Supporting Information

Electronic communication between Co and Ru sites decorated on nitrogen-doped carbon nanotubes boost the alkaline hydrogen evolution reaction

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1. Synthesis of $C_{60}(OH)_n$

The $C_{60}(OH)_n$ was prepared with a modified procedure according to the literature [1]. Firstly, C_{60} (100 mg) was dissolved into a 250 ml flask containing 100 ml of toluene. Then 2 ml of TBAH and 10 ml of H_2O_2 were added to the purple solution of C_{60}. After continuously stirring at 60 °C for 36 h, the upper toluene layer turned into a colorless transparent solution. The bright yellow and muddy water solution at the bottom of flask was separated by separatory funnel. When 50 ml of MeOH was added, a brown turbid precipitate formed immediately. After centrifugation and decantation, the precipitate was dissolved in 100 ml of deionized water and concentration by rotary evaporation. Then the yellow-brown solid was dehydrated by freeze drying under vacuum to obtain a yellow-brown powder sample.

2. Synthesis of CoRu@N-CNTs

The preparation procedure of CoRu@N-CNTs was schematically illustrated in Scheme 1. Briefly, 1.2 g of melamine,150 mg of $C_{60}(OH)_n$, 0.5 mmol of $CoCl_2$ and 0.5 mmol of $RuCl_3$ were dissolved into 70 ml of deionized water. The mixture solution was then transferred to a stainless-steel capped Teflon autoclave. After hydrothermal treatment at 150 °C for 24 h, the solid precursor of CoRu@N-CNTs was obtained by extraction filtration. Then the obtained powder was carbonized in a tube furnace under Ar/H_2 (5%) flow for 3 h at 600 ◦C with a raising rate of 5 ◦C min^{-1}. Then the CoRu@N-CNTs, black and fine powder, was successfully prepared by grinding and collection.

3. Synthesis of CoRu@NC

The synthesis process of CoRu@NC was the same to CoRu@N-CNTs without addition of $C_{60}(OH)_n$.

4. Synthesis of Co@N-CNTs

The synthesis process of Co@N-CNTs was the same to CoRu@N-CNTs except that the amount of $CoCl_2$ was 1 mmol without $RuCl_3$.

5. Synthesis of Ru@NC

The synthesis process of Ru@NC was the same to CoRu@N-CNTs except that the amount of $RuCl_3$ was 1 mmol without $CoCl_2$.

