Supporting Information for

General Fabrication of RuM (M=Ni, Co) Nanoclusters for Boosting Hydrogen Evolution Reaction Electrocatalysis

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Experimental section

Chemicals

Potassium hydroxide (KOH, analytical reagent), nickel (Ⅱ) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, ≧98.0%), cocalt (Ⅱ) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, ≧99.0%), , sodium borohydride ($NaBH_4$, 96.0%), and ethanol (C_2H_5OH) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ruthenium trichloride ($RuCl_3$) was purchased from Energy Chemical. Hydrogrn peroxide (H_2O_2, 30%) was purchased from Shanghai Lingfeng Chemical Reagent CO.LTD. Carbon fiber cloth (CFCs) were purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4, industrial grade, 98%) was purchased from experimental materials supply center of Soochow University. All the chemicals were used without further purification.

Synthesis of RuNi/CFCs

The CFCs were pre-treated by immersed in H_2SO_4/H_2O_2 (30%)=3:1(volume ratio) overnight, then ultrasound with acetone, ethanol and deionized water was performed successively for 30 minutes. The 50mg acid-treated CFCS was dispersed into 50mL ethylene glycol (EG) under ultrasonication for 1h. Afterwards, 16.53 mg $RuCl_3$ and 15.84 mg $NiCl_2 \cdot 6H_2O$ were added for preparing RuNi/CFCs, and the resulting mixture was stirred for three hours. Then the temperature of the solution was increased to 120 °C and $NaBH_4$ solution (15 mL, 10 mg mL^{-1}) was added drop by drop under magnetic stirring. After 30 min reaction, the mixture was cooled down to room temperature, centrifuged and rinsed several times with DI water. The collected black powders were dried in a vacuum oven at 70 °C for 24 hours. RuCo/CFCs were synthesized using the same procedures as that of RuNi/CFCs except changing $NiCl_2 \cdot 6H_2O$ to $CoCl_2 \cdot 6H_2O$. Ru/CFCs were synthesized using the same procedures as that of RuNi/CFCs in the absence of $NiCl_2 \cdot 6H_2O$.

Characterizations

Transmission electron microscopy (TEM) and high-angle annular dark-field (HAADF)-scanning TEM (STEM) images were taken using an FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. The samples were prepared by dropping ethanol dispersion of samples onto carbon-coated copper TEM grids using pipettes and dried under ambient condition. Powder X-ray diffraction (PXRD) patterns were collected on an X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). The concentrations of catalysts were determined by ICP-AES (710-ES, Varian, ICP-AES). X-ray photoelectron spectroscopy (XPS) was performed on an SSI S-Probe XPS spectrometer.

Electrochemical tests

The electrochemical performance tests in 1 M KOH electrolyte media or 0.5 M H_2SO_4 were performed on a CHI760e electrochemical workstation without iR compensation, using an Ag/AgCl electrode, a graphite rod, and as-prepared bimetal supported by carbon fiber cloth electrodes as the reference electrode, the counter electrode, and the working electrode, respectively. The content of RuNi on CFCs is as follows:

Equation S1: Content of RuNi= $\frac{(52.3-50.0)\ mg}{1*3\ cm^2} = 0.77 mg\ cm^{-2}$,

Therefore, the mass loading of RuNi anchored on carbon fiber cloth was 0.77 mg cm⁻

[2].The EIS tests were measured by ac impedance spectroscopy in the frequency range of 10^5 to 0.1 Hz. According to the Nernst equation:

Equation S2: $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197$,

Where E_{RHE} is the potential vs a reversible hydrogen electrode, $E_{Ag/AgCl}$ is the potential vs an Ag/AgCl electrode, and pH is the pH value of the electrolyte. The effective surface areas of catalysts was estimated through measuring the capacitances of double layer at the solid-liquid interface by cyclic voltammograms (CVs) collected in the region of -0.047-0.153 V vs. RHE. The electrochemical active surface area is calculated using the following formula:

Equation S3: $A_{ECSA} = C_{dl} / C_s$

Where C_s is specific capacitance = 0.04 mF cm^{-2} in 0.5 M H_2SO_4. The specific activity is obtained by normalizing the apparent current to A_{ECSA}.

Supporting Figures and Tables

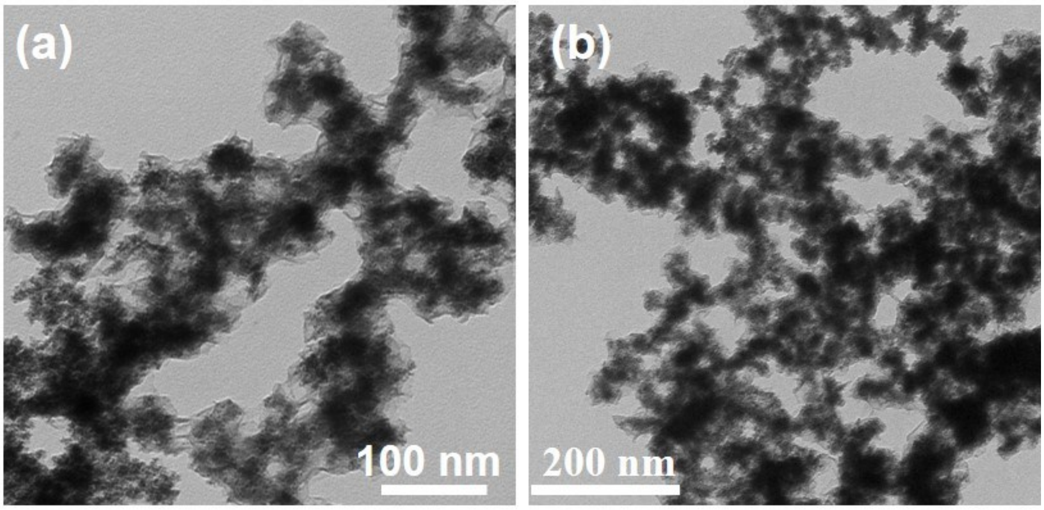

Fig. S1. Representative TEM images of RuNi/CFC with different magnifications.

