All electrochemical performances were performed by a CHI 760E electrochemical workstation. An as-prepared NF-based electrocatalysts, a graphite rod, and saturated calomel electrode (SCE) were used as working electrode, counter electrode, and reference electrode, respectively. The iR-compensation (80%) polarization curves of HER performances were tested in 1 M KOH and 1 M PBS solution (pH=7.0) by linear sweep voltammetry (LSV) at a scan rate of 5 mV s<sup>-1</sup>. For overall water splitting, the iR-compensation (80%) polarization curve in a two-electrode system was tested in 1 M KOH by LSV from 1.0 to 2.0 V at a scan

rate of 5 mV s<sup>-1</sup>. The accelerated durability tests were conducted by performing up to 4000 CV cycles in 1 M KOH with a sweep rate of 0.1 V s<sup>-1</sup> in the potential range of 0.3 to 0 V (vs. RHE). The electrochemically active surface areas (ECSA) were measured via cyclic voltammograms (CVs) at various scan rates in small potential range. The electrochemical impedance spectroscopy (EIS) at -0.132 V (vs. RHE) was collected with frequency range from 0.1 Hz to 100 KHz and alternating voltage of 5 mV. All potentials for HER were calibrated reversible hydrogen electrode using to (RHE) the equation:  $E_{RHE}=E_{SCE}+0.0591\times pH+0.2412$ , where  $E_{RHE}$  and  $E_{SCE}$  are the potentials versus RHE and the measured potentials versus SCE reference electrode, respectively. Oxygen and hydrogen evolution for overall water splitting were collected in an air-tight cell applied at 10 mA cm<sup>-2</sup>. The amount of gases was measured with a gas chromatograph (Shimadzu, GC-2014C) every 20 min.

#### 3. Characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out using Zeiss Supra55 and JEM 2100F microscope for morphology observation. X-ray photoelectron spectroscopic (XPS) analysis was conducted on an ESCALAB 250Xi using a monochromatic Al K $\alpha$  X-ray source. Renishaw inVia Microscope Raman were taken using a Raman spectrometer with a laser wavelength of 532 nm. Electron Paramagnetic Resonance (EPR) spectra of the samples were recorded on a JEOL-JES-FA-200 spectrometer at -150 °C. Atomic force microscopy (AFM) were taken on the Dimension Edge for structure observation. The crystal structure and orientation properties of the obtained films were studied by X-ray diffraction measurements (Rigaku, SmartLab). 2theta-beta maps (beta: the direction along Debye rings) were obtained with a two-dimensional (2D) pixel area detector (Dectris, PILATUS 100 K), and a collimator with 200 micro-m diameter. The detector length from the samples was fixed at 105 mm.

#### 4. DFT calculation

All DFT calculations were carried out by Vienna ab-Initio Simulation Package (VASP).<sup>2</sup> Core electrons are described by pseudopotentials generated from the projector augmented wave method,<sup>3</sup> and valence electrons are expanded in a plane-wave basis set with an energy cutoff of 450 eV. The Perdew-Burke- Ernzerh (PBE) exchange correlation functional with the on-site Coulomb Repulsion U term was used. According to previous literatures,<sup>4</sup> the value of U is selected 4.3 eV for Fe and 4.0 eV for Co. The 2D CoFe-LDHs is modeled by a  $(2\times 2)$ supercell consisting of 80 atoms and a vacuum of 16 Å. For the sampling of Brillouin-zone integrals, Gamma centered k-points grid of  $4 \times 4 \times 1$  was used. All the atom positions in the CoFe-LDHs were optimized. The convergence criterions of force and energy were set as 0.01 eV Å<sup>-1</sup> and 10<sup>-4</sup> eV, respectively. Generally, the HER rate of catalyst was affected by the adsorption/desorption energetics of H\* intermediate on its surface. It is widely accepted that the value of free energies of hydrogen adsorption ( $\Delta G_{\rm H}$ ) on the catalyst can be used as a good descriptor for its activity toward HER. To estimate  $\Delta G_H$  at zero potential and pH = 0, we calculated the binding energies  $\Delta E_H$  of H\* intermediate and corrected them with zero point energy (ZPE) and entropy (TS) using  $\Delta G_H = \Delta E_H + \Delta ZPE - T\Delta S$ . Here,  $\Delta E_H$  and  $\Delta G_H$  are calculated with respect to  $H_2(g)$ .

