Supporting Information

RuCo alloy nanoparticles embedded into N-doped carbon for high efficiency hydrogen evolution electrocatalyst

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1 Materials characterization

X-ray diffraction (XRD) was performed on a D8 ADVANCE (BRUKER) powder diffractometer with Cu-Kα (λ = 1.54 Å) as the radiation source, operating at 40 kV and 40 mA. The morphological information of samples was characterized using a FEI XL30 ESEM FEG scanning electron microscope (SEM). Transmission electron microscopy (TEM), selected area electron diffraction (SAED), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping analysis were conducted on a Philips TECNAI G2 electron microscope operating at 200 kV. The porous structure of the samples was investigated by N_2 adsorption at −196 °C using a Micromeritics ASAP 2020 automatic adsorption instrument. The contents of elements in catalysts and precursors were determined by an X Series 2 (Thermo Fisher Scientific) inductively coupled plasma mass spectrometry (ICP-MS). X-ray photoelectron spectroscopy (XPS) was recorded on a Shimadzu AXIS ultra DLD spectrometer.

2 Electrochemical measurements

The electrochemical measurements for HER were carried out on a EG&G Princeton Applied Research Model 273A Potentiostat/Galvanostat (USA) using a conventional three-electrode system at room temperature. In this three-electrode system, a glass carbon electrode (GCE) with a diameter of 3 mm coated with catalyst was used as the working electrode and a graphite rod serve as counter electrode. Hg/Hg_2SO_4 and Hg/HgO electrodes were acted as reference electrodes in 0.5 M sulfuric acid and 1.0 M KOH, respectively. The catalyst ink was fabricated as follows: After the catalyst was fully ground, 5 mg of catalyst was ultrasonically dispersed in a mixture of 50 μL Nafion (5 wt.%) solution and 950 μL ethanol. Next, drop 5 μL of ink onto a clean and smooth surface of GCE and vaporize the solvent at room temperature. The mass loading was about 0.35 mg cm^{-2}.

Above all, the catalyst surface was cleaned and activated using the electrochemical cyclic voltammetry (CV) method before the test began. Linear sweep voltammetry (LSV) was recorded to evaluate the electrocatalytic activity of samples at a scan rate of 5 mV s^{-1} in 1.0 M KOH and 0.5 M H_2SO_4. All potential values from LSV were calibrated to the reversible hydrogen electrode (RHE) with *iR* compensation.

E(RHE) = E(Hg/Hg_2SO_4) + 0.701 V, in 0.5 M H_2SO_4

E(RHE) = E(Hg/HgO) + 0.926 V, in 1.0 M KOH

Electrochemical impedance spectroscopy (EIS) is measured in the frequency range of 0.1 to 10000 Hz. To assess the durability of samples, cyclic voltammetry (CV) was tested for 1500 cycles and 3000 cycles in alkaline and acidic media, respectively, and the I–t test at 10 mA cm^{-2} were performed for 15 h. Electrochemical surface area (ECSA) was evaluated through the double-layer capacitance (C_{dl}) obtained from the CV curves at different scan rates including 10, 20, 40, 50, 60, 80, 90 and 100 mV s^{-1}.