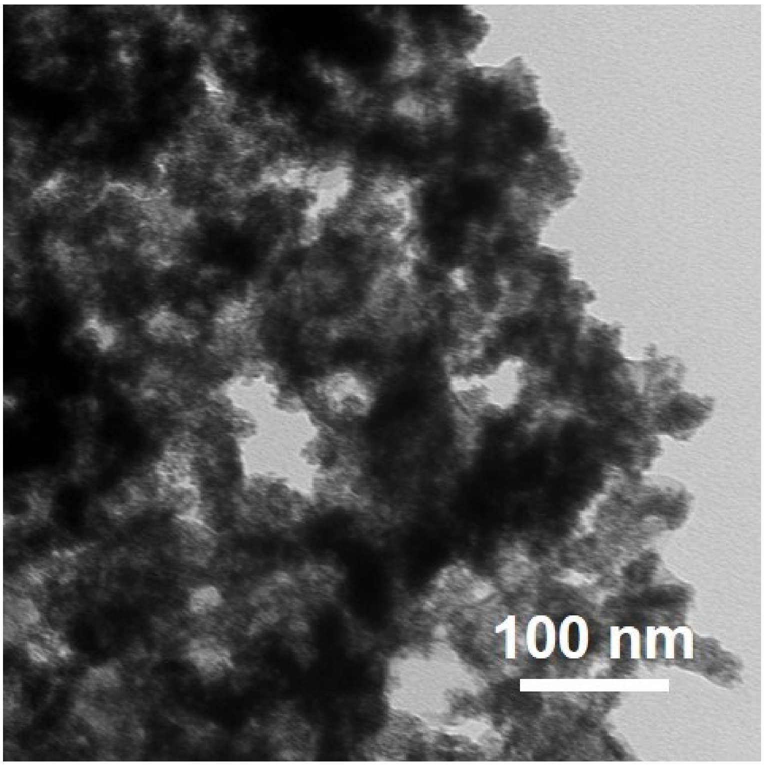

Fig. S2. Representative TEM image of RuCo/CFC.

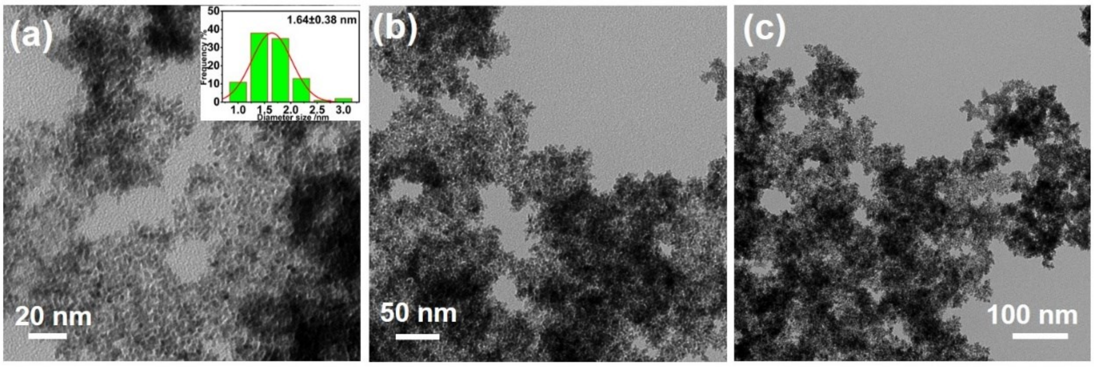

Fig. S3. Representative SEM images of Ru/CFC with different magnifications.

