Supporting Information

Photoelectrochemical Nitrogen Reduction to Ammonia on Cupric and Cuprous Oxide Photocathodes

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Experimental

Synthesis of CuO electrodes. CuO electrodes were prepared by a previously reported electrodeposition method.¹ A conventional undivided three-electrode cell was used. A fluorine-doped tin oxide (FTO) slide (Hartford Glass, Inc.) was used as the working electrode and Pt-coated glass was used as the counter electrode. Pt electrodes were prepared by sputter-coating a 100 nm thick Pt layer over a 20 nm thick Ti layer onto clean glass slides (LGA Thin Films). The reference electrode was an Ag/AgCl electrode (4 M KCl). Copper hydroxy double salt (Cu-HDS) films served as precursors to CuO films and were first deposited potentiostatically at 0.1 V vs Ag/AgCl for 10 min from an unstirred aqueous solution composed of 100 mM Na₂SO₄ (Aldrich), 20 mM CuSO₄ (Aldrich), and 50 mM *p*-benzoquinone (Aldrich) at a temperature of 80 °C. The pH of the plating solution was adjusted to 5 with NaOH (Aldrich) prior to performing the deposition. The Cu-HDS precursor films were first converted to fibrous Cu(OH)₂ by soaking in 1 M NaOH solution (pH 14) at room temperature for ~15 s. These films were then annealed at 500 °C for 3 h (ramp rate 2 °C/min) to produce the fibrous CuO films. More details about the synthesis can be found elsewhere.¹

Synthesis of Cu₂O electrodes. Cu₂O electrodes were prepared by electrodeposition performed in a conventional undivided three-electrode cell using Au-coated glass as the working electrode and Pt-coated glass as the counter electrode. The Au electrodes were prepared by sputtercoating a 100 nm thick Au layer over a 20 nm thick Ti layer onto clean glass slides (LGA Thin Films). The reference electrode used was an Ag/AgCl electrode (4 M KCl). Cu₂O films were deposited potentiostatically at 0.45 V vs Ag/AgCl from an unstirred aqueous solution containing 20 mM CuSO₄ (Alfa Aesar), 50 mM KH₂PO₄ (Electron Microscopy Sciences), and 0.4 M DL-Lactic acid (Aldrich) at a temperature of 60 °C. The pH of the plating solution was adjusted to 12 with KOH (Aldrich) prior to performing the deposition. The depositions were rinsed with water and dried with a stream of air after the deposition. To improve the photocurrent of the Cu₂O electrodes (**Figure S2**), the resulting electrodes were heated for 30 s at a power level of 1 in a microwave oven. A Si wafer was used as a susceptor during the microwave treatment.

Characterization. The crystal structures of CuO and Cu₂O electrodes were investigated by powder X-ray diffraction (XRD) (Bruker D8 diffractometer, Ni-filtered Cu K α radiation, $\lambda = 1.5418$ Å). The morphologies of the electrodes were examined by scanning electron microscopy (SEM) (LEO Supra55 VP operated at an accelerating voltage of 2 kV). The chemical compositions and oxidation states at the surface of the CuO and Cu₂O electrodes were investigated using X-ray photoelectron spectroscopy (XPS) (Thermo Scientific equipped with Al K α excitation). The binding energies of Cu 2p were calibrated with respect to the carbon 1s peak at 284.8 eV.

Photoelectrochemical N_2 **Reduction.** All photoelectrochemical N_2 reduction experiments (J-V and J-t measurements) were performed under simulated solar illumination in an undivided, three-electrode, gas-tight cell where CuO or Cu₂O photocathodes were used as working electrodes with a graphite rod counter electrode and an Ag/AgCl (4 M KCl) reference electrode. The simulated solar illumination was generated from a 300 W Xe lamp and was passed through an AM 1.5G filter and an IR (water) filter. Illumination was through the FTO side for CuO (back side-illumination) and electrode side for Cu₂O (front side-illumination). The power density of light was calibrated to be 1 sun (100 mW/cm²) by using an NREL certified GaAs

reference cell. The photocathodes were masked with epoxy to expose comparable geometrical illumination areas (1–1.2 cm² for J-V measurements and \sim 3.4 cm² for J-t measurements).

