Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Localized Surface Plasmon Resonance Effect Enhanced Cu/TiO_2 Core-Shell Catalyst for boosting CO_2 Hydrogenation Reaction

Lizi Shi [a], Huimin Liu [b*], Shangbo Ning [a] and Jinhua Ye [a, c*]

a. TJU-NIMS International Collaboration Laboratory, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, P. R. China

b. School of Chemical and Environmental Engineering, Liaoning University of Technology, Jinzhou 121001, China.

c. International Center for Materials Nanoarchitectonics (WPI-MANA), National Institutes for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

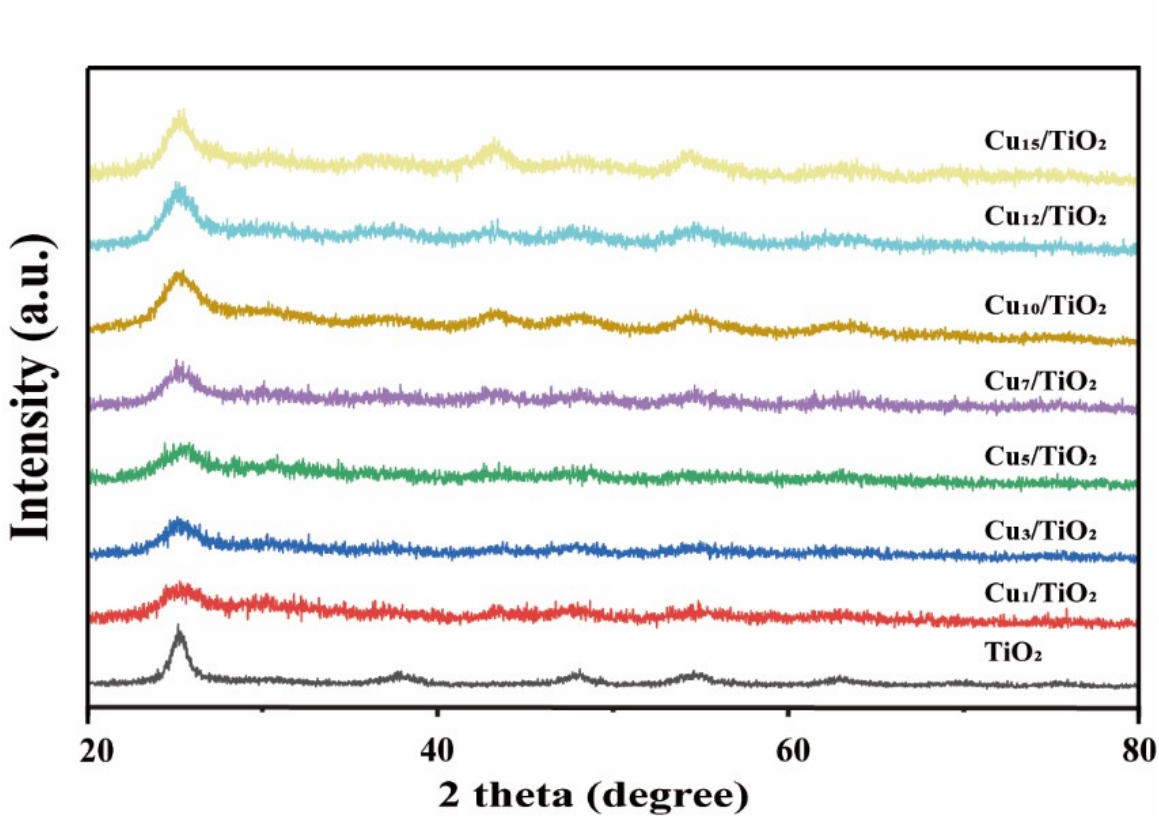

Figure S1. XRD patterns of photo-reduced Cu_x/TiO_2 (x=1, 3, 5, 7, 10, 12, 15).

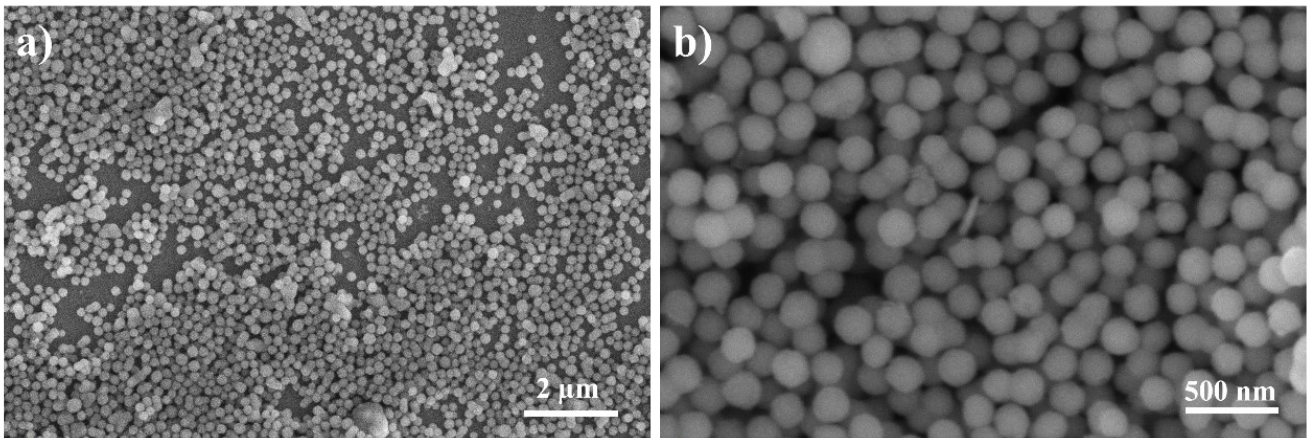

Figure S2. SEM images of SiO_2 nanoparticals: (a) large scale and (b) local distribution.

