Electronic Supplementary Information

Experimental section

Materials: Stannous chloride ($SnCl_2 \cdot 2H_2O$) was abtained from Chengdu jinshan Chemical Reagent Factory, China. Sodium nitroferricyanide dihydrate ($C_5FeN_6Na_2O \cdot 2H_2O$), salicylic acid ($C_7H_6O_3$), sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), and para-(dimethylamino) benzaldehyde (*p*-$C_9H_{11}NO$) were purchased from Aladdin Ltd, Shanghai, China. Dipotassium hydrogen phosphate (K_2HPO_4) was purchased from Tianjin ruijinte chemical Co., Ltd. Ethyl alcohol (C_2H_5OH), Sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (KOH), sodium borohydride ($NaBH_4$), 1, 10-phenanthroline ($C_{12}H_8N_2 \bullet H_2O$), tin (Ⅱ) 2-ethylhexanoate ($C_{16}H_{30}O_4Sn$) and Potassium dihydrogen phosphateand (KH_2PO_4) were bought from Chengdu Kelong Chemical Reagent Factory, China. Ammonium chloride (NH_4Cl), hypochlorite solution (NaClO), hydrazine monohydrate ($N_2H_4 \cdot H_2O$) and Sn foil (99.99%) were purchased from Beijing Chemical Corp, China. High-purity Ar (99.999%) and N_2 (99.999%) were purchased from Chengdu Xuyuan Chemical Co., Ltd, China. All reagents were analytical reagent grade without further purification. The ultrapure water used throughout all experiments was purified through a Millipore system.

Synthesis Sn dendrite on Sn foil (Sn D/SF): Sn dendrite is prepared by a simple electrodeposition method.[1] First, SF was polised with sandpaper and cleaned by deionized water and ethanol, last 0.1 M HCl. Then, 1 M HCl aqueous solution including 0.05 M $SnCl_2$ was prepared. In the three-electrode electrochemical system, Sn foil (0.5 × 1 cm^2) was used as working electrolysis, saturated calomel electrode (SCE) and Pt foil were used as reference electrode and counter electrode respectively. The Sn dendrite was synthesised by constant potential at –2.0 V (V *vs*. SCE) for 20 s. After deposition, The Sn dendrite was cleaned with deionized water and baked in an oven at 50℃ for 1h.

Synthesis Sn nanoparticles (Sn NPs): In a typical synthesis process [2], 0.33 g of tin (Ⅱ) 2-ethylhexanoate and 0.1 g of 1, 10-phenanthroline were mixed in 60 mL anhydrous methanol solution. The solution was then mechanically stirred intensively for 2 h.Then, 0.2 g of sodium borohydride was added to the solution and the reaction continued for another 2 h at room temperature. After the reaction completed, the obtained products were centrifugally separated at 8000 r/min for 30min and rinsed several times with a large amount of absolute ethanol, and finally dried in vacuum at 60℃ for 4 h.

Preparation of Sn NPs/SF： 5 mg of Sn NPs and 20 μL of Nafion solution (5 wt%) was dispersed in 980 μL ethanol/water (1:1) solution follow by 20 min sonication to form a homogeneous ink. Finally, 30 μL ink was loaded on a piece of SF (0.5×1 cm^{-2}) and dried under ambient condition.

Characterization: X-ray diffraction (XRD) patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). Scanning electron microscopy (SEM) images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The structures of the samples were determined by Transmission electron microscopy (TEM) images on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. X-ray photoelectron spectroscopy graphs were obtained from a Thermo Scientific K-Alpha+. The absorbance data of spectrophotometer were measured on UV-Vis spectrophotometer.

Electrochemical measurement: Electrochemical NRR measurements were performed in a two-compartment cell separated by Nafion 117 membrane using a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai). Nafion 117 membrane was ultrasonicated in 1 M H_2SO_4, and deionized water at 80 ˚C for 1 h, respectively. Then it was thoroughly rinsed in deionized water several times. The electrochemical experiments were carried out with a three-electrode H-type electrolytic cell using

graphite rod as the counter electrode and Ag/AgCl/saturated KCl as the reference electrode. The working electrode was Sn D/SF of 0.5 × 1 cm^2 (Sn dendrite loading: 0.30 mg cm^{-2}) The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E(RHE) = E(Ag/AgCl) + 0.059 × pH + 0.197 V and the presented current density was normalized to the geometric surface area. Before all NRR test, Sn D/SF electrodes were pretreated by cyclic voltammograms (CVs) range from –0.24 to –0.60 V for cycling 30 times in Ar-.saturated 0.1 M PBS electrolyte until the oxide layer reduction currents fully disappeared. The double layer capacitance is measured by cyclic voltammetry. A potential range from 0.4 to 0.5V *vs*. RHE is chosen for the CV test under different scan rates of 20, 60, 100, 140, 180, 220 mV s^{-1} without faradic current. The differences of positive and negative current density at the potential-range center were plotted *vs*. scan rates, the slope of curves were double capacitance. The chrono-amperometry tests were conducted in N_2-saturated 0.1 M PBS solution (the PBS electrolyte was purged with N_2 for 30 min before the measurement).

