Supplementary information

Ultrafine Ru nanoparticles as efficient HER electrocatalyst for large current density in alkaline media by electronic communication of Ru-O bonds

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Materials

All reagents were used as received without any purification. Ruthenium trichloride ($RuCl_3$), Pt/C (20 wt%), Nafion solution (5%) and potassium hydroxide (KOH, ≧95%) were purchased from Sigma-Aldrich. Fullerene (C_{60}) was purchased from Xiamen Funano New Material Technology Co., Ltd.. Toluene (C_7H_8,≧99.5%), isopropyl alcohol (IPA, $(CH_3)_2CHOH$, ≧99.7%), ethanol (EtOH, CH_3CH_2OH, 99.7%), methanol (MeOH, CH_3OH, 99%), tetrabutylammonium hydroxide (TBAH, 50% in water) and hydrogen peroxide (H_2O_2, 40%)) were received from Sinopharm Chemical Reagent Co., Ltd.. Deionized water (DW, 18.25 MΩ/cm) was obtained from the ultra-pure purification system (ULUPURE, UPDR-I-10T).

Materials Characterization.

X-ray diffraction (XRD) patterns of the electrocatalysts were tested on a Rigaku D/max-2200PC diffractometer (Japan) using Cu Kα radiation (λ = 1.5406 Å). High-resolution Transmission Electron Microscope (HRTEM) images and EDS mapping images were recorded using a JEOL JEM-2010 field-emission transmission electron microscope with an accelerating voltage of 200 kV. The chemical bonding states and compositions of the samples were processed by Fourier transform infrared spectroscopy (FT-IR) in the range of 4000 to 400 cm^{-1} on a Bruker vector-80 installation. Raman spectra was collected on a Renishaw-invia Microscopic confocal laser Raman spectrometer with 532 nm as the excitation laser. The pyrolysis process of the precursors was characterized by thermogravimetry and differential thermal analysis (TG/DTA) using Universal V4.5A TA Instruments from room temperature to 800 °C in an N_2 atmosphere with a heating rate of 5 °C min^{-1}. Deionized water (DW, 18.25 MΩ/cm) was obtained from the ultra-pure purification system (ULUPURE, UPDR-I-10T).

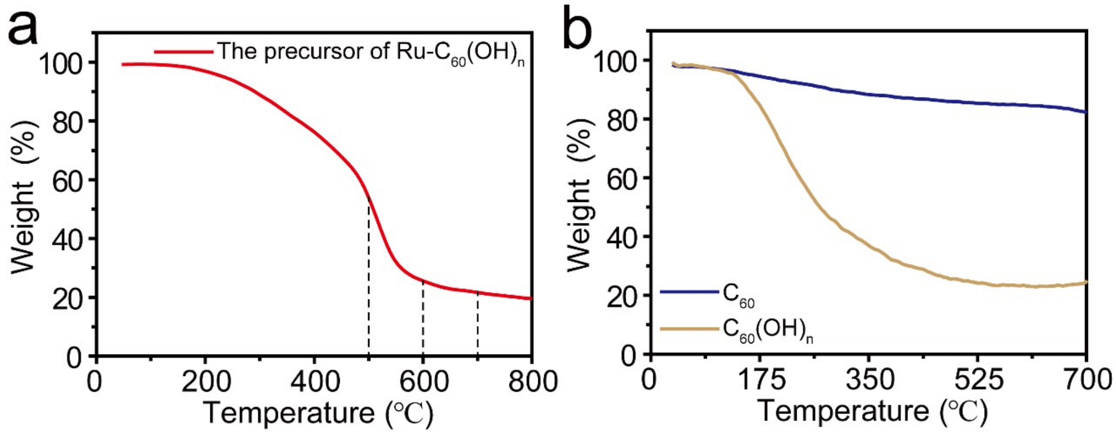

Fig. S1. Typical TG analysis of a) the precursor of Ru-$C_{60}(OH)_n$. and b) C_{60} and $C_{60}(OH)_n$.

