Electronic Supplementary Information for

Bimetallic mesoporous RhRu film for electrocatalytic nitrogen reduction to ammonia

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Experimental section

Materials: Potassium hexachlororhodate (K_3RhCl_6), ruthenium(III) chloride ($RuCl_3$), tetrahydrofuran (THF), sodium hydroxide (≥98%, NaOH), sodium citrate dihydrate (≥99%, $C_6H_5Na_3O_7 \cdot 2H_2O$), sodium salicylate (≥99.5%, $C_8H_5NaO_3$), dioctadecyl dimethyl ammonium chloride (DODAC), sodium sulfate (99%, Na_2SO_4), and sodium hypochlorite solution (6.0-14.0%, NaClO) were purchased from Aladdin. Polyethylene oxide–polypropylene oxide–polyethylene oxide (P123), Pluronic F127, ammonium chloride (NH_4Cl) and sodium nitroferricyanide dihydrate ($C_5FeN_6Na_2O \cdot 2H_2O$) were purchased from MACKLIN Inc. Hydrazine monohydrate ($N_2H_4 \cdot H_2O$) and hydrochloric acid (37%, HCl) were bought from Beijing Chemical Reagent. Poly(ethylene oxide)-*b*-poly(methyl methacrylate) (PEO_{10500}-*b*-$PMMA_{18000}$) block copolymer and polystyrene-block-polyethylene oxide (PS-*b*-PEO) block copolymer was purchased from Polymer Source. Inc. Deionized water, Nafion 211 membrane, N_2 gas (99.999%) and Ar gas (99.99%) were used for the electrochemical measurements. The $^{15}N_2$ was purchased from WUHAN NEWRADAR SPECIAL GAS Co., LTD.

Preparation of mRhRu/NF: Mesoporous RhRu film was electrodeposited on Ni foam in the electrolyte contained PEO_{10500}-*b*-$PMMA_{18000}$ micelles as a pore-directing agent. Electrodeposition was conducted in a conventional three-electrode cell using a CHI 660E electrochemical analyzer. The electrode used for electrochemical deposition consists of foam nickel (1 × 1.5 cm), Pt wire and Ag/AgCl as working electrode, counter electrode and reference electrode. Electrolyte was prepared as follows. In typical, 5 mg of PEO-*b*-PMMA was first dissolved in 0.5 mL of THF by ultrasound. Then, 3.5 mL of ultrapure water, 0.2 mL of K_3RhCl_6 (40 mM), 0.3 mL $RuCl_3$ (40 mM) were sequentially added to the above solution under sonication for 10 min. Chronoamperometric measurement operated at -0.6 V for 4000 s. The obtained sample was washed several times with ethanol and water, and then immersed in the ethanol overnight. Finally, the sample was dried in the desiccator.

Characterizations: The morphology of the RhRu film was assessed by scanning electron microscope (SEM, ZEISS SUPRA 55) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2010 instrument equipped with an energy dispersive X-ray spectroscopy (EDX) system. X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert Pro MPD with Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA for the crystal information of samples. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source. The superconducting-magnet nuclear magnetic resonance (NMR) spectrometer (Bruker AVANCE III HD 500 MHz) was used to test ^1H NMR spectra. The amount of the elements in samples was investigated by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Nitrogen temperature-programmed desorption (N_2-TPD) measurement was obtained by Micromeritics Autochem 2910. The absorbance datas of spectrophotometer were measured on TU-1900 ultraviolet-visible (UV–vis) spectrophotometer.

Electrochemical investigations: Electrocatalytic nitrogen reduction tests were performed with a CHI 660E electrochemical analyzer using a standard three-electrode system using mRhRu/NF as working electrode, and carbon rod and saturated Ag/AgCl were used as the counter electrode and reference electrode in a H-type cell separated by a Nafion 211 membrane. First of all, 40 mL of electrolyte (0.1 M Na_2SO_4, pH = 7.0) was added to the cathode and anode sections of the electrolytic cell, simultaneously, the electrolyte in the cathode cell was purged with ultra-highpurity N_2 gas for 30 min. Next, the chronoamperometric measurements were conducted at different potentials for 2 h in N_2-saturated 0.1 M Na_2SO_4 solution (during the test, nitrogen was continuously bubbled in in the cathode section).

