Supporting Information

Ru/La_2S_3 nanorods as electrocatalyst for efficient N_2 fixation under ambient conditions

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Ⅰ. Experimental Section

Process of the Nafion membrane

Step 1: Boiling it in a 3 wt% H_2O_2 solution at 80 °C for 1 h. Step 2: Washing it in deionized water several times. Step 3: Boiling it for 1 h in 80 °C sulfuric acid. Step 4: Soaking it for 30 min and repeating several times in deionized water.

Determination of ammonia (NH_3)

Typically, the indophenol blue method was adopted to quantify the NH_3 in 0.1 M electrolyte. In 0.1 M Na_2SO_4, 4 mL the electrolyte was taken from the cathode chamber and was mixed with 50 μL oxidizing solution prepared by NaClO (ρCl = 4−4.9) and 0.75 M NaOH, 500 μL coloring solution (0.4 M $C_7H_5O_3Na$ and 0.32 M NaOH), and 50 μL catalyst solution (1 wt% $Na_2[Fe(CN)_5NO]_2H_2O$). After standing in a lightless environment ambient temperatures for 1 h, such solution was analyzed via the UV-Vis spectroscopy at the wavelength of 670 nm. The standard curve is (Y = 0.682X+0.005 R^2=0.999), which was calibrated using a standardized NH_4Cl solution with five progressive concentrations.

Determination of hydrazine (N_2H_4)

The hydrazine was identified using the Watt and Chrisp method. Typically, 5 mL electrolyte solution was added with 5 mL hydrazine chromogenic agent prepared by 5.99 g $C_9H_{11}NO$, 30 mL HCl and 300 mL ethanol. Followed by 20 min complete stir, the absorbance of such solution at the wavelength of 455 nm was measured to quantify the hydrazine yields with a standard curve of hydrazine (Y = 2.58529X + 0.12902, R^2 = 0.998).

Calculations of NH_3 formation rate and FE

Rate of NH_3 formation was calculated using the following equation:

$$NH_3 \text{ yield} = [NH_3] \times V / (m_{cat} \times t)$$

FE was calculated according to following equation:

$$FE\ (NH_3) = 3 \times F \times [NH_3] \times V / (17 \times Q) \times 100\%$$

Where $[NH_3]$ is the measured NH_4Cl concentration; V is the volume of the cathode reaction electrolyte; t is the potential applied time; m is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.

II. Supplementary Figures

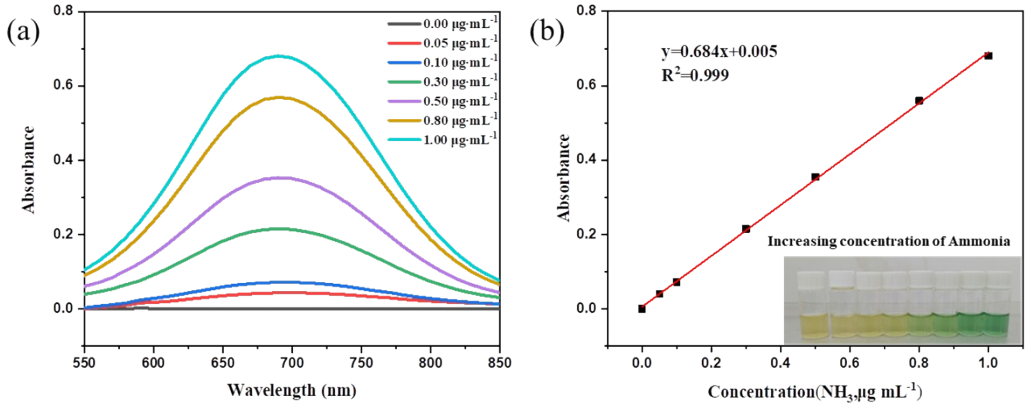

Fig. S1. (a) UV-Vis absorption spectra of indophenol assays performed with different concentrations of NH_3 in 0.1 M Na_2SO_4. (b) A calibration curve used for estimating the NH_3 concentration.

