

## Supporting Information

# **Multivalent ruthenium immobilized by self-supported NiFe-organic frameworks for durable electrocatalytic overall water splitting**

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## 1. Experimental

### 1.1 Materials

All chemicals and reagents were of analytical grade and used without further purification. H<sub>2</sub>BDC-NH<sub>2</sub> was purchased from Aladdin Reagent Co. Ltd. RuCl<sub>3</sub>•xH<sub>2</sub>O was obtained from Macklin Reagent Co. Ltd. N,N'-dimethylformamide (DMF) was offered from Tianjin Tiantai Chemicals Co. Ltd. Commercial NFF (thickness: 1.5 mm) was provided by Longshengbao Co. Ltd.

### 1.2 Characterization

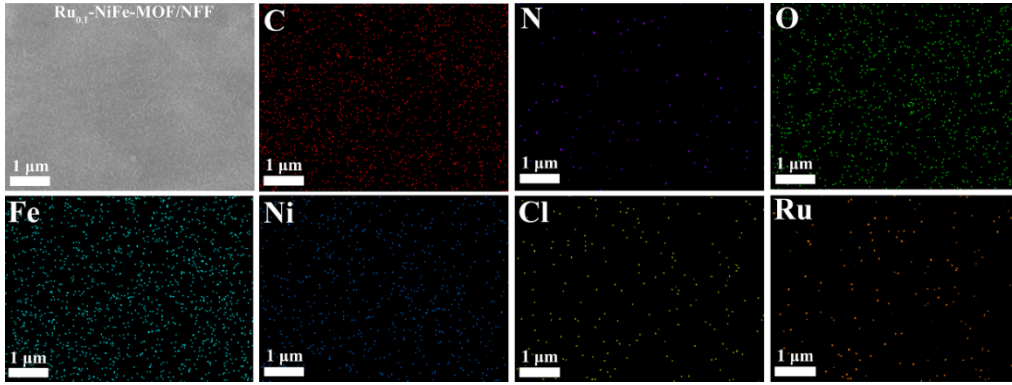
X-ray powder diffraction (XRD) pattern characterization was recorded on a PC2500 diffractometer. Scanning electron microscopy (SEM) images were taken on a HITACHI-Regulus8100 scanning electron microscope. The functional groups of catalysts were characterized through Fourier transformed infrared (FT-IR, Thermoscientific Nicolet 4700). Corresponding energy-dispersive X-ray spectroscopy (EDX) elemental maps were gained using a UltimMax65 equipped with an Oxford energy dispersive spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB250X X-ray photoelectron spectrometer.

### 1.3 Construction of Ru-doped NiFe-MOF powder

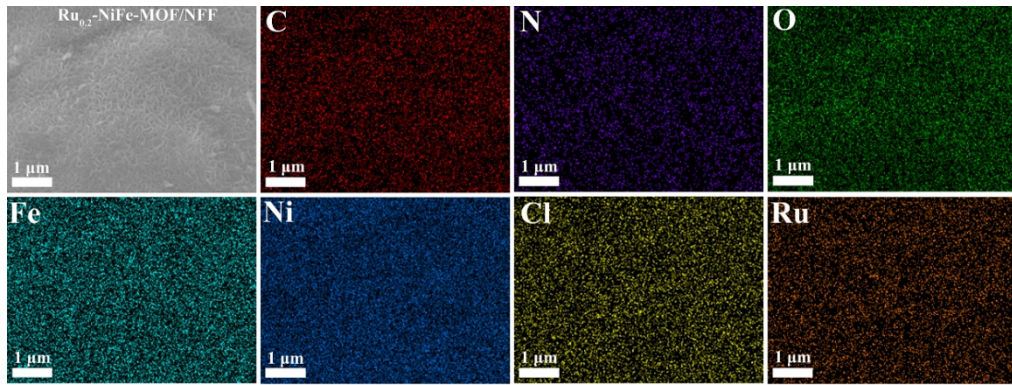
Firstly, 540.4 mg of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 135.1 mg of FeCl<sub>3</sub>•6H<sub>2</sub>O, and 362.4 mg of H<sub>2</sub>BDC-NH<sub>2</sub> were added in the the Teflon autoclave with 44.8 mL of DMF and 6.4 mL of ethanol. Subsequently, the Teflon autoclave was sealed and heated at 150°C for 3 h to obtain NiFe-MOF powder. After cleaned with ethanol and dried, the obtained NiFe-MOF powder was added to a 50 mL of ethanol solution containing 10 mg of RuCl<sub>3</sub> and then heated at 80°C for 12 h. After cooling down to room temperature, the Ru-doped NiFe-MOF powder was washed with ethanol and dried at 60°C.