Production determination: In order to determine the concentration of ammonium ion in the electrolyte after the test, the concentration-absorbance curve was obtained as the reference substance by the indophenol blue method.[1] In detail, 4 mL of electrolyte, 0.5 mL of colorant (0.32 M NaOH and 0.4 M $C_7H_5NaO_3$), 50 μL of oxidant and 50 μL of catalyst solution (1 wt% $C_5FeN_6Na_2O$) were mixed in the centrifuge tube, then the mixture was placed for an hour in the dark. The oxidant is composed of 300 mg NaOH, 0.325 mL NaClO, and 9.675 mL of deionized water. The produced ammonia was estiamted by ultraviolet-visible (UV-vis) spectrophotometer at a wavelength of 685 nm. Calculations of NH_3 yield and Faradaic efficiency: NH_3 yield was calculated using the following equation:

$$r_{\mathrm{NH3}} = (c_{\mathrm{NH3}} \times V)/t \times m_{\mathrm{cat.}} \qquad (1)$$

FE was calculated according to following equation:

$$\mathrm{FE} = 3\mathrm{F} \times n_{\mathrm{NH3}}/Q \qquad (2)$$

where c_{NH3} is the mass concentration of produced NH_3, V is the volume of the cathodic reaction electrolyte, t is the potential applied time, $m_{\mathrm{cat.}}$ is the loaded quality of sample, F is the Faraday constant, $\mathrm{n}_{\mathrm{NH3}}$ is the mole of produced NH_3 and Q is the total the quantity of applied electricity during the whole reaction process.

The by-production of hydrazine in the electrolyte solution was estimated by the Watt and Chrisp method.[2] The colorant is composed of 5.99 g *p*-(dimethylamino) benzaldehyde, 30 mL concentrated HCl (12 M) and 300 mL ethanol. N_2H_4 was measured by mixing 5 mL electrolyte and 5 mL colorant for 10 min at room temperature. The concentration-absorbance curve was obtained by taking the known concentration of hydrazine solution as the reference substance.

$^{15}N_2$ Isotope Labeling Experiments: The isotopic labeling experiments were performed to clarify the source of NH_3 using $^{15}N_2$ as the feed gas. The $^{15}N_2$ gas was purified using 3 M H_2SO_4 solution before flowing into the electrochemical chamber. After ^{15}NRR measurement at -0.05 V for 12 h in 0.1 M Na_2SO_4, the obtained electrolyte was freeze-dried to a solid powder, which was dissolved in 3 mL of dilute sulfuric acid solution. The $^{15}NH_4^+$ was determined by ^{1}H NMR (600 MHz). Similarly, the amount of $^{14}NH_4^+$ was estimated using $^{14}N_2$ as the feed gas.

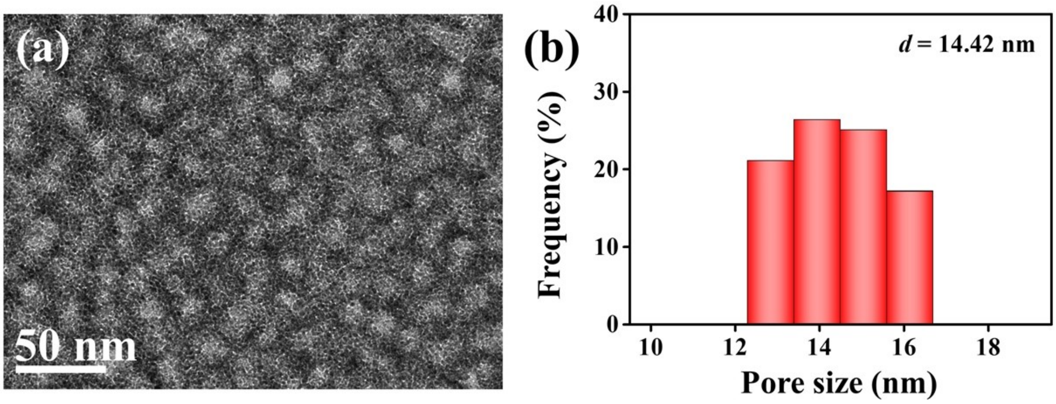
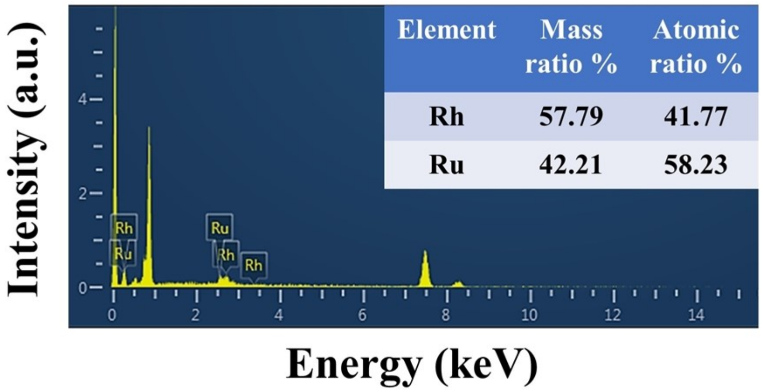