Determination of NH_3: Concentration of produced NH_3 was spectrophotometrically determined by the indophenol blue method.[3] Typically, 2 mL electrolyte was taken from the cathodic chamber, and then 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. Subsequently, 1 mL of 0.05 M NaClO and 0.2 mL of 1% $C_5FeN_6Na_2O{\cdot}2H_2O$ were add into the above solution. After standing at room temperature for 2 h, UV-Vis absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using the standard NH_4Cl solution with NH_3 concentrations of 0.0, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 μg mL^{-1} in 0.1 M PBS. The fitting curve (y = 0.364x + 0.057, R^2 = 0.999) shows good linear relation of absorbance value with NH_3 concentration by three times independent calibrations.

Determination of N_2H_4: N_2H_4 presented in the electrolyte was estimated by the method of Watt and Chrisp.[4] The mixed solution of 5.99 g *p*-$C_9H_{11}NO$, 30 mL HCl and 300 mL ethanol was used as a color reagent. Calibration curve was plotted as

follow: firstly, preparing a series of reference solutions; secondly, adding 5 mL above prepared color reagent and stirring 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 455 nm, and the yields of N_2H_4 were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using $N_2H_4 \cdot H_2O$ solutions of known concentration as standards, and the fitting curve shows good linear relation of absorbance with $N_2H_4 \cdot H_2O$ concentration ($y = 0.75x + 0.051$, $R^2 = 0.999$) by three times independent calibrations.

Calculations of NH_3 yield and Faradaic efficiency (FE): The FE for N_2 reduction was defined as the amount of electric charge used for synthesizing NH_3 divided the total charge passed through the electrodes during the electrolysis. The total amount of NH_3 produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH_3 molecule, the FE could be calculated as follows:

$$FE = 3 \times F \times [NH_3] \times V / (17 \times Q)$$

The rate of NH_3 yield (V_{NH3}) was calculated using the following equation:

$$V_{NH3} = [NH_3] \times V / (S_{cat.} \times t)$$

The amount of NH_3 was calculated as follows:

$$m_{NH3} = [NH_3] \times V$$

Where F is the Faraday constant (96500 C mol^{-1}); $[NH_3]$ is the measured NH_3 concentration; V is the volume of the electrolyte in the cathodic chamber (35 ml); Q is the total quantity of applied electricity; $S_{cat.}$ is area of catalyst on Sn foil and t is the reduction time (7200 s).

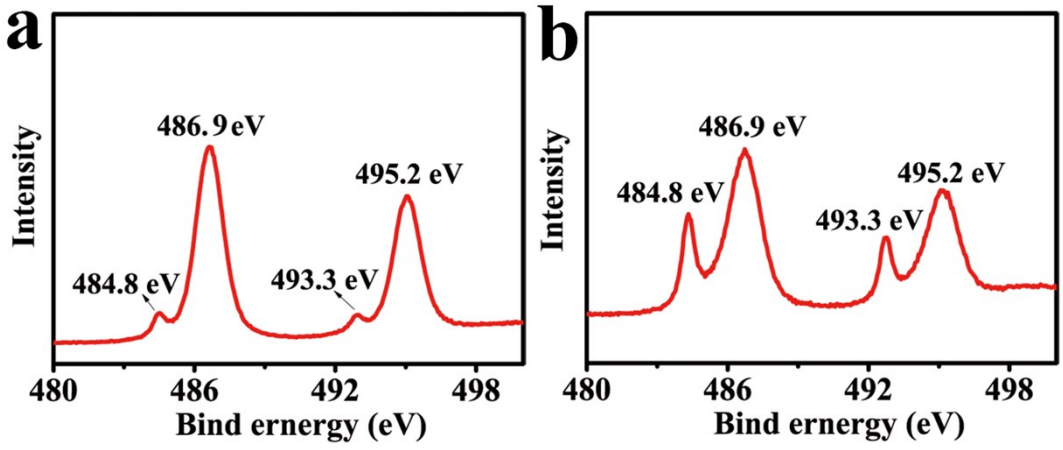

Fig. S1. XPS images of Sn dendrite: (a) Before test. (b) After test.

