

Electronic Supplementary Information

Morphology-dependent electrocatalytic nitrogen reduction on Ag triangular nanoplates

Wen-Yan Gao, Yu-Chen Hao, Xin Su, Li-Wei Chen, Tong-An Bu, Nan Zhang, Zi-Long Yu, Zhejiaji Zhu and An-Xiang Yin*

W. Y. Gao, Y. C. Hao, X. Su, L. W. Chen, T. A. Bu, N. Zhang, Z. L. Yu, Z. Zhu, Prof. A. X. Yin
Ministry of Education Key Laboratory of Cluster Science, Beijing Key Laboratory of
Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering,
Beijing Institute of Technology, Beijing 100081 (P. R. China)
E-mail: yin@bit.edu.cn

Materials and Methods

Chemicals

Sodium borohydride (NaBH_4), potassium sulfate (K_2SO_4 , 99%), carbon black (CB) were all purchased from Alfa Aesar (USA). Sulfuric acid (H_2SO_4 , 98%), silver nitrate (AgNO_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 98%) and hydrogen peroxide (H_2O_2 , 30 wt%) were purchased from Beijing Chemical Reagent Co. Ltd. (Beijing, China). Nafion (5% in methanol) was purchased from Sigma-Aldrich (USA). The carbon paper (CP) was purchased from TORAY. The Nessler's reagent was purchased from Aladdin (China). The water (18 M Ω cm) used in all experiments was prepared by passing through an ultra-pure purification system (Milli-Q). All chemicals are of analytical grade without any further purification. High-purity nitrogen (N_2 , 99.9999%) and argon (Ar , 99.9999%) were purchased from Beijing AP BAIF Gases Industry Co., Ltd (Air Products).

Preparation of Ag triangular nanoplates (AgTPs) and Ag nanoparticles (AgNPs)

AgTPs were prepared through a modified method reported previously.^[1–3] Typically, a 24.75 mL aqueous solution containing silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL) and H_2O_2 (30 wt%, 60 μL) was vigorously stirred at room temperature. Sodium borohydride (NaBH_4 , 100 mM, 250 μL) was rapidly injected into the mixture solution to initiate the reduction of Ag^+ , immediately leading to a light-yellow solution. After about 3 min, the colloidal solution turned to deep yellow. Afterwards, the solution color changed from deep yellow to red, green, and finally blue in 2–3 min. The resulting product was collected by centrifugation and washed with deionized water. The preparation of AgNPs was similar to that for the AgTPs except that no H_2O_2 was added to the synthesis solution. The obtained nanocrystal dispersions were mixed with 2 mg of CB and sonicated for 40 minutes, centrifuged and washed with deionized water for three times.

Structure and composition characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex 600 diffractometer with a $\text{Cu-K}\alpha$ X-ray radiation source ($\lambda = 0.154056$ nm) at the scan rate of 1 $^\circ/\text{min}$. Transmission electron microscopy (TEM) studies were performed on a JEM-2100 (JEOL, Japan) transmission electron microscope operating at 200 kV. All the absorbance of samples was measured by the UV-vis spectrophotometer (Shimadzu, UV-2600).

Electrochemical tests

All the electrochemical measurements were carried out in a standard two-compartment cell (H cell) using saturated calomel electrode (SCE) as the reference electrode, a platinum plate as the counter electrode and the catalyst loading carbon paper as the working electrode. In a typical test, 3.04 mg of

CB-supported Ag catalysts (1.04 mg of Ag catalyst and 2 mg of CB) were dispersed in a mixed solvent containing 200 μL of deionized water, 64 μL of ethanol and 32 μL of Nafion to form a homogeneous ink after 1 h of sonication. The catalysts were then applied to a carbon paper ($0.6 \times 1.2 \text{ cm}^2$) with a total loading of 0.15 mg through the dip-coating method. The working electrodes (Ag/CB/CP) were dried in Argon at room temperature before testing. The Nafion 115 membrane separating the cathodic was pretreated in boiled 5% H_2O_2 solution for 1 h, then in boiled 0.5 M H_2SO_4 solution for another 1 h, and finally washed with deionized water for several times. All potentials in this study were measured against the SCE and converted to the reversible hydrogen electrode (RHE) reference scale.