Fig. S1 (a) TEM image and (b) corresponding pore size distribution of the mRhRu film.



Element	Mass ratio %	Atomic ratio %
Rh	57.79	41.77
Ru	42.21	58.23

Fig. S2 The EDX spectrum of the mRhRu/NF and corresponding mass and atomic ratios.

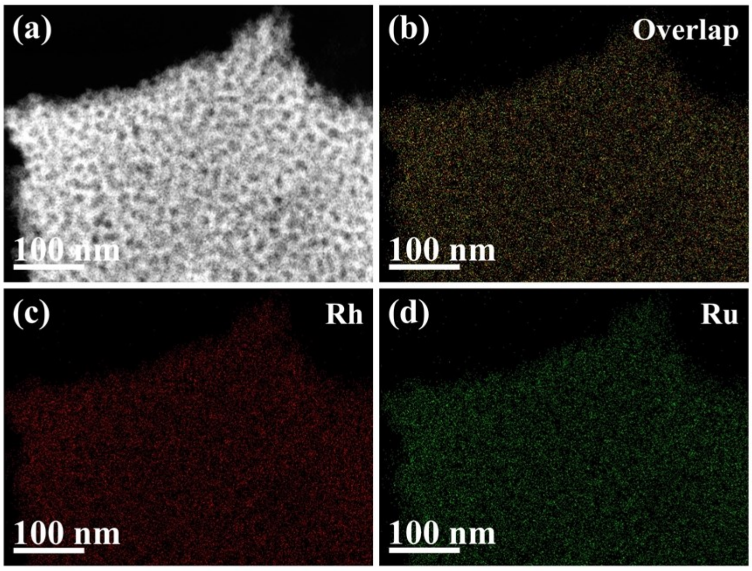


Fig. S3 (a) HAADF-STEM image and (b-d) EDX elemental mapping images of the mRhRu flim.

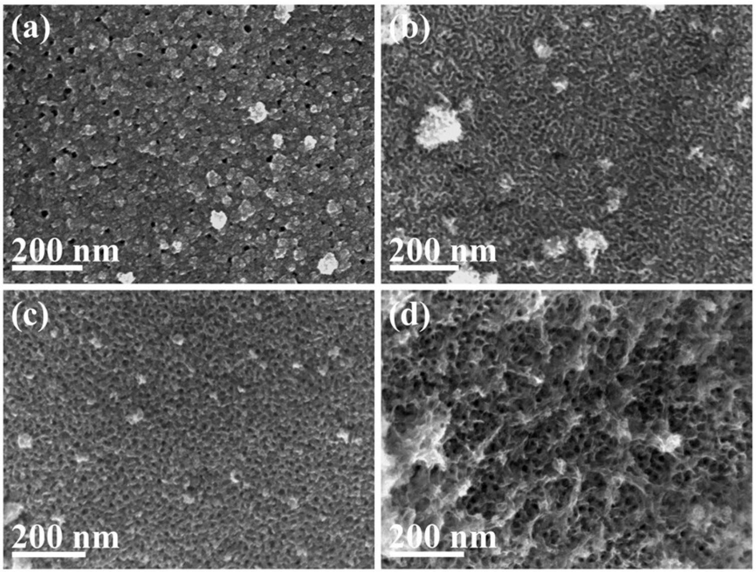


Fig. S4 SEM images of samples obtained from different molar concentrations of metallic precursors: (a) 5:0, (b) 4:1, (b) 1:4, and (d) 0:5.

