Electronic Supplementary Information

Fabrication of uniform Ru-doped NiFe₂O₄ nanosheets as efficient hydrogen evolution electrocatalyst

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Experimental Section

Electrodeposition of NiFe LDH on Ni foam (NiFe LDH/NF).

Commercial Ni foam (NF, cut into an area of $1\times 2 \text{ cm}^2$) was washed with 1.5 M HCl under ultrasonication condition for 10 min and washed with ultrapure water for several times. Then, the NF was washed with ethanol for 10 min under ultrasonication followed by rinsed with ethanol for several times before dried in a vacuum oven. NiFe LDH was electrodeposited on NF according to a previous work.¹ The NF was used as the working electrode in a conventional three-electrode setup, while the Pt foil and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrolyte for electrodeposition consisted of Ni(NO₃)₂·6H₂O (0.15 M) and FeSO₄·7H₂O (0.15 M) with a continuous N₂ flow to prevent the oxidation of Fe²⁺.The potentiostatic deposition was carried out at a potential of -1 V vs. SCE for 300 s with NF area of 1×1 cm² immersed in the electrolyte. The as-synthesized NiFe LDH/NF was rinsed with ultrapure water and then dried in the oven for further use.

Electrodeposition of Ru-doped NiFe LDH on Ni foam (Ru (atomic ratio)-NiFe LDH/NF).

Ru-doped NiFe LDH was synthesized with the similar method by partially substituting Fe with certain atomic ratio (1%, 2.5%, 4%, 5.5% and 7%) Ru dopants, where RuCl₃·xH₂O was used as Ru source. The electrolyte for electrodeposition consisted 0.15 M Ni(NO₃)₂·6H₂O and the total metal ions concentration was 0.3 M.

Preparation of NiFe₂O₄/NF and Ru-NiFe₂O₄/NF.

The synthesized precursors (NiFe LDH/NF or Ru-doped NiFe LDH/NF) were heated to 300 °C under Ar atmosphere in a tube furnace at a rate of 2 °C min⁻¹ and maintained at 300 °C for 2 h. The obtained materials were NiFe₂O₄/NF and Ru-NiFe₂O₄/NF for further use.

Characterization

X-ray diffraction (XRD) data were recorded on a Rigaku D/MAXRC X-ray diffractometer (45.0 kV, 50.0 mA) using Cu target as the anticathode to produce corresponding X-ray radiation. Raman spectra were collected on a Renishaw inVia confocal microRaman spectroscopy system using the TE air-cooled 576×400 CCD array with a 532 nm excitation laser. The incident laser power was kept at 0.1 mW, and a total accumulation time of 10 s was employed. X-ray photoelectron spectra (XPS) were recorded on a PHI 5700 ESCA system with AI K α radiation as excitation source (h ν = 1486.6 eV). The scanning electron microscopic (SEM) images were obtained on a Quanta 200 S (FEI) with samples mounted on aluminium studs by graphite tape and sputter coated with gold before

analysis. Transmission electron microscopy (TEM) images were obtained on a Tecnai F20 operating at an accelerating voltage of 200 kV. The Ru loading was calculated according to the inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer (PE) Optima 8300) test result. **Electrode preparation and electrochemical measurements**

