

Supplementary Information

Facile Fabrication of Bimetallic Cu-Ag Binary hybrid Nanoparticles and their application in Catalysis

Yuxi Meng^a, Hanyu Gao^a, Shuang Li^a, Fang Chai^{*ab}, Lihua Chen^{*b}

^a Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province; Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, Harbin, 150025, Heilongjiang, China.

* Corresponding author. E-mail: fangchai@gmail.com

^b Shandong Key Laboratory of Biochemical Analysis; College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China.

E-mail: Lihuachen@qust.edu.cn

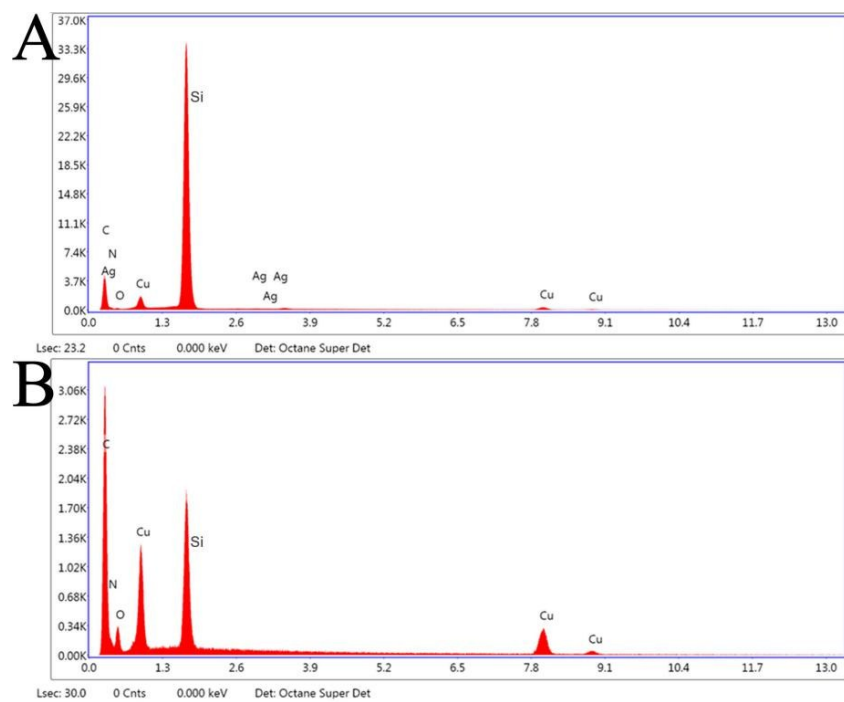


Fig. S1. EDS spectrum of (A) Trp-Cu-Ag NPs (B) Trp-Cu NPs. Both of the two sample were gained at 120 °C, 6 h.

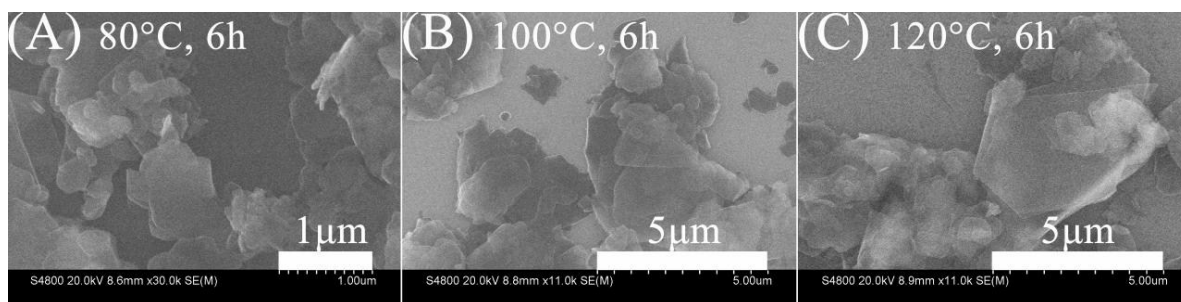


Fig. S2. SEM image of Trp-Cu NPs at different reaction condition: (A) 80 °C, 6 h; (B) 100 °C, 6 h; (C) 120 °C, 6 h.

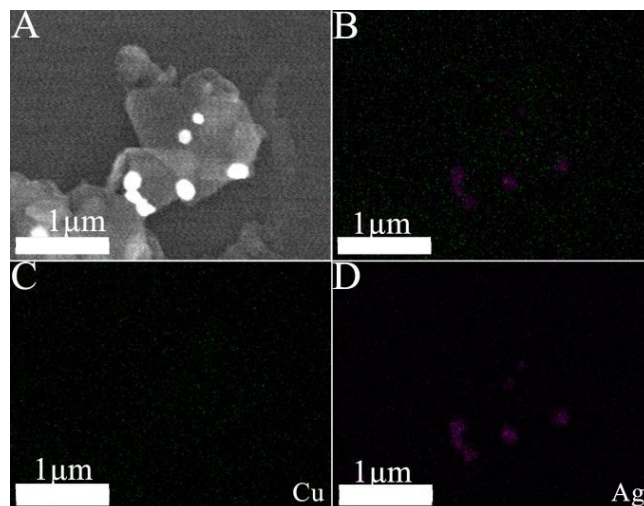


Fig. S3. Elemental mappings showing the spatial distribution of Cu (C, green), and Ag (D, pink) in a part of Trp-Cu-Ag NPs.