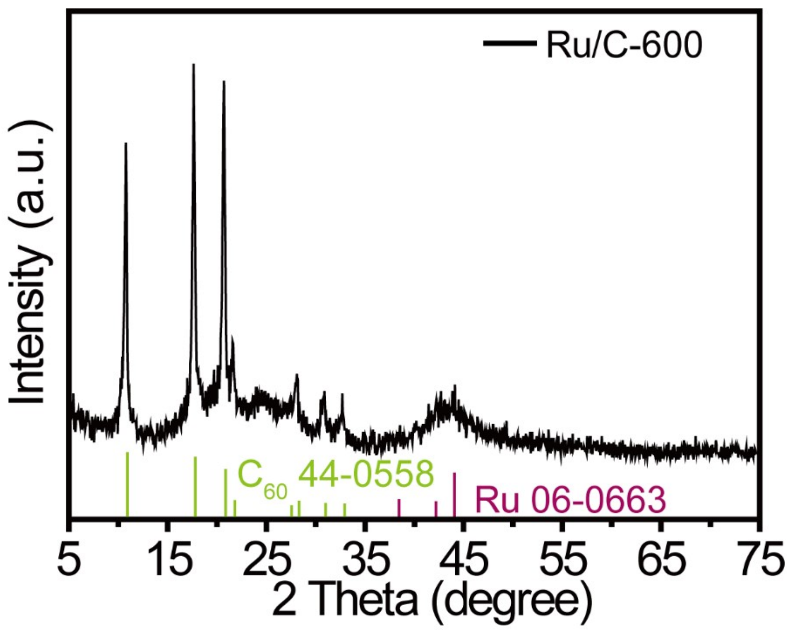

Fig. S2. The XRD pattern of Ru/C-600.

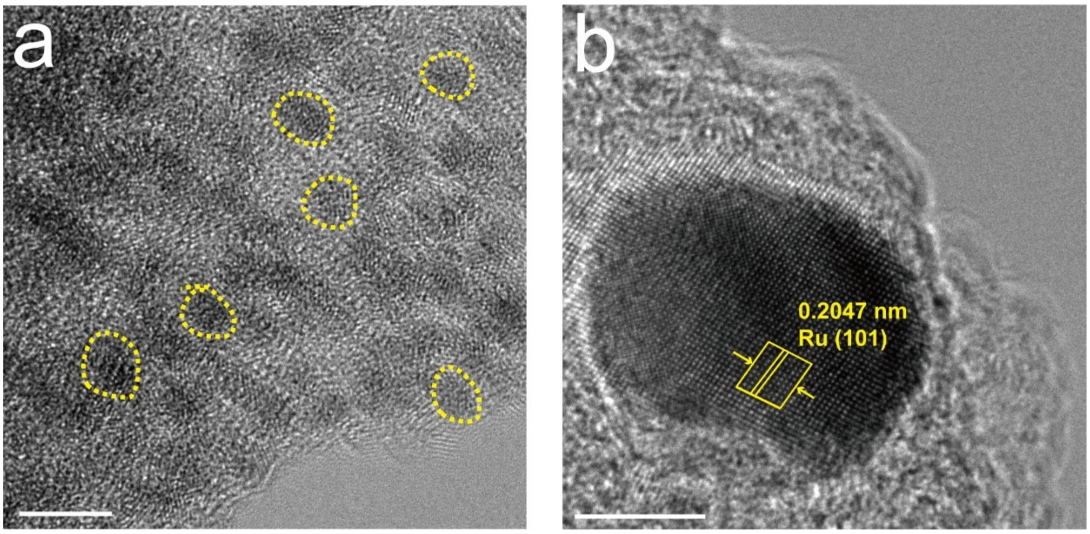

Fig. S3. HRTEM images of a) Ru-O/C-500 and b) Ru-O/C-700. Scale bar: 5 nm.

