Supporting Information

Sowing Ru atoms on Defects CoAl LDHs for Boosting Alkaline Water Splitting

Yingjie Li[a]*****, *Shuangwu Bao*[a], *Zhihua Feng*[a], *Xing Li,*[a] *Sheng Yin*[a], *Jiexiang Xia*[a]*****, *Huaming Li*[b]

a. School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

b. School of Chemistry and Chemical Engineering, Institute for Energy Research, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China

Chemicals

$Al(NO_3)_3\cdot 9H_2O$ (>=99%), NH_4F (>=96%), urea ($CO(NH_2)_2$, >=99%) and NaOH (>=96%) were purchased from Sinopharm Chemical Reagent Co., Ltd, $RuCl_3\cdot xH_2O$ (36-40% Ru), $Co(NO_3)_2\cdot 6H_2O$ (99%) were obtained from Macklin Biochemical Technology Co., Ltd.

Preparation of CoAl LDHs nanosheets

The CoAl LDHs nanosheets grown on Ni foam were prepared via hydrothermal method. Briefly, 1 mmol $Co(NO_3)_2\cdot 6H_2O$, 0.5 mmol $Al(NO_3)_3\cdot 9H_2O$, 4 mmol NH_4F, and 10 mmol $CO(NH_2)_2$ were put into a 100 mL beaker, 36 mL deionized water was added, and the solution was stirred until it became clear and transparent. Then, the solution was transferred to a 40 mL polytetrafluoroethylene container and the clean Ni foam was put into it. Ni foam with a size of 2.5 cm◊3 cm was ultrasonically cleaned in HCl solution (6 mol L^{-1}), deionized water, and ethanol in order for 5 minutes. Finally, the polytetrafluoroethylene container in the sealed autoclave was placed in an oven and kept at 120 ˚C for 12 hours. After the autoclave cooled naturally, the sample was taken out, washed with deionized water, and dried overnight at 60 ˚C.

Preparation of D-CoAl LDHs nanosheet arrays

The CoAl LDHs was immersed in NaOH solution (5 mol L^{-1}) for 2 hours at room temperature. After the etching was completed, the sample was thoroughly washed with deionized water and dried overnight at 60 ˚C.

Preparation of Ru/D-CoAl LDHs nanosheet arrays

The D-CoAl LDHs was immersed in 0.25 mg mL^{-1} $RuCl_3$ solution for 6 hours. Then, the sample was thoroughly washed with deionized water and dried overnight at 60 ˚C.

Preparation of Ru/CoAl LDHs nanosheet arrays

The CoAl LDHs was immersed in 0.25 mg mL^{-1} $RuCl_3$ solution for 6 hours. Then, the sample was thoroughly washed with deionized water and dried overnight at 60 ˚C.

Electrochemical measurements

All electrochemical tests were carried out on a CHI 760E electrochemical workstation. The HER and OER performances of the as-prepared materials was evaluated in 1 M KOH solution using three-electrode system. The prepared samples were used as the working electrode, while the carbon rod and Hg/HgO electrodes were used as the counter electrode and reference electrode, respectively. For comparison, the commercial Pt/C and RuO_2 were also tested as working electrode. The linear sweep voltammetry (LSV) curves were recorded with a scan rate of 5 mV s^{-1}, and all LSV curves were corrected by iR compensation. For TMAOH test, the LSV curves were collected via negative potential sweep, and the other LSV curves were obtained by positive potential sweep. The Tafel slope was obtained according to the LSV curves. The electrochemical stability of the catalyst was tested using chronoamperometry (i-t) technology at a given overpotential. The electrochemical double-layer capacitance (C_{dl}) was used to quantitatively calculate the electrochemical active surface area (ECSA), The value of C_{dl} was calculated based on cyclic voltammetry curves with the range of 0.05 - 0.10 V vs. Hg/HgO at a scan rate of 10-50 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) data were recorded at -1.24 V vs. Hg/HgO for HER and 0.49 V vs. Hg/HgO for OER in the frequency range of 0.1 to 100 kHz, respectively. TOF is calculated from the formula：$TOF = j * A/(Z * F * n)$.

j represents the current density at a given overpotential. A is the area of the catalyst electrode at work. Z is the number of electrons transferred during an individual reaction. F is the faraday constant (96485 C mol^{-1}). n is the number of moles of the Ru atoms.

