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Micropore-Boosted Layered Double Hydroxide Catalysts: EIS Analysis in Structure and Activity for Effective Oxygen Evolution Reaction

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ABSTRACT Since the oxygen evolution catalysis process is vital yet arduous in the energy conversion and storage devices, it is highly desirable but extremely challenging to engineer earth-abundant, noble-metal-free nanomaterials with superior electrocatalytic activity toward effective oxygen evolution reaction (OER). Herein, we construct a prism-like cobalt-iron layered double hydroxide (Co-Fe LDH) with a Co/Fe ratio of 3:1 utilizing a facile self-templated strategy. Instead of carbon species-coupled treatment, we focus on ameliorating the intrinsic properties of LDHs as an OER electrocatalyst accompanied with hierarchical nanoflake shell, well-defined interior cavity and numerous microporous defects. In contrary to conventional LDHs synthesized *via* a one-pot method, Co-Fe LDHs fabricated in this work possess a huge specific surface area up to 294.1 m² g⁻¹ that not only provide abundant active sites, but also expedite the kinetics of

OER process. The as-prepared Co-Fe LDH electrocatalysts exhibit advanced electrocatalytic performance, and a dramatic stability of OER in an alkaline environment. Particularly, the contribution of micropore defects is clearly discussed according to the EIS analysis, in which the time constant of OER at the micropore defect is several orders of magnitude smaller than that at the exterior of Co-Fe LDHs, forcefully verifying the intrinsic catalytic activity enhancement derived from the micropore defects. This work provides a promising model to improve OER electrocatalysts activity *via* produce defects and research the contribution of micropore defects.

KEYWORDS: LDH electrocatalysts, micropore defects, EIS analysis, oxygen evolution reaction, wettability

INTRODUCTION

As the rapid consumption of fuel resources led to an increasingly serious environmental problem, efficient electrolytic water splitting has been considered as an promising strategy to meet the urgent demands of converting and storing energies.¹⁻⁴ Unfortunately, the anodic oxygen evolution reaction (OER) of water splitting involves a four-proton-coupled electron transfer process with high overpotential and sluggish kinetics, which hinders overall water splitting efficiency.^{5,6} Generally, superior electrocatalysts with a low overpotential in OER process are those state-of-the-art noble-metal-based catalysts, such as IrO₂ and RuO₂, which are costly with finite resource.^{7,8} Nevertheless, recent studies reported that it is feasible to use noble-metal-free materials as electrocatalysts for efficient OER.⁹⁻¹¹ And among these promising alternatives, transition metal layered double hydroxides (LDHs) have attracted much attention due to their tunable chemical composition, environment-friendly peculiarity, and cost effectiveness.¹²⁻¹⁴ They

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3 have a universal formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} \cdot [A^{n-}_{x/n}]^{x-} \cdot mH_2O$, and consist of positively-
4 charged host layers and weakly bound charge-balancing interlayer hydrated anions. In particular,
5 LDHs possess high ionic conductivity and superior stability in alkaline environment, which
6 makes it potential to be applied as efficient electrocatalyst for OER.^{15,16}
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13 LDHs bid fair to be high-performance electrocatalysts with the first row transition-metal
14 elements containing Co, Fe or Ni in the host layer composition.¹⁷⁻¹⁹ More recently, to pursue
15 enhanced catalytic activity, efforts have been devoted into the synergistic effects and charge-
16 transfer kinetics of carbon species-coupled LDHs. However, little attention has been paid to the
17 intrinsic properties of LDHs.²⁰⁻²² It is well-known that the oxidation reaction facilitates the
18 production of a catalytical active phase with the high valence, but in some aspects the process
19 can be hindered by the close-packed basal planes.^{3,23-25} The key to promoting the intrinsic
20 catalytic activity of LDHs is to rationally adjust surface properties or increase the number of
21 active sites.¹⁹ A facile self-templated strategy has the potential to engineer LDH nanostructures
22 for achieving advanced electrocatalytic performance,²⁶⁻²⁸ in comparison with the one-pot
23 strategies, such as electrodeposition, hydrothermal reaction, and others.^{29,30}
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39 Nowadays, the self-templated strategy, directly and efficiently converting templates into
40 hollow structures especially with complex architectures, has attracted increasing attention.³¹⁻³³
41 Lou's group pioneered in advanced self-templated methods and elegantly divided them into three
42 categories, including "Selective etching", "Outward diffusion" and "Heterogeneous
43 contraction".²⁷ To establish well-defined multiple or hierarchical hollow structure, "Outward
44 diffusion" is applied by relocating the mass in templates from inner region to outer region.^{27,28}
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Based on the self-templated strategy, structural defects are expected to arise in LDHs fabrication process. It is worth mentioning that the structural defects are beneficial to boost the activity of

