Supporting Information

Efficient Electrocatalytic Reduction of Nitrate to Nitrogen Gas by Cubic Cu_2O Film with Predominated (111) Orientation

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Experimental section

Chemicals and materials

Cu foam was purchased from KunShan GuangJiaYuan new materials Co. Ltd. KNO_3, K_2SO_4, $CuSO_4$, H_2SO_4, KOH, DL-Lactic acid and NaOH were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without any further purification.

Electrode preparation

The Cu foam (10 × 20 × 1.6 mm^3) slices were carefully cleaned with acetone, ethanol and deionized water for 10 min in sequence. Cu_2O films were electrodeposited from an alkaline electrolyte solution containing 0.3 M $CuSO_4$ and 3 M lactic acid based on a previously reported work.[1] The solution was adjusted to pH 12 with 5 M NaOH. The Cu foam was immersed in the electrolyte solution as working cathode. A Pt and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Deposition was performed at -0.5 V vs. the SCE for a duration varying between 30 and 180 min at room temperature (25 °C).[1]

Characterization

The crystal structure was determined by X-ray powder diffraction (XRD, X'Pert-Pro MPD, PANalytiacl) with Cu Kα1 (λ= 1.54 Å) radiation operated at 40 kV and 40 mA. Field emission scanning electron microscope (FE-SEM) images were collected on a Hitachi SU8020. The transmission electron microscope (TEM) images and energy dispersive X-ray (EDX) analysis were achieved on JEOLJEM-2010 with a 200 keV accelerated electron beam. The concentration of nitrate and nitrite in solution was detected by Thermo Scientific Dionex Aquion ion chromatography (Aquion) equipped with Dionex IonPac AS11-HC analytical column (4×250 mm), shown in Fig. S5. Its eluent is potassium hydroxide based on an automatic eluent generator. The concentration of ammonia in solution was detected by Thermo Scientific Dionex Ion Chromatography (ICS-600) equipped with Dionex IonPac CS16 analytical column (4×250 mm), shown in Fig. S5. The eluent is 30mM methylsulfonic acid. The detectors in both Aquion and ICS-600 are conductivity detector.

Electrochemical nitrate reduction

The nitrate removal experiments were carried out in an 80 mL single three-electrode cell (Fig. S4). Unless otherwise mentioned, 50 mL of 40 mg L^{-1} nitrate containing 0.05 M K_2SO_4 was prepared as the test sample. The pH of the solution was tuned by KOH or H_2SO_4. The immersed area of the cathode was 1 cm^2 (1 × 1 cm^2). Pt foil and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. All the electrochemical experiments were performed on CHI660 electrochemical workstation, and a potential of −1.4 V vs. Ag/AgCl was applied for 2 h with violently stirring. About 2 mL of solution was taken out regularly to determine the concentration of nitrate, nitrite and ammonia ions during the catalytic reaction. The calculation of selection for nitrogen gas, nitrite, and ammonia were followed as

$$C_t(TN) = C_t\left(NO_3^-\right) + C_t\left(NO_2^-\right) + C_t\left(NH_4^+\right)$$

$$S(N_2) = \frac{C_0\left(NO_3^-\right) - C_t(TN)}{C_0\left(NO_3^-\right) - C_t\left(NO_3^-\right)} \times 100\%$$

$$S(NO_2^-) = \frac{C_t\left(NO_2^-\right)}{C_0\left(NO_3^-\right) - C_t\left(NO_3^-\right)} \times 100\%$$

$$S(NH_4^+) = \frac{C_t\left(NH_4^+\right)}{C_0\left(NO_3^-\right) - C_t\left(NO_3^-\right)} \times 100\%$$

$$R = \frac{C_0\left(NO_3^-\right) - C_t\left(NO_3^-\right)}{C_0\left(NO_3^-\right)} \times 100\%$$

Here, C_0 is the initial concentration and C_t is the concentration at the sampling time (t), for NO_3^-, NO_2^-, NH_4^+, and total nitrogen (TN) element in solution. Besides, it is an approximate evaluation of the system performance that does not consider other soluble species such as chloramines or other volatile species such as NO_x. However, because the most nitrous oxides are water-soluble and can be finally reduced to dinitrogen exclusively with excess hydrogen based on previous reports,[2,3] this calculation method was wildly used in previous works.

