

Supplementary information

Ammonia photosynthesis via an association
pathway using a plasmonic photoanode and a
zirconium cathode

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1. Quantitative determination of H₂ evolution

The quantity of evolved H₂ was determined using gas chromatography-thermal conductivity detector (GC-TCD 2014, Shimadzu) respectively. We analyzed the area counts for the peaks, and the gas was identified using the calibrated carrier times. The reaction system is same as photoelectrochemical reaction system except that 0.9 mL of N₂ gas was injected into the sealed cathodic chamber instead of the continuous N₂ bubbling as shown in Figure S1. The GC-TCD was equipped with a 6.0 m packed column (Shincarbon ST 50/80, Shimadzu), and Ar flowed at 30 mL/min as the carrier gas. After the irradiation of Xe light (410-800 nm) into the anode for 6 hours, 10.0 μL of the evolved gas from the cathodic chamber was injected. The column and sample injections were performed at 120°C and 200°C, respectively. The detector temperature was 200°C. The amount of evolved H₂ and the FE were estimated as 75 nmol and 48%, respectively.

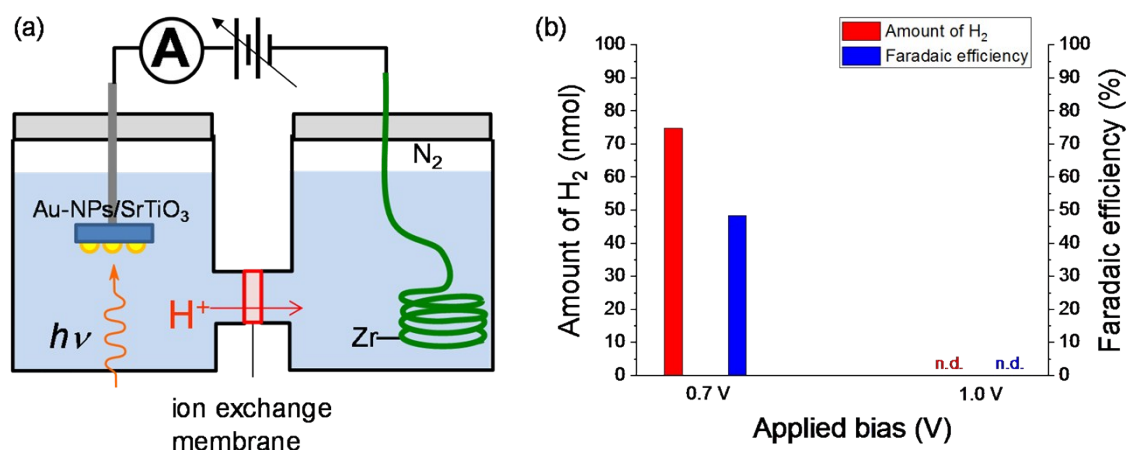


Figure S1. (a) The schematics of the reaction cell for H₂ production measurement using Au-NPs/SrTiO₃|Zr coil. The cathodic chamber was bubbled with N₂ with 200 sccm for 15 min and sealed before the reaction. The cathodic chamber was filled with 9.1 mL H₂SO₄aq (pH3) and 0.9 mL N₂ gas. The applied bias was 0.7-1.0 V, and the irradiation wavelength was from 410 to 800 nm. (b) The amount of H₂ after 6 h irradiation and the Faradaic efficiencies for H₂ production. n.d. indicates the detection limit of GC-TCD (less than 2 nmol of H₂).

2. Electrochemical analysis of NH₃ formation

The electrochemical analysis of N₂ reduction on the cathode was performed using the same equipment as the photoelectrochemical reaction except for using the conventional three-electrode system. Zr wire was used as a working electrode. Pt wire and Ag/AgCl electrodes were used as a counter and reference electrode, respectively. The N₂ or Ar was bubbled in the cathodic chamber with 50 sccm during the reaction. Figure S2 shows that quasi-steady state current as functions of applied potential under N₂ (I_{N_2}) and Ar (I_{Ar}) bubbling conditions, and the current enhancement by N₂ calculated as $(I_{N_2}-I_{Ar})/I_{N_2}$.

