# Supporting Information
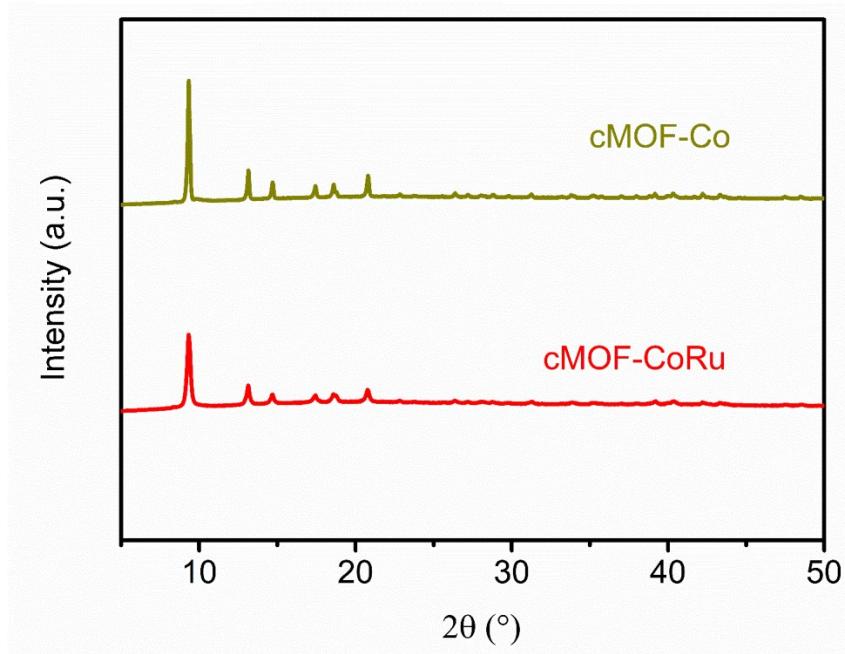
Fig. S1. X-ray diffraction patterns of cMOF-Co and cMOF-CoRu.
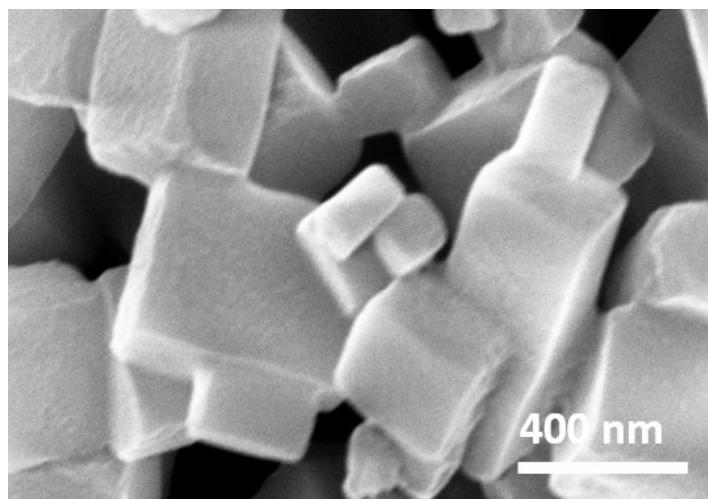

Fig. S2. SEM image of cMOF-Co.
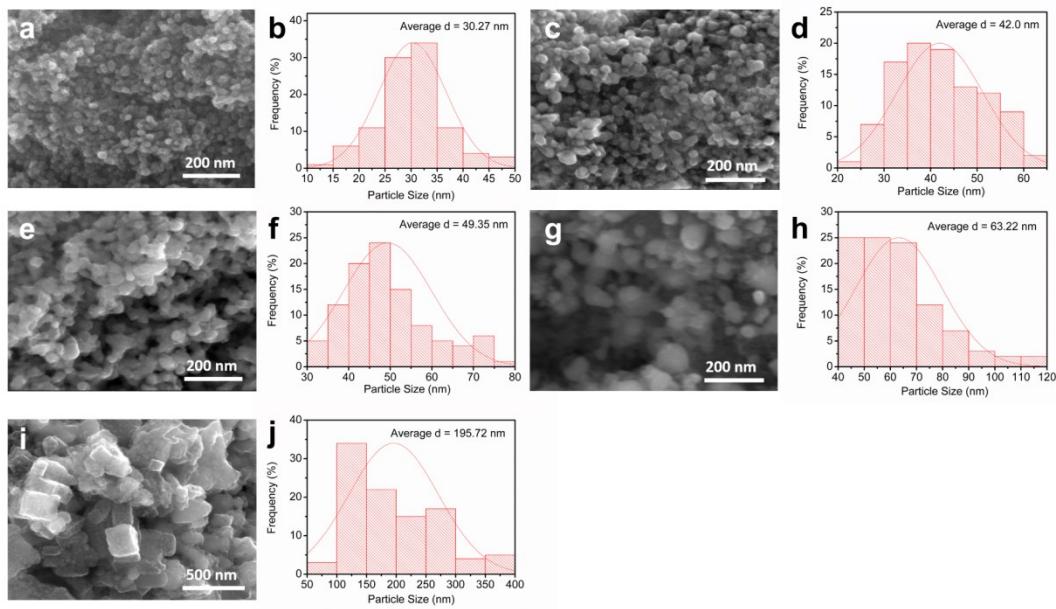
Fig. S3. SEM images of (a) RuCo@NC-500, (c) RuCo@NC-600, (e) RuCo@NC-700, (g) RuCo@NC-800 and (i) Co@NC-600. Particle size distribution diagrams of (b) RuCo@NC-500, (d) RuCo@NC-600, (f) RuCo@NC-700, (h) RuCo@NC-800 and (j) Co@NC-600.
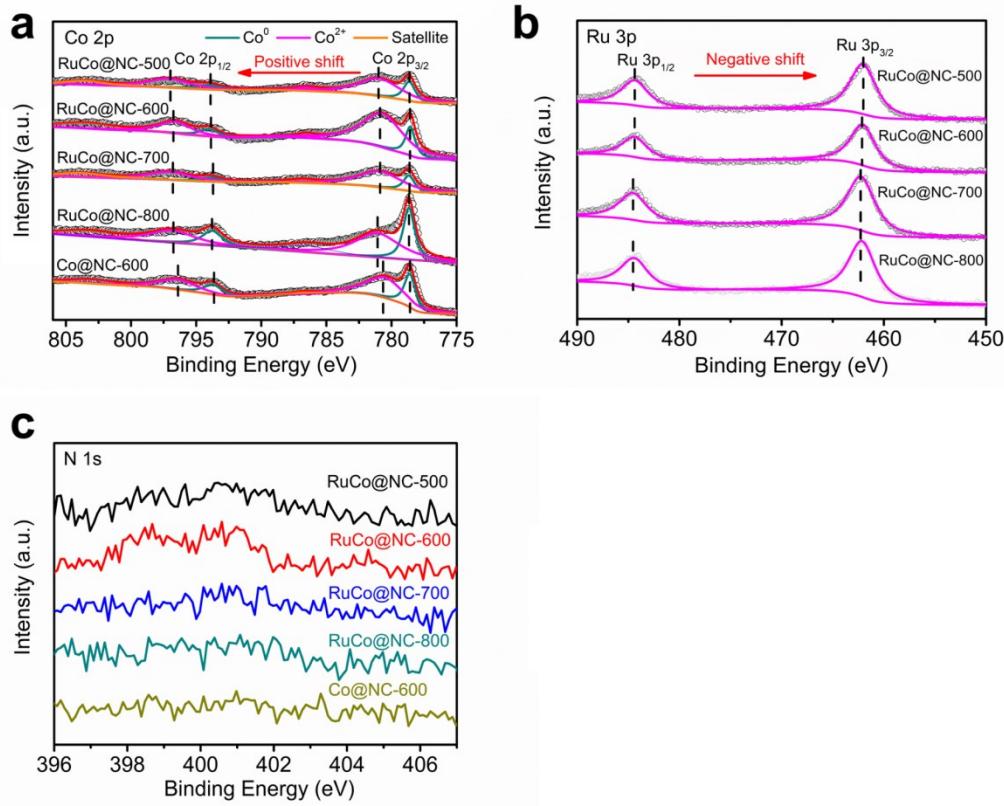

