Electronic Supplementary Information

A two-dimensional MXene-supported CuRu catalyst for efficient electrochemical nitrate reduction to ammonia

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Preparation of working electrode

A homogeneous catalyst ink was created by dissolving 10 mg of the produced Ru-Cu/Cu$_2$O@Ti$_3$C$_2$ catalyst in 1 mL of isopropanol, adding 30 L of 5 wt% Nafion solution, and then sonicating the mixture for 30 minutes. Then, 20 μL of catalyst ink was deposited onto a glassy carbon electrode with a 5 mm diameter and allowed to dry in the open air.

Electrochemical Measurements

The electrocatalytic NO$_3$RR and NRR tests were performed on a CHI760E electrochemical workstation in Shanghai, used for the three-electrode test system. Platinum wire as a counter electrode, Ag/ AgCl as reference electrode, 0.1 M KOH and 0.1 M KNO3 as electrolyte. 10 mg of catalyst and 30 μL of Nafion solution (5 wt%) were dispersed in 970 μL of isopropanol and sonicated for 1 h to obtain a homogeneous suspension. Then, 20 μL of catalyst dispersion was dropped onto a smooth glassy carbon working electrode (effective area 0.196 cm^2), which was naturally dried and used as the working electrode. All potentials obtained in the experiments were converted to reversible hydrogen electrodes (RHE).

Before the electrochemical NO$_3$RR test, high-purity Ar should be introduced into the electrolyte for up to 30 min to ensure complete discharge of dissolved impurity gases, followed by a linear scanning voltammetric curve (LSV) test at a scan rate of 5 mV s^{-1}. In this study, NO$_3$RR experiments were conducted utilizing a chrono-current approach (i-t) with a continuous scan at potentials ranging from -0.1 V to -0.8 V (vs. RHE) for 2 hours. Ar was continuously supplied throughout the testing to create a gas protection

barrier. The reproducibility test was carried out by reconstituting the working electrode after each 2-hour NO_3RR procedure, and the stability cycle test was carried out by scanning the electrochemical NO_3RR procedure using the chrono-current method for 24 hours. Both tests were carried out at optimal potentials. The nitrogen source and protective gas for NRR was N_2, the electrolyte was 0.1 M KOH, and the other experimental conditions were as stated above.

Determination of NH_3: The determination of NH_3 was determined by the indophenol blue and spectrophotometric methods in this experiment. 5 g of sodium salicylate and 5 g of sodium tartrate were dissolved in 100 mL of 1 M KOH as color developer (A). Then 5 mL of NaCIO (14% effective chlorine content) was added to 100 mL of deionized water to prepare color developer (B). Finally, as color developer C, 0.2 g sodium nitrosoferricyanide was dissolved in 20 mL of deionized water. The concentrations of 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 μg/mL ammonium chloride were prepared as standard solutions. Then, 2 ml of standard solution was added to the test tube, followed by 2 ml of color developer A, 1 ml of color developer B and 0.2 mL of color developer C. The mixed solution was then shaken well. After standing for 1 hour, the hybrid solution was transferred to a cuvette and detected by UV-Vis spectrophotometer. The UV-Vis absorption spectrum was obtained according to the absorbance at 655 nm. The concentration-absorbance curve (Figure S4) was obtained using a series of standard NH_4Cl solutions, and was fitted by linear regression, y = 0.30609x-0.00644; R^2 = 0.9995.

The following equation calculates the NH_3 production rate.

NH$_3$ production rate = (c x V)/(t x A)   (1) t

is the electrochemical test time (h), and A is the effective geometric area of the working

electrode (cm^{-2}). Where, c is the measured ammonia concentration and V is the volume

(mL).

FE can be calculated by the following equation.

FE= 8F x c x V /17 x Q   (2),

where one NH$_3$ molecule requires the production of 8 electrons, F is Faraday's constant,

and Q is the amount of electricity consumed in the electrochemical test.

