

Supporting Information

Synergetic interface between metal Cu nanoparticles and CoO for highly efficient hydrogen production from ammonia-borane

Hongmei Li, Wenxue He, Liuxin Xu, Ya Pan, Ruichao Xu, Zhihu Sun*, and Shiqiang Wei

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, P. R. China.

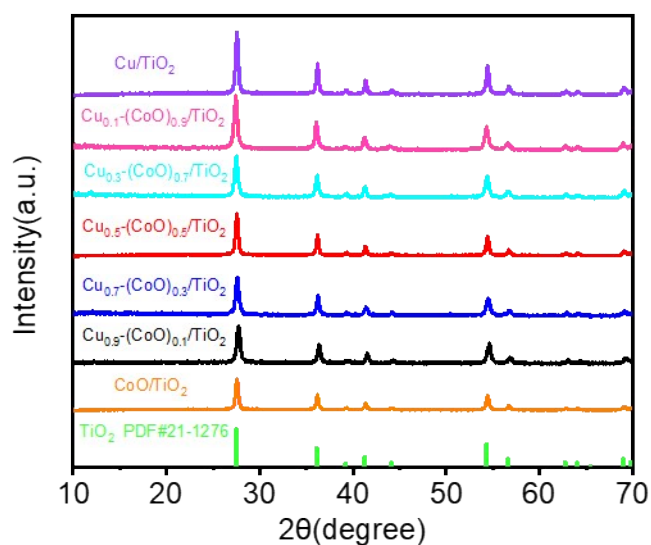


Figure S1. XRD patterns of different catalysts.

*Corresponding author. Email: zhsun@ustc.edu.cn.