### 1.3 Electrochemical measurements

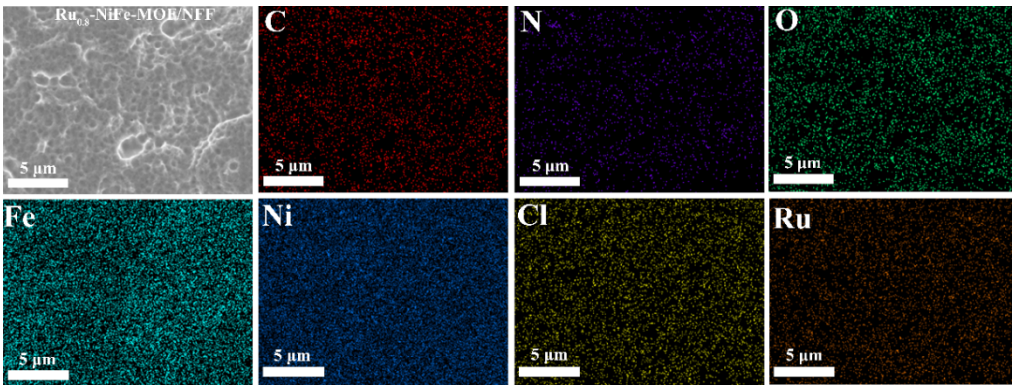
All electrochemical tests of HER and OER were represented on a PGSTAT-302 N (Metrohm) electrochemical analyzer at room temperature. A typical three-electrode system was used, with a saturated calomel electrode as the reference electrode, carbon rod as the counter electrode, and each self-supported catalyst as the working electrode. The electrochemical test was carried out in 1 M KOH solution saturated with N<sub>2</sub>. The voltage range of LSV curve is 0.306 V-0.706 V and (-0.924 V)-(-1.124 V) with 80% iR compensation, and the sweep speed is 1 mV/s. The slope of Tafel is calculated by the formula  $\eta=a+b\cdot\log(j)$ . The impedance is measured in the range of 0.1-100 KHz with an amplitude of 5 mV. The Faraday efficiencies of hydrogen and oxygen production were measured at voltages -0.95 V and 0.51 V, respectively. In addition, Ru<sub>9,1</sub>-NiFe-MOF/NFF participated in electrochemical reaction with an area of 0.09 cm<sup>2</sup> and a loading capacity of 4.1 mg cm<sup>-3</sup>. The loading capacity of RuO<sub>2</sub>/NFF and Pt/C/NFF electrodes is 2.5 mg cm<sup>-2</sup>.



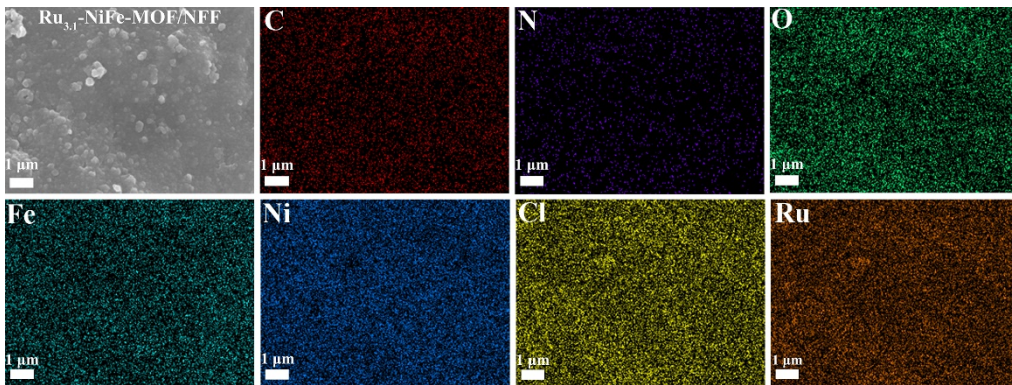
(a)



