Supporting Information

Nitrogen-doped RuS_2 Nanoparticles with in-situ Reduced Ru as Efficient Electrocatalyst for Hydrogen Evolution

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Experimental details

Synthesis of RuS_2. 500 mg $RuCl_3$ was placed in the tube furnace, which was heated to 400 °C with 10 °C/min and kept at this temperature for 2 h in air. The resulting black powder is the precursor of RuS_2. Took 50 mg the precursor of RuS_2 in the tube furnace and place 500mg sulfur powder upstream of quartz tube, then heated it to 400 °C for 1 h under the protection of inert gas argon. When the temperature control procedure finished, we shut down the power of the tube furnace and waited it to be naturally cooled down under argon protection. The end product is RuS_2.

Synthesis of RuS_2/Ru. To prepare RuS_2/Ru, the RuS_2 was put in the tube furnace to anneal at 400 °C for 30 min under argon protection.

Synthesis of N-RuS_2/Ru. The preparation process is the same as that of *RuS_2/Ru* except that argon is changed into ammonia.

Physical characterization. The crystal structure of the samples was study by X-ray diffraction (XRD, X' Pert PRO PHILIPS with Cu Kα radiation). X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra) was used to study the elementary composition and the bonding characteristics of the samples. The morphology and high-resolution images were observed by the scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, TecnaiTM G2 F30, FEI, USA). Electrochemical measurements were performed in a standard three-electrode electrochemical cell using an electrochemical workstation (CHI660e).

Electrochemical measurements. We carried out the electrochemical tests at room temperature via a three-electrode configuration using an electrochemical workstation (CHI660e). 50 mL 0.5 M H_2SO_4 was added into the cell for HER as acidic electrolyte. Saturated silver chloride electrode (Ag/AgCl) and graphite rod electrode were used as the reference electrode and counter electrode in acidic electrolytes, respectively. The glassy carbon electrode coated with catalyst ink was directly connected with the working electrode. To value and compare the catalytic efficiency of catalyst fabricated in this work, commercial Pt/C (20 wt.% Pt) was tested under equal conditions. The polarization curves were measured to explore the electrocatalytic performance under a sweep rate of 5 mV/s by linear sweep voltammetry method. The measured potentials (vs. Ag/AgCl) were converted to RHE by the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.197$). Electrochemical tests were performed at room temperature and the curves were reported with iR-correct, where the value of R is 1~3 ohm. The electrochemical impedance spectroscopy (EIS) spectrum was tested at −0.150 V (vs. RHE) with the frequency changing from 10k Hz to 0.1 Hz. Its electrochemical stability was tested at continuous cycle for over 10000 cycles at a scan rate of 100 mV/s. Chronoamperometry test was conducted at cathodic potential of -100 mV (vs. RHE) for 40 hours.

Calculation of turnover frequency (TOF). Here, we selected an electrochemical method to obtain the active site density at the surface. It was supposed that nearly all the surface active sites are accessible to the electrolyte, then it is possible to evaluate the TOF values by the equation as follows:

$$\mathrm{TOF} = \frac{I}{2nF}$$

Here these physical variables F, n, and I represent the Faraday constant (~ 96485 C/mol), active site density (mol), and the current (A) during hydrogen evolution, respectively. The factor 1/2 is because water electrolysis requires two electrons to evolve one hydrogen molecule from two protons. The electrochemical measurements were performed to collect the CV curves in 0.2 M PBS electrolyte (pH = 7) from −0.2 V to +0.6 V (vs. RHE) with a scan rate 50 mV/s. Assuming a one-electron process for both reduction and oxidation, we can evaluate the upper limit of the active site number (n) according to the follow formula:

$$n = \frac{Q}{2F}$$

Where F and Q correspond to the Faraday constant and the whole charge of CV curve, respectively.

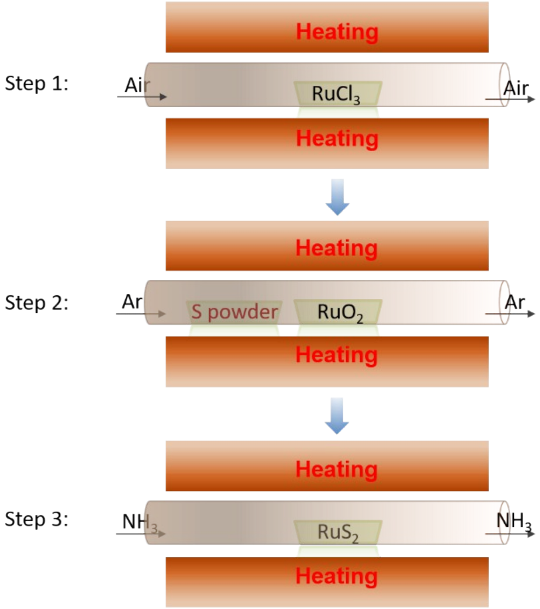

Figure S1. Fabrication process of the N- RuS_2/ Ru.