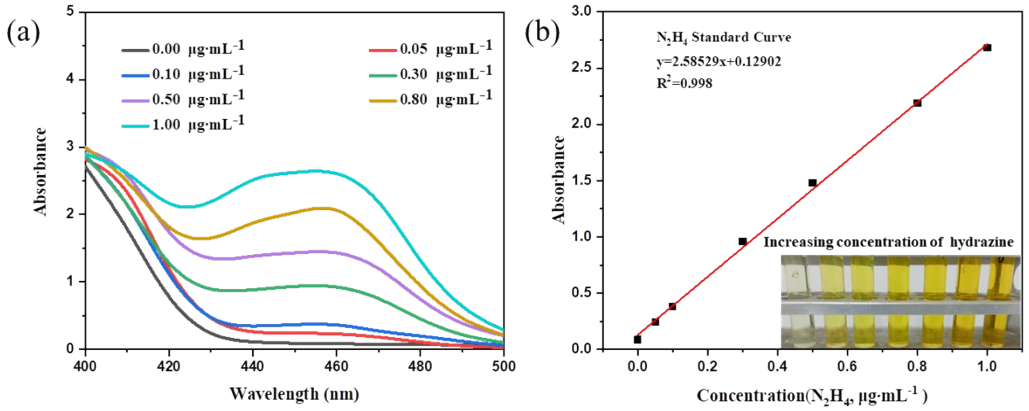

Fig. S2. (a) UV-Vis spectra of various N_2H_4 concentrations after adding into chemical indicator by the Watt and Chrisp method. (b) A calibration curve used for the calculation of N_2H_4 concentrations.