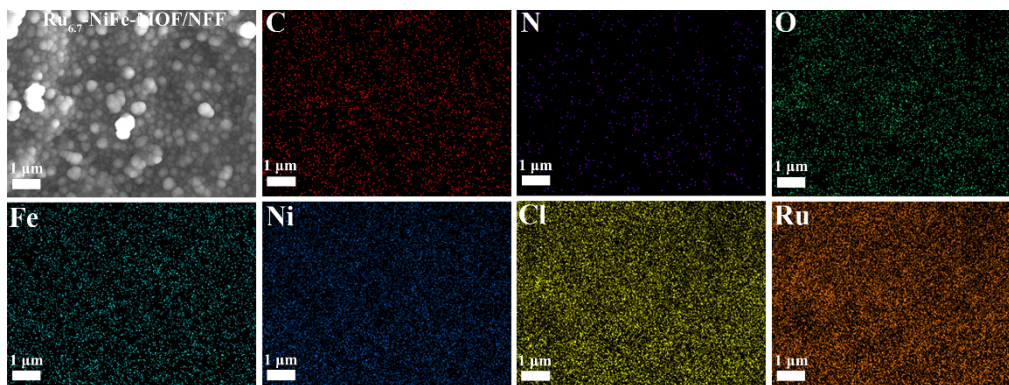
(b)



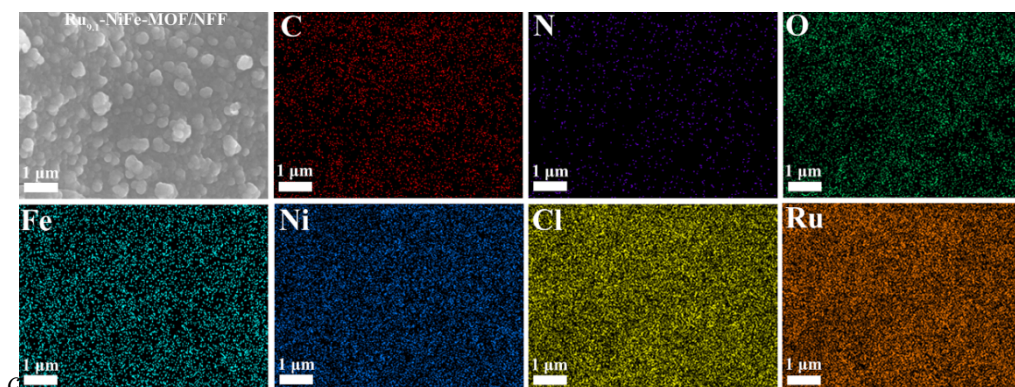
(c)



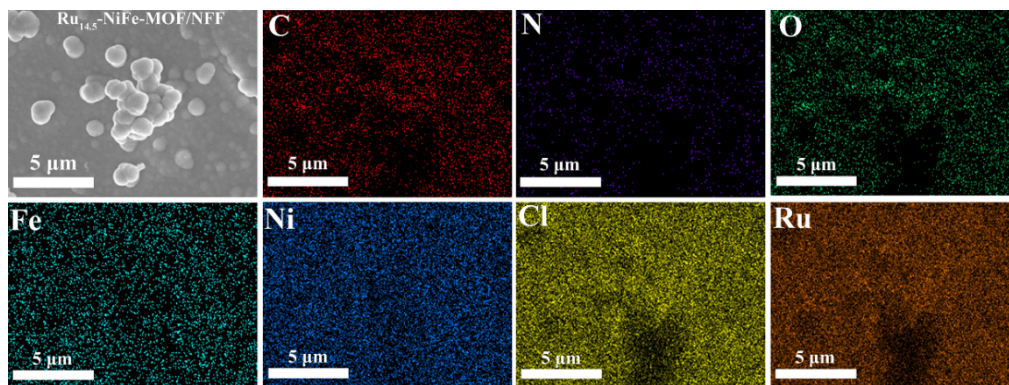
(d)



(e)



(f)



(g)

**Fig. S1.** The EDS-mapping of Ru<sub>0.1</sub>-NiFe-MOF/NFF (a), Ru<sub>0.2</sub>-NiFe-MOF/NFF (b), Ru<sub>0.8</sub>-NiFe-MOF/NFF (c), Ru<sub>3.1</sub>-NiFe-MOF/NFF (d), Ru<sub>6.7</sub>-NiFe-MOF/NFF (e), Ru<sub>9.1</sub>-NiFe-MOF/NFF (f), Ru<sub>14.5</sub>-NiFe-MOF/NFF(g).