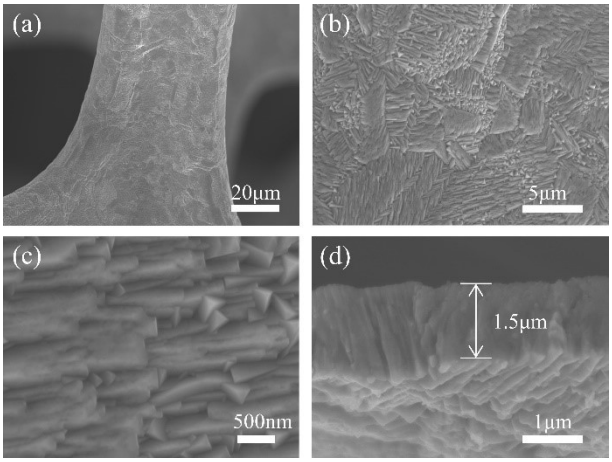

Figure S1. (a-c) SEM images of the surface and (d) cross-section view of electrodeposited Cu_2O thin films on Cu foam for 2 hours.

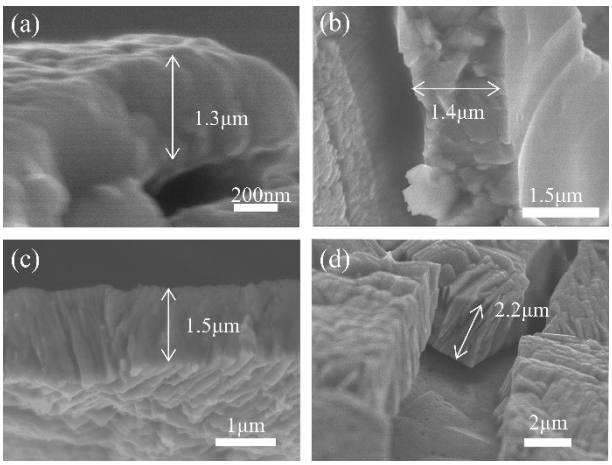

Figure S2. SEM images of the cross-section view of electrodeposited Cu_2O thin films on Cu foam with electrodeposition duration for (a) 0.5, (b) 1, (c) 2 and (d) 3 h.

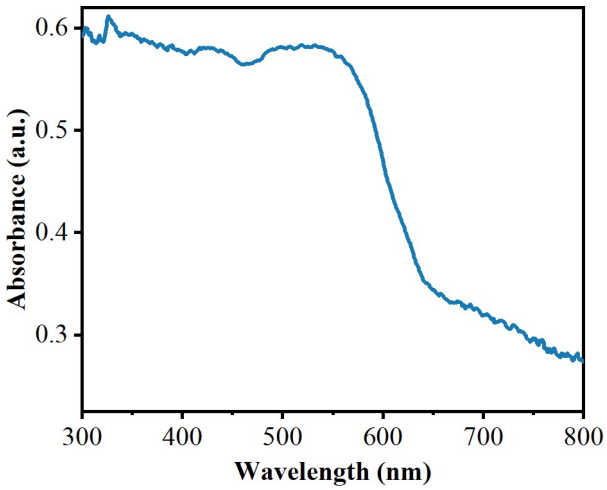

Figure S3. The UV-vis absorption spectra of the as-prepared Cu_2O@CF composite electrode.

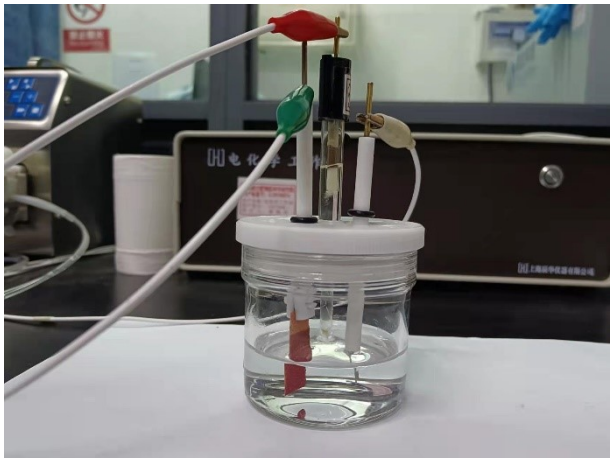

Figure S4. Photo of the used electrocatalytic reactor in this work.