Prior to use, the electrolyte, 0.1 M KOH (pH 13) (40 mL), was purged with Ar gas (99.999%) for 20 min in order to remove any gas impurities in the cell. For N₂ reduction, the solution was saturated with isotopically labeled ¹⁵N₂ gas by purging for 10 min before sealing the cell. The purity of the isotopically labeled ¹⁵N₂ is 98 atom % ¹⁵N and \geq 99.0% N₂ (¹⁵N₂ + ¹⁴N₂). The impurities (< 1.0%) identified by the manufacturer are Argon, O₂, CO₂, N₂O, and C₂H₆. In this study, only ¹⁵NH₃ produced by ¹⁵N₂ reduction was quantified to calculate the Faradaic efficiency (FE) for NH₃ production. This eliminates any concern that environmental ¹⁴NH₃ contamination may result in overestimation of the FE for NH₃ production. J-V measurements were taken while sweeping the potential to the negative direction at a scan rate of 5 mV/s. The J-t measurements were performed for 1 hour at 0.6 V vs RHE for CuO and 0.4 V vs RHE for Cu₂O.

After the J-t measurement, the produced ¹⁵NH₃ was quantified using proton nuclear magnetic resonance spectroscopy (¹H NMR) (Bruker Avance III HD 600 MHz equipped with a TCI-F cryoprobe with z-gradient). For this process, the electrolyte was first acidified to pH ~3 by adding HCl (Aldrich, 37 %) to convert ${}^{15}NH_3$ to ${}^{15}NH_4^+$ and then condensed to 4 mL via reduced pressure distillation.² The solutions for NMR study were prepared by mixing the condensed $^{15}\text{NH}_4^+$ solutions with volume % D_2O 5 (Aldrich) containing trimethylsilylpropanoic acid (TSP) as an internal reference for locking. In order to remove the ¹H signal from water, all NMR analyses were carried out with water suppression using excitation sculpting. The transmitter frequency for all solutions was adjusted to be centered on the water frequency (~4.7 ppm, adjusted for every sample). Water suppression did not affect the quantification of ${}^{15}NH_4^+$ produced because the ${}^{15}NH_4^+$ signals were observed at 7 ppm. The NMR spectra were collected using 1024 scans, an acquisition time of 3 s, and a relaxation delay of 1.5 s. The concentration of produced ¹⁵NH₄⁺ was determined based on a calibration curve, obtained by integrating the ¹⁵NH₄⁺ signals of a set of standard solutions of known concentrations in the range of 0.1 - 2 mM. The standard solutions were prepared by dissolving ¹⁵NH₄Cl (Aldrich, 99.5%) in 0.1 M KOH, followed by the aforementioned acidification and mixing with D₂O (5 vol %) containing TSP for locking. In this study, ¹H NMR was used instead of ¹⁵N NMR because ¹H NMR provides better sensitivity for the detection of ¹⁵NH₄⁺ due to the extremely low gyromagnetic ratio of ¹⁵N.³ Differentiation between ¹⁵NH₄⁺ and ¹⁴NH₄⁺ is possible in ¹H NMR because ¹⁴N is a spin-1 nucleus and ¹⁵N is a spin-1/2 nucleus. This means that the coupling between ¹H and ¹⁵N in ¹⁵NH₄⁺ results in a doublet with a spacing of 73 Hz while the coupling between ¹H and ¹⁴N in ¹⁴NH₄⁺ results in a triplet with a spacing of 52 Hz.

We note that when control experiments were performed with CuO and Cu₂O photocathodes in the dark at the potentials used for the J-t measurements or at their open circuit potentials, no $^{15}NH_3$ was detected. In these experiments, all other conditions were the same as those used for photoelectrochemical N₂ reduction.

The formation of N₂H₄, another possible product of photoelectrochemical N₂ reduction, was examined spectrophotometrically by the method developed by Watt and Chrisp, which is more sensitive than ¹H NMR for N₂H₄ detection (detection limit: $\sim 0.5 \times 10^{-5} \mu$ M).^{4,5} After photoelectrochemical N₂ reduction, 2 mL of electrolyte was collected and mixed with 2 mL of an ethanol solution containing 0.7 M HCl (Aldrich, 37%) and 0.12 M 4- (dimethylamino)benzaldehyde (Aldrich, 99%). After keeping the solution for 1 h at room temperature, the absorbance of the mixed solution was measured at 455 nm using a UV-Vis spectrophotometer (Varian, Cary 300 Bio UV-Visible spectrophotometer). The concentration of the produced N₂H₄ was evaluated based on the calibration curve generated from a set of standard solutions of known concentrations of N₂H₄ measured at 455 nm. The standard

solutions were prepared by adding N_2H_4 (Aldrich 50-60%) to the electrolyte used for photoelectrochemical N_2 reduction. The results showed that neither of the photocathodes investigated in this study produced N_2H_4 during photoelectrochemical N_2 reduction.