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3 electrocatalyst *via* the vast active sites exposure and superior charge transport capabilities,
4 certified by more and more studies.¹⁹ Although more and more studies have certified the
5 significant effect of defects on electrocatalyst, the contribution and cause of structural defects to
6 the overall electrocatalytic performance of catalyst is rarely studied. Generally, electrochemical
7 impedance spectroscopy (EIS) is an effective technique, in which the impedance of an
8 electrochemical system is studied as a function of the frequency of an applied a.c. wave. When a
9 steady-state system is perturbed (say by an applied a.c. voltage), it relaxes to a new steady state.
10 The time (in seconds) taken for this relaxation is known as the time constant “ τ ”, and the analysis
11 of relaxation process would provide information about the system. In the case of the frequency
12 domain, the fast processes with a low time constant occur at high frequencies, while the slow
13 processes with a high time constant occur at low frequencies.^{34,35}

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29 Herein, we constructed a highly efficient and LDHs-based OER catalyst through the self-
30 templated strategy. The defective Co-Fe LDHs exhibit remarkable OER activity and excellent
31 stability primarily by integrating the advantages of defect-boosted structure and superior charge
32 transport capability. More importantly, we clearly observe the defects structure and deeply
33 discusses the contribution of micropore defects. On account of EIS data, the time constant of
34 OER at the micropore defects is several orders of magnitude smaller than that at the exterior of
35 Co-Fe LDHs, forcefully certifying the good electrocatalytic activity derived from the micropore
36 defect. In addition, the good wettability of the defective Co-Fe LDHs further contribute to high
37 electrocatalytic performance. The findings in this work are conducive to the development of a
38 viable route to designing cost-effective electrocatalysts for OER.

53 **EXPERIMENTAL SECTION**

Synthesis of the Co precursor

The Co precursor was synthesized according to the literature work with a little modification.²⁸ C₄H₁₄CoO₈ (0.35 g) and PVP (0.75 g) were dissolved and ultrasonically mixed for 5 min in ethanol (50 mL) at room temperature. The obtained mixture was transferred into a 250 mL round-bottom flask, and then heated and refluxed at 90 °C under vigorous magnetic stirring for 5 h. Afterwards, the product was washed by centrifuging (5 min, 10000 rpm) with ethanol and ultrapure water for several times, and dried under vacuum to collect the Co precursor.

Synthesis of the Co-Fe layered double hydroxide (LDH)

The Co precursor (20 mg) was ultrasonically dispersed in ethanol (2 mL) as solution A. FeSO₄·7H₂O (10 mg) was ultrasonically dissolved in ultrapure water (5 mL) followed by the addition of ethanol (5 mL), and this solution was denoted as solution B. Next, solution A and solution B were mixed quickly, and aged for 10 min under N₂ protection. A green precipitate of Co-Fe LDHs was collected, followed by centrifuging and washing with ethanol for several times, and drying in vacuum oven.

Electrochemical Performance

All electrochemical measurements were executed on a workstation (CHI 660E, CHI Instruments Inc, Shanghai) in a three-electrode setup, coupled with a graphite electrode as a counter electrode, Hg/HgO (1 M NaOH) electrode as a reference electrode, and a modified rotating disk electrode (RDE, $\Phi = 4$ mm) as a working electrode. To prepare the working electrode, the catalyst powder (2 mg) was added in a solution (1 mL) of ethanol-ultrapure water (1:1 by vol) and Nafion (1 wt.%), and ultrasonically dispersed to obtain homogeneous catalyst ink. Then, the ink (2 mg mL⁻¹, 10 μ L) was dropped onto the well-polished RDE surface, and air-dried at

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3 ambient environment. KOH solution (1 M) was utilized as the electrolyte during the whole test,
4 and the rotation rate of the RDE is 1600 rpm. The polarization curves were surveyed by the
5 linear sweep voltammetry (LSV) in the range of 0.2 ~ 0.8 V vs. Hg/HgO at a scan rate of 5 mV s⁻¹
6 with 95% *iR* correction. Particularly, 20 cycles of cyclic voltammetry (CV) measurements at a
7 scan rate of 50 mV s⁻¹ were executed to stabilize the current before the LSV test. To dynamically
8 evaluate the OER kinetics of catalysts, polarization curves were plotted by the potential versus
9 logarithm current density (*j*). The stability was studied using LSV and amperometric *i-t* methods
10 at a fixed potential. Electrochemical impedance spectroscopy (EIS) was measured by applying
11 an AC amplitude of 5 mV over the frequency range of 10⁶ ~ 10⁻¹ Hz. In this study, the recorded
12 potential was all quoted against the reversible hydrogen electrode (RHE) by the equation: $E_{\text{RHE}} =$
13 $E_{\text{Hg/HgO}} + 0.098 + 0.059 \text{ pH}$. The overpotential (η) was calculated based on the following
14 formula: $\eta = E_{\text{RHE}} - 1.23 \text{ V}$. The current density was calibrated *via* dividing the current by
15 geometric area of the working electrode.
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34 RESULTS AND DISCUSSION