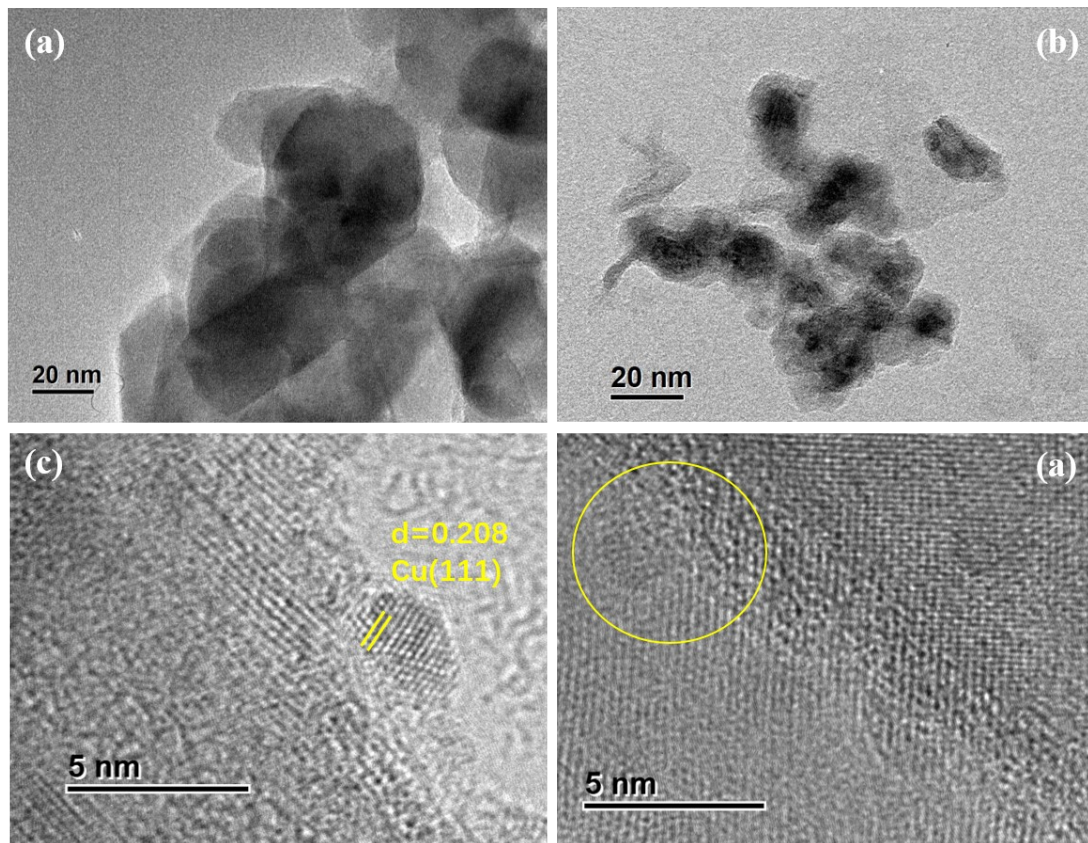


Figure S2. TEM images of (a) TiO_2 and (b) $\text{Cu}_{0.5}\text{-(CoO)}_{0.5}$. HRTEM images of (c) Cu/TiO_2 and (d) CoO/TiO_2 .

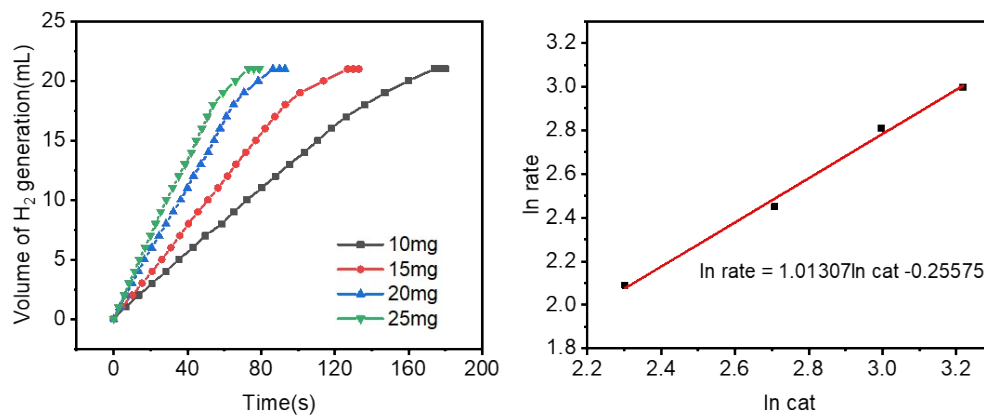


Figure S3. Hydrogen production over time for the hydrolysis of ammonia borane catalyzed by $\text{Cu}_{0.5}\text{-(CoO)}_{0.5}/\text{TiO}_2$ at different catalysts amounts (left), and the relationships between the H₂ generation rate and catalysts amounts in natural logarithmic scale (right).

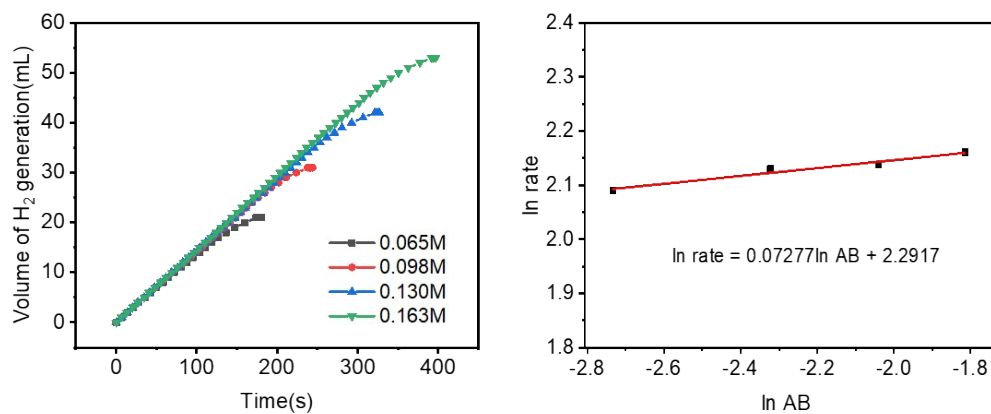


Figure S4. Hydrogen production over time for the hydrolysis of ammonia borane catalyzed by $\text{Cu}_{0.5}\text{-(CoO)}_{0.5}/\text{TiO}_2$ at different ammonia borane concentrations (left), and the relationships between the H₂ generation rate and ammonia borane concentrations in natural logarithmic scale (right).