Determination of N$_2$H$_4$: The color developer is 4g of dimethylbenzaldehyde dissolved

in a mixture of 20ml of concentrated hydrochloric acid and 200 ml of ethanol. 1ml of

1000μg/ml hydrazine standard solution was placed in a 100ml volumetric flask and

fixed with 0,1 M KOH, followed by the configuration of standard solutions with

concentrations of 0.2, 0.4, 0.8, 1.2, 1.8μg/ml, respectively. Add 1.5 mL of standard

solution or sample solution into the centrifuge tube, add 1.5ml of color developer, shake

to make the color developer fully act, leave it for 1 h, measure the concentration of

N$_2$H$_4$ in the solution using UV-vis spectrophotometer, and plot the standard curve with

absorbance as the y-axis and the concentration of N$_2$H$_4$ as the x-axis.
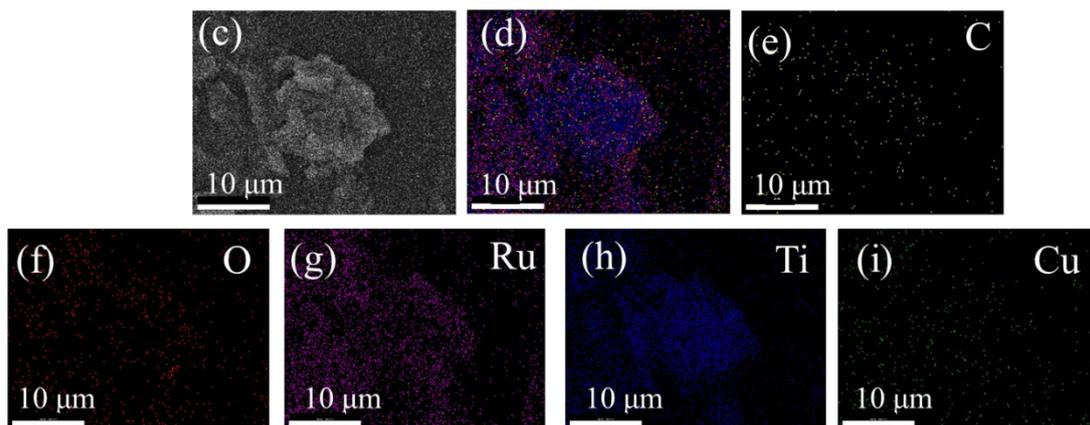
