

Electronic Supplementary Information *for*

**Metal-metalloid alloys: mesoporous Rh-Te films for electrocatalytic nitrogen
fixation**

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Experimental section

Materials and chemicals

Potassium hexachlororhodate (K_3RhCl_6), sodium tellurite (Na_2TeO_3), tetrahydrofuran (THF), ethanol, hydrochloric acid (37%, HCl), sodium hydroxide (NaOH), sodium salicylate ($C_7H_5NaO_3$) and sodium sulfate (99%, Na_2SO_4), ammonium chloride (NH_4Cl), sodium hypochlorite solution (6.0-14.0%, NaClO) and sodium nitroferricyanide dihydrate ($C_5FeN_6Na_2O \cdot 2H_2O$, 99%) were ordered from Aladdin. Poly(ethylene oxide)-*b*-poly(methyl methacrylate) (PEO-*b*-PMMA) and polystyreneblock-polyethylene oxide (PS-*b*-PEO) was produced by Polymer Source Inc.

Synthesis of the mRhTe/CP

The carbon paper (CP) was first immersed in 3 M HCl for 15 min, followed by cleaning with water. Then, 5 mg of PEO₁₀₅₀₀-*b*-PMMA₁₈₀₀₀ was dissolved in 0.5 mL of THF, followed by homogeneously mixing with 0.5 mL of 40 mM K_3RhCl_6 , 0.5 mL of 5 mM Na_2TeO_3 , and 3.5 mL of H_2O . Electrodeposition was performed by electrochemical workstation (CHI 660E) in a three-electrode cell at -0.2 V for 3200 s, in which Pt wire, clean CP and Ag/AgCl were employed as counter electrode, working electrode and reference electrode. Finally, the sample was cleaned with ultra-pure water and ethanol, and soaked in ethanol overnight.

Characterization

Scanning electron microscope (SEM, ZEISS SUPRA 55) and transmission electron microscopy (TEM, JEM-2100) equipped with energy dispersive X-ray spectroscopy (EDX) were conducted to investigate the morphology and microstructure of samples. X-ray diffraction (XRD, PANalytical X'Pert Pro MPD) and X-ray photoelectron spectroscopy (XPS, ESCALAB MK II) were performed to study the crystal and electronic structures of samples.

Electrochemical measurements

The NRR tests were performed under ambient conditions in a standard three-electrode cell using obtained samples, Ag/AgCl electrode and carbon rod as working electrode, reference electrode and counter electrode, respectively. Prior to each NRR test, electrolytes (0.1 M Na₂SO₄) were purged with nitrogen for 0.5 h. Then the *i-t* tests were carried out for 2 h with continual flow of N₂. All linear sweep voltammetry (LSV) tests were performed at a sweep rate of 5 mV s⁻¹ with *iR* compensation and all potentials were converted to reversible hydrogen electrode (RHE) potential. Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range of 100 kHz to 0.1 Hz.

Product detection

To determine the NH₃ production, the indophenol blue method was utilized.¹ For preparing the colorant, C₇H₅NaO₃ (1.28 g) and NaOH (0.256 g) were dissolved in water (20 mL). The oxidation solution was prepared by dissolving NaOH (0.3 g) in NaClO (0.325 mL) and deionized water (10 mL), while the color development solution was synthesized by dissolving C₅FeN₆Na₂O (0.1 g) in water (10 mL). Then, 4 mL of electrolytes were mixed with 500 μL of colorant, 50 μL of oxidation solution, and 50 μL of color development solution in the dark for an hour, which were measured by ultraviolet-visible (UV-vis) at room temperature. The NH₃ yield was then calculated using standard NH₄Cl solutions and concentration-absorbance curves. The NH₃ yield (r_{NH_3}) and Faraday efficiency (FE) were determined using the following equations, in which the c_{NH_3} is the mass concentration of produced NH₃, the V is the volume of the cathodic reaction electrolyte, t is the time of applied potential, m_{cat} is the loaded mass, F is the Faraday constant and Q is the total applied charge.