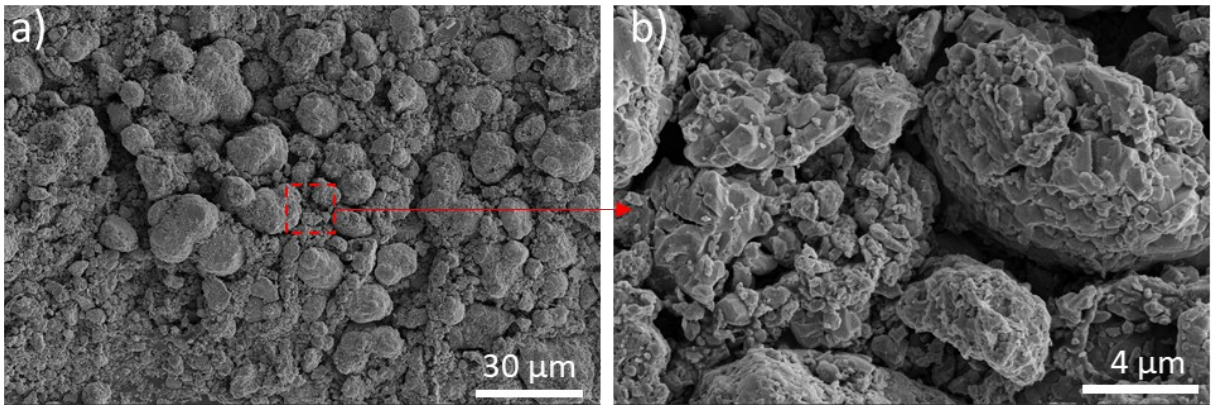

Figure S3. SEM images of Cu after calcining at 700 ℃ for 2h. Cu was severe sintered at high temperature (700°C)

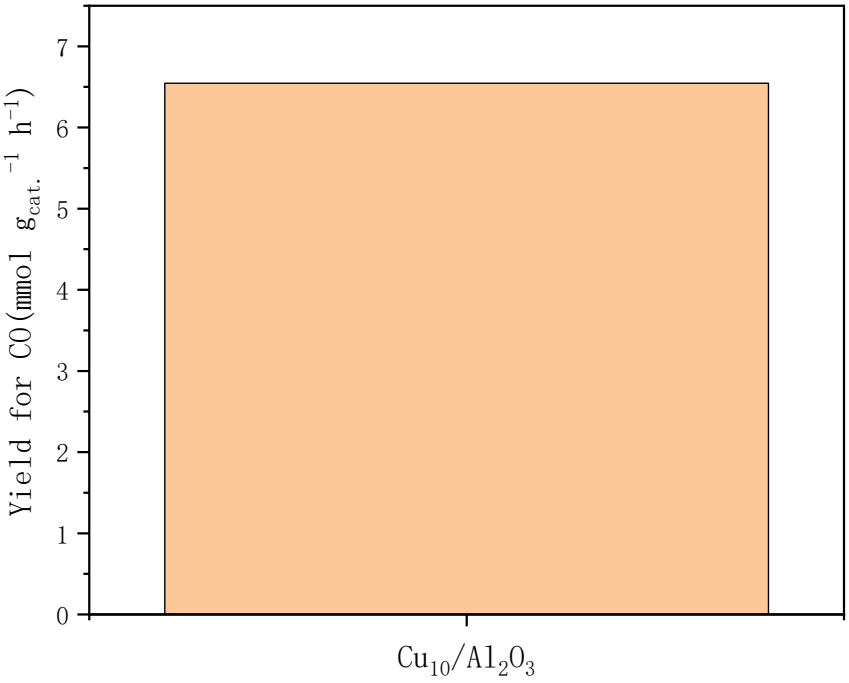

Figure S4. CO yield on Al_2O_3 under light illumination.

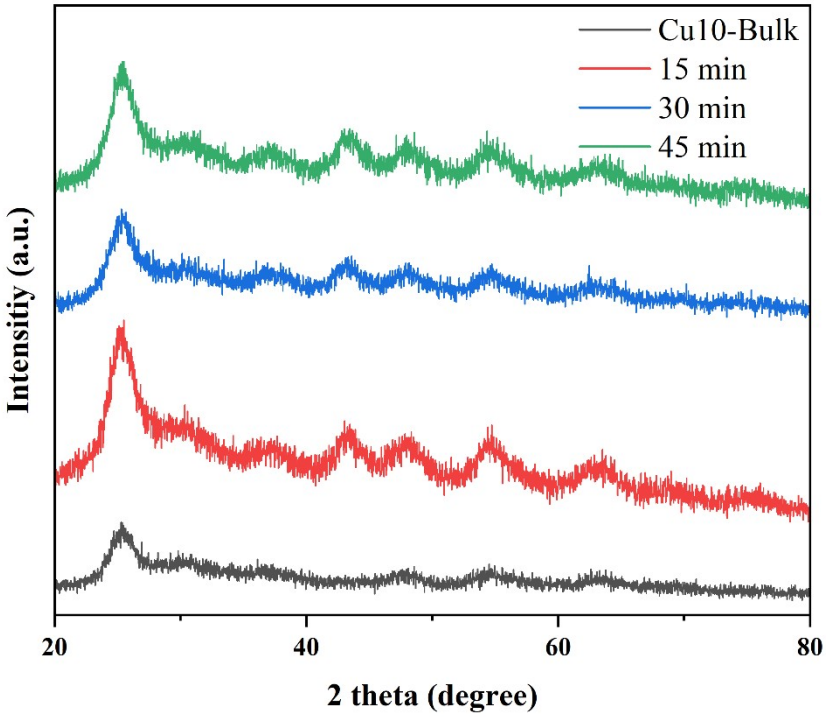

Figure S5. XRD patterns of Cu_{10}/TiO_2 for before photoreduction (Cu10-Bulk) and different photoreduction time (10~45 min).