Figure S5. Photo of the Thermo Scientific Dionex Aquion Ion Chromatography System used in this work (On the left is AquionLcs, the right is ICS-600).

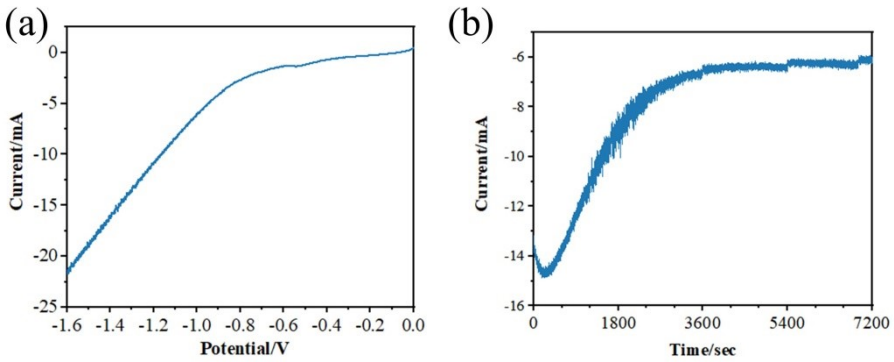

Figure S6. (a) LSV measurement of the Cu_2O@Cu foam and (b) the corresponding current-time curve (reaction conditions: 40 mg L^{-1} NO_3^-, pH=7, applied potential = −1.4 V vs. Ag/AgCl, 0.05 M K_2SO_4).

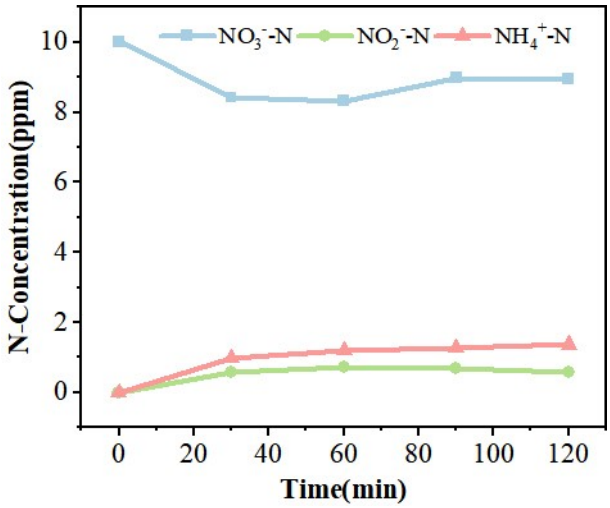

Figure S7. The time-dependent concentration evolution of NO_3^--N, NO_2^--N and NH_4^+-N using the lone Cu foam cathode.