A two-electrode system was used to assess the performance of overall water splitting. The prepared catalysts were used as the anode and cathode. The electrolyte and scan rate were the same as three-electrode system. The EIS test was carried out at 1.47 V vs. Hg/HgO in the frequency range of 0.1 to 100 kHz, and the stability test was carried out by i-t technology.

Characterizations

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded on HITACHI Regulus-8100 at 20 kV and HITACHI HT-7800 at 100 kV, respectively. High resolution TEM (HRTEM) operated on Thermo Fisher TF-G20 at 200 kV. The atomic resolution high angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and corresponding energy dispersive spectroscopy (EDS) mapping were operated on JEMARM200F TEM at an accelerating voltage of 300 kV. X-ray diffraction (XRD) data were collected by a Shimadzu XRD-6000 instrument at 40 kV with scanning rate of 5°/min (Cu Kα radiation, 2θ=10-80°). Fourier transform infrared (FT-IR) spectra were measured by a Nicolet iS50 spectrophotometer. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was operated on Agilent 5110 instrument. X-ray Photoelectron Spectroscopy (XPS) spectra were collected on Thermo ESCALAB 250XI.

The influence of $RuCl_3$ concentration

The influence of $RuCl_3$ solution concentration on the performances of electrochemical activities was studied, as shown in Figures S1. Figure S1a and S1b showed that the HER performance slightly improved as the concentration of $RuCl_3$ solution increased. When the $RuCl_3$ concentration was further increased up to 0.25 mg mL^{-1}, the HER overpotential at 100 mA cm^{-2} was significantly reduced to 170 mV. The Ru/D-CoAl LDHs with 0.35 mg mL^{-1} $RuCl_3$ solution immersion exhibited the best HER performance with an overpotential of only 125 mV to reach a current density of 100 mA cm^{-2}. Subsequently, Figure S1c and S 1d displayed the OER performances of a series of Ru/D-CoAl LDHs with different $RuCl_3$ immersion concentration. Unlike HER, the OER activity was significantly enhanced when the Ru was introduced. As the concentration of $RuCl_3$ solution increased, the OER activity slightly improved from 332 mV at 100 mA cm^{-2} in 0.10 mg mL^{-1} $RuCl_3$ solution to 326 mV and 325 mV in 0.25 mg mL^{-1} and 0.35 mg mL^{-1} $RuCl_3$ solution, respectively. Although the Ru/D-CoAl LDHs immersed in 0.35 mg mL^{-1} $RuCl_3$ solution showed the best HER and OER performance among the various Ru/D-CoAl LDHs samples, the particles on the surface of the Ru/D-CoAl LDHs impregnated in 0.35 mg/mL $RuCl_3$ solution was observed by TEM characterization (Figure S2a). Significantly, there is no obvious particles for the Ru/D-CoAl LDHs with immersion of 0.25 mg mL^{-1} $RuCl_3$ solution (Figure S2b). Considering the economic efficiency and aggregation of nanoparticles, impregnation in 0.25 mg/mL $RuCl_3$ solution was selected as the optimal loading condition. The Ru/D-CoAl LDHs sample with immersion of 0.25 mg mL^{-1} $RuCl_3$ solution was used as the main research object, named as Ru/D-CoAl LDHs.

The influence of alkali etching time

To explore the optimal conditions of alkali etching time, the electrochemical performances under different etching times were systematically investigated. As displayed in Fig. S3, the sample treated with alkali etching for 2 h exhibited the superior HER performance compared with those etched for 0.5 h, 1 h, 5 h and 12 h. Namely, an overpotential of 170 mV was required to achieve a current density of 100 mA cm^{-2} (Fig. S3a). For OER, the samples etched for 1h and 2 h delivered an overpotential of 323 and 326 mV at 100 mA cm^{-2}, respectively, which were superior than those samples obtained by 0.5 h, 5 h, 12 h alkali etching (Fig. S3b). Taking into account the performances of both HER and OER, CoAl LDHs with 2 h alkali etching was selected as the main research subject for subsequent experiments.