$$r_{\text{NH}_3} = (c_{\text{NH}_3} \times V) / (t \times m) \quad (1)$$

$$\text{FE} = 3F \times c_{\text{NH}_3} \times V / (17 \times Q) \quad (2)$$

By-product of hydrazine was also measured by the Watt and Chrisp method.² Typically, 5 mL of color reagent and 5 mL of electrolyte were mixed, in which the color reagent contained p-(dimethylamino) benzaldehyde (5.99 g), HCl (30 mL) and ethanol (300 mL). After maintaining for 10 min, the resultant solutions were conducted by UV–vis spectrophotometry to measure absorbance. The absorbance-concentration curve was first obtained from standard hydrazine hydrate solution with known concentration, and the by-product hydrazine content was calculated by means of the concentration-absorbance curve.

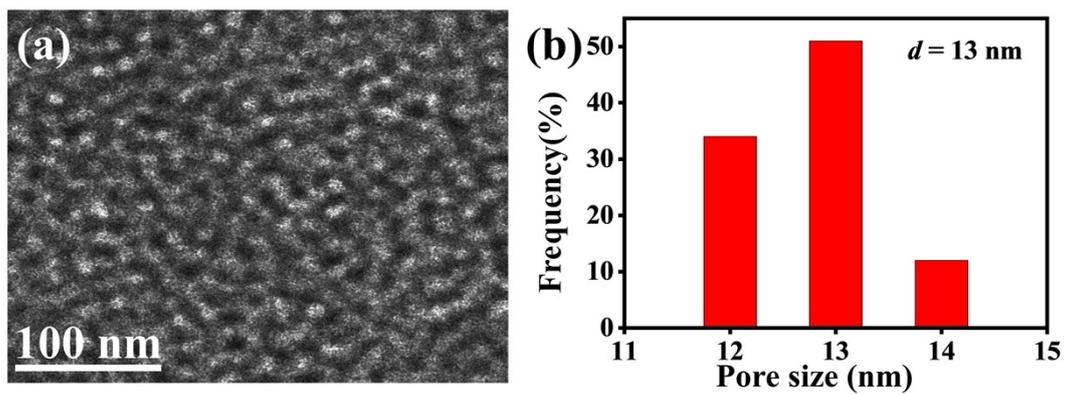


Fig. S1 TEM image and (b) corresponding pore size distribution of the mRhTe/CP.

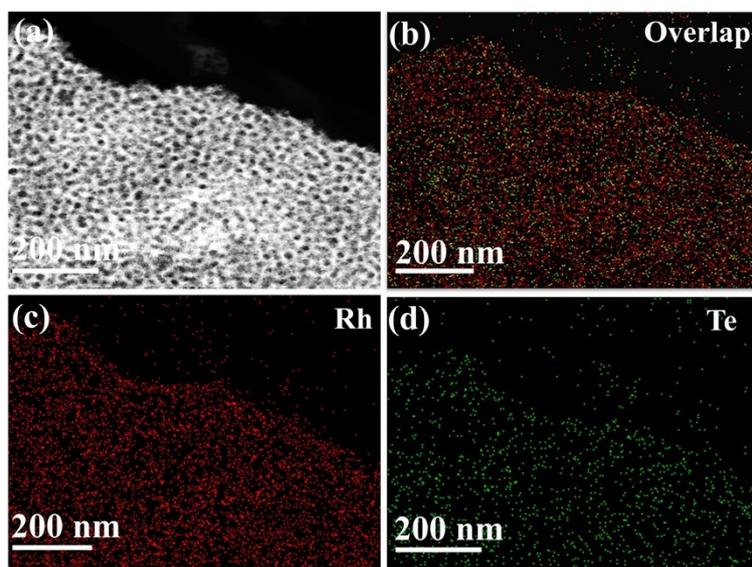


Fig. S2 (a) HAADF-STEM image and (b-d) EDX elemental mapping images of the mRhTe films.

