Supporting Information:

Ultralow Ruthenium modification of Cobalt Metal–Organic Frameworks for Enhanced Efficient Bifunctional Water Splitting

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1.Experimental section

1.1 Chemicals and reagents

Nickel foam (NF, 1.5 mm-thick, 200 × 300 mm) was purchased from Suzhou Keshenghe Metal Materials and was pretreated. Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), ruthenium trichloride hydrate ($RuCl_3·xH_2O$), and 2-methylimidazole (Hmim) were purchased from Aladdin. Hydrochloric acid (HCl) was purchased from Sinopharm Chemical Reagent Co.

Treatment of foam nickel：

First, nickel foam was placed in a hydrochloric acid (1 M) solution and sonicated for 10 min. Thereafter, the material was washed twice with deionised water, placed in an absolute ethanol solution, and sonicated for 10 min. Subsequently, the foamed Ni was washed twice with deionised water, followed by ultrasonication in deionised water for 5 min. The oxides and pollutants on the surface of the nickel foam (1 cm × 6 cm) were removed, and the foam was dried at room temperature.

1.2 Synthesis of Co–MOF/NF

First, cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, 0.29 g) and dimethylimidazole (0.656 g) were dissolved in deionised water (20 mL). The solution was then mixed with dimethylimidazole in a cobalt nitrate solution and stirred for 5 min, after which the treated NF was immersed in the solution and stirred for 4 h to obtain Co–MOF/NF. The prepared Co–MOF/NF samples were sonicated three times in anhydrous ethanol, then washed three times with deionised water, and dried at 60 ^oC under vacuum for 6 h.

1.3 Synthesis of $CoRu_{0.06}$–MOF/NF

First, cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, 0.29 mg), ruthenium trichloride hydrate ($RuCl_3·xH_2O$, 25 mg), and dimethylimidazole (0.656 mg) were dissolved in deionised water (20 mL). A Hmim solution was then poured into the mixed metal solution and stirred for 5 min, and the treated NF was immersed in the solution and stirred for 4 h to obtain $CoRu_{0.06}$–MOF/NF. Finally, the $CoRu_{0.06}$–MOF/NF samples

were sonicated three times with anhydrous ethanol, then washed three times with deionised water, and dried at 60 °C under vacuum for 6 h.

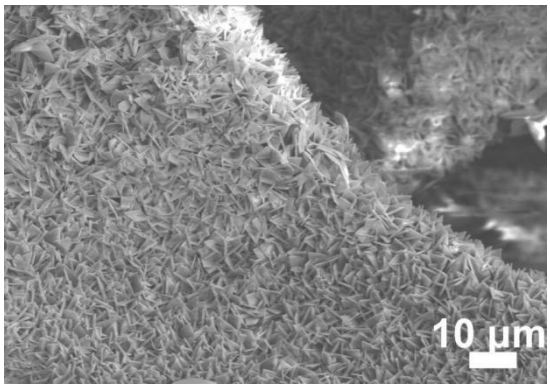

Fig. S1. SEM images of Co-MOF/NF.

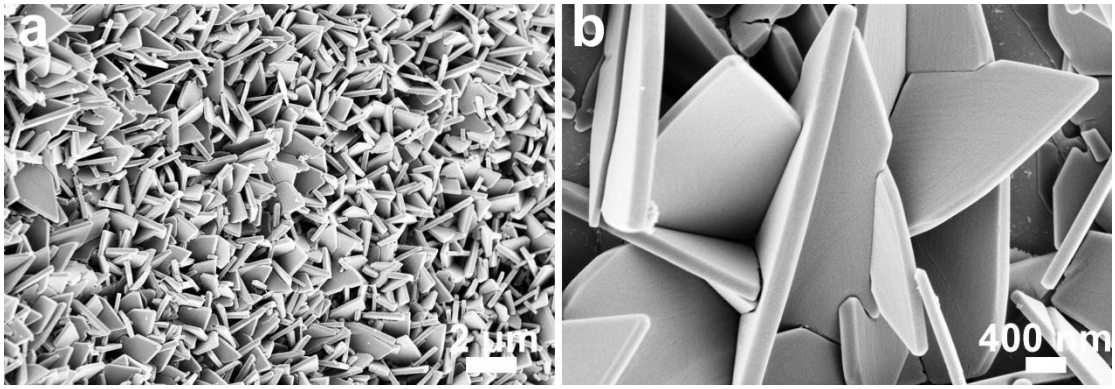

Fig. S2. (a,b) SEM images of $CoRu_{0.06}$-MOF.