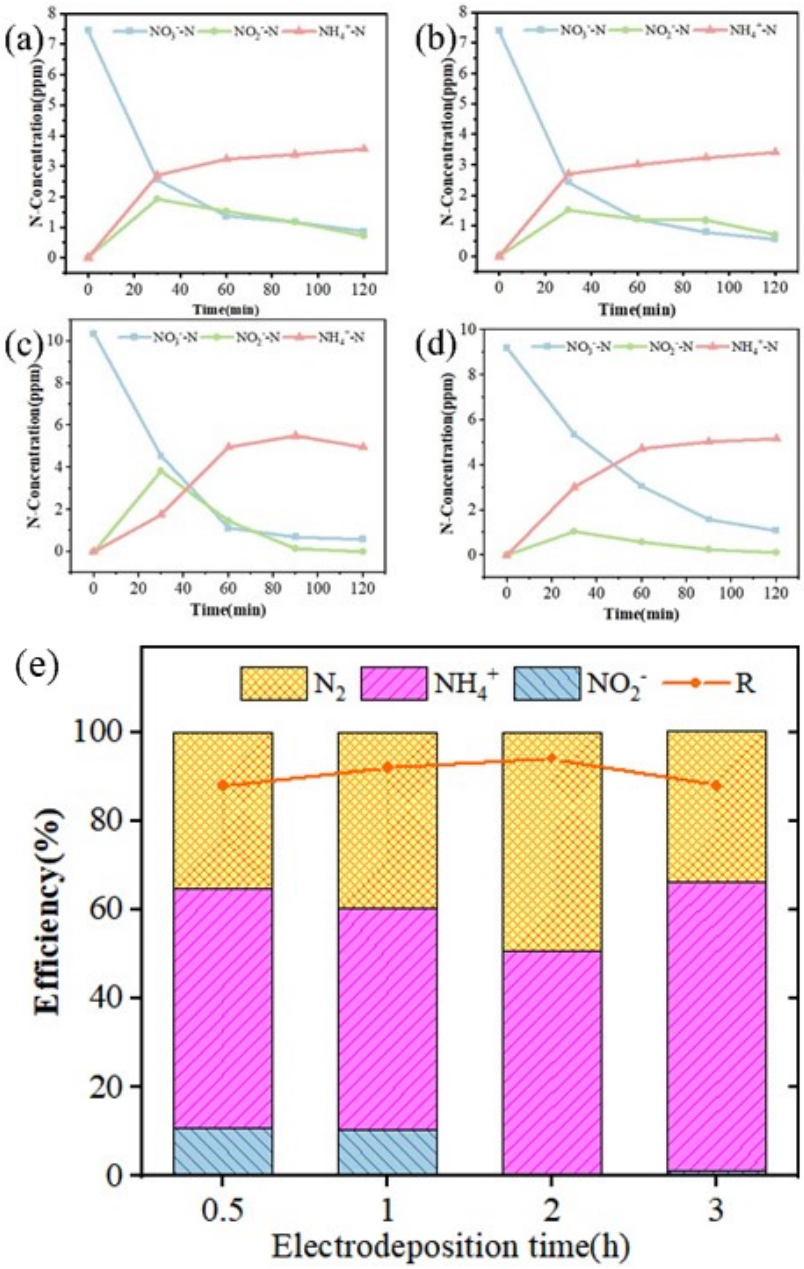

Figure S8. The time-dependent concentration evolution of NO_3^--N, NO_2^--N and NH_4^+-N at electrodes with different thickness of Cu_2O film based on electrodeposition durations of (a) 0.5, (b) 1, (c) 2 and (d) 3 h; (e) Nitrate removal efficiency and product selectivity with electrodes achieved through different electrodeposition durations.