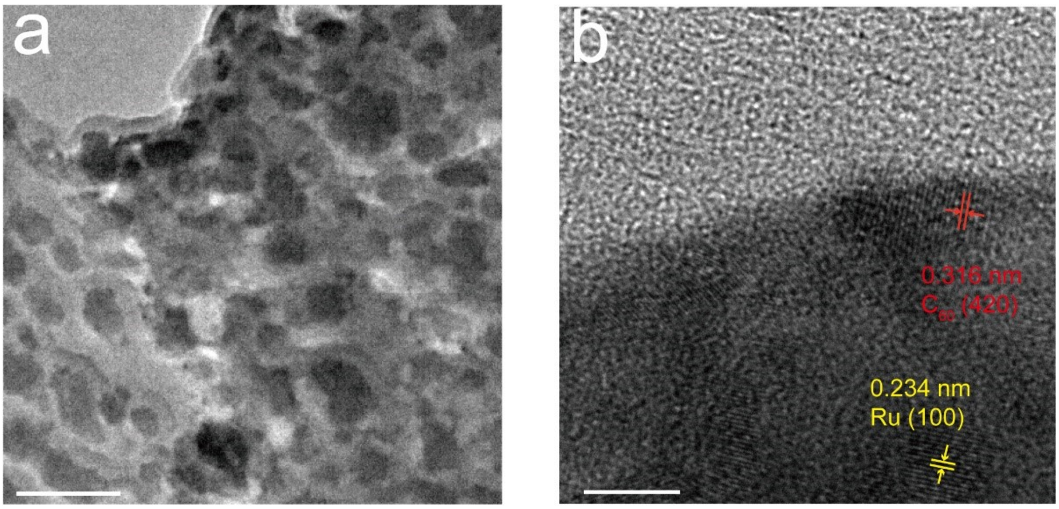

Fig. S4. TEM images of Ru/C-600. Scale bar a) and b): 100 nm and 5 nm.

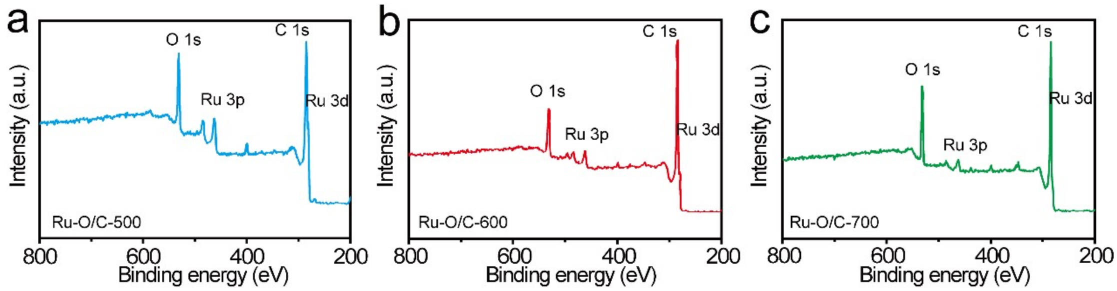

Fig. S5. X-ray photoelectron spectroscopy studies. XPS full survey spectra of (a) Ru-O/C-500, (b) Ru-O/C-600, and (c) Ru-O/C-700.

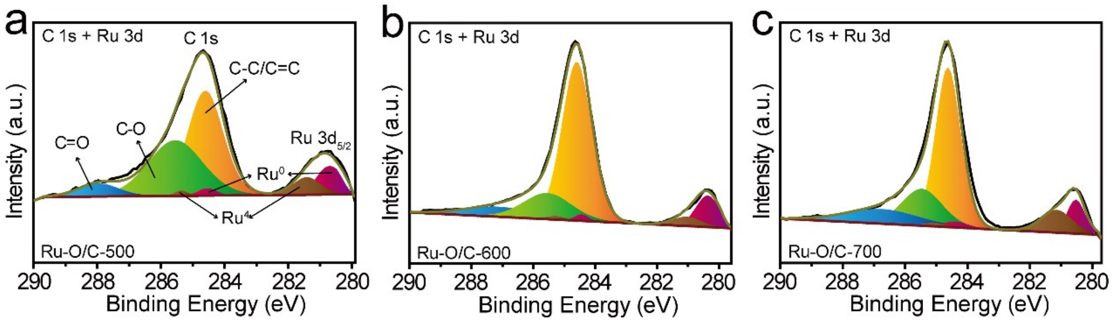

Fig. S6. High-resolution XPS spectra for C 1s and Ru 3d of (a) Ru-O/C-500, (b) Ru-O/C-600, and (c) Ru-O/C-700.