Figures

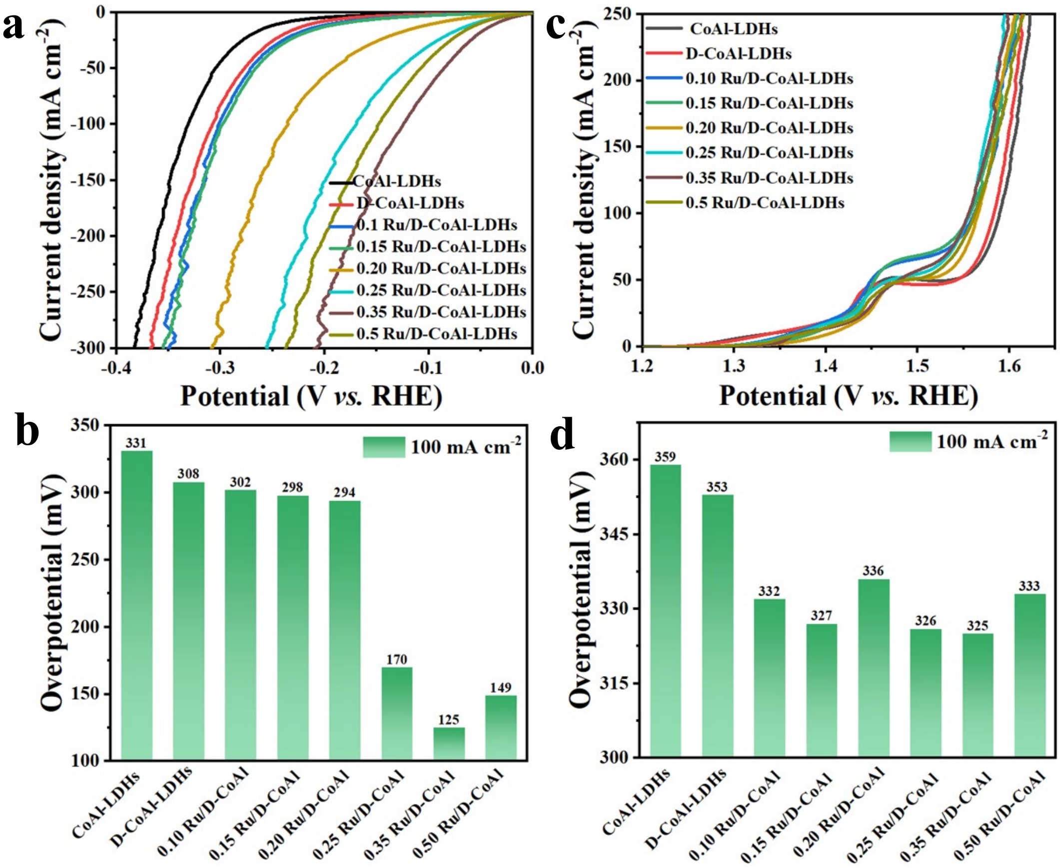

Fig. S1. (a) HER and (c) OER LSV polarization curves of CoAl LDHs, D-CoAl LDHs and Ru/D-CoAl LDHs with different concentration of $RuCl_3$ solution, and corresponding (b) HER and (d) OER overpotentials at 100 mA cm^{-2}.

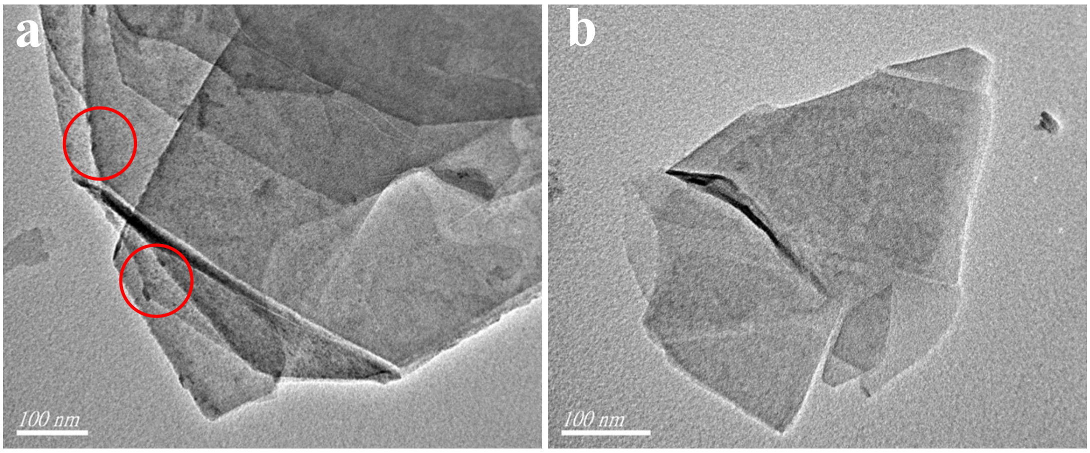

Fig. S2. TEM images of (a) 0.35 Ru/D-CoAl LDHs and 0.25 Ru/D-CoAl LDHs.