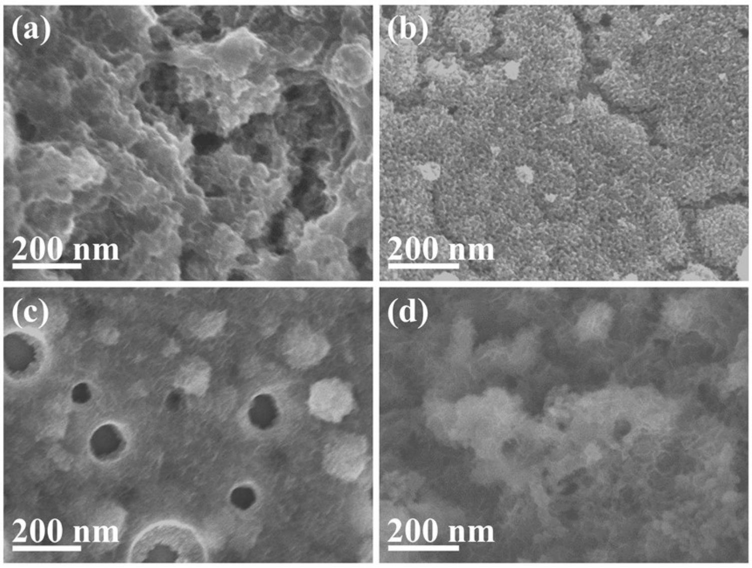


Fig. S5 SEM images of the mRhRu/NF prepared with (a) DODAC, (b) F127, (c) P123, and (d) PS-*b*-PEO.

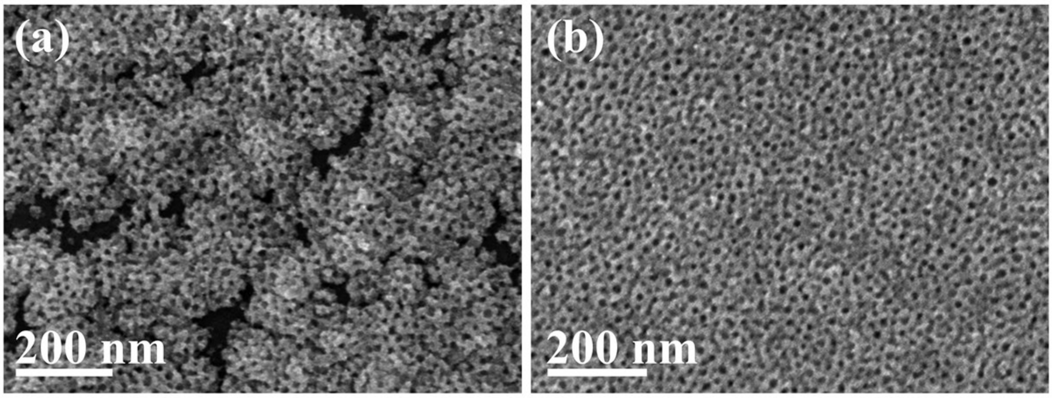


Fig. S6 SEM images of the mRhRu film prepared on (a) carbon paper and (b) titanium sheet.

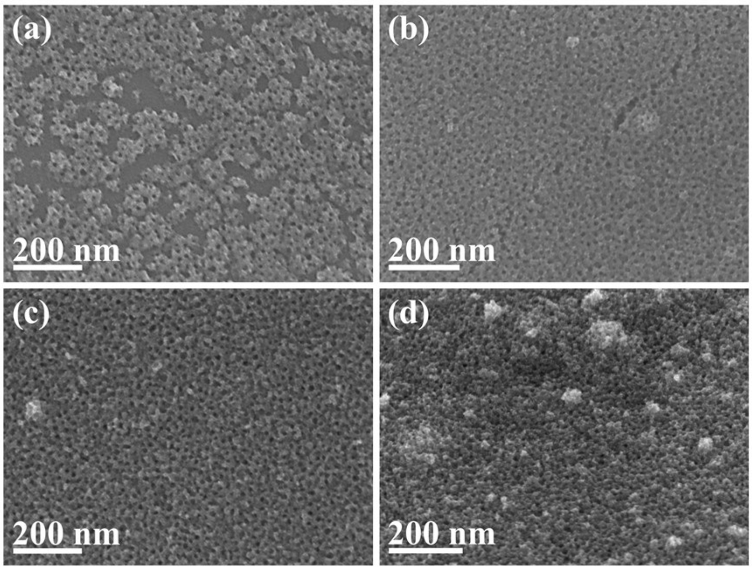


Fig. S7 SEM images of samples at different electrodeposition times: (a) 500 s, (b) 1000 s, (c) 2000 s, and (d) 6000 s.

