Supplementary Information

Construction of Ruthenium Doped CoFe-Layered Double Hydroxide as a Bifunctional Electrocatalyst for Overall Water Splitting

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Experimental sections

Materials: Ferric nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, 99.0%) was purchased from Energy Chemical Co., Ltd. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, AR), 2-methylimidazole (2-MIM, AR) and ruthenium trichloride (RuCl$_3$, 45-55% Ru) were purchased from Shanghai Macklin Biochemical Co., Ltd. Ethanol (C$_2$H$_5$OH, AR) and urea (CH$_4$N$_2$O, 99.5%) were purchased from Shanghai Titan Scientific Co., Ltd. Potassium hydroxide (KOH, 85.0%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. All the chemicals mentioned above were used without further purification.

Synthesis of ZIF-67@NF precursor: Firstly, a piece of NF (1*1 cm^2) was sequentially preprocessed in acetone, ethanol, 3 M hydrochloric acid, and ethanol for 15 min to remove the oil stains and oxide layer on NF surface. After rising with deionized (DI) water, NF was dried in vacuum oven (60 °C) for subsequent use. Then ZIF-67 precursor was synthesis in a typical way as followed. 0.5 mmol Co(NO$_3$)$_2$·6H$_2$O was dissolved in 10 mL DI water with NF immersed in for 10 min, in order to make Co(NO$_3$)$_2$·6H$_2$O penetrate in NF adequately. 4 mmol 2-MIM was also dissolved in 10 mL DI water, and the solution was dropped swiftly in Co(NO$_3$)$_2$·6H$_2$O solution thereafter. After standing for 2 h in mixture solution, NF with ZIF-67 in-situ grown on (ZIF-67@NF) was rinsed with DI water and ethanol 3 times alternately, and then it was dried in vacuum oven (60 °C, overnight) for subsequent use.

Synthesis of CoFe-ZLDH@NF and CoFe-ZLDH/Ru@NF: Afterwards, ZIF-67@NF was immersed into 20 mL of solution containing 0.35 mmol Fe(NO$_3$)$_3$·9H$_2$O and 3.33 mmol urea. After etching and coprecipitation under 70 °C for an hour, CoFe-ZLDH precipitated on the NF (CoFe-ZLDH@NF) was obtained. It requires that CoFe-ZLDH@NF should be thoroughly washed with DI water and ethanol 3 times alternately and dried further in vacuum oven (60 °C) overnight. CoFe-ZLDH/Ru@NF was synthesized in a similar way except for adding 17.5 mg RuCl$_3$ in the mixture solution of Fe(NO$_3$)$_3$·9H$_2$O and urea.

Synthesis of CoFe-ZLDH and CoFe-ZLDH/Ru: Similar to the preparation of ZIF@NF, 0.5 mmol Co(NO$_3$)$_2$·6H$_2$O and 4 mmol 2-MIM were separately dissolved in 10 mL DI water. Then mixed two kinds of solution swiftly and let it stand for 2 h at room temperature. After the treatment of centrifuge, the ZIF-67 sediment was taken out and dried in vacuum oven (60 °C, overnight) for subsequent use. Afterwards, ZIF-67 was added into 20 mL of solution containing 0.35 mmol Fe(NO$_3$)$_3$·9H$_2$O and 3.33 mmol urea. Under the condition of 70 °C for an hour, CoFe-ZLDH bulk was obtained through centrifugation 3 times and further dried in vacuum oven (60 °C) overnight. The synthesis method of CoFe-ZLDH/Ru is similar with that of CoFe-ZLDH, only requiring to add 17.5 mg RuCl$_3$ in mixture solution of Fe(NO$_3$)$_3$·9H$_2$O and urea.

