Supporting Information

Surface Distortion of FeRu Nanoparticles Improves Hydrogen Evolution Reaction Performance in Alkaline Media

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Experimental Section

Chemical

Iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, 99.99%, Aldrich), Ru(III) chloride hydrate (RuCl$_3$·xH$_2$O, ReagentPlus grade, Sigma-Aldrich, degree of hydration ≤1), tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich), triethanolamine (TEA, 99%, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB, 98%, Sigma), 1-hexadecanethiol (HDT, ≥ 95%, Aldrich), oleic acid (OA, 90%, Aldrich), sodium hydroxide (NaOH, 99%, Jinchemical Co., Ltd), methyl alcohol (MeOH, 99.9%, Daejung Chemicals Co., Ltd), ethyl alcohol (EtOH, 99.9%, Daejung Chemicals Co., Ltd), hydrochloric acid (HCl, 35.0%, Daejung Chemicals Co., Ltd), HF (48.0 ~ 51.0%, J. T. Baker), potassium hydroxide (KOH, Sigma-Aldrich, 99.999%) and all other reagents purchased from commercial sources were used as obtained without further purification

Material characterization

X-ray diffraction (XRD, Rigaku Miniflex II (4.5 kW) diffractometer using Cu-Kα radiation at 30 kV and 15 at the Advanced Bio-Interface Core Research Facility, Sogang University), scanning electron microscopy (SEM, Magellan 400 operated at 2 kV), transmission electron microscopy (TEM, JEOL JEM-2100F operated at 200 kV) with selected area electron diffraction (SAED) patterns, and aberration-corrected field scanning TEM (JEOL ARM-200CF operated at 200 kV) equipped with electron probe corrector and energy dispersive X-ray spectroscope (EDX) were conducted to characterize FeRu NPs. Samples for TEM and STEM investigation were prepared by dropping the diluted samples in EtOH or hexane on a 300 mesh carbon support Cu grid (Ted Pella, Inc.) and amorphous Si grid (SPI Supplies, US100-A05Q33A, Membrane thickness 5 nm), respectively. The Fe/Ru ratios in the catalysts were determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Agilent 7700). Thermogravimetric Analysis (TGA, TA instruments TA-Q50) was performed on a thermal analysis from 30 to 900 °C under N$_2$ atmosphere by heating the sample at a heating rate of 30 °C min^{-1} and maintaining at 900 °C for 150 min. X-ray absorption spectroscopy data were obtained at the 8A1 beamline of the Pohang Accelerator Laboratory (PAL); specifically Fe L-edge including those of Ru was obtained. High-resolution photoemission spectroscopy experiments were also performed at the 8A1 beamline at the PAL,

and were carried out with an electron analyzer (Physical Electronics, PHI-3057). Photon energy was set to 380 eV to obtain Ru 3d core level spectra.

Synthesis of MSN

MSN were prepared through a modified stöber method.[1] CTAB (0.40 g, 1.10 mmol), TEA (6.0 g, 40.0 mmol), and 17 mL of EtOH were added in 53 mL of deionized water, and the mixture was stirred at 80 °C for 10 min, followed by addition of TEOS (2.8 mL, 12.5 mmol). After continuous stirring for 3 h at this temperature, the synthesized solid product was collected by centrifuged and repeatedly washed with distilled water and EtOH. To completely removal the surfactant incorporated into the silica, the synthesized solid product was heat for 3 h at 60 °C in EtOH (100 mL) containing 2 mL of concentrated HCl. The resulting MSN were collected by centrifugation and repeatedly washed with distilled water and EtOH, and then dried in an oven at 80 °C to yield a white powder.

Preparation of HF-treated FeRu NPs/C

To prepare HF-treated FeRu NPs/C catalyst, the FeRu NPs@MSN was added to carbon support (Vulcan carbon XC-72) with a weight ratio of 2.4:1 in EtOH (20 mL) and sonicated the mixture for 1 h. Thereafter, we added 2% HF EtOH solution (20 mL) to the mixture under sonication and continued for another 1 h. We collected the carbon supported catalyst by centrifugation and thoroughly washed with distilled water and EtOH.