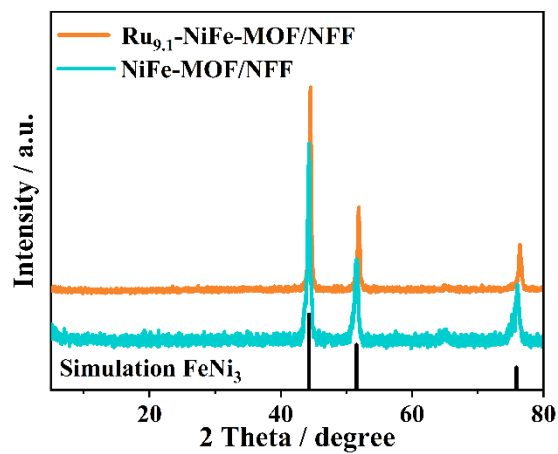


Fig. S2. XRD patterns of NiFe-MOF/NFF and Ru<sub>9,1</sub>-NiFe-MOF/NFF.

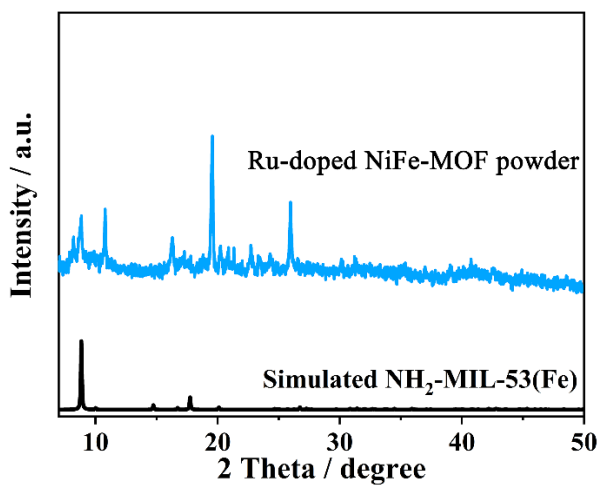
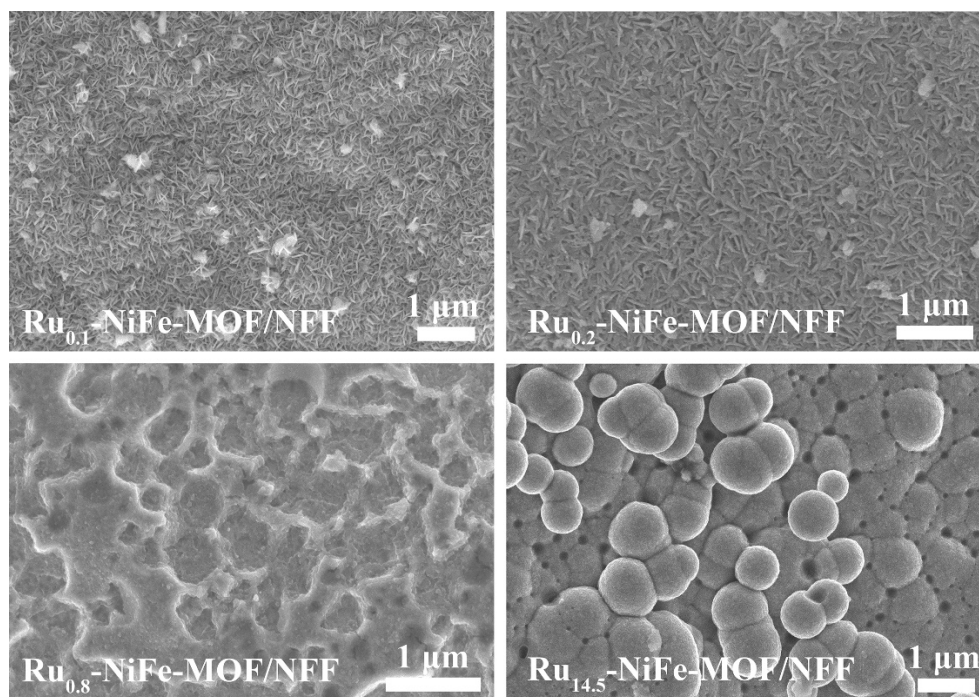
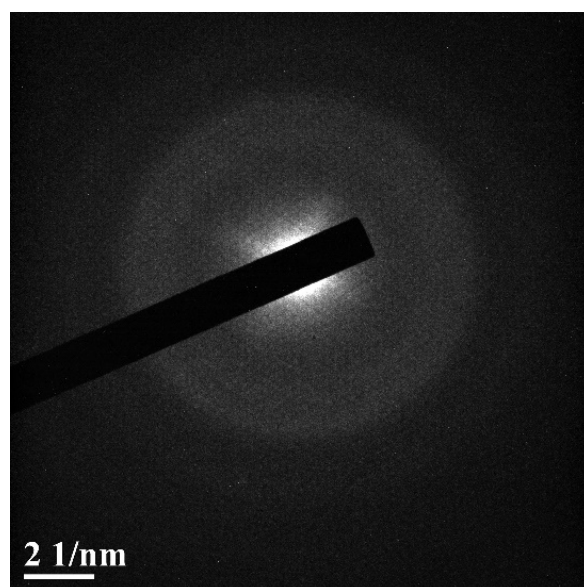