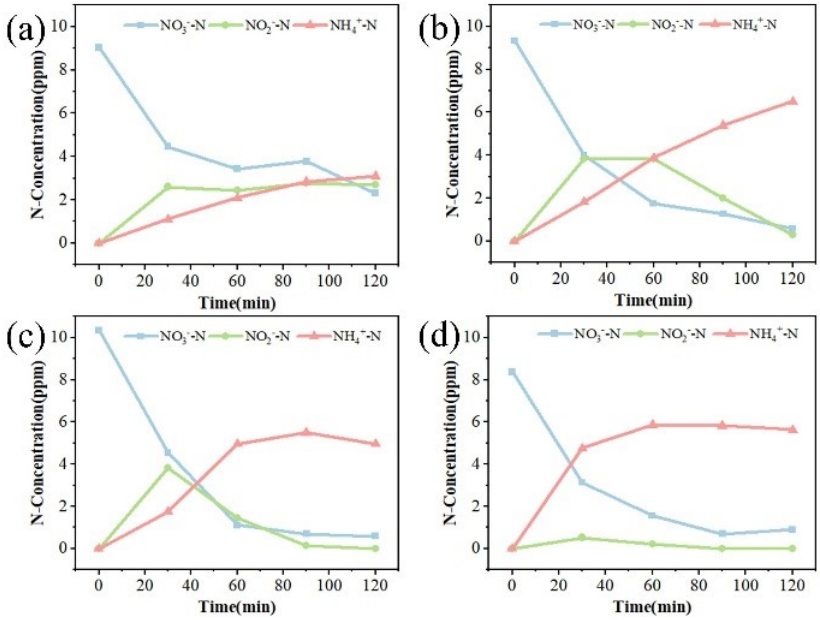

Figure S9. The time-dependent concentration evolution of NO_3^--N, NO_2^--N and NH_4^+-N at potentials of (a) -1.0, (b) -1.2, (c) -1.4 and (d) -1.6V.

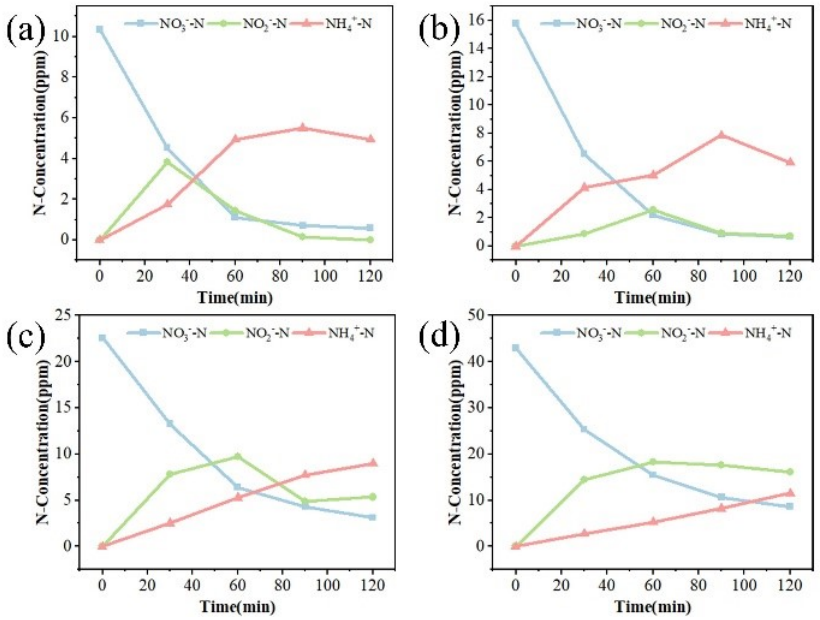

Figure S10. The time-dependent concentration evolution of NO_3^--N, NO_2^--N and NH_4^+-N at different initial nitrate concentrations with (a) 40, (b) 70, (c) 100 and (d) 200 ppm.

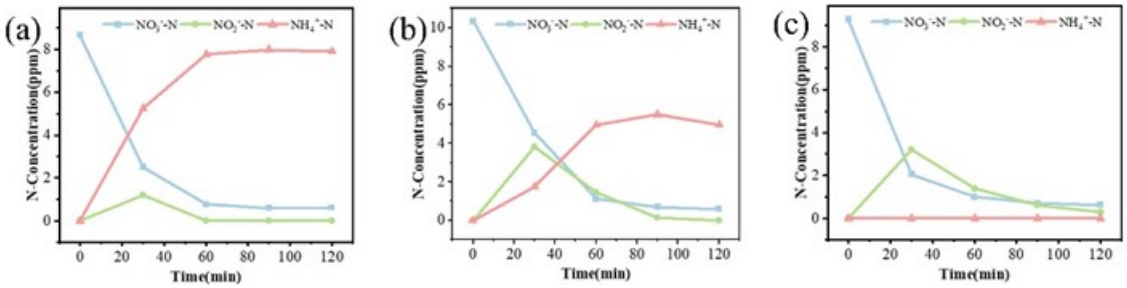

Figure S11. The time-dependent concentration evolution of NO_3^--N, NO_2^--N and NH_4^+-N at different initial pH values of (a) 3, (b) 7 and (c) 11.