$$\text{Potential (V vs RHE)} = \text{Applied potential (V vs SCE)} + 0.241 \text{ V} + 0.0592 \times \text{pH} \quad (1)$$

The electrochemical nitrogen reduction was carried out in N_2 -saturated acidic 0.5 M K_2SO_4 solution (pH = 3.5) at room temperature and pressure. To produce enough ammonia for quantification, the electrolysis reaction was kept for 4000 s or even longer. Before electrolysis, we bubbled high-purity N_2 (99.9999%) gas into the cathodic electrolyte for at least 30 min to realize nitrogen gas saturation.

Linear sweep voltammogram (LSV) curves were collected at a scan rate of 50 mV s^{-1} . N_2 (99.9999%) was continuously bubbled into the cathodic electrolyte with magnetic stirring (300 rpm) during the electrolysis measurements. Electrochemical measurements with Ar as gas supply were carried out under the same experiment condition. All current densities were normalized to the geometrical area of electrode.

Quantification of NH_3 using Nessler's reagents

The concentration of produced NH_3 was spectrophotometrically determined by colorimetric assays using the Nessler's reagent. Before UV-vis adsorption tests, all the test solution was kept in dark place at 25°C for 20 min. Then we took the absorbance test at 420 nm with a UV-vis spectrophotometer (Shimadzu, UV-2600). The calibration curve (ammonium concentration versus absorbance) was plotted by measuring the UV-vis absorbance at 420 nm of series reference solutions at known concentrations of NH_4Cl . The concentration of ammonia in electrolytes can be calculated through the standard curve.

Quantification of NH_3 using indophenol-blue method

The quantity of the produced ammonia could also be measured with the indophenol-blue method.^[4] Typically, 2 mL of sample solution was taken from the cathodic compartment and transferred into a 10 mL plastic tube. Then, 2 mL of 1 M NaOH solution (containing 5% salicylic acid and 5% sodium citrate), 1 mL of 0.05 M NaClO and 0.2 mL of 1% $\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$ were added into the above solution. After being kept in dark at 25°C for 2 h, the UV-Vis absorption at the wavelength of 660 nm

for the solution was measured. The calibration curve was calibrated using standard NH_4Cl solution with a series of concentrations. The concentration of ammonia in the electrolytes can be calculated through the standard curve.

Quantification of N_2H_4 using Watt and Chrisp method

Typically, a mixture solution of hydrochloric acid (concentrated, 30 mL), ethanol (300 mL) and 4-(dimethylamino) benzaldehyde (5.99 g) was used as color reagent. A series of reference solutions with suitable $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ concentrations were made to measure their UV-vis absorbance at 455 nm to obtain the calibration curve. After ENRR experiments, 5 mL of electrolyte was pipetted out and mixed with 5 mL of the above as-prepared color reagent.^[4] Then, the mixture solution was kept under dark condition at 25 °C for 20 min before UV-vis adsorption tests. At last, the concentration of hydrazine in electrolytes was calculated via the as-obtained calibration curve.

Nuclear magnetic resonance (NMR) measurements

After electrochemical nitrogen reduction reactions, 100 μL of 20% DMSO- d_6 (Sigma) was mixed with 500 μL of the resultant electrolytes and then measured with a Bruker Ascend 700-MHz NMR system.

Faradaic efficiency calculation

The NH_3 concentration was calculated from the calibration curve and the NH_3 yield (r) normalized to catalyst (Ag) mass was calculated using the following equation:

$$r = (17 \times c(\text{NH}_3) \times V) / (m \times t) \quad (2)$$

The Faradic efficiency (FE) for N_2 reduction could be calculated as follows:

$$\text{FE} = [3 \times F \times c(\text{NH}_3) \times V / Q] \times 100\% \quad (3)$$

where the amount of the produced ammonia is in mole measured by colorimetry with Nessler's reagent, F is the Faradaic constant (96485 C mol^{-1}), V is the volume of the electrolytes in the cathodic compartment, m is the mass of catalyst (Ag), t is the total reaction time for nitrogen reduction, and Q is the electric charge (in C).