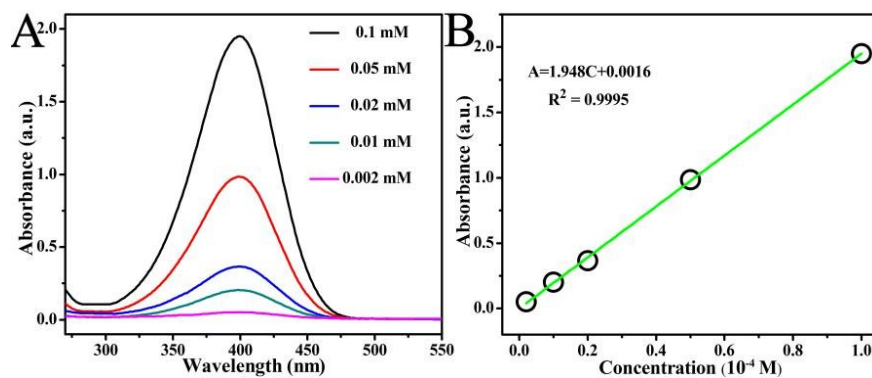


Fig. S4. Absorption spectra of aqueous mixture solutions of 4-NP and NaBH₄ at different concentrations of 4-NP. (b) Plot of the peak absorbance against the concentration of 4-NP.

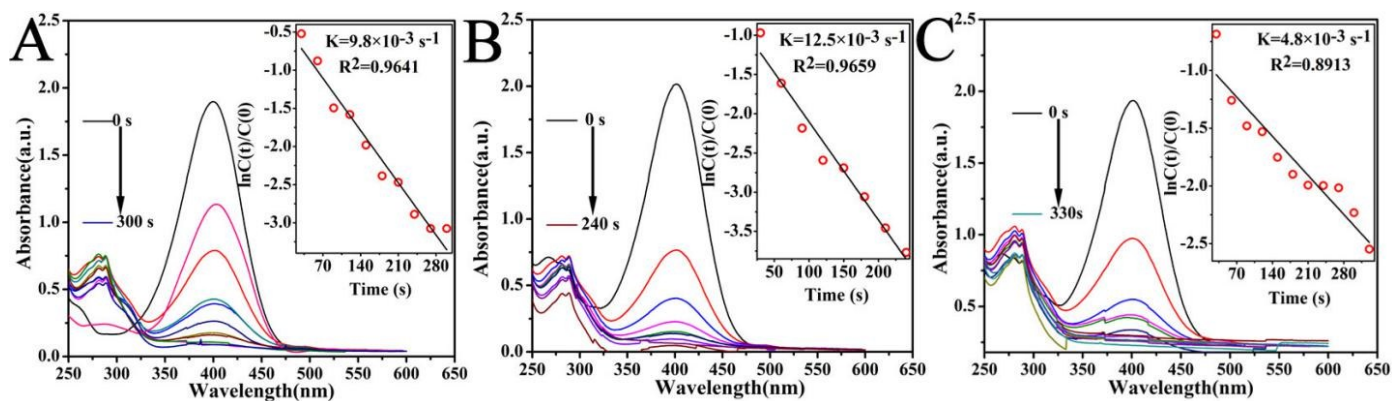


Fig. S5. UV-vis absorption spectra of reduction of 4-NP by NaBH_4 under the catalysis of Trp-Cu NPs reacted at various condition: (A) 80 °C, 6 h; (B) 100 °C, 6 h; (C); (D) 120 °C, 6 h. (Insets: the corresponding $\ln(C(t)/C(0))$ versus reaction time for reduction of 4-NP).