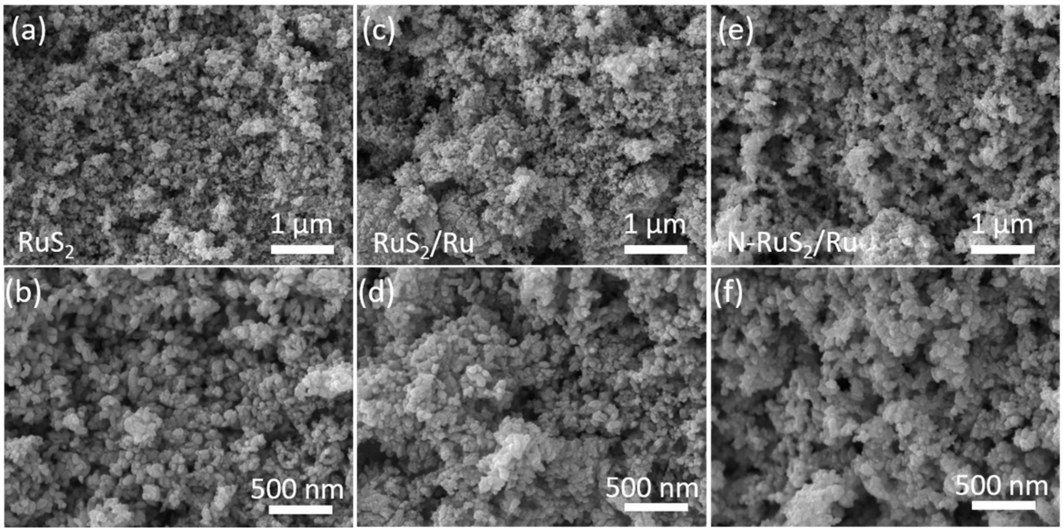

Figure S2. The low-magnification SEM images of (a) RuS_2, (c) RuS_2/Ru and (e) N-RuS_2/Ru. The high-magnification SEM images of (b) RuS_2, (d) RuS_2/Ru and (f) N-RuS_2/Ru.

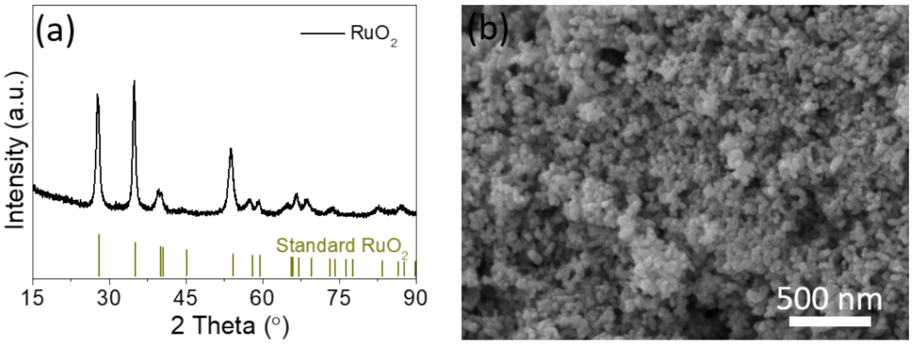

Figure S3. (a) The XRD pattern and (b) the SEM image of the precursor of RuS_2.