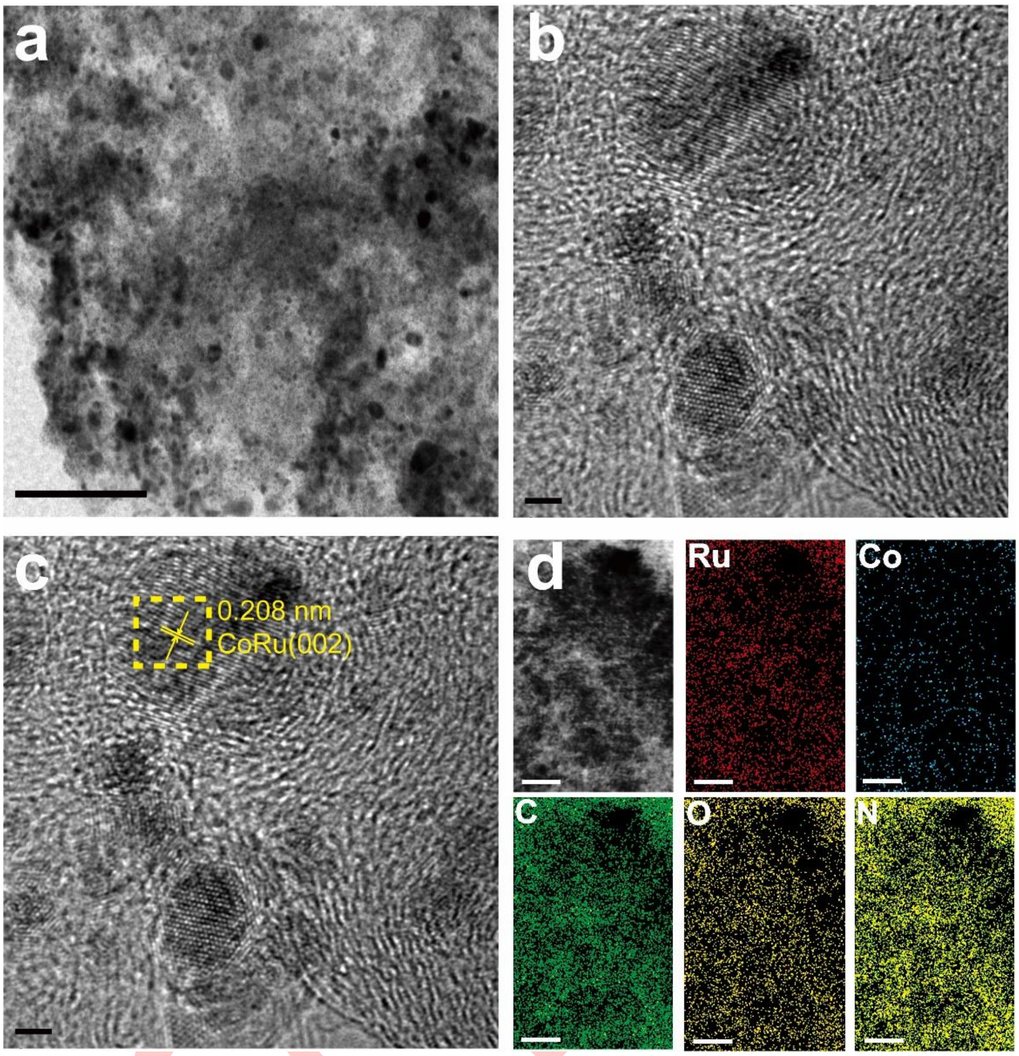

Fig. S1. Structure characterization of CoRu@NC. (a) TEM, (b) and (c) HRTEM, (d) the corresponding elemental mapping of Co, Ru, O, C and N for CoRu@NC. Scale bar in (a-f) are 200 nm, 2 nm, 2 nm, 100 nm, respectively.

