Support information (SI)

Photo-assisted thermal catalytic Fischer-Tropsch Synthesis over Co-Cu/CeO_2

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Content

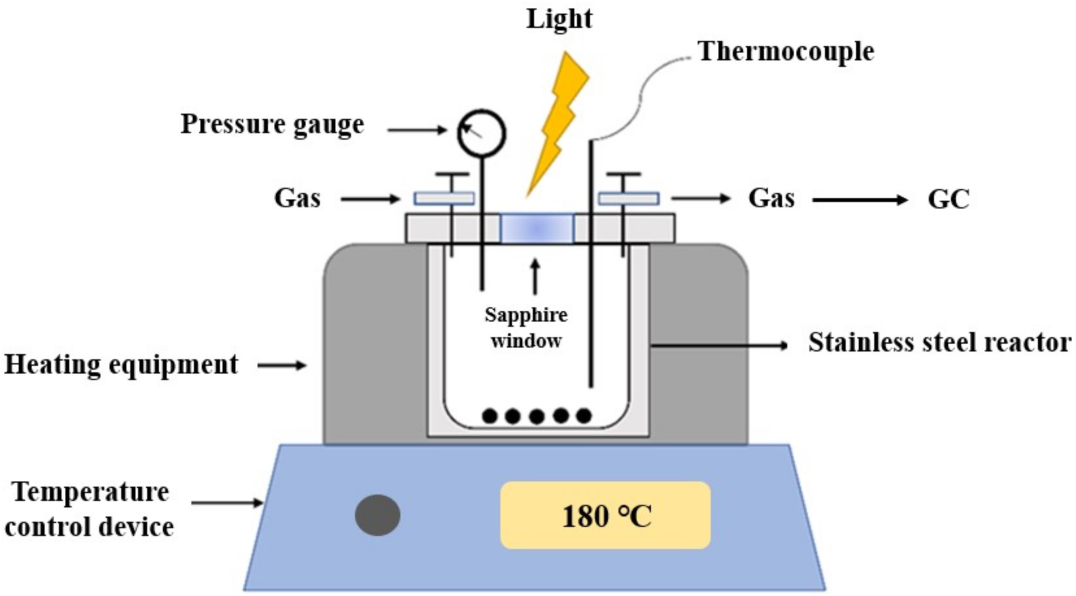

Figure S1. Schematic diagram of the reaction device

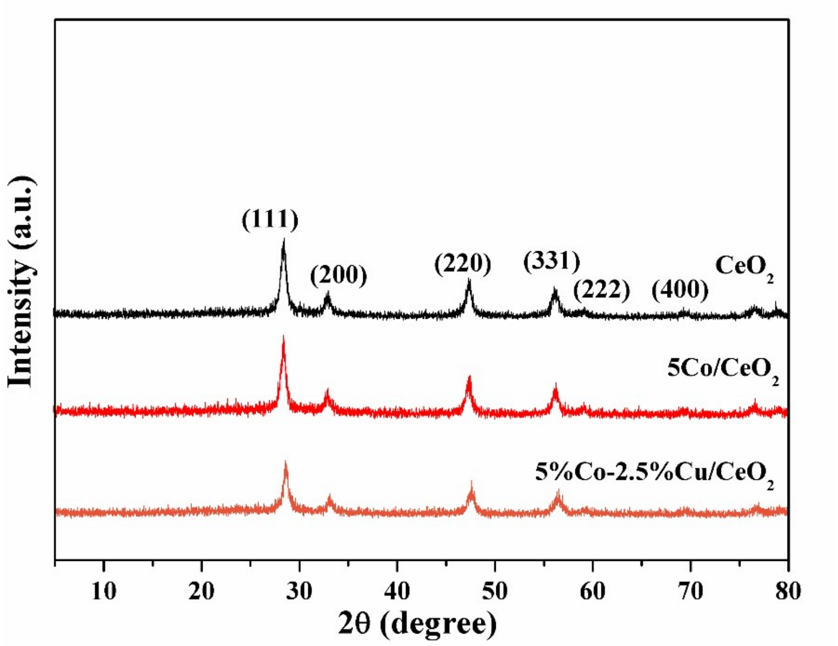

Figure S2. X-ray powder diffraction patterns of (a) CeO_2, (b) Co/CeO_2, (c) $Co-Cu/CeO_2$