Table S1. BET surface areas of different samples.

Sample	Cu_{10}/TiO_2 Rutile	Cu/P25	Cu_{10}/TiO_2 Before Reduction	Cu/ Al_2O_3
BET surface area (m^2/g)	10.113	26.155	73.937	147.688
Pore diameter (nm)	3.706	64.632	3.940	5.797

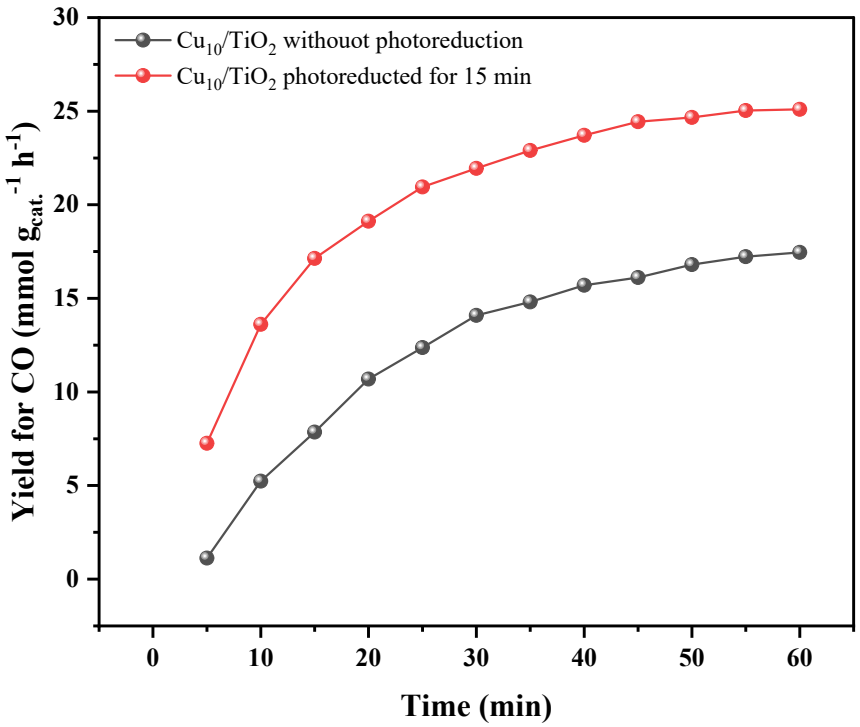

Figure S6. CO yield of Cu_{10}/TiO_2 catalyst under different treatment: without photoreduction and photo-reduced for 15 min.

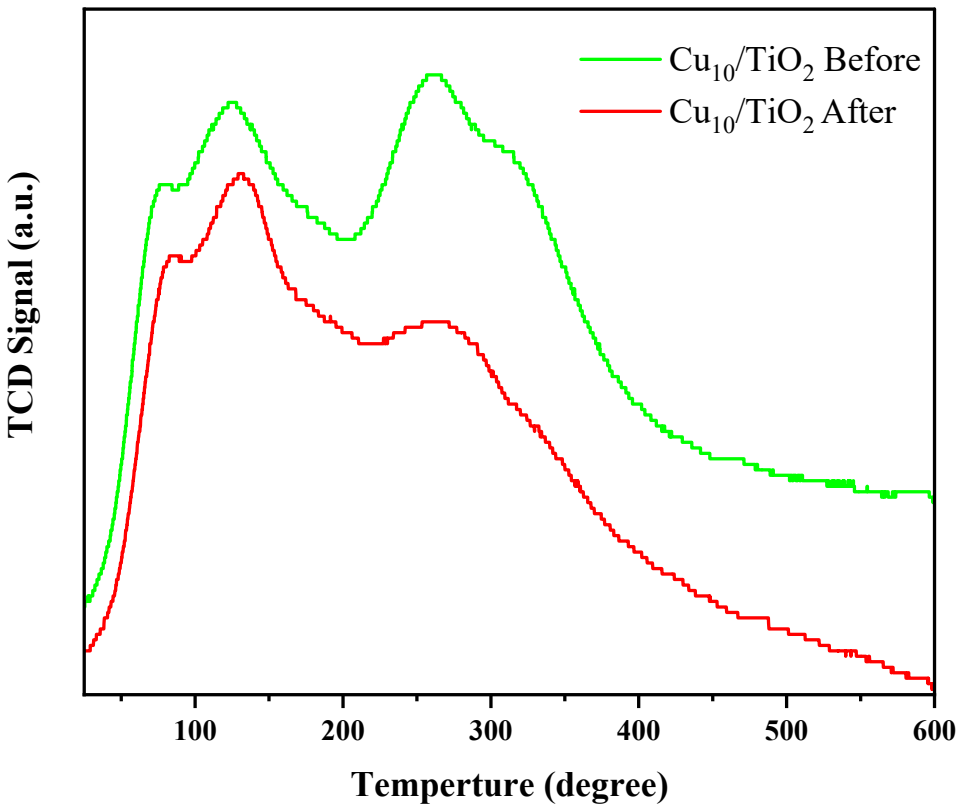

Figure S7. TPD CO_2 desorption profiles for Cu_{10}/TiO_2 before and after photoreduction.

