Electronic Supplementary Information

Ir^{4+}-doped NiFe LDH to Expedite Hydrogen Evolution Kinetics as Pt-like Electrocatalyst for Water Splitting

Qian-Qian Chen,[ab] Chun-Chao Hou,[a] Chuan-Jun Wang,[a] Xiao Yang,[ab] Rui Shi[a] and Yong Chen*[ab]

[a] Key Laboratory of Photochemical Conversion and Optoelectronic Materials & HKU-CAS Joint Laboratory on New Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[b] University of Chinese Academy of Sciences Beijing 100149, People's Republic of China

*Corresponding author

E-mail: chenyong@mail.ipc.ac.cn

Materials: All chemicals used in the experiments were analytical grade and used without further treatments.

The synthesis of NiFeIr LDH/NF: The NiFeIr LDH was grown in situ under hydrothermal conditions. Ni foam (1 cm × 3.6 cm × 1.6 mm) was ultra-sonicated for 30 min in 3 M HCl, deionized water and ethanol, respectively. In a typical procedure, 88 mg $Ni(NO_3)_2 \cdot 6H_2O$ and 130 mg urea were first dissolved in 15 mL H_2O. Then, 97 mg $Fe(NO_3)_3 \cdot 9H_2O$ were added to the above solution. Finally, 3 mL 20 mM H_2IrCl_6 solution was added to the solution and stirred for 30 min to obtain a clear solution. The final solution was poured into a 25 mL reaction vessel containing a piece of Ni foam. The sealed reactor was put into an oven at 120 ^{o}C with a heating rate of 3.5 ^{o}C min^{-1} and kept at this temperature for 12 h. The weight of catalyst is about 1.43 mg cm^{-2}.

The preparation of Pt/C electrode: In a typical synthesis, 25 mg commercial 10% Pt/C was dispersed in 1 mL water containing 100 μL Nafin solution, and then the mixture was ultra-sonicated for more than 1 h to generate a catalyst ink. Next, 15 μL of the dispersion was dropped onto 0.5 × 0.5 cm^{-2} Ni foam (1.5 mg cm^{-2}). Finally, the as-prepared electrode was dried at room temperature for two days.

Characterization

The structure of the catalysts were investigated by Powder X-ray patterns (PXRD) on a Bruker AXSD8 X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å). The Scanning electron microscope (SEM) images of catalysts and corresponding energy-dispersion X-ray mapping were obtained at a Hitachi S-4800 field emission scanning electron microscope. Samples for transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were analyzed by using a transmission electron microscope (JEM 2100). X-ray photoelectron spectroscopy (XPS) spectra were firstly deoxygenated under Ar overnight and then investigated on a ThermoScientific ESCALAB 250XI spectroscopy equipped with an Al Kα X-ray source and a power of 250 W was used. The charge effect was calibrated using the binding energy of C (1s) (284.8 eV). Raman spectroscopy measurements were performed on an inVia-Reflex confocal laser micro-Raman spectrometer using Ar^+ laser excitation (λ_{ex} = 532 nm). Hydrogen was measured by a gas chromatograph (GC-14C, Shimadzu, with Ar as a carrier gas), which was equipped with a 5 Å molecular sieve column (3 m × 2mm) and a thermal-conductivity detector.

Electrochemical measurements

The electrochemical tests were performed on CHI660E electrochemical workstation and carried out in a standard three-electrode cell in 1 M KOH solution (pH = 13.7), using a carbon rod as the counter electrode for HER (but for OER using a Pt foil) and Ag/AgCl (3.5 M) as the reference electrode, which was calibrated by reversible hydrogen electrode (RHE): E(RHE) = E (Ag/AgCl) +0.059 * pH + 0.2046. Ni foam (0.5 cm × 1.2 cm) was used as the working electrode, but the actual area immersed in the electrolyte is 0.5 cm × 0.5 cm. During the measurement, H_2 is bubbled through electrolyte. The scan rate for the electrochemical measurements was 5 mV s^{-1}. The ECSA was obtained by electrical double layer capacitor (C_{dl}) in a small non-faradaic potential range from -0.6 to -0.7 V vs. Ag/AgCl. The Faradaic efficiency of NiFeIr LDH for HER was measured with chronopotentiometry model in N_2 saturated 1 M KOH solution.