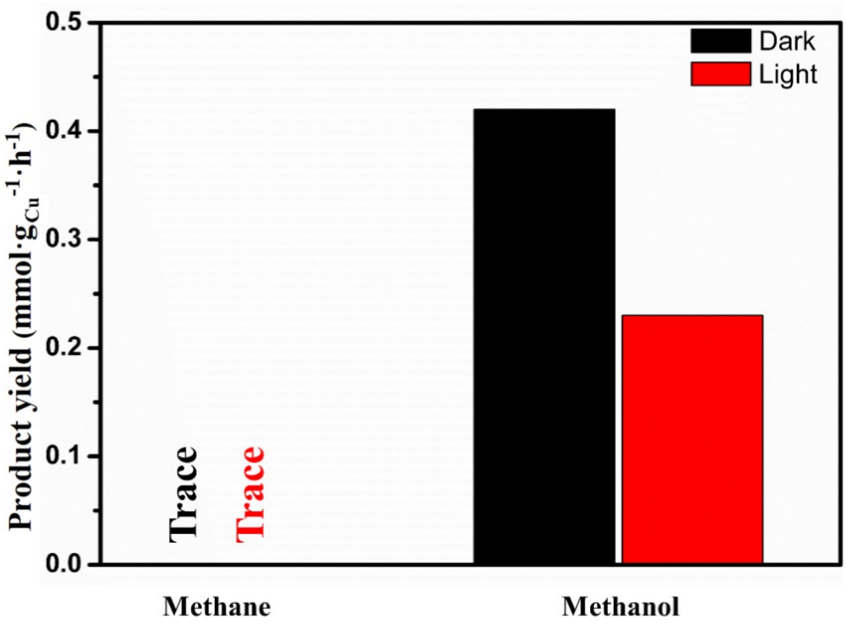

Figure S3. Catalytic performances of Cu/CeO_2 for $CO+H_2$ reaction at 180°C and 30 Bar under UV-irradiation or in dark.

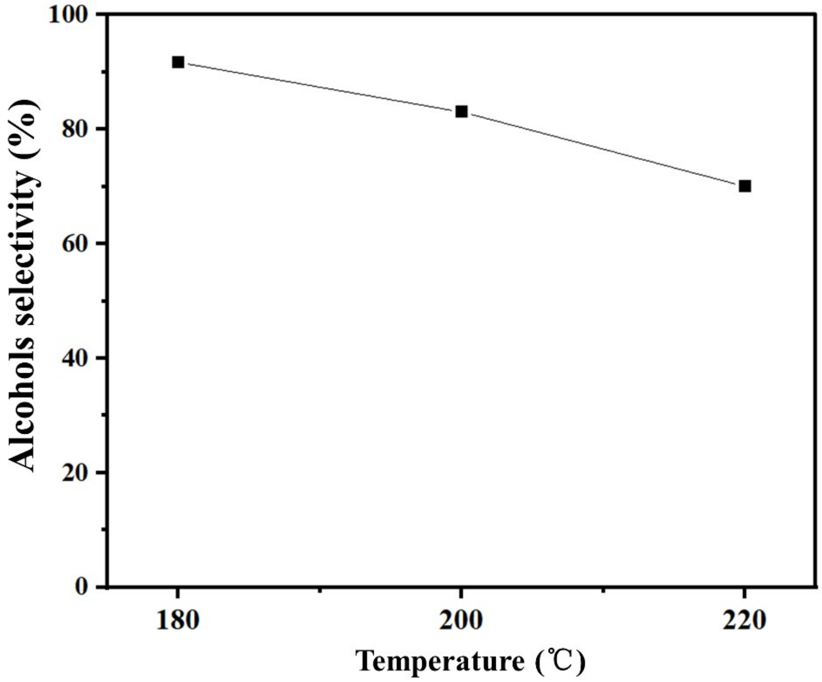

Figure S4. Selectivity of alcohols of Cu-Co/CeO_2 at different temperatures.