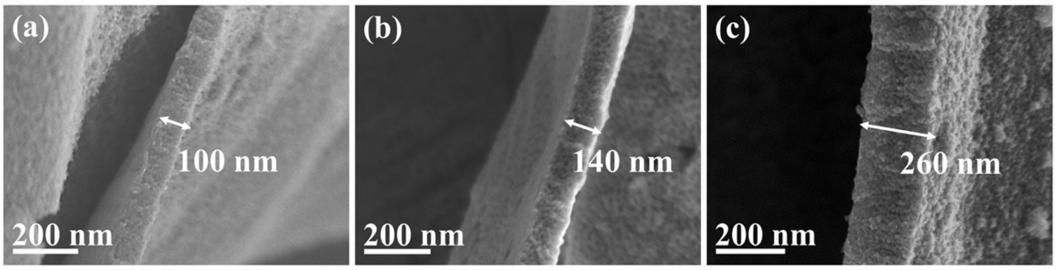


Fig. S8 Cross-section SEM images of typical samples at different electrodeposition times: (a) 1000 s, (b) 2000 s, and (c) 6000 s.

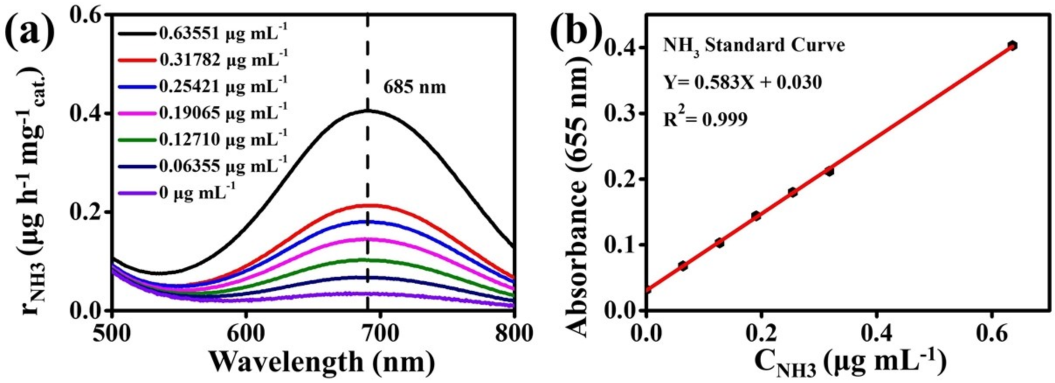


Fig. S9 (a) UV-vis spectra at various ammonia concentrations after being incubated for 1 h at room temperature, and (b) the corresponding calibration curve.

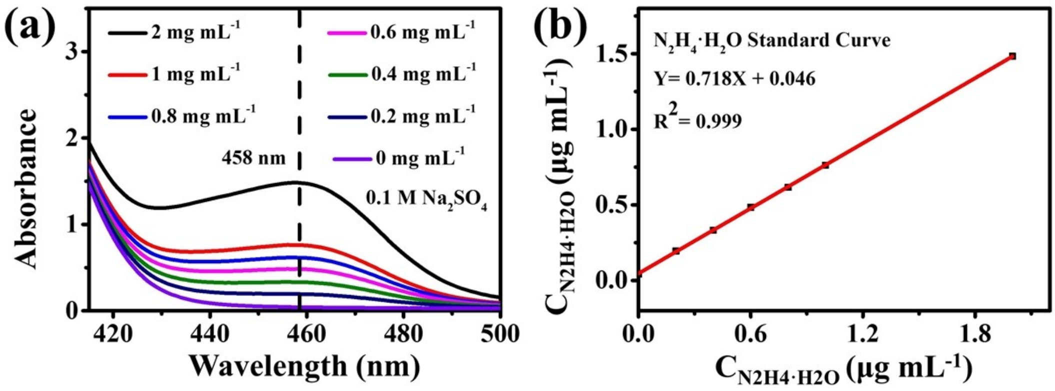


Fig. S10 (a) UV-vis spectra at various hydrazine concentrations after being incubated for 15 min under ambient conditions, and (b) the corresponding calibration curve.