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39 Figure 1a depicts the fabrication process of defect-boosted Co-Fe LDHs based on a self-
40 templated strategy using a Co precursor. The crystal structures of the as-prepared samples were
41 inquired by X-ray diffraction (XRD). As illustrated in Figure S1, the XRD pattern of the Co
42 precursor reveals the diffraction peaks that could be assigned to cobalt acetate hydroxide (JCPDS
43 No. 22-0582). When a suitable content of Fe ions was incorporated, all the broadened diffraction
44 peaks in Figure 1b could be indexed to Co-Fe LDHs (JCPDS No. 50-0235). The results
45 demonstrated LDH structures are produced effectively. In the rest of the paper, unless otherwise
46 stated, we mention Co-Fe LDHs as that with a Co/Fe ratio of 3:1 for convenience, which refers
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3 to the initial ratio in the synthetic process. From field-emission scanning electron microscopy
4 (FESEM) images (Figure 1c, d), it can be seen that the individual Co precursor exhibits a smooth
5 prismatic architecture and the prisms have a length of approximately 500 nm. Transmission
6 electron microscopy (TEM) images of the Co precursor further illustrate the compact and solid
7 characteristics of the samples (Figure S2). For Co-Fe LDHs, FESEM image confirms the
8 retention of the prismatic architecture (Figure 1e), however, the smooth surface eventually
9 becomes hierarchical shells composed of disorderly oriented nanoflakes. For comparison, the
10 FESEM images with various Co/Fe ratios are shown in Figure S3. The results illustrate the
11 obvious influence of Fe incorporation towards the morphology of samples with various Co/Fe
12 ratios, in which the prismatic architectures are gradually collapse into disordered nanoflakes with
13 the increasing amount of Fe ions. Figure 1f displays the results of energy-dispersive X-ray
14 spectroscopy (EDX) mapping, which clearly confirms the presence and the uniform distribution
15 of Co and Fe in LDH structures. LDH prisms with hierarchical shells and well-defined inner
16 cavity are further exhibited in TEM images (Figure 1g, h), where abundant porous structure with
17 loosely interconnected Co-Fe LDH nanoflakes can be observed. Figure 1i, S4 show high-
18 resolution TEM (HRTEM) images of Co-Fe LDHs, from which a set of dislocations, lattice
19 distortions, and micropore defects are observed. This unique structural feature provides rich
20 active sites and a brilliant mass transfer pathway. Besides, the TEM images with various Co/Fe
21 ratios are shown in Figure S5. Integrating the FESEM and TEM images towards the Co/Fe ratios
22 of 6:1, 3:1, 3:2, and 1:1, prismatic architectures are gradually collapse into disordered nanoflakes
23 with the increasing amount of Fe ions, while we can only observe the abundant porous structure
24 with loosely interconnected nanoflakes in the Co/Fe ratio of 3:1. The results illustrate the
25 obvious influence of Fe ions incorporation towards the morphology of Co/Fe ratios, and only the
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3:1 ratio resulted in the complete formation of Co-Fe LDH structures, which is consistent with the generally acknowledged phenomena that x in the universal formula of LDHs should lie in the range 0.2-0.33 to stabilize LDH compounds.³⁹ Figure 1j exhibits lattice fringes with a d -spacing of 0.26 nm that can be indexed to (012) lattice planes of Co-Fe LDHs. The inset in Figure 1j shows the corresponding Fast Fourier Transform (FFT) pattern, corresponding well to XRD results in Figure 1b.