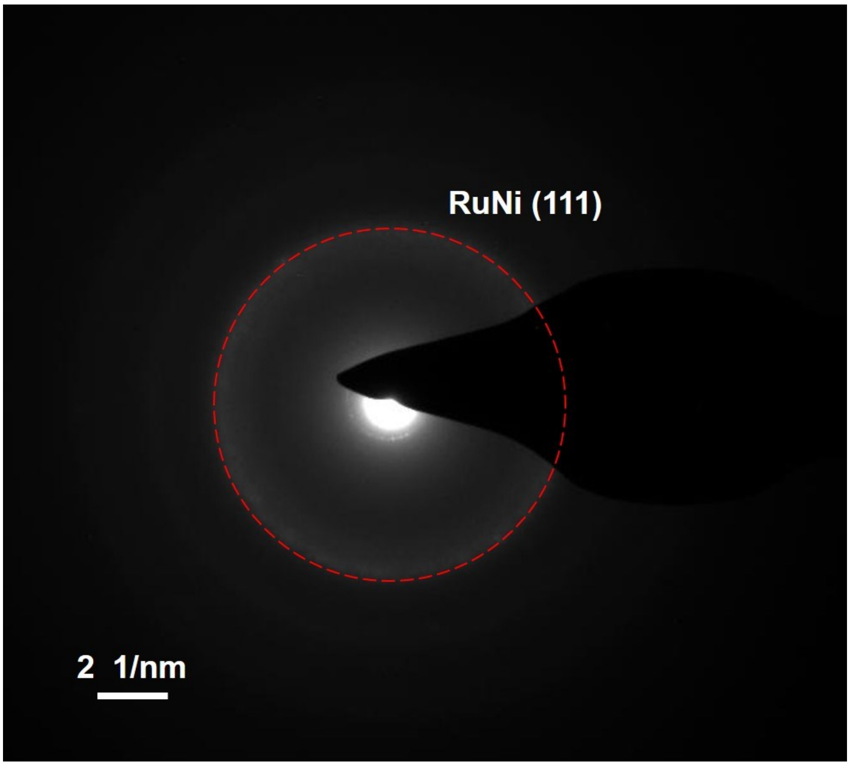

Fig. S4 SAED pattern of RuNi/CFC

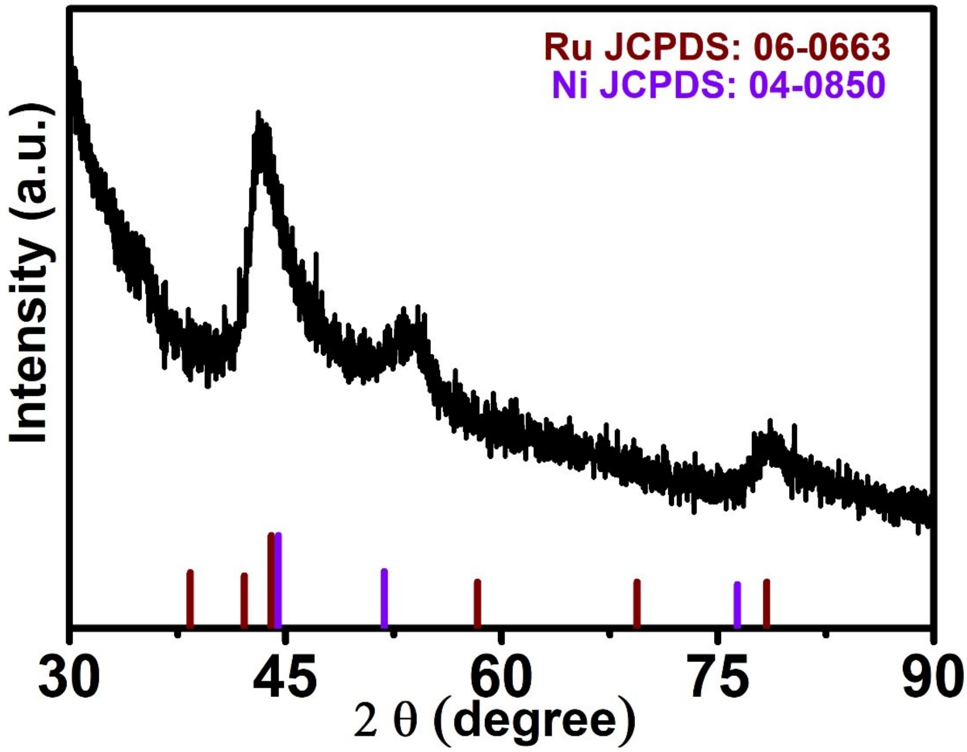

Fig. S5. PXRD pattern of RuNi/CFC.

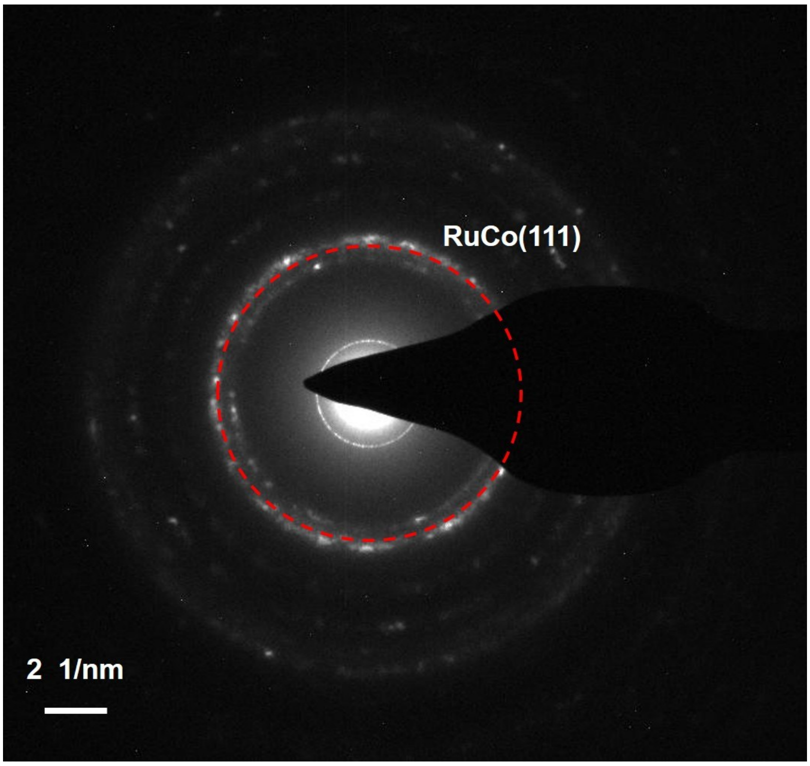

Fig. S6 SAED pattern of RuCo/CFC

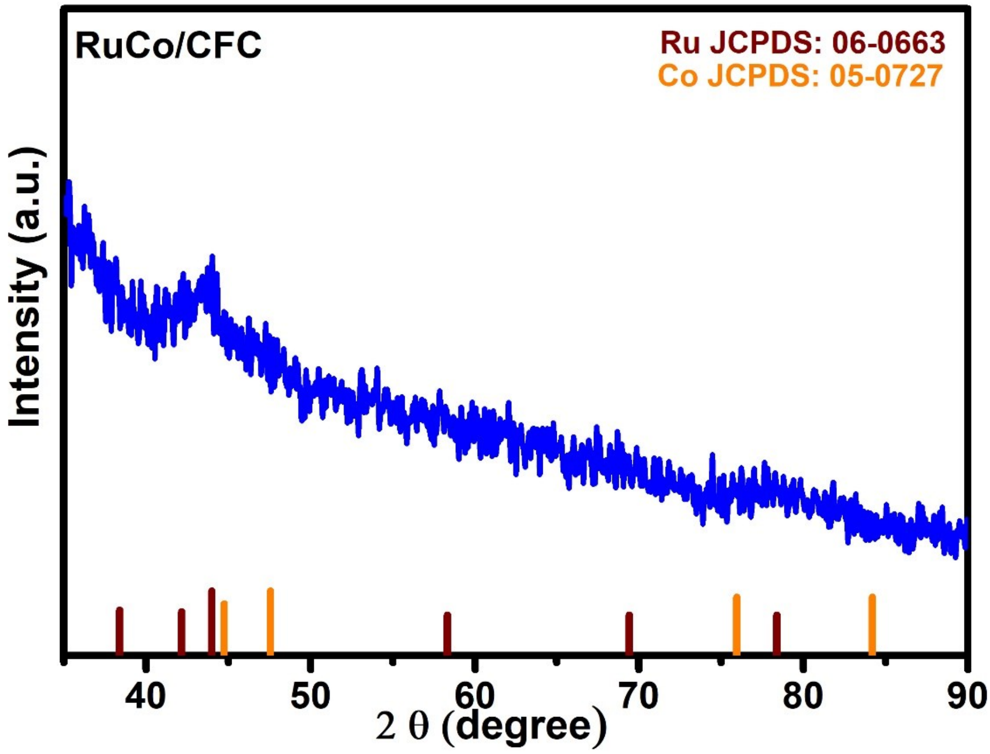

Fig. S7. PXRD pattern of RuCo/CFC.