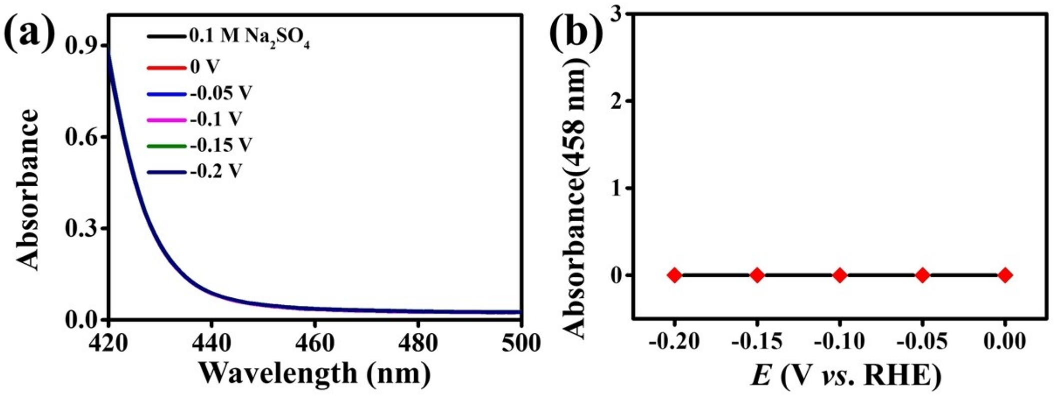


Fig. S11 UV-vis spectra of the electrolytes after 2-h electrolysis at different potentials, and (b) the $N_2H_4 \cdot H_2O$ concentration of the electrolyte.

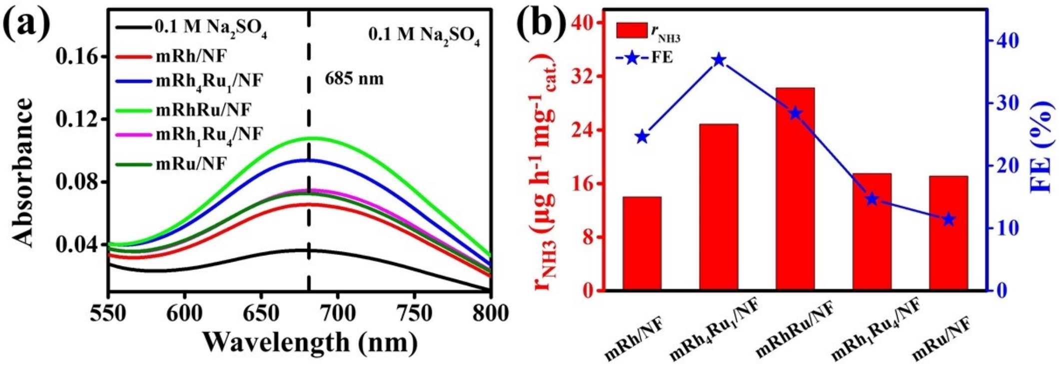


Fig. 12 UV-vis absorption spectra of the electrolytes after electrolysis for different samples at -0.05 V and (b) correndonding NH_3 production rates and Faradaic efficiencies.

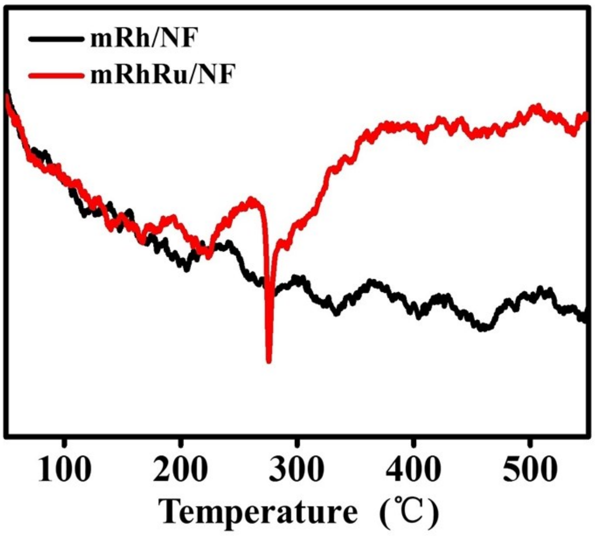


Fig. 13 N_2-TPD patterns of mRhRu/NF and mRh/NF.