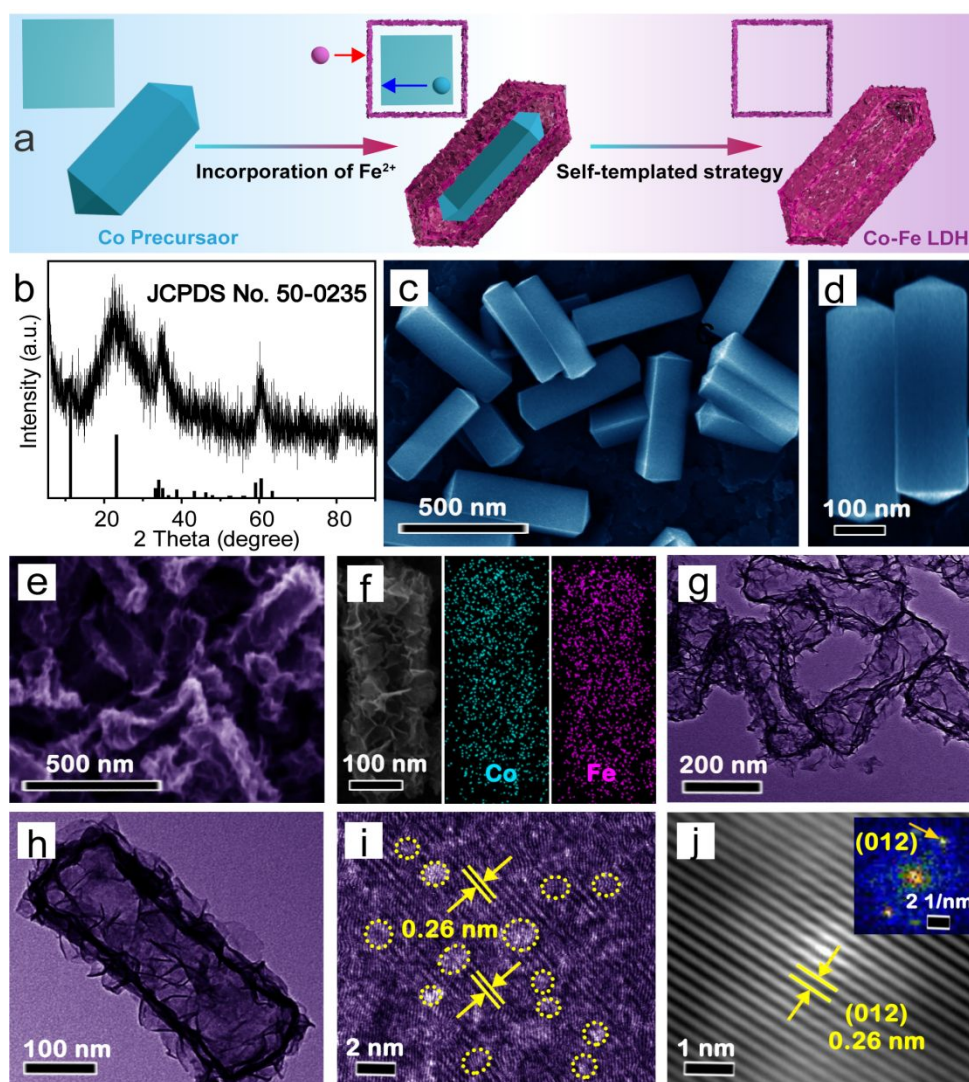


Figure 1. a) The fabrication process of defect-busted Co-Fe LDHs. b) XRD pattern of Co-Fe LDHs. FESEM images of c, d) Co precursor, and e) Co-Fe LDHs. f) Elemental mapping of an individual Co-Fe LDH prism. g) TEM image, h, i) HRTEM image, and j) simulated HRTEM image and FFT pattern (inset) of Co-Fe LDHs.

Typical X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical composition and surface electronic states of Co-Fe LDHs. As shown in Figure S6a, the overview survey spectrum indicates the coexistence of Co, Fe, O, and C elements in samples with different binding energies (BE). The spectral peaks at 531.8 and 284.5 eV belong to O1s and C1s, respectively (Figure S6b, c). The high-resolution XPS of Co 2p spectrum (Figure 2a) is split into Co 2p_{3/2} and Co 2p_{1/2}, located at 781.4 and 797.5 eV, respectively, accompanied by two satellite peaks. The prominent Co 2p_{3/2} satellite peak is generally considered an indicator of a high-spin Co²⁺ state.^{14,20} The Fe 2p spectrum has been fitted into two BE peaks at 711.6 and 725.4 eV due to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Figure 2b). Considering the BE difference of 13.8 eV, it is believed that the Fe species exist in the form of Fe³⁺.²³ Figure 2c displays the Raman spectrum of Co-Fe LDHs. Characteristic peaks at 456 and 535 cm⁻¹ are observed, and attributed to the vibration modes of Metal-Oxygen-Metal (M-O-M) bond.³⁶ These results unambiguously confirm the successful formation of Co-Fe LDHs.