The Cu-Co/CeO_2 activity at different temperatures was tested. As shown in Figure S4, an increase in temperature caused an increase in methane activity, but the activity of alcohols all decreased, resulting in a final decrease in the selectivity of alcohols as the temperature increased.

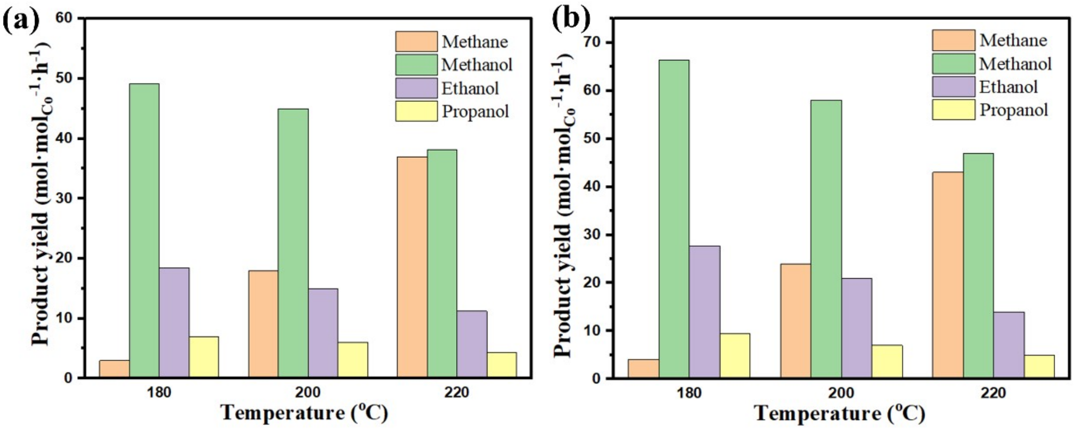

Figure S5. Co-Cu/CeO_2 catalyst activity at different temperatures. (a) Dark condition (b) Light condition

The stability of the Co-Cu/CeO_2 is shown in Figure S5. It can be seen that with the increase of temperature, the activity of CH_4 increases significantly, but the activity of alcohols decreases. The same trend was shown in both dark and light conditions. Of course, methanol is still one of the main products. The production of CH_4 and CH_3OH is a competitive reaction, and the increase in temperature is not conducive to the production of CH_3OH. The increase in methane activity results in less CO conversion to alcohols.