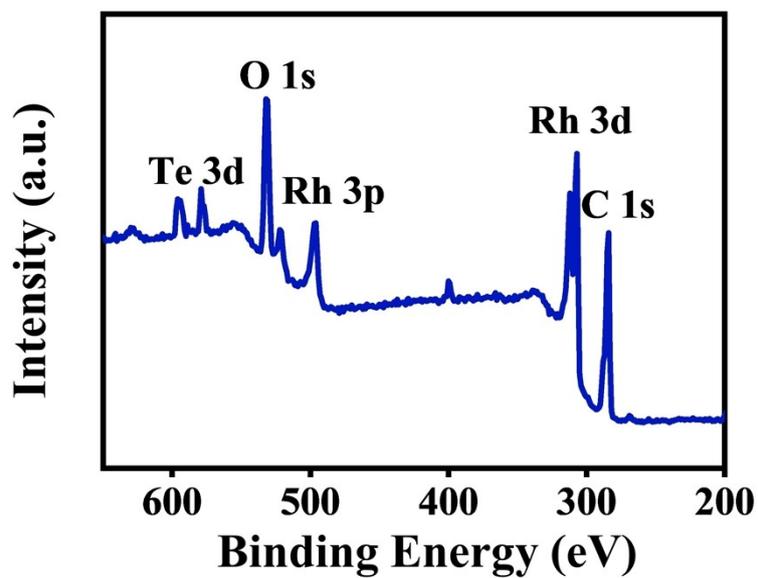


Fig. S3 XPS survey spectrum of mRhTe/CP

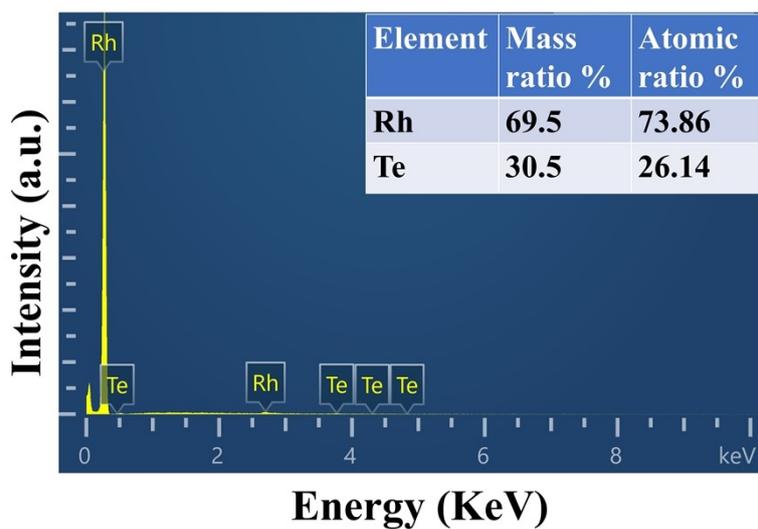


Fig. S4 EDX spectrum of the mRhTe/CP and corresponding element amount.

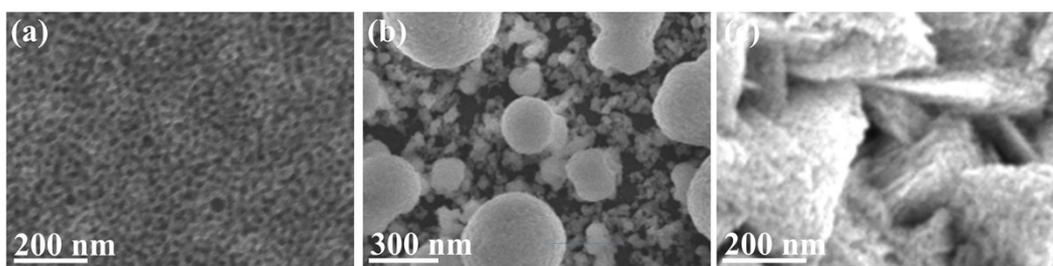


Fig. S5 SEM images of samples obtained from different molar concentrations of metallic precursors:

(a) 1:0, (b) 1:1 and (c) 0:1.