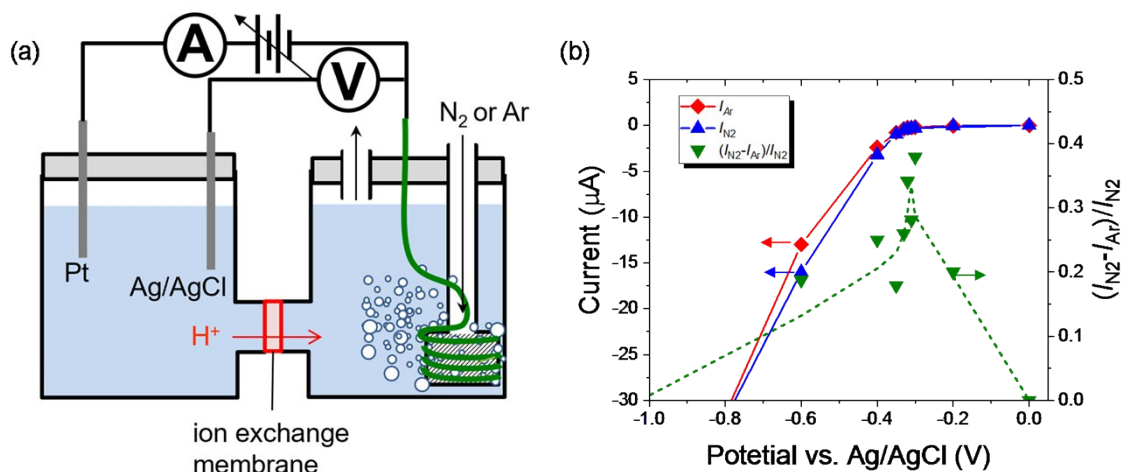


Figure S2. I - V characteristics of zirconium working electrode under N₂ and Ar bubbling (a), and the current enhancement under N₂ bubbling compared to Ar bubbling (b). The broken line in green is adjacent-averaging fitting of the current enhancement.

3. Time dependence of pH during NH₃ photosynthesis reaction

To understand the proton transportation, we measured pH changes as a function of reaction time (Figure S3). The reaction system shown in Figure 1b was employed. The pH value was measured by a pH meter (AS600, AS ONE). As a result, the pH increment (lack of proton) was not observed during the reaction.

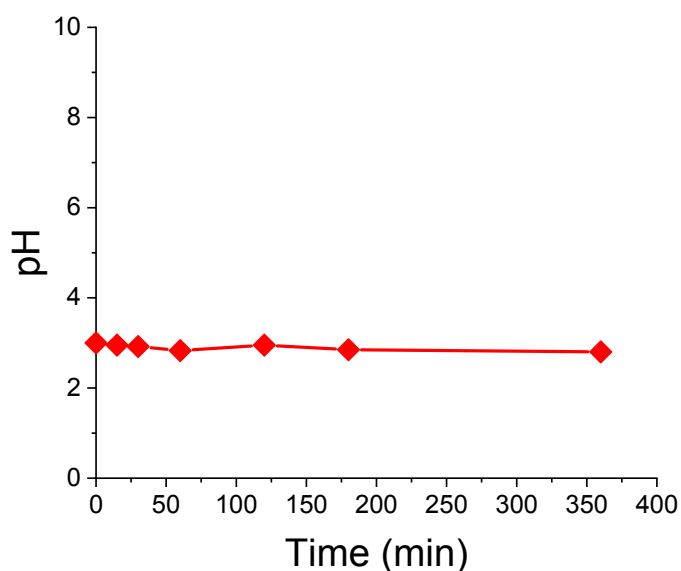


Figure S3. The time dependence of pH during NH₃ photosynthesis reaction. The applied bias was 1.0 V, and the irradiation wavelength was from 410 to 800 nm.