Fig. S4. (a) XPS spectra of Co 2p and (b) Ru 3p for RuCo@NC-T and Co@NC-600. (c) High-resolution XPS spectrum of N 1s for RuCo@NC-T and Co@NC-600.
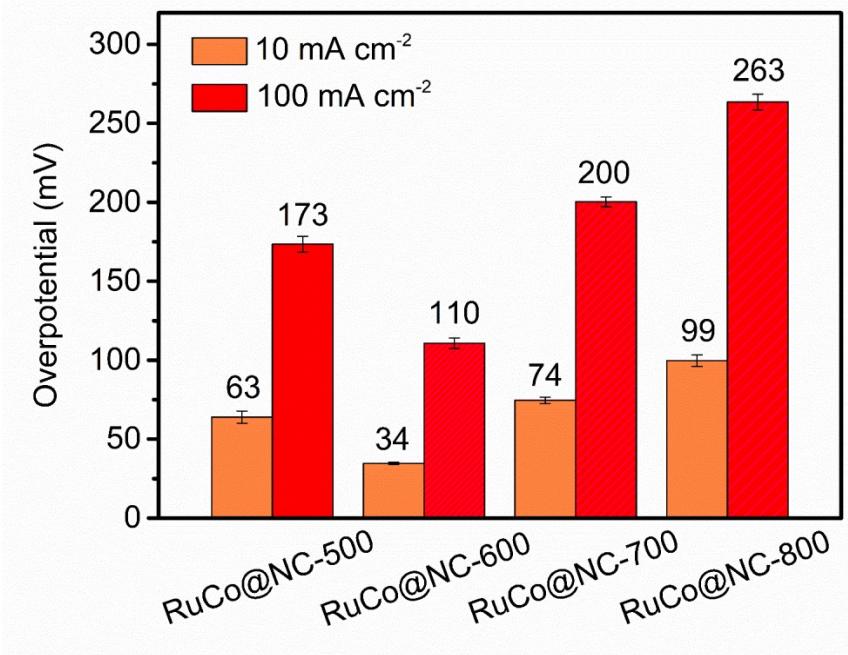
Fig. S5. Overpotential at -10 and -100 mA cm^{-2} for RuCo@NC-T catalysts in 1.0 M KOH solution.
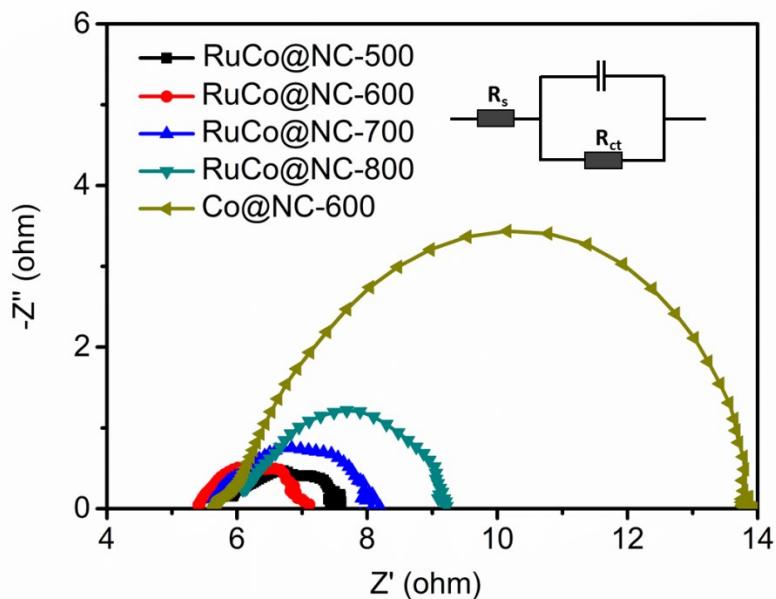
Fig. S6. Nyquist plots of RuCo@NC-T and Co@NC-600 in 1.0 M KOH solution.
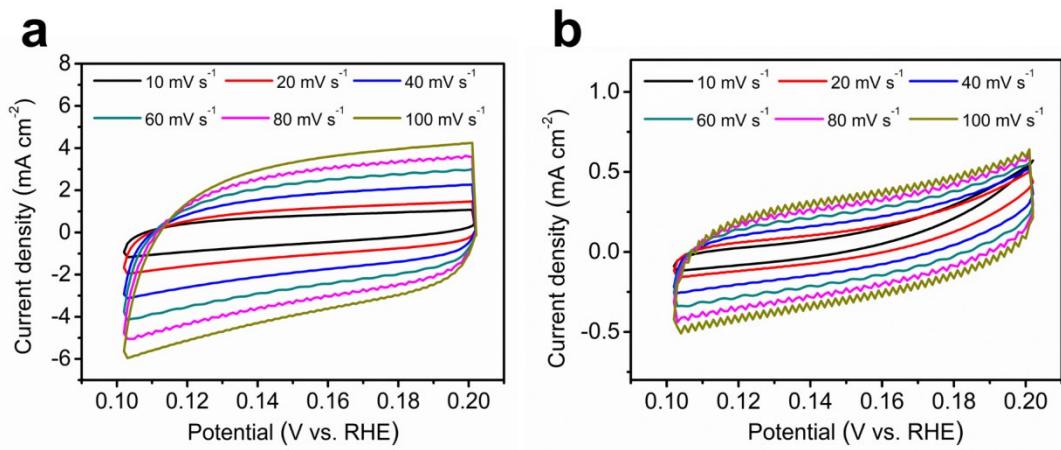
Fig. S7. The cyclic voltammetry (CV) measurements tested within the range of 0.1 to 0.2 V