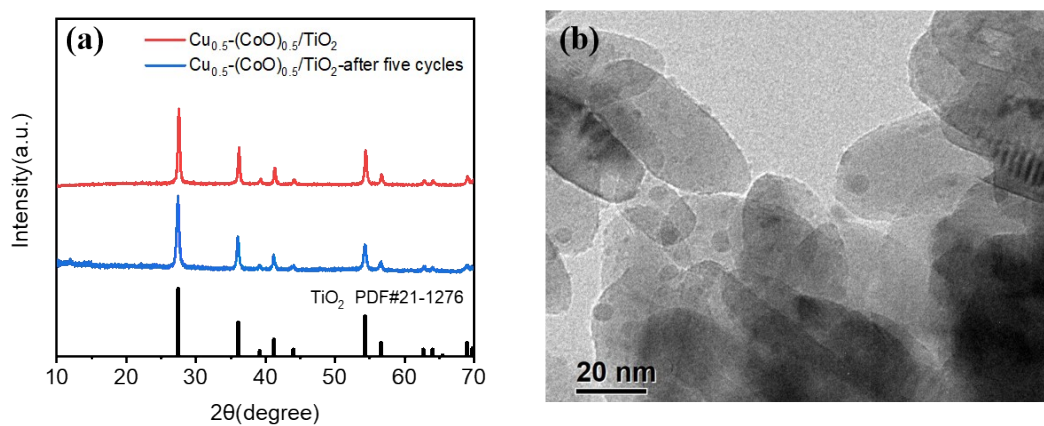


Figure S5. The (a) XRD patterns and (b) TEM images of $\text{Cu}_{0.5}\text{-(CoO)}_{0.5}\text{/TiO}_2$ after five cycles.

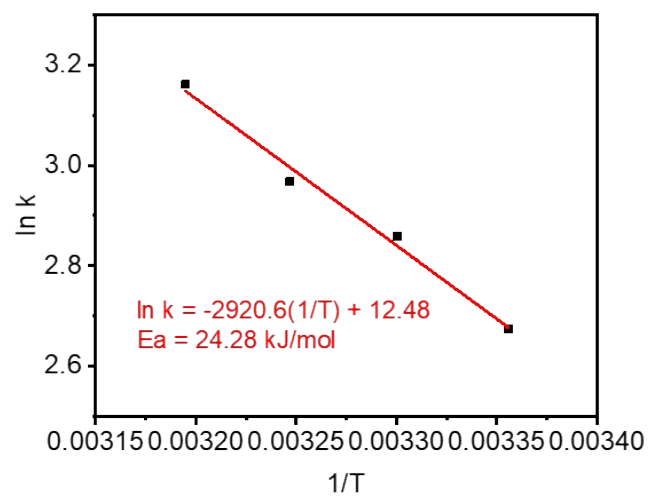


Figure S6. The Arrhenius plot and the E_a of $\text{Cu}_{0.5}\text{-(CoO)}_{0.5}/\text{TiO}_2$ for hydrolysis of ammonia borane in 0.2 M NaOH within the temperature range from 298 to 313 K.