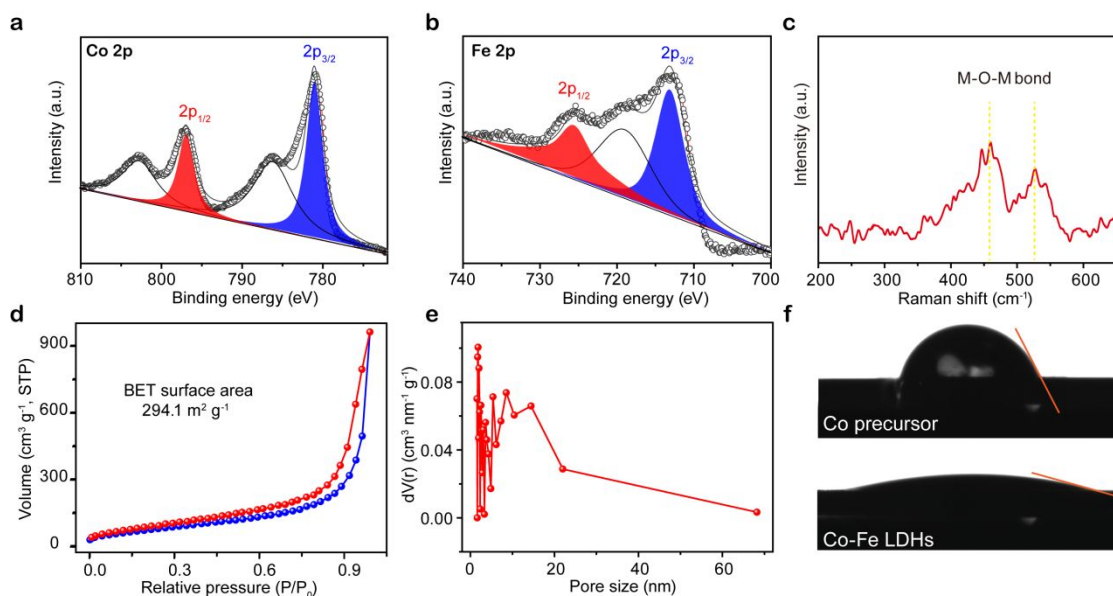


Figure 2. XPS analysis of a) Co 2p region, and b) Fe 2p region for Co-Fe LDHs. c) Raman spectrum of Co-Fe LDHs. d) Nitrogen adsorption–desorption isotherm, and e) the corresponding pore size distribution of Co-Fe LDHs. f) Contact angle measurements.

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3 As a key factor for electrocatalyst, Brunauer-Emmett-Teller (BET) specific surface area and
4 porosity distribution were evaluated by N₂ adsorption/desorption isotherms (Figure 2d, e) using
5 Barrett–Joyner–Halenda (BJH) method. Co-Fe LDHs with hierarchical prismatic structure have a
6 high BET surface area of 294.1 m² g⁻¹ which is greater than that of recently reported LDH
7 electrocatalysts.^{17,19} The average pore diameter is calculated as 1.4 nm. The hysteresis of the
8 curve initiating from a low P/P₀ value implies the microporous structure of the loosely packed
9 LDH nanoflakes, which is consistent with TEM observations in Figure 1i. As we discussed in the
10 previous section, the incorporation of Fe ions in Co precursor generated numerous micropore
11 defects in crystal lattices of Co-Fe LDHs. Undoubtedly, engineering affluent defects into Co-Fe
12 LDHs facilitates exposure of abundant active sites, thereby enhancing electrocatalytic activity.
13 Figure 2f depicts the static contact angles of Co precursor and Co-Fe LDHs. Co-Fe LDHs have a
14 much smaller contact angle than that of the Co precursor, revealing a more hydrophilic surface of
15 the former. The good surface wettability of the catalyst facilitates electrolyte penetration and
16 accelerates hydroxyl group migration and oxygen release.³⁶ Therefore, this result portends the
17 good OER performance derived from the defect-rich structures based on the self-templated
18 strategy.

19 We thoroughly explored and analyzed the key factors related to electrocatalytic activity and
20 gained insight into OER performance. The effect of Co/Fe ratio in LDH prisms on polarization
21 curves was investigated. As depicted in Table S1 and Figure 3a, LDH prisms with a Co/Fe ratio
22 of 3:1 possess the lowest onset potential and the highest current density at 1.65 V (vs. RHE). To
23 analyze the electrochemical active surface area (ECSA), the double-layer capacitance (*C_{dl}*) was
24 characterized by CV at a suitable potential range without a redox process (Figure S7). Figure 3b
25 shows the *C_{dl}* of samples at the Co/Fe ratios of 6:1, 3:1, 3:2, and 1:1, respectively. The sample

with a Co/Fe ratio of 3:1 displayed the largest C_{dl} in accordance with the analysis result of polarization curves, certifying that the incorporation of Fe ions in an appropriate ratio contributed to the improvement of OER activity. In addition, the turnover frequencies (TOFs), directly related to actual number of active sites, are calculated to reveal the inherent properties of Co-Fe LDHs for OER. As shown in Figure 3c, as-prepared Co-Fe LDHs with a Co/Fe ratio of 3:1 have a TOF of 0.312 s^{-1} , which is the largest among Co-Fe LDH samples in this work.