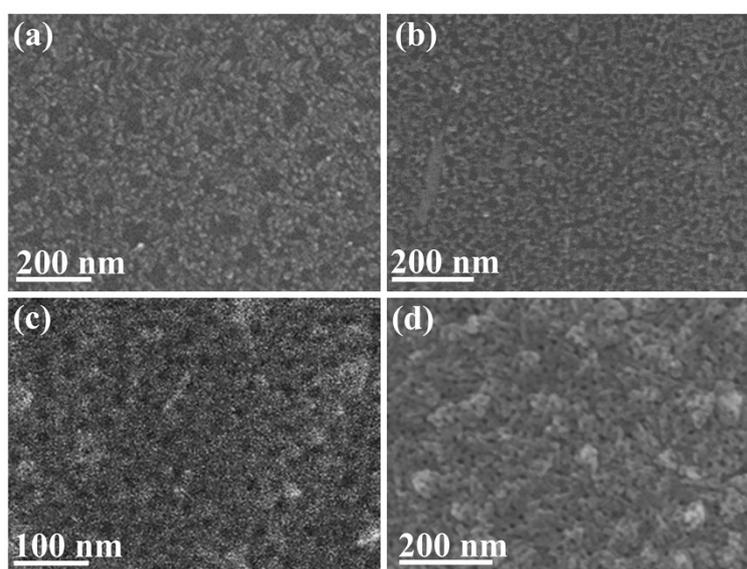


Fig. S6 SEM images of typical samples at different electrodeposition times for (a) 1000 s, (b) 2000 s, (c) 3000 s, and (d) 4000 s.

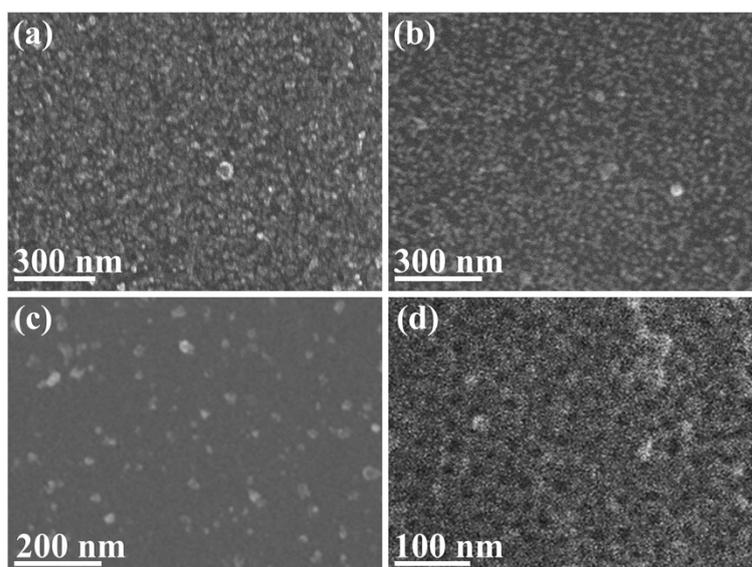


Fig. S7 SEM images of the mRhTe/CP prepared by changing surfactant with (a) PS-b-PEO, (b) F127, (c) P123, and (d) PEO-b-PMMA.