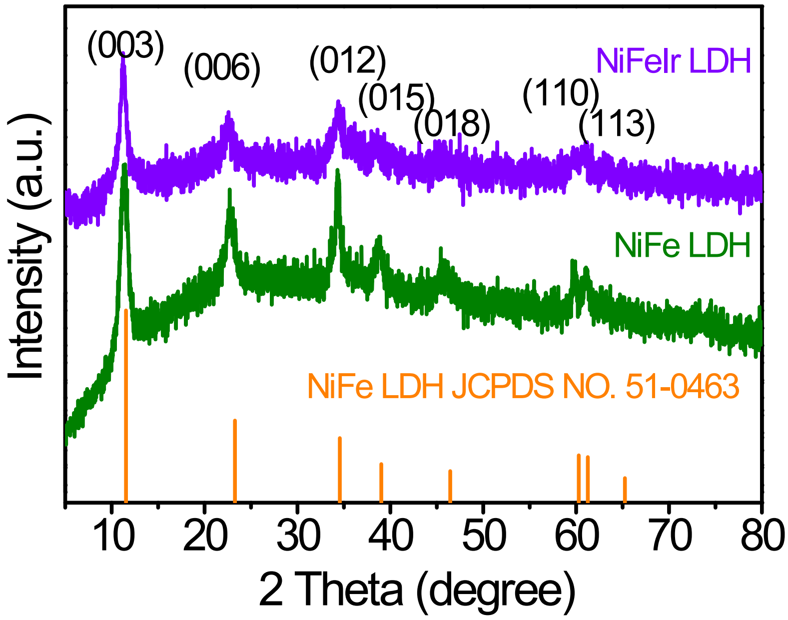

Fig. S1 XRD spectra of NiFe LDH and NiFeIr LDH prepared without Ni foam substrate.

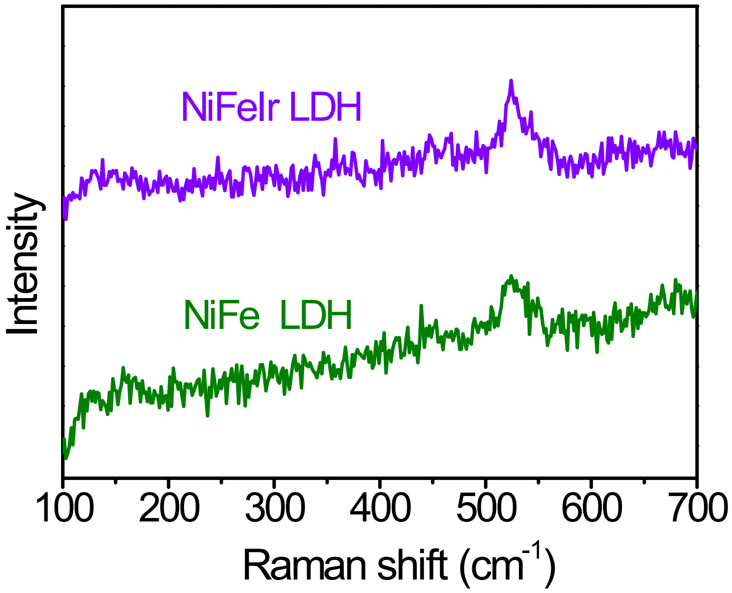

Fig. S2 Raman spectra of NiFe LDH and NiFeIr LDH.