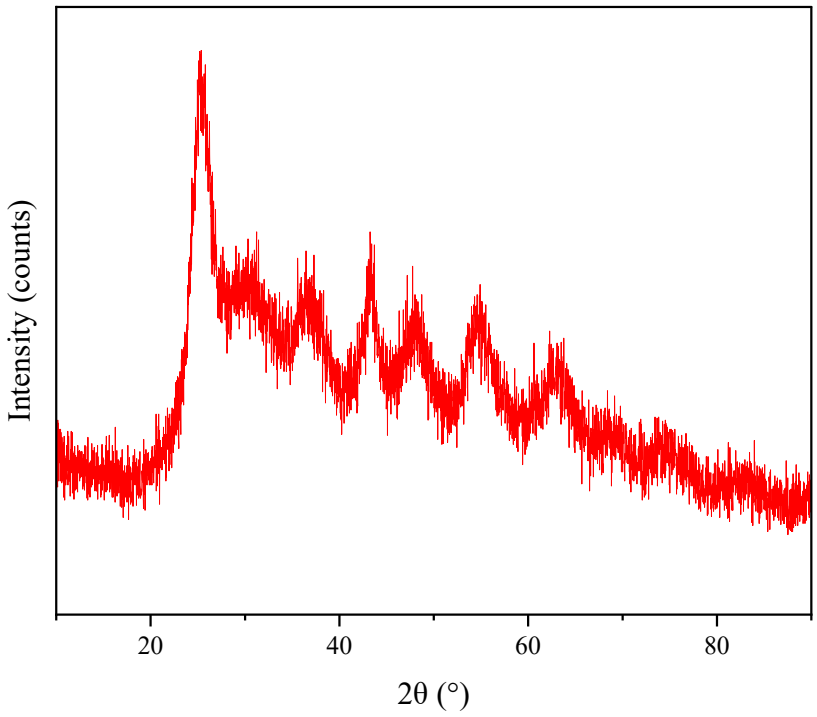

Figure S8. XRD patterns of Cu_{10}/TiO_2 after reduction at 10% H_2/Ar atmosphere 450 ℃ for 2 hours.

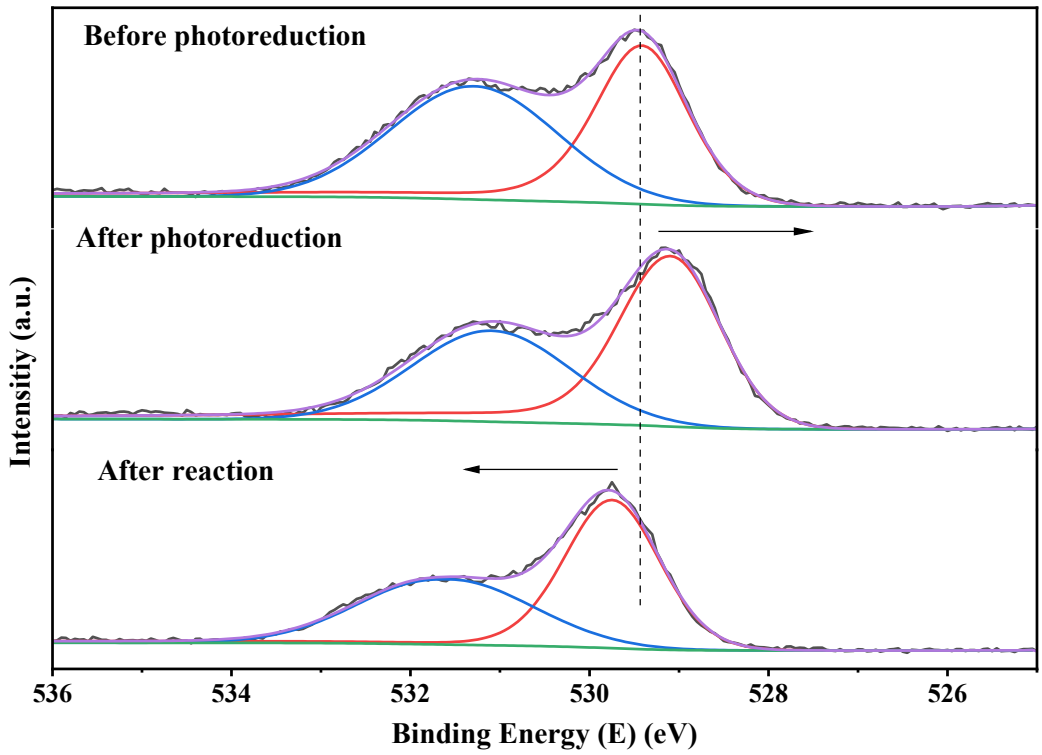

Figure S9. High resolution XPS image of O element at different sample condition (Cu_{10}/TiO_2, before photoreduction, after photoreduction and after reaction).

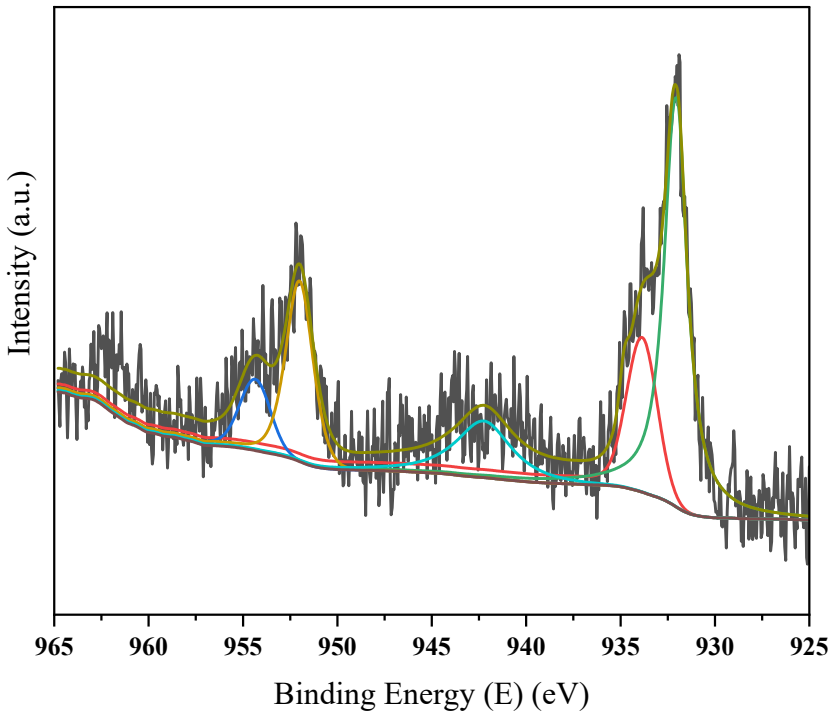

Figure S10. Cu 2p high resolution XPS spectra of Cu_{10}/TiO_2.