Characterization: The morphology and composition analyses were based on the following methods. Scanning electron microscope (SEM) images were obtained by using Japan Hitachi Scanning Electron Microscope (S4800). Transmission electron microscopy (TEM) characterization was performed using ThermoFisher Talos F200X, and the corresponding energy dispersive X-ray spectroscopy (EDS) graphs were carried out using 4 in-column Super-X detectors. The crystal structure of sample was characterized by X-ray diffraction (XRD, 18 KW/D/max 2550 VB/PC) and Fourier transform infrared spectrometer (FT-IR, Nicolet is50). The composition as well as valence states of the elements were examined by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi) and laser micro-Raman spectrometer (Raman, LabRAM HR). The peak positions in XPS spectrum for each element are all calibrated by the C 1s peak at 284.8 eV.

Electrochemical measurements: Given the catalysts were synthesized through in-situ growth on conductive base NF, those catalysts can be used as electrodes directly. Electrochemical measurements were performed using an electrochemical station (CHI 660E) in a three-electrode compartment (H-cell) with CoFe-ZLDH@NF or CoFe-ZLDH/Ru@NF serving as the working electrode, an Ag/AgCl/3.5 M KCl electrode as the reference electrode and Pt mesh as the counter electrode. The Ag/AgCl/3.5 M KCl reference electrode was calibrated to RHE in the 1.0 M KOH solution with Pt mesh as the counter electrode. With regard to catalysis of overall water splitting, electrochemical measurements were tested in standard two-electrode system (single cell). Besides, anode and cathode both utilized the same catalysts which were in-situ grown on NF.

All LSV curves were tested at a scan rate of 5 mV s^{-1} in 1.0 M KOH solution at room temperature and corrected with *iR* compensation (85%). For OER, the CV tests were acquired at different scan rates (20, 40, 60, 80, and 100 mV·s^{-1}) with a range of 0.44 ~ 0.54 V and 0.45 ~ 0.55 V (vs. RHE) for CoFe-ZLDH/Ru@NF and CoFe-ZLDH@NF, respectively. While for HER, the CV tests were acquired with a range of -0.80~ -0. 70 V (vs. RHE) at different scan rates (60, 80, 100, 120, and 140 mV·s^{-1}). Due to ECSA and C_{dl} satisfying this relation: ECSA = $C_{dl-catalyst}$ / C_s, comparison of ECSA among samples can be simplified to comparison of C_{dl}, which was acquired from CV curves. The EIS spectrum were tested at a frequency range of 10^5 to 0.01 Hz under the potential of 1.474 V and -0.076 V (vs. RHE) for OER and HER, respectively. For the stability measurement, the chronopotentiometry curve was tested at the constant current density of 100 mA cm^{-2} with 85% *iR* compensation. For the reason of considerable change of solution resistance in single cell, LSV curves and chronopotentiometry curve were corrected with 80% *i*R compensation.