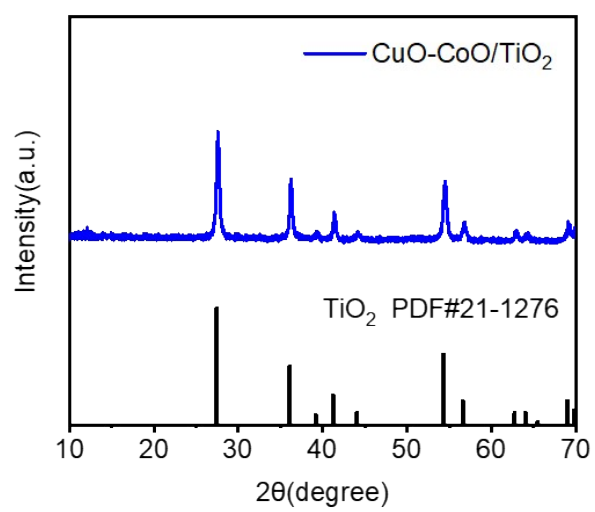


Figure S7. XRD pattern of CuO-CoO/TiO₂.

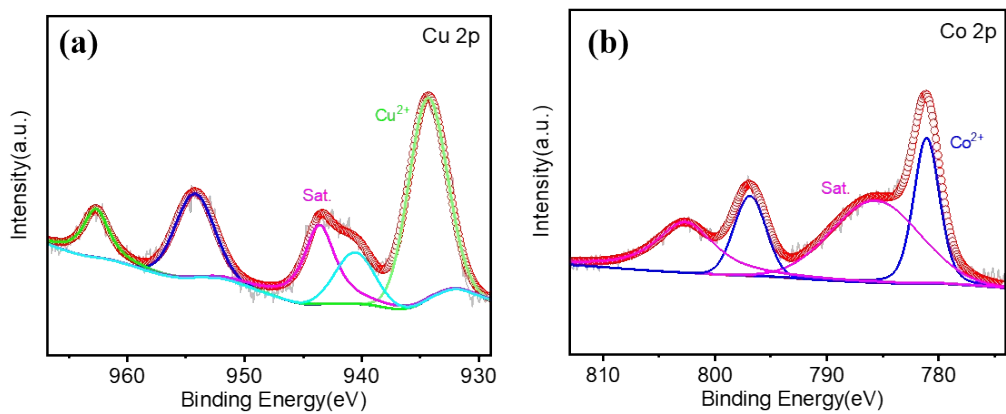


Figure S8. The high-resolution XPS spectra of (a) Cu 2p and (b) Co 2p of CuO-CoO/TiO₂.

Table S1. The content of Co and Cu in samples by ICP-AES.

Sample	Cu (wt%)	Co (wt%)
CoO/TiO ₂	0	5.0
Cu _{0.1} -(CoO) _{0.9} /TiO ₂	0.6	4.6
Cu _{0.3} -(CoO) _{0.7} /TiO ₂	1.8	3.6
Cu _{0.5} -(CoO) _{0.5} /TiO ₂	2.9	2.5
Cu _{0.7} -(CoO) _{0.3} /TiO ₂	4.4	1.7
Cu _{0.9} -(CoO) _{0.1} /TiO ₂	5.6	0.6
Cu/TiO ₂	5.7	0
CuO-CoO/TiO ₂	3.0	2.7
Cu/TiO ₂ + CoO/TiO ₂	2.9	2.5
Cu _{0.5} -(CoO) _{0.5}	46.1	36.2

Table S2. TOF values of different catalysts.

Catalysts	TOF ($\text{mol}_{\text{H}_2} \text{mol}_{\text{metal}}^{-1} \text{min}^{-1}$)
$\text{Cu}_{0.1}\text{-(CoO)}_{0.9}/\text{TiO}_2$	14.9
$\text{Cu}_{0.3}\text{-(CoO)}_{0.7}/\text{TiO}_2$	23.4
$\text{Cu}_{0.5}\text{-(CoO)}_{0.5}/\text{TiO}_2$	40.8
$\text{Cu}_{0.7}\text{-(CoO)}_{0.3}/\text{TiO}_2$	20.3
$\text{Cu}_{0.9}\text{-(CoO)}_{0.1}/\text{TiO}_2$	16.2
CoO/TiO_2	0.0
Cu/TiO_2	1.0
$\text{CuO-CoO}/\text{TiO}_2$	19.0
$\text{Cu}/\text{TiO}_2 + \text{CoO}/\text{TiO}_2$	9.9
$\text{Cu}_{0.5}\text{-(CoO)}_{0.5}$	2.4

Table S3. TOF values of different non-noble metal catalysts reported in the literature.