#### References

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**Figure S1**. SEM images of (a) CoFe LDH, (b) V-CoFe LDH, (c) Ce/CoFe LDH, and (d) V-Ce/CoFe LDH. Scale bars: (a-d) 200 nm.



Figure S2. AFM images of (a-c) CoFe LDH and (d-f) V-CoFe LDH.



Figure S3. (a,d,e) TEM images, (b) SAED pattern, and (c) FFT image of CoFe LDH.



Figure S4. (a,d,e) TEM images, (b) SAED pattern, and (c) FFT image of V-CoFe LDH.

The lattice of 0.26 nm corresponds to (012) and (311) phases of CoFe LDH and CoFe<sub>2</sub>O<sub>4</sub>, respectively. Besides, the lattice of 0.21 nm can be attributed to (107) and (400) phases of CoFe LDH and CoFe<sub>2</sub>O<sub>4</sub>, respectively.



Figure S5. TEM images Ce/CoFe LDH.



Figure S6. TEM images V-Ce/CoFe LDH.



Figure S7. AFM images of (a-c) Ce/CoFe LDH and (d-f) V-Ce/CoFe LDH.



Figure S8. SEM images of CoFe LDH powder.









Ce/CoFe LDH





Figure S9. (a) XRD patterns, (b) 2D XRD mappings, and (c,d) the lattice strains of CoFe LDH powder and Ce/CoFe LDH powder with  $N_2$  plasma treatment at 500 W for different times.

In **Figure R9**, both CoFe LDH and Ce/CoFe LDH were plasma etched in various times (0, 10, 30, 120, 300, and 600 s) for comparison. Clearly, it shows a similar tendency for both CoFe LDH and Ce/CoFe LDH after etching. The (003) and (006) peaks representing LDH become weak with increasing plasma time from 10 s to 30 s, following with the disappearance after 120 s. On the contrary, the (111) peak representing CoFe<sub>2</sub>O<sub>4</sub> shows a little bit strong intensity with increasing plasma time. These results are consistent with XRD data shown in Figure S9a. It provided an evidence that both CoFe<sub>2</sub>O<sub>4</sub> and CoFe LDJ existed before plasma treatment, while the original CoFe<sub>2</sub>O<sub>4</sub> kept and CoFe LDH transformed to CoFe<sub>2</sub>O<sub>4</sub> during plasma process.



**Figure S10.** (a) Co 2p, (b) Fe 2p, and (c) O 1s spectra of CoFe LDH and V-CoFe LDH; (d) corresponding element ratio of Co, Fe, O, and C.

The Co and Fe are with atomic ratio of 1:1 (Co: 1.03 at%; Fe: 1.51 at%) before plasma treatment. After plasma treatment, the Co and Fe are with the ratio of 1:2 (Co: 1.68 at%; Fe: 3.78 at%).



**Figure S11.** (a) Co 2p, (b) Fe 2p, (c) O 1s, and (d) Ce 3d XPS spectra of Ce/CoFe LDH and V-Ce/CoFe LDH; (e) corresponding element ratio of Co, Fe, Ce, O, and C.

Co, Fe, and Ce are with a ratio of 3:6:1 for both samples.



Figure S12. Raman spectra of CoFe LDH and V-CoFe LDH.



Figure S13. Flat-band potentials of CoFe LDH and V-CoFe LDH from Mott-Schottky plots.



Figure S14. EPR of CoFe LDH and V-CoFe LDH.



Figure S15. IR-corrected polarization curves for CoFe LDH in  $N_2$  plasma treatment for 10 s with different power densities.



**Figure S16.** (a) IR-corrected polarization curves for Ce/CoFe LDH with various Ce concentrations; (b) IR-corrected polarization curves for 2%Ce doped CoFe LDH with  $N_2$  plasma treatment for 10 s with different power densities; (c) IR-corrected polarization curves for 2%Ce doped CoFe LDH with  $N_2$  plasma treatment at 500 W for different times.