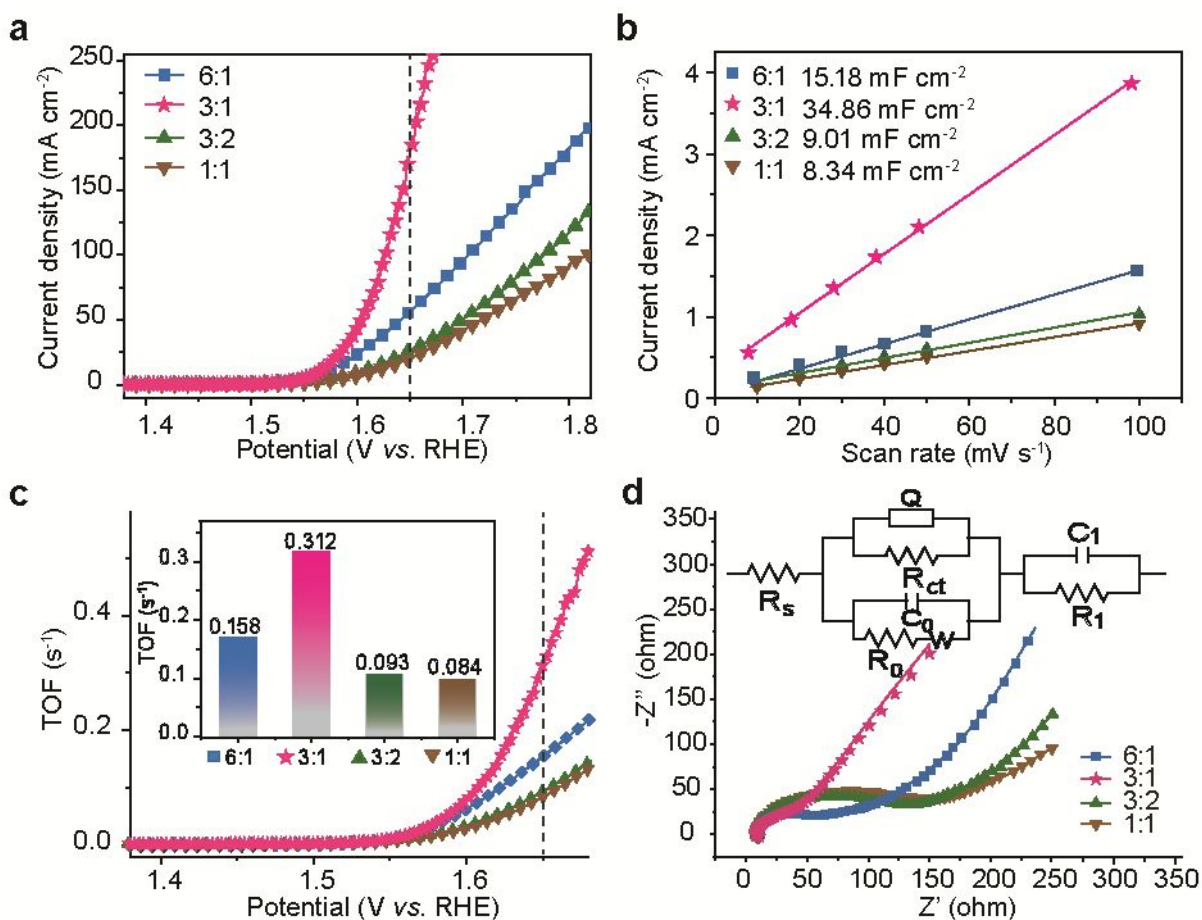


Figure 3. a) Polarization curves, b) Current density differences plotted against scan rates under a non-Faradaic range. c) TOFs of Co-Fe LDHs at different Co/Fe ratios of 6:1, 3:1, 3:2 and 1:1 (inset shows the TOF values at 1.65 V vs. RHE for different Co/Fe ratios of Co-Fe LDHs). d) Nyquist plots with a fitted equivalent circuit (inset).

Both the electrochemical measurements provide electrocatalytic properties averaged over all active sites on the surface of LDHs, thereby obscuring the true contribution of elementary processes. In order to understand in depth the contribution of micropore defects to the overall electrocatalytic performance, we performed electrochemical impedance spectroscopy (EIS) measurements on Co-Fe LDH samples, taking into account that EIS was a powerful tool for decoupling the electrochemical processes in complex electrodes. Figure 3d presents the Nyquist plots and fitting results for EIS measurements with a proper equivalent circuit model for Co-Fe LDHs with different Co/Fe ratios. In the equivalent circuit model, R_s corresponds to the series resistance of the electrolyte, the electrodes, and the circuit leads. The two RC circuits in the middle of the diagram describe the charge kinetics at the interface between the electrolyte and the outer surface as well as the micropore defects of Co-Fe LDHs, respectively. The third RC circuit is associated with adsorption/desorption of the intermediates of the OER. Obviously, the Nyquist plot of LDHs with a Co/Fe ratio of 3:1 possesses the smallest semicircle diameter in the high frequency region, indicating that proper incorporation of Fe ions in LDH prisms enabled ultrafast charge transfer at the electrolyte/electrode interface. The minimum R_s value also indicates that LDHs with a Co/Fe ratio of 3:1 has the highest conductivity among the four compositions. In Table S2, we can unambiguously assign the high frequency semicircle in EIS curves to the kinetic process at the interface between the electrolyte and the micropores in the working electrode. The much smaller time constant provides conclusive evidence that the active sites on the surface of the micropore defects are much more effective in electrocatalytic OER, in good agreement with previous observations by other researchers.^{3,9,34} It was proposed that the synergistic effect of Co and Fe in LDHs lowered the energy barrier of OER, thereby accelerating the reaction kinetics.³⁷⁻³⁹ We found that the synergistic effect is more effective for the active sites

at the surface of the micropore defects. The capacitance of the micropore defects is much larger than that of the outer surface of the electrodes, further confirming the higher electrocatalytic activity of the micropore defects in Co-Fe LDHs. The contribution to the larger capacitance is partly due to the much larger specific surface area of the micropore defects than that of the outer surface of the electrodes (Table S3). The capacitance of the adsorption and the desorption process implies that the active sites for electrocatalytic OER account for only a small part of the overall surface lattice atoms, and there is still great potential to improve the performance of Co-Fe LDH electrocatalysts *via* more advanced structural design in future work.