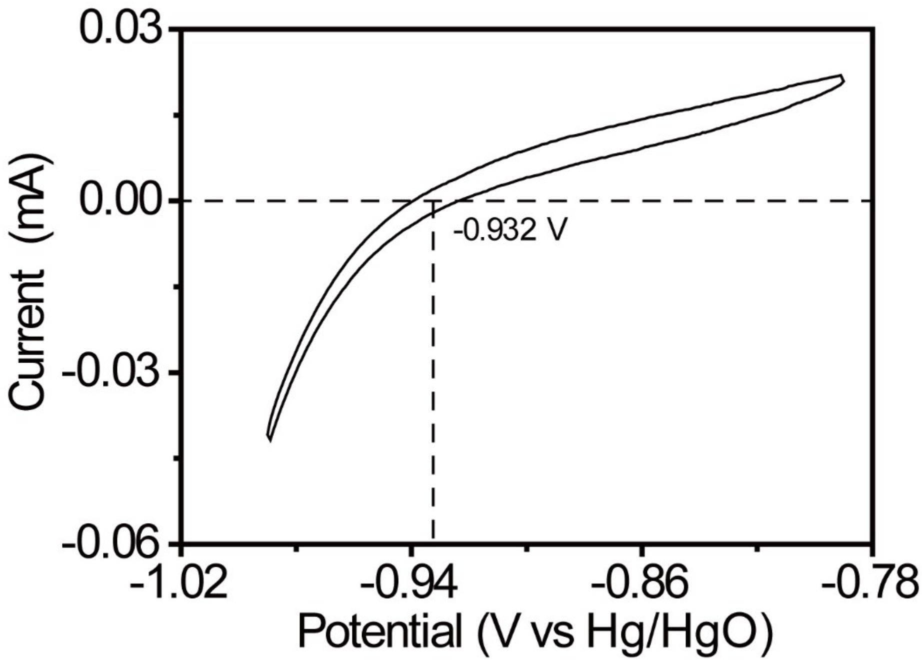

Fig. S7. Polarization curve of the Hg/HgO reference electrode calibrated against RHE in H_2-saturated 1M KOH electrolyte[1]. Potential scan rate at 10 mV s^{-1}

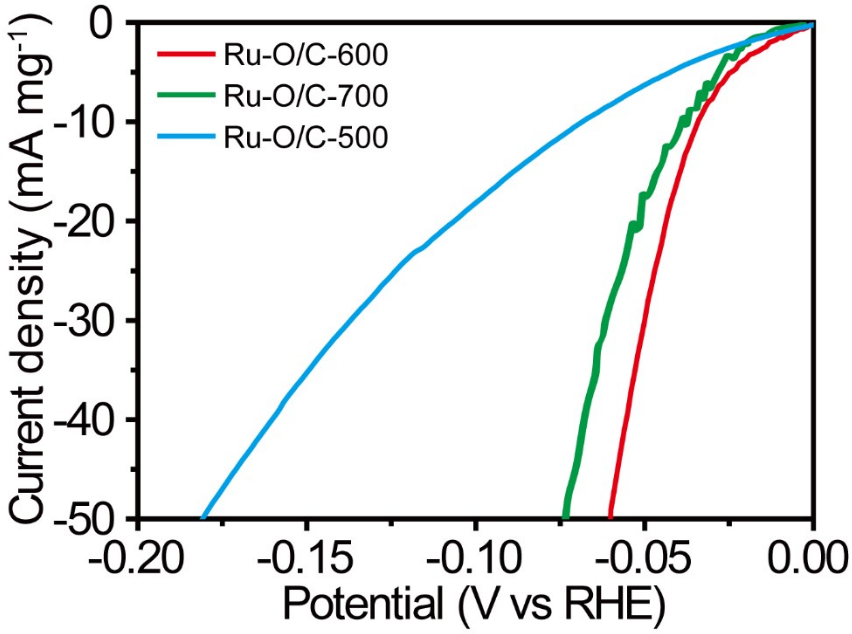

Fig. S8. LSV curves of the Ru-O/C-500, Ru-O/C-700, and Ru-O/C-600 normalized by Ru content in each sample.