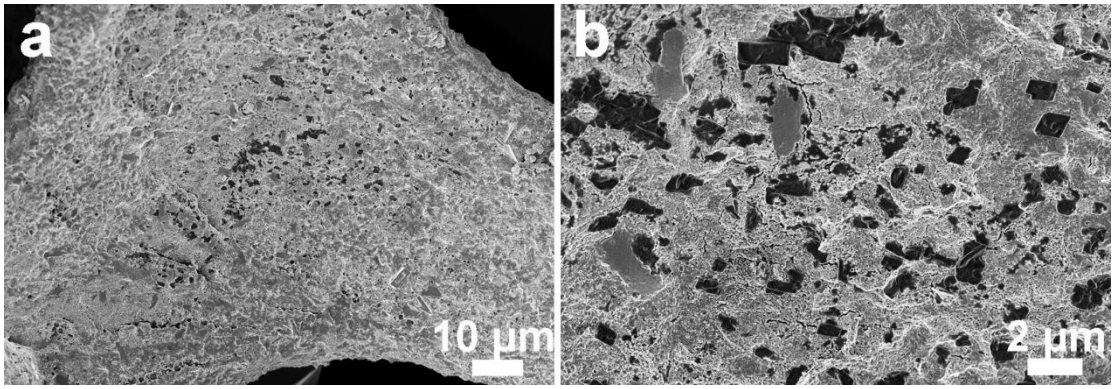

Fig. S3. (a,b) SEM image of $CoRu_{0.06}$-MOF after OER.

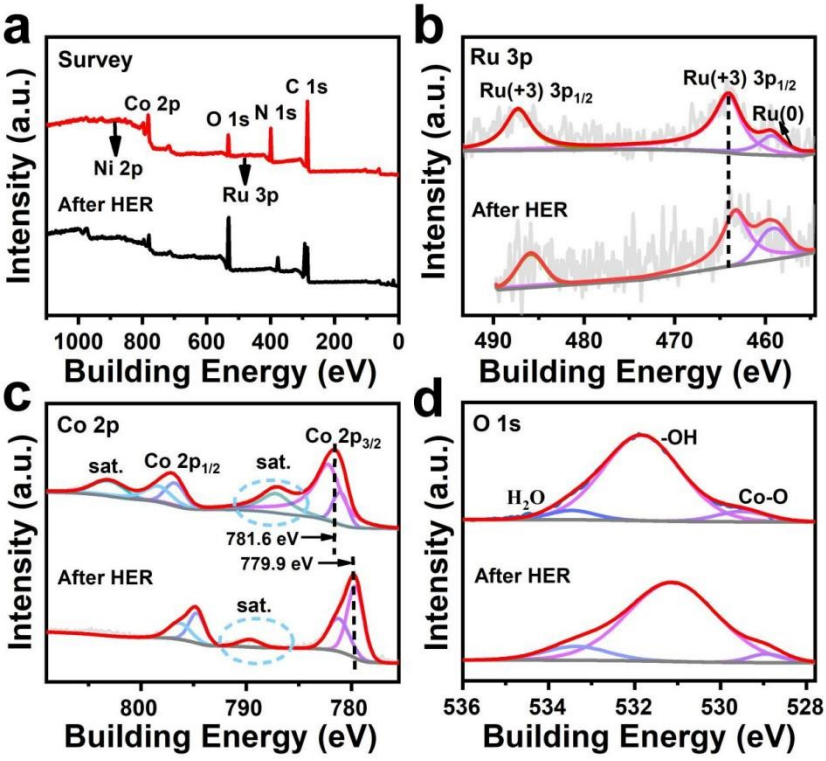

Fig. S4. (a) XPS measured spectra of $CoRu_{0.06}$-MOF/NF, $CoRu_{0.06}$-MOF/NF and Co-MOF/NF of (b) Ru 3p (c) Co 2p and (d) O1s in high resolution XPS spectra.