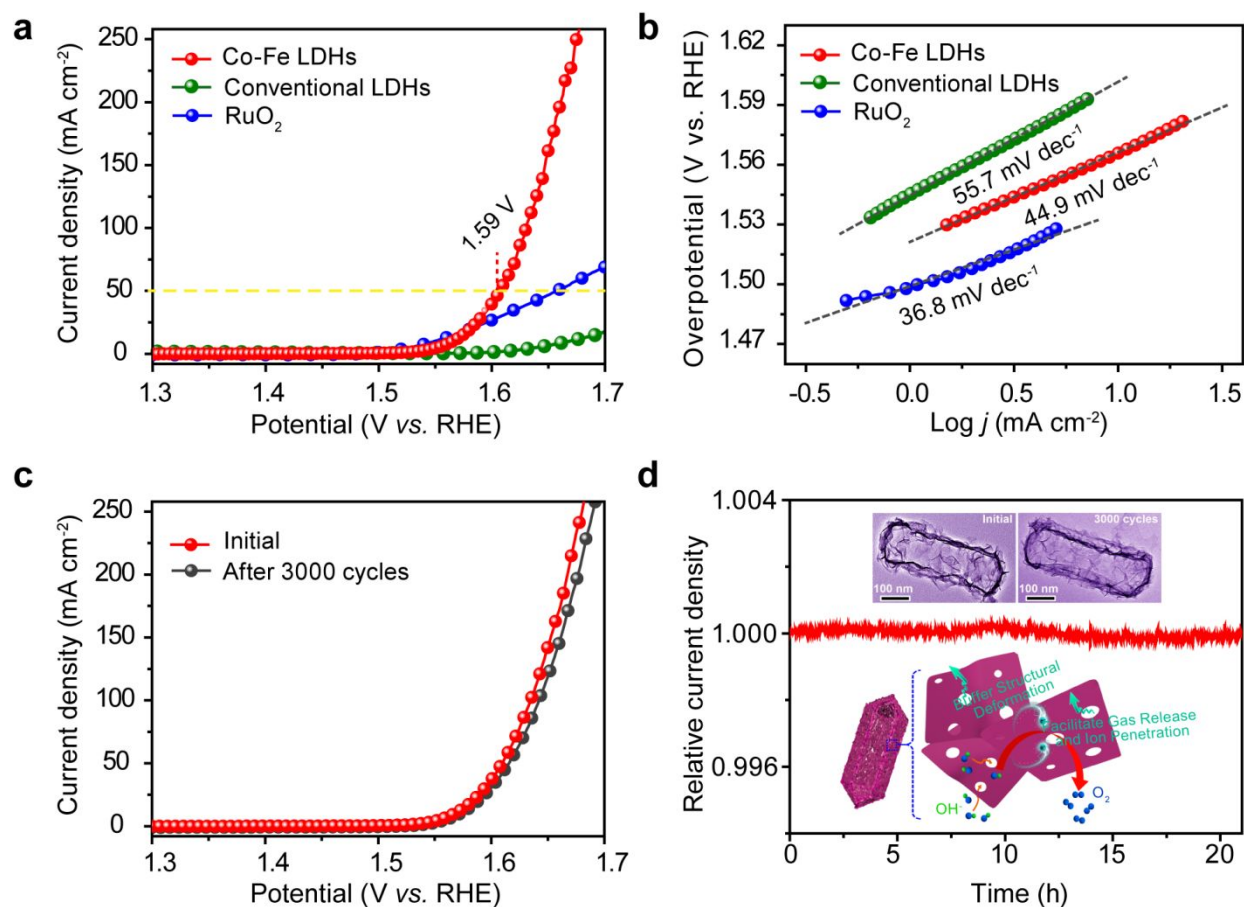


Figure 4. a) Polarization curves and b) Tafel plots in 1 M KOH. c) LSV curves of Co-Fe LDHs before and after 3000 cycles of CV scanning. d) Chronoamperometric measurement at a fixed operating potentials (the inset shows the corresponding TEM images before and after 3000 cycles (upside), and illustration of OER process over Co-Fe LDHs (underside)).