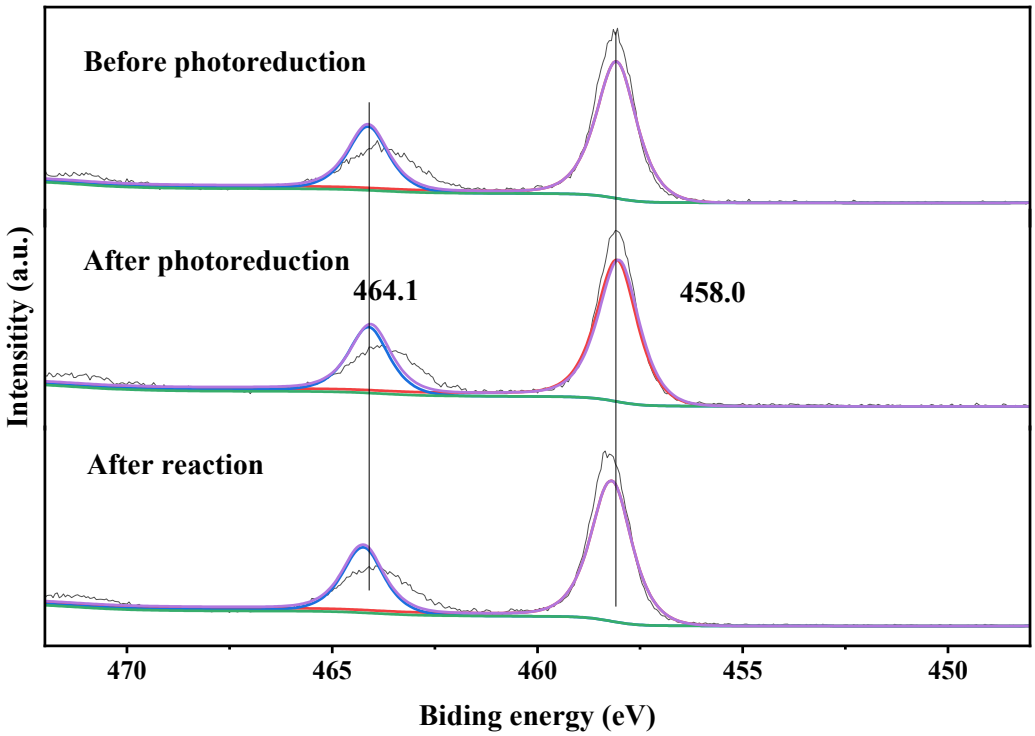

Figure S12. Comparison of chemical state of Ti element in different conditions (Cu_{10}/TiO_2, before photoreduction, after photoreduction and after reaction).

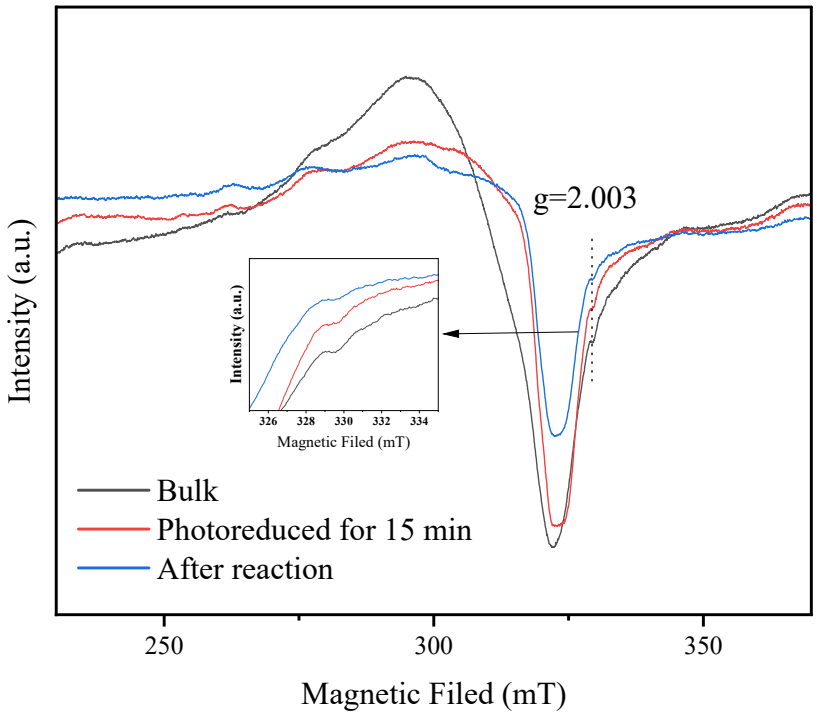

Figure S13. X-Band EPR spectra for Cu_{10}/TiO_2 under different conditions. "Bulk" means that Cu_{10}/TiO_2 was used for test without any reduction, neither photoreduction nor thermal reduction at H_2/Ar atmosphere.