vs. RHE at different scan rates (0.01-0.1 V s^{-1}) for (a) RuCo@NC-600 and (b) Co@NC-600 in 1.0 M KOH solution.
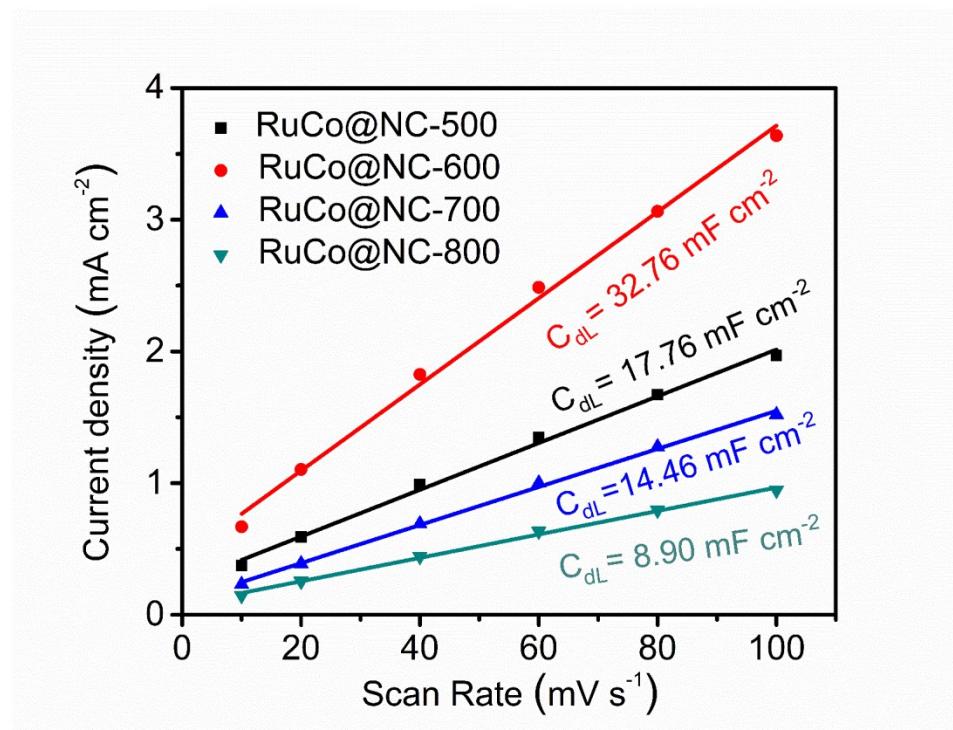
Fig. S8. Linear fitting of the capacitive currents versus CV scan rates for RuCo@NC-T in 1.0 M KOH solution.
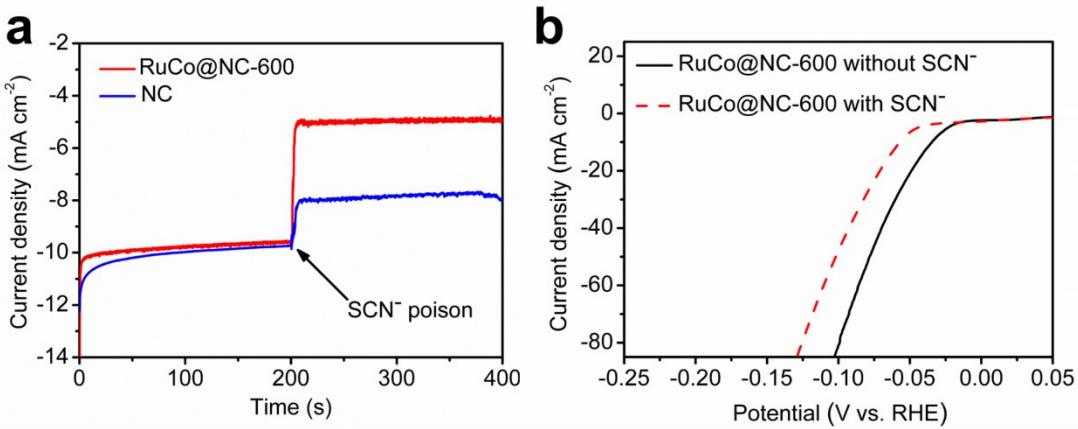
**Fig. S9.** (a) Current-time curve of RuCo@NC-600 and NC samples before and after the introduction of SCN⁻ ions. (b) LSV polarization curves for HER on RuCo@NC-600 in 1.0 M KOH without (solid line) and with (dot line) 10 mM KSCN.