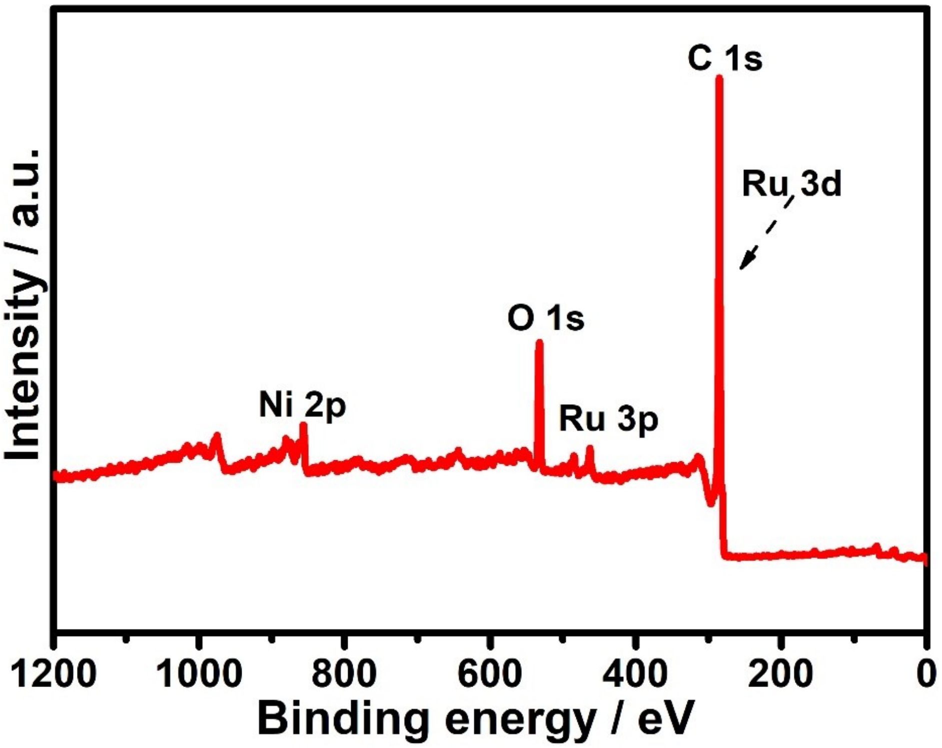

Fig. S8. XPS survey spectrum of RuNi/CFC.

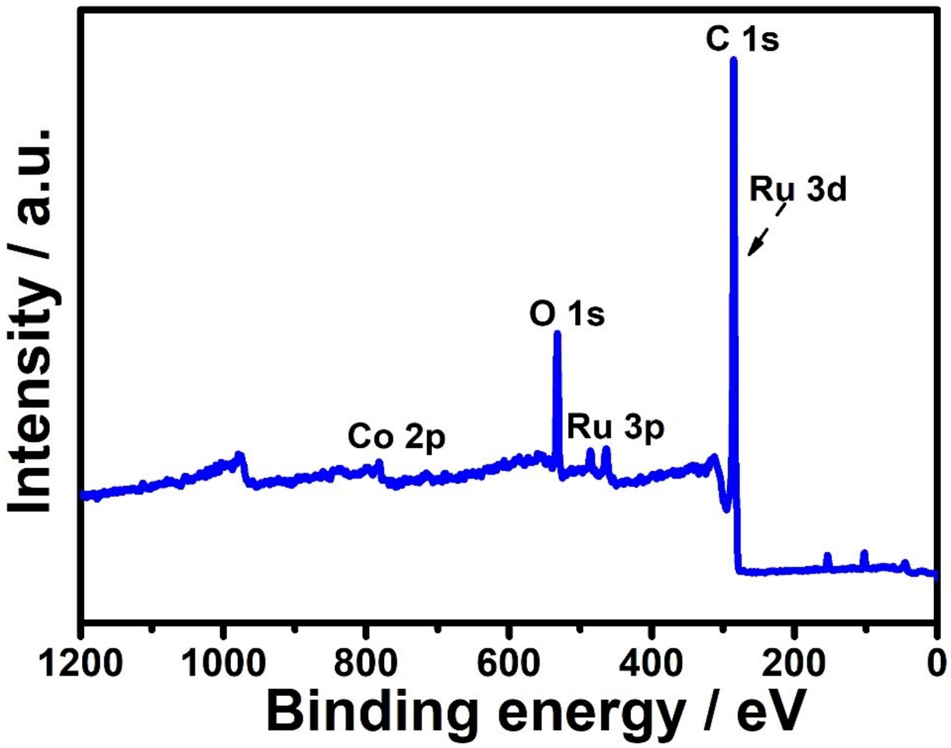

Fig. S9. XPS survey spectrum of RuCo/CFC.

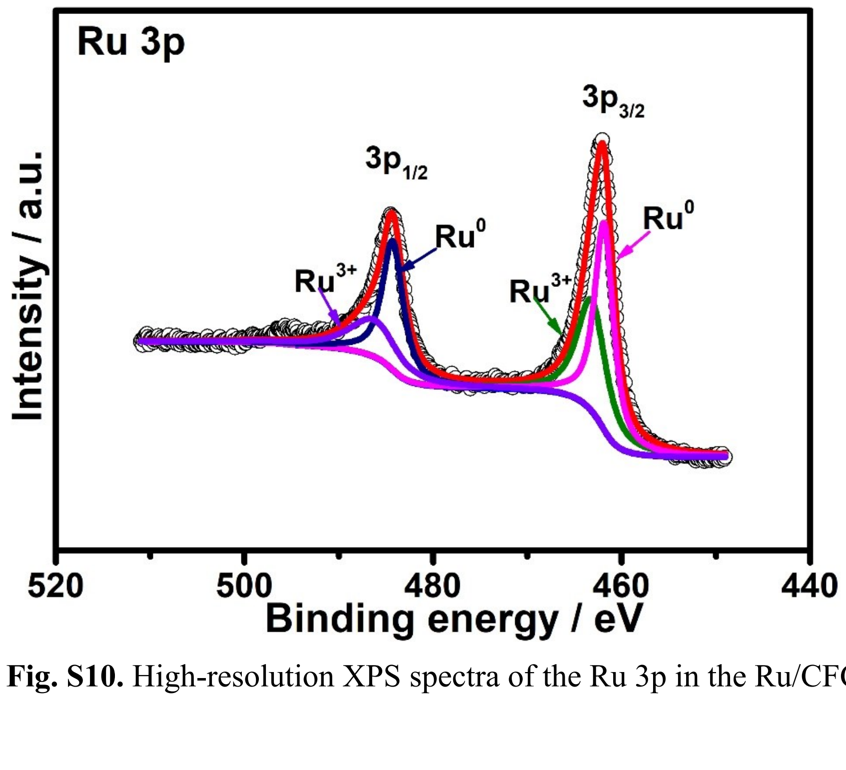

Fig. S10. High-resolution XPS spectra of the Ru 3p in the Ru/CFC.