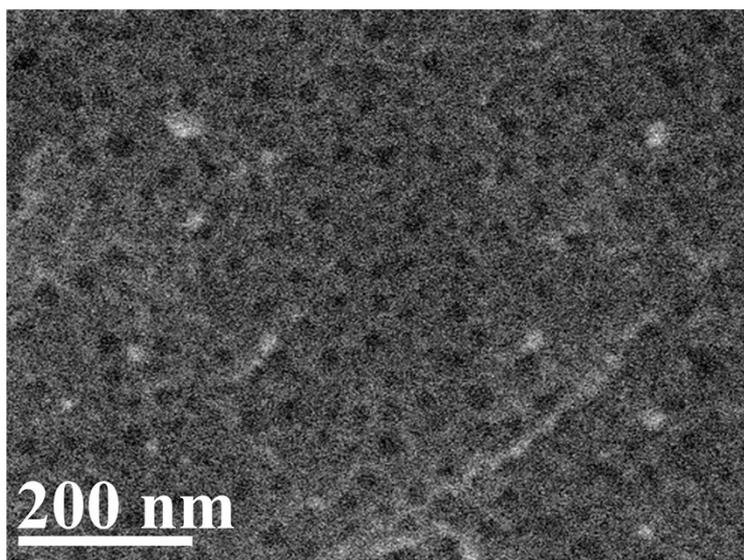


Fig. S8 SEM image of mRhTe/NF.

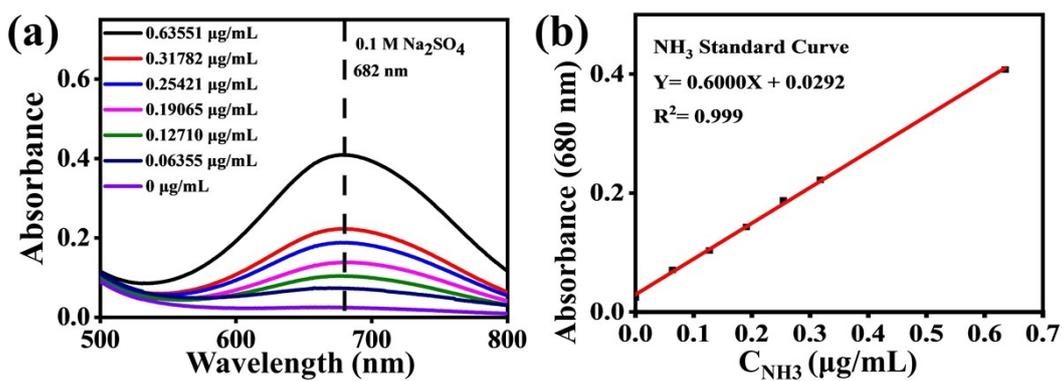


Fig. S9 (a) UV-vis absorption spectra of various NH_4^+ concentrations with the color reagent for 1 h at room temperature. (b) Calibration curve used to estimate the concentrations of NH_3 .

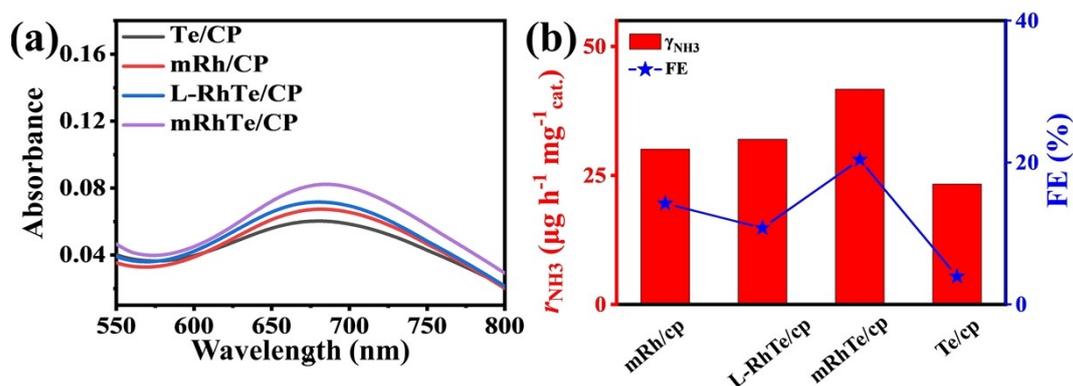


Fig. S10 (a) UV-vis absorption spectra of RhTe/CP obtained by electrodeposition of potassium hexachlororhodate and sodium tellurite solutions with different molar concentrations, and (b) NH_3 yield and Faraday efficiency at 0.1 V.