3 Figures and tables

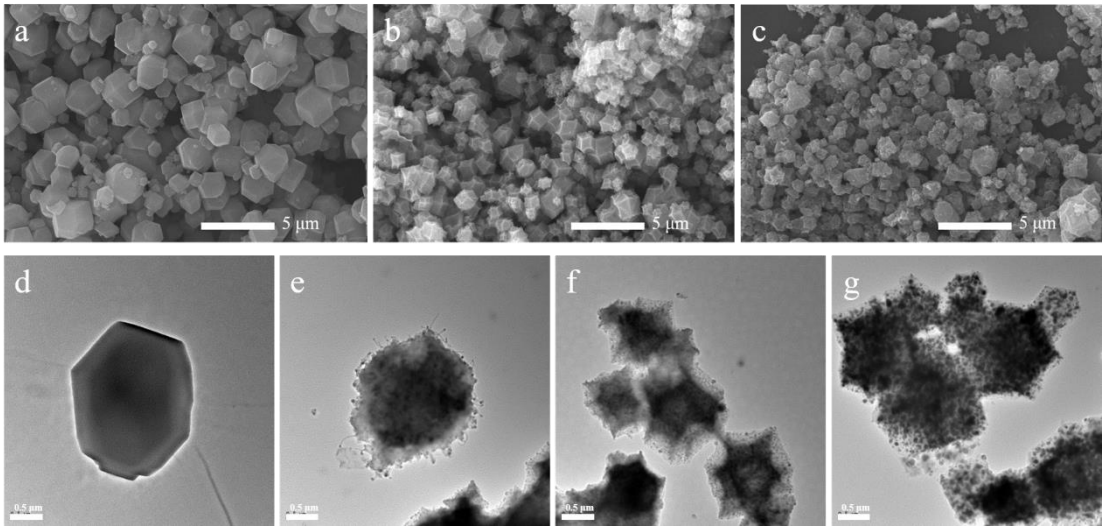

Figure S1. SEM images of (a) ZIF67, (b) C_{ZIF67}-750 and (c) 1-RuCo500@NC750. TEM images of (d) ZIF67, (e) 1-RuCo300@NC750, (f) 1-RuCo500@NC750 and (g) 1-RuCo700@NC750.

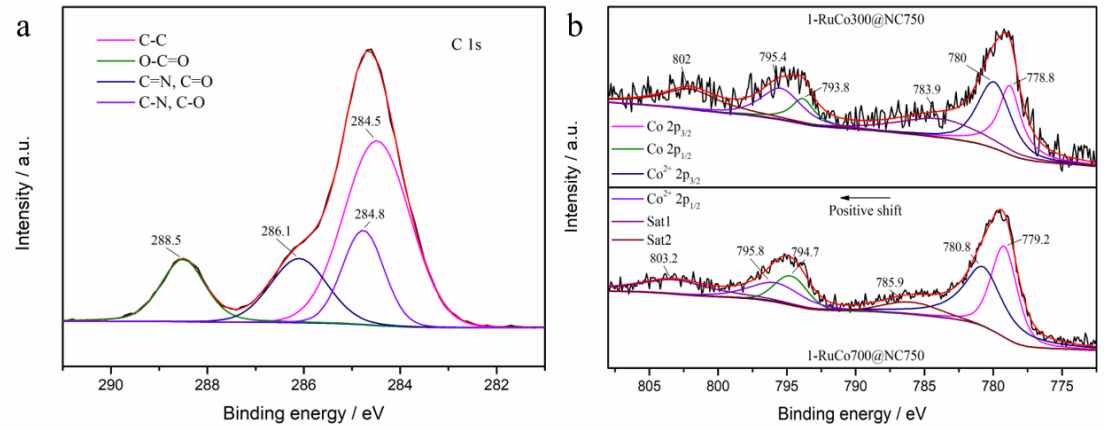

Figure S2. (a) C 1s XPS spectrum of C_{ZIF67}-750. (b) Co 2p XPS spectra of 1-RuCo300@NC750 and 1-RuCo700@NC750.

