Supporting Information

Low-loaded Ru on hollow SnO$_2$ for enhanced electrocatalytic hydrogen evolution

Yousaf Saira,[a] Zhijuan Li,*[b] Yu Zhu,[a] Qicheng Liu,[a] Wenkai Luo,[b] Yu Wang,[b] Mingxing Gong,[c] Gengtao Fu*[a] and Yawen Tang*[a]

[a] Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Centre of Biomedical Functional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China.
E-mail: gengtaofu@njnu.edu.cn (G. Fu); tangyawen@njnu.edu.cn (Y. Tang)

[b] School of Environmental Science and Nanjing Key Laboratory of Advanced Functional Materials, Nanjing Xiaozhuang University, Nanjing 211171, China.
E-mail:zhijuanlibbd@163.com (Z. Li)

[c] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430078, China.

Materials and Methods

1. Materials

Tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$), ammonium fluoride (NH_4F), and L-Ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene glycol (EG) was purchased from Macklin Biochemical Technology Co., Ltd. Ruthenium (III) chloride hydrate ($RuCl_3 \cdot xH_2O$) was purchased from Dibai Biological Science and Technology Co., Ltd. All the reagents were of analytical grade and utilized as received without any further purification. Deionized water was used throughout the experimental process.

2. Preparation of SnO$_2$

In a typical synthesis, 0.5 mmol $SnCl_2 \cdot 2H_2O$ was added to 40 mL deionized water and stirred at room temperature for 1 hour. Then 1mmol NH_4F was added and kept stirring for another 1 h. The homogeneous solution was transferred into a 50 mL teflon-lined autoclave. The autoclave was sealed and maintained at 180 °C for 24 h. The final product was washed with deionized water and alcohol and dried at 60 °C in the oven. Then the sample was put in the tube furnace and annealed at 400 °C in air for 2 h at a rate of 2 °C min^{-1} to get the hollow SnO_2.

3. Preparation of Ru-SnO$_2$

For the synthesis of Ru-SnO$_2$-0.073 (Ru-SnO$_2$), Ru-SnO$_2$ electrocatalyst was synthesized by an alcohol-reduction process by first adding 40 mg as prepared SnO_2, and 0.073 mmol $RuCl_3 \cdot xH_2O$ into 20 mL EG solution and ultrasonicated for 10 min. After that 50 mg of AA was added to the solution and stirred for another 30 min. The resulting mixture was kept under reflux at 150 °C for 3 h before being filtered, washed with abundant water and alcohol and dried. For the synthesis of Ru-SnO$_2$-0.144 and Ru-SnO$_2$-0.036, the same process was followed with an adjustment of $RuCl_3 \cdot xH_2O$ content to 0.144 and 0.036mmol, respectively.

4. Characterization

The crystalline structure information of the prepared sample was measured by X-ray powder diffraction (XRD) on a D/max-rC X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). X-ray

photoelectron spectroscopy (XPS) data were measured on Thermo VG Scientific ESCALAB 250 spectrometer with an Al Kα radiator. Scanning electron microscopy (SEM) images were measured on JEOL JSM7500F. Transmission electron microscopy (TEM) was inquired with JEOL JEM-2100F TEM/STEM at an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDX) and elemental mapping images were measured on an FEI Tecnai G2 F20 microscope, an accessory built on the JEOL JEM 2100F. The Brunauer–Emmett–Teller (BET) specific surface area was collected on a Micromeritics ASAP 2050 instrumenant at 77 K.