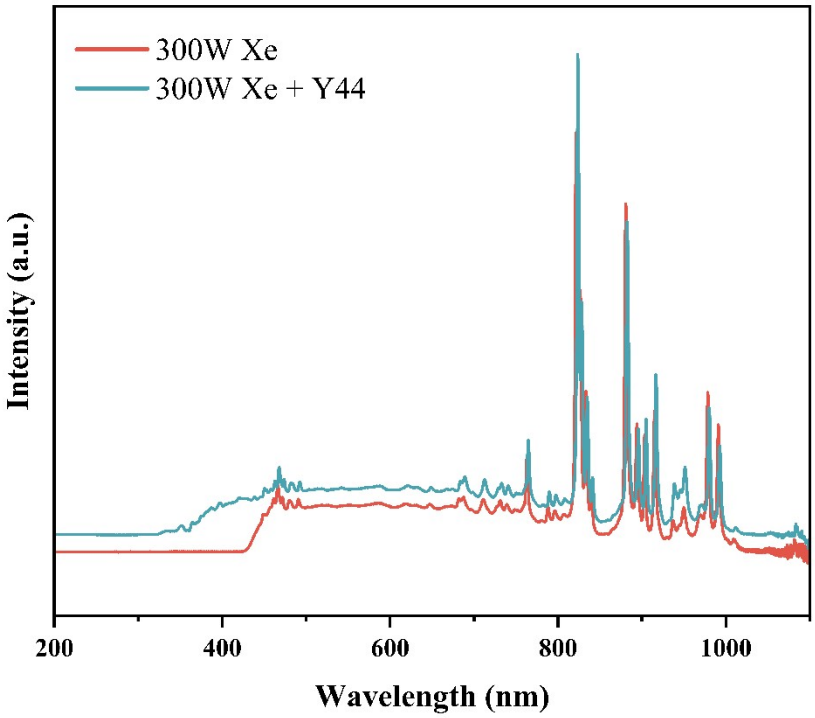

Figure S14. Spectrum of 300W Xe lamp without any filter and with Y44 filter.

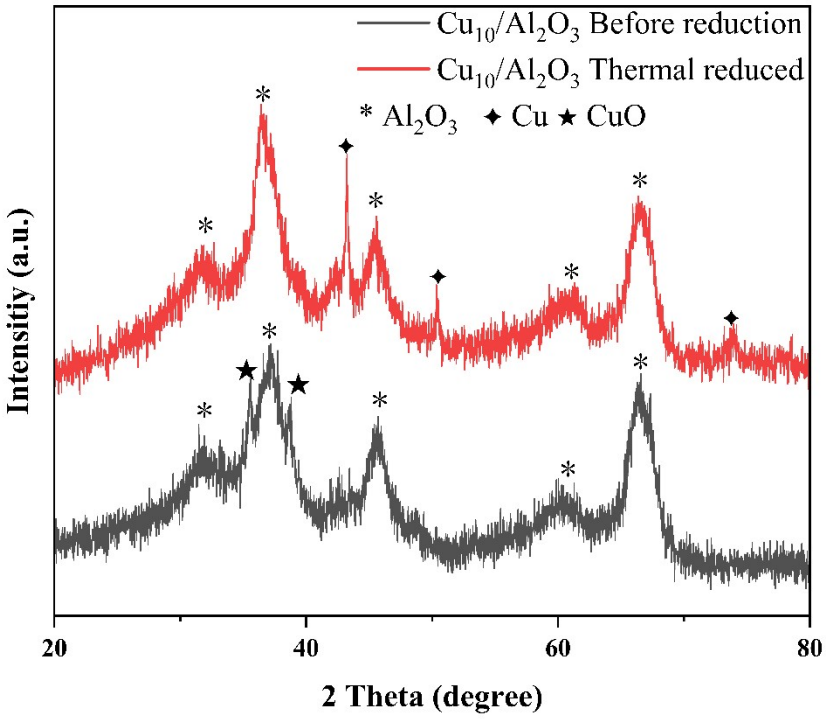

Figure S15. XRD patterns of Cu_{10}/Al_2O_3 before and after thermal reduction. Thermal reduction was taken place in a H_2/Ar atmosphere for two hours at 450 °C.

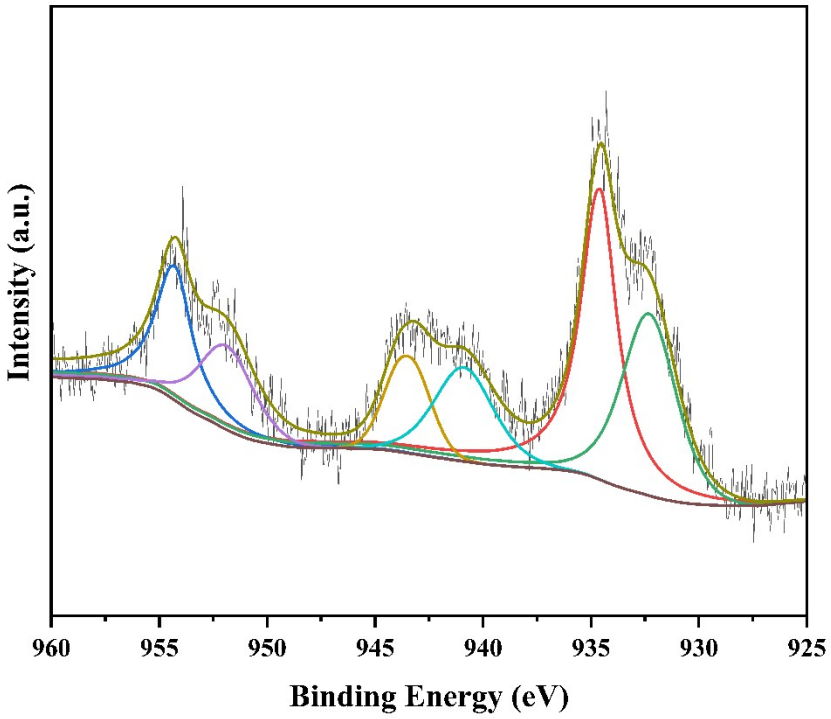

Figure S16. Cu 2p high resolution XPS spectra of Cu_{10}/Al_2O_3 after thermal reduction. Thermal reduction was taken place in a H_2/Ar atmosphere for two hours at 450 ℃. Cu (II) is primarily formed as a result of oxidation while waiting for the test.