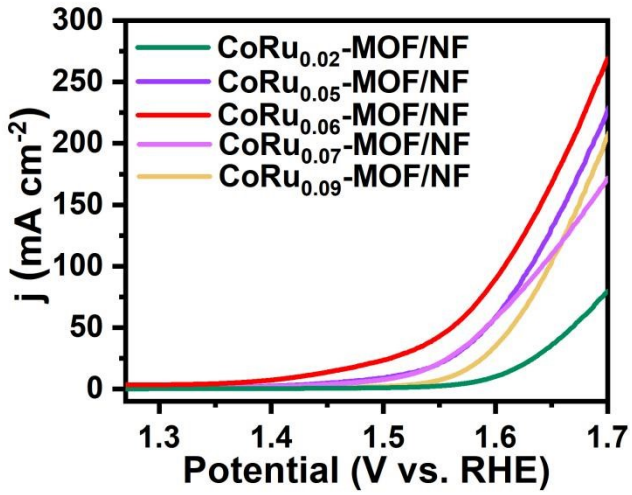

Fig. S5. LSV curves of OER test for catalysts with different Ru concentrations in alkaline media.

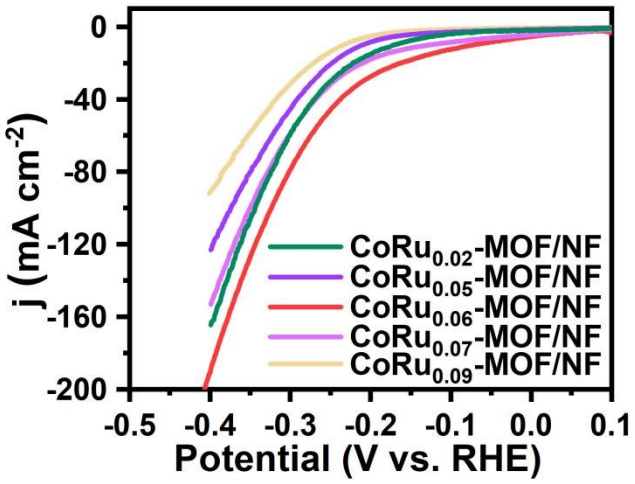

Fig. S6. LSV curves of HER test for catalysts with different Ru concentrations in alkaline media.

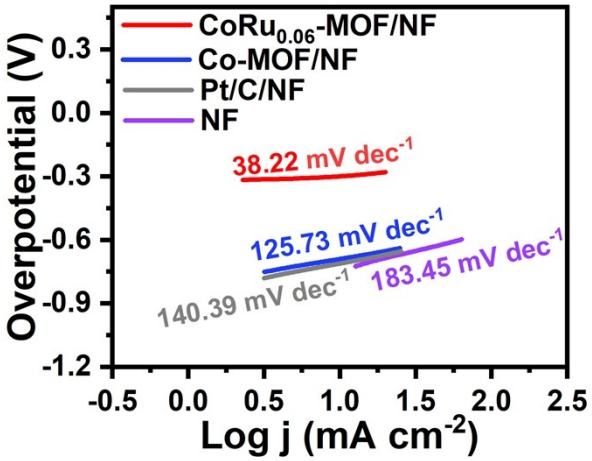

Fig. S7. Tafel slope plots of $CoRu_{0.06}$–MOF/NF, Co–MOF/NF, RuO_2/NF and NF.