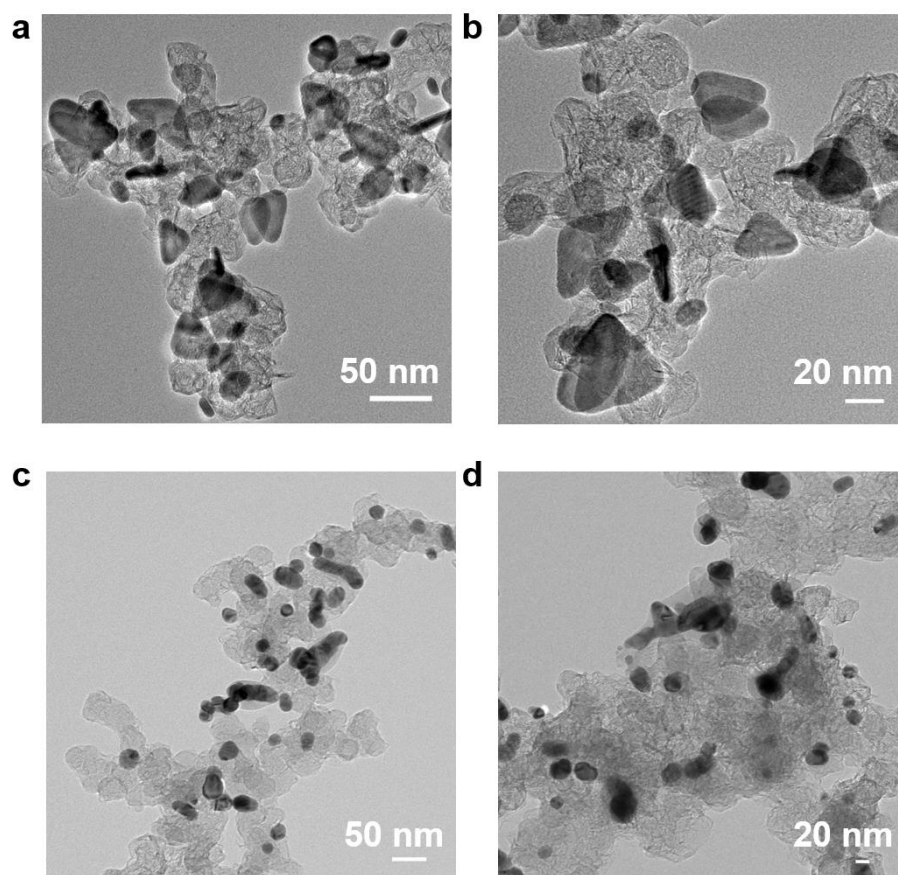


Fig. S1 Transmission electron microscopy (TEM) images for the carbon black (CB) supported Ag catalysts. (a–b) AgTPs/CB and (c–d) AgNPs/CB.

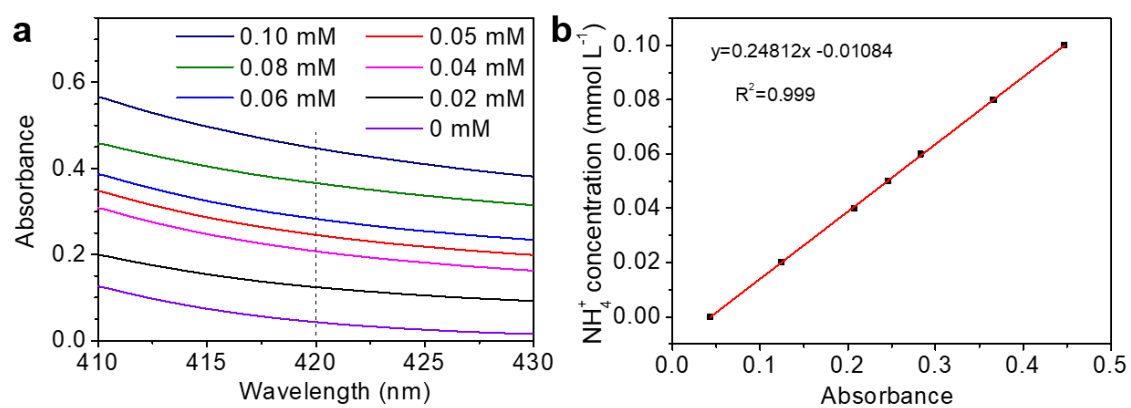


Fig. S2 UV-vis measurements of the concentrations of ammonium in standard solutions with Nessler's reagents. (a) UV-vis spectra for standard solutions. (b) Calibration curve for ammonium concentration vs absorbance. $R^2 = 0.999$.