Preparation of FeRu alloy NPs/C

In a typical synthesis of FeRu alloy NPs/C, 16 mg of $RuCl_3$, 12.8 mg of $Fe(acac)_3$, and 24 mg of Vulcan-XC72 carbon were dispersed in 10 mL of EG in a glass vial. The vial was pre-heated at 130 °C for 30 min in an oil bath under magnetic stirring. Then, the vial was maintained at 170 °C for 6 h. The resulting RuFe alloy NPs/C was collected by centrifugation at 12,000 rpm, and then washed three times with ethanol and dried in Ar.

Electrochemical measurements

All electrochemical measurements were performed with a three-electrode cell using potentiostats (CHI 600E from CH Instruments and VSP from Bio-Logic) at room temperature. A Hg/HgO electrode was used as a reference electrode and calibrated with respect to the reversible hydrogen electrode (RHE). A graphite rod and a glassy carbon electrode (GCE, 5

mm in diameter) were used as a counter and a working electrode, respectively. To prepare the electrocatalyst inks, a catalyst and 10 μL Nafion (5 wt% in a mixture of lower aliphatic alcohol and water, Aldrich) were dispersed in 2.5 mL of 4:1 v/v water/isopropanol and further ultrasonic agitation for 10 min. The resulting catalyst loaded on GCE was 0.28 mg cm^{-2}. The electrochemical measurements were carried out in a teflon beaker for alkaline electrolytes to avoid any glass contamination. The working electrodes were pre-cycled in Ar-saturated 1.0 M KOH electrolytes for 20 cycles between 0.08 and 0.8 V_{RHE} at a scan rate of 100 mV s^{-1}. Before the electrochemical tests, the electrolytes were bubbled with H_2 gas for 10 min. The polarization curves were obtained from the linear sweep voltammetry with a scan rate of 2 mV s^{-1}. Electrochemical impedance spectroscopy was performed in H_2-saturated 1.0 M KOH electrolytes at a constant potential of -0.04 V_{RHE} from 100 kHz to 0.10 Hz with an AC potential magnitude of 5 mV. Z' and Z" are the real and imaginary parts of the impedance Z, respectively. Cu underpotential deposition (Cu_{UPD}) on Pt and Ru has proven to be an ideal method for qualifying their corresponding active sites. In this approach, the number of active sites (n) can be qualified based on the Cu_{UPD} stripping charge (Q_{Cu}, $Cu_{UPD} \rightarrow Cu^{2+} + 2e^-$) with the following equation:

$$n = Q_{Cu} / 2F$$

, where F is the Faraday constant (C mol^{-1}). The electrochemically active surface area were obtained from the charges associated with the stripping of Cu_{UPD} on the all catalysts by assuming 420 μC cm^{-2} for a full monolayer coverage of Cu on Ru facets. The Cu_{UPD} was conducted in an Ar-saturated solution containing 0.1 M H_2SO_4 and 0.02 M $CuSO_4$. The turnover frequency (TOF) (H_2 s^{-1}) can be calculated with the following equation:

$$TOF = I / (2Fn)$$

, where I is the current (A) during linear sweep measurement and n is the number of active sites (mol). The factor 1/2 is based on the consideration that two electrons are required to form one hydrogen molecule. For CO stripping experiments, CO was adsorbed on the precleaned electrode by holding the potential at 0.1 V_{RHE} for 10 min in a CO-saturated 1.0 M KOH electrolyte. The CO stripping curve was then recorded after the extra CO in the solution had been removed by purging Ar for 10 min. Accelerated durability tests were performed at room temperature in 1.0 M KOH electrolytes by applying cyclic potential sweeps between 0.05 V