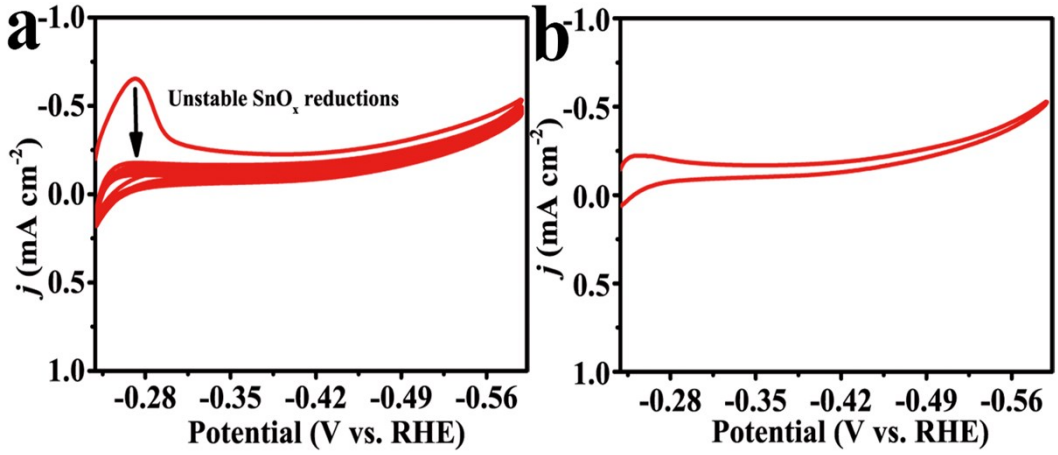

Fig. S2. (a) Stabilization of the Sn D/SF through cyclic voltammetry sweeping in Ar-bubbled 0.1 M PBS electrolyte. (b) CV of Sn D/SF after NRR test in Ar-bubbled 0.1 M PBS electrolyte.

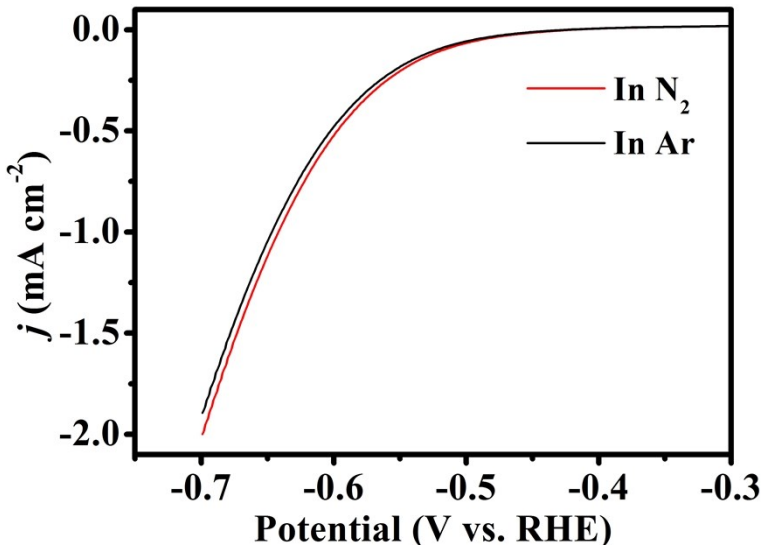

Fig. S3. LSV curves of Sn D/SF in Ar-saturated and N_2-saturated 0.1 M PBS with a scan rate of 5 mV s^{-1}.

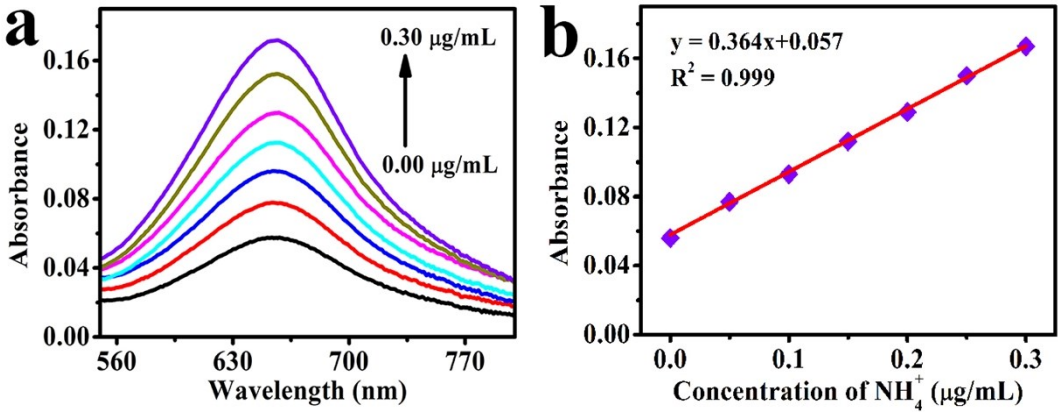

Fig. S4. (a) UV-Vis curves of indophenol assays with NH_3 after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_3.