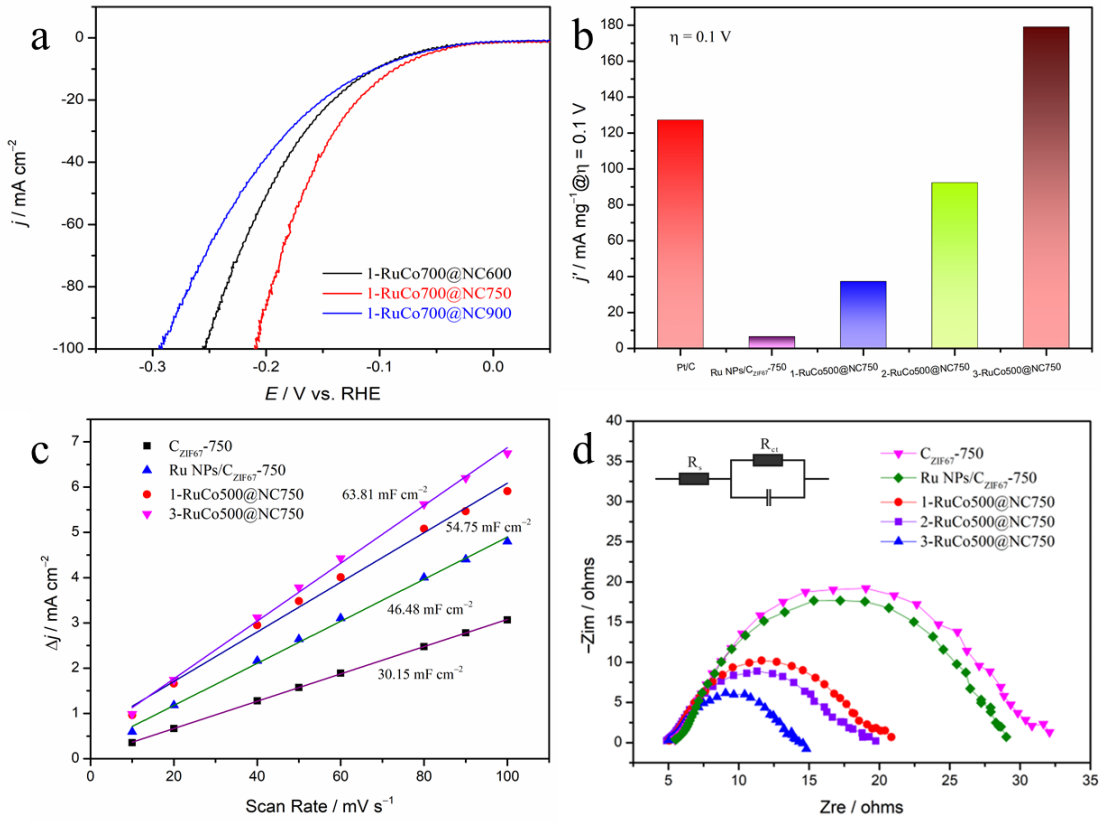

Figure S3. (a) HER polarization curves of 1-RuCo700@NC-T_1 in 1.0 M KOH. (b) HER mass activity of Ru NPs/C_{ZIF67}-750, 20% Pt/C and *n*-RuCo500@NC750 at −0.1 V. (c) Linear fitting of capacitance current to CV scan rate for Ru NPs/C_{ZIF67}-750, 1/3-RuCo500@NC750 and C_{ZIF67}-750. (d) Nyquist plots of Ru NPs/C_{ZIF67}-750, C_{ZIF67}-750 and *n*-RuCo500@NC750.