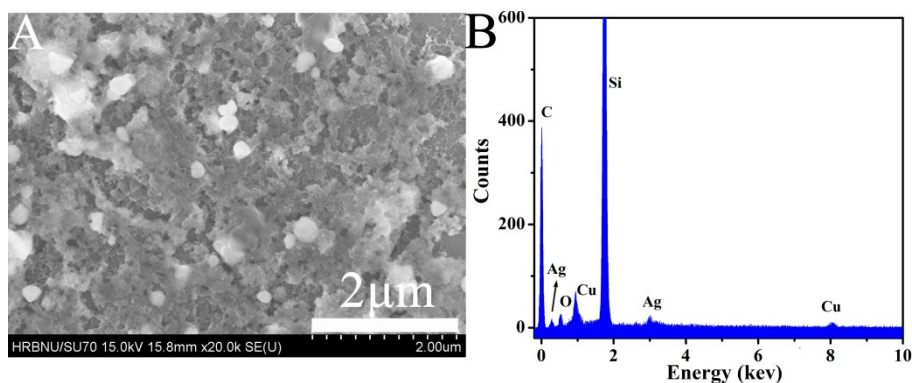


Fig. S6. (A) SEM image of Trp-Cu-Ag NPs after catalytic reduction of 4-NP for multiple (10) times circularly and (B) the corresponding EDS spectrum.

Table S1. React time and rate constant of reduction of 4-NP by NaBH₄ under the catalysis of Trp-Cu-Ag NPs reacted at various condition: (A) 80 °C, 2 h; (B) 80 °C, 4 h; (C) 80 °C, 6 h; (D) 100 °C, 2 h; (E) 100 °C, 4 h; (F) 100 °C, 6 h; (G) 120 °C, 2 h; (H) 120 °C, 4 h; (I) 120 °C, 6 h.

Sample		React time (t)	Rate constant (k)
80 °C	2 h	300 s	$14.5 \times 10^{-3} \text{ s}^{-1}$
80 °C	4 h	180 s	$21.1 \times 10^{-3} \text{ s}^{-1}$
80 °C	6 h	270 s	$15.4 \times 10^{-3} \text{ s}^{-1}$
100 °C	2 h	510 s	$5.1 \times 10^{-3} \text{ s}^{-1}$
100 °C	4 h	150 s	$27.4 \times 10^{-3} \text{ s}^{-1}$
100 °C	6 h	150 s	$33.9 \times 10^{-3} \text{ s}^{-1}$
120 °C	2 h	90 s	$37.9 \times 10^{-3} \text{ s}^{-1}$
120 °C	4 h	390 s	$8.7 \times 10^{-3} \text{ s}^{-1}$
120 °C	6 h	330 s	$13.0 \times 10^{-3} \text{ s}^{-1}$

Table S2. Comparison of pseudo-first-order rate constants for 4-NP reduction by metal nanomaterials containing Trp-Cu-Ag NPs.

Materials	Concentration of 4-NP	Amount of catalyst	K_{app}	References
Trp-Cu-Ag NPs	0.01 M	2 mg/mL	$37.9 \times 10^{-3} \text{ s}^{-1}$	This work
highly branched Pt@Ag NPs	$1 \times 10^{-4} \text{ M}$	1 mg/mL	$5.9 \times 10^{-3} \text{ s}^{-1}$	[1]
PCP@Au-Ag composites	$2 \times 10^{-4} \text{ M}$	1 mg/mL	$2.87 \times 10^{-3} \text{ s}^{-1}$	[2]
PdNiP/RGO	$5 \times 10^{-3} \text{ M}$	1 mg/mL	$23.5 \times 10^{-3} \text{ s}^{-1}$	[3]
CeO ₂ @Au@CeO ₂ -MnO ₂	$3 \times 10^{-7} \text{ M}$	5 mg/mL	$3.2 \times 10^{-3} \text{ s}^{-1}$	[4]
Fe-Fe ₂ O ₃ @PDA NCs	$2 \times 10^{-4} \text{ M}$	0.1 mg/mL	$15 \times 10^{-3} \text{ s}^{-1}$	[5]
bio-Pd/Au-NPs	$1.08 \times 10^{-3} \text{ M}$	8.3 mg/mL	$2.8 \times 10^{-3} \text{ s}^{-1}$	[6]

References

- [1] Z. Lv, X. Zhu, H. Meng, J. Feng and A. Wang. *J. Colloid Interf. Sci.* 2019, **538**, 349.
- [2] J. Fu, S. Wang, J. Zhu, K. Wang, M. Gao, X. Wang and Q. Xu. *Mater. Chem. Phys.* 2018, **207**, 315.
- [3] X. Gao, H. Zhao, Y. Liu, Z. Ren, C. Lin, J. Tao and Y. Zhai. *Mater. Chem. Phys.* 2019, **222**, 391.
- [4] G. Chen, Y. Wang, Y. Wei, W. Zhao, D. Gao, H. Yang and C. Li. *ACS Appl. Mater. Interfaces* 2018, **10**, 11595.
- [5] S. Wang, J. Fu, K. Wang, M. Gao, X. Wang, Z. Wang, J. Chen and Q. Xu. *Appl. Surf. Sci.* 2018, **459**, 208.
- [6] H. Zhang and X. Hu. *Enzyme Microb. Tech.* 2018, **113**, 59.