Figure S1 Ru-Cu/Cu$_2$O@Ti$_3$C$_2$ low-magnification EDS spectrum and corresponding elemental distribution
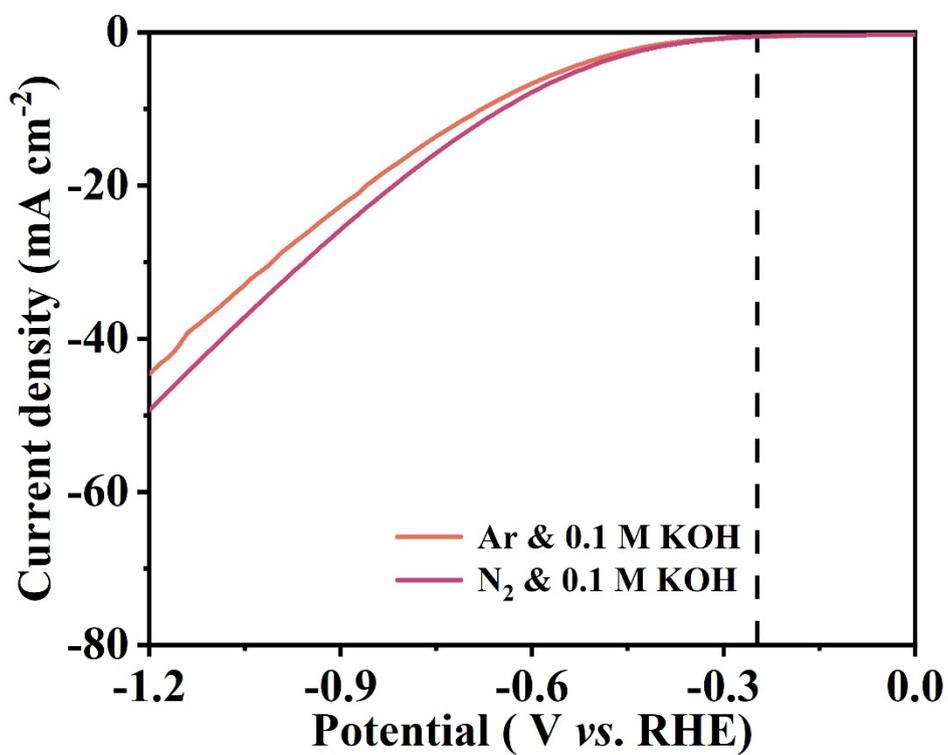
Figure S2 LSV curves of Ru-Cu/Cu$_2$O@Ti$_3$C$_2$-catalyzed NRR
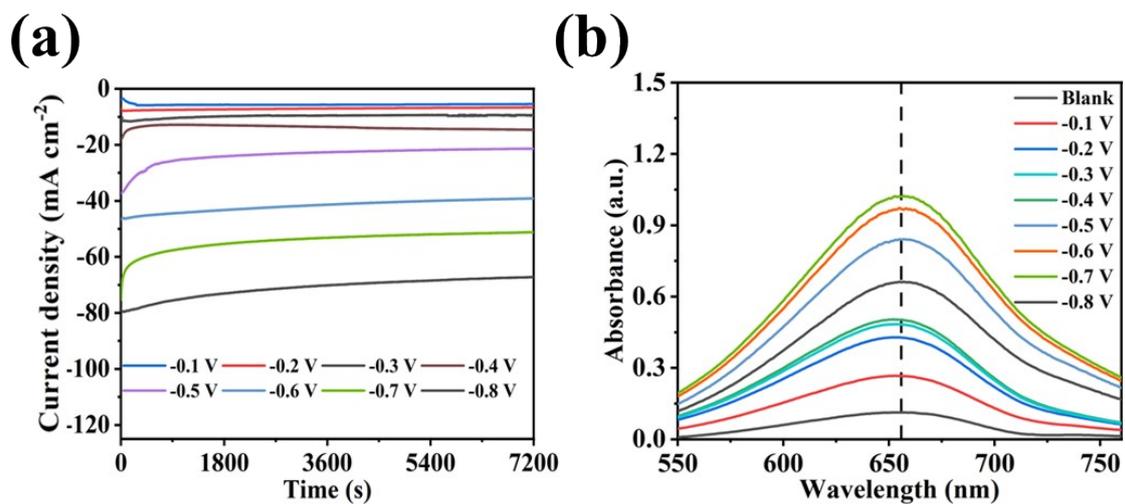
Figure S3 Ru-Cu/Cu$_2$O@Ti$_3$C$_2$-catalyzed NO$_3$RR: (a) i-t test curve; (b) UV absorbance test of NH$_4^+$ in electrolyte
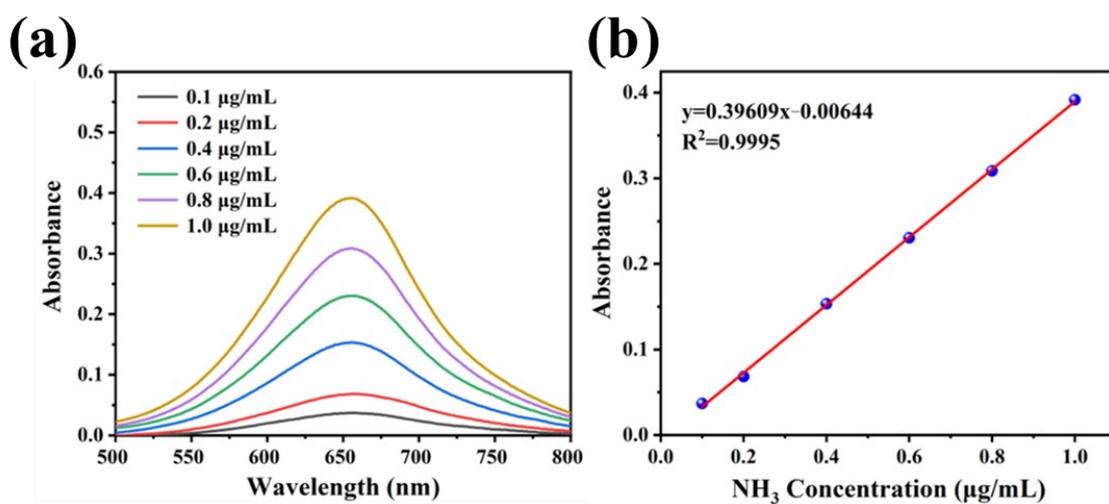
Figure S4 Plotting of standard curve of NH$_3$ in 0.1 M KOH solution.