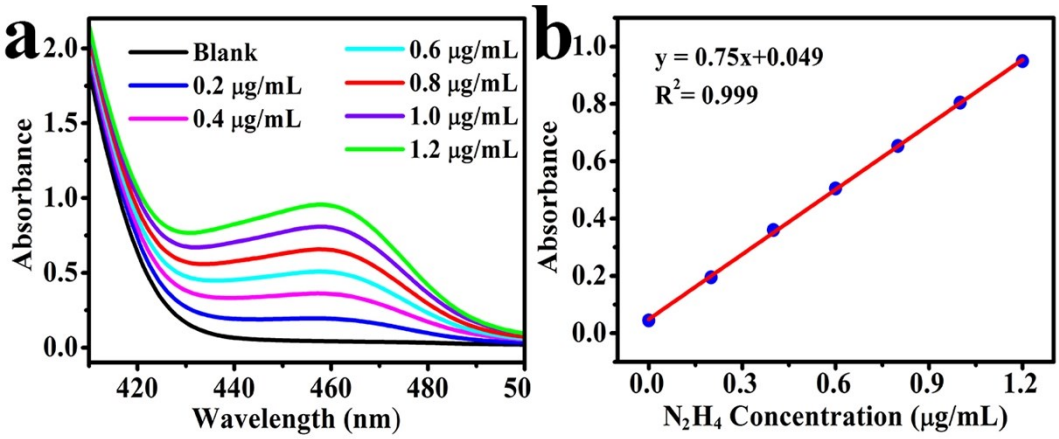

Fig. S5. (a) UV-Vis curves of various N_2H_4 concentrations after adding into chemical indicator by the method of Watt. (b) Calibration curve used for calculation of N_2H_4 concentrations.

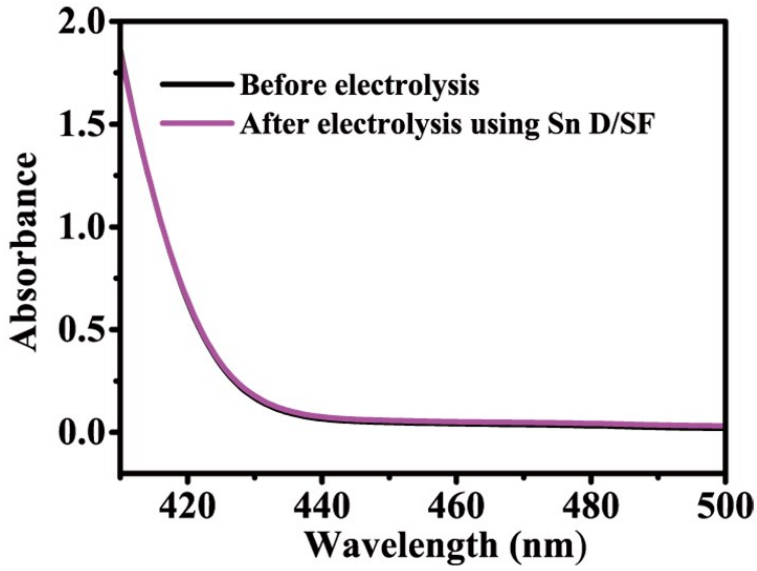

Fig. S6. UV-Vis absorption spectra of electrolytes stained with para-(dimethylamino) benzaldehyde indicator before and after 2 h electrolysis at –0.60 V.

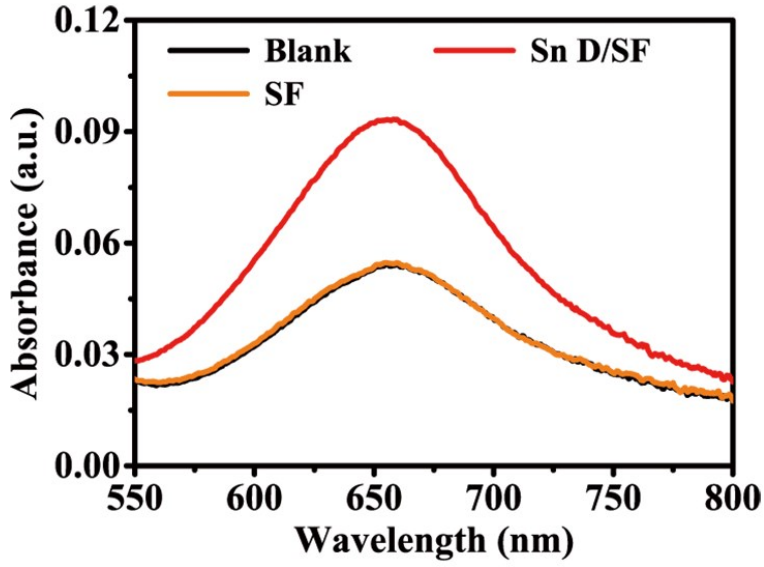

Fig. S7. UV-Vis absorption spectra of the electrolytes colored with indophenol indicator after 2 h electrolysis using different electrodes.