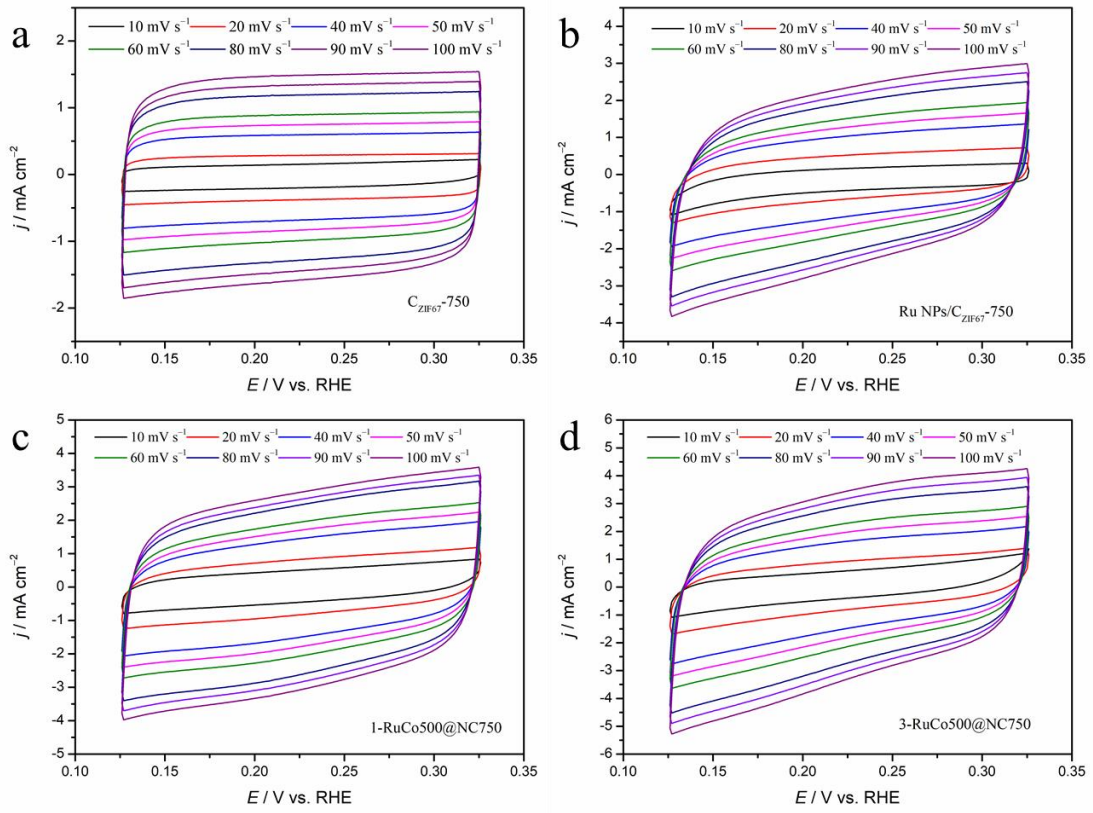

Figure S4. Cyclic voltammetry curves of C_{ZIF67}-750, Ru NPs/C_{ZIF67}-750 and 1/3-RuCo500@NC750 at different scan rates in 1.0 M KOH.

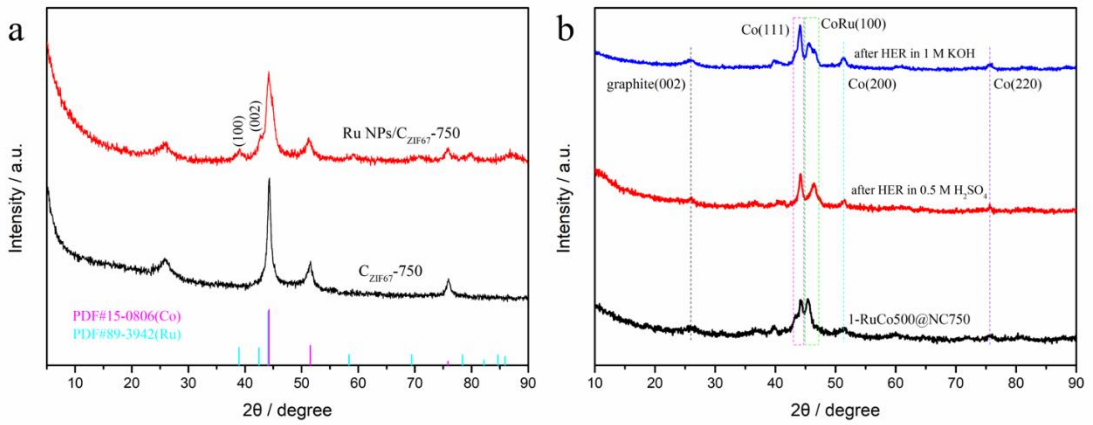

Figure S5. XRD patterns of (a) Ru NPs/C_{ZIF67}-750 and (b) the 1-RuCo500@NC750 before and after HER test.