and −0.1 V_{RHE} at a scan rate of 100 mV s^{-1} for 5000 cycles. Chronopotentiometric curves were obtained in Ar-saturated 1.0 M KOH electrolytes for 12 h at a current density of 10 mA cm^{-2}.
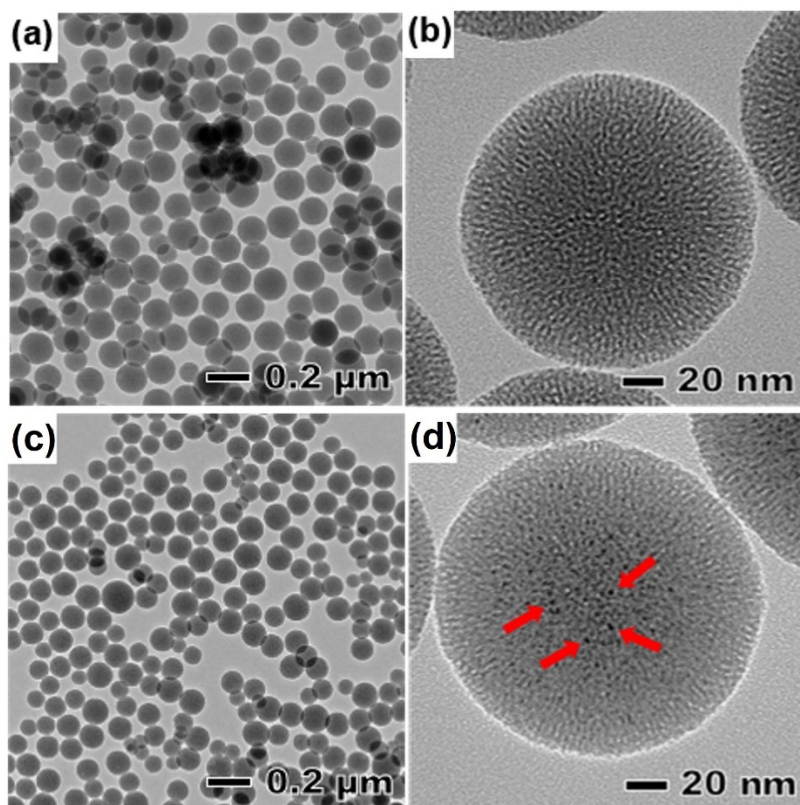
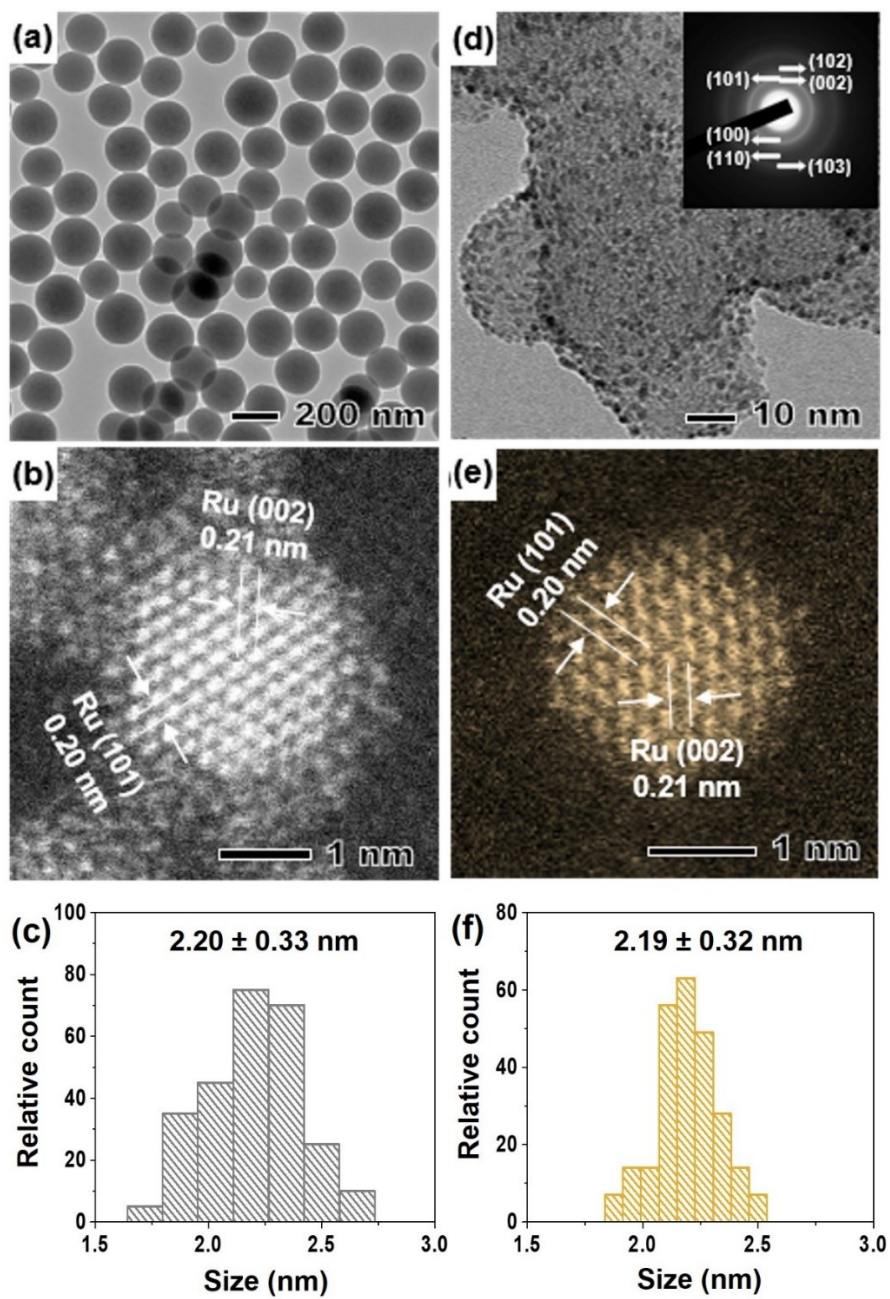**Fig. S1** TEM images