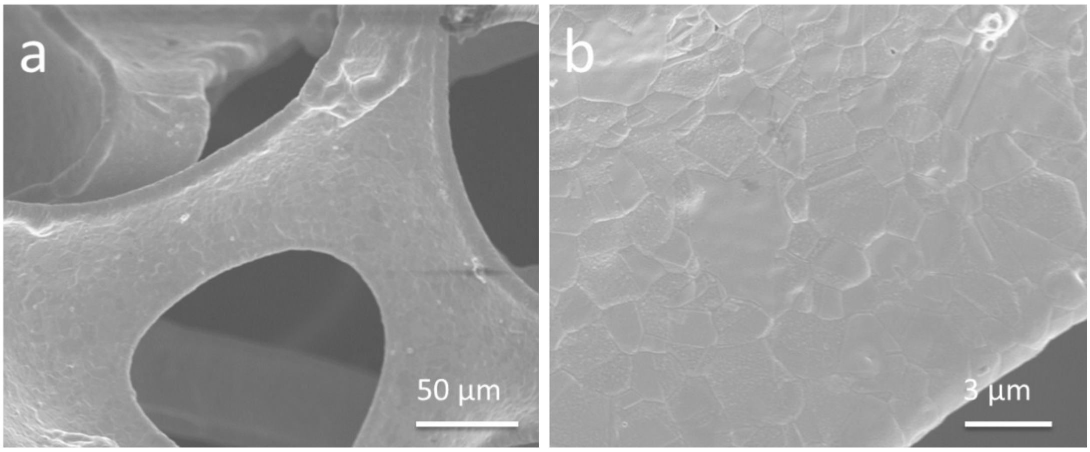

Fig. S3 SEM images of Ni foam.

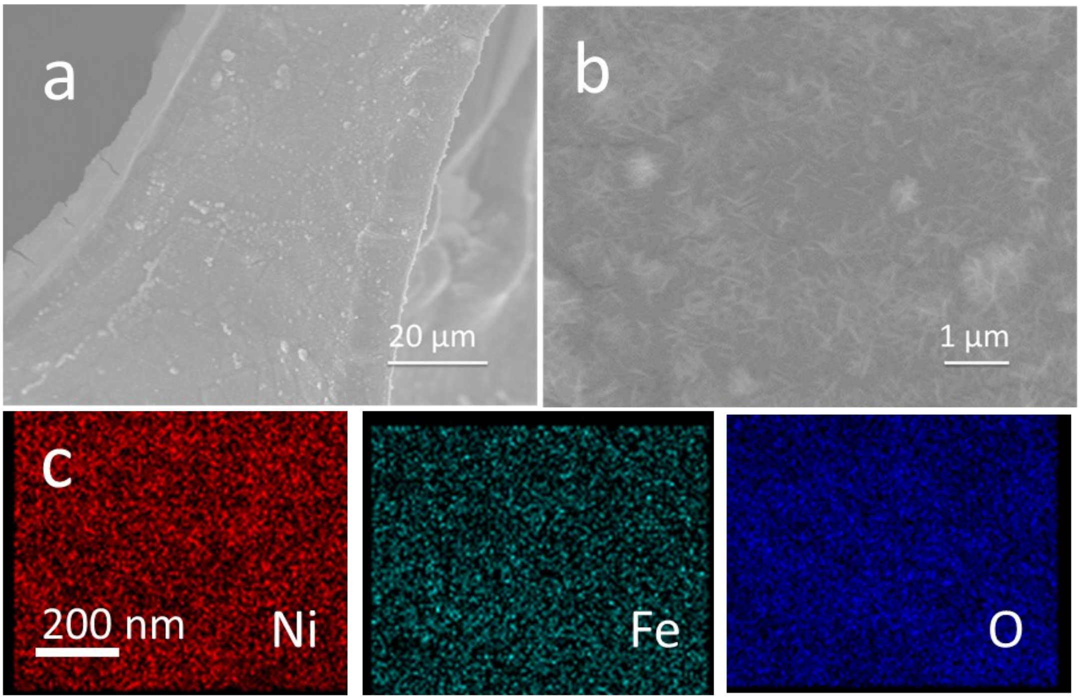

Fig. S4 SEM images and EDS-corresponding mapping of NiFe LDH.

