

Coupling Cu with Au for enhanced electrocatalytic activity of nitrogen reduction reaction

Yongqin Liu^{a,b}, Liang Huang^b, Xinyang Zhu^b, Youxing Fang^b and Shaojun Dong^{*,a,b}

^aCollege of Chemistry, Jilin University, Changchun, Jilin 130012, P.R. China

^bState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, Jilin 130022, P.R. China

*Corresponding author E-mail: dongsj@ciac.ac.cn

Experimental section

Ammonia determination

The absorbance of the produced NH_3 was spectrophotometrically quantitatively determined via indophenol blue method. In this method, ammonia reacted with phenol and hypochlorite in alkaline solution, sodium nitroferricyanide as the catalyst, producing blue-green indophenol blue dye for quantitative determination. In detail, the electrolyte (2 mL) after NRR test was mixed thoroughly with NaOH (2 mL) solution containing salicylic acid and sodium citrate, NaClO (1 mL, 0.05 mol L^{-1}) and $\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$ (0.2 mL, 1 wt%), then the mixed solution was preserved undisturbed for 2 h at room temperature. The absorbance of produced indophenol blue was measured by UV-Vis spectrophotometer at a wavelength of 655 nm. Meanwhile, the absorbance of the blank sample was subtracted for background correction. The calibration curve was obtained using a series of known concentrations of NH_4^+ as standard in 0.05 mol L^{-1} H_2SO_4 solution. Then, the determined concentration of NH_4^+ could be calculated from the linear equation (Absorbance = $0.369 C_{\text{NH}_4^+} + 0.0233$, $R^2 = 0.9999$). The measurements of background solution were performed in all spectrum experiments.

Hydrazine determination

In an acidic environment, hydrazine (N_2H_4) could react with p-dimethylaminobenzaldehyde to produce yellow compounds with the absorption spectrum at a wavelength of 455 nm, which served as the basis for spectrophotometric determination of hydrazine. The preparation of the color reagent was as follows: p-dimethylaminobenzaldehyde (0.8 g) was dissolved in anhydrous ethanol (40.0 mL) and hydrochloric acid (12 mol L^{-1} , 4.0 mL) mixture solution. 5 mL electrolyte after 2 h electrolysis was added into as-obtained color reagent (5 mL) for 10 min at room temperature. Subsequently, the absorbance at 455 nm were measured

by UV-Vis spectrophotometer. For background correction, 10 mL electrolyte before electrolysis was measured likewise.

Faradic efficiency (FE) and NH₃ yield rate

The faradic efficiency of NRR is the ratio of the amount of electric charge consumed for the production of NH₃ to the total amount of charge through the electrode during the electrolysis process. FE can be calculated according to the following formula:

$$FE = 3 \times C_{NH_3} \times V_{electrolyte} \times F / (17 \times Q) \quad (1)$$

NH₃ yield rate formula as follows:

$$v_{NH_3} = C_{NH_3} \times V_{electrolyte} / (t \times m_{cat}) \quad (2)$$

Where constant 3 is the transfer electron number of produced NH₃, C_{NH_3} ($\mu\text{g mL}^{-1}$) is the concentration of produced NH₃, $V_{electrolyte}$ (20 mL in our work) is the volume of the H₂SO₄ electrolyte, F (96485 C mol⁻¹) is the Faraday constant, constant 17 is the molar mass of NH₃, Q (C) is the normalized area of current and time after electrolysis, t (2 h) is the time for electrolysis and m_{cat} ($3 \mu\text{L} \times 0.5 \text{ mg mL}^{-1}$) is the loading mass of electrocatalyst.

The obtained absorbance and Q value on Au₁Cu₁/GCE at -0.2 V were used for sample calculation. Sample data:

Potential	Abs-1	Abs-2	Abs-3	Q	C _{NH3-1}	C _{NH3-2}	C _{NH3-3}
-0.2 V	0.0319	0.0320	0.0317	0.0144	0.0233	0.0236	0.0228