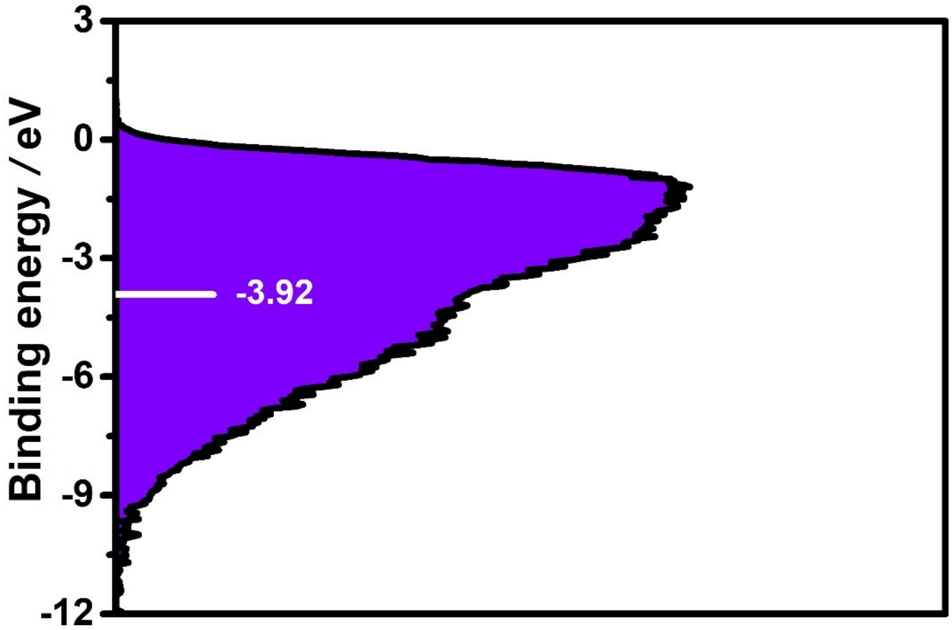

Fig. S11. The d-band center of the metal atoms where hydrogen atoms are adsorbed on the surface of Ru/CFC.

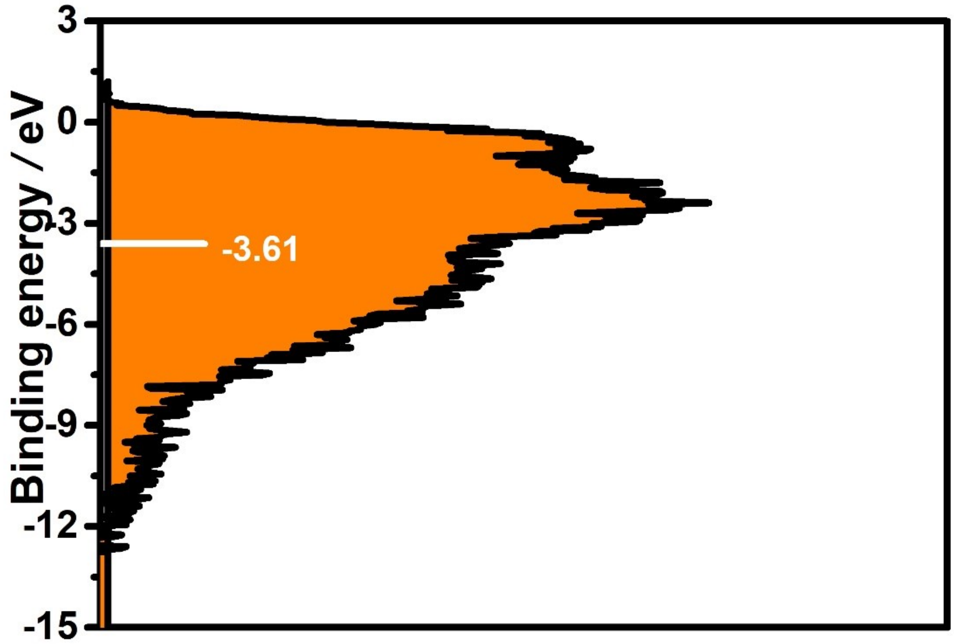

Fig. S12. The d-band center of the metal atoms where hydrogen atoms are adsorbed on the surface of RuCo/CFC.

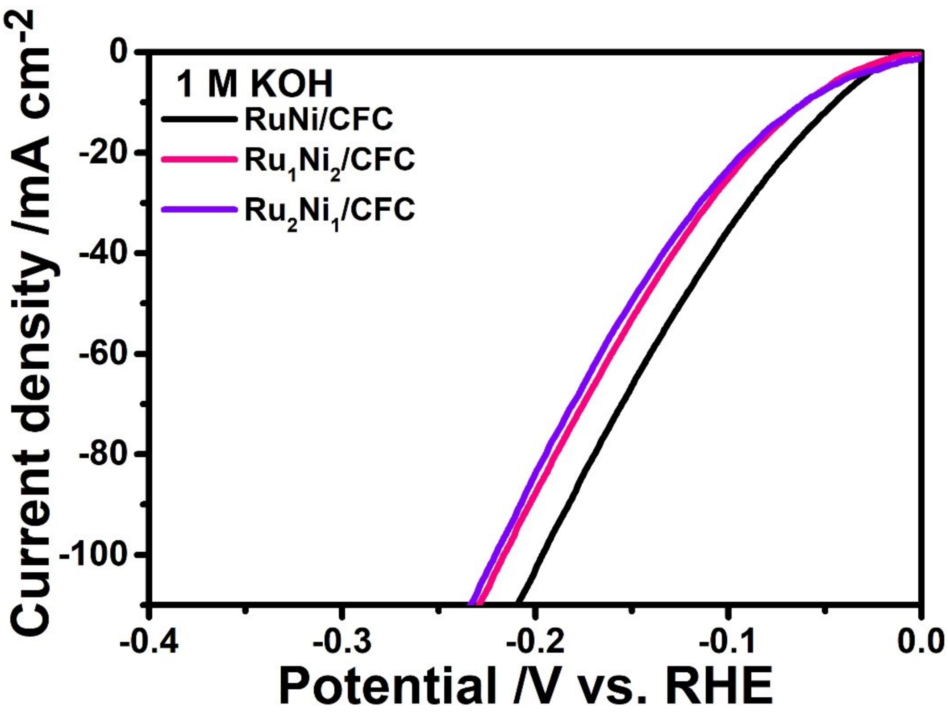

Fig. S13. LSV polarization curves of RuNi/CFC, Ru_1Ni_2/CFC, and Ru_2Ni_1/CFC catalysts toward HER in 1 M KOH electrolyte