Calculation of the Turnover Efficiency (TOF)

The TOF value of samples can be calculated based on the following equation:

$$\text{TOF (H}_2 \text{ s}^{-1}) = j*S/(2*F*n)$$

Here, j represents the current density during linear sweeping. S represents the surface area of electrode. F is the Faradaic constant (96485.3 C mol⁻¹). 1/2 indicates two electrons are required to form a hydrogen molecule. n represents the number of active sites.[S1]

The number of active sites (n) can be measured according to the formula:[S2]

$$n \text{ (mol)} = \text{metal loading on GCE*metal content/molar mass of metal}$$

All the Ru and Co atoms on the RuCo@NC-T surface are assumed to be the active sites for HER. The metal content was determined by XPS shown in Table. S2. For example, the TOF of RuCo@NC-500 at -0.1 V can be calculated as follows:

$$n_{Ru} \text{ (mol)} = (2.55*10^{-4} \text{ g cm}^{-2}*0.196 \text{ cm}^2*23 \text{ wt\%})/101.07 \text{ g mol}^{-1}=1.137*10^{-7} \text{ mol}$$

$$n_{Co} \text{ (mol)} = (2.55*10^{-4} \text{ g cm}^{-2}*0.196 \text{ cm}^2*8 \text{ wt\%})/58.93 \text{ g mol}^{-1}=6.785*10^{-8} \text{ mol}$$

$$n_{total} \text{ (mol)} = n_{Ru} \text{ (mol)}+ n_{Co} \text{ (mol)} =1.81*10^{-7} \text{ mol}$$

$$\text{TOF (H}_2 \text{ s}^{-1}) =(0.02775 \text{ A cm}^{-2} * 0.196 \text{ cm}^2)/(2*96485.3 \text{ C mol}^{-1} * 1.81*10^{-7} \text{ mol})=0.156 \text{ s}^{-1}$$
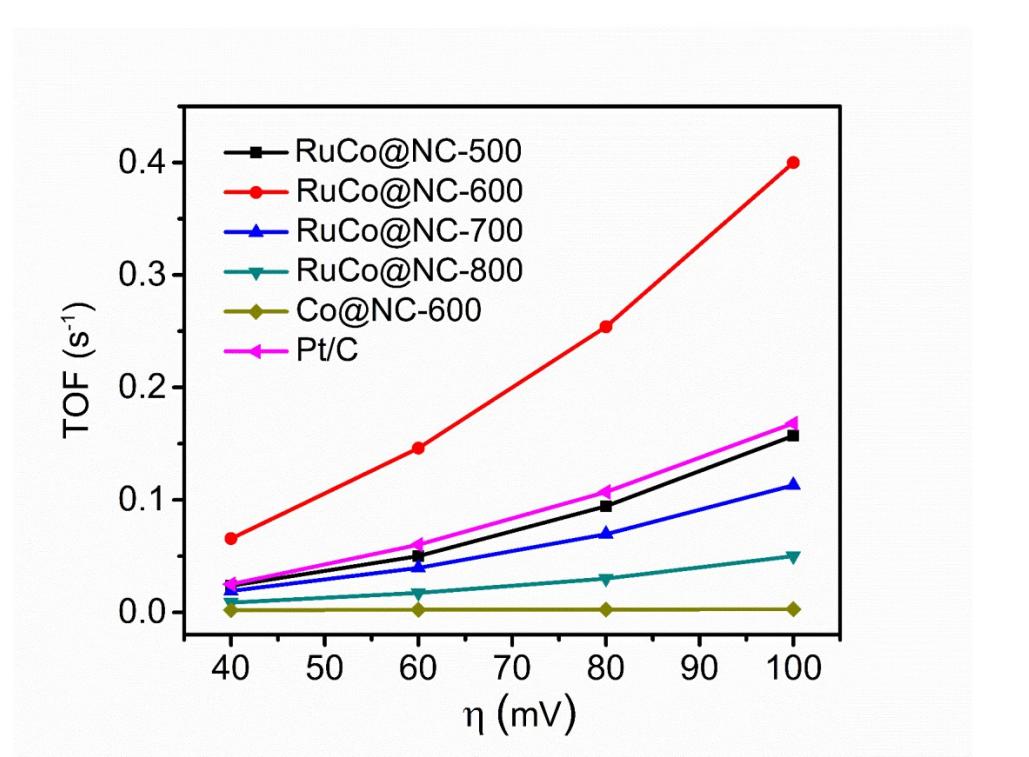
Fig. S10. The TOF values of samples calculated at different overpotentials (η=20, 40, 60, 80 and 100 mV) in 1.0 M KOH sollution.
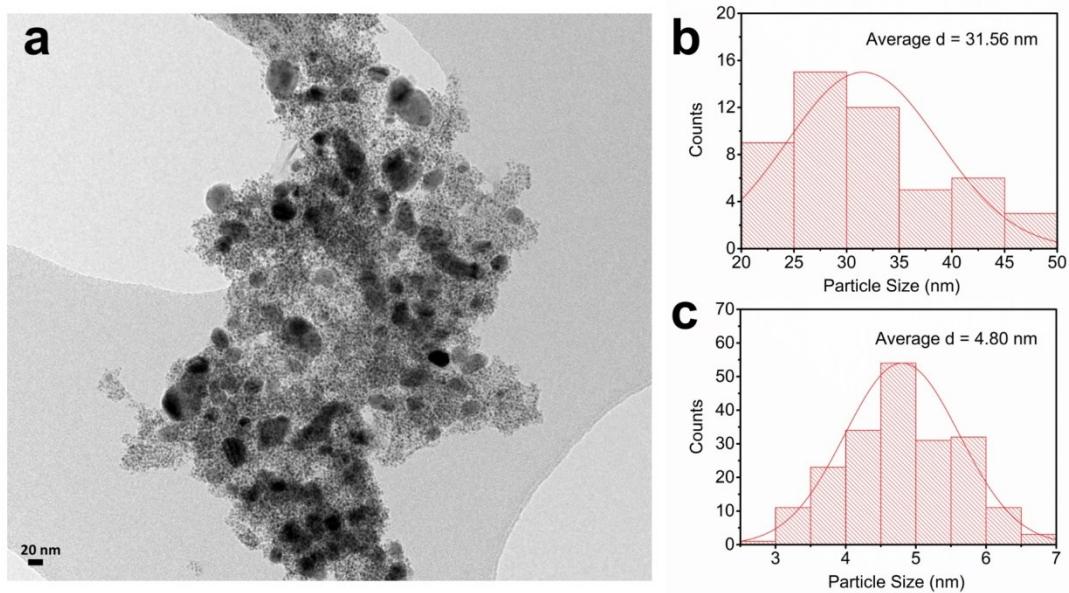
Fig. S11. (a) TEM image of RuCo@NC-600 and corresponding particle size distribution diagrams of (b) large and (c) small RuCo alloy NPs after the electrocatalytic HER stability test in 1.0 M KOH solution.