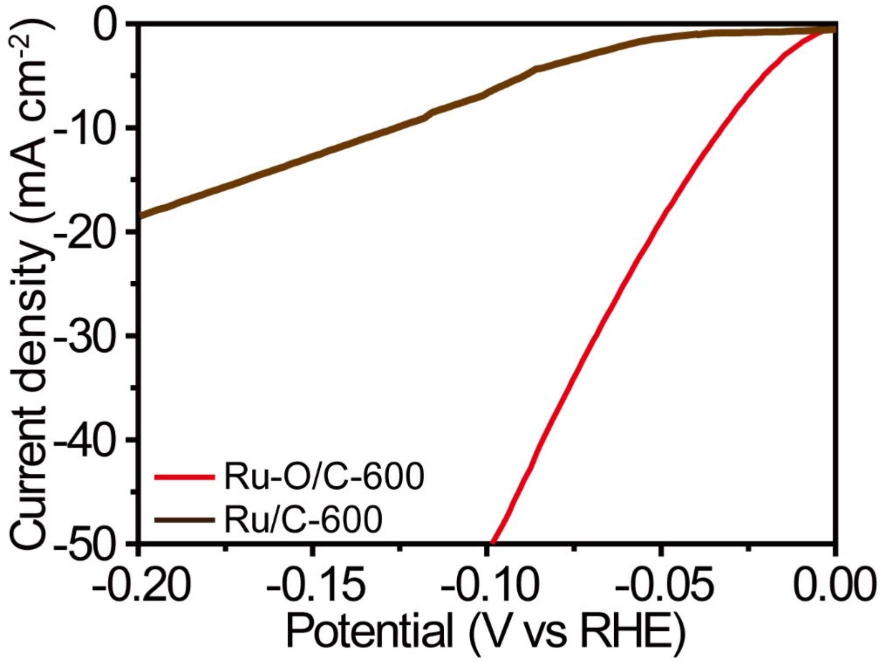

Fig. S9. LSV curves of the Ru/C-600 and Ru-O/C-600.

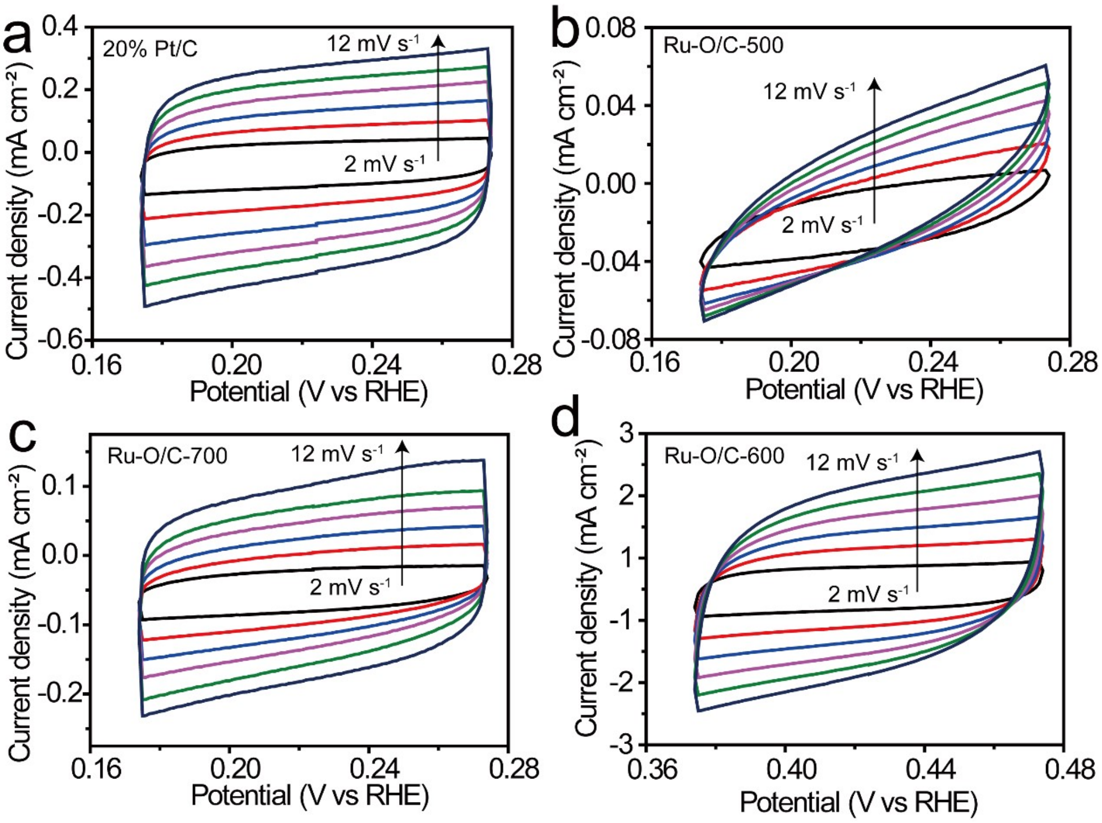

Fig. S10. a), b), c) and d) HER CV curves of the 20% Pt/C, Ru-O/C-500, Ru-O/C-700, and Ru-O/C-600 obtained at different scan rates between 2 mV and 12 mV in 1 M KOH[2, 3], respectively.