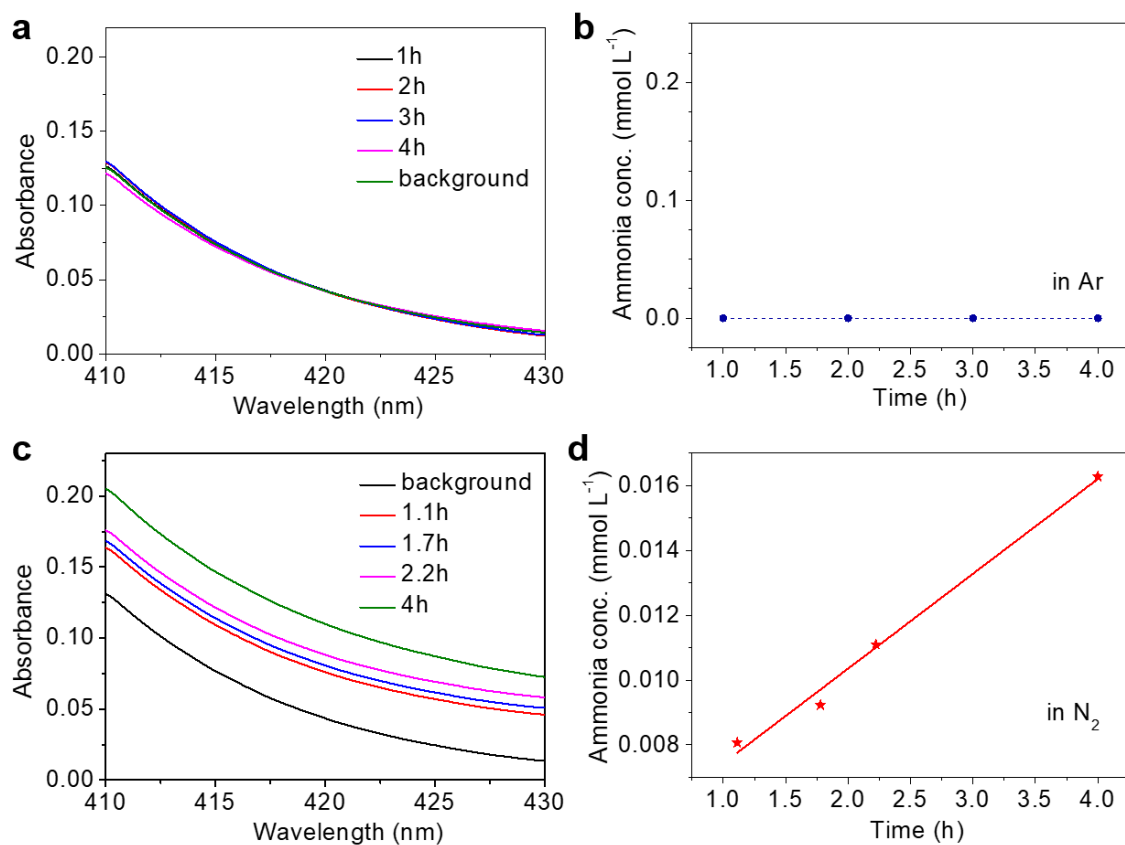


Fig. S3 UV-vis measurements of the electrolytes with Ar and N₂ as gas feed, respectively. (a) UV-vis spectra for electrolytes after electro-reduction reactions under Ar atmosphere. (b) None ammonium can be detected during the 4 h of electrolysis reduction. (c) UV-vis spectra for after nitrogen electro-reduction reactions with N₂ as feed gas. (d) Ammonia yield increases linearly with time.