All electrochemical measurements were carried out at room temperature in a conventional threeelectrode cell on an electrochemical workstation (CHI 660E). Graphite rod (Alfa Aesar, 99.9995%) was used as the counter electrode and Hg/HgO (1 M KOH solution) as the reference electrode, respectively. Prior to the electrochemical measurements, the reference electrode was calibrated according to the published work using Pt sheets (Aldrich) as both the working and the counter electrodes in 1 M KOH (aq).² All the potentials were referred to reversible hydrogen electrode (RHE) and all the electrochemical measurements were operated in 1 M KOH (aq) solution. Before the polarization curves were obtained, the working electrode was cycled at a scan rate of 50 mV s⁻¹ for 30 cycles to activate the electrode in the electrolyte. Linear sweep voltammetry (LSV) was carried out at a scan rate of 1 mV s⁻¹ to measure HER performance. Cyclic voltammograms at different scan rates (20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV s⁻¹) were collected in the range of 1.15-1.25 V vs. RHE to estimate the double-layer capacitance (C_{dl}). The electrochemical impedance spectroscopy (EIS) measurements were tested at the potential of -0.2 V vs. RHE for HER with the frequency ranging from 10^6 to 0.1 Hz. Multi-current process carried out in 1 M KOH was used to test the mass transport property of the Ru-NiFe₂O₄/NF electrode. The current density was normalized from the apparent area of the NF (1×1 cm²). For preparation of commercial electrodes, 2 mg of Pt/C and 2 mg of IrO_2 powders were dispersed into 0.4 mL of water/ethanol mixed solution (1:1) and sonicated to get ink. Then, the ink was dropcasted onto NF used as working electrode for test. The stability tests were carried out by continuous 1000 cycles CV scans at the scan rate of 50 mV/s and chronopotentiometry test. All presented data were corrected with series resistance (R_s $^{2}\Omega$) determined from EIS experiments for the Ohm losses to better compare the intrinsic catalytic activity of the different catalysts.

Calculation of C_{dl}, ECSA

Electrochemical active surface area (ECSA) was determined based on the double-layer capacitance (C_{dl}) by measuring the CV curves of the electrode at different scan rates in a non-Faradic region (1.15–1.25 V). C_{dl} was determined as the linear slope by plotting anodic current density at 1.2 V against the scan rates (20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV s⁻¹) (Equation 1).

$$C_{\rm dl} = i_{\rm c}/\nu \tag{1}$$

Supplementary figures and tables



Fig. S1 XRD patterns of the as-synthesized NiFe LDH and Ru-doped NiFe LDH.



Fig. S2 (a) SEM image, (b) TEM image and (c) HRTEM image of NiFe LDH/NF.



Fig. S3 (a) SEM image, (b) TEM image and (c) HRTEM image of Ru-doped NiFe LDH/NF.



Fig. S4 (a) SEM image, (b) TEM image and (c) HRTEM image of NiFe₂O₄/NF.



Fig. S5 XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) Ru 3p and (d) O 1s of NiFe LDH/NF (top) and Ru-doped NiFe LDH /NF(bottom).



Fig. S6 XPS full spectra of NiFe₂O₄/NF and Ru-doped NiFe₂O₄/NF.



Fig. S7 Polarization curves of NiFe₂O₄/NF and Ru-doped NiFe₂O₄/NF with different Ru content for HER catalysis in 1 M KOH.



Fig. S8 Cyclic voltammetry curves of NiFe LDH/NF, Ru-doped NiFe LDH/NF, NiFe₂O₄/NF and Rudoped NiFe₂O₄/NF with different ratio under different scan rates, in the region of 1.15-1.25 V vs. RHE. These data were used to present the plots showing the extraction of the C_{dl} for different samples shown in Figure 4d in the main text.



Fig. S9 SEM image of Ru-doped NiFe₂O₄/NF after HER process.



Fig. S10 (a) TEM image and (b) HRTEM image of Ru-doped NiFe₂O₄ after HER process. (c) HAADF-STEM image of Ru-doped NiFe₂O₄ after hydrogen evolution process and corresponding elemental mapping.



Fig. S11 Raman spectra of Ru-doped NiFe₂O₄/NF before and after HER process.



Fig.S12 XPS spectra of Ru 3p of Ru-doped NiFe₂O₄/NF after 1000 CV cycles.