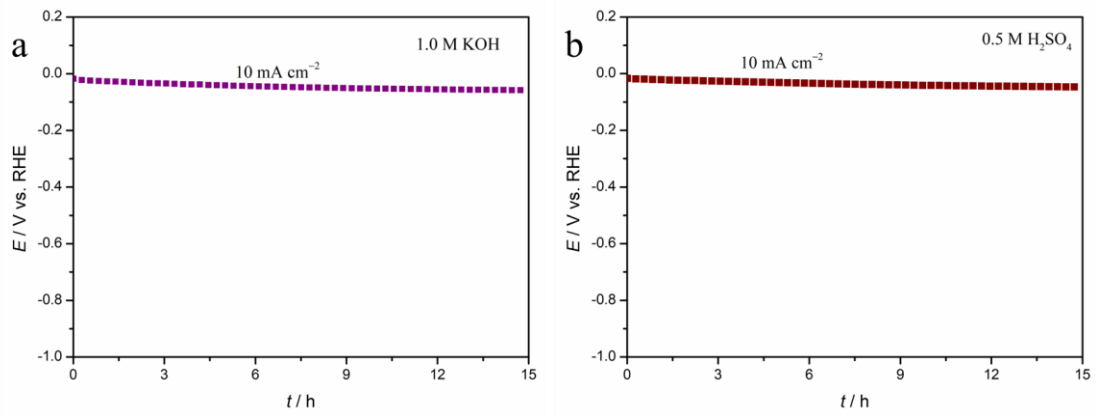

Figure S6. The chronopotential response of 3-RuCo500@NC750 at the constant cathodic current density of −10 mA cm^{-2} in (a) 1.0 M KOH and (b) 0.5 M H_2SO_4.

Table S1. The amount of $RuCl_3$ added in synthesis.

Sample	$RuCl_3$/mmol
Ru NPs/C_{ZIF67}-750	0.098
1-RuCo-T_2@NC-T_1	0.098
2-RuCo-T_2@NC-T_1	0.147
3-RuCo-T_2@NC-T_1	0.196

Table S2. The Ru and Co content determined by ICP-MS and XPS.

Sample	ICP-MS		XPS	
	Co (wt.%)	Ru (wt.%)	Co (wt.%)	Ru (wt.%)
1-RuCo500@NC750	38.45	7.56	14.49	8.27
2-RuCo500@NC750	33.62	10.64		
3-RuCo500@NC750	29.77	12.83		
Ru NPs/C_{ZIF67}-750	42.17	8.63		

Table S3. BET surface areas and pore volumes of samples.

Sample	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})
C_{ZIF67}-600	57.21	0.330
C_{ZIF67}-750	330.11	0.287
C_{ZIF67}-900	247.56	0.259
1-RuCo500@NC750	580.92	0.617

Table S4. Compared with the reported performance of alkaline HER electrocatalysts.

Catalyst	Electrolyte	Overpotetial/mV (10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Reference
1D-RuO_2-CN_x	0.5 M KOH	95	70	[57]
Ni_2P-$Ni_{12}P_5$/NF	1.0 M KOH	76	68	[58]
Ru_1CoP/CDs	1.0 M KOH	51	73.4	[59]
MoN-MnO	1.0 M KOH	35	30.2	[60]
W_1Mo_1-NG	1.0 M KOH	67	45	[61]
V_8C_7/CoP-0.18	1.0 M KOH	130	109	[62]
F-Ni_3S_4	1.0 M KOH	29	46.2	[63]
Ni_xRh_{1-x}@200°C	1.0 M NaOH	37	36.7	[64]
RhPdH NSs/C	1.0 M KOH	40	35.7	[65]
CS-PdPt	1.0 M KOH	46	88	[66]
3-RuCo500@NC750	1.0 M KOH	31	47	This work

Table S5. Compared with the reported performance of acidic HER electrocatalysts.

Catalyst	Electrolyte	Overpotetial/mV (10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Reference
1D-RuO_2-CN_x	0.5 M H_2SO_4	93	40	[57]
CoMoS/C	0.5 M H_2SO_4	90	50	[67]
Ru/RuS_2	0.5 M H_2SO_4	45	47.2	[68]
Au@$AuIr_2$	0.5 M H_2SO_4	29	15.6	[1]
Ru_1CoP/CDs	0.5 M H_2SO_4	49	51.6	[59]
Ag_2S/rGO	0.5 M H_2SO_4	120	49.1	[69]
ECM@Ru	0.5 M H_2SO_4	63	47	[70]
Au/MoS_2 QDs	0.5 M H_2SO_4	112	83	[71]
Co-Pd-MoS_2	0.5 M H_2SO_4	49.3	43.2	[72]
CS-PdPt	0.5 M H_2SO_4	26	33	[66]
3-RuCo500@NC750	0.5 M H_2SO_4	22	52	This work