5. Electrocatalytic HER Measurement

Electrocatalytic hydrogen evolution test in 1 M KOH: The HER test was performed by a three-electrode test system with a glassy carbon electrode (d=3 mm) modified with catalysts as a working electrode, a graphite rod as the auxiliary electrode as well as a saturated calomel reference electrode (SCE) as the reference electrode and is equipped with a Shanghai Chenhua Instrument Co., Ltd. electrochemical workstation model CHI760E to assess its catalytic activity. The catalysts ink was prepared by mixing 5 mg of catalyst, 1 mL mixed solvent consisting of 0.6 mL ethanol, 0.3 mL H_2O, and 0.1 mL Nafion solution with the following sufficient sonication. 9 μL catalyst ink was used to modify the glassy carbon electrode. All of the electrochemical tests were carried out in 1 M KOH electrolyte with a scan rate of 5 mV s^{-1}. The long-term stability was recorded using chronopotentiometry at the current density of 10 mA cm^{-2}. The accelerated durability test (ADT) of CVs is performed between the potential range of -0.05 V-0.05 V vs. RHE at a scan rate of 100 mV s^{-1}. The electrochemical double-layer capacitance (C_{dl}) was calculated from the CV curves tested in a non-Faradic region under different scan rates from 20 to 100 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) plots were performed at a voltage of 0.5 V over a scanning frequency range from 100 kHz to 0.01Hz. All electrode potentials were quoted versus reversible hydrogen electrodes (RHE).
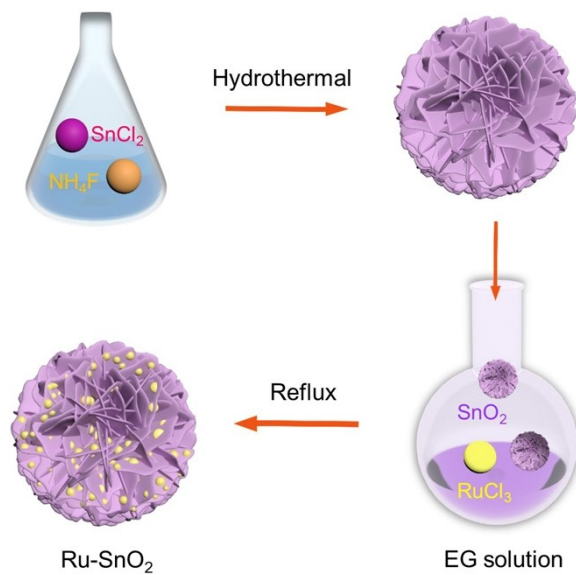
Figures and tables

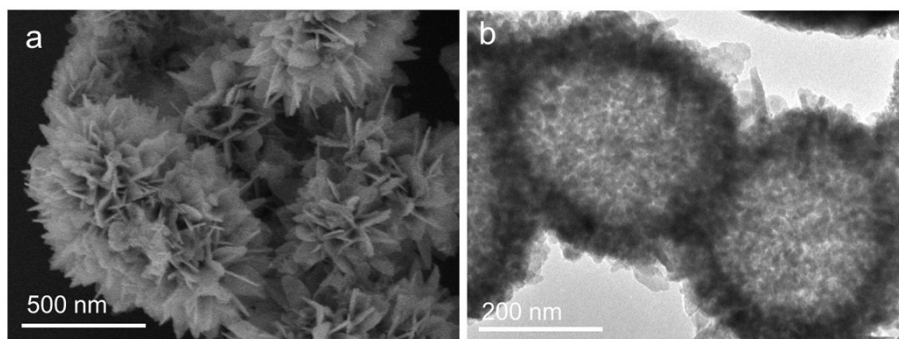**Figure S1.** Schematic illustration for the preparation of Ru-SnO$_2$.