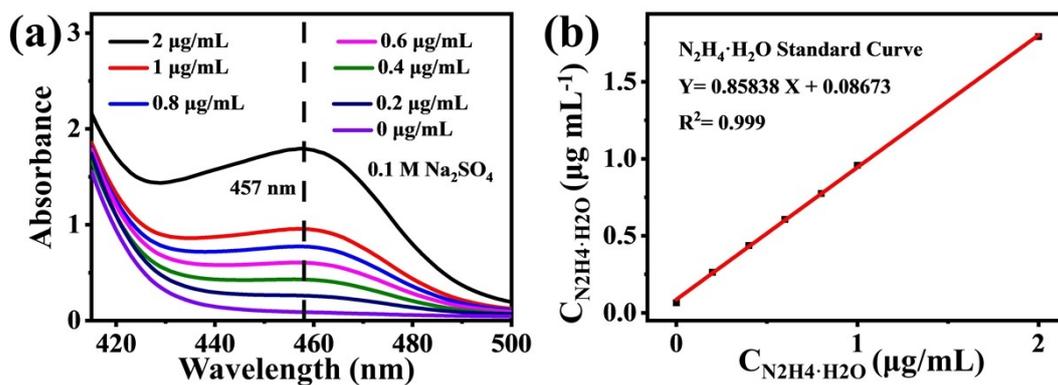


Fig. S11 (a) UV-Vis absorption spectra of different concentrations of hydration solution were measured after incubated for 15 min at 25 °C. (b) Calibration curve used for estimation of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentration.

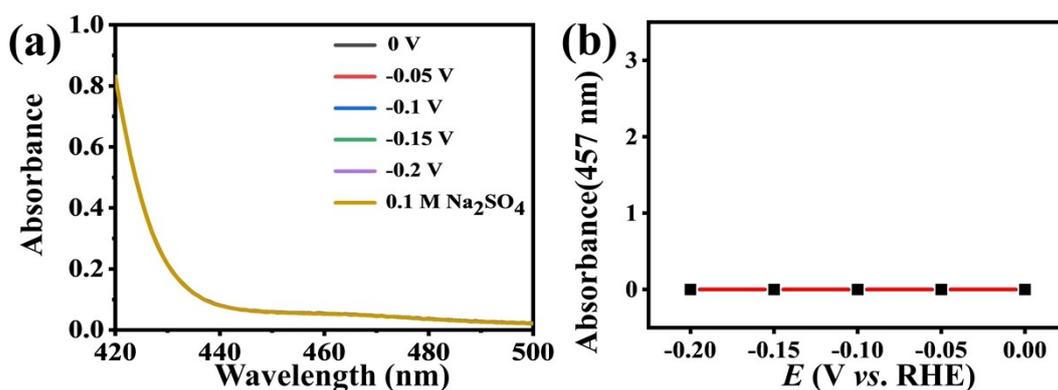


Fig. S12 UV-vis absorption spectra of the electrolytes after 2 h electrolysis in nitrogen at different potentials, and (b) the N_2H_4 concentration of the electrolyte.