Moreover, for overall water splitting measurements at the ampere-level current density, which is proximate to the conditions of industrial production, an AEM unit cell ($1 * 1.2$ cm^2) with flowing solution (1 M KOH) was assembled. The same as-prepared catalysts (CoFe-ZLDH/Ru@NF or CoFe-ZLDH@NF) were directly performed as both anode and cathode catalysts, which were separated by an anion exchange membrane (Sustainion X37-FA Membrane). The LSV curves were run at a scan rate of 5 mV s^{-1} at room temperature without *iR* compensation owning to the resistance tolerance brought by high current density in AEM. For long-term stability test, the chronopotentiometry curves were carried out at room temperature under the current of 500 mA (~417 mA cm^{-2}) and 1 A (~833 mA cm^{-2}).
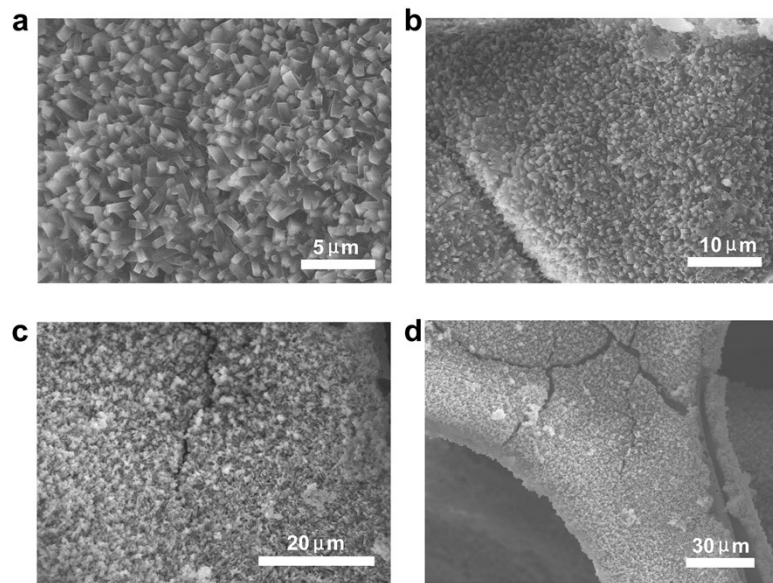
Fig. S1 SEM images of (a, b) ZIF-67 and (c, d) CoFe-ZLDH/Ru@NF at different magnifications.
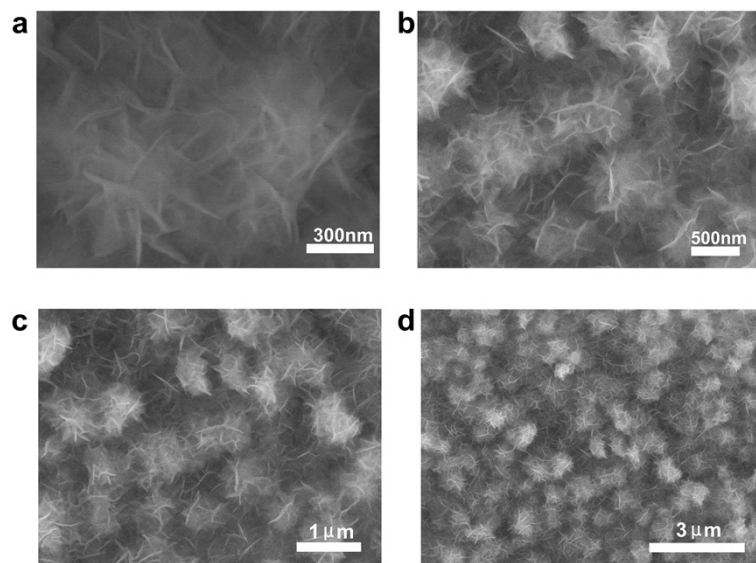
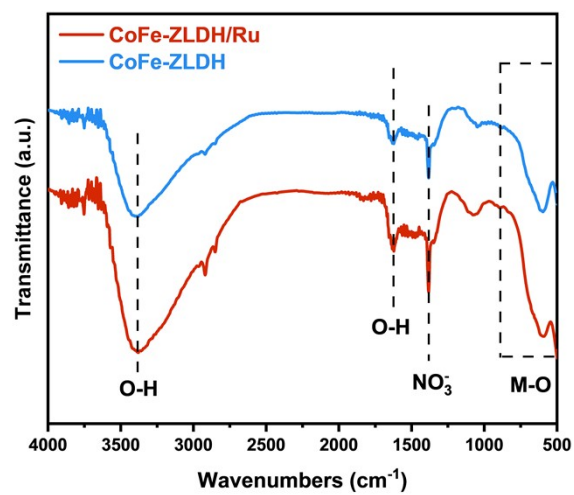**Fig. S2** SEM images of CoFe-ZLDH@NF at different magnifications.
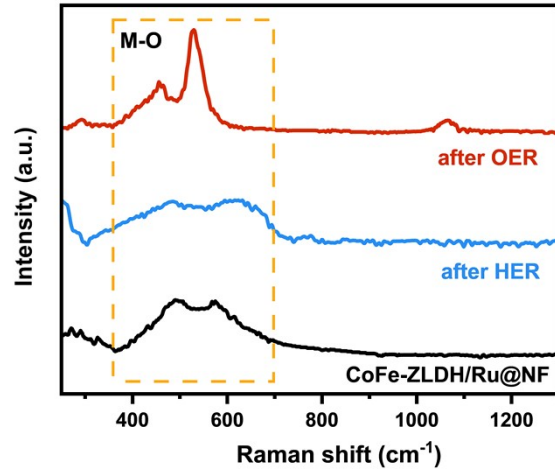
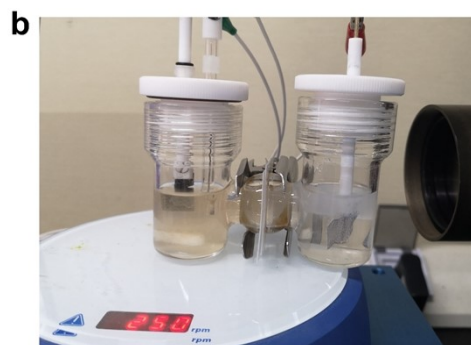**Fig. S3** FTIR spectra of CoFe-ZLDH/Ru and CoFe-ZLDH.