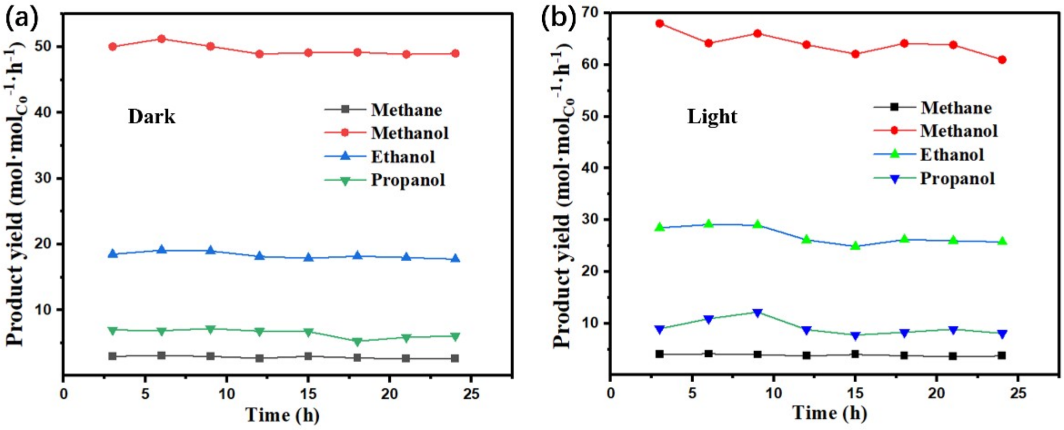

Figure S6. Stability diagram of Co-Cu/CeO_2 under light and dark conditions

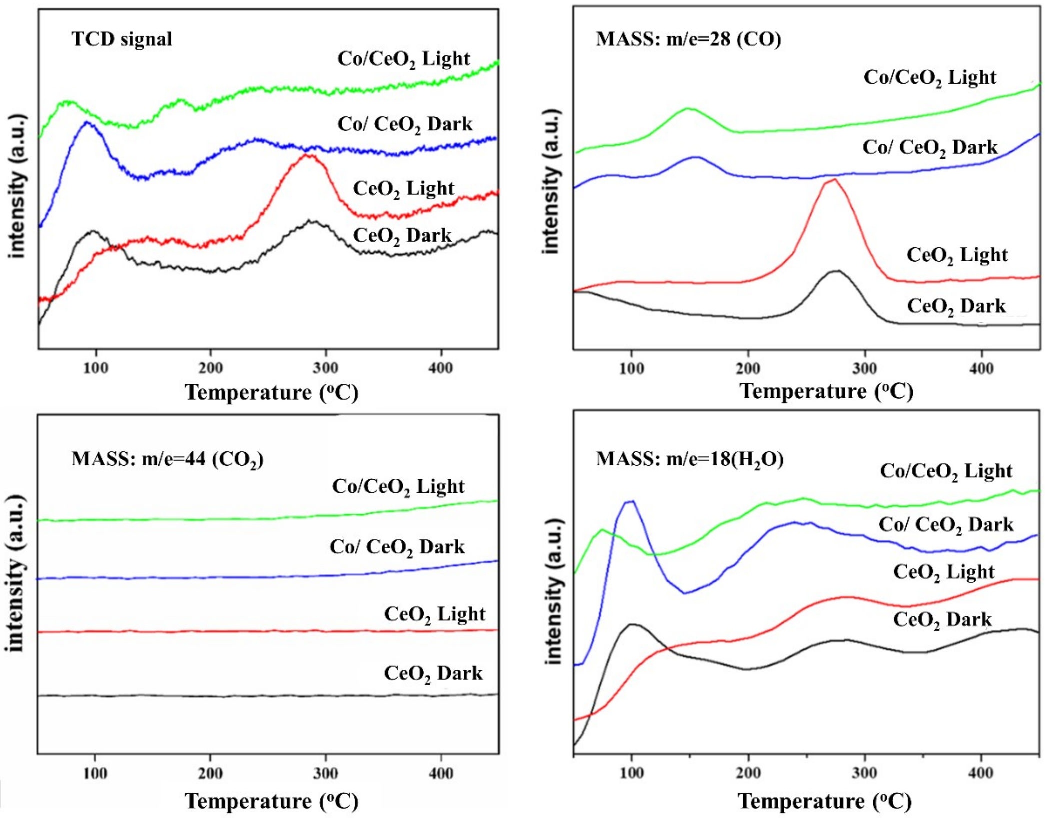

Figure S7. TPD-MS spectra of Co/CeO_2 and CeO_2 at dark and light conditions respect.

Figure S7 shows the TPD signal curve of CeO_2 and Co/CeO_2. In Figure S5a, it can be seen that CeO_2 has a clear peak at 200 to 310°C, and the peak is significantly enhanced after illumination. Combining Figure S7c-d, we can think that light is beneficial to the adsorption of CO by CeO_2. This is due to the fact that light is beneficial to the generation of oxygen vacancies, which is consistent with previous reports. For Co-CeO_2, an obvious peak also appears at 150 to 180 °C, which is also attributed to the adsorption of CO. Light promoted the adsorption of CO by Co-CeO_2.