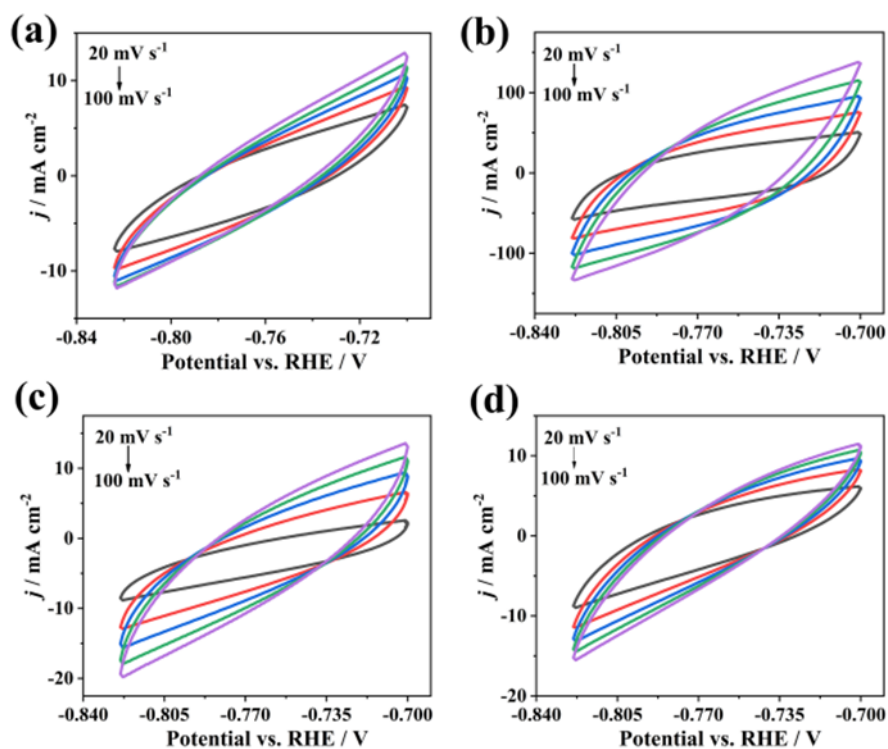
Fig. S3. XRD patterns of Ru-doped NiFe-MOF powder.