Catalysts	TOF ($\text{mol}_{\text{H}_2} \text{mol}_{\text{metal}}^{-1} \text{min}^{-1}$)	T (K)	Ref.
$\text{Cu}_{0.72}\text{Co}_{0.18}\text{Mo}_{0.1}$ NPs	119.0 ^a	298	1
$\text{Cu}_{0.5}\text{-(CoO)}_{0.5}/\text{TiO}_2$	104.0 ^a	298	This work
Cu@CuCoO_x	98.2 ^a	298	2
Ni/ZIF-8	85.7 ^a	298	3
$\text{CuO-NiO/Co}_3\text{O}_4$	79.1 ^a	298	4
Cu-Ni-Co@MIL-101	72.1	298	5
$\text{Cu}_{0.8}\text{Co}_{0.2}\text{O-GO}$	70	298	6
$\text{Cu}_{0.6}\text{Co}_{0.4}\text{O@CN}$	57.7 ^a	298	7
$\text{Cu/Cu}_{0.76}\text{Co}_{2.24}\text{O}_4\text{-V60}$	50.33 ^a	298	8
$\text{Cu}_{0.5}\text{-(CoO)}_{0.5}/\text{TiO}_2$	40.8	298	This work
CoCuO@CoCu-C	38 ^a	298	9
$\text{CuNi/Co}_3\text{O}_4$	31.5 ^a	298	10
$\text{Cu}_{0.5}\text{Co}_{0.5}/\text{PDDA-HNT}$	30.8	298	11
Ni@MSC-30	30.7	298	12
CoCu/Ni	30.5 ^a	298	13
$\text{Ni}_{0.9}\text{Mo}_{0.1}$ NPs	27.3	298	14
$\text{MoO}_3\text{-doped MnCo}_2\text{O}_4$	26.4 ^a	298	15
$\text{Ni}_{0.75}\text{Cu}_{0.25}/47\text{-SiO}_2$	25.3	298	16
Co@Ni-MOF NCA	20.54	298	17
CuCo NPs@MIL-101	19.6	298	18
$\text{Co}_{40}\text{Cu}_{60}\text{@S16LC-20}$	16.36	298	19
$\text{Co/CoFeO}_x\text{-25}$	12.25	298	20
CuCo NPs/graphene	9.18	298	21
$\text{Cu}_{0.4}\text{Co}_{0.6}$ NPs/BNNFs	8.42	298	22
Co@N-C-700	5.6	298	23

^aThe reaction was tested in the presence of NaOH.

Table S4. The area and proportion of each atom measured by XPS of CuO-CoO/TiO₂.

Name	Area (P)	Atomic percentage (%)
Cl 2p	693.73	0.2
Ti 2p	187515.12	25.9
O 1s	211056.32	67.3
Co 2p	72649.99	4.1
Cu 2p	58021.11	2.5