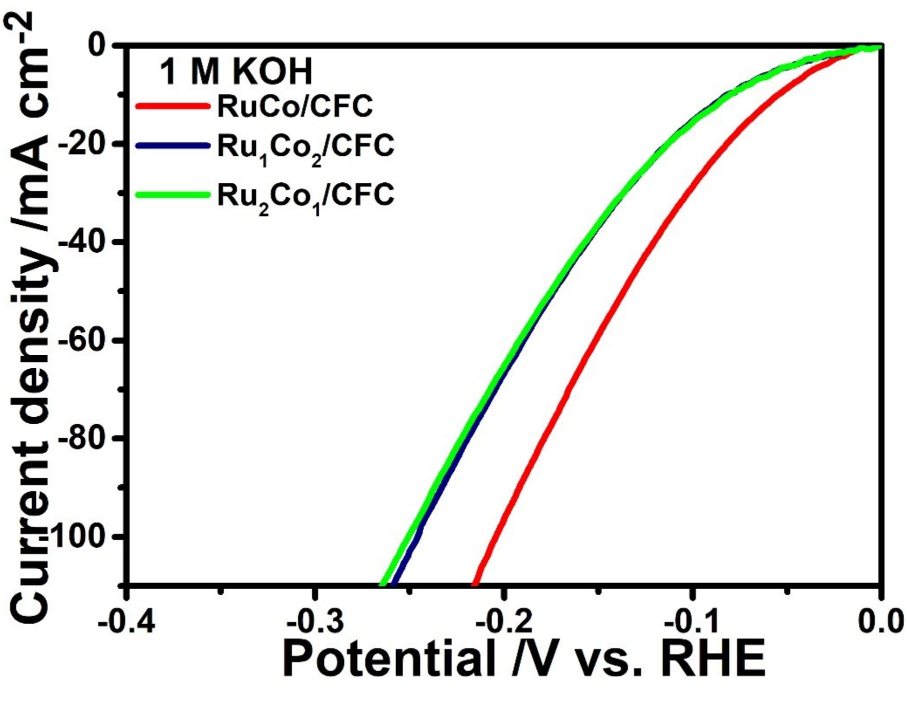

Fig. S14. LSV polarization curves of RuCo/CFC, Ru_1Co_2/CFC, and Ru_2Co_1/CFC catalysts toward HER in 1 M KOH electrolyte

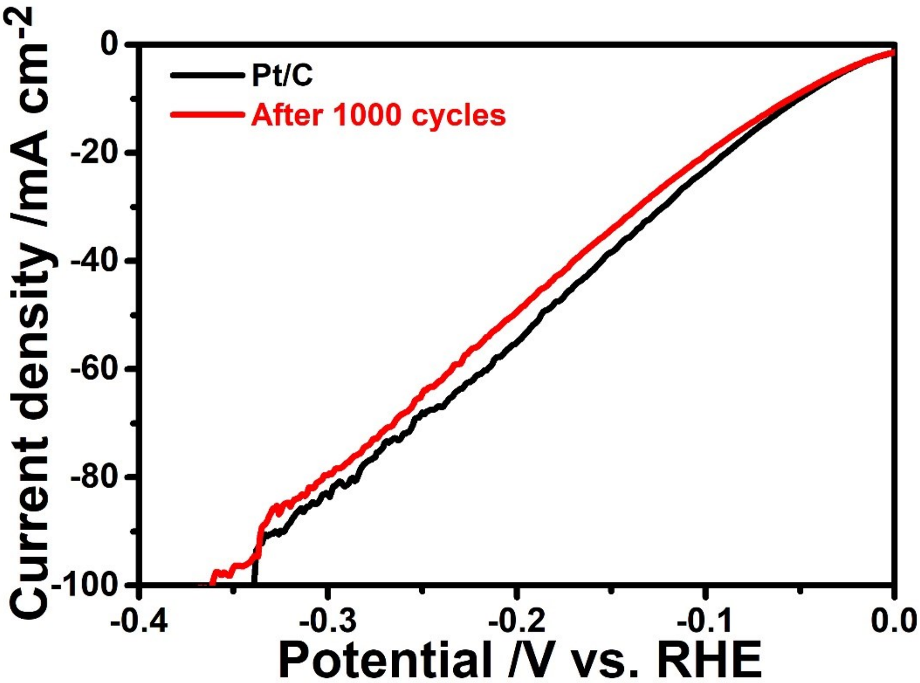

Fig. S15 LSV polarization curves of Pt/C before and after 1000 CV cycles.

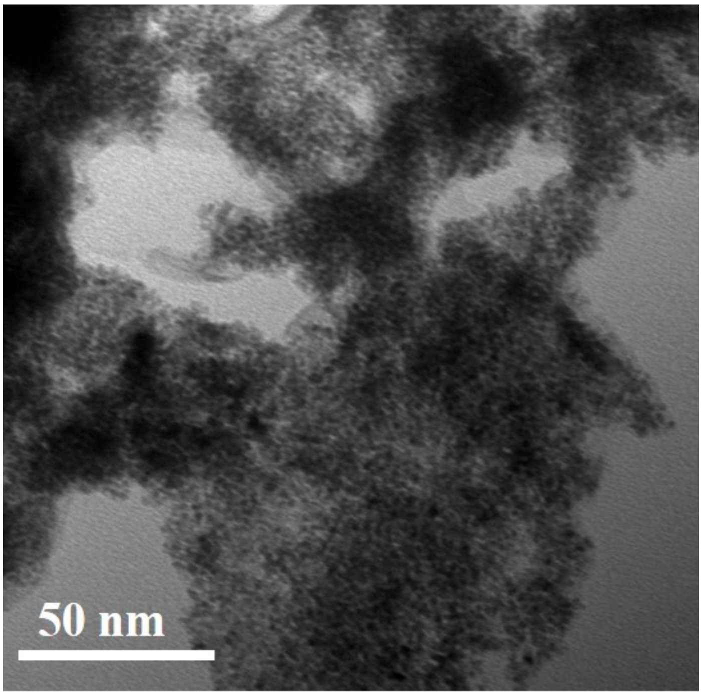

Fig. S16 Representative TEM image of RuNi/CFC after 40 h CP test in 1 M KOH solution.