of (a,b) MSN and (c,d) FeRu NPs@MSN. Red arrows in (d) indicating the embedded FeRu NPs.
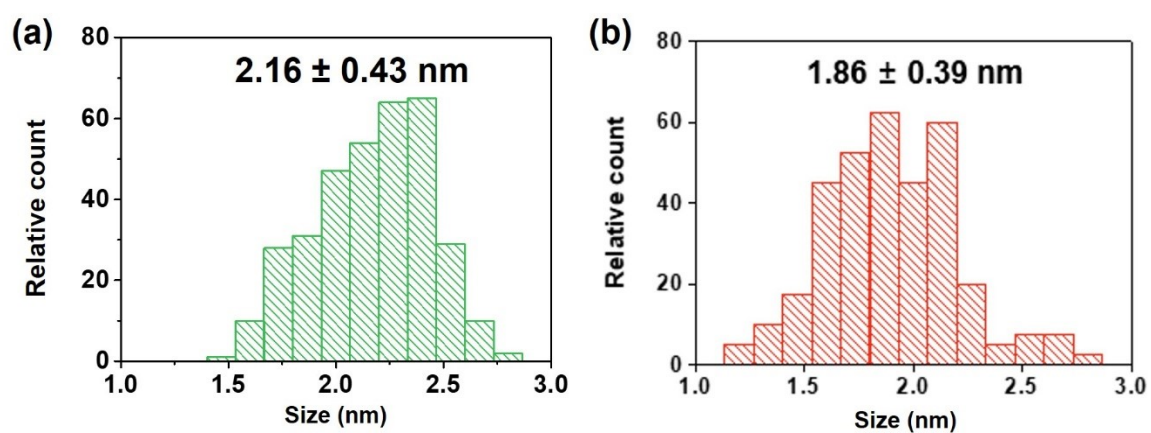
Fig. S2 Particle size distribution histograms of FeRu NPs in (a) FeRu NPs@MSN and (b) HF-treated FeRu NPs/C.
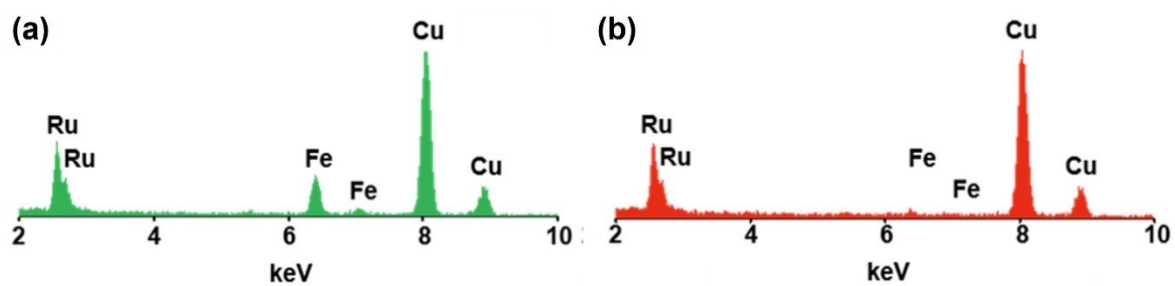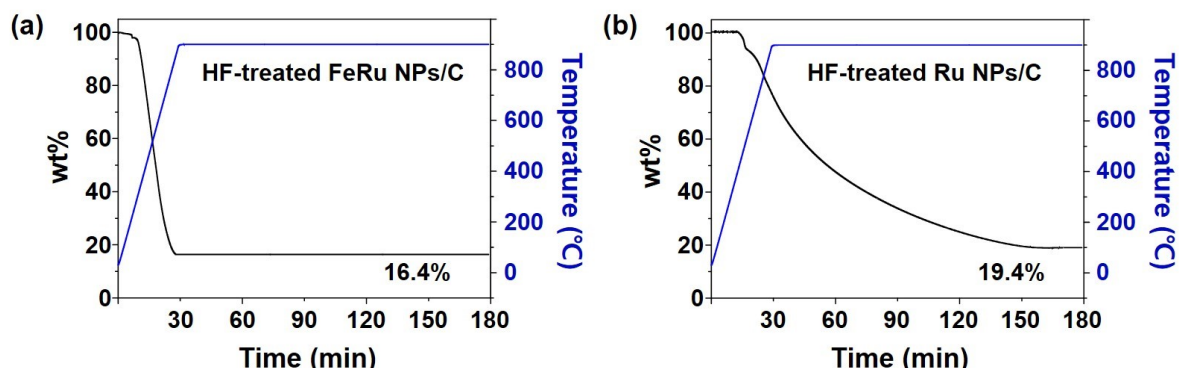