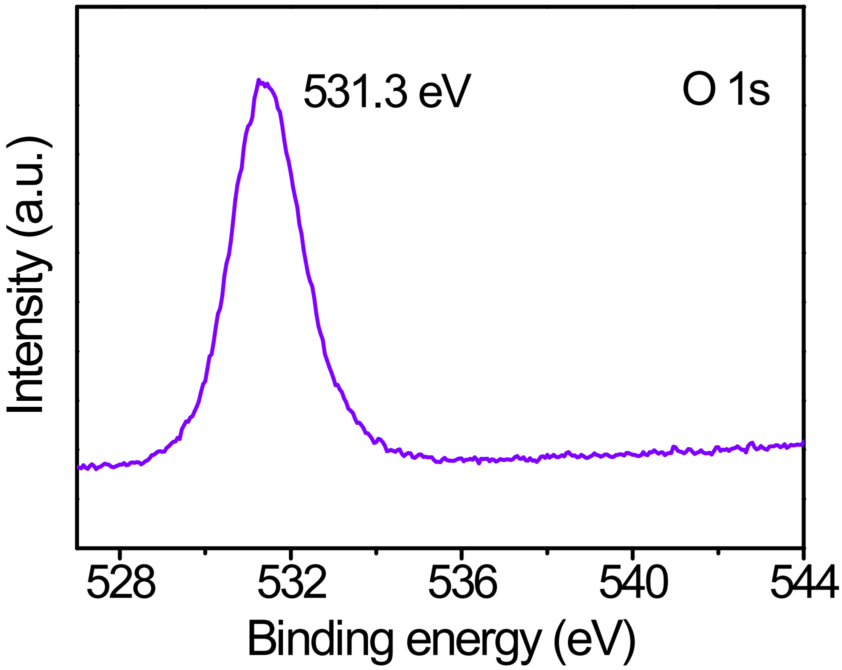

Fig. S5 XPS spectrum of O 1s for NiFeIr LDH.

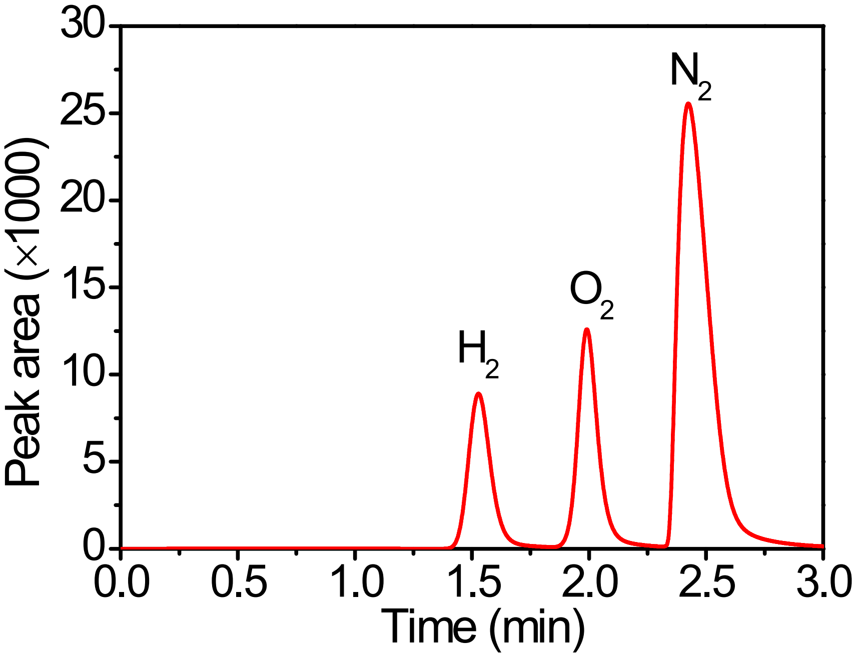

Fig. S6 GC signals obtained from the closed electrolytic cell.