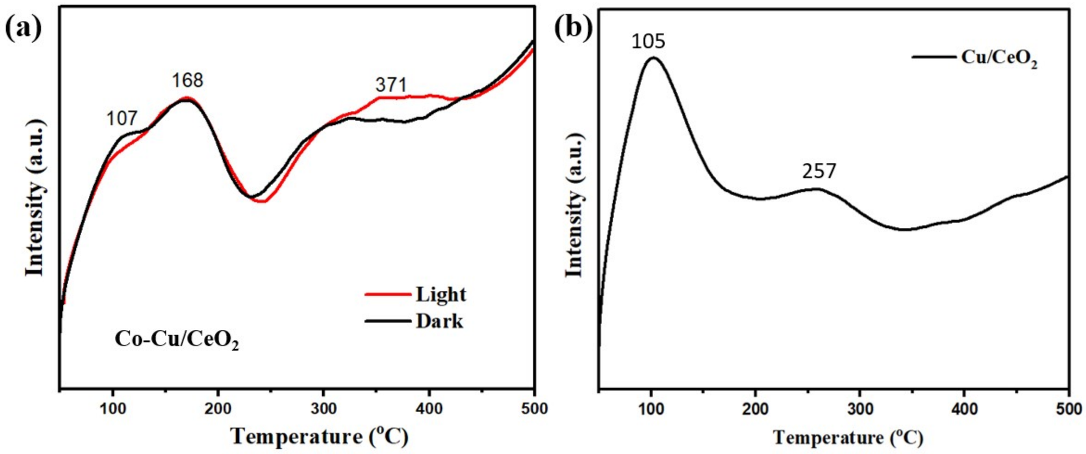

Figure S8. (a) H_2-TPD spectra of Co-Cu/CeO$_2$ and (b) CO-TPD spectra of Cu/CeO$_2$

The H_2-TPD of Co-Cu/CeO$_2$ is shown in Figure S8a, an obvious peak appeared at 371 °C under illumination, which also implies that adding light is beneficial to the adsorption of hydrogen by Co-Cu/CeO$_2$. The CO-TPD of Cu/CeO$_2$ is shown in Figure S8b. The main CO desorption peaks are located at 105 and 257 °C.

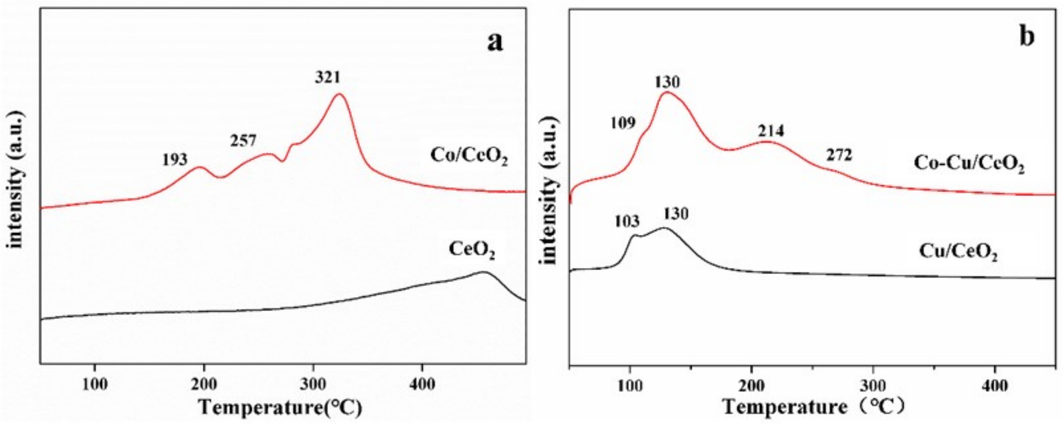

Figure S9. Temperature-programmed reduction profiles of CeO_2 and Co/CeO_2(a), Co-Cu/CeO_2 and Cu/CeO_2 catalysts(b)