Faradaic efficiency

The Faradaic efficiency (FE) of hydrogen (H_2) can be calculated based on the formula: FE%=n*Z*F/Q*100%. Here, n represents the detected amount of H_2 generated from HER. Z represents the specific number of electrons to form a hydrogen molecule (Z=2). F is the Faradaic constant (96485.3 C mol^{-1}). Q represents the total charge passed through the working electrode.[S3,S4]
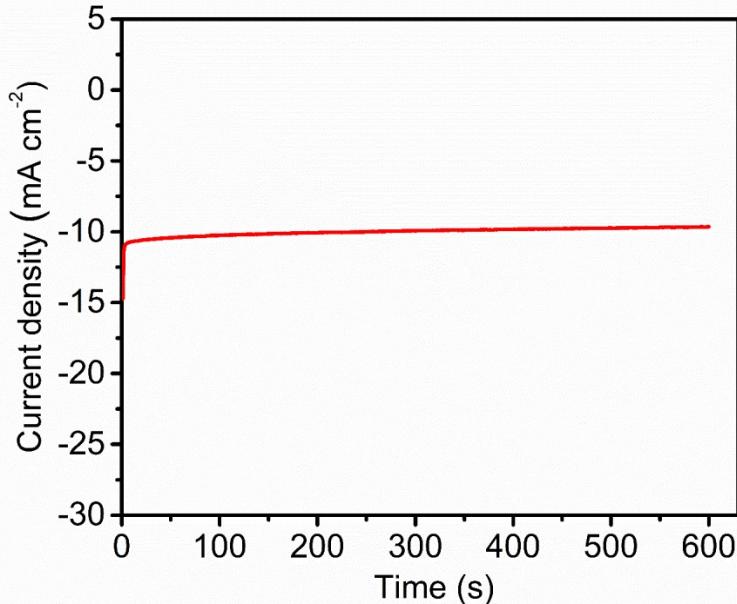
Fig. S12. Chronoamperometric curves of RuCo@NC-600 obtained at -0.045 V vs RHE for hydrogen quantification in 1.0 M KOH.

When 1.2 C of charge (Q) passed through the working electrode, the amount of H_2 (n) measured from gas chromatography (GC) was 6.1 μmol. Considering the systematic error such as the release of H_2 from the electrochemical cell during the transport to GC, approximately ± 2% error bar is provided.