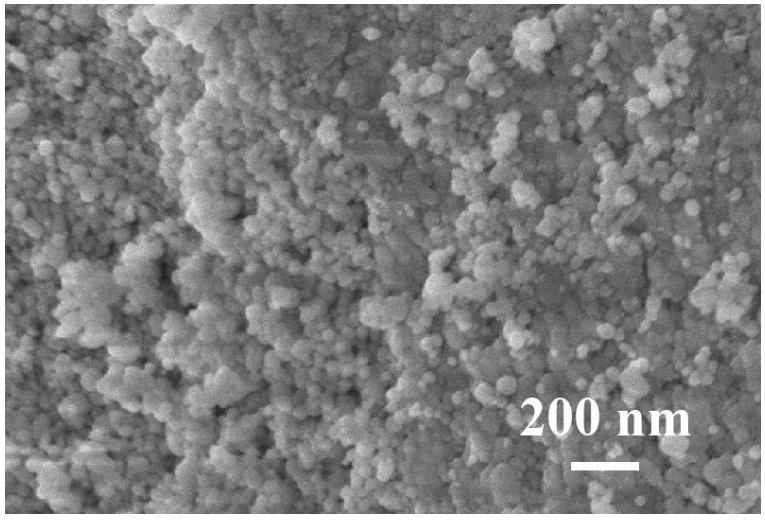

Fig. S8. SEM image of Sn nanoparticles

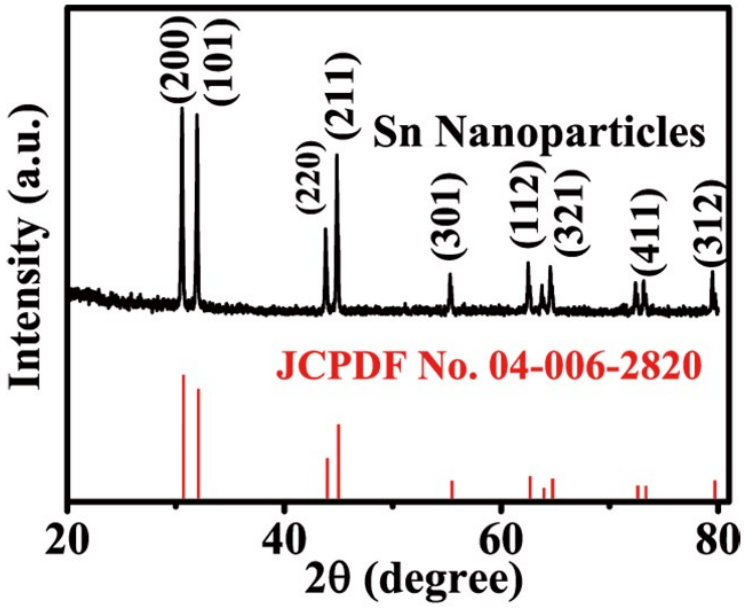

Fig. S9. XRD pattern of Sn nanoparticles

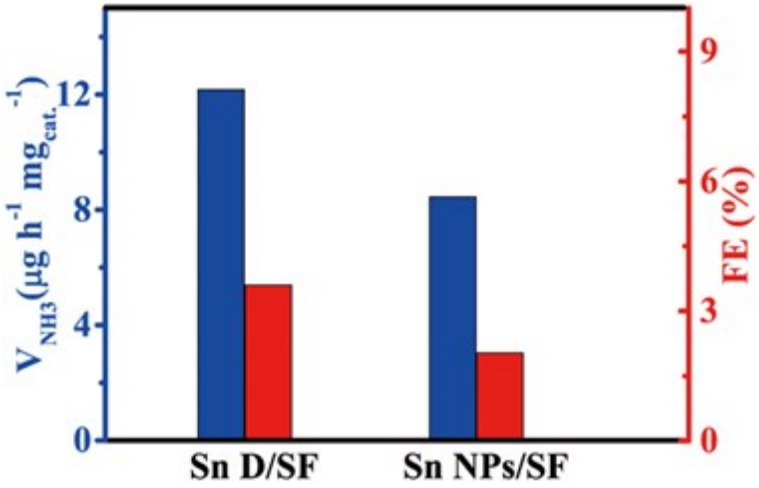

Fig. S10. NH_3 yields and FEs at –0.60 V for 2 h over Sn D/SF and Sn NPs/SF after 2-h testing.