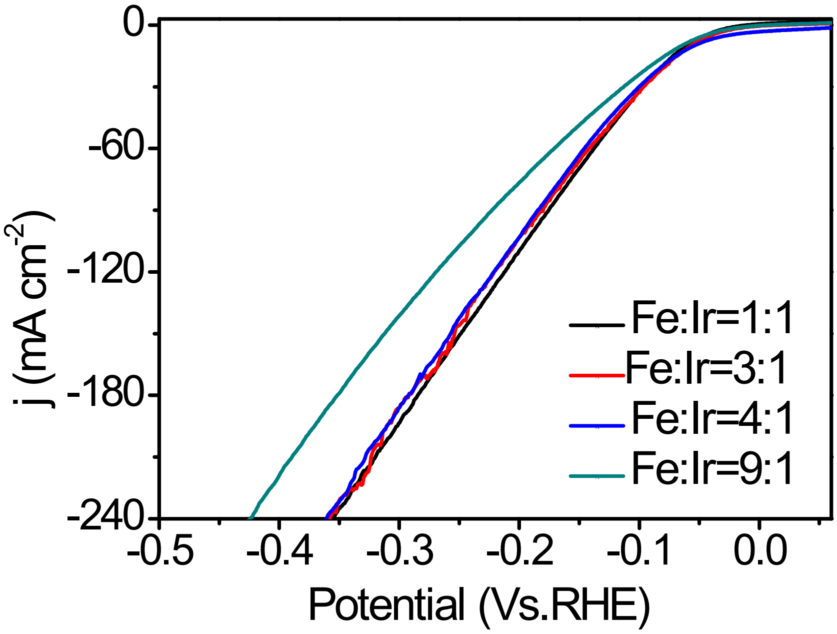

Fig. S7 LSV curves of NiFeIr LDH in 1 M KOH with different feed ratio without iR compensation.

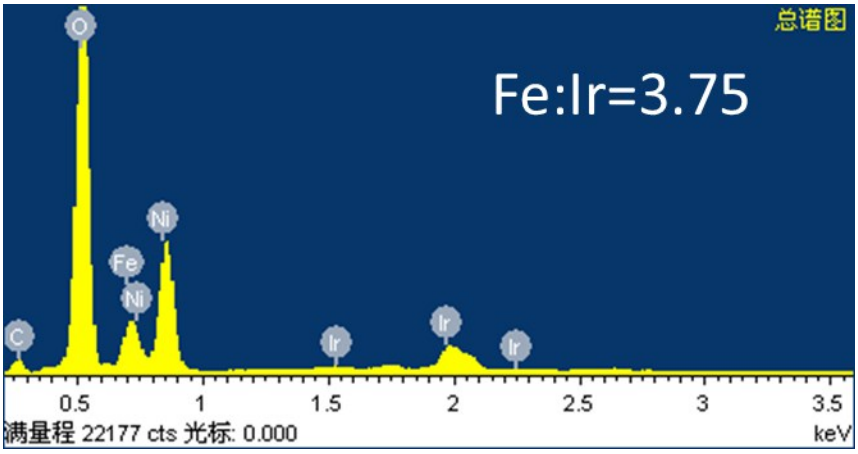

Fig. S8 SEM-EDS spectrum of NiFeIr LDH.

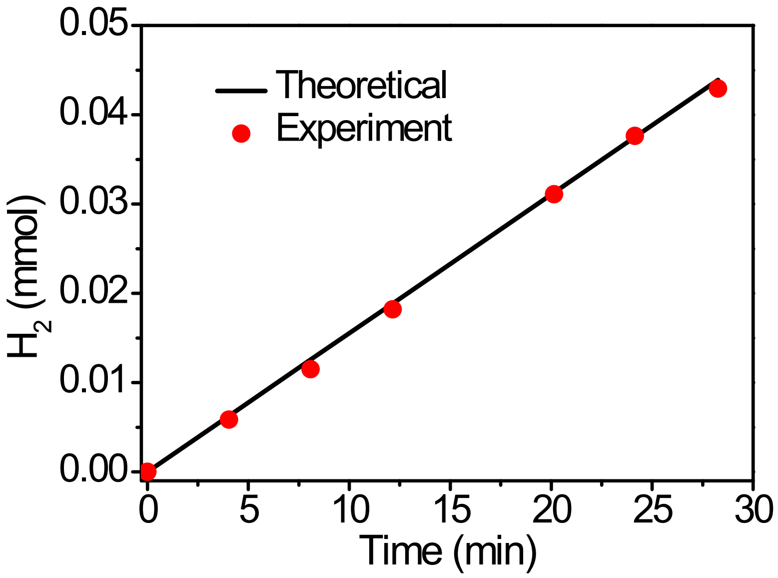

Fig. S9 Theoretical and experiment hydrogen evolution at a current of 5 mA using NiFeIr LDH in 1 M KOH.