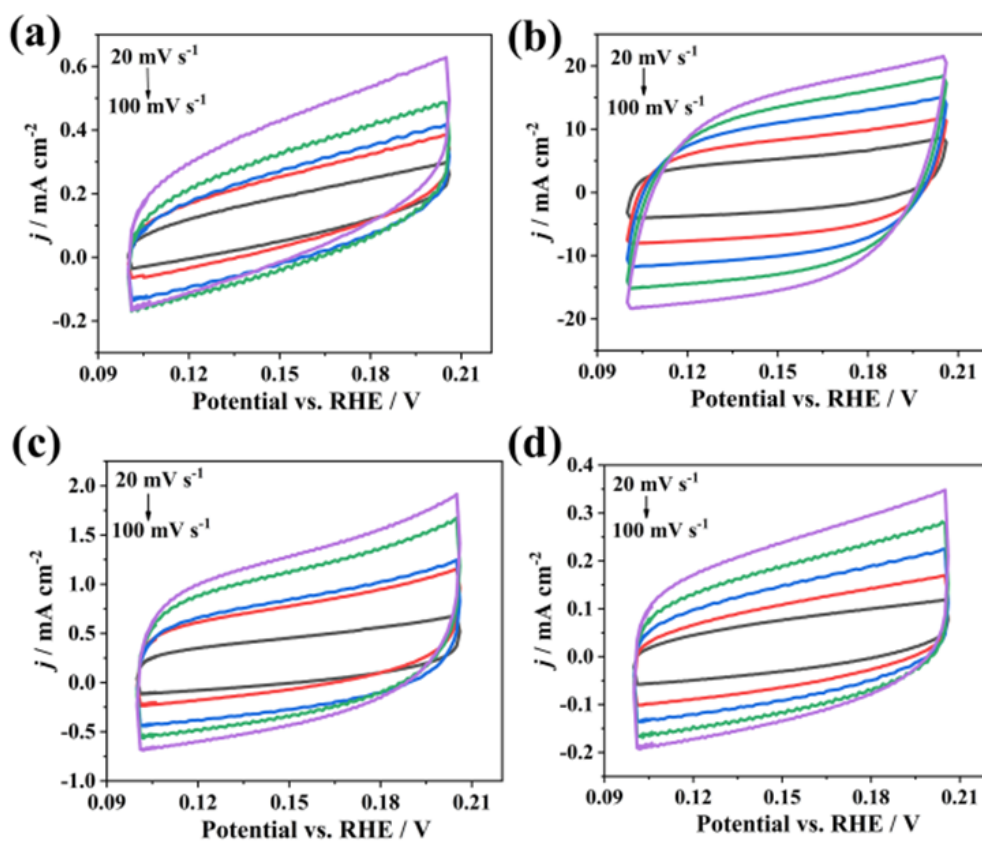
**Fig. S4.** SEM images of (a) Ru<sub>0.1</sub>-NiFe-MOF/NFF, (b) Ru<sub>0.2</sub>-NiFe-MOF/NFF, (c) Ru<sub>0.8</sub>-NiFe-MOF/NFF and (d) Ru<sub>14.5</sub>-NiFe-MOF/NFF.



**Fig. S5.** The SAED pattern of Ru<sub>0.1</sub>-NiFe-MOF/NFF.



**Fig.S6.** Cyclic voltammograms of (a) NiFe-MOF/NFF, (b) Ru<sub>9,1</sub>-NiFe-MOF/NFF, (c) 20Ru/NFF and (d) NFF at scan rates from 20 to 100 mV s<sup>-1</sup> for HER.



**Fig. S7.** Cyclic voltammograms of (a) NiFe-MOF/NFF, (b) Ru<sub>9,1</sub>-NiFe-MOF/NFF, (c) 20Ru/NFF

and (d) NFF at scan rates from 20 to 100 mV s<sup>-1</sup> for OER

**Table S1** The actual doping percent (at%) of Ru species in Ru<sub>x</sub>-NiFe-MOF/NFF determined by repeated EDS.

	Area 1	Area 2	Area 3	Average
Ru <sub>0.1</sub> -NiFe-MOF/NFF	0.1	0.1	0.1	0.1
Ru <sub>0.2</sub> -NiFe-MOF/NFF	0.2	0.2	0.2	0.2
Ru <sub>0.8</sub> -NiFe-MOF/NFF	0.8	0.6	0.9	0.8
Ru <sub>3.1</sub> -NiFe-MOF/NFF	3.4	2.9	3.2	3.1
Ru <sub>6.7</sub> -NiFe-MOF/NFF	6.2	6.9	7.0	6.7
Ru <sub>9.1</sub> -NiFe-MOF/NFF	7.8	9.9	9.5	9.1
Ru <sub>14.5</sub> -NiFe-MOF/NFF	16.4	13	14	14.5

**Table S2** The corresponding actual doping content of Ru species with different amount of RuCl<sub>3</sub> usage.

RuCl <sub>3</sub> usage (mg)	Actual doping content of Ru (%)
2	0.1
5	0.2
10	0.8
13	3.7
16	6.7
20	9.1
50	14.5

**Table S3** The actual doping percent (at%) of Cl species in Ru<sub>9.1</sub>-NiFe-MOF/NFF before and after catalysis determined by repeated EDS.

	Area 1	Area 2	Area 3	Average
before catalysis	4.2	4.9	3.6	4.2
after catalysis	0.1	0.2	0.3	0.2