Figure S9a-b is the TPR spectrum of Co-CeO_2, Cu/CeO_2, and Co-Cu/CeO_2. It can be clearly seen that the reduction peaks of Co- CeO_2 are located at 193°C, 257°C, and 321°C after loading. The reduction peak of Cu- CeO_2 is less than 150°C. When the bimetal is loaded, the reduction peak becomes 109, 130°C, 214°C, and 272°C. On the one hand, it proves that the metal and the carrier have formed a strong interaction force, and on the other hand, it implies that the same force is formed between Co-Cu[1].

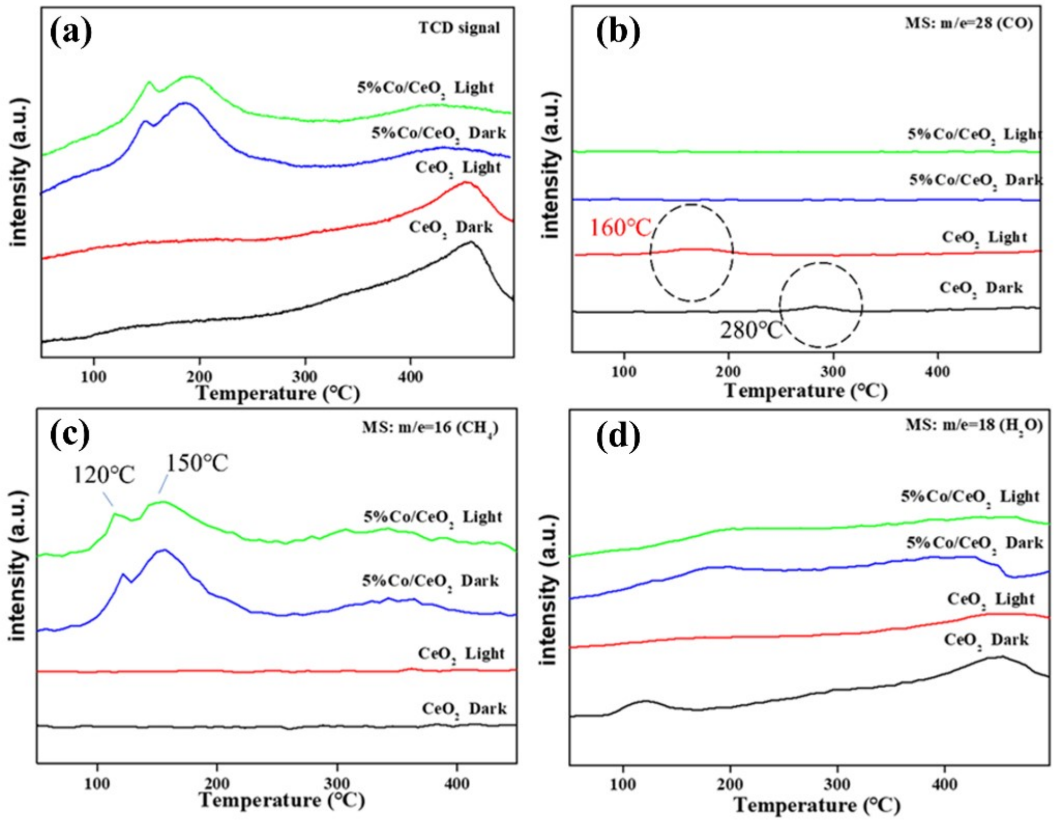

Figure S10. TPSR spectra of pre-adsorbed CO over Co/CeO_2 and CeO_2 catalysts under irradiation and dark respect.