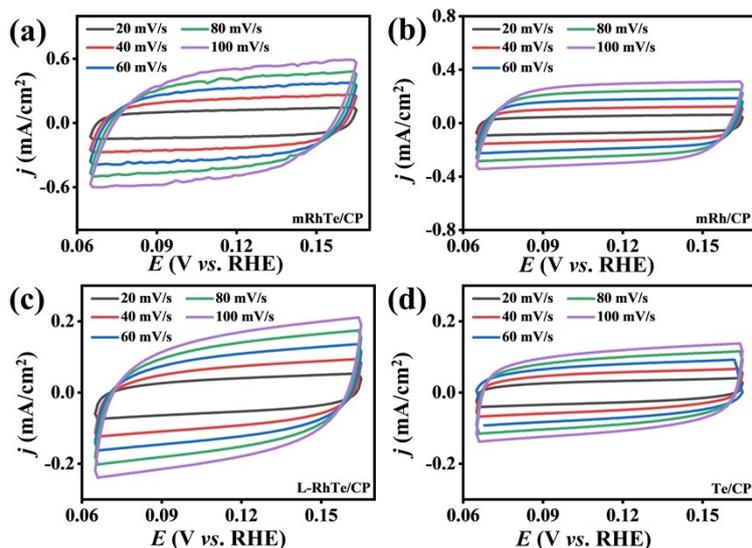


Fig. S13 CV curves of samples in the range of 0.06 to 0.16 V.

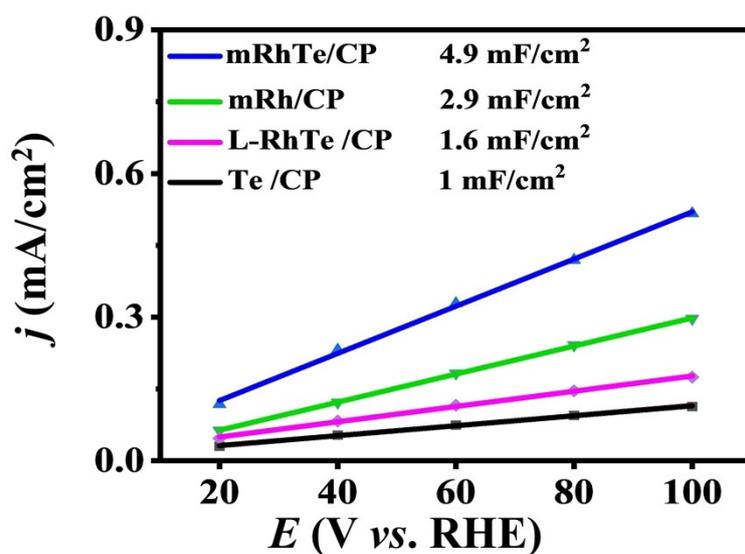


Fig. S14 Capacitive current densities at 0.745 V derived from CVs against scan rates for different samples.

Table S1 The comparison of NRR performance for mRhTe/CP with recently reported catalysts under the ambient conditions.

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
mRhTe/CP	0.1 M Na₂SO₄	41.7 μg h⁻¹ mg⁻¹_{cat.}	20.4	This work
S-mAu film	0.1 M Na ₂ SO ₄	22.7 μg h ⁻¹ cm ⁻²	17.2	3
mPd-PdO/NF	0.1 M Na ₂ SO ₄	24.8 μg h ⁻¹ mg ⁻¹ _{cat.}	16.64	4
pAu/NF	0.1 M Na ₂ SO ₄	9.42 μg h ⁻¹ cm ⁻²	13.36	5
PdCuIr-LS	0.1 M Na ₂ SO ₄	13.43 μg h ⁻¹ mg ⁻¹ _{cat.}	5.29	6
mAu ₃ Rh/NF	0.1 M Na ₂ SO ₄	26.29 μg h ⁻¹ mg ⁻¹ _{cat.}	23.84	7
nPdB/NF	0.1 M Na ₂ SO ₄	29.0 μg h ⁻¹ mg ⁻¹ _{Cat.}	17.9	8
BNS	0.1 M Na ₂ SO ₄	13.22 μg h ⁻¹ mg ⁻¹ _{Cat.}	4.04	9
nPd/NF	0.1 M Na ₂ SO ₄	18.27 μg h ⁻¹ mg ⁻¹ _{cat}	10.36	10
dendritic Cu	0.1 M HCl	25.63 μg h ⁻¹ mg ⁻¹ _{Cat.}	15.12	11
Bi nanodendrites	0.1 M HCl	25.86 μg h ⁻¹ mg ⁻¹ _{cat.}	10.8	12

References

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