Fig. S3 EDX spectra of (a) FeRu NPs@MSN and (b) HF-treated FeRu NPs/C. *Copper is from the TEM grids.
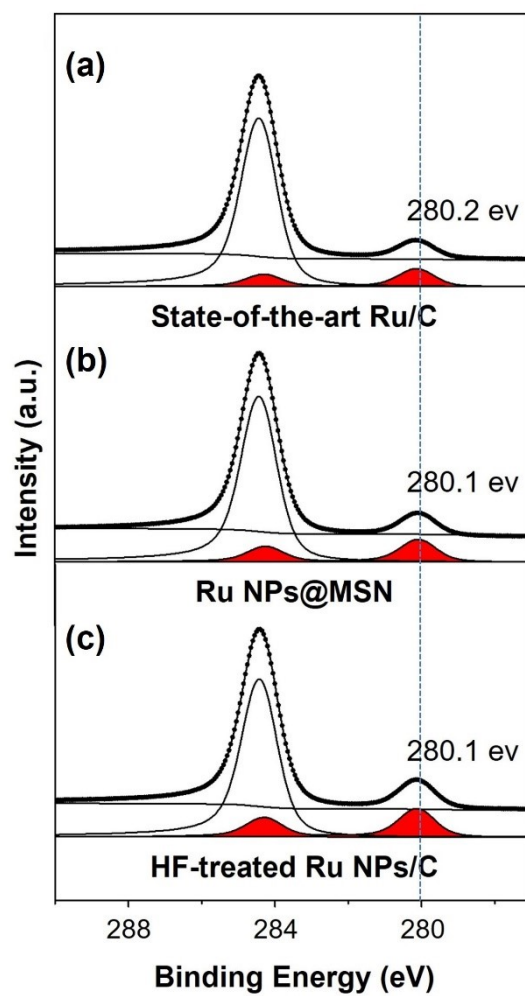
Fig. S4 TEM, HAADF-STEM images, and particle size distribution histograms of (a,b,c) the Ru NPs@MSN and (d,e,f) HF-treated Ru NPs/C.