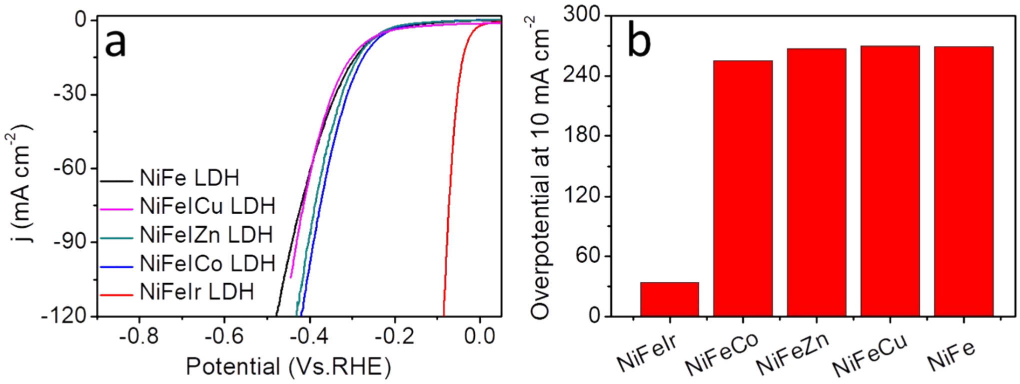

Fig. S10 (a) LSV curves and (b) overpotentials at 10 mA cm^{-2} for NiFe LDH, NiFeCu LDH, NiFeZn LDH, NiFeCo LDH and NiFeIr LDH.

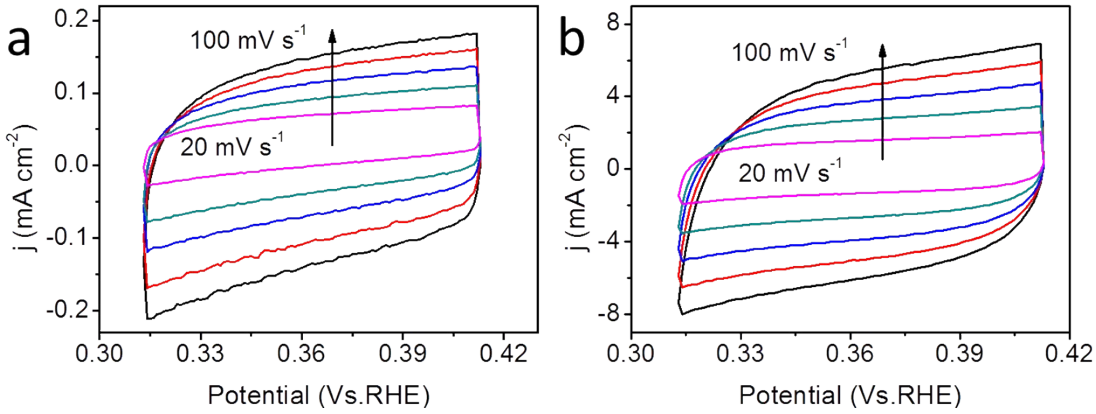

Fig. S11 CV curves for the as-prepared NiFe LDH (a) and NiFeIr LDH (b).