For example, after 2 h electrolysis on Au₁Cu₁/GCE at -0.2 V, the obtained absorbance by three successive measurements with indophenol blue method at the wavelength of 655 nm are 0.0319 0.0320 and 0.0317, respectively. Based on the linear equation for NH₄⁺ determination (Absorbance = 0.369 C_{NH₄⁺} + 0.0233, R² = 0.9999), we can calculate the produced NH₄⁺ concentration (0.0233 $\mu\text{g mL}^{-1}$, 0.0236 $\mu\text{g mL}^{-1}$ and 0.0228 $\mu\text{g mL}^{-1}$). Therefore, we can obtain corresponding FE through formula (1):

$$\begin{aligned} FE &= 3 \times C_{NH_3} \times V_{electrolyte} \times F / (17 \times Q) \\ &= 3 \times 0.0233 \mu\text{g mL}^{-1} \times 20 \text{ mL} \times 96485 \text{ C mol}^{-1} / (17 \text{ g mol}^{-1} \times 0.0144 \text{ C}) \times 10^{-4} \% \\ &= 55.10\% \end{aligned}$$

$$\begin{aligned} \text{Similarly, } v_{NH_3} &= C_{NH_3} \times V_{electrolyte} / (t \times m_{cat}) \\ &= 0.0233 \mu\text{g mL}^{-1} \times 20 \text{ mL} / (2 \text{ h} \times 3 \mu\text{L} \times 0.5 \text{ mg mL}^{-1}) \\ &= 155.33 \mu\text{g h}^{-1} \text{ mg}_{cat}^{-1} \end{aligned}$$

So, we can calculate the NH₃ yield rate and corresponding FE at different potentials through the obtained NH₄⁺ concentration and Q value.

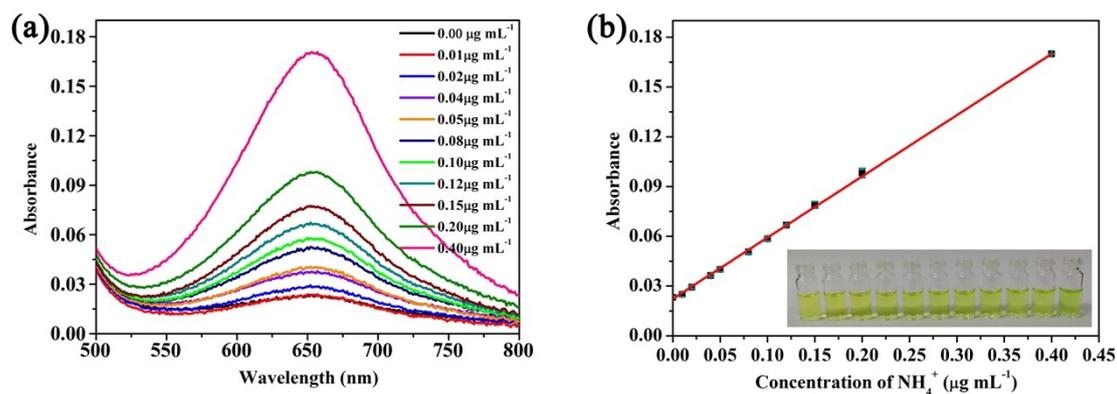


Fig. S1 (a) UV-Vis spectra of indophenol blue method with multiple known NH_4^+ concentrations after incubated for 2 h at room temperature. (b) Calibration curve is used to calculate the produced NH_4^+ concentration after 2h electrolysis in $0.05 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolyte.

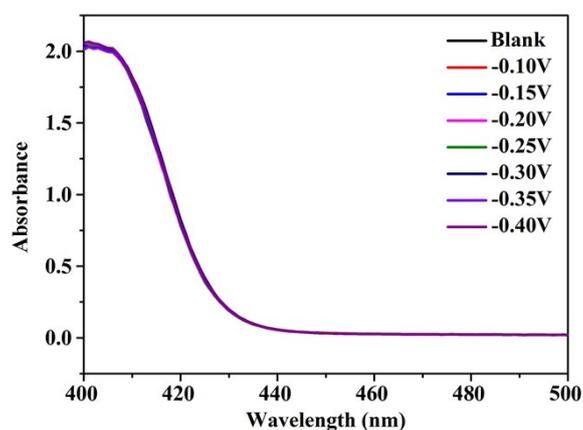


Fig. S2 UV-Vis spectra of the electrolyte after electrolysis for 2 h on $\text{Au}_1\text{Cu}_1/\text{GCE}$ at different potentials stained with the indicator for $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