Fig. S5 TGA profiles of (a) HF-treated FeRu NPs/C and (b) HF-treated Ru NPs/C. TGA was performed on a thermal analysis from 30 to 900 °C under N_2 by heating at a ramping rate of 30 °C min^{-1} and maintaining at 900 °C for 150 min.

Fig. S6 HRPES spectra of Ru 3d for (a) the state-of-the-art Ru/C, (b) Ru NPs@MSN, and (c) HF-treated Ru NPs/C.
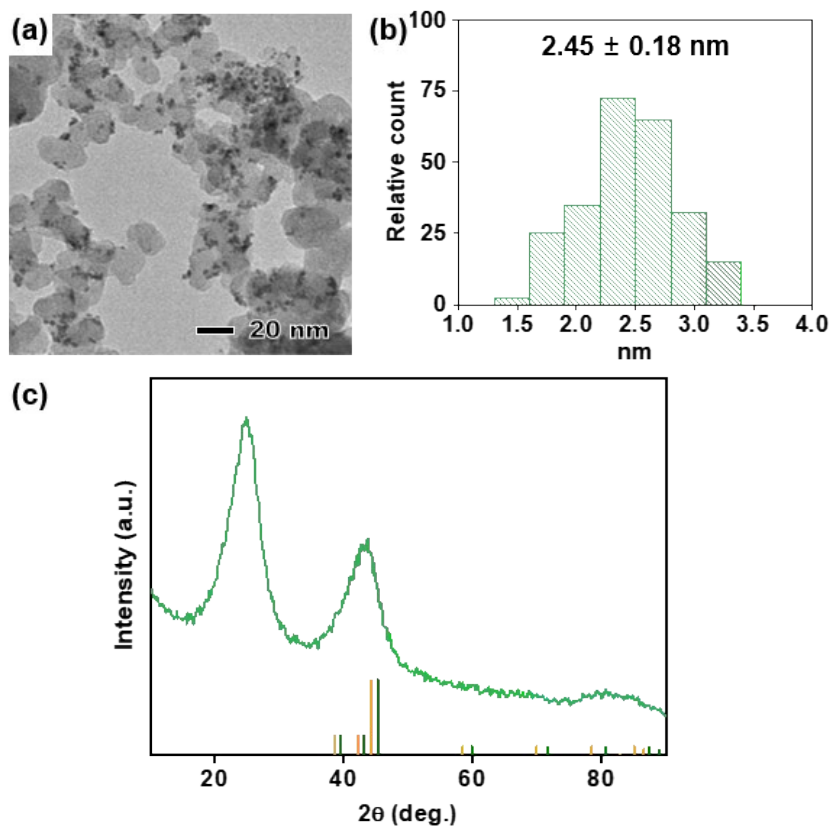
Fig. S7 (a) TEM image, (b) particle size distribution histogram, and (c) XRD pattern of the FeRu alloy NPs/C. The vertical lines in (c) showing the hcp phases of the Ru (yellow) and FeRu references (green).
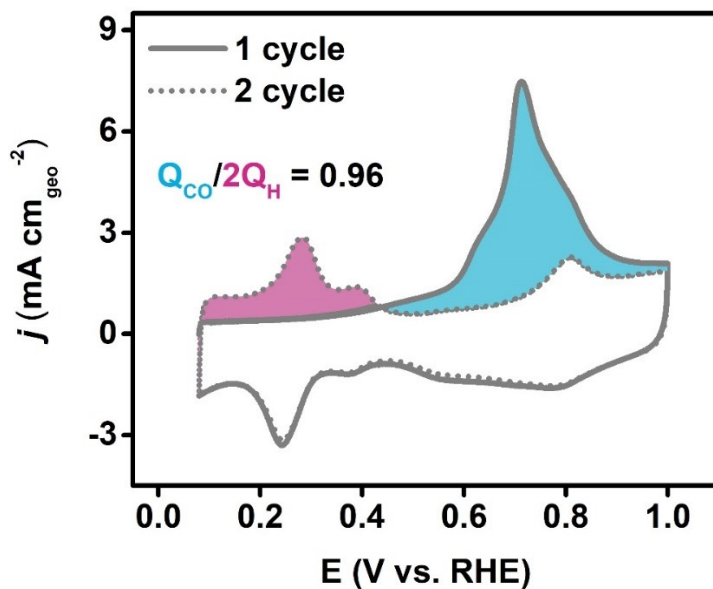
Fig. S8 First and second cycles of CO stripping experiment recorded in Ar-saturated 1.0 M KOH electrolytes at a scan rate of 50 mV s^{-1} for the state-of-the-art Pt/C. Peak areas related to H$_{upd}$ desorption and CO electrooxidation colored in purple and blue.