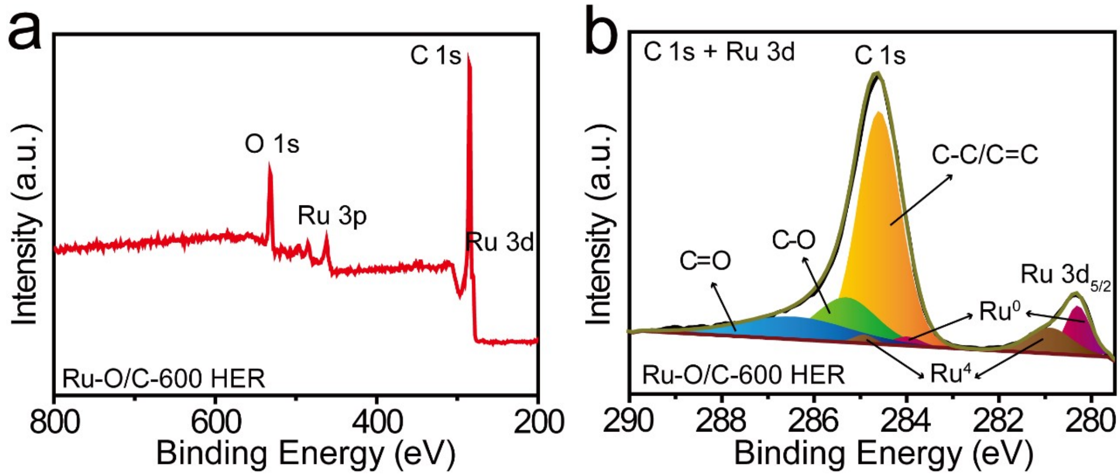

Fig. S11. (a) XPS survey spectra of Ru-O/C-600 after long-time stability test. (b) High-resolution XPS spectra for C 1s and Ru 3d of Ru-O/C-600 after long-time stability test.

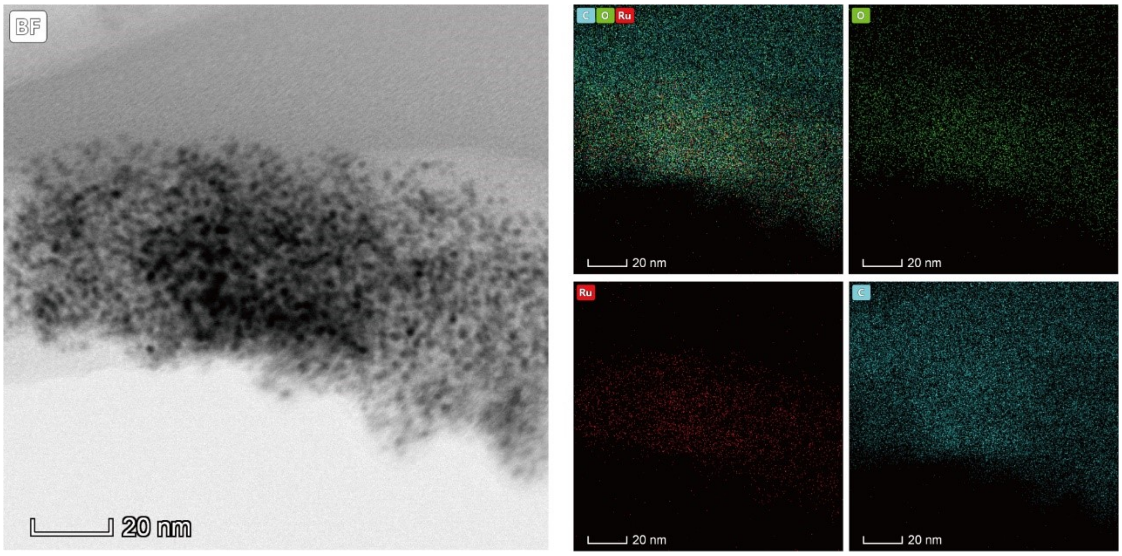

Fig. S12. TEM and element mapping images of Ru-O/C-600 after HER. Scale bar: 20 nm.

Table S1. a) I_D/I_G radio of Raman spectra among Ru-O/C-600, Ru-O/C-700 and Ru-O/C-500.

Sample	**I_D/I_G**
Ru-O/C-600	0.82
Ru-O/C-700	0.78
Ru-O/C-500	0.98

Table S2. Comparison of HER activity data for test catalysts in this experiment.