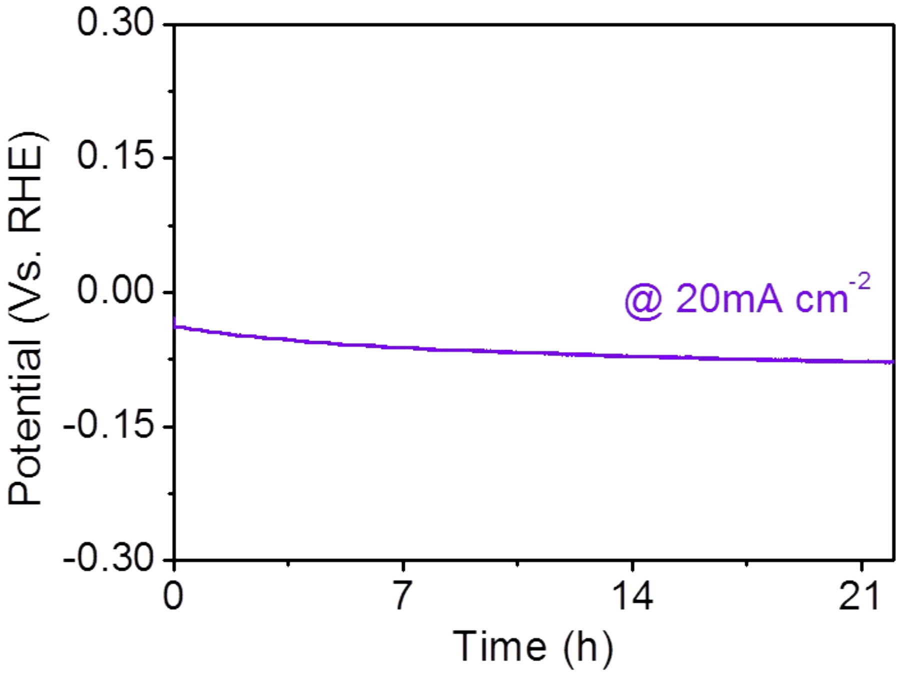

Fig. S12 The long-time stability of NiFeIr LDH in a three-electrode system at 20 mA cm^{-2}.

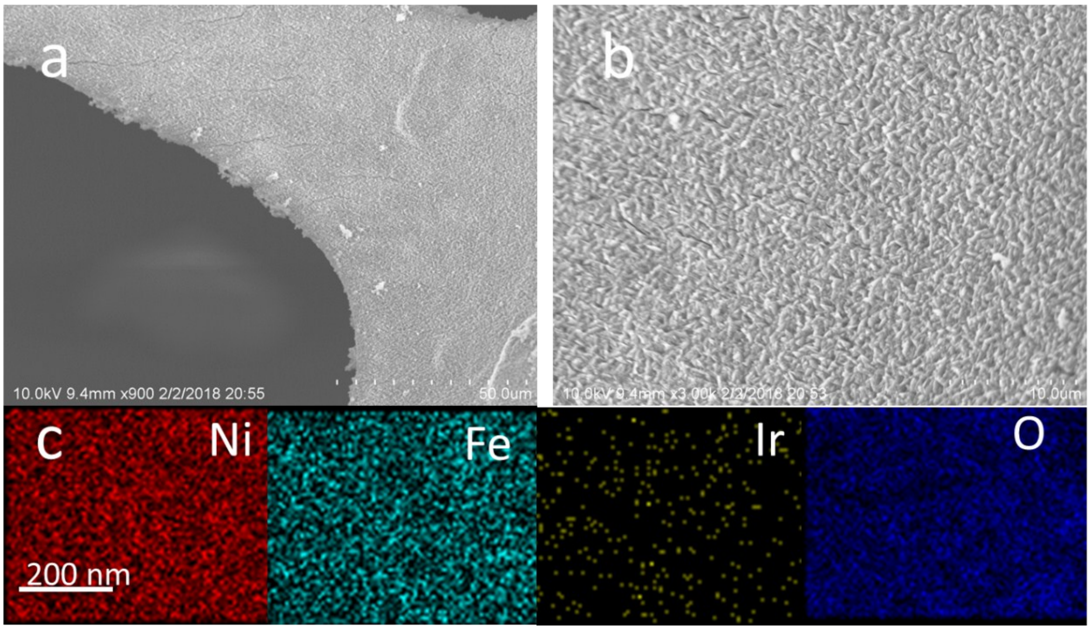

Fig. S13 (a) SEM image, (b) Imaged SEM image and the corresponding EDX of NiFeIr LDH after stability test.