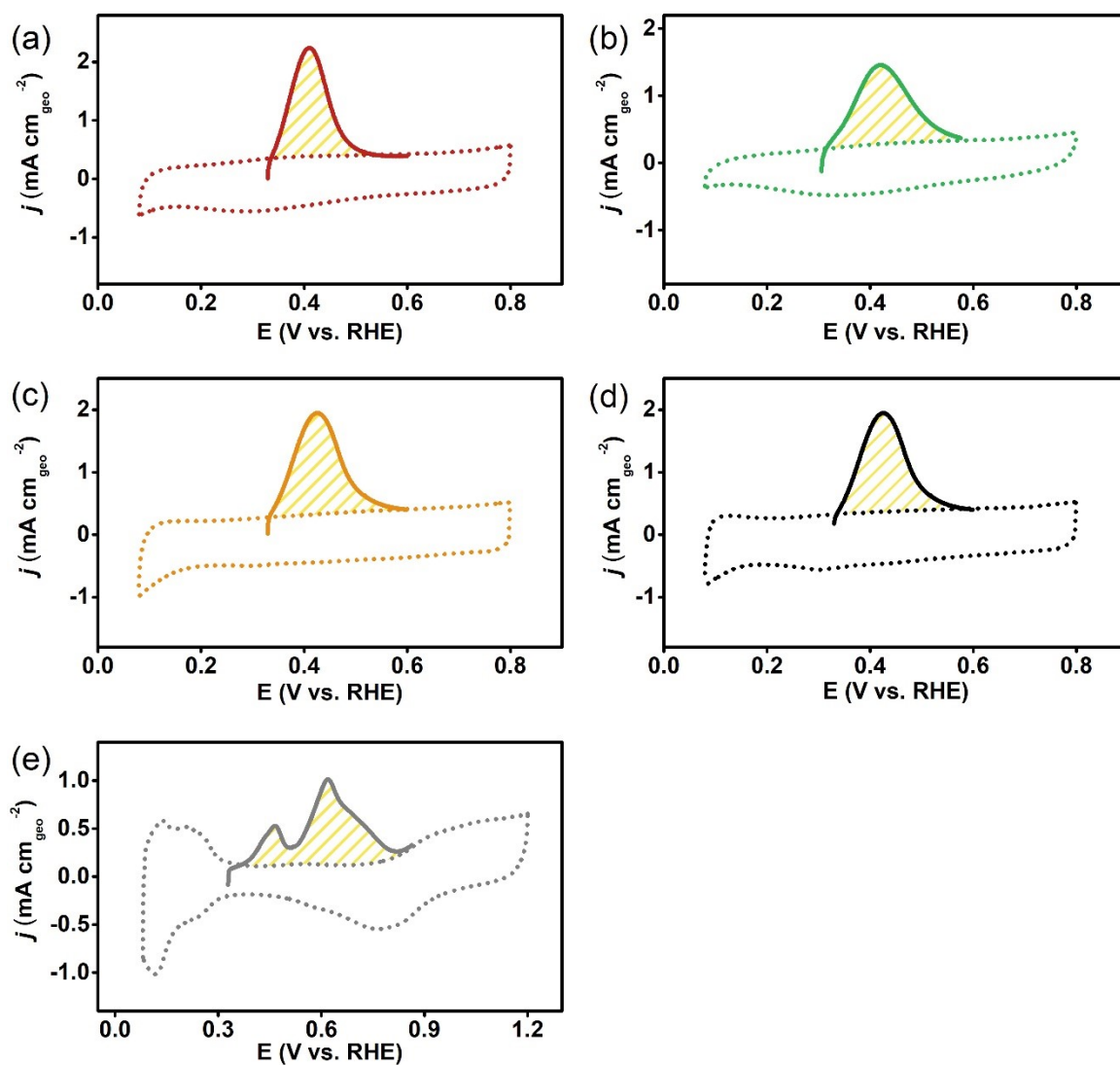
Fig. S9 Cu underpotential deposition (Cu_{UPD}) curves obtained in 0.1 M H$_2$SO$_4$ in the absence (dashed line) and presence (solid line) of 0.02 M CuSO$_4$ for the (a) HF-treated FeRu NPs/C, (b) FeRu alloy NPs/C, (c) HF-treated Ru NPs/C, (d) the state-of-the-art Ru/C, and (e) Pt/C.
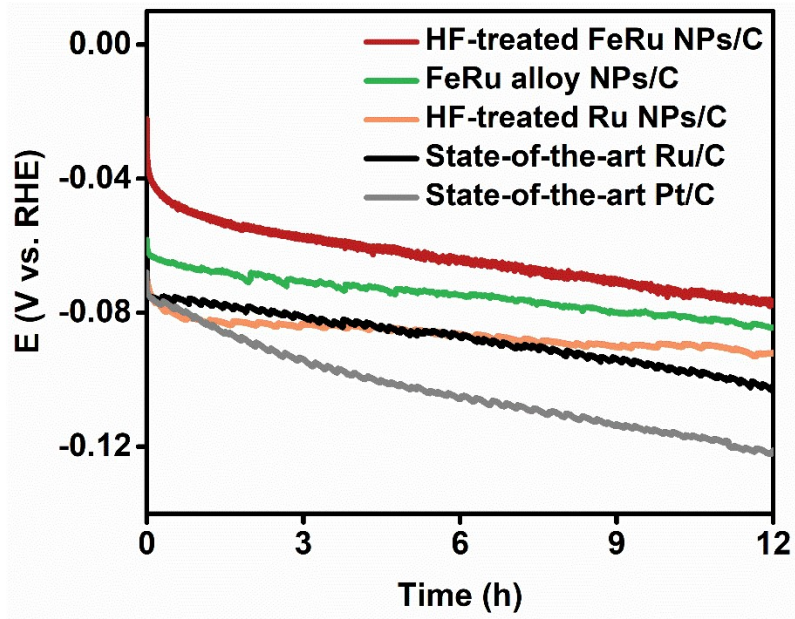
Fig. S10 Chronopotentiometry curves of the different catalysts in 1.0 M KOH electrolytes at the current density of -10 mA cm^{-2} for 12 h.
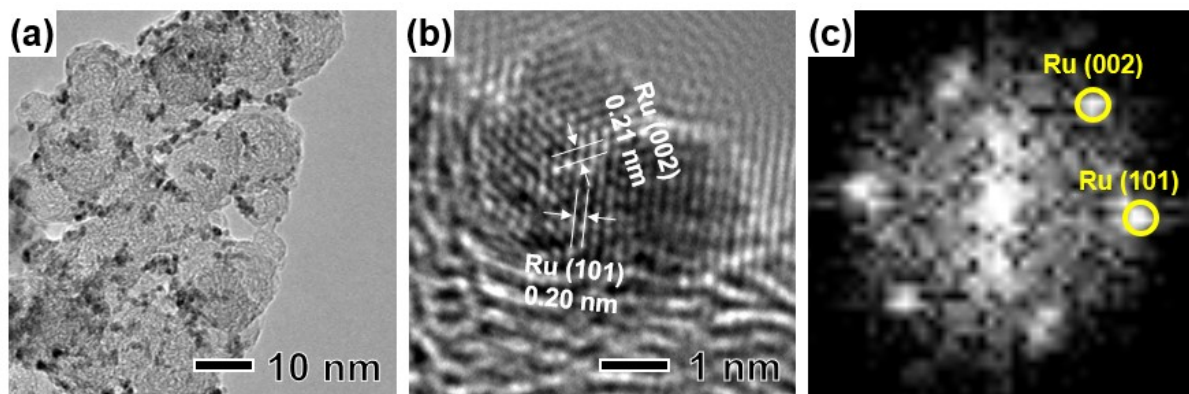
Fig. S11 (a) TEM and (b) HRTEM images and (c) fast Fourier-transform pattern of the HF-treated FeRu NPs/C after 5000 times of cyclic potential sweeps.