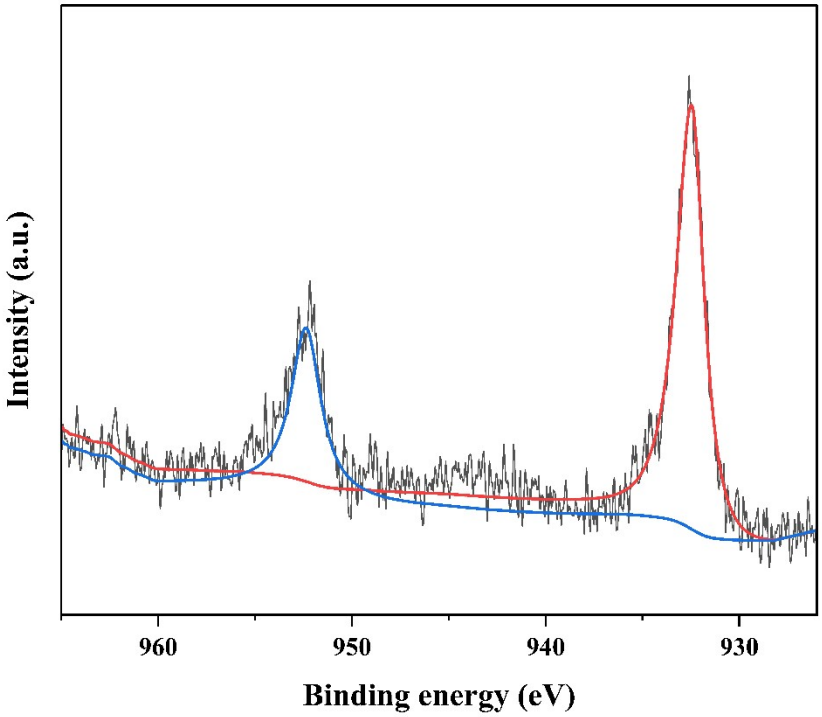

Figure S17. Cu 2p high resolution XPS spectra of Cu_{10}/TiO_2 after thermal reduction. Thermal reduction was taken place in a H_2/Ar atmosphere for two hours at 450 ℃.

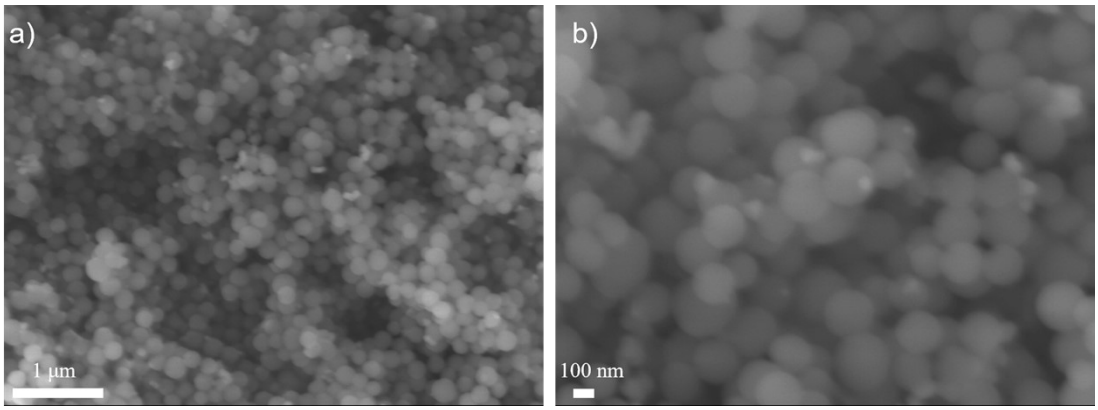

Figure S18. SEM images of Cu_{10}/TiO_2 after reaction. (a) Large scale, 1 μm; (a) Local scale, 100 nm. The bright spots in the picture are suspected to be aggregated Cu (0).

Table S2. Catalyst activity under different reduction time and reduction ways: photo-reduced varies from 0 to 45 min and reduced at 10% H_2/Ar atmosphere 450 ℃ for 2 hours.

Reduction Parameters	Photo-reduced for 0 min	Photo-reduced for 5 min	Photo-reduced for 10 min	Photo-reduced for 15 min	Photo-reduced for 30 min	Photo-reduced for 45 min	Reduction with H_2/Ar at 450 ℃ for 2h
CO yield (mmol g^{-1} h^{-1})	17.453	10.007	19.631	25.100	19.778	22.247	23.06

Table S3. Recent works relevant to photothermal CO_2 hydrogenation reactions.

Catalyst	Type of Reactor	Light Source	Temperature (℃)	CO_2:H_2 Ratio	Yield of CO （mmol g^{-1} h^{-1}）	Yield of CH_4 （mmol g^{-1} h^{-1}）	Selectivity of CO_2 (%)	Year	Reference
Ni/$TiO_{2-x}H_x$	Flow	300 W Xe lamp	441.2	1:1	~1.0	~2.7	/	2022	[1]
FeCe-300 [a]	Flow	300 W Xe lamp, (2.2 W cm^{-2})	450	1:4	19.61	Trace	~100	2020	[2]
Ni-600 [b]	Flow	300 W Xe lamp	~260	1:4	Trace	278.8	~0	2021	[3]
Fe_3O_4	Flow	300 W Xe lamp, (2.05 W cm^{-2})	~350	1:2	11.3	Trace	~100	2020	[4]
Ni/SiO_2·Al_2O_3	Batch	300 W Xe lamp, (1.3 W cm^{-2})	113.7	1:1	4.53	11.6	/	2020	[5]
$CsPbBr_3$ @$CsPb_2Br_5$	Batch	300 W Xe lamp, (220 mW cm^{-2})	200	1:3	0.069	/	/	2022	[6]
In_2O_{3-x}	Batch	300 W Xe lamp	262	1:1	2.38	~0	~100	2020	[7]
Ni-BTO	Batch	300 W Xe lamp, (293 mW cm^{-2})	/	1:4	Trace	257	3.6	2021	[8]
RuO_2/STO	Batch	300 W Xe lamp, (108 mW cm^{-2})	150	1:4	/	14.6	/	2019	[9]
Ru-Al_2O_{3-x}-L	Batch	300 W Xe lamp	236.4	1:4	/	14.04	/	2022	[10]
Pt/H_xMoWO_y	Flow	500W Hg-Xe short arc lamp, λ>450nm	140	1:1	3.1	Trace	~100	2022	[11]
0.35Ru @NVO	Batch	300 W Xe lamp, (2.0 W cm^{-2})	350	1:4	/	114.9	5	2021	[12]
Ni@C-600 [c]	Flow	300 W Xe lamp, (4.3 W cm^{-2})	272	1:4	/	154	2.3	2021	[13]
Ni/$N_{5.0}$-CeO_2	Batch	300 W Xe lamp, (2.11 W	350	1:1	20.9	Trace	~100	2021	[14]