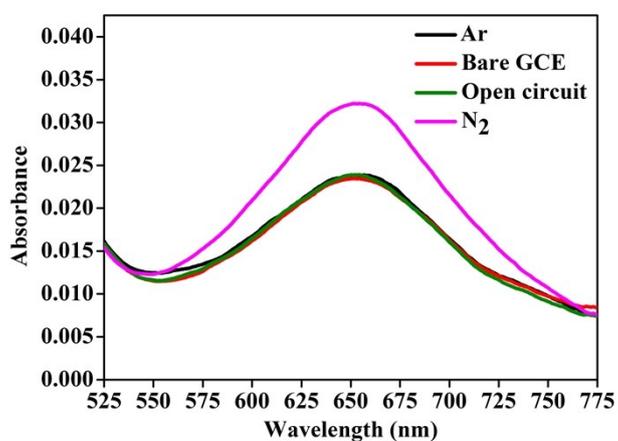


Fig. S3 UV-Vis spectra of the electrolyte after 2 h electrolysis stained with indophenol indicator.

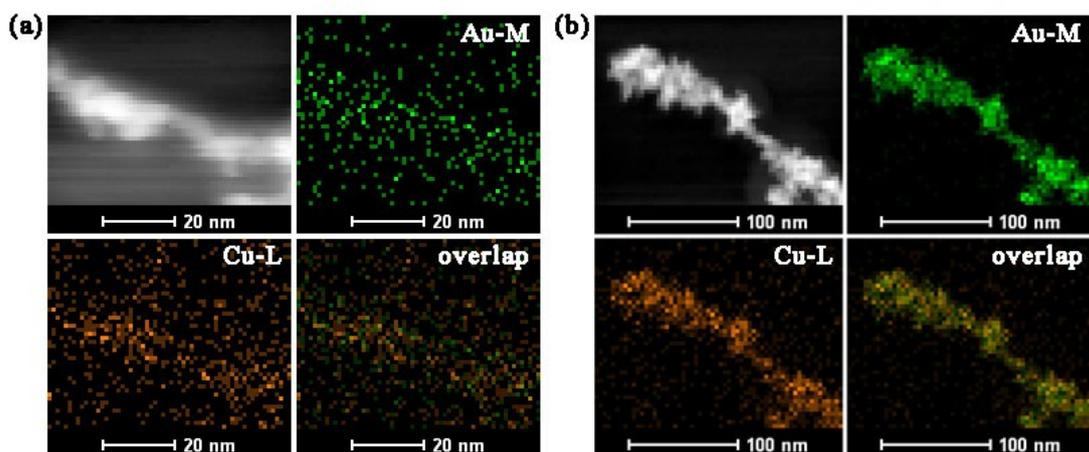


Fig. S4 (a, b) HAADF-STEM image and EDX mapping images of Au₃Cu₁ (a) and Au₁Cu₃ (b) nanowires.