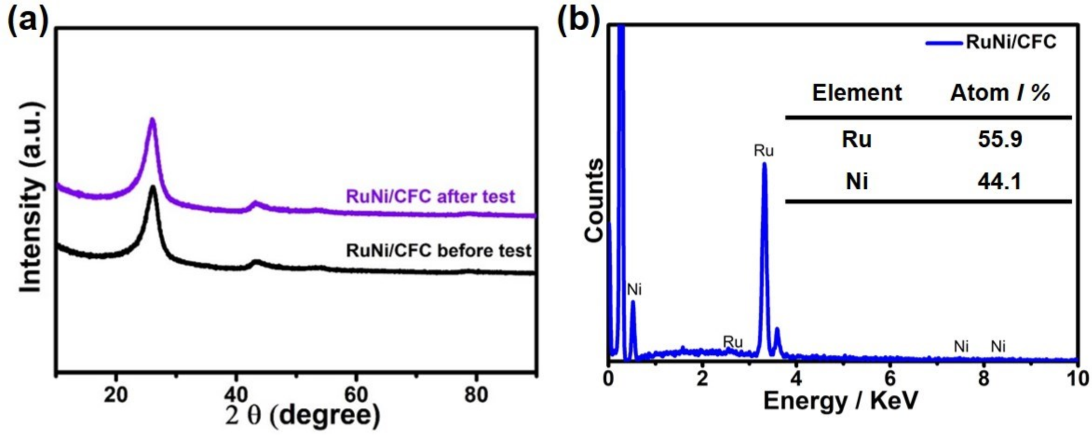

Fig. S17 (a) PXRD pattern and (b) SEM-EDX spectrum of the RuNi/CFCs after 40 h CP test in 1 M KOH solution.

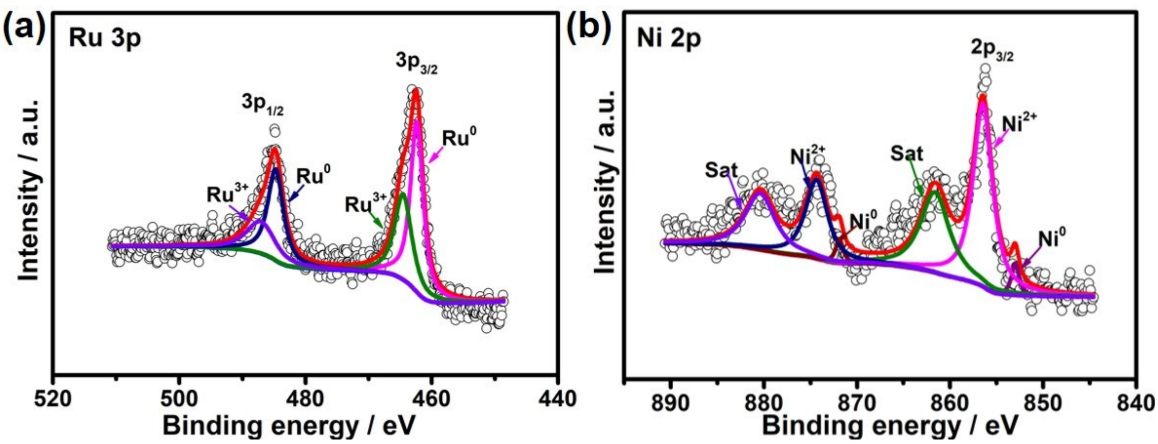

Fig.18 High-resolution XPS spectra of the (a) Ru 3p and (b) Ni 2p in the RuNi/CFCs after 40 h CP test in 1M KOH solution.

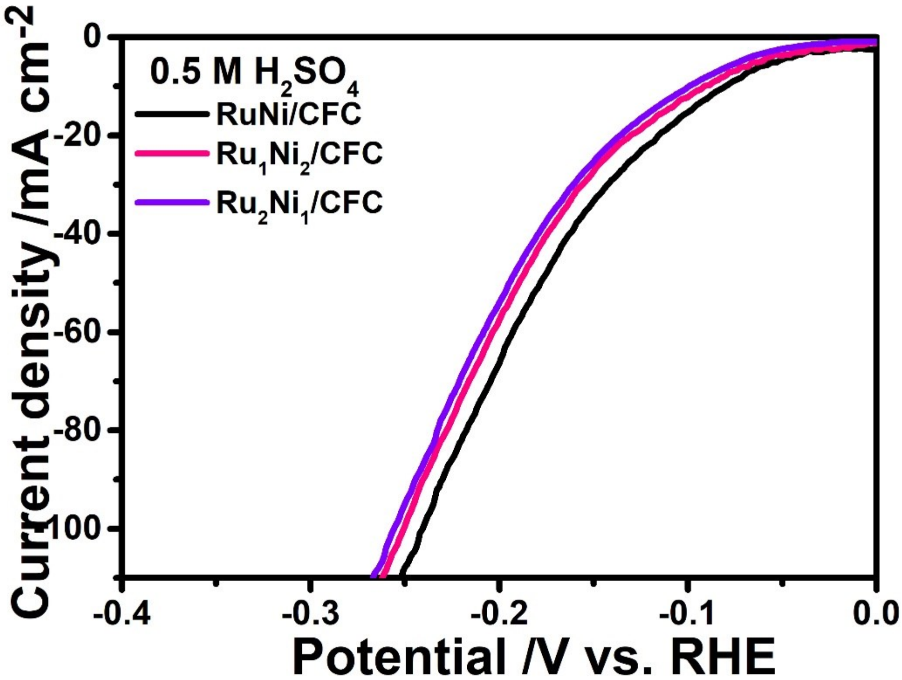

Fig. S19. LSV polarization curves of RuNi/CFC, Ru_1Ni_2/CFC, and Ru_2Ni_1/CFC catalysts toward HER in 0.5 M H_2SO_4 electrolyte