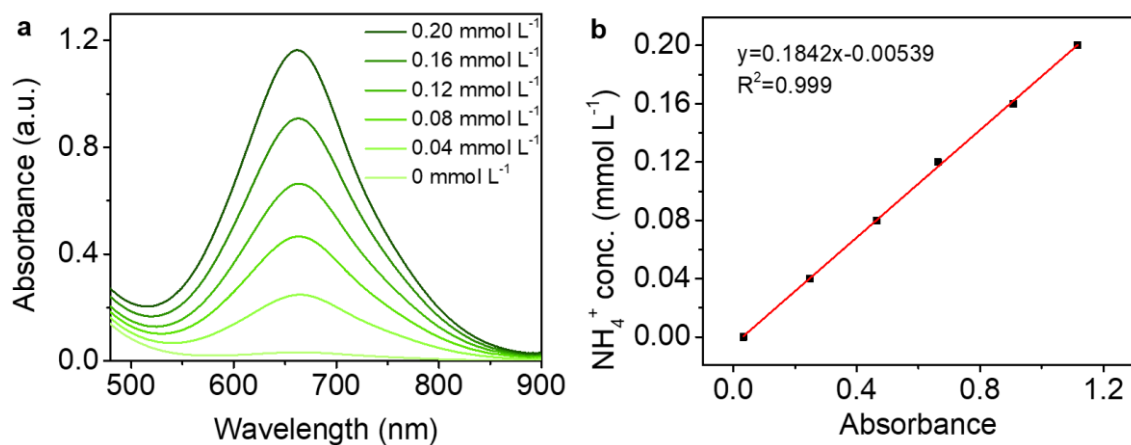


Fig. S4 UV-vis measurements of the concentrations of ammonium in standard solutions with the indophenol-blue method. (a) UV-vis spectra for standard solutions. (b) Calibration curve for ammonium concentration vs absorbance at 660 nm. $R^2 = 0.999$.

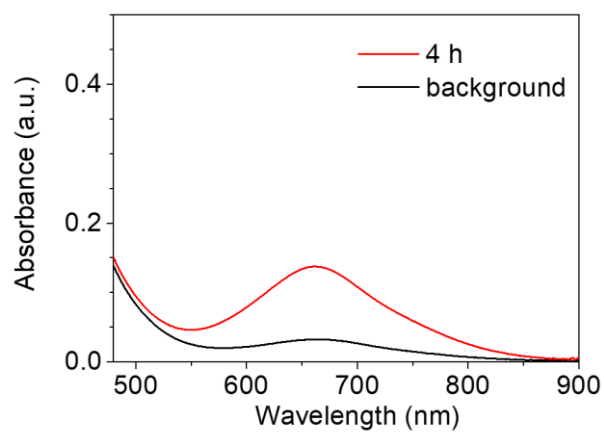


Fig. S5 UV-vis spectra for electrolytes after 4 h of nitrogen reduction reactions. The corresponding FE for ammonia was calculated to be 23.9% with the ammonia yield of $56.5 \text{ mg g}_{\text{Ag}}^{-1} \text{ h}^{-1}$.