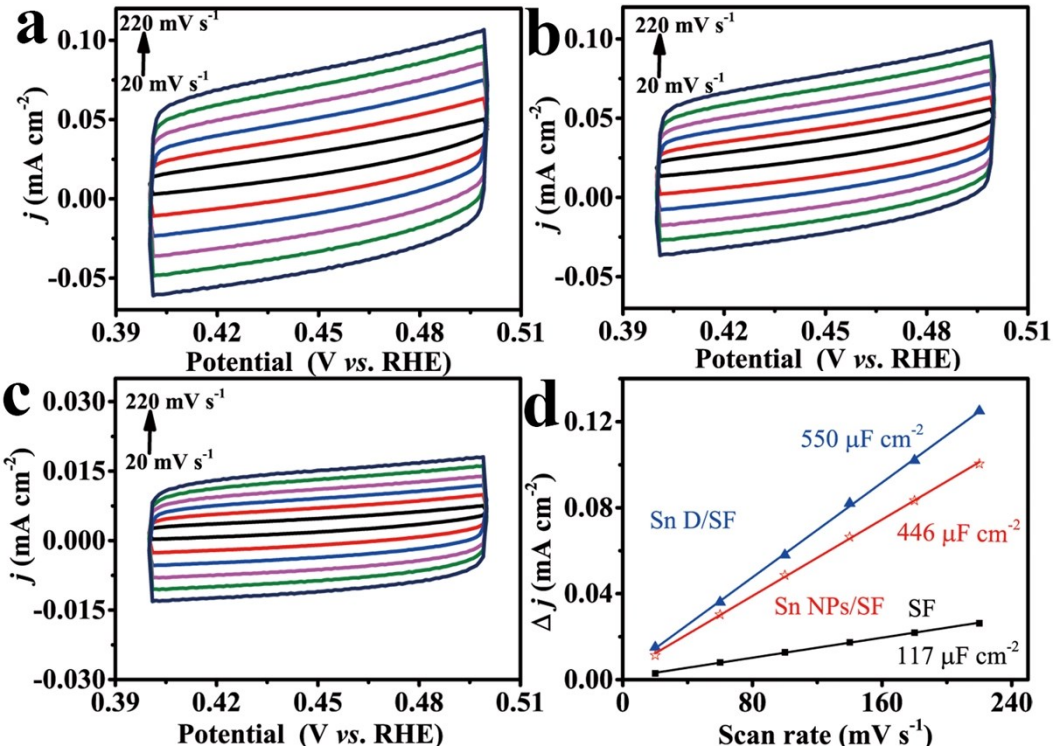

Fig. S11. CVs of (a) Sn D/SF, (b) Sn NPs/SF and (c) bare SF in the non-faradaic capacitance current range with various scan rates (20-220 mV s^{-1}) in the region of 0.40 to 0.50 V *vs*. RHE. (d) Corresponding capacitive currents at 0.45 V vs. RHE as a function of scan rates for Sn D/SF, Sn NPs/SF and SF.

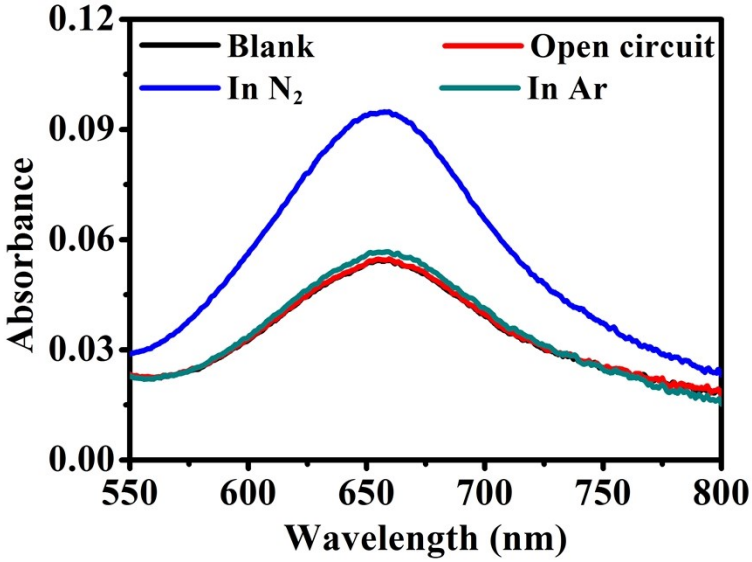

Fig. S12. UV-Vis absorption spectra of the electrolytes colored with indophenol indicator after 2 h electrolysis under different conditions.

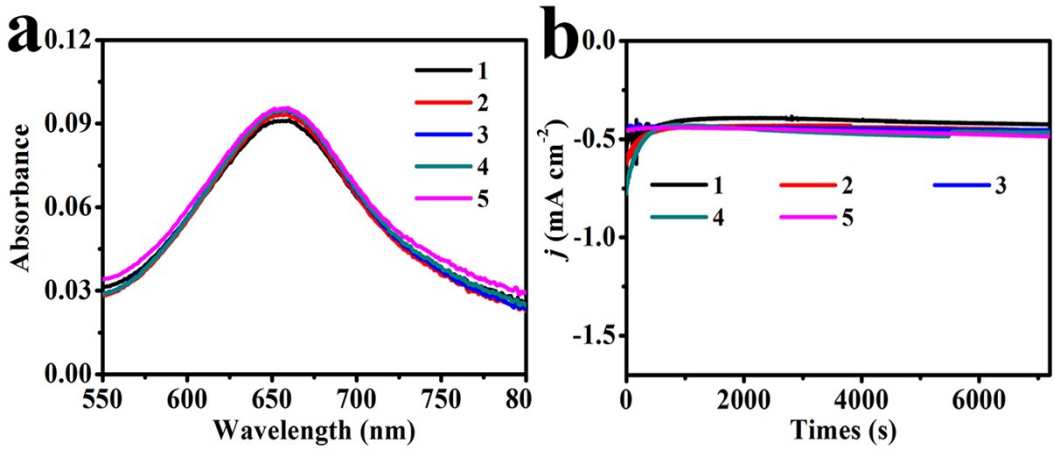

Fig. S13. (a) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h NRR electrolysis at –0.60V over 5 cycles. (b) Time-dependent current density curves of Sn/SF electrode at –0.60 V for 5 cycles.