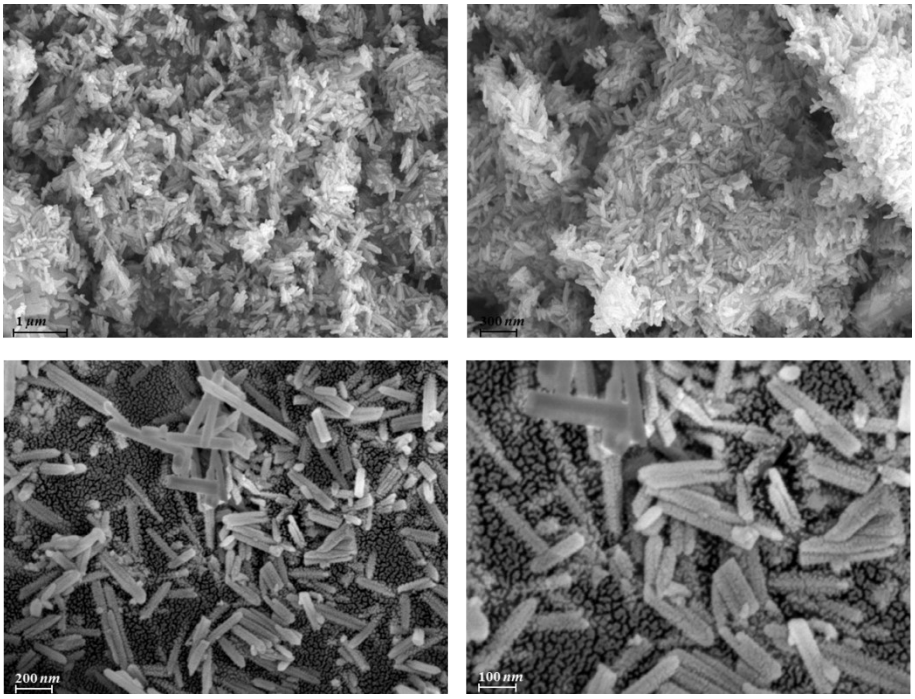

Fig. S3. SEM micrograph of La_2S_3

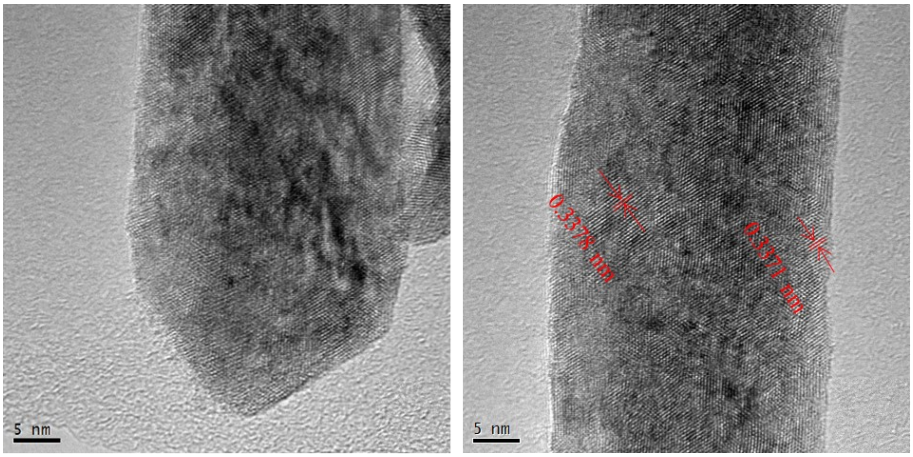

Fig. S4. HRTEM micrograph of La_2S_3

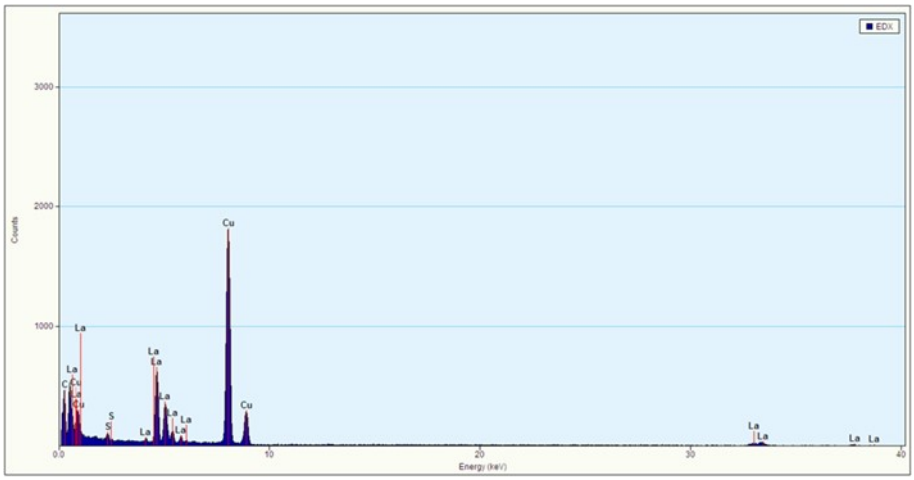

Fig. S5**.** EDX spectrum of La_2S_3

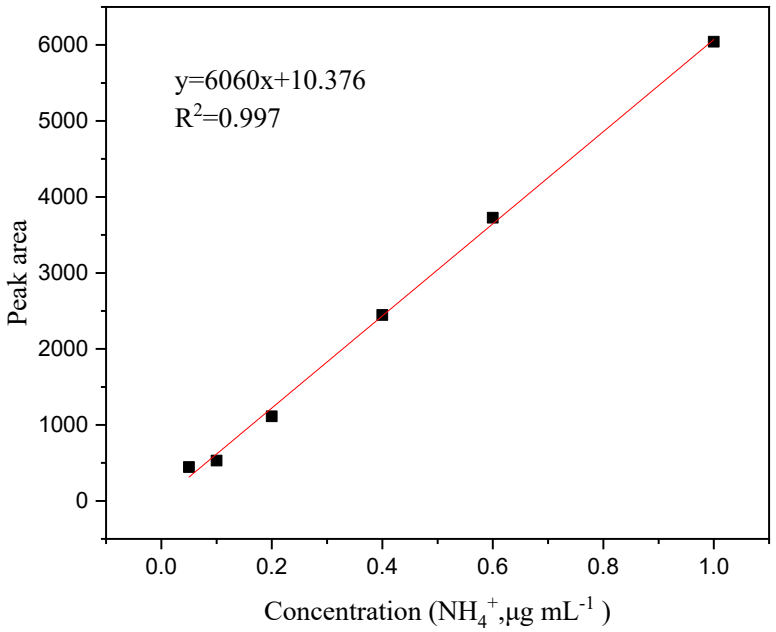

Fig. S6. Calibration curve for ion chromatographic of NH_3 concentration

Table S1. Ion chromatography was compared with salicylic acid method

Number	Ion chromatography (NH_4^+,μg/mL)	Absorbance	Indophenol method (μg/mL)	Different (μg/mL)
1	0.060	0.034	0.061	0.001
2	0.069	0.038	0.071	0.002
3	0.112	0.058	0.119	0.007
4	0.156	0.071	0.152	0.004
5	0.256	0.120	0.271	0.015

Table S2. Comparison of the NRR electrocatalytic activity of Ru/La_2S_3 catalyst under ambient conditions with other catalysts.

Catalyst	Electrolyte	NH_3 Yield Rate	FE(%)	Ref
Ag NPs-rGO	0.1 M HCl	2.8	4.80	[1]
Au/Ni	0.05 M H_2SO_4	7.4	67.80	[2]
a-Au/Cex-RGD	0.1 M HCl	8.3	10.10	[3]
Ru NPs	0.1 M KOH	1.3	5.40	[4]
$Ru@ZrO_2/NC$	0.1 M HCl	3.7	15	[5]
Au_1/C_3N_4	0.05 M H_2SO_4	2.0	11.10	[6]
Ru/MoS_2	0.01 M HCl	6.98	17.60	[7]
MoS_2	0.1M Na_2SO_4	4.94	1.17	[8]
DR MoS_2	0.1M Na_2SO_4	11.72	8.34	[9]
MoS_2-rGO	0.1 M $LiClO_4$	24.82	4.58	[10]
$CoS_2/NS-G$	0.05 M H_2SO_4	10.00	25.90	[11]
$FeS_2-Mo_{17.3}$	0.1 M KOH	25.2	14.41	[12]
Fe_3S_4	0.1 M HCl	75.4	6.45	[13]

References:

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