4. Evaluation of NH₃ and N₂H₄

NH₃ and N₂H₄ were quantified according to the procedure written in the experimental section in the main manuscript. Figure S4 shows typical absorption spectra and the calibration curves for the estimation of NH₃ and N₂H₄.

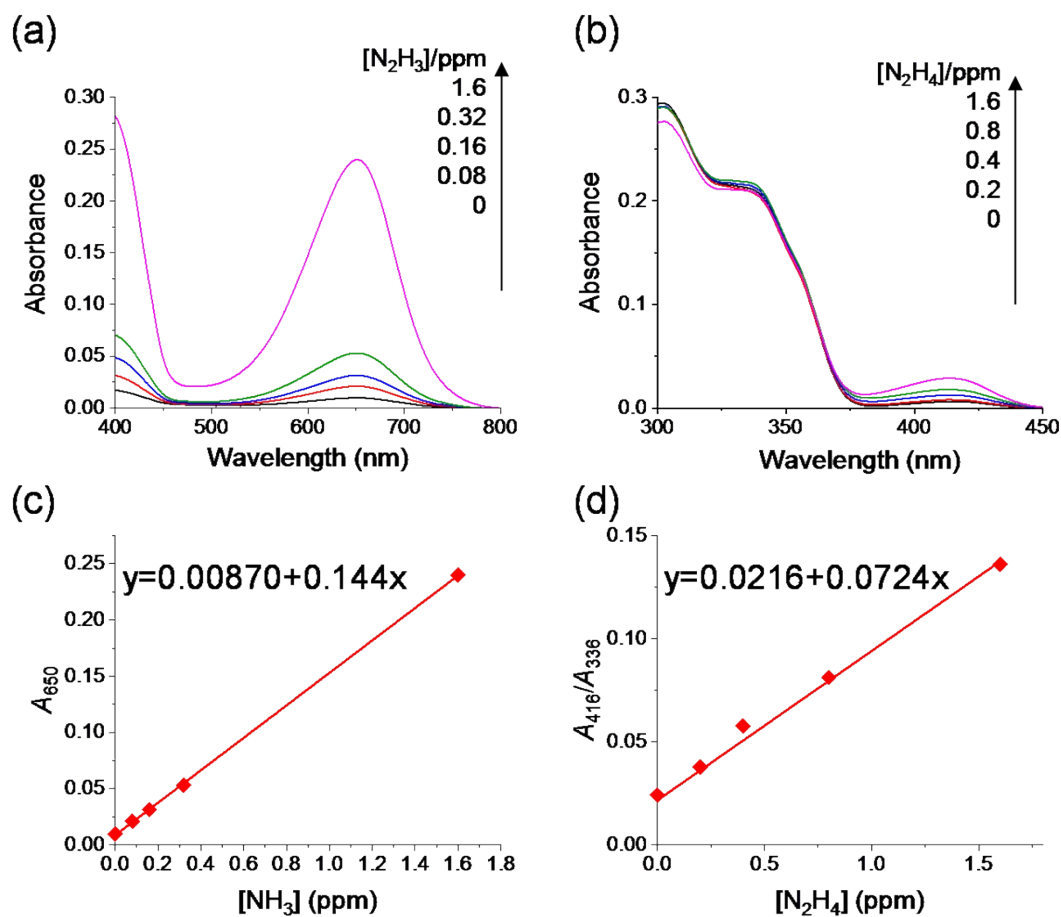


Figure S4. Absorption spectra for NH₃ (a) and N₂H₄ (b) estimation. The calibration curves for NH₃ (a) and N₂H₄ (b) quantification. A_{650} , A_{416} , A_{336} indicate the absorbance at the wavelength of 650, 416, and 336 nm, respectively.

5. Reaction scheme for CHCL synthesis and N₂H₄ detection

Scheme S1. Synthesize and degradation of 3-cyanocumarin-7-levulinate