Fig. S13 (a) 1 cycle cyclic voltammograms (CV) was conducted at a scan rate of 5 mV s⁻¹ to measure OER performance of IrO_2/NF , $NiFe_2O_4/NF$ and Ru-doped $NiFe_2O_4/NF$, (b) Electrochemical impedance spectroscopy Nyquist plots (c) Multicurrent process obtained with Ru-doped $NiFe_2O_4/NF$ electrode in 1 M KOH without *iR* correction. The current density started at 60 mA/cm² and finished at 180 mA/cm², with an increment of 20 mA/cm² after every 300 s.



Fig. S14 (a) Polarization curves of Ru-doped NiFe₂O₄/NF|| Ru-doped NiFe₂O₄/NF and PtC/NF||IrO₂/NF in 1.0 M KOH (the inset is the digital photograph of the two-electrode electrolyzer). (b) The chronopotentiometric curve of Ru-doped NiFe₂O₄/NF in the two-electrode configuration for overall water splitting.

Materials	η (mV vs. RHE)	Tafel Slope	Ref.
	@ -10 mA/cm ²	(mV/dec)	
Ru-doped NiFe ₂ O ₄ /NF	18	27.2	This work
Ru-doped	33.6	30.7	This work
NiFe LDH/NF			
Ru@NC	26	36	Angew. Chem. Int. Ed. 2018,
			<i>57</i> (20) <i>,</i> 5848-5852.
Ru@CN	32	64	Energy Environ. Sci., 2018,
			11, 800-806.
Ru/C	53	47	Appl. Catal. B: Environ.
			2019, 258, 117952
NiFeRu-LDH/NF	29	31	Adv. Mater. 2018, 30 (10),
			1706279.
RuO ₂ /NiO/NF	22	50.5	Small 2018, 14 (16),
			1704073.
WS ₂ /Pt	~40	65	Adv. Mater. 2018, 30 (7),
			1704779
Pt-Ni ASs	27	27.7	Adv. Mater. 2018, 30 (30),
			1801741
Pt SASs/AG	12	29.33	Energy Environ. Sci., 2019,
			12, 1000-1007
Rh–Rh ₂ O ₃ -NPs/C	63	70	J. Mater. Chem. A, 2018, 6,
			23531-23541
Rh NP/C	7	19	Adv. Energy Mater. 2018, 8,
			1801698
Pd@MoO ₃	180		ACS Appl. Mater. Interfaces
			2019, 11, 27798-27804
Pd@Ru	30	30	ACS Appl. Mater. Interfaces
			2018, 10, 34147–34152

Table S1 Comparative characteristics of HER activity on Ru-based electrocatalysts in alkaline media.

Catalyst	Theoretical Ru content (atom%)	Theoretical Ru content (wt%)ª	Actual Ru content (wt%) ^b
Ru (3%)-NiFe ₂ O ₄ /NF	1.0	1.8	3.3
Ru (9%)-NiFe ₂ O ₄ /NF	2.5	5.2	9.2
Ru (15%)-NiFe ₂ O ₄ /NF	4.0	9.0	14.9
Ru (17%)-NiFe ₂ O ₄ /NF	5.5	11.8	17.2
Ru (18%)-NiFe ₂ O ₄ /NF	7.0	14.9	18.2

Table S2. The Ru content in the Ru-doped $NiFe_2O_4/NF$ electrocatalysts according to ICP-AES and their feeding amount.

a. Theoretical Ru content is calculated by the amount of metal precursor.

b. Actual Ru content is measured by ICP-AES. The actual Ru content is higher than the theoretical Ru amount as the Ksp of $Ru(OH)_3$ is much less than $Ni(OH)_2$ and $Fe(OH)_3$.

References

1. Li, Z.; Shao, M.; An, H.; Wang, Z.; Xu, S.; Wei, M.; Evans, D. G.; Duan, X., *Chem. Sci.* **2015**, *6* (11), 6624-6631.

2. Silva, R.; Voiry, D.; Chhowalla, M.; Asefa, T., J. Am. Chem. Soc. **2013**, 135 (21), 7823-7826.