		cm^{-2})							
ASA-c-Ag_8Cu_1	Batch	300 W Xe lamp, (3.7 W cm^{-2})	>300	1:1	5.4	19.9	/	2022	[15]
Cu_{10}/TiO_2	Batch	300 W Xe lamp, (2.4 W cm^{-2})	334	1:1	25.1	Trace	~100	/	This Work

a. An FeCe-300 catalyst with an Fe:Ce molar ratio of 2:1, The final products are denoted as FeCe-x, where x refers to the reduction temperature. For the FeCe-300 catalysts, the Fe: Ce molar

b. The number '600' means the Ni-based catalysts (Ni-x) have been prepared by reducing NiAl-LDH nanosheets precursor at 600 ℃

c. The precursor was placed in the reactor under continuous flow of N_2 followed by direct carbonization at 600 °C for 6 h under N_2 (25 mL min^{-1}) using a heating ramp of 2 °C min^{-1}. After cooling down of the reactor the samples were passivated in continuous flow of N_2 (25 mL min^{-1}) and Air (5 mL min^{-1}) for 2 hours.

Note: "/" means that the author did not provide relevant information in their article.

References

1 Y. Li, Z. Zeng, Y. Zhang, Y. Chen, W. Wang, X. Xu, M. Du, Z. Li and Z. Zou, *ACS Sustainable Chemistry and Engineering*, , DOI:10.1021/ACSSUSCHEMENG.2C01081/ASSET/IMAGES/LARGE/SC2C01081_0004.JPEG.

2 J. Zhao, Q. Yang, R. Shi, G. I. N. Waterhouse, X. Zhang, L. Z. Wu, C. H. Tung and T. Zhang, *NPG Asia Materials*, , DOI:10.1038/s41427-019-0171-5.

3 Z. Li, R. Shi, J. Zhao and T. Zhang, *Nano Research 2021 14:12*, 2021, **14**, 4828–4832.

4 C. Song, X. Liu, M. Xu, D. Masi, Y. Wang, Y. Deng, M. Zhang, X. Qin, K. Feng, J. Yan, J. Leng, Z. Wang, Y. Xu, B. Yan, S. Jin, D. Xu, Z. Yin, D. Xiao and D. Ma, *ACS Catalysis*, 2020, **10**, 10364–10374.

5 M. J. Cai, C. R. Li and L. He, *Rare Metals*, 2020, **39**, 881–886.

6 P. Gao, Z. Cui, X. Liu, Y. Wu, Q. Zhang, Z. Wang, Z. Zheng, H. Cheng, Y. Liu, Q. Li, B. Huang and P. Wang, *Chemistry – A European Journal*, 2022, e202201095.

7 L. Wang, Y. Dong, T. Yan, Z. Hu, A. A. Jelle, D. M. Meira, P. N. Duchesne, J. Y. Y. Loh, C. Qiu, E. E. Storey, Y. Xu, W. Sun, M. Ghoussoub, N. P. Kherani, A. S. Helmy and G. A. Ozin, *Nature Communications 2020 11:1*, 2020, **11**, 1–8.

8 D. Mateo, N. Morlanes, P. Maity, G. Shterk, O. F. Mohammed, J. Gascon, D. Mateo, N. Morlanes, G. Shterk, J. Gascon, P. Maity and O. F. Mohammed, *Advanced Functional Materials*, 2021, **31**, 2008244.

9 D. Mateo, J. Albero and H. García, *Joule*, 2019, **3**, 1949–1962.

10 X. Liu, C. Xing, F. Yang, Z. Liu, Y. Wang, T. Dong, L. Zhao, H. Liu and W. Zhou, *Advanced Energy Materials*, 2022, **2201009**, 2201009.

11 H. Ge, Y. Kuwahara, K. Kusu, H. Kobayashi and H. Yamashita, *Journal of Materials Chemistry A*, 2022, **10**, 10854–10864.

12 Y. Chen, Y. Zhang, G. Fan, L. Song, G. Jia, H. Huang, S. Ouyang, J. Ye, Z. Li and Z. Zou, *Joule*, 2021, **5**, 3235–3251.

13 I. S. Khan, D. Mateo, G. Shterk, T. Shoinkhorova, D. Poloneeva, L. Garzón-Tovar and J. Gascon, *Angewandte Chemie International Edition*, 2021, **60**, 26476–26482.

14 Z. Jia, S. Ning, Y. Tong, X. Chen, H. Hu, L. Liu, J. Ye and D. Wang, *ACS Applied Nano Materials*, 2021, **4**, 10485–10494.

15 T. Shao, X. Wang, H. Dong, S. Liu, D. Duan, Y. Li, P. Song, H. Jiang, Z. Hou, C. Gao, Y. Xiong, T. Shao, X. Wang, H. Dong, S. Liu, D. Duan, Y. Li, H. Jiang, Z. Hou, C. Gao and Y. Xiong, *Advanced Materials*, 2022, **34**, 2202367.