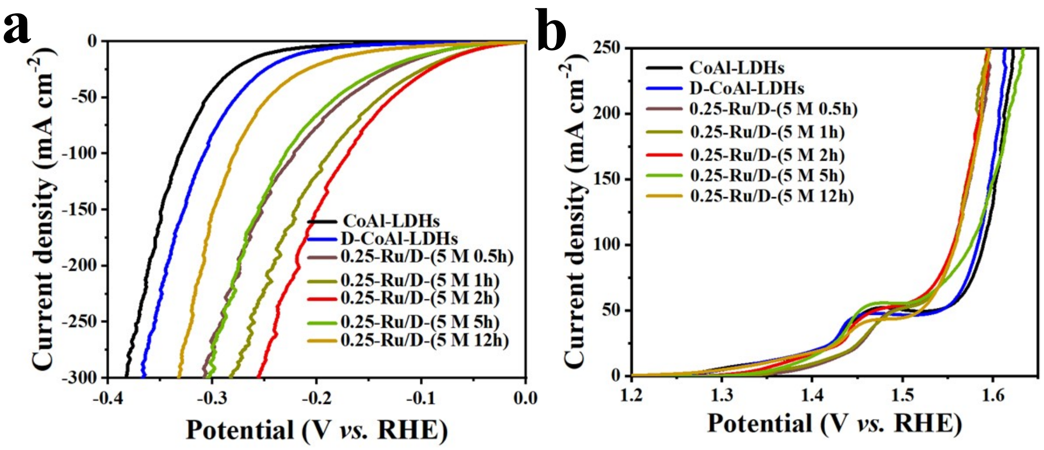

Fig. S3. Comparison of the (a) HER and (b) OER performance of samples with different etching times in 0.25 mg mL^{-1} $RuCl_3$ solution

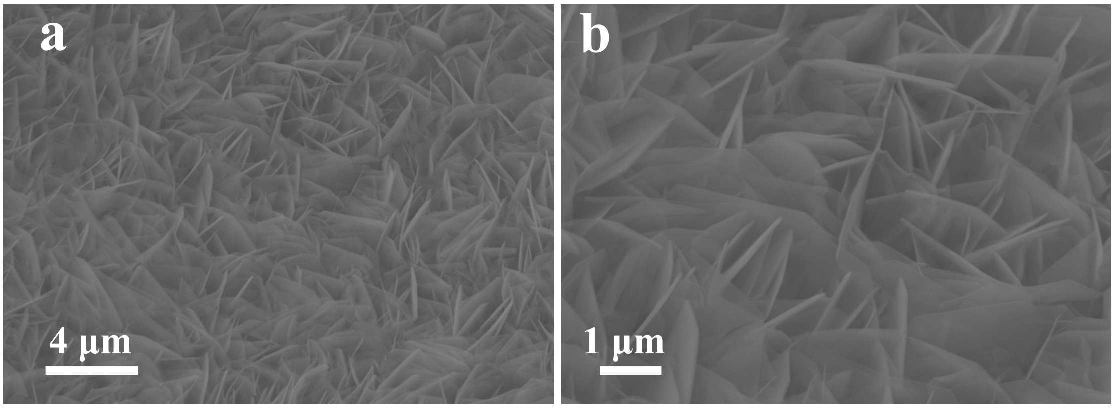

Fig. S4. (a) and (b) SEM images of CoAl LDHs.