Fig. S4 Raman spectroscopy of CoFe-ZLDH/Ru@NF before and after OER and HER.

a CoFe-ZLDH@NF for OER

b CoFe-ZLDH/Ru@NF for OER

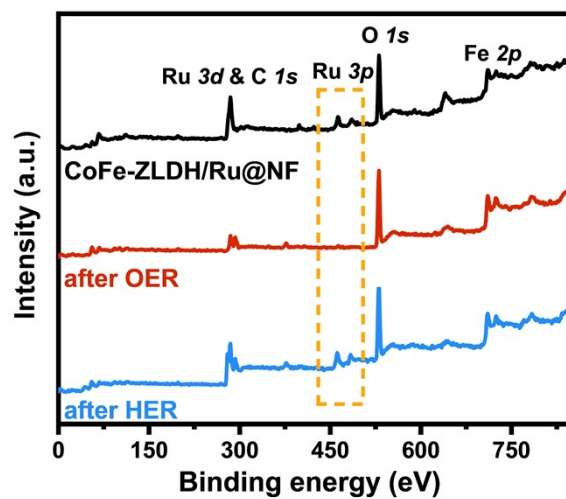**Fig. S5** Digital photos of (a) CoFe-ZLDH@NF and (b) CoFe-ZLDH/Ru@NF when tested in alkaline three-electrode system (H-cell) for OER.