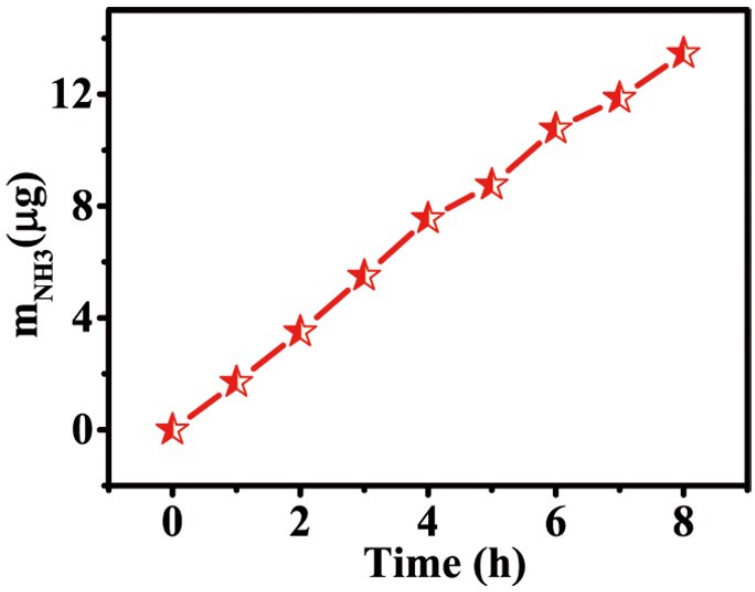

Fig. S14. m_{NH3} *vs*. time recorded at –0.6 V in N_2-saturated solution

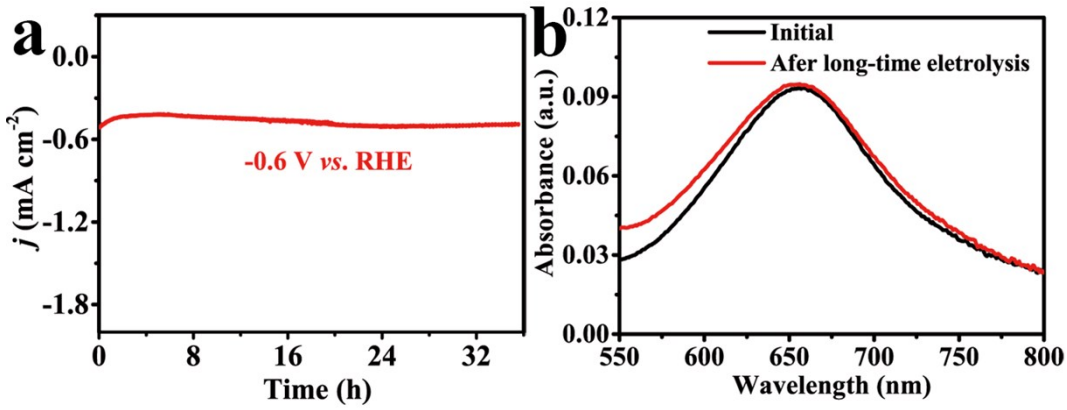

Fig. S15. (a) Time-dependent current density curve for Sn D/SF at –0.60 V for 36 h. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator at –0.60 V after electrolysis for 2 h with the initial and post-NRR electrolysis of Sn D/SF.

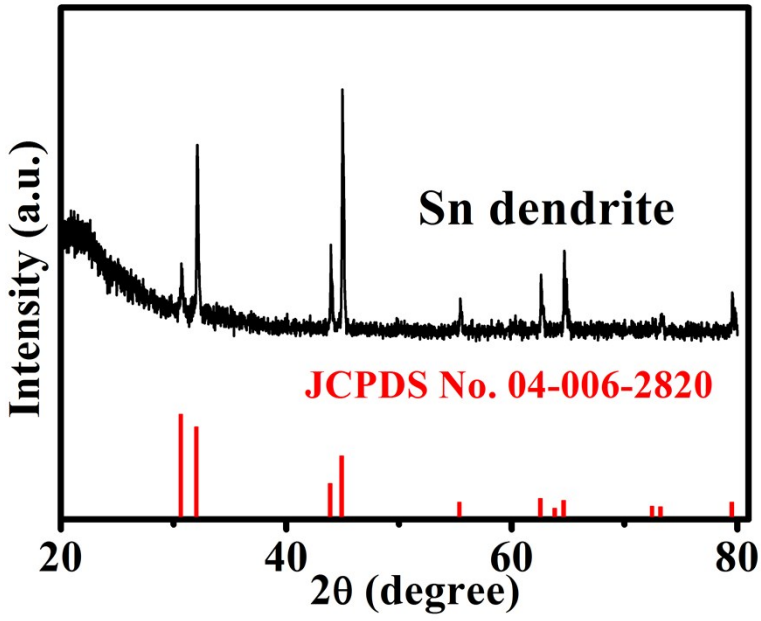

Fig. S16. XRD pattern of Sn dendrite scratched down from Sn foil after stability test.