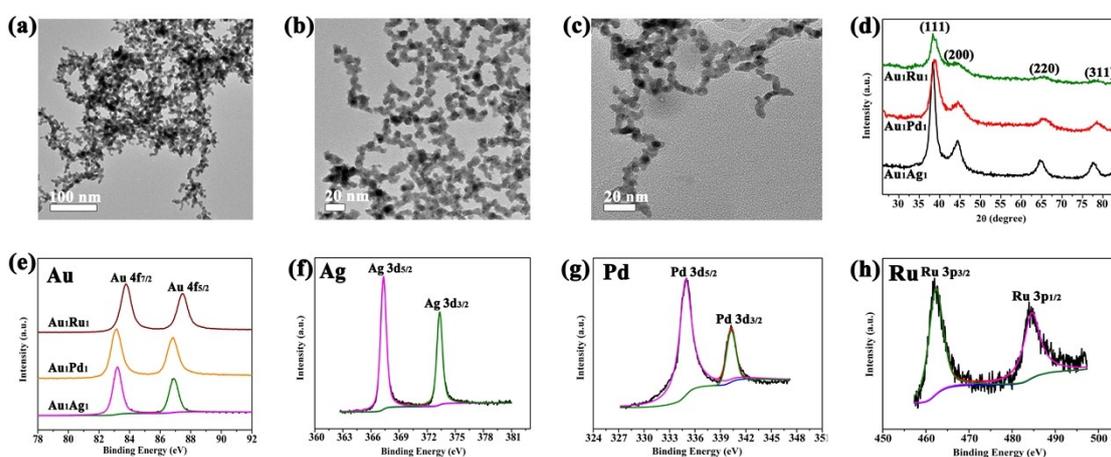


Fig. S5 (a-c) TEM images of Au₁Ag₁, Au₁Pd₁ and Au₁Ru₁ nanowires, respectively. (d) XRD patterns of Au₁Ag₁, Au₁Pd₁ and Au₁Ru₁ nanowires, respectively. (e-h) XPS spectra of Au 4f region (Au 4f_{7/2} and Au 4f_{5/2}) (e), Ag 2p region (Ag 3d_{5/2} and Ag 3d_{3/2}) (f), Pd 3d region (Pd 3d_{5/2} and Pd 3d_{3/2}) (g), and Ru 3p region (Ru 3p_{3/2} and Ru 3p_{1/2}) (h) of Au₁Ag₁, Au₁Pd₁ and Au₁Ru₁ nanowires.

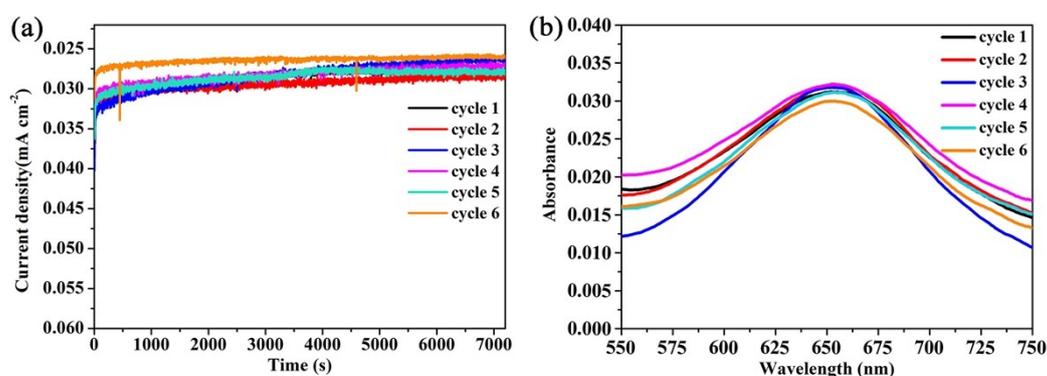


Fig. S6 (a) Cycling tests on Au₁Cu₁/GCE at -0.2 V; (b) corresponding UV-Vis spectra of the electrolytes after 2 h electrolysis stained with indophenol indicator.

Table S1. Comparison of the electrocatalytic NRR activity of Au₁Cu₁ nanocatalyst with other reported NRR catalysts under ambient condition.

Electrode Material	electrolyte	FE(%)	NH ₃ yield rate	Ref.
Au ₁ Cu ₁ /GCE	0.05 M H ₂ SO ₄	54.96	154.91 μg h ⁻¹ mg _{cat} ⁻¹	This work
PdCu/rGO	0.1 M KOH	0.6	2.8 μg h ⁻¹ mg ⁻¹ _{cat}	1
Pd-Co/CuO	0.1 M KOH	2.16	10.04 μg h ⁻¹ mg ⁻¹ _{cat}	2
PdRu nanorod	0.1 M HCl	2.4	34.2 μg h ⁻¹ mg ⁻¹ _{cat}	3
Ag nanosheet	0.1 M HCl	4.8	4.62×10 ⁻¹¹ mol s ⁻¹ cm ⁻²	4
AuAg@ZIF	THF-based electrolyte	18	0.61 μg h ⁻¹ cm ⁻²	5
TA-reduced Au/TiO ₂	0.1 M HCl	8.11	21.4 μg h ⁻¹ mg ⁻¹ _{cat}	6
THH Au NRs	0.1 M KOH	4.1	1.648 mg h ⁻¹ cm ⁻²	7
pAu/NF	0.1 M Na ₂ SO ₄	13.36	9.42 μg h ⁻¹ cm ⁻²	8
Au/C ₃ N ₄	5 mM H ₂ SO ₄	11.1	1,305 μg h ⁻¹ mg _{Au} ⁻¹	9
Au/CeO _x	0.1 M HCl	10.1	37.3 μmol h ⁻¹ mg _{Au} ⁻¹	10
AuHNCs/ITO	0.5 M LiClO ₄	30.2	3.9 μg cm ⁻² h ⁻¹	11
Au flowers	0.1 M HCl	6.05	25.57 μg h ⁻¹ mg ⁻¹ _{cat}	12
Ru SAs/N-C	0.05 M H ₂ SO ₄	29.6	120.9 μg h ⁻¹ mg ⁻¹ _{cat}	13
Ru NPs	0.01 M HCl	5.4	21.4 mg h ⁻¹ m ⁻²	14
Ru@ZrO ₂ /NC	0.01 M HCl	21	3.665 mg _{NH₃} h ⁻¹ mg _{Ru} ⁻¹	15
Bi/carbon black	pH 3.5, 1.0 M K ⁺	66	200 mmol NH ₃ g ⁻¹ h ⁻¹	16