Figure S2. (a) SEM and (b) TEM images of the as-fabricated SnO$_2$.
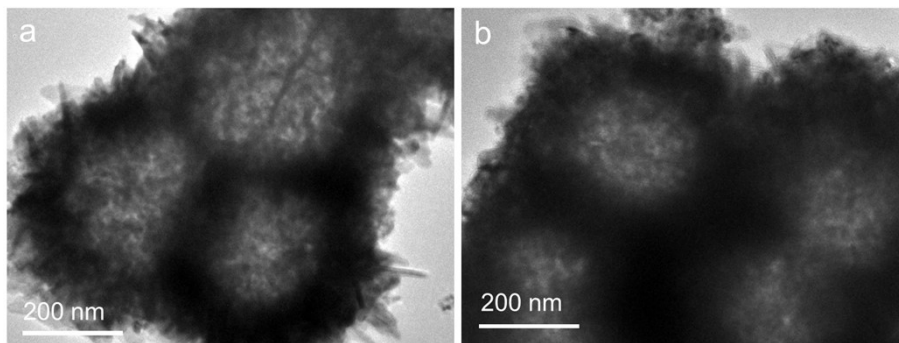
Figure S3. TEM images of Ru-SnO$_2$ with different Ru contents: (a) 0.036 mmol and (b) 0.144 mmol.
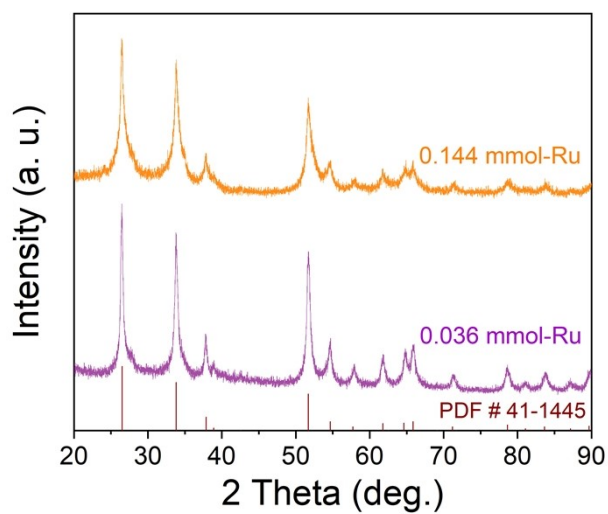

Figure S4. XRD patterns of Ru-SnO$_2$ with different Ru contents.
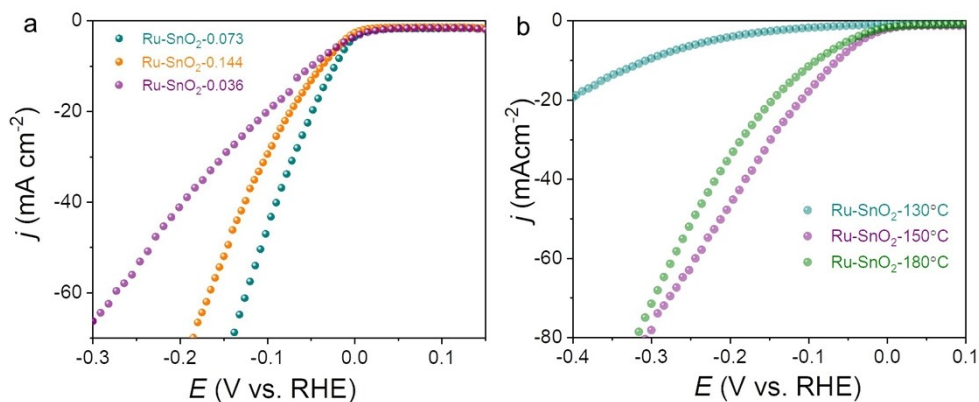
Figure S5. (a) LSV curves of catalysts with different Ru contents; (b) LSV curves of catalysts with reflux temperature recorded in 1.0 M KOH at 5 mV s^{-1}.
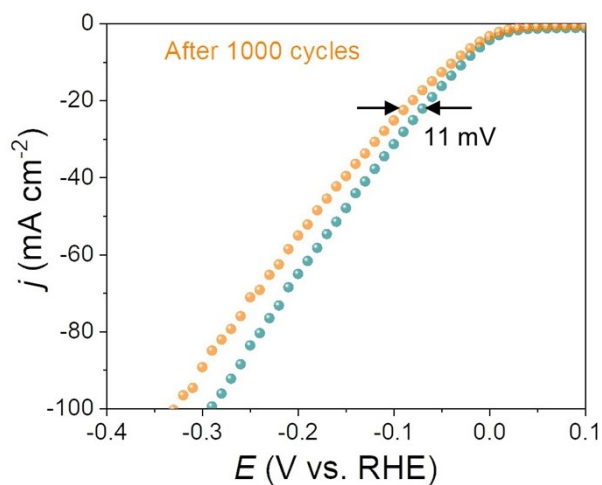