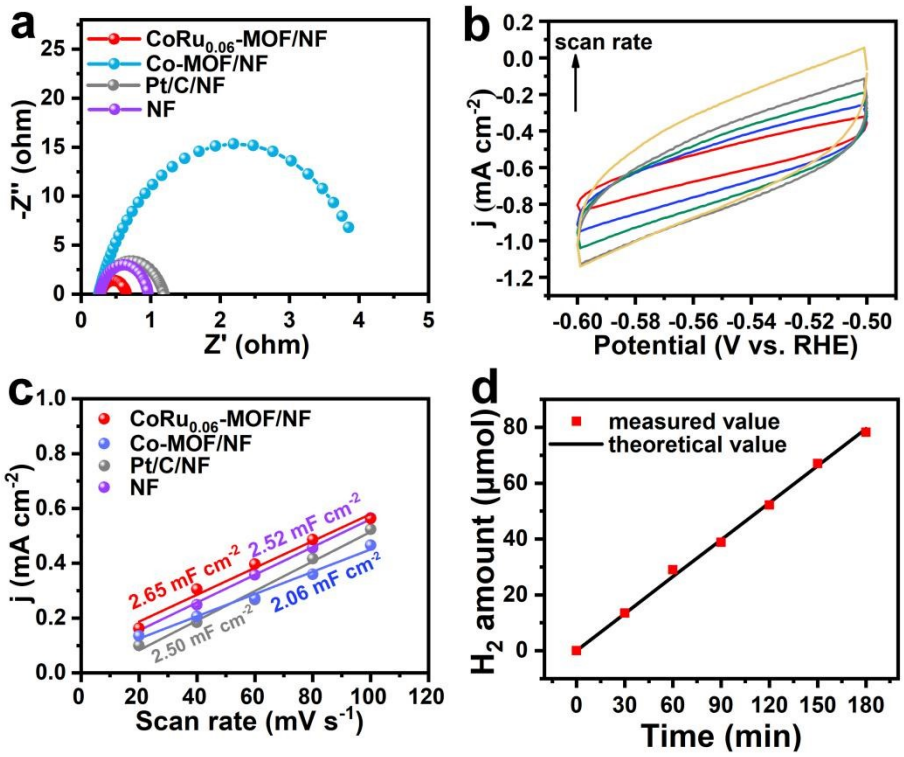

Fig. S8. (a) EIS Nyquist plots of $CoRu_{0.06}$-MOF/NF, Co-MOF/NF, Pt/C/NF and NF. (b) Cyclic Voltammetry curves of $CoRu_{0.06}$-MOF/NF. (c) The plots of the current density versus the scan rate of $CoRu_{0.06}$-MOF/NF, Co-MOF/NF, RuO_2/NF and NF. (d) Electrocatalytic efficiency of $CoRu_{0.06}$-MOF/NF for HER at an overpotential of 10 mA cm^{-2}.

Table S1. Comparison of the electrocatalytic performance of $CoRu_{0.06}$-MOF/NF with some representative elelctrocatalysts reported recently for HER and OER.

Catalyst	Electrolyte solution	HER/ OER	Current density (j)	Overpotential (η)	Stability test	Reference
$CoRu_{0.06}$-MOF/NF	**1 M KOH**	**HER**	**10 mA cm^{-2}**	**37 mV**	**95 h**	**This work**
		OER		**181 mV**	**110 h**	
Co-LDH@ZIF-67	1 M KOH	OER	10 mA cm^{-2}	187 mV	50 h	Adv. Sci., 2021, 8(2): 2002631
Ru-$NiSe_2$/NF	1 M KOH	HER	10 mA cm^{-2}	29 mV	40 h	Small, 2022,18 (6): 2105305
		OER		210 mV	25 h	
Ni_1Co_3@BC	1 M KOH	OER	10 mA cm^{-2}	309 mV	20 h	Appl. Surf. Sci., 2020, 532, 147381.
Ru-NiCoP/NF	1 M KOH	HER	10 mA cm^{-2}	44 mV	30 h	Appl. Catal. B Environ., 2020, 279: 119396
		OER	20 mA cm^{-2}	216 mV	30 h	
Co（OH）$_2$/Co-MOF	1 M KOH	OER	10 mA cm^{-2}	196 mV	54000 s	Chem. Eng. J., 2021, 408: 127319.
CoNi-MOF	1 M KOH	HER	10 mA cm^{-2}	110 mV	20 h	Adv. Mater. Interfaces, 2018, 5(21): 1800849.
		OER		265 mV		
Ru-Co_3O_4-NiO-NF	1 M KOH	HER	10 mA cm^{-2}	44 mV	60 h	Chem. Eng. J., 2021, 426: 131300.
MOF-Fe/Co	1 M KOH	OER	10 mA cm^{-2}	238 mV	50000 s	Angew. Chem. Int. Ed., 2021, 60, 12097–12102
$Ni_{0.5}Co_{0.5}$-MOF-74	1 M KOH	OER	10 mA cm^{-2}	198 mV	1800 s	Nat. Energy, 2020, 5(11): 881-890.
Ru-SAs/AC-FeCoNi	1 M KOH	OER	10 mA cm^{-2}	205 mV	48 h	Adv. Energy. Mater., 2021, 11(1): 2002816