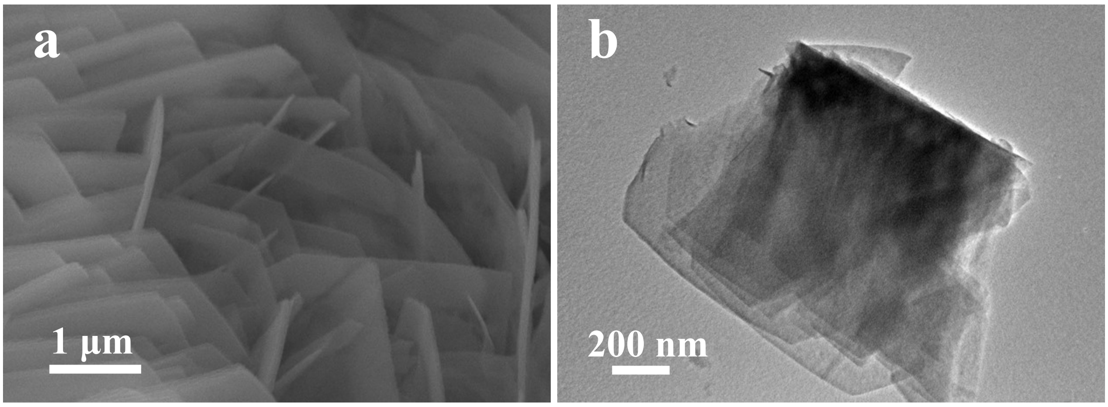

Fig. S5. (a) SEM and (b) TEM images of D-CoAl LDHs.

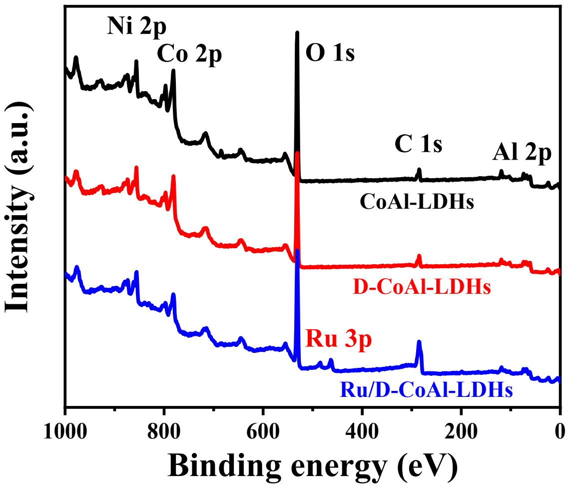

Fig. S6. XPS full spectra of CoAl LDHs, D-CoAl LDHs and Ru/D-CoAl LDHs.

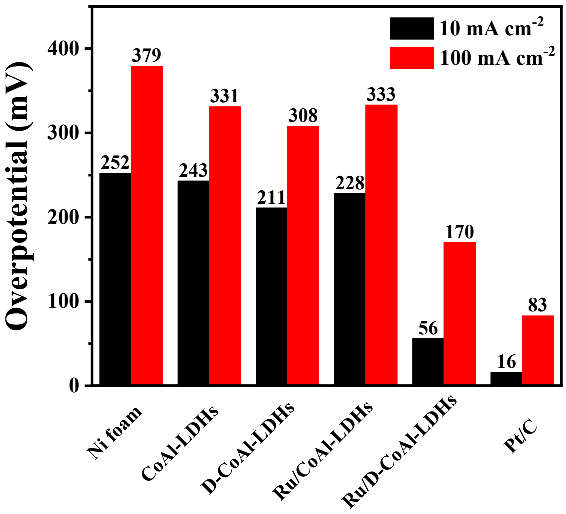

Fig. S7. The overpotentials at the current densities of 10 mA cm^{-2} and 100 mA cm^{-2} for catalyzing HER.