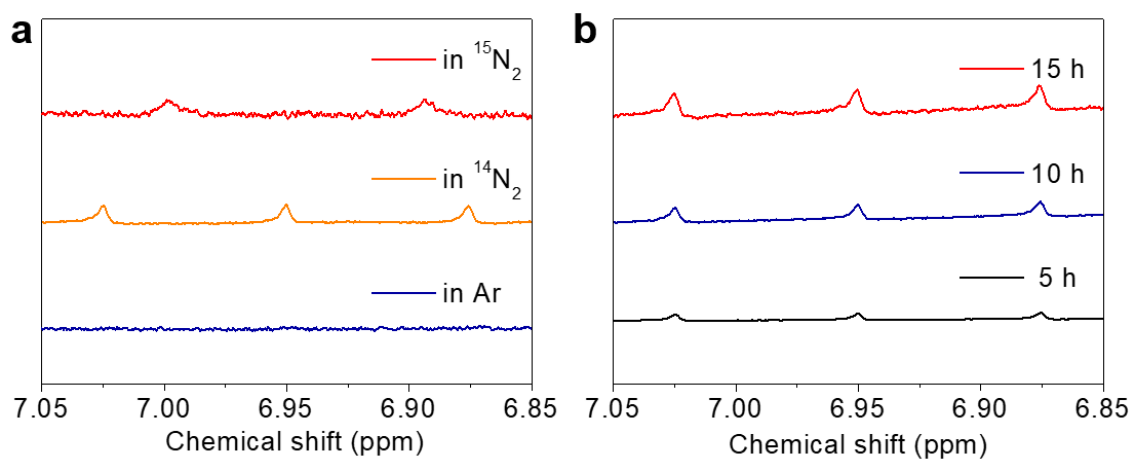


Fig. S6 NMR & isotope-labelled experiments. (a) NMR spectra for the resultant electrolytes after 5 h of electrolysis with $^{15}\text{N}_2$, $^{14}\text{N}_2$ and Ar as feed gas, respectively. (b) NMR spectra for NH_4^+ in the electrolytes extracted from the ENRR system at 5, 10 and 15 h, respectively, showing the increasing amount of NH_4^+ during the electroreduction reaction.

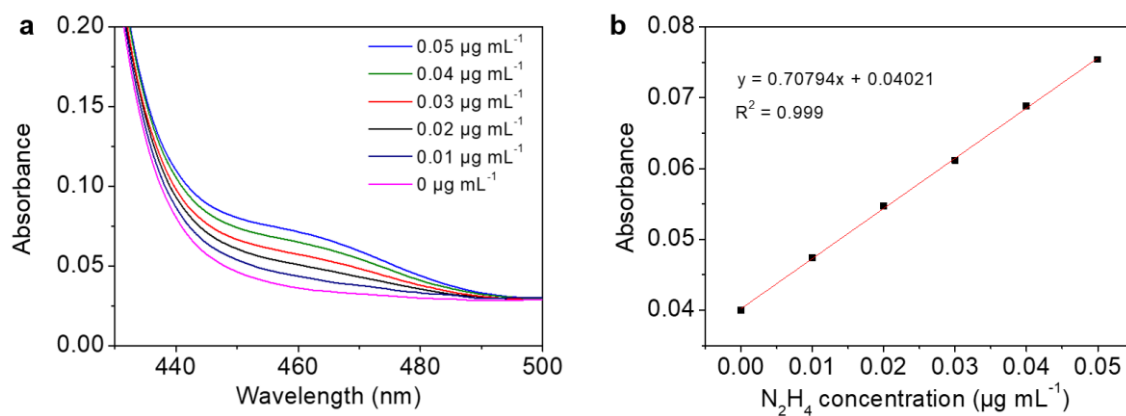


Fig. S7 Quantification of N_2H_4 with the Watt and Chrisp method. (a) UV-vis spectra for standard solutions. (b) Calibration curve for N_2H_4 concentrations. $R^2 = 0.999$.

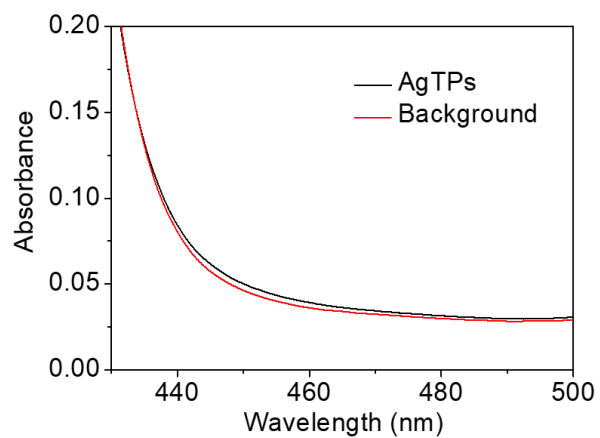


Fig. S8 UV-vis absorption spectra for the electrolytes after 7000 s of electrolysis at -0.25 V for hydrazine quantification. Negligible hydrazine could be found ($\text{FE} < 0.4\%$).