The produced H_2 gas was quantified using a gas chromatograph-mass spectrometer (GCMS-QP2010 Ultra equipped with a ShinCarbon ST packed column (Restek) and a secondary electron detector) where He (99.999%) was used as the carrier gas. For GCMS measurements, 0.5 mL of gas from the headspace of the cell was collected using a gas-tight syringe and injected manually into the GCMS.

The Faradaic efficiency (FE) was calculated using the following equation where the amount of charge used to produce a desired product was divided by the amount of total charge passed during the J-t measurement. In the equation, F is Faraday's constant (96485 C/mol) and n is the number of electrons required to produce one NH_3 or H_2 molecule (3 or 2, respectively).

$$FE (\%) = \frac{n \times mol \ of \ product \times F(C/mol)}{Total \ charge \ passed \ (C)} \times 100$$

All results in this work are presented with respect to the reversible hydrogen electrode (RHE) for easy comparison with reports using various pH conditions. Potentials vs Ag/AgCl were converted to potentials vs RHE as follows:

$$E (vs RHE) = E (vs Ag/AgCl) + E_{Ag/AgCl} + 0.0591 V \times pH$$

where $E_{Ag/AgCl}$ (reference electrode, 4 M KCl) = 0.1976 V vs NHE at 25°C

The reduction potential of N_2 to NH_3 in pH 13 solution against RHE can be calculated using the following considerations. Depending on the solution pH, the major product of N_2 reduction can be either NH_4^+ or NH_3 and a different equation needs to be used for each case⁶:

When NH ₄ ⁺ is the major product (pH \leq 9.27): N ₂ (g) + 8H ⁺ + 6e ⁻ \rightleftharpoons 2NH ₄ ⁺ (aq)	$E^o = 0.275$ V vs SHE	(1)
When NH ₃ is the major product (pH \ge 9.27): N ₂ (g) + 6H ⁺ + 6e ⁻ \rightleftharpoons 2NH ₃ (aq)	$E^o = 0.092$ V vs SHE	(2)

Since the $e^-:H^+$ ratios in these two equations are not the same, the shift of the reduction potential per unit pH change in these two cases is different. This also means that when the reduction potential of N₂ is reported against RHE, it cannot be a constant value throughout the entire pH range since the effects of pH on water reduction and N₂ reduction are not the same at every pH. The acid-base equilibrium of NH₃/NH₄⁺ that affects their concentrations is another factor that can affect the equilibrium reduction potential of N₂ when N₂ reduction is performed at a pH near its pK_a (9.27)

At pH 13 where NH₃ is the major product, eq 2 is used and the N₂ reduction potential was calculated to be 0.092 V vs RHE with the assumption that N₂ and NH₃ are in their standard states.



Figure S1. (a) ¹H NMR spectra of ¹⁵NH₄⁺ standard solutions (0.1-2.0 mM) and (b) the resulting calibration curve; (c) ¹H NMR spectra of ¹⁵NH₄⁺ obtained by acidifying ¹⁵NH₃ produced from photoelectrochemical ¹⁵N₂ reduction by CuO and Cu₂O photocathodes.



Figure S2. J-V plots (scan rate = 10 mV/s) of as-prepared (red) and microwaved (blue) Cu₂O for O₂ reduction that shows the effect of the microwave treatment. All measurements were carried out in 0.1 M KOH (pH 13) solution purged with O₂. The dashed lines show J-V curves obtained in the dark and the solid lines show J-V curves obtained under AM 1.5G (100 mW/cm^2) illumination.

Table S1. $^{15}\rm NH_3$ produced by CuO and Cu₂O photoelectrodes via photoelectrochemical N_2 reduction during the J-t measurement for 1 hour.

Photocathode	Potential	Yield of NH ₃	Rate of NH ₃ Production
	(vs RHE)	(µg)	$(\mu g \text{ cm}^{-2} \text{ h}^{-1})$
CuO	0.6 V	18.1	5.3
Cu ₂ O	0.4 V	24.4	7.2

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