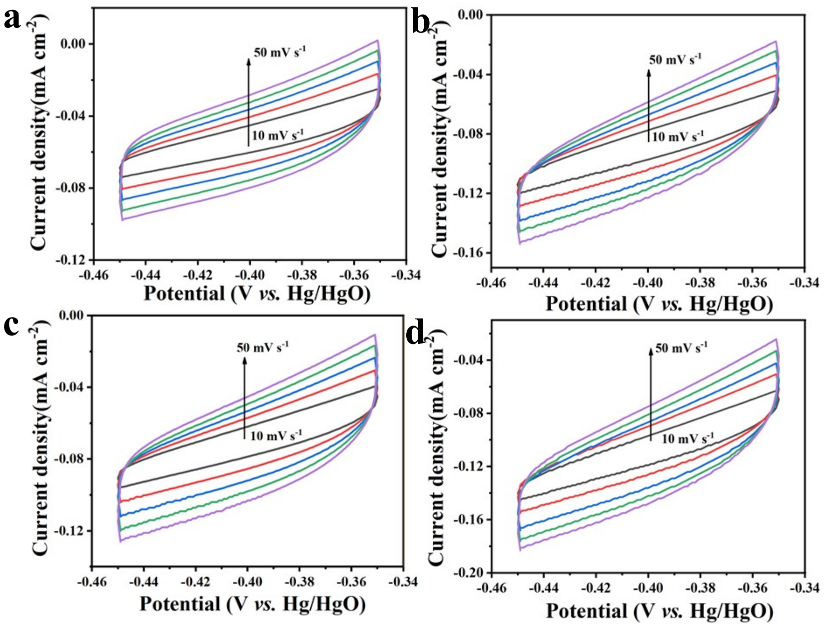

Fig. S8. Cyclic voltammetry curves of the samples at different scan rates (a) CoAl LDHs, (b) D-CoAl LDHs; (c) Ru/CoAl LDHs and (d) Ru/D-CoAl LDHs.

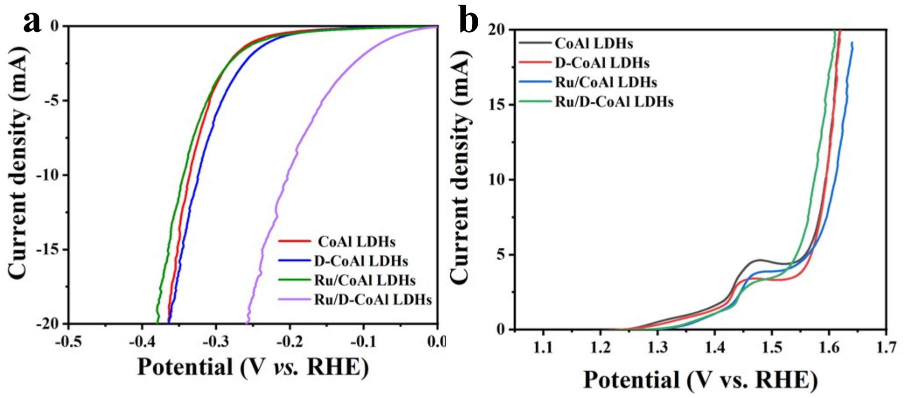

Fig. S9. The polarization curves of (a) HER and (b) OER normalized by ECSA.

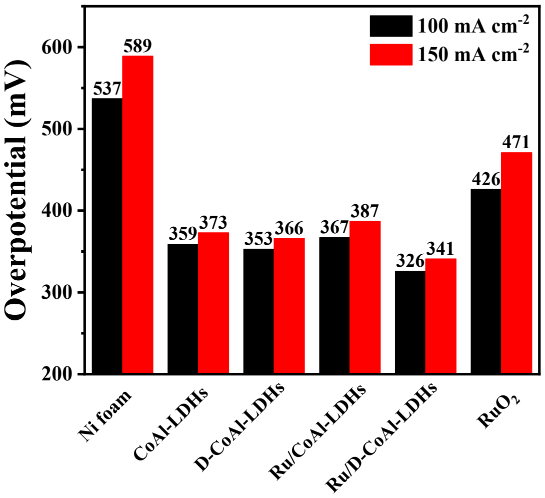

Fig. S10. The overpotentials at the current densities of 100 mA cm^{-2} and 150 mA cm^{-2} for catalyzing OER.

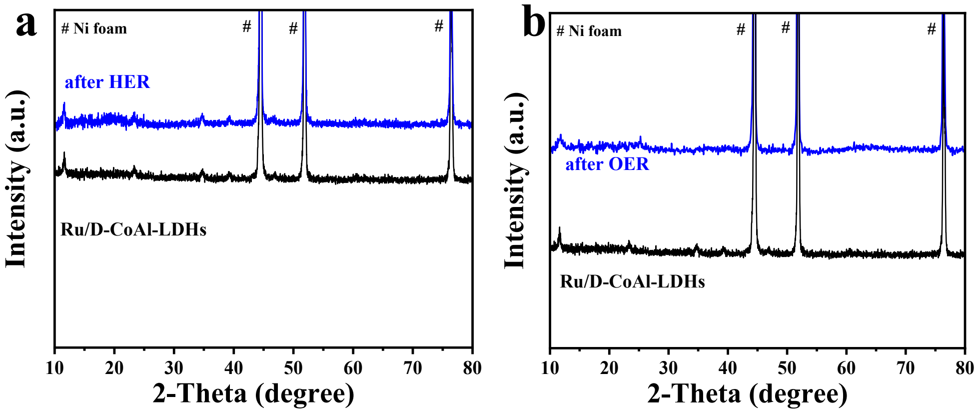

Fig. S11. XRD patterns of Ru/D-CoAl LDHs. (a) before and after HER stability test; (b) before and after OER stability test.