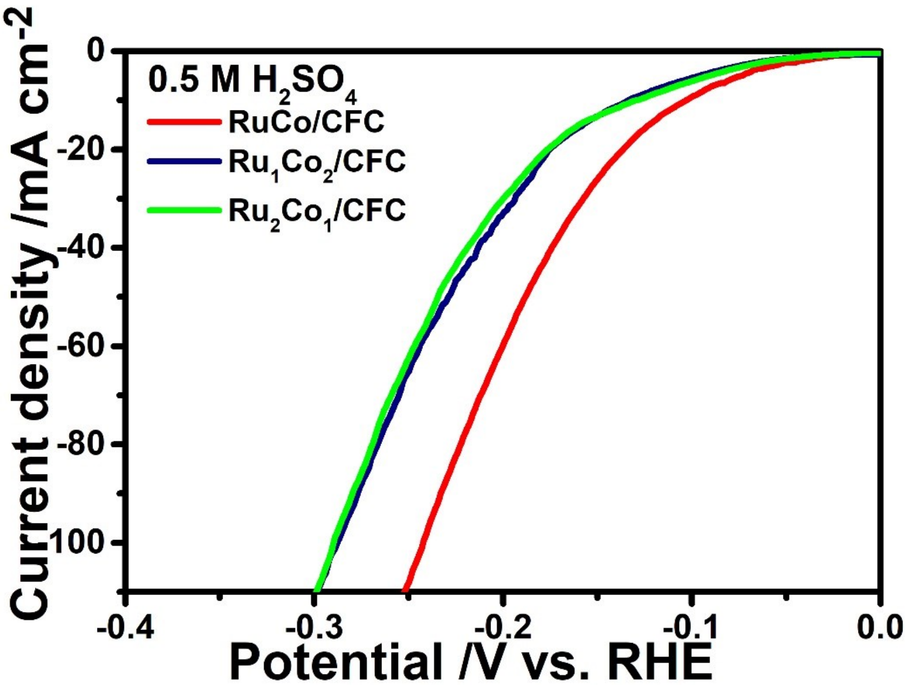

Fig. S20. LSV polarization curves of RuCo/CFC, Ru_1Co_2/CFC, and Ru_2Co_1/CFC catalysts toward HER in 0.5 M H_2SO_4 electrolyte

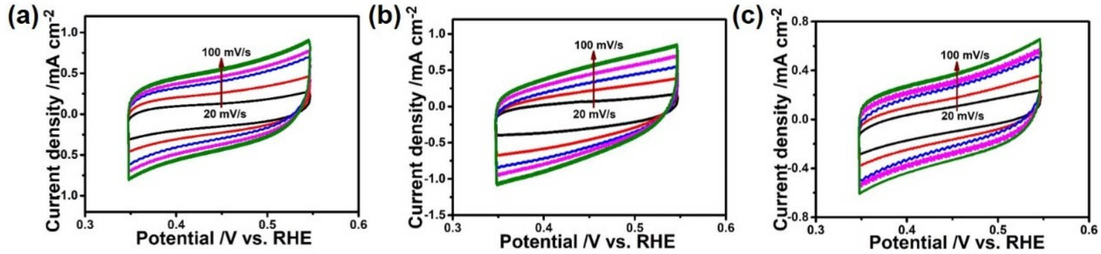

Fig. S21 CV curves of (a) RuNi/CFC, (b) RuCo/CFC and (c) Ru/CFC in 0.5 M H_2SO_4 solution at the scan rates between 20 mV/s to 100 mV/s.

Table S1 HER activity comparison of the as-synthesized RuNi/CFC and RuCo/CFC with previously reported catalysts.

Catalysts	Electrolyte	Overpotential(mV)		Reference
		10 mA cm^{-2}	100 mA cm^{-2}	
RuNi/CFC RuCo/CFC	1 M KOH 0.5 M H_2SO_4 1 M KOH 0.5 M H_2SO_4	43.0 80.2 54.7 103.1	186.8 240.7 204.5 242.2	**This work**
Ru@CN	1 M KOH 0.5 M H_2SO_4	32 126	- -	Energy Environ. Sci. 2018, 11, 800
Ru NPs	0.5 M H_2SO_4	148	-	J. Am. Chem. Soc. 2018,140, 2731
Ru/C_3N_4/C	1 M KOH 0.5 M H_2SO_4	79 70	- -	J. Am. Chem. Soc. 2016, 138, 16174
$Cu_{2-x}S$@Ru	1 M KOH	82	-	Small 2017, 13, 1700052
Ru/MoS_2/CP	0.5 M H_2SO_4	96	-	Nanoscale 2017, 9, 16616
P-Co_2Mo_3Se/CFC	1 M KOH	71	120	J. Mater. Chem. A, 2017, 5, 12043–12047
Ru-$Co(OH)_2$/CC	1 M KOH	55	212	J. Taiwan Inst. Chem. E, 2020, 109, 71-78212
RuFeP-NCs/CNF	1 M NaOH 0.5 M H_2SO_4	16 66	111 132	Appl. Catal. B-Environ, 2021, 283, 119583
NiCo	-	-	-	Electrochim.

diselenide/C C composites	0.5 M H_2SO_4	108	-	Acta, 2017, 225, 503-513
NiΦCFC	1 M KOH	131.5	-	Carbon, 2017, 122, 710-717

Table S2 EIS fitting parameters from equivalent circuits of samples during electrocatalytic process in 1 M KOH.

Samples	R_s / Ω cm^{-2}	R_0 / Ω cm^{-2}	Q_1 / S s-n	R_{ct} / Ω cm^{-2}	Q_2 / S s-n
RuNi/CFC	7.3E-1	9.2	5.7E-6	4.3	3.8E-3
RuCo/CFC	7.6E-1	1.0	3.3E-3	40.2	1.2E-3
Ru/CFC	5.9E-1	0.6	1.0E-2	124	4.5E-3

Table S3 EIS fitting parameters from equivalent circuits of samples during electrocatalytic process in 0.5 M H_2SO_4.

Samples	R_s 1 / Ω cm^{-2}	R_0 7 / Ω cm^{-2}	Q_1 5 / S s-n	R_{ct} 4 / Ω cm^{-2}	Q_2 2 / S s-n
RuNi/CFC	7.4E-1	1.5E6	9.2E4	2.2	2.9E-3
RuCo/CFC	5.5E-1	5.5E-1	1.6E-2	12.7	2.96E-3
Ru/CFC	6.1E-1	7.1E-1	3.4E-3	99.7	3.8E-5