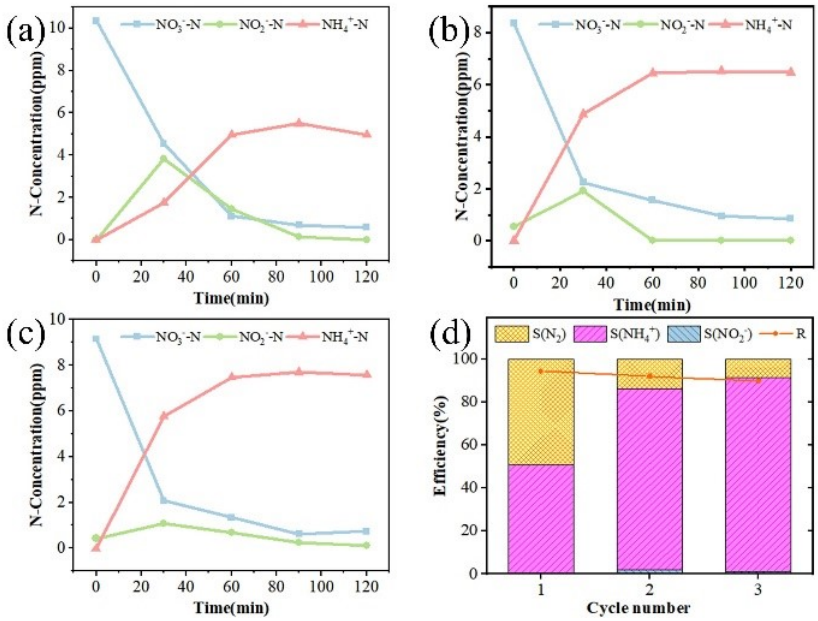

Figure S12. The time-dependent concentration evolution of NO_3^--N, NO_2^--N and NH_4^+-N using the same electrodes after different applied cycle: (a) 1st, (b) 2nd and (c) 3rd; (d) Nitrate removal efficiency and product selectivity based on the same electrode after different experimental cycles.

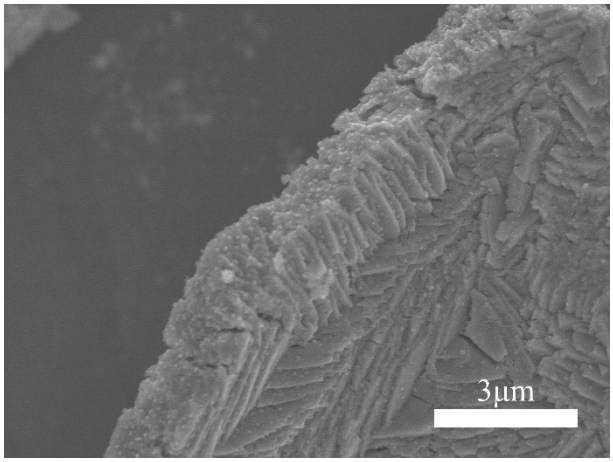

Figure S13. SEM image of the surface of the electrodeposited Cu_2O film on Cu foam after 3 cycles of nitrate reduction experiments (reaction conditions: 40 mg L^{-1} NO_3^-, pH=7, applied potential = −1.4 V vs. Ag/AgCl, 0.05 M K_2SO_4).

References

(1) Wu, L.; Tsui, L.-k.; Swami, N.; Zangari, G. Photoelectrochemical Stability of Electrodeposited Cu_2O Films. *J. Phys. Chem. C* **2010**, *114*, 11551-11556.

(2) Chen, M.; Wang, H. F.; Zhao, Y. Y.; Luo, W.; Li, L.; Bian, Z. F.; Wang, L. J.; Jiang, W.; Yang, J. P. Achieving high-performance nitrate electrocatalysis with PdCu nanoparticles confined in nitrogen-doped carbon coralline. *Nanoscale* **2018**, *10*, 19023-19030.

(3) Su, L.; Han, D. D.; Zhu, G. J.; Xu, H.; Luo, W.; Wang, L. J.; Jiang, W.; Dong, A. G.; Yang, J. P. Tailoring the Assembly of Iron Nanoparticles in Carbon Microspheres toward High-Performance Electrocatalytic Denitrification. *Nano Lett.* **2019**, *19*, 5423-5430.