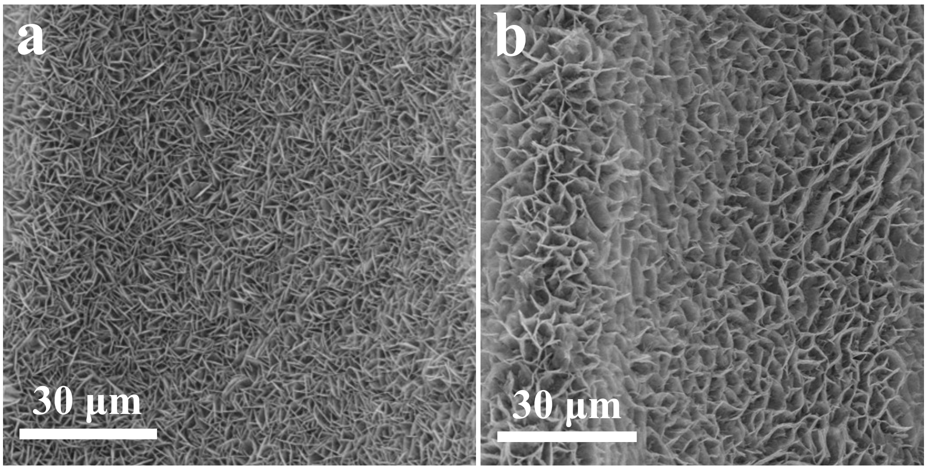

Fig. S12. SEM images of Ru/D-CoAl LDHs. (a) after HER stability test; (b) after OER stability test.

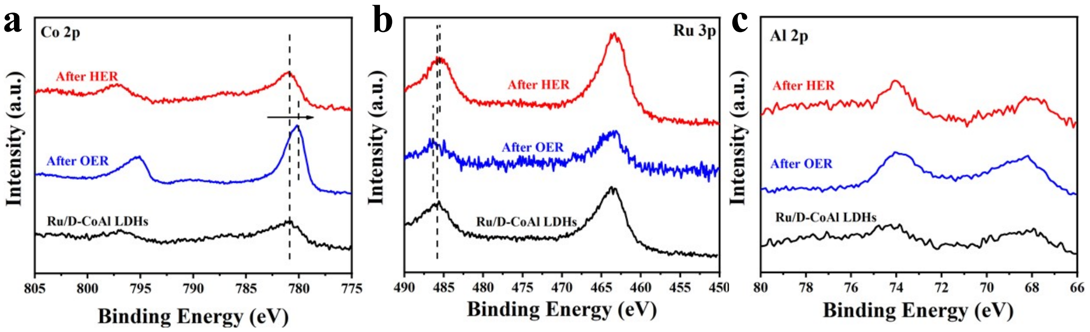

Fig. S13. The XPS spectra of (a) Co 2p, (b) Ru 3p and (c) Al 2p before and after HER/OER test.

Table S1. The atomic concentration of Co, Al and Ru on the surface

Materials	Co	Al	Ru
CoAl LDHs	5.95	7.30	-
CoAl LDHs	10.87	4.81	-

Ru/D-CoAl LDHs	2.11	1.08	0.41

Table S2. The values based on fitted equivalent circuit.