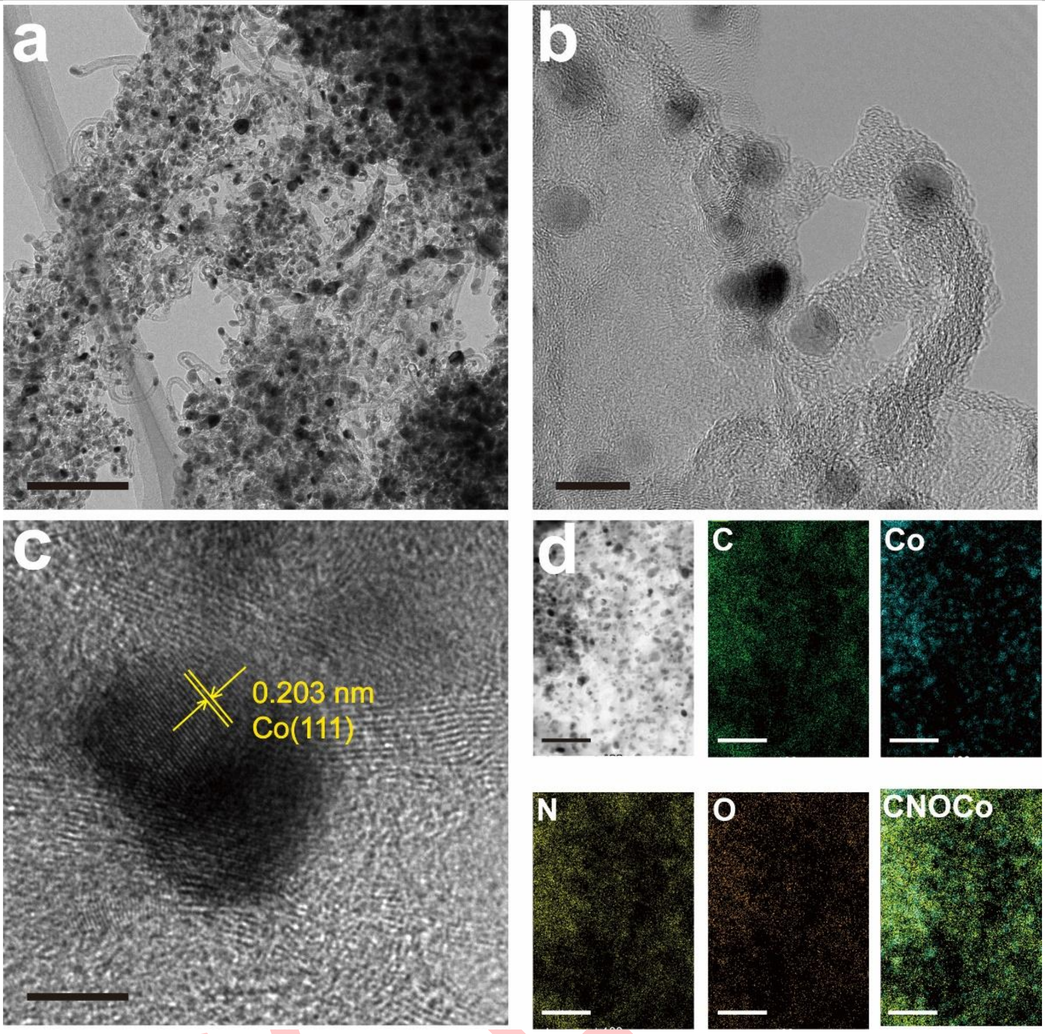

Fig. S2. Structure characterization of Co@N-CNTs. (a) TEM, (b) and (c) HRTEM, (d) the corresponding elemental mapping of Co, O, C and N for Co@N-CNTs. Scale bar in (a-d) are 200 nm, 20 nm, 5 nm, 100 nm, respectively.

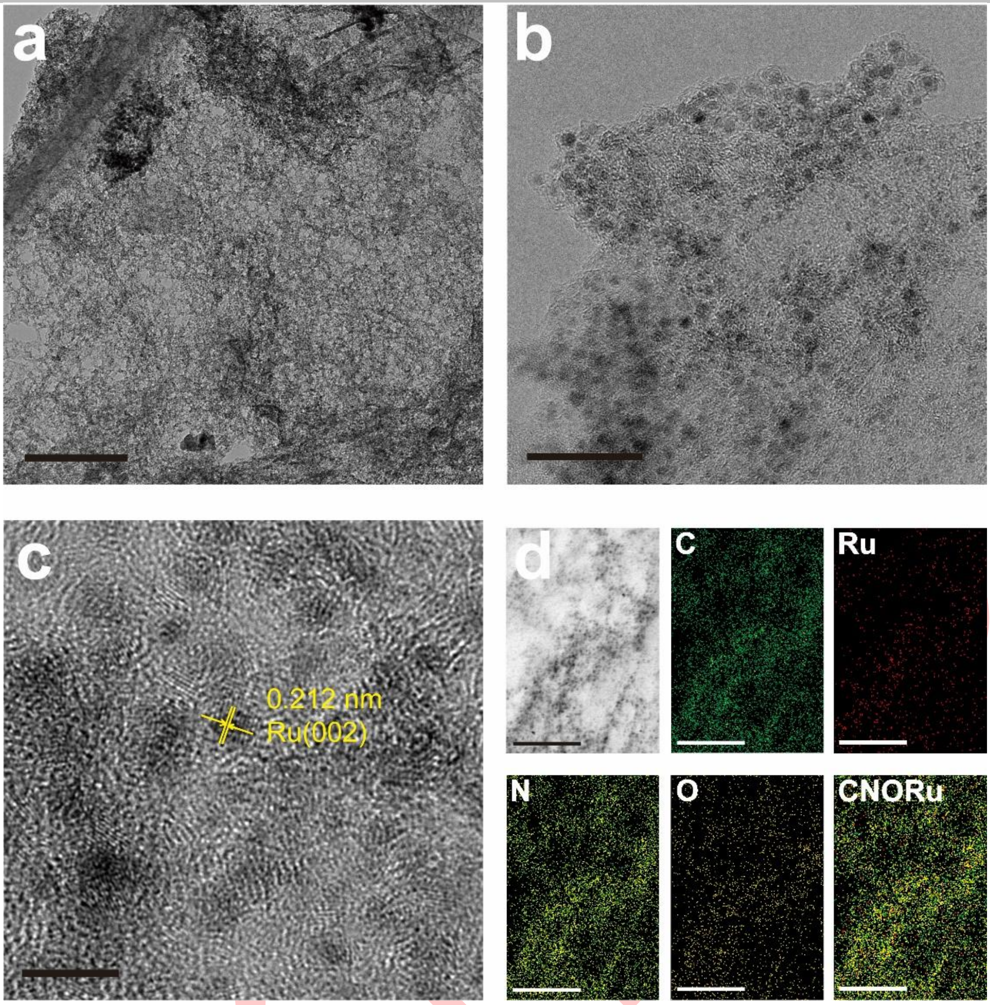

Fig. S3. Structure characterization of Ru@NC. (a) and (b) TEM, (c) HRTEM, (d) the corresponding elemental mapping of Ru, O, C and N for Ru@NC. Scale bar in (a-d) are 200 nm, 20 nm, 5 nm, 50 nm, respectively.