FE%=n*Z*F/Q*100%=(6.1*10^{-6} mol*2*96485.3 C mol^{-1})/1.2 C*100%=98.1% ± 2%.
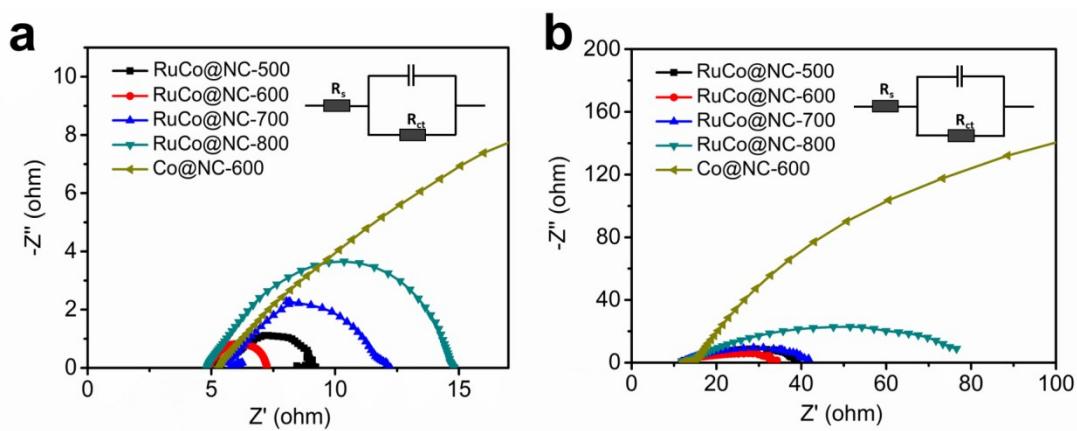
Fig. S13. Nyquist plots of RuCo@NC-T and Co@NC-600 in (a) 0.5 M H_2SO_4 and (b) 1.0 M PBS solutions.
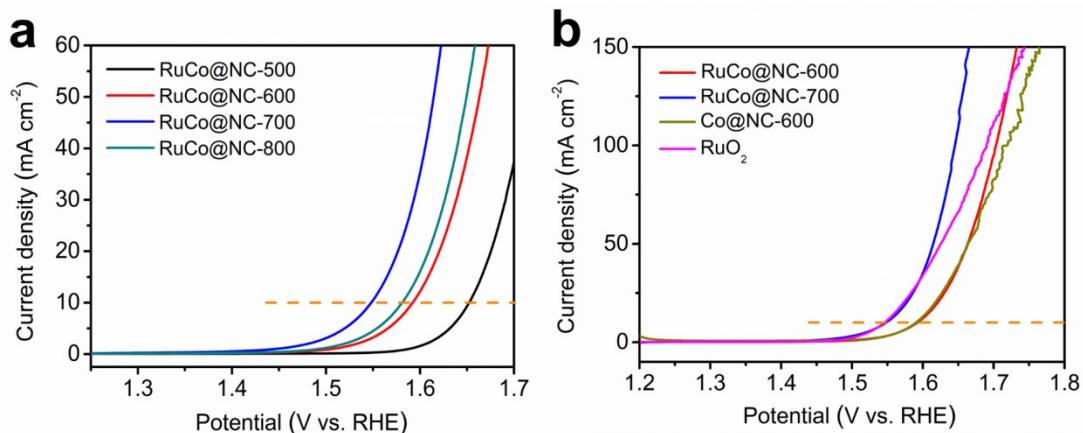
Fig. S14. (a, b) The OER polarization curves of samples at a scan rate of 5 mV s^{-1} in 1.0 M KOH solution.
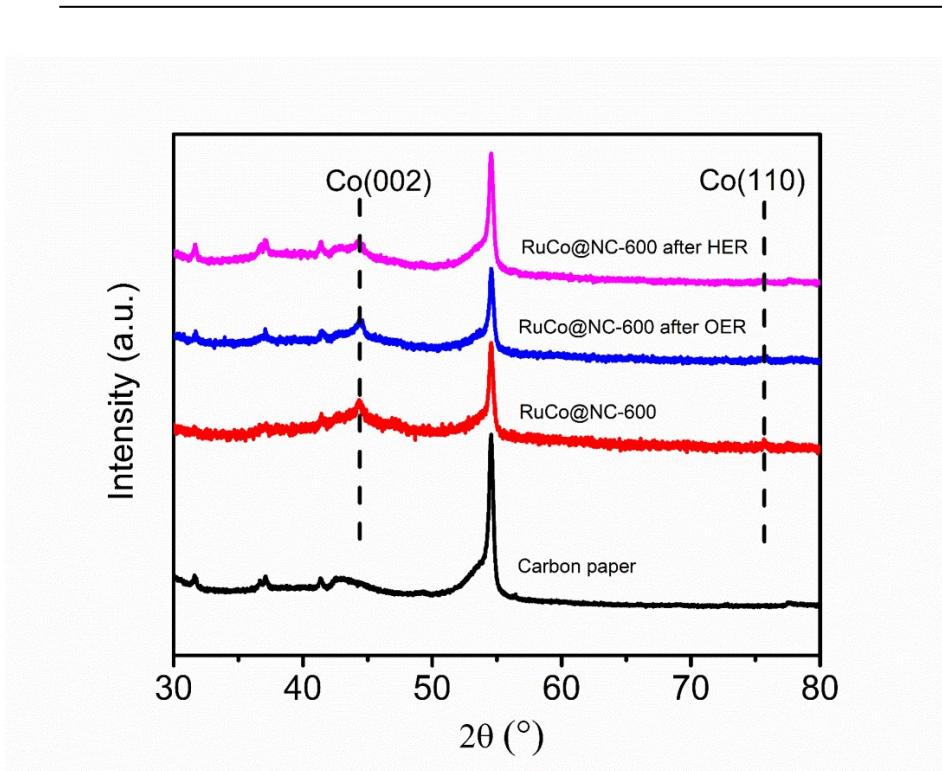
Fig. S15. X-ray diffraction patterns of the RuCo@NC-600 loaded on carbon paper before and after water splitting test, and blank carbon paper.
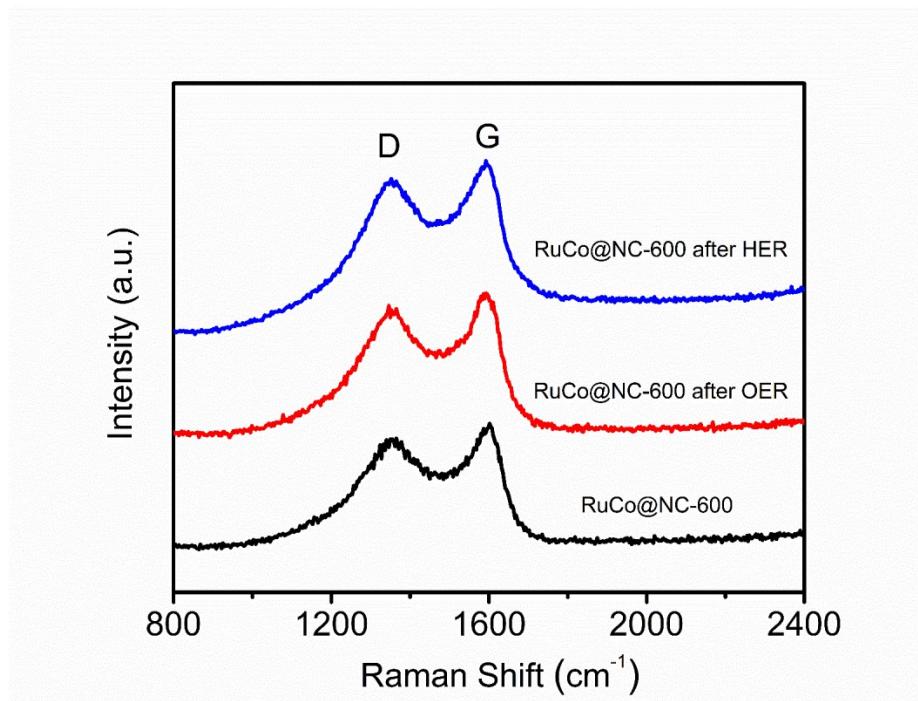
Fig. S16. Raman spectra of the RuCo@NC-600 loaded on carbon paper before and after water splitting test.