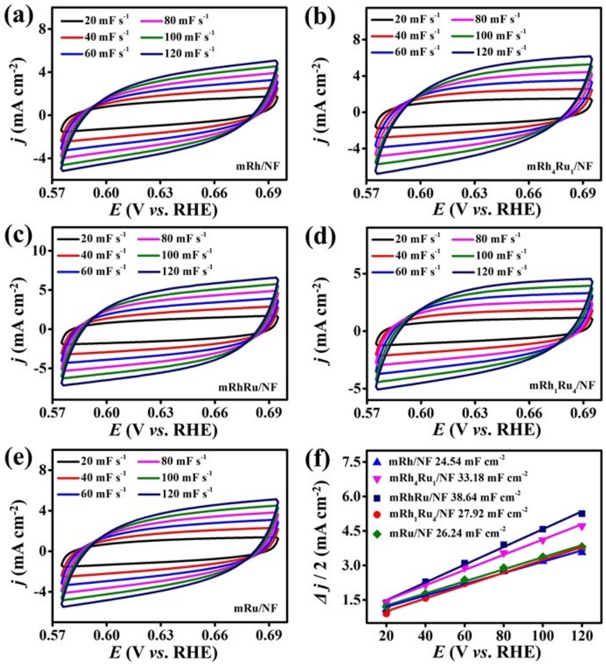


Fig. 14 (a-c) Cyclic voltammetry curves of mRh/NF, mRh_4Ru_1/NF, mRhRu/NF, mRh_1Ru_4/NF and mRu/NF in the range of 0.575 and 0.695 V. (d) Capacitive current densities at 0.635 V derived from CVs against scan rates for different samples.

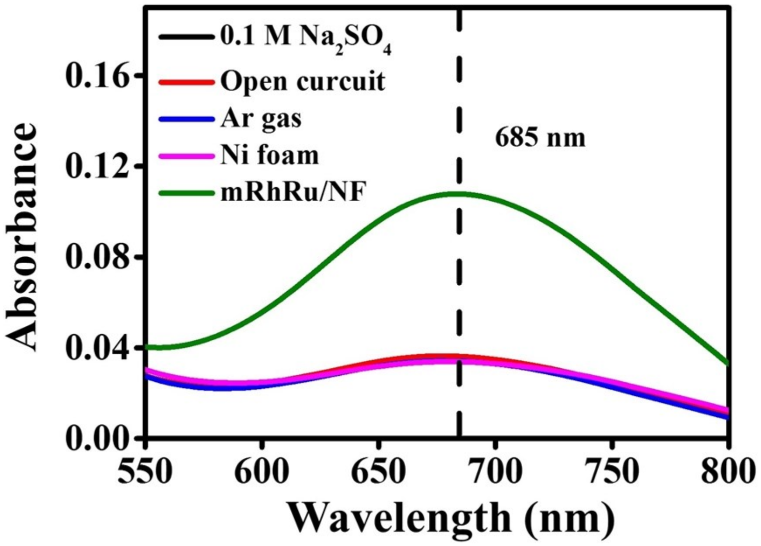


Fig. S15 UV-vis absorption spectra of the electrolytes under different conditions.