Inspired by the high ionic conductivity and reasonable stability of defect-boosted LDHs in an alkaline environment, we evaluated the appealing OER activity of as-prepared Co-Fe LDHs in a 1 M KOH solution, compared with the conventional LDHs and commercial RuO₂. As illustrated in Figure 4a, Co-Fe LDHs have a low operating potentials of 1.59 V (*vs.* RHE) corresponding to a low overpotential value of 360 mV at a current density (*j*) of 50 mA cm⁻¹, which is much lower than that of conventional LDHs and commercial RuO₂. As the overpotential increases, the difference of current density of Co-Fe LDHs augments faster than that of RuO₂ and conventional LDHs. To deeply delve into the reaction kinetics of Co-Fe LDHs, we have executed a relevant Tafel analysis, and Figure 4b displays the Tafel slope. The value for Co-Fe LDHs (44.9 mV dec⁻¹) is much lower than that of conventional LDHs (55.7 mV dec⁻¹) and commercial RuO₂ (44.9 mV dec⁻¹). Figure S8 reveals the results of C_{dl}, TOF, and EIS between as-prepared Co-Fe LDHs and conventional LDHs. Compared to the as-prepared Co-Fe LDHs, conventional LDHs manifest lower Tafel slope and TOF values. Besides, their Nyquist plot possesses the larger semicircle diameter in the high frequency region. As expected, the as-prepared Co-Fe LDHs have better performance, which could be caused their hierarchical prismatic structure with a high BET surface area since the conventional LDHs have a lower BET surface area of 20.59 m² g⁻¹ (Figure S9). To further reveal the intrinsic activities, the LSV curves of different samples were normalized by electrochemical surface area (non-Faradic double layer capacitance), in which the electrochemical surface areas are calculated from double-layer charging curves, assuming a C_{dl} value of 0.06 mF cm⁻² for a smooth oxide surface.⁴⁰ As seen in Figure S10, the as-prepared Co-Fe LDHs shows the lowest overpotential at a fixed current density, which is basically matched with that in Figure 3a,4a. Altogether, those results demonstrate the prominent catalytic kinetics of Co-Fe LDHs in an alkaline environment. As listed in Table S4, the OER activity of Co-Fe

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3 LDHs in this work is superior or at least comparable to those reported noble-metal-free catalysts
4 of LDHs. Furthermore, the durability and the stability of Co-Fe LDHs for OER in an alkaline
5 environment were investigated. When a sequential CV scanning of 3000 cycles was carried out,
6 the decrease of the current density is negligible compared to the initial density (Figure 4c).
7 Figure 4d exhibits the relative constant current density, referring to the ratio of current density (j)
8 to initial current density (j_0), at a fixed operating potentials, which further demonstrates the
9 promising long-term stability of Co-Fe LDHs. Moreover, as displayed in Figure S11 and the
10 inset (upside) in Figure 4d, the morphology of Co-Fe LDHs remain almost unchanged after the
11 electrochemical aging, and well-defined hierarchical LDH prisms were conserved. After the
12 long-term OER, XRD and XPS characterizations were further executed for the as-prepared Co-
13 Fe LDHs. As seen in Figure S12, the crystal structures of the mentioned sample were inquired,
14 and all the broadened diffraction peaks are nearly indexed to Co-Fe LDHs (JCPDS No. 50-
15 0235). Figure S13 displays the related chemical composition and surface electronic states
16 through XPS analysis. The results of XRD and XPS characterizations towards the as-prepared
17 Co-Fe LDHs after the long-term OER further verify the good stability, as seen in Figure S12,13.

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38 The OER process over the Co-Fe LDHs is depicted in the inset (underside) of Figure 4d. And
39 the structural benefits of LDHs in OER catalysis derived from the intrinsic catalytic activity
40 enhancement can be summarized as the following: (i) the hierarchical prismatic structure of Co-
41 Fe LDHs endows a high BET surface area for ion interaction, thus facilitating the charge
42 transport; (ii) the abundant microporous defects can not only produce wealthy active phase
43 around the pores and notably enrich the active phase, but also provide wettable channels for ion
44 penetration and intimate contact, which is crucial for the remarkably enhanced OER; (iii) the
45 well-distributed microporous defects can serve as an effective buffer area for the volume change,
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3 and then ensure the good electrochemical stability, which refrains from material swelling or
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5 severe mechanical deformation during the continuous OER operation.
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8 9 **CONCLUSIONS**

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13 In short, defect-boosted Co-Fe LDHs were prepared *via* a facile self-templated strategy and
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15 applied as highly efficient OER catalysts. Benefiting from the rich micropore defects with a large
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17 number of active sites, the as-prepared Co-Fe LDHs show impressive electrocatalytic
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19 performance and stability. It is worth mentioning that the versatility of the microporous structure
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21 not only endows the hierarchical LDH prisms with abundant active site exposure, enhanced
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23 charge/mass transfer capability, and fast reaction kinetics, but also promises a huge exposed
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25 surface and excellent wettability between the electrocatalyst and the electrolyte. The study
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27 highlights a cost-effective route to improving the inherent characteristic of noble-metal-free
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29 catalysts for gaining deeper insights into electrocatalytic design.
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35 36 **ASSOCIATED CONTENT**

37 38 39 **Supporting Information**

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43 Sectional description of the experimental and corresponding analytical data as well as
44
45 some additional results
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48 49 **AUTHOR INFORMATION**

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Notes

The authors declare no competing financial interest.

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