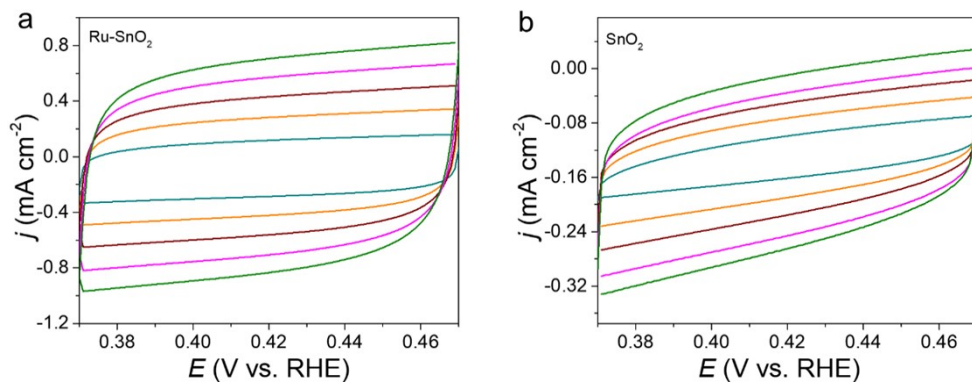**Figure S6.** LSV curves of commercial Pt/C before and after 1000 CV cycles.

Figure S7. Cyclic voltammetry curves of (a) Ru-SnO$_2$, and (b) SnO$_2$ at different scan sweeping rates from 20 mV s^{-1} to 100 mV s^{-1} in 0.1 M KOH solution.
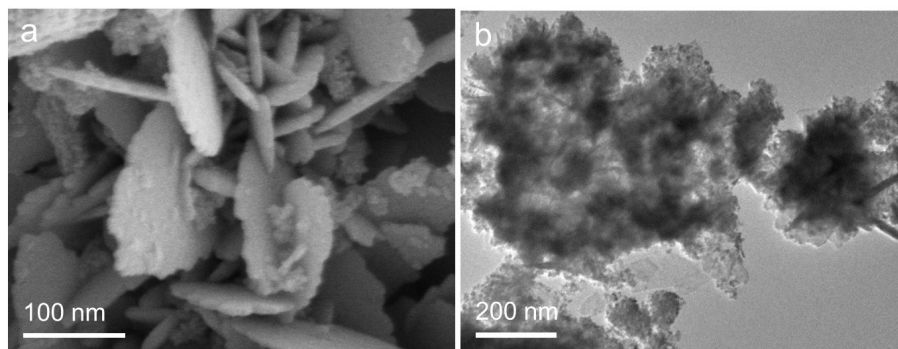