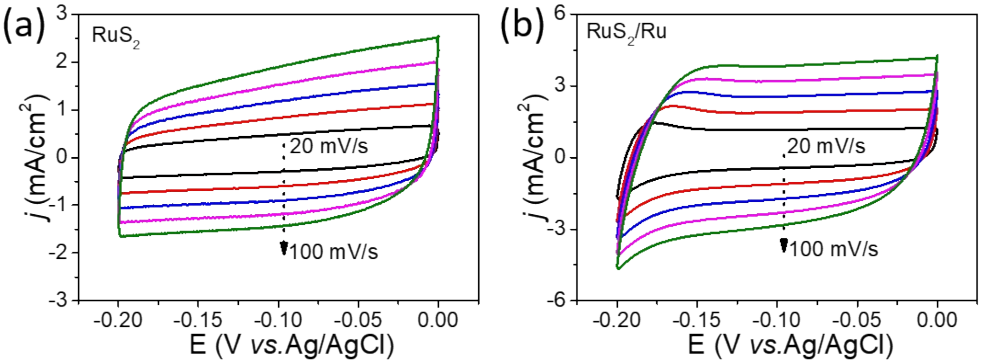

Figure S4. CV scans of double-layer capacitance measurement of (a) RuS_2 and (b) RuS_2/Ru at different scanning rates.

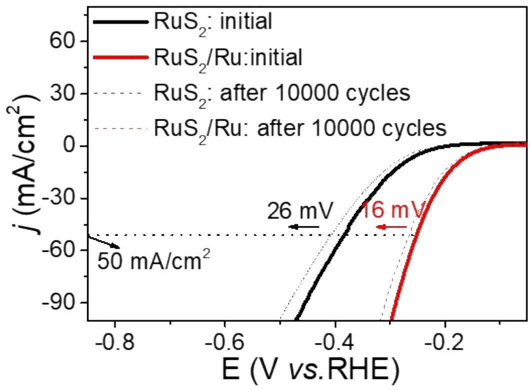

Figure S5. Polarization curves of RuS_2 and RuS_2/Ru before and after 10000 CV cycles from −0.2 to 0 V (vs. RHE).

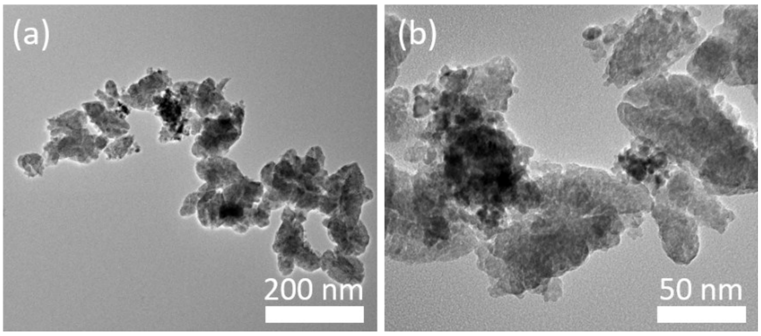

Figure S6. TEM images of N- RuS_2/Ru after stability test.

Table S1. Comparison of the electrocatalytic activity of N-Ru/RuS_2 with some representative powder HER catalysts recently reported under acidic electrolyte.

Catalysts	Overpotential at the 10 mA/cm^2	Tafel slope	Reference
N-RuS_2/Ru	**120 mV**	**53 mV/dec**	**This work**
s-RuS_2/S-rGO	69 mV	64 mV/dec	*ACS Appl. Mater. Inter.*, 2018, 10, 34098.
$Cu_{2-x}S$@Ru NPs	129 mV	51 mV/dec	*Small*, 2017, 13, 1700052.
Ru/MeOH/THF	83 mV	46 mV/dec	*Chem. Commun.*, 2017, 53, 11713-11716.
RuS_2/CNT	226 mV	74 mV/dec	*Chem. Eur. J.*, 2019, 25, 8579
Ru@CN	126 mV	--	*Energy Environ. Sci.*, 2018, 11, 800-806.
Ru@NiCoP	49 mV	49 mV/dec	*Chem. Commun.*, 2017, 53, 13153-13156.
Ru/SiNW-42.9	200 mV	81 mV/dec	*Electrochem. Commun.*, 2015, 52, 29-33.
1D-RuO_2-CNx	93 mV	40 mV/dec	*ACS Appl. Mater. Inter.*, 2016, 8, 28678.
Pd@Ru(2.6)	102 mV	83 mV/dec	*CrystEngComm.*, 2018, 20, 4230-4236

Table S2. Comparison of the electrocatalytic activity of RuS_2, Ru/RuS_2 and N-Ru/RuS_2.

Catalysts	Overpotential at the 10 mA/cm^2	Tafel slope (mV/dec)	C_{dl} (mF/cm^2)	TOF at −200 mV vs. RHE

RuS_2	276 mV	125	16	$0.107\ s^{-1}$
RuS_2/Ru	177 mV	74	32	$0.438\ s^{-1}$
N-RuS_2/Ru	120 mV	53	41	$2.115\ s^{-1}$