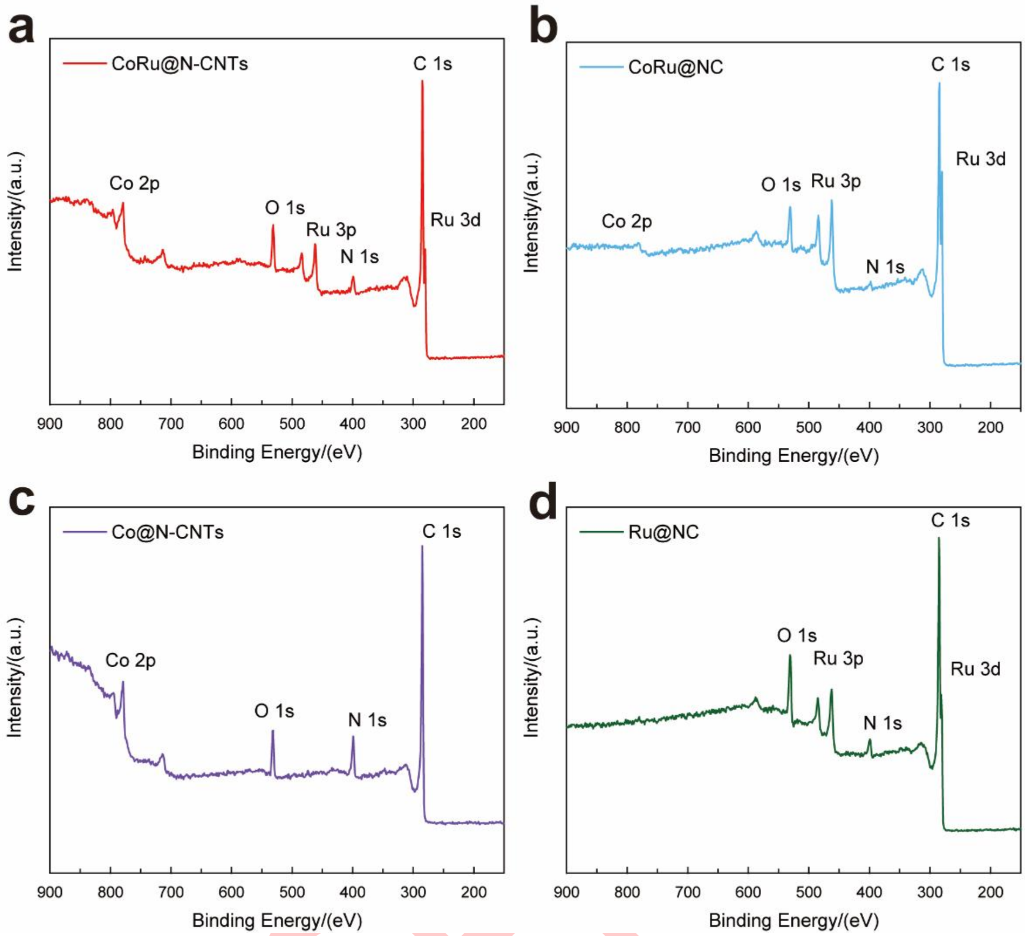

Fig. S4. XPS survey spectra of (a) CoRu@N-CNTs, (b) CoRu@NC, (c) Co@N-CNTs and (d) Ru@NC