Figure S8. (a) SEM and (b) TEM images of the recovered Ru-SnO$_2$ after the stability test.
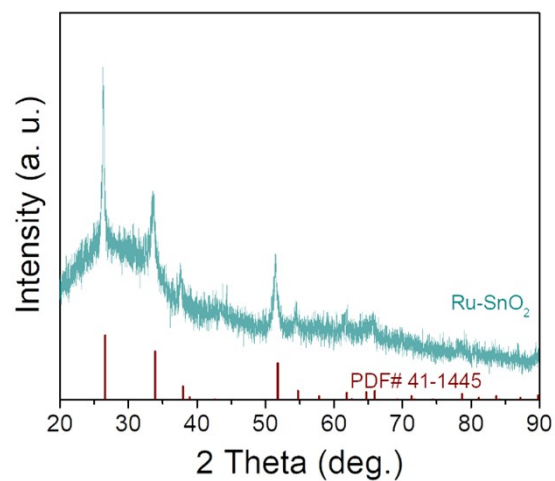
Figure S9. XRD pattern of the recovered Ru-SnO$_2$ after the stability test.
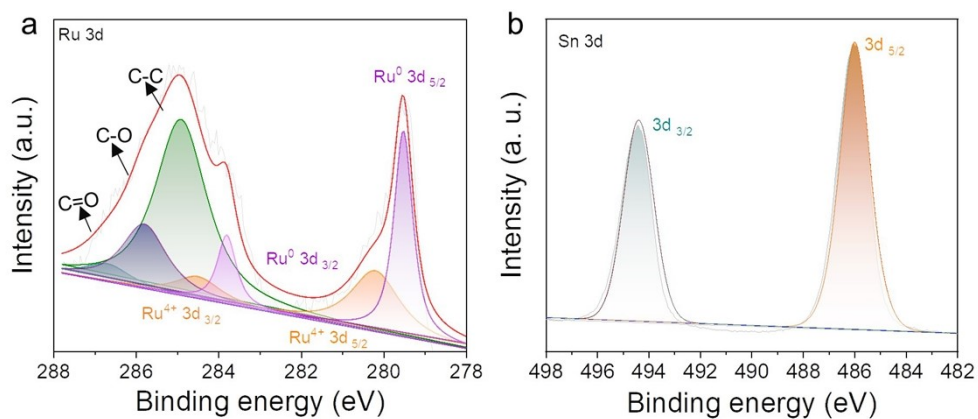

Figure S10. (a) Ru 3d XPS spectrum and (b) Sn 3d XPS spectrum of the recovered Ru-SnO$_2$ after the stability test.

Table S1. Comparison of HER performance with recently reported HER catalysts in 1.0 M KOH.

Catalysts	Overpotential (mV@10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Reference
Ru-SnO$_2$	23	52.5	This work
mRu@PANI/CP	24	75	J. Mater. Chem. A 2022, 10, 14435.
RuP/CN/C	30	60	J. Alloys Compd. 2023, 939, 168717.
Ru/BCN	33	72	Int. J. Hydrog. Energy 2023, 48, 9682.
PtNPs@MXene/Ppy	40	64	Electrocatalysis 2022, 13, 469.
Ni(OH)$_2$-PtO$_2$ NS/Ti	44.8	64	J. Mater. Chem. A 2018, 6, 1967.
Ru-KB-H-6H	52	58.9	ChemElectroChem 2021, 8, 447.
NiRu-MOF/NF	51	90	ACS Appl. Mater. Interfaces 2020, 12, 34728.
Ru-CoP-2.5 NAs	52	70.1	J. Colloid. Interface Sci. 2022, 625457.
PtNBs/NiNRs	61.6	113	Int. J. Hydrog. Energy 2023, 48, 30382.
Ru/Ta$_3$N$_5$ NBs	64.6	84.92	Molecules 2023, 28, 1100.
Ru/NPC-2	64	74.7	Fuel 2023, 341, 126996.
PtNi10/C	66	117.19	J. Colloid. Interface Sci. 2023, 634, 897.
Co$_3$Mo$_3$N-Mo$_2$C/CNFs	76	82.8	Inorg.Chem. 2023,62, 11207.
Ru/CoO	85	70	J. Energy. Chem. 2019, 37, 143.
Ru-MnO@C NWs	92	57.8	Chem. Eng. J. 2022, 446, 136816.
Ru-Ti$_3$C$_2$T$_x$@600	96	150.6	J. Phys. Chem. Lett. 2021, 12, 8016.
Ru/LCO	150	110.25	Inorg. Chem. 2022, 61, 19407.
PtSe$_2$	173	91	Nano Lett. 2021, 21, 3857.
Dr-Pt	26	52	Adv. Mater. 2022, 34, 2106973.
PtSe$_2$/Pt	42	53	Angew. Chem. Int. Ed. 2021, 60, 23388.