Fig. S6 XPS survey spectra of CoFe-ZLDH/Ru@NF before and after OER and HER tests.
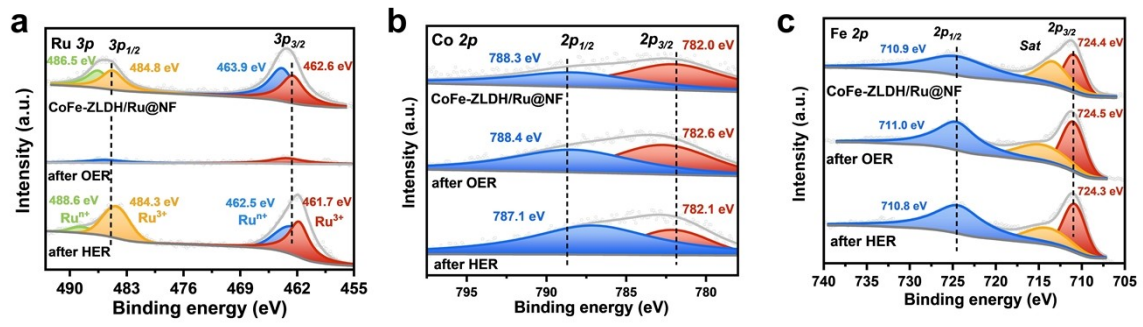
Fig. S7 High-resolution XPS spectra of (a) Ru 3p, (b) Co 2p and (c) Fe 2p in CoFe-ZLDH/Ru@NF before and after OER and HER tests.
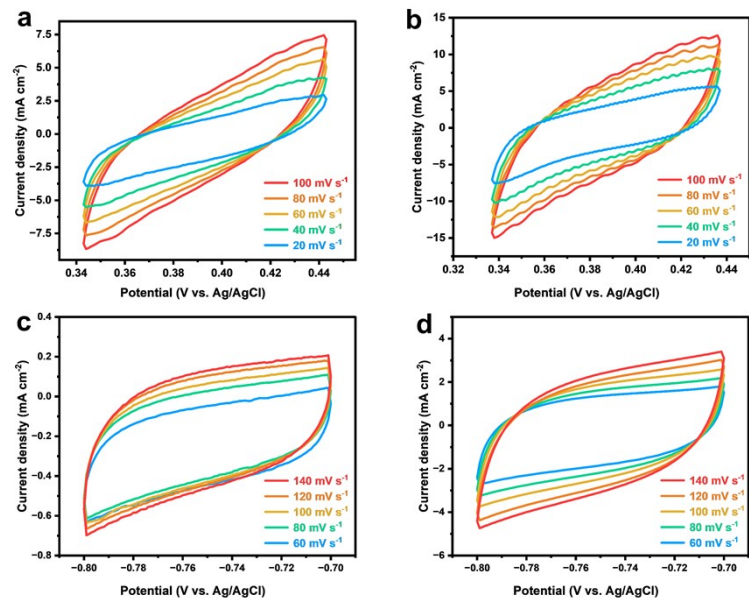
Fig. S8 CV curves of (a) CoFe-ZLDH @NF and (b) CoFe-ZLDH/Ru @NF at the scan rate of 20, 40, 60, 80, 100 mV s⁻¹ for OER catalysis, CV curves of (c) CoFe-ZLDH @NF and (d) CoFe-ZLDH/Ru @NF at the scan rate of 60, 80, 100, 120, 140 mV s⁻¹ for HER catalysis.
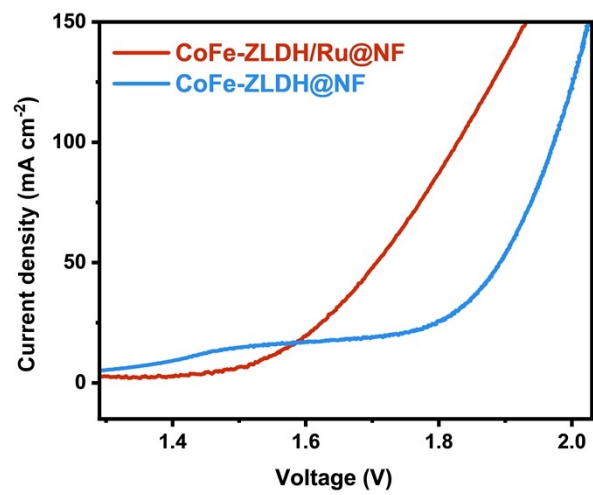
Fig. S9 LSV curves of CoFe-ZLDH/Ru@NF and CoFe-ZLDH@NF for overall water splitting in two-electrode system (single cell).
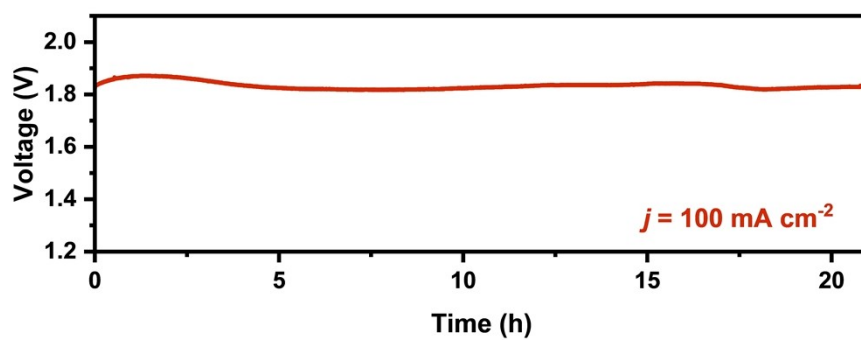
Fig. S10 Chronopotentiometry curve of CoFe-ZLDH/Ru@NF for overall water splitting in two-electrode system (single cell) at a current density of 100 mA cm^{-2}.