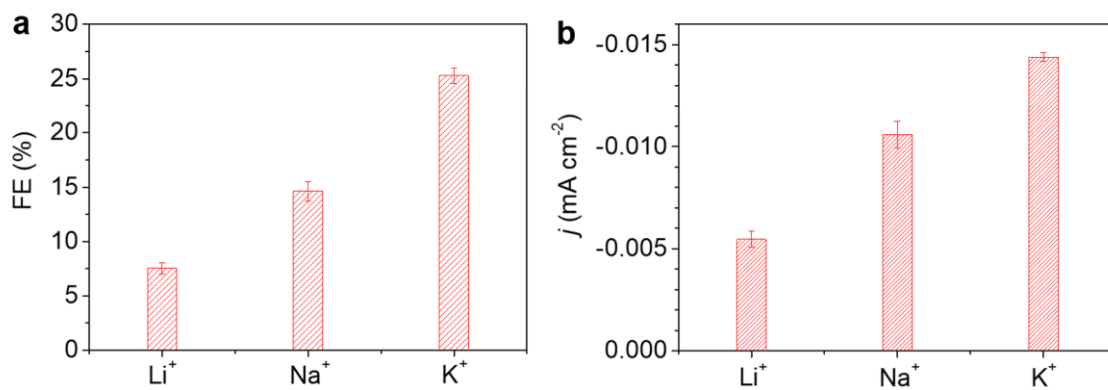


Fig. S9 Promotion of nitrogen reduction by different alkali metal cations (e.g. Li⁺, Na⁺, K⁺) (1.0 mol L⁻¹). (a) FE for ENRR on AgTPs at -0.25 V vs RHE. K⁺ cations exhibited superior ENRR promotion to the other two alkali metal cations. Na⁺ and Li⁺ cations showed lower FE of 15.64% and 7.35%, respectively. (b) Effective current density for ENRR on AgTPs at -0.25 V vs RHE.

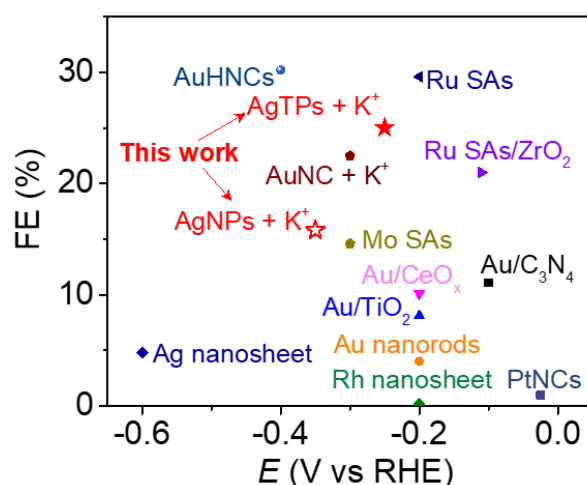


Fig. S10 Comparison in the ENRR selectivity for typical transition metal catalysts in aqueous solutions under ambient conditions. AgTPs (FE = 25% at -0.25 V, solid star, this work), AgNPs (FE = 16% at -0.35 V, open star, this work), AuHNCs (FE = 30.2% at -0.4 V, *Nano Energy* 2018, **49**, 316–323), RuSAs (FE = 29.6% at -0.2 V, *Adv. Mater.* 2018, **30**, 1803498), RuSAs/ZrO₂ (FE = 21% at -0.11 V, *Chem.* 2019, **5**, 204–214), AuNC (FE = 22.5% at -0.3 V, *Nat. Catal.* 2019, **2**, 448–456), MoSAs (FE = 14.6 ± 1.6% at -0.3 V, *Angew. Chem. Int. Ed.* 2019, **58**, 2321–2325), Au/CeO_x (FE = 10.1% at -0.2 V, *Adv. Mater.* 2017, **29**, 1700001), Au/C₃N₄ (FE = 11.1% at -0.1 V, *Sci. Bull.* 2018, **63**, 1246–1253), Au/TiO₂ (FE = 8.11% at -0.2 V, *Adv. Mater.* 2017, **29**, 1606550), Au nanorods (FE = 4.02% at -0.2 V, *Adv. Mater.* 2017, **29**, 1604799), Ag nanosheets (FE = 4.8% at -0.6 V, *Chem. Commun.* 2018, **54**, 11427–11430), Rh nanosheets (FE = 0.217% at -0.2 V, *J. Mater. Chem. A* 2018, **6**, 3211–3217), PtNCs (FE = 1.0% at -0.025 V, *Nat. Catal.* 2019, **2**, 448–456).