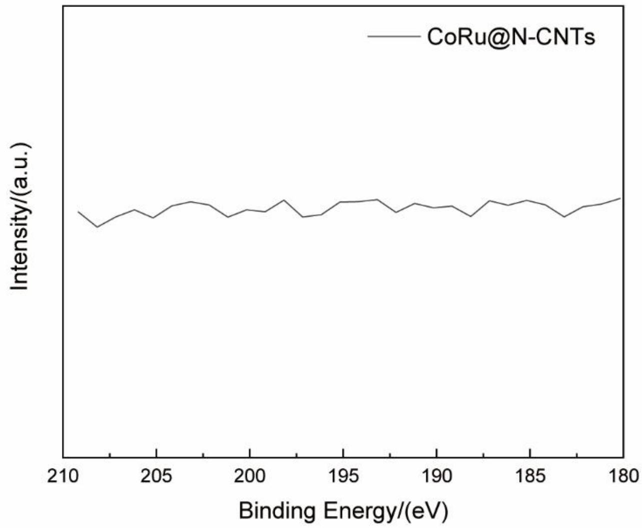

Fig. S5. XPS spectrum of CoRu@N-CNTs at binding energies of 180~210 eV.

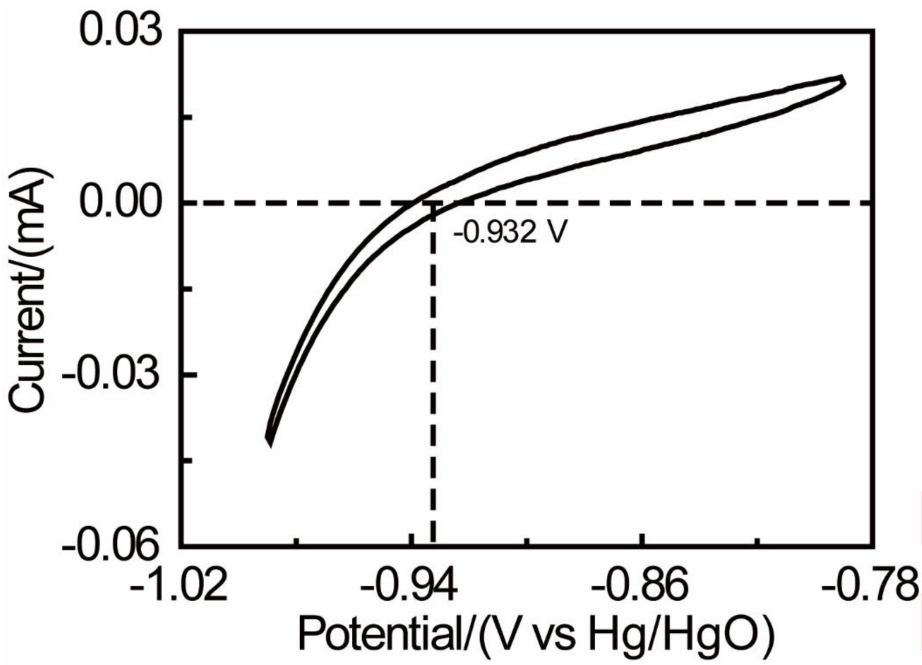

Fig. S6. Polarization curve of the Hg/HgO reference electrode calibrated against RHE in H_2-saturated 1M KOH electrolyte. Potential scan rate at 10 mV s^{-1}