Sample	η_{10} (mV)	Tafel plots (mV dec^{-1})	Rct (Ω)	C_{dl} (mF cm^{-2})
Ru-O/C-600	32	51.8	12.8	117.5
Ru-O/C-700	75	99.8	40.5	10.8
Ru-O/C-500	190	236.9	81.5	1.5
20% Pt/C	46	61.2	29.8	26.1

Table S3. Summary of recently reported HER catalysts in 1 M KOH electrolyte.

No.	Catalyst	η_{10} (mV)	reference
1	Pd@Ru NRs	30	ACS Appl. Mater. Interfaces 2018, 10, 34147-34152.
2	Ru/Co_3O_4 NWs	30.98	Nano Energy 2021, 85, 105940.
3	Ru-Ni@Ni_2P-HNRs	31	J. Am. Chem. Soc. 2018, 140, 2731-2734.
4	Ru-O/C-600	32	this work
5	NiRu@N−C (S-2)	32	J. Mater. Chem. A 2018, 6, 1376-1381.
6	Ru/Ni-MoS_2	32	Appl. Catal. B 2021, 298, 120557.
7	Ru-MoO_2	35	J. Mater. Chem. A 2017, 5, 5474.
8	Ru@NG-4	40	Sustain. Energy Fuels 2017, 1, 1028-1033.
9	Ru_2Ni_2 SNs	40	Nano Energy 2018, 47, 1-7.
10	RuO_2/N-C	40	ACS Sustainable Chem. Eng. 2018, 6, 11529-11535.
11	a-$RuTe_2$ PNRs	41	Nat. Commun. 2019, 10, 5692.
12	Pd_3Ru/C	42	ACS Catal.2019, 9, 9614.
13	Ru ND/C	43.4	Chem. Commun. 2018, 54, 4613-4616.
14	CoRu@NC	45	Nanotechnology 2018, 29, 225403.
15	STRO	46	Nat. Commun. 2020, 11, 5657.
16	RuNC700	47	Nat. Commun. 2019, 10, 631.
17	Ru@CoN-CNTs-2	48	ACS Sustainable Chem. Eng. 2020, 8, 24, 9136-9144.
18	Ru_2P@PNC/CC-900	50	ACS Appl. Energy Mater. 2018, 1, 314-3150.
19	Ru_1CoP/CDs-1000	51	Angew. Chem. Int. Ed. 2021, 60, 7234-7244.

20	$Ni_{1.5}Co_{1.4}P$@Ru	52	Chem. Commun. 2017, 53, 13153-13156.
21	RuP_2@NPC	52	Angew. Chem. Int. Ed. 2017, 56, 11559-11564.
22	Ru/Co_4N-CoF_2	53	Chem. Eng. J. 2021, 414, 128865.
23	Ru/C-H_2O/CH_3CH_2OH	53	Appl. Catal. B. 2019, 258, 117952.
24	Sr_2RuO_4	61	Nat. Commun. 2019, 10, 149.
25	ah-RuO_2@C	63	Nano Energy 2019, 55, 49-58.
26	RuP_x@NPC	74	ChemSusChem 2018, 11, 743-752.
27	SA-Ru-MoS_2	76	Small Methods 2019, 1900653.
28	RuP_2PC	79	J. Mater. Chem. A, 2021, 9, 12276-12282.
29	$Cu_{2-x}S$@Ru NPs	82	Small 2017, 13, 1700052.
30	CoRu-OA@HNC-2	85	ACS Appl Mater Interfaces, 2020, 12, 51437-51447.
31	RuO_2-NWs@g-CN	95	ACS Appl. Mater. Interfaces 2016, 8, 28678-28688.

Reference

1. C. Wei, R. R. Rao, J. Peng, B. Huang, I. E. L. Stephens, M. Risch, Z. J. Xu and Y. Shao-Horn, Recommended practices and benchmark activity for hydrogen and oxygen electrocatalysis in water splitting and fuel cells, *Adv. Mater.*, 2019, **31**, e1806296.
2. J. Wang, F. Xu, H. Jin, Y. Chen and Y. Wang, Non-noble metal-based carbon composites in hydrogen evolution reaction: fundamentals to Applications, *Adv Mater*, 2017, **29,** 1605838.
3. D. Voiry, M. Chhowalla, Y. Gogotsi, N. A. Kotov, Y. Li, R. M. Penner, R. E. Schaak and P. S. Weiss, Best practices for reporting electrocatalytic performance of nanomaterials, *ACS Nano*, 2018, **12**, 9635-9638.