Table S1. BET results of RuCo@NC-T and Co@NC-600.

Sample	S_{BET} (m^2 g^{-1})	$S_{Micropore}$ (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})	$V_{Micropore}$ (cm^3 g^{-1})
RuCo@NC-500	186.5	67.1 (36.0 %)	0.631	0.028 (4.4 %)
RuCo@NC-600	165.7	49.0 (29.6 %)	0.528	0.021 (4.0 %)
RuCo@NC-700	130.8	49.1 (37.5 %)	0.391	0.021 (5.4 %)
RuCo@NC-800	102.6	25.0 (24.4 %)	0.307	0.011 (3.6 %)
Co@NC-600	159.3	36.1 (22.7%)	0.238	0.015 (6.3 %)

Table S2. The Ru and Co content in RuCo@NC-T and Co@NC-600 characterized by XPS spectrum.

Sample	Ru content (at%)	Co content (at%)	Atomic ratio of Ru to Co (at%/at%)
RuCo@NC-500	3.73	2.22	1.68
RuCo@NC-600	3.66	3.34	1.10
RuCo@NC-700	3.64	2.11	1.73
RuCo@NC-800	3.58	3.26	1.10
Co@NC-600	-	4.69	-

Table S3. Comparison of catalytic performance of RuCo@NC-600 with reported representative state-of-the-art HER electrocatalysts in 1.0 M KOH.

| Catalysts	Substrate	Loading amount (mg cm^{-2})	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	References
RuCo@NC-600	Glass carbon	0.255	34	36	This work
0.4-Ru@NG-750	Glass carbon	N.A.[a]	40	36	*ACS Catal.* **2019**, *9*, 9897
Ru$_1$Ni$_1$-NCNFs	Glass carbon	0.612	35	30	*Adv. Sci.* **2020**, *7*, 1901833
RuP$_2$@NPC	Glass carbon	1.0	52	69	*Angew. Chem. Int. Ed.* **2017**, *56*, 11559
Ru@CN	Glass carbon	0.273	32	53	*Energy Environ. Sci.* **2018**, *11*, 800

Catalysts	Substrate	Loading amount (mg cm^{-2})	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	References
NiRu@N–C	Glass carbon	0.273	32	64	*J. Mater. Chem. A* **2018**, *6*, 1376
CoRu@NC-2	Glass carbon	0.273	45	66	*Nanotechnology* **2018**, *29*, 225403
Ru/C$_3$N$_4$/C[b]	Glass carbon	0.204	79	N.A.	*J. Am. Chem. Soc.* **2016**, *138*, 16174
SA-Ru-MoS$_2$	Glass carbon	0.285	76	21	*Small Methods* **2019**, *3*, 1900653
RuO$_2$/Co$_3$O$_4$	Glass carbon	0.285	89	91	*RSC Adv.* **2017**,*7*, 3686
Cu$_{2-x}$@RuNPS	Glass carbon	0.23	82	48	*Small* **2017**, *13*, 1700052
Ru$_1$@Co/NC	Glass carbon	0.163	103	210	*Angew. Chem. Int. Ed.* **2019**, *58*, 11868
Ni-MOF@Pt	Glass carbon	0.2	102	88	*Nano Lett.* **2019**, *19*, 8447
IrCo@NC-500	Glass carbon	0.285	45	80	*Adv. Mater.* **2018**, *30*, 1705324
Co$_2$Ni$_1$N	Carbon cloth	N.A.	102.6	60	*ACS Appl. Mater. Interfaces* **2019**, *11*, 8018
CoMoS$_x$	Ni foam	2	89	94	*Angew. Chem. Int. Ed.* **2020**, *59*, 1659
S-CoWP@(S,N)-C	Glass carbon	0.75	67	66	*ACS Energy Lett.* **2018**, *3*, 1434

Note: CNF, Carbon nanofibers.   [a]: N. A. = Not available. [b]: The electrolyte is 0.1 M KOH.

Table S4. Comparison of catalytic performance of RuCo@NC-600 with reported representative state-of-the-art HER electrocatalysts in 0.5 M H$_2$SO$_4$.