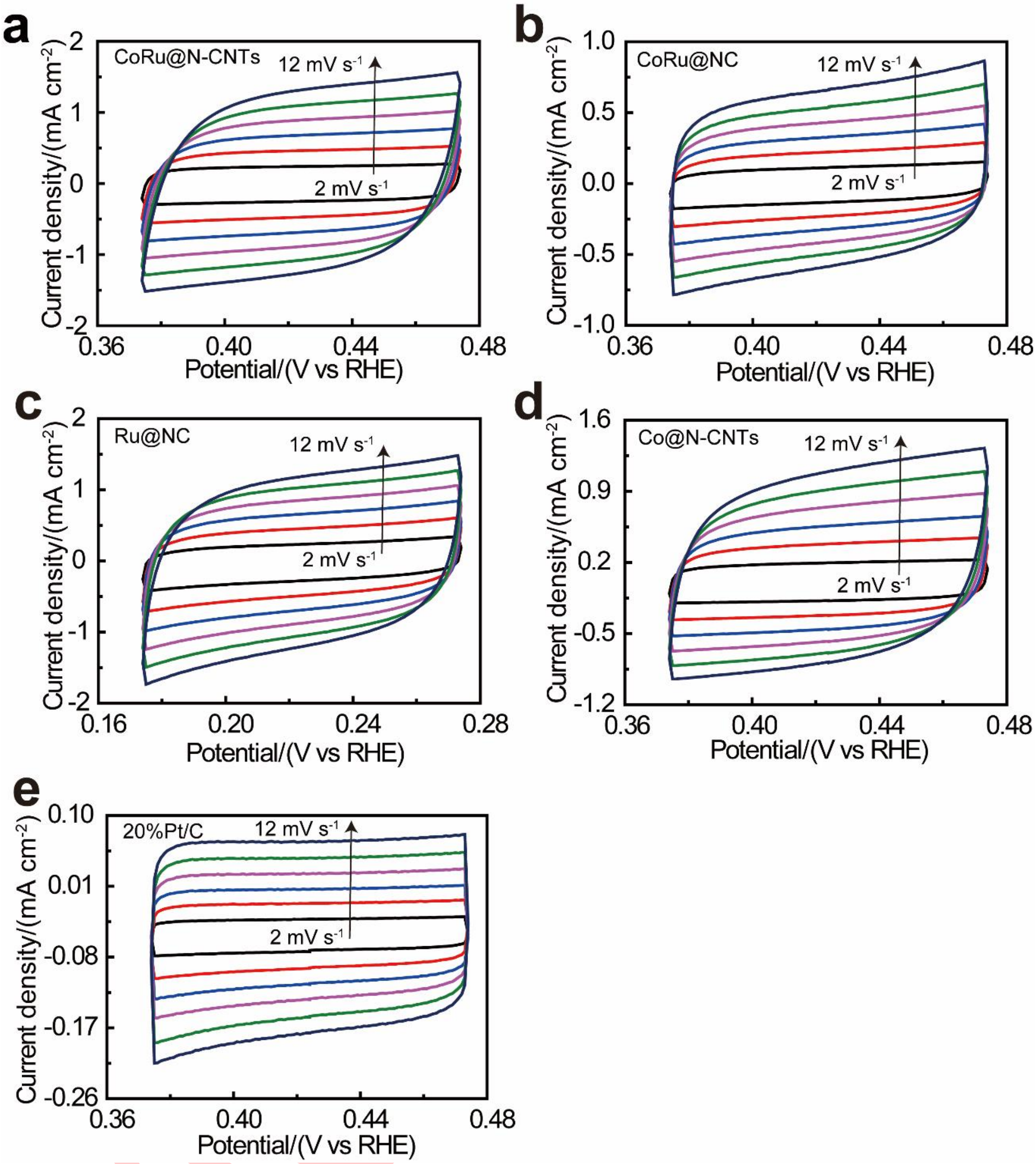

Fig. S7. CV patterns of (a) CoRu@N-CNTs, (b) CoRu@NC, (c) Ru@NC (d) Co@N-CNTs, and (e) 20%Pt/C with a scan rate ranging from 2-12 mV s^{-1}.

