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$_3$)$_2$·6H$_2$O and 0.5 mmol Fe(NO$_3$)$_3$·9H$_2$O (with Co/Fe molar ratios of 1:1 were dissolved in 30 mL of deionized water. Then 0.8 mmol Na$_2$CO$_3$ 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.$^1$ 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$^{-1}$. 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\(^{-1}\). 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\(^{-1}\) 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 to reversible hydrogen electrode (RHE) using the equation: 

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \times pH + 0.2412 \]

where \( E_{\text{RHE}} \) and \( E_{\text{SCE}} \) 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\(^{-2}\).

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).\(^2\) Core electrons are described by pseudopotentials generated from the projector augmented wave method,\(^3\) 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,\(^4\) 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 (2×2) supercell consisting of 80 atoms and a vacuum of 16 Å. For the sampling of Brillouin-zone integrals, Gamma centered k-points grid of 4×4×1 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\(^{-1}\) and \(10^{-4}\) 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 (\(\Delta G_H\)) 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

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$_2$O$_4$, respectively. Besides, the lattice of 0.21 nm can be attributed to (107) and (400) phases of CoFe LDH and CoFe$_2$O$_4$, 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.
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 N₂ 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 CoFe₂O₄ 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 CoFe₂O₄ and CoFe LDJ existed before plasma treatment, while the original CoFe₂O₄ kept and CoFe LDH transformed to CoFe₂O₄ 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 N₂ 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 N₂ plasma treatment for 10 s with different power densities; (c) IR-corrected polarization curves for 2%Ce doped CoFe LDH with N₂ 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$_2$O$_4$ 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$_2$ and O$_2$ 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.
**Table S1.** Comparison of the HER performances of CoFe LDH-based electrocatalysts in 1 M KOH.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Substrate</th>
<th>Overpotential (10 mA cm⁻²) (mV vs. RHE)</th>
<th>Tafel (mV dec⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-Ce/CoFe LDH</td>
<td>Nickel foam</td>
<td>73</td>
<td>69</td>
<td>This work.</td>
</tr>
<tr>
<td>Co₃₀Fe₇₀₋₄₋LDH/g-CN₆</td>
<td>Glassy carbon</td>
<td>270</td>
<td>79</td>
<td>ACS Appl. Energy Mater. 2018, 1, 1200</td>
</tr>
<tr>
<td>CoFe LDH</td>
<td>Copper foam</td>
<td>194</td>
<td>46.5</td>
<td>Appl. Catal. B: Environ. 2019, 244, 583.</td>
</tr>
<tr>
<td>CoFe</td>
<td>Nickel foam</td>
<td>110</td>
<td>35</td>
<td>Small 2017, 14, 1702568.</td>
</tr>
<tr>
<td>α-CoFe(OH)$_x$</td>
<td>Nickel foam</td>
<td>122</td>
<td>/</td>
<td>ChemElectroChem 2019, 6, 2415.</td>
</tr>
<tr>
<td>CoFe-LDH@g-C₃N₄</td>
<td>Glassy carbon</td>
<td>417</td>
<td>71</td>
<td>Mater. Chem. Front. 2019, 3, 520.</td>
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<tr>
<td>Co$<em>{0.75}$Fe$</em>{0.25}$-LDH</td>
<td>Nickel foam</td>
<td>205</td>
<td>98</td>
<td>ACS Appl. Mater. Interfaces 2018, 10, 42453</td>
</tr>
<tr>
<td>Co$<em>{0.75}$Fe$</em>{0.25}$-NC</td>
<td>Glassy carbon</td>
<td>202</td>
<td>68</td>
<td>J. Power Sources 2018, 389, 249.</td>
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