REFERENCES

1. Q. Yao, K. Yang, X. Hong, X. Chen and Z.-H. Lu, *Catal. Sci. Technol.*, 2018, **8**, 870-877.
2. J. Li, X. Ren, H. Lv, Y. Wang, Y. Li and B. Liu, *J Hazard Mater*, 2020, **391**, 122199.
3. C. Wang, J. Tuninetti, Z. Wang, C. Zhang, R. Ciganda, L. Salmon, S. Moya, J. Ruiz and D. Astruc, *J Am Chem Soc*, 2017, **139**, 11610-11615.
4. J. Liao, Y. Feng, W. Lin, X. Su, S. Ji, L. Li, W. Zhang, B. G. Pollet and H. Li, *Int. J. Hydrogen Energy*, 2020, **45**, 8168-8176.
5. Z. Liang, X. Xiao, X. Yu, X. Huang, Y. Jiang, X. Fan and L. Chen, *J. Alloys Compd.*, 2018, **741**, 501-508.
6. K. Feng, J. Zhong, B. Zhao, H. Zhang, L. Xu, X. Sun and S. T. Lee, *Angew Chem Int Ed Engl*, 2016, **55**, 11950-11954.
7. W. Xu, S. Zhang, R. Shen, Z. Peng, B. Liu, J. Li, Z. Zhang and B. Li, *Energy & Environmental Materials*, 2022, DOI: 10.1002/eem2.12279.
8. C. Wang, Y. Ren, J. Zhao, S. Sun, X. Du, M. Wang, G. Ma, H. Yu, L. Li, X. Yu, X. Zhang, Z. Lu and X. Yang, *Applied Catalysis B: Environmental*, 2022, **314**, 121494.
9. S. Guan, Y. Guo, H. Zhang, X. Liu, Y. Fan and B. Liu, *Sustain Energy Fuels*, 2022, **6**, 1753-1761.
10. J. Zhou, X. Feng, Y. Zhao, R. Cui, D. Wang and B. Zhang, *J. Alloys Compd.*, 2022, **923**, 166345.
11. Y. Liu, J. Zhang, H. Guan, Y. Zhao, J.-H. Yang and B. Zhang, *Appl. Surf. Sci.*, 2018, **427**, 106-113.
12. P. Z. Li, A. Aijaz and Q. Xu, *Angew Chem Int Ed Engl*, 2012, **51**, 6753-6756.
13. J. Liao, F. Lv, Y. Feng, S. Zhong, X. Wu, X. Zhang, H. Wang, J. Li and H. Li, *Catal. Commun.*, 2019, **122**, 16-19.
14. K. Yang, Q. Yao, W. Huang, X. Chen and Z.-H. Lu, *Int. J. Hydrogen Energy*, 2017, **42**, 6840-6850.
15. D. Lu, Y. Feng, Z. Ding, J. Liao, X. Zhang, H. R. Liu and H. Li, *Nanomaterials(Basel)*, 2019, **9**, 1112.
16. K. Guo, Y. Ding, J. Luo, M. Gu and Z. Yu, *ACS Appl. Energy Mater.*, 2019, **2**, 5851-5861.
17. D. R. Kumar, S. Prabu, K. Y. Chiang and T. H. Oh, *Int. J. Energy Res.*, 2022, **46**, 18134-18145.
18. J. Li, Q.-L. Zhu and Q. Xu, *Catal. Sci. Technol.*, 2015, **5**, 525-530.
19. J. R. Deka, D. Saikia, N.-F. Lu, K.-T. Chen, H.-M. Kao and Y.-C. Yang, *Appl. Surf. Sci.*, 2021, **538**, 148091.
20. J. Wang, Y. Chen, S. Guan, J. Shi, M. Li and B. Liu, *Journal of Alloys and Compounds*, 2022, **913**, 165215.
21. J.-M. Yan, Z.-L. Wang, H.-L. Wang and Q. Jiang, *Journal of Materials Chemistry*, 2012, **22**, 10990.
22. X. Yang, Q. Li, L. Li, J. Lin, X. Yang, C. Yu, Z. Liu, Y. Fang, Y. Huang and C. Tang, *J. Power Sources*, 2019, **431**, 135-143.
23. H. Wang, Y. Zhao, F. Cheng, Z. Tao and J. Chen, *Catal. Sci. Technol.*, 2016, **6**, 3443-3448.