**Figure S17.** IR-corrected polarization curves for Ce/CoFe LDH and V-Ce/CoFe LDH on carbon cloth in 1 M KOH.

From **Figure S9**, the Ce/CoFe LDH powder sample shows the CoFe<sub>2</sub>O<sub>4</sub> phase after plasma etching at 500 W for 5 min. It indicates that the LDH transfers to the cobalt-iron oxide. The samples without and with plasma etching were further dropped on carbon cloth for LSV measurement. From **Figure S17** it is sure that the V-Ce/CoFe LDH shows an improved HER activities.



**Figure S18.** (a-d) Cyclic voltammetry curves as a function of scan rate of (a) CoFe LDH, (b) Ce/CoFe LDH; (c) V-CoFe LDH, and (d) V-Ce/CoFe LDH in 1 M KOH.



Figure S19. XPS N 1s spectra for V-Ce/CoFe LDH.



**Figure S20.** IR-corrected polarization curves for CoFe LDH, V-CoFe LDH, Ce/CoFe LDH, and V-Ce/CoFe LDH in PBS solution (pH=7).



Figure S21. SEM images of CoFe LDH: (a,c) thick LDH; (b,d) thin LDH used in this work.



**Figure S22.** IR-corrected polarization curves for CoFe LDH and V-CoFe LDH (thick LDH) in 1 M KOH. The sample was plasma-treated at 500 W for 10 s.



**Figure S23.** IR-corrected polarization curves for (a) NiFe LDH and (b) NiCo LDH without and with plasma etching in 1 M KOH. The Ce/CoFe LDH was plasma-treated at 500 W for 10 s.



Figure S24. (a) SEM and (b-d) TEM images of V-Ce/CoFe LDH after 4000 cycling measurement.



**Figure S25.** (a) Co 2p, (b) Fe 2p, (c) O 1s, and (d) Ce 3d XPS spectra of V-Ce/CoFe LDH before and after 4000 cycling measurements; (e) corresponding element ratio of Co, Fe, Ce, O, and C.

After cycling measurement, Co, Fe, and Ce are with a ratio of 4:5:1.



**Figure S26.** H<sub>2</sub> and O<sub>2</sub> evolution and faradic efficiency produced by overall water-splitting device using CoFe LDH as anode and V-Ce/CoFe LDH as cathode.



Figure S27. UPS spectra of Ce/CoFe LDH and V-Ce/CoFe LDH.

Electrocatalyst	Substrate	Overpotential (10 mA cm <sup>-2</sup> ) (mV vs. RHE)	Tafel (mV dec <sup>-1</sup> )	Reference
V-Ce/CoFe LDH	Nickel foam	73	69	This work.
CoFe LDH-F	Nickel foam	166	92	ACS Appl. Mater. Interfaces 2016, 8,
				34474.
CoFe LDH	Nickel foam	320	127	Appl. Catal. B: Environ. <b>2019</b> , 253, 131.
Co <sub>0.4</sub> Fe <sub>0.6</sub> LDH/g-CN <sub>x</sub>	Glassy carbon	270	79	ACS Appl. Energy Mater. 2018, 1, 1200
CoFe LDH	Copper foam	194	46.5	Appl. Catal. B: Environ. <b>2019</b> , 244, 583.
CoFe-H-2	Nickel foam	199	171	Nano Energy <b>2017</b> , 41, 327
СоFе	Nickel foam	110	35	Small <b>2017</b> , 14, 1702568.
Co-Fe NPs	Carbon fiber	220	73	Catal.Today <b>2019</b> ,
	paper			DOI:10.1016/j.cattod.2019.01.060.
α-CoFe(OH) <sub>x</sub>	Nickel foam	122	/	ChemElectroChem <b>2019</b> , 6, 2415.
CoFe-LDH@g-C <sub>3</sub> N <sub>4</sub>	Glassy carbon	417	71	Mater. Chem. Front. <b>2019</b> , 3, 520.
	Carbon fiber			
NiCoFe	cloth	200	70	ACS Energy Lett. 2016, 1, 445.
Co <sub>1-x</sub> Fe <sub>x</sub> -LDH	Nickel foam 205	205	98	ACS Appl. Mater. Interfaces
		205		<b>2018</b> , 10, 42453
Co0.75Fe0.25-NC	Glass carbon	202	68	J. Power Sources <b>2018</b> , 389, 249.

**Table S1.** Comparison of the HER performances of CoFe LDH-based electrocatalysts in 1 MKOH.