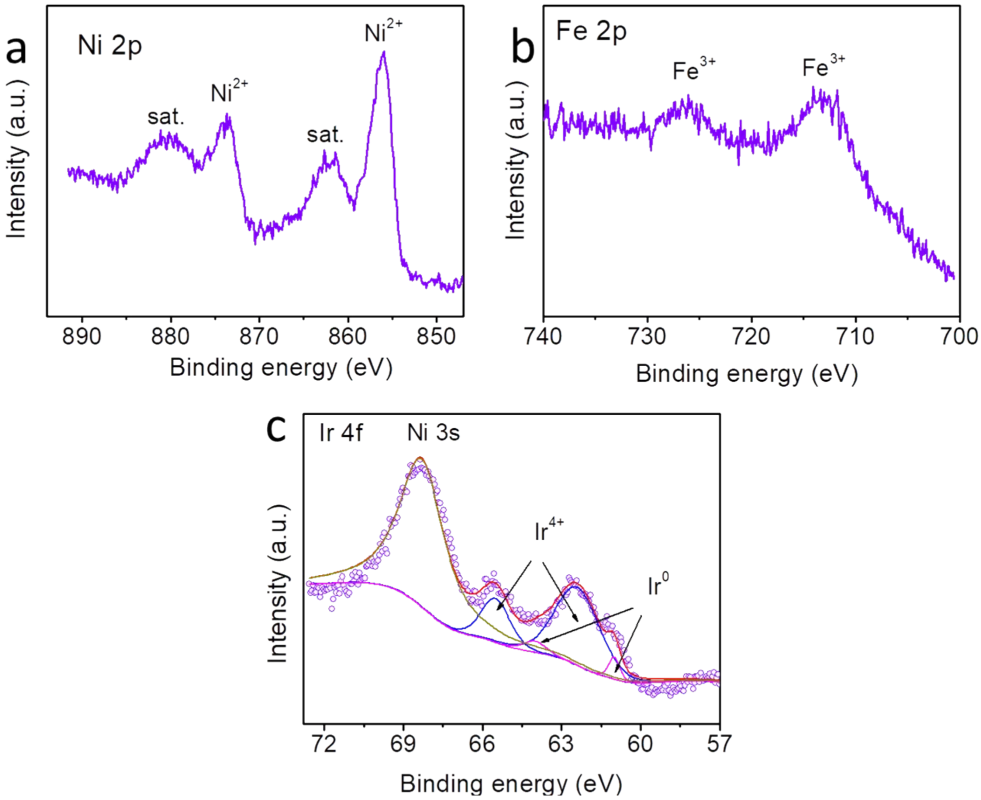

Fig. S14 XPS spectra of a) Ni 2p, (b) Fe 2p and (c) Ir 4f for NiFeIr LDH after 22 h of HER at 20 mA cm^{-2}.

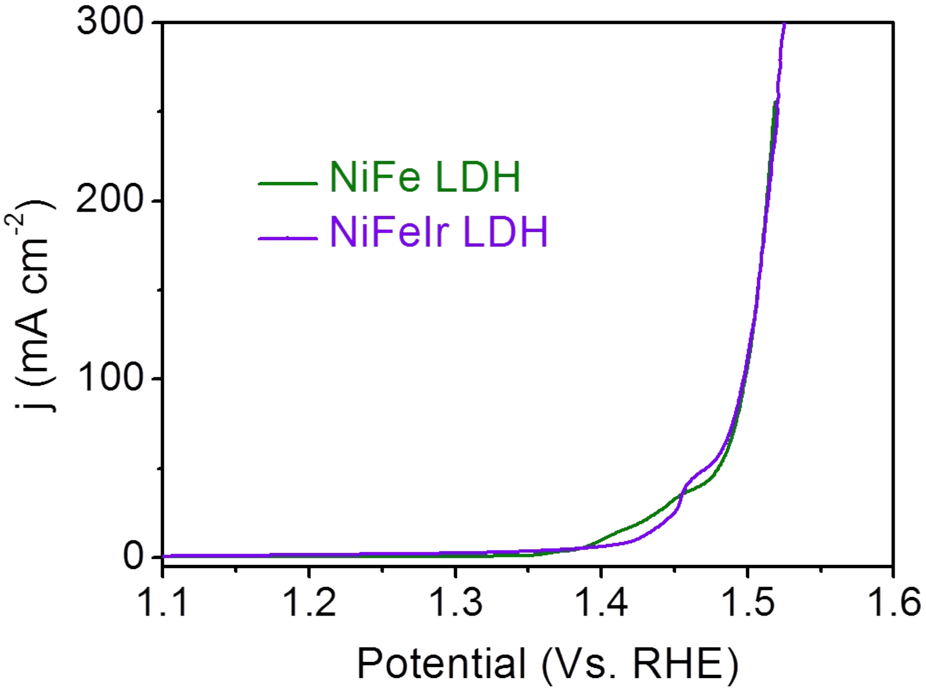

Fig. S15 OER LSV curves of NiFe LDH and NiFeIr LDH in 1 M KOH with iR compensation.