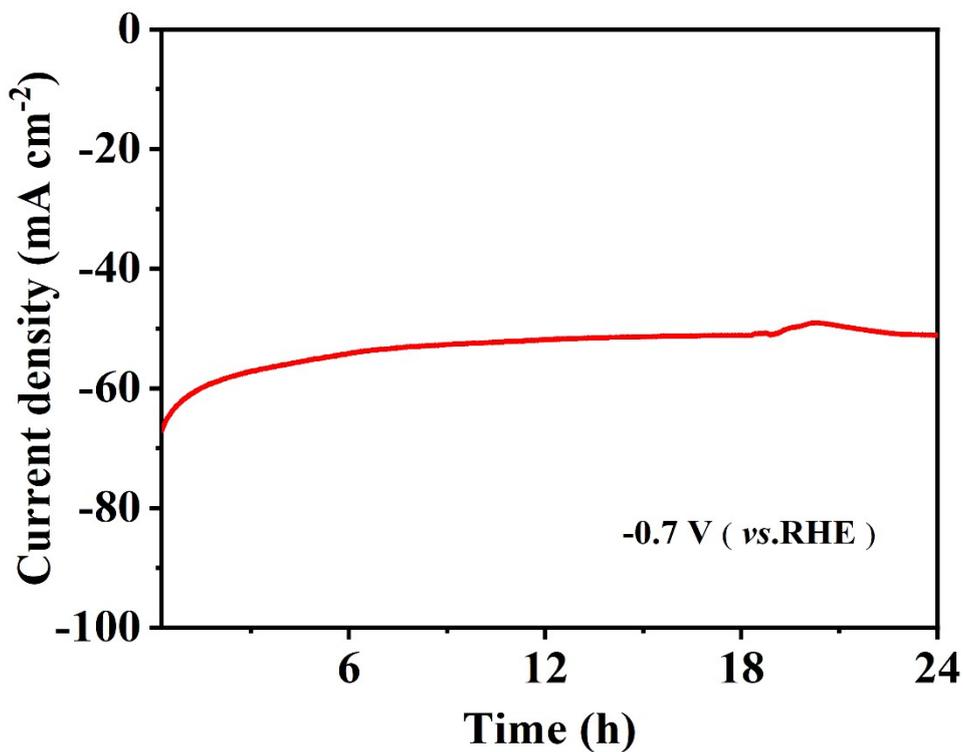
Figure S5 24-h current density variation of Ru-Cu/Cu$_2$O@Ti$_3$C$_2$-catalyzed NO$_3$RR
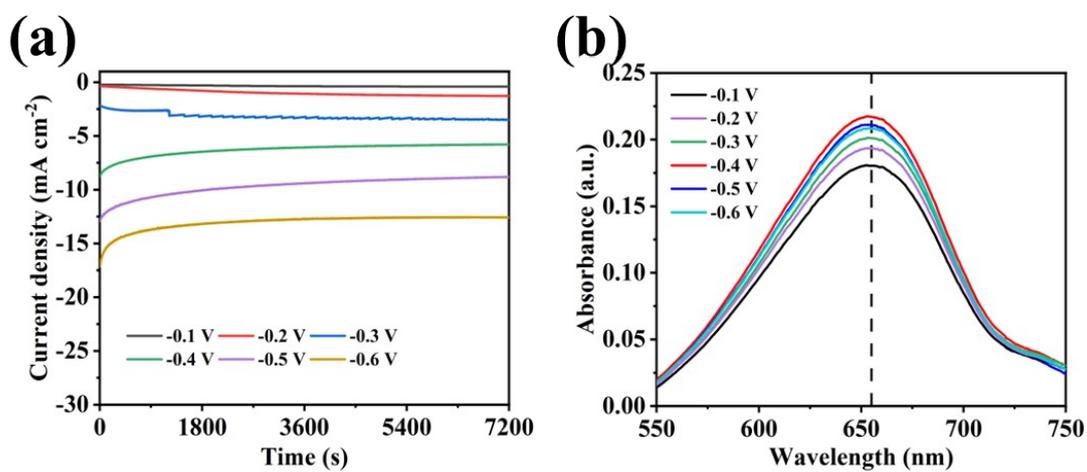
Figure S6 Ru-Cu/Cu$_2$O@Ti$_3$C$_2$-catalyzed NRR; (a) i-t test curve; (b) absorbance test of NH$_4^+$ in electrolyte
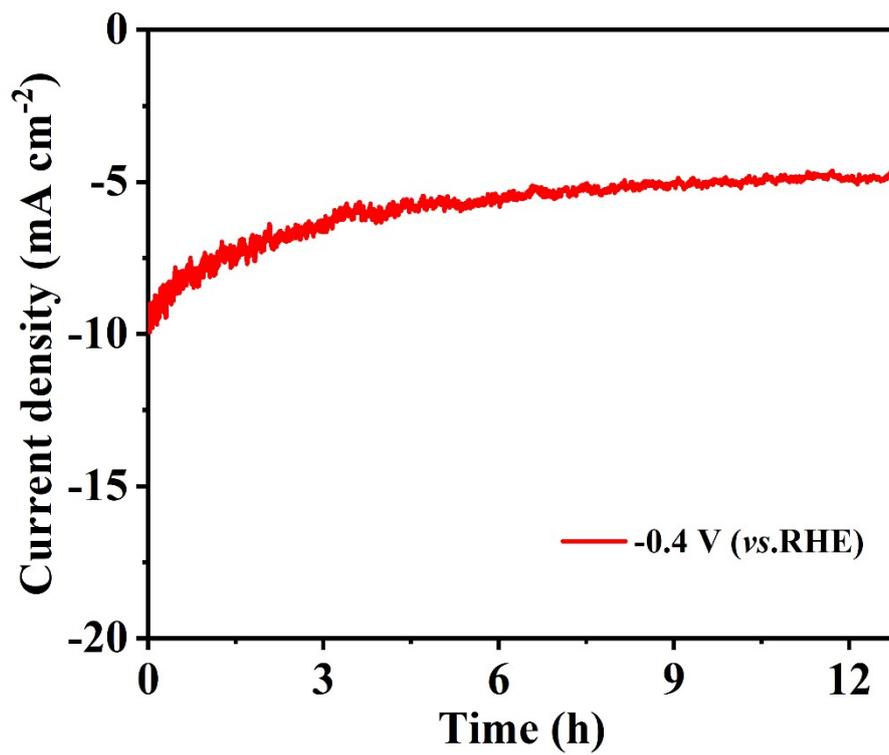
Figure S7   12-h current density test of Ru-Cu/Cu$_2$O@Ti$_3$C$_2$-catalyzed NRR