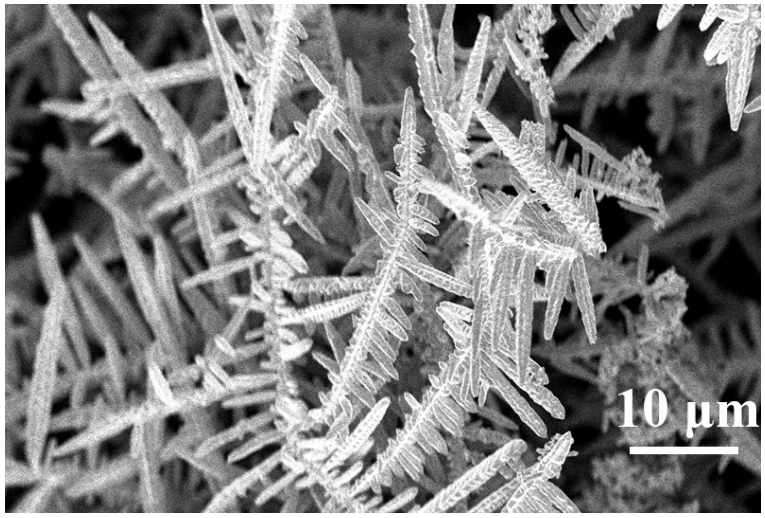

Fig. S17. SEM image of Sn D/SF after stability test.

Table S1. Comparison of the NH_3 yields and FEs for Sn/SF with other NRR electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH_3 yield	FE (%)	Ref.
Sn D/SF	**0.1 M PBS**	**5.66×10^{-11} mol s^{-1} cm^{-2}** **12.17 μg h^{-1} mg_{cat}^{-1}**	**3.67**	**This work**
SnO_2	0.1 M Na_2SO_4	4.3 μg h^{-1} mg_{cat}^{-1}	2.17	5
F-SnO_2 nanosheet	0.1 M Na_2SO_4	19.3 μg h^{-1} mg_{cat}^{-1}	8.6	6
SnO_2/rGO	0.1 M Na_2SO_4	25.6 μg h^{-1} mg_{cat}^{-1}	7.1	7
Fe_2O_3-CNT	0.1 M HCl	3.58×10^{-11} mol s^{-1} cm^{-2}	0.15	8
Ru/C	2.0 M KOH	3.44×10^{-11} mol s^{-1} cm^{-2}	0.28	9
Mo nanofilm	0.01 M H_2SO_4	3.09×10^{-11} mol s^{-1} cm^{-2}	0.72	10
Fe_2O_3 nanorod	0.1 M Na_2SO_4	15.9 μg h^{-1} mg^{-1}	0.94	11
MoN nanosheets array	0.1 M HCl	3.01×10^{-10} mol s^{-1} cm^{-2}	1.15	12
NPC	0.05 M H_2SO_4	1.40 mmol g^{-1} h^{-1}	1.42	13
Fe_3O_4 nanorod	0.1 M Na_2SO_4	5.6×10^{-11} mol s^{-1} cm^{-2}	2.6	14
PEBCD/C	0.5 M Li_2SO_4	2.01 μg h^{-1} cm^{-2}	2.85	15
Au nanorods	0.1 M KOH	2.69×10^{-11} mol s^{-1} cm^{-2}	4.0	16
Ag nanosheet	0.1 M HCl	4.62×10^{-11} mol s^{-1} cm^{-2}	4.8	17
Fe/Fe_3O_4	0.1 M PBS	0.19 μg h^{-1} cm^{-2}	8.29	18
NCM-Au NPs	0.1 M KOH	0.36 g m^{-2} h^{-1}	22	19
B nanosheet	0.1 M Na_2SO_4	13.22 μg h^{-1} mg^{-1}	4.04	20
W_2N_3	0.05 M H_2SO_4	3.80×10^{-11} mol s^{-1} cm^{-2}	11.67	21
DyF_3	0.1 M Na_2SO_4	10.9 μg h^{-1} $mg^{-1}_{cat.}$	8.8	22
$CoFe_2O_4$/rGO	0.1 M Na_2SO_4	4.2×10^{-11} mol s^{-1} cm^{-2}	6.2	23
$NiWO_4$	0.1 M Na_2SO_4	23.14 μg h^{-1} $mg^{-1}_{cat.}$	10.18	24
NiCoS/C	0.1 M Li_2SO_4	26.0 μg h^{-1} $mg^{-1}_{cat.}$	12.9	25

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