Catalysts	Rs (Ω)	Rct (Ω)	CPE
Ni foam	1.357	32.4	0.85032
CoAl-LDHs	1.068	2.151	0.96468
D-CoAl-LDHs	1.068	1.293	0.97676
Ru/CoAl-LDHs	1.192	2.211	0.94346
Ru/D-CoAl-LDHs	1.136	0.53115	0.94705
Pt/C	1.412	0.49365	0.70737

Table S3. The comparison of TOF values for various HER catalysts

Catalysts	TOF(s^{-1})	Overpotential (mV)	Electrolyte	Ref.
Ru/D-CoAl LDHs	1.03	100	1 M KOH	This work
Cu-dopedRu/$RuSe_2$ NSs/C	0.88	100	1M KOH	[1]
Ru–Mo	0.12	100	1M KOH	[2]
S_V-Ru/Ni_xS_y-4	0.02	150	1M KOH	[3]
Ru/TiO_2-A	2.38	100	1 M KOH	[4]
Ru_{1+NPs}/N−C	0.58	100	1M KOH	[5]
RuO_{2NB}/C	1.82	70	1 M KOH	[6]
Ru-RuO_2	0.69	50	1 M KOH	[7]
Pt/C	0.049	100	1 M KOH	[8]
Ru-CoP/Ni_2P	0.75	100	1 M KOH	[8]

Table S4. The comparison of TOF values for various OER catalysts

Catalysts	TOF (s^{-1})	Overpotential (mV)	Electrolyte	Ref.
Ru/D-CoAl LDHs	1.16	300	1 M KOH	This work
RuO_{2NB}/C	0.49	300	1 M KOH	[6]
Ru-NiFeP/NF	0.04628	220	1 M KOH	[9]
Ru-Ni-Co-P/NC	0.47	300	1 M KOH	[10]
Ru@Cr-FeMOF	0.215	250	1 M KOH	[11]
Ru-CoNi@NC-2	8.27	370	1 M KOH	[12]
2D D-RuO_2/G	1.25	270	1 M KOH	[13]
Ru-CoP/Ni_2P	0.017	171	1 M KOH	[8]

References

[1] K. Wang, J. Zhou, M. Sun, F. Lin, B. Huang, F. Lv, L. Zeng, Q. Zhang, L. Gu, M. Luo and S. Guo, *Adv. Mater.*, 2023, **35**, 2300980

[2] Z. Chen, H. Zeng, C. Zhang, H. Cai, Y. Jiang, J. Hu, H. Wang, J. Wang, Y. Cui, *Nano Res.*, 2025, **18**, 94907346

[3] J. Chen, H. Xu, X. Qian, Y. Liu, L. Jin, K. Wang, G. He, H. Chen, *Int. J. Hydrogen Energy,* 2025, **139**, 621-629

[4] E. Li, Y. Shen, Y. Li, Y. Zong, W. Xiao, G. Xu, J. Wang, H. Li, T. Ma, Z. Wu, L. Wang, *Appl. Catal. B Environ. Energy,* 2026, **382**, 126022

[5] S. Wang, M. Wang, Z. Liu, S. Liu, Y. Chen, M. Li, H. Zhang, Q. Wu, J. Guo, X. Feng, Z. Chen and Y. Pan, *ACS Appl. Mater. Interfaces*, 2022, **14**, 15250-15258

[6] J. Chen, S. Feng, C. Lu, J. Huang, *Chem. Eng. J.*, 2023, **468**, 143761.

[7] Y. Cong, D. Dou, L. Zhang, H. Wang, M. Liu, L. Chen, Q. Zhao, C. Li, *Fuel*, 2024, 367, 131472

[8] H. Zhang, W. Liu, Z. Li, L. Qiao, K. Chi, X. Guo, D. Cao, D. Cheng, *Adv. Sci.*, 2024, **11**, 2401398.

[9] Y. Lin, M. Zhang, L. Zhao, L. Wang, D. Cao, Y. Gong, *Appl. Surf. Sci.*, 2021, **536**, 147952.

[10] D. Wang, L. Gu, X. Luo, R. Su, Y. Shang, Y. Wang, S. Hao, Y. Yang, *J. Electroanal. Chem.*, 2022, **924**, 116875.

[11] C. Zhao, J. Wang, Y. Gao, J. Zhang, C. Huang, Q. Shi, S. Mu, Q. Xiao, S. Huo, Z. Xia, J. Zhang, X. Lu and Y. Zhao, *Adv. Funct. Mater.*, 2024, **34**, 2307917.

[12] W. Wang, S. Xi, Y. Shao, W. Sun, S. Wang, J. Gao, C. Mao, X. Guo, G. Li, *ACS Sustainable Chem. Eng.,* 2019, **7**, 17227-17236.

[13] Y. Li, Y. Wang, J. Lu, B. Yang, X. San, Z. Wu, *Nano Energy*, 2020, **78**, 105185.