Catalysts	Substrate	Loading amount (mg cm^{-2})	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	References
RuCo@NC-600	Glass carbon	0.255	6	26	This work

Ru@C$_2$N	Glass carbon	0.285	22	30	*Nature Nanotech.* **2017**, *12*, 441
Ru$_1$Ni$_1$-NCNFs	Glass carbon	0.612	23	29	*Adv. Sci.* **2020**, *7*, 1901833
PtRu@RFCS-6h	Glass carbon	0.354	19.7	27.2	*Energy Environ. Sci.* **2018**, *11*, 1232
RuCu NSs/C-250 °C	Glass carbon	N.A.[a]	19	26	*Angew. Chem. Int. Ed.* **2019**, 58, 13983
hcp-Ru@N	Glass carbon	0.28	27.5	37	*ACS Catal.* **2018**, *8*, 5714
Mo$_2$C@Ru	Glass carbon	0.275	24.6	58.4	*ACS Appl. Mater. Interfaces* **2018**, *10*, 32171
RuP$_2$@NPC	Glass carbon	1.0	38	38	*Angew. Chem. Int. Ed.* **2017**, *56*, 11559
Ru@CN	Glass carbon	0.273	126	47	*Energy Environ. Sci.* **2018**, *11*, 800
NiRu@N–C	Glass carbon	0.273	50	31	*J. Mater. Chem. A* **2018**, *6*, 1376
CoRu@NC-2	Glass carbon	0.273	32	47	*Nanotechnology* **2018**, *29*, 225403
Ru@N-g-CN	Glass carbon	0.85	43.7	55	*J. Mater. Chem. A* **2018**, *6*, 13859
Ru@Co-SAs/N-C	Glass carbon	0.285	57	55	*Nano Energy* **2019**, *59*, 472
Ru-MoO$_2$	Glass carbon	0.285	55	44	*J. Mater. Chem. A* **2017**, *5*, 5475
Ru-HPC	Glass carbon	0.2	61.6	66.8	*Nano Energy* **2019**, *58*, 1
C$_3$N$_4$–Ru	Glass carbon	0.153	140	57	*J. Mater. Chem. A* **2017**, *5*, 18261
Ru SAs@PN	Carbon paper	1.0	24	38	*Angew. Chem. Int. Ed.* **2018**, *57*, 9495
Ru$_{SA}$-N-S-Ti$_3$C$_2$T$_x$	Carbon paper	1.0	76	90	*Adv. Mater.* **2019**, *31*, 1903841

Ru/MeOH/THF	Glass carbon	0.352	83	46	*Chem. Commun.* **2017**, *53*, 11713
Ni-MOF@Pt	Glass carbon	0.2	43	30	*Nano Lett.* **2019**, *19*, 8447
IrCo@NC-500	Glass carbon	0.285	24	23	*Adv. Mater.* **2018**, *30*, 1705324
PtCoFe@CN	Glass carbon	0.285	45	32	*ACS Appl. Mater. Interfaces* **2017**, *9*, 3596
CoPd@NC	Glass carbon	0.285	80	31	*ACS Appl. Mater. Interfaces* **2016**, *8*, 13378
Co_2Ni_1N	Carbon cloth	N.A.	92	55.3	*ACS Appl. Mater. Interfaces* **2019**, *11*, 8018
CuCo@NC	Glass carbon	0.182	145	79	*Adv. Energy Mater.* **2017**, *7*, 1700193
S-CoWP@(S,N)-C	Glass carbon	0.75	35	35	*ACS Energy Lett.* **2018**, *3*, 1434

Note: CNF, Carbon nanofibers; RFCS, Resorcinol-formaldehyde carbon spheres; NS, Nanosheet; hcp, Hexagonal-closed-packed; HPC, Hierarchically porous carbon; HPN, Amorphous phosphorus nitride imide nanotubes. [a]: N. A. = Not available.

Table S5. Comparison of catalytic performance of RuCo@NC-600 with reported representative state-of-the-art HER electrocatalysts in 1.0 M PBS.

Catalysts	Substrate	Loading amount ($mg\ cm^{-2}$)	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope ($mV\ dec^{-1}$)	References
RuCo@NC-600	Glass carbon	0.255	60	38	This work
Ru@Co-SAs/N-C	Glass carbon	0.285	55	82	*Nano Energy* **2019**, *59*, 472
RuP_2@NPC	Glass carbon	1.0	57	87	*Angew. Chem. Int. Ed.* **2017**, *56*, 11559
Ru/MeOH/THF[a]	Glass carbon	0.352	83	80	*Chem. Commun.* **2017**, *53*, 11713

Ru@CN[a]	Glass carbon	0.273	100	N.A.[b]	*Energy Environ. Sci.* **2018**, *11*, 800
Ru@N-g-CN[a]	Glass carbon	0.85	144	133	*J. Mater. Chem. A* **2018**, *6*, 13859
D-RuO$_2$-CNx	Glass carbon	0.28	135	135	*ACS Appl. Mater. Interfaces* **2016**, *8*, 28678
Ni$_{0.33}$Co$_{0.67}$S$_2$ nanowire	Glass carbon	0.3	72	67.8	*Adv. Energy Mater.* **2015**, *5*, 1402031
Co$_2$Ni$_1$N	Carbon cloth	N.A.	152.8	90.3	*ACS Appl. Mater. Interfaces* **2019**, *11*, 8018
NiRu@N–C	Glass carbon	0.273	482	N.A.	*J. Mater. Chem. A* **2018**, *6*, 1376
CoRu@NC-2	Glass carbon	0.273	425	N.A.	*Nanotechnology* **2018**, *29*, 225403

Note: [a]: The electrolyte is 0.1 M PBS. [b]: N. A. = Not available.

Reference

S1   T. Feng, G. Yu, S. Tao, S. Zhu, R. Ku, R. Zhang, Q. Zeng, M. Yang, Y. Chen, W. Chen, W. Chen, B. Yang, *J. Mater. Chem. A*, 2020, 8, 9638-9645.

S2   H. Wang, C. Gao, R. Li, Z. Peng, J. Yang, J. Gao, Y. Yang, S. Li, B. Li, Z. Liu, *ACS Sustainable Chem. Eng.*, 2019, 7, 18744-18752.

S3   S. Dutta, H. Han, M. Je, H. Choi, J. Kwon, K. Park, A. Indra, K. M. Kim, U. Paik, T. Song, *Nano Energy*, 2020, 67, 104245.

S4   Z. Li, J. Fu, Y. Feng, C. Dong, H. Liu, X. Du, *Nat. Catal.*, 2019, 2, 1107-1114.