References

1. M.-M. Shi, D. Bao, S.-J. Li, B.-R. Wulan, J.-M. Yan and Q. Jiang, *Advanced Energy Materials*, 2018, **8**, 1800124.
2. W. Fu, Y. Cao, Q. Feng, W. R. Smith, P. Dong, M. Ye and J. Shen, *Nanoscale*, 2019, **11**, 1379-1385.
3. H. Wang, Y. Li, D. Yang, X. Qian, Z. Wang, Y. Xu, X. Li, H. Xue and L. Wang, *Nanoscale*, 2019, **11**, 5499-5505.
4. H. Huang, L. Xia, X. Shi, A. M. Asiri and X. Sun, *Chemical Communications*, 2018, **54**, 11427-11430.
5. H. K. Lee, C. S. L. Koh, Y. H. Lee, C. Liu, I. Y. Phang, X. Han, C.-K. Tsung and X. Y. Ling, *Science Advances*, 2018, **4**, 3208.
6. M. M. Shi, D. Bao, B. R. Wulan, Y. H. Li, Y. F. Zhang, J. M. Yan and Q. Jiang, *Advanced Materials*, 2017, **29**.
7. D. Bao, Q. Zhang, F. L. Meng, H. X. Zhong, M. M. Shi, Y. Zhang, J. M. Yan, Q. Jiang and X. B. Zhang, *Advanced Materials*, 2017, **29**.

8. H. Wang, H. Yu, Z. Wang, Y. Li, Y. Xu, X. Li, H. Xue and L. Wang, *Small*, 2019, **15**, e1804769.
9. X. Wang, W. Wang, M. Qiao, G. Wu, W. Chen, T. Yuan, Q. Xu, M. Chen, Y. Zhang, X. Wang, J. Wang, J. Ge, X. Hong, Y. Li, Y. Wu and Y. Li, *Science Bulletin*, 2018, **63**, 1246-1253.
10. S. J. Li, D. Bao, M. M. Shi, B. R. Wulan, J. M. Yan and Q. Jiang, *Advanced Materials*, 2017, **29**.
11. M. Nazemi, S. R. Panikkanvalappil and M. A. El-Sayed, *Nano Energy*, 2018, **49**, 316-323.
12. Z. Wang, Y. Li, H. Yu, Y. Xu, H. Xue, X. Li, H. Wang and L. Wang, *ChemSusChem*, 2018, **11**, 3480-3485.
13. Z. Geng, Y. Liu, X. Kong, P. Li, K. Li, Z. Liu, J. Du, M. Shu, R. Si and J. Zeng, *Advanced Materials*, 2018, DOI: 10.1002/adma.201803498, e1803498.
14. D. Wang, L. M. Azofra, M. Harb, L. Cavallo, X. Zhang, B. H. R. Suryanto and D. R. MacFarlane, *ChemSusChem*, 2018, **11**, 3416-3422.
15. H. Tao, C. Choi, L.-X. Ding, Z. Jiang, Z. Han, M. Jia, Q. Fan, Y. Gao, H. Wang, A. W. Robertson, S. Hong, Y. Jung, S. Liu and Z. Sun, *Chem*, 2019, **5**, 204-214.
16. Y.-C. Hao, Y. Guo, L.-W. Chen, M. Shu, X.-Y. Wang, T.-A. Bu, W.-Y. Gao, N. Zhang, X. Su, X. Feng, J.-W. Zhou, B. Wang, C.-W. Hu, A.-X. Yin, R. Si, Y.-W. Zhang and C.-H. Yan, *Nature Catalysis*, 2019, **2**, 448-456.