Table S1. Atomic ratio of Fe:Ru measured by EDX and ICP-MS for FeRu NPs@MSN and HF-treated FeRu NPs/C.

Sample	Atomic ratio of Fe:Ru	
	EDX	ICP-MS
FeRu NPs@MSN	44.4 : 55.6	44.5 : 55.5
HF-treated FeRu NPs/C	4.9 : 95.1	5.6 : 94.4

Table S2. Comparison of reported Ru-based electrocatalysts for HER in alkaline media.

Catalyst	Overpotential at -10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	Reference
HF-treated FeRu NPs/C	23	43	1.0 M KOH	This work
Ru@C$_2$N	17	38	1.0 M KOH	2
Ru/C$_3$N$_4$/C	79	69	0.10 M KOH	3
Ru SAs/N-Mo2C NSs	43	38.67	1.0 M KOH	4
Ru$_2$P/RGO-20	13	56	1.0 M KOH	5
RuNi/CQDs-600	13	40	1.0 M KOH	6
Ru/CQDs	10	47	1.0 M KOH	7
Ru-MoS$_2$/CNT	50	62	1.0 M KOH	8
CoRu$_{0.25}$@N-C	27	73	1.0 M KOH	9
Ru@CN-0.16	32	53	1.0 M KOH	10
Au-Ru-2 NWs	50	30.8	1.0 M KOH	11
Ru@GNs-300	40	28	1.0 M KOH	12

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