Table S1. The metal content of the as-prepared metal/CB catalysts determined by ICP-AES and the metal loading on working electrodes

Sample	Metal content (wt.%)	Ag/CB loading on CP (μg)	Ag loading on CP (mg cm^{-2})
AgTPs/CB on CP	25.3	150.0	0.053
AgNPs/CB on CP	25.0	150.0	0.052

Table S2. Quantification of ion content in electrolytes before and after reaction by ion chromatography method.

Sample	NH_4^+ (mg L ⁻¹)	NO_3^- (mg L ⁻¹)	NO_2^- (mg L ⁻¹)
1	<0.05 (50 ppb)	<0.05 (50 ppb)	<0.05 (50 ppb)
2	<0.05 (50 ppb)	<0.05 (50 ppb)	<0.05 (50 ppb)
3	0.32	<0.05 (50 ppb)	<0.05 (50 ppb)

No detectable NH_4^+ , NO_3^- or NO_2^- could be found (i.e. the concentrations were well below the detection limit of ion chromatography, <50 ppb) in the electrolytes (30 mL) bubbled by direct nitrogen flow (Sample 1, 50 mL min⁻¹, 4 h) or cycling nitrogen (Sample 2, 1 L, 4 h).

After 4 hours of electrolysis reaction, a significant increase (0.32 mg L⁻¹) in ammonia concentration could be detected in the electrolyte (Sample 3) while no NO_3^- or NO_2^- could be found.

The corresponding FE was calculated to be 25.7%, which was in well agreement with the results acquired by the colorimetric methods.

Table S3. ENRR Performance for typical transition metal electrocatalysts.

Catalyst	Electrolyte	T (°C)	Potential (V vs RHE)	NH ₃ yield	FE (%)	Ref.
AgTPs	0.5 M K ₂ SO ₄ pH = 3.5	25	−0.25	58.5 mg g _{Ag} ^{−1} h ^{−1}	25	This work
AgNPs	0.5 M K ₂ SO ₄ pH = 3.5	25	−0.35	38 mg g _{Ag} ^{−1} h ^{−1}	16	This work
Ag nanosheet	0.1 M HCl	25	−0.6	1.66 × 10 ^{−7} mol cm ^{−2} h ^{−1}	4.8	4
Au nanorod	0.1 M KOH	25	−0.2	1.648 μg cm ^{−2} h ^{−1}	4.02	5
Au/TiO ₂	0.1 M HCl	20	−0.2	21.4 mg g _{cat} ^{−1} h ^{−1}	8.11	6
Au/CeO _x -rGO	0.1 M HCl	RT	−0.2	8.3 mg g _{cat} ^{−1} h ^{−1}	10.1	7
Au/C ₃ N ₄	5 mM H ₂ SO ₄	RT	−0.1	1305 mg g _{Au} ^{−1} h ^{−1}	11.1	8
MoSAs	0.1 M KOH	RT	−0.3	(34.0 ± 3.6) mg g _{cat} ^{−1} h ^{−1}	14.6 ± 1.6	9
AuHNCs	0.5 M LiClO ₄	20	−0.4	3.9 μg cm ^{−2} h ^{−1}	30.2	10
Rh nanosheet	0.1 M KOH	25	−0.2	23.88 mg g _{cat} ^{−1} h ^{−1}	0.217	11
RuSAs@ZrO ₂	0.1 M HCl	RT	−0.11	3665 mg g _{Ru} ^{−1} h ^{−1}	21	12
RuSAs/N-C	0.05 M H ₂ SO ₄	RT	−0.2	120.9 mg g _{cat} ^{−1} h ^{−1}	29.6	13
AuNCs/CB	0.5 M K ₂ SO ₄ pH = 3.5	25	−0.3	13 mmol g _{Au} ^{−1} h ^{−1}	22.5	14
PtNCs	0.5 M K ₂ SO ₄ pH = 3.5	25	−0.025	1.3 mmol g _{Pt} ^{−1} h ^{−1}	1.0	14

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