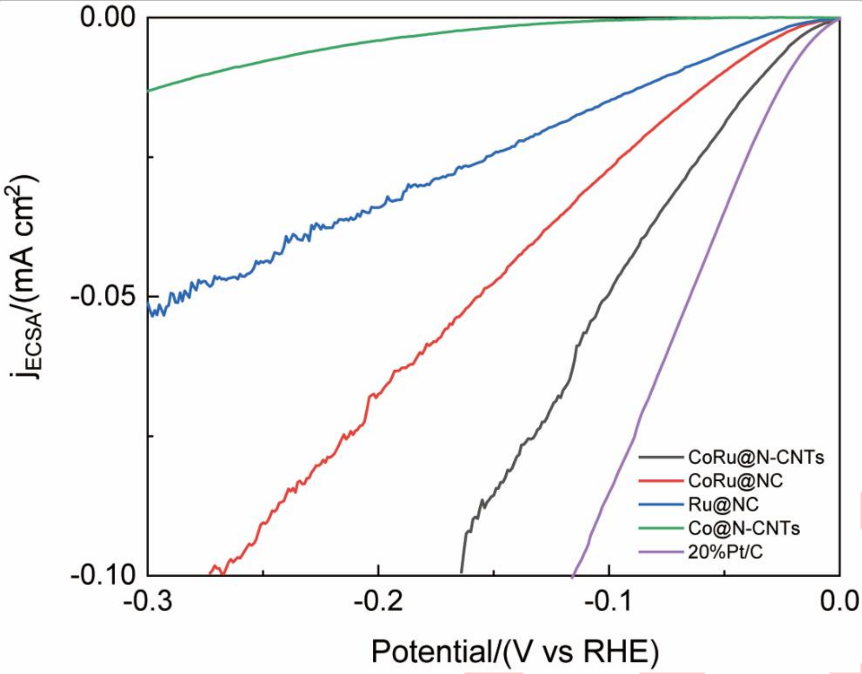

Fig. S8. The ECSA-normalized LSV curves of the CoRu@N-CNTs , CoRu@NC, Co@N-CNTs, Ru@NC and 20%Pt/C electrocatalysts for HER performance.

Table. S1. Element atomic content (%) of CoRu@N-CNTs, CoRu@NC, Co@N-CNTs and Ru@NC

	Co	Ru	C	N	O
CoRu@N-CNTs	2.92	3.27	78.58	6.88	8.35
CoRu@NC	1.49	11.41	68.68	3.64	14.77
Co@N-CNTs	2.68	-	80.96	9.88	6.49
Ru@NC	-	4.48	74.2	6.96	14.36

Table S2. The performance of CoRu@N-CNTs compared with the recently-reported Co/Ru-based HER electrocatalysts measured in 1 M KOH.

Catalyst	η_{10} (mV)	Reference
(Ru-N)@Pt	10	J. Mater. Chem. A, 2021, 9(26): 14941-14947
Ru/Co@OG	13	Angew. Chem., 2021, 133(29): 16180-16186
Ru/Mo_2C@NC	13	J. Mater. Chem. A, 2021, 9(36): 20518-20529
Ru-SNC	14	J. Mater. Chem. A, 2021, 9(31): 16967-16973
Ru S/DAs + Ru NCs	15	SmartMat, 2022, 3(2): 249-259
Ru1/DNiFe LDH	18	Nat. Commun., 2021, 12(1): 4587
Ru-Ru_2P	18	InfoMat, 2022, 4(5): e12287
Ru/Co-N-C-800	19	Adv. Mater., 2022, 34(21): 2110103
CoRu@N-CNTs	19	This work
Ru/Ni-MOF	22	Angew. Chem. Int. Ed., 2021, 60(41): 22276-22282
Ru_2P@Ru/CNT	23	Chinese J.Catal., 2022, 43(4): 1148-1155
Ru MNSs	24	Adv. Mater., 2022, 34(21): 2110103
RuIr@NrC	28	This work
Co_5Ru_1@NCNT/PF	28	Angew. Chem. Int. Ed., 2021, 60(41): 22276-22282
Ru/MoO_{2-x}	29	Appl. Catal. B-Environ., 2022, 307: 121204
Ru@NC	29	Catal. Sci. Tech., 2020, 10(13): 4405-4411
Ru-NiFeP/NF	29.3	Appl. Surf. Sci., 2021, 536: 147952
Ru/np-MoS_2	30	Nat. Commun., 2021, 12(1): 1687

ld-Ru@a-Co/Ti	33.5	Chem. Commun., 2022, 58(98): 13588-13591
M-Co NPs@Ru SAs/NC	34	Small, 2021, 17(49): 2105231
CNT-V-Fe-Ru	38	ACS Catal., 2022, 13(1): 49-59
Ru/N-C	39	ACS Appl. Mater. Interfaces, 2022, 14(13): 15250-15258
Ru-NiCoP/NF	44	Appl. Catal. B-Environ., 2020, 279: 119396
Co-SAC/RuO_2	45	Angew. Chem., 2022, 134(4): e202114951
Ru@Co/N-CNTs	48	ACS Sustain. Chem. Eng., 2020, 8(24): 9136-9144
Ni_5P_4-Ru	54	Adv. Mater., 2020, 32(11): 1906972
Co-Ru-MoS_2	55	Small, 2020, 16(13): 2000081
Ru@B-Ti_3C_2Tx	62.9	Small, 2021, 17(38): 2102218
Co-Ru/NCN	70	J. Energy Chem., 2023, 87: 286-294
Ru/Co$(OH)_2$ NWAs	96	Int. J. Hydrogen Energ., 2024, 51: 769-776

Reference

[1] K. Kokubo, S. Shirakawa, N. Kobayashi, H. Aoshima, T. Oshima, *Nano Res.* **2011,** 4, 204.