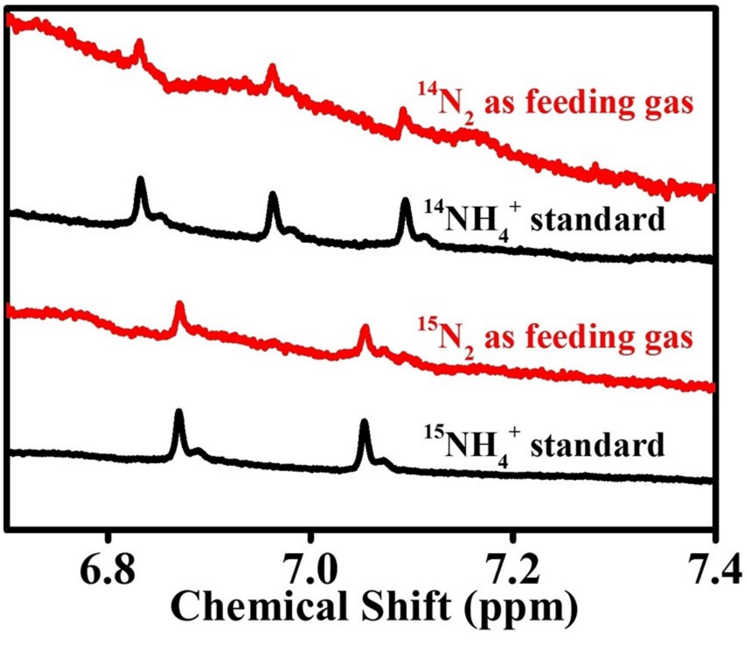


Fig. S16 ^{1}H-NMR spectra of standard samples of $^{14}NH_4^+$, $^{15}NH_4^+$, and the electrolyte produced from the NRR reaction using $^{14}N_2$ and $^{15}N_2$ as the N_2 source.

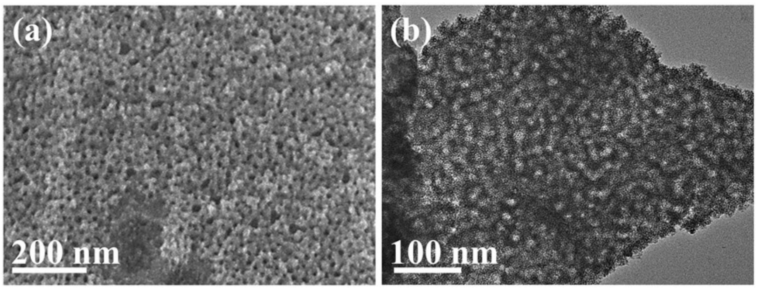


Fig. S17 SEM and TEM images of RhRu film after stability test.

Table S1 The mass percentage of Rh and Ru in different samples.

Samples	**Rh (wt%)**	**Ru (wt%)**
mRh_4Ru_1/NF	78.37	21.63
mRh_1Ru_4/NF	23.03	76.97

Table S2 The performance comparisons of the mRhRu/NF with the recently reported catalysts under ambient conditions.

Catalyst	Electrolyte	NH_3 yield	FE (%)	Ref.
mRhRu/NF	**0.1 M Na_2SO_4**	**30.28 μg h^{-1} $mg^{-1}_{cat.}$**	**28.33**	**This work**
mAu_3Rh/NF	0.1 M Na_2SO_4	26.29 μg h^{-1} mg-$^{1}_{cat.}$	23.84	3
Cr_2O_3 nanofiber	0.1 M Na_2SO_4	28.13 μg h^{-1} mg^{-1}_{cat}	8.56	4
MBN	0.1 M Na_2SO_4	18.2 μg h^{-1} $mg^{-1}_{cat.}$	5.5	5
Ag_3Cu BPNs	0.1 M Na_2SO_4	24.59 μg h^{-1} $mg^{-1}_{cat.}$	13.28	6
Pd NPs	0.1 M Na_2SO_4	24.12 μg h^{-1} $mg^{-1}_{cat.}$	9.49	7
BNS	0.1 M Na_2SO_4	13.22 μg h^{-1} $mg^{-1}_{cat.}$	4.04	8
MoS_2 nanoflowers	0.1 M Na_2SO_4	29.28 μg h^{-1} $mg^{-1}_{cat.}$	8.34	9
Pd-Ag-S porous nanosponges	0.1 M Na_2SO_4	9.73 μg h^{-1} $mg^{-1}_{cat.}$	18.41	10
nPd/NF	0.1 M Na_2SO_4	18.27 μg h^{-1} $mg^{-1}_{cat.}$	10.36	11
Porous bromide derived Ag film	0.1 M Na_2SO_4	1.27 μg h^{-1} cm^{-2}	7.36	12

References

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