From figure S10, CeO_2 has an obvious peak above 400°C, and the combined figure c-d can be attributed to the H_2O peak. From figure S7b, it can be seen that CeO_2 has a peak at 280°C under dark conditions. When light is irradiated, the peak position shifts to 160°C. Therefore, for CeO_2, we think that light is beneficial to the activation of CO. The desorption peak of Co/CeO_2 is mainly located from 100 to 220°C, and these two peaks combined with the b-d diagram are mainly attributed to CH_4. Compared with the dark reaction, the peak area is reduced after illumination. We suspect that illumination is more conducive to the conversion of CO to alcohols.

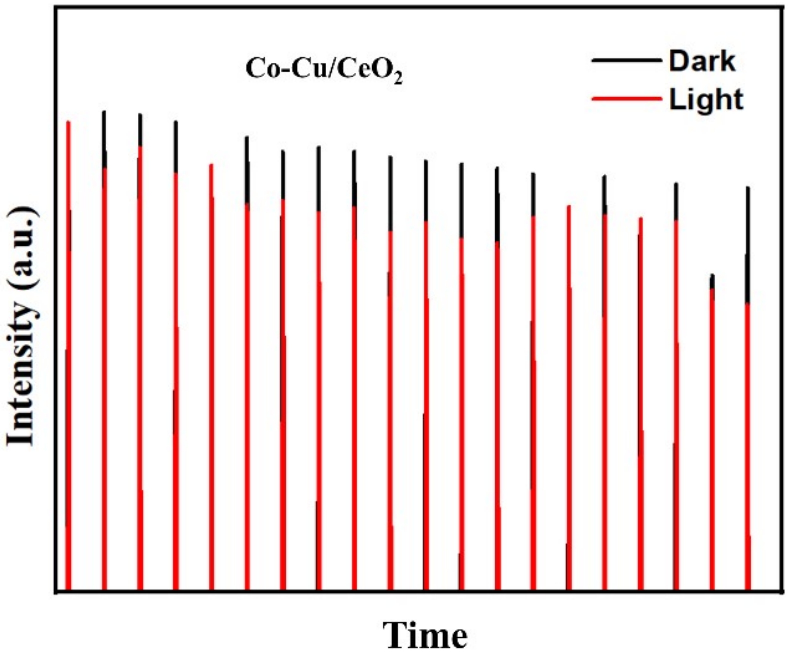

Figure S11. *In situ* H_2-chemisorption on Co-Cu/CeO_2 under dark and light irradiation

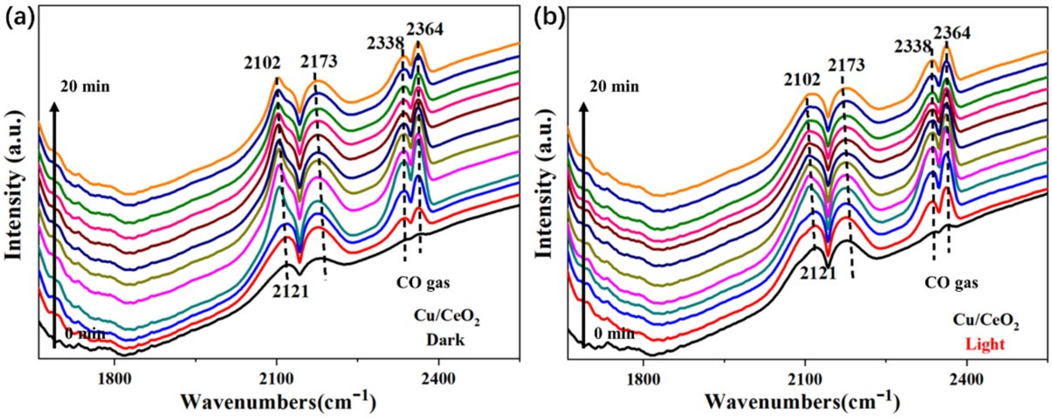

Figure S12. *In situ* DRIFTS spectra of CO absorption at the various condition: (a) under dark condition (b) under irradiation condition 180°C over Cu/CeO_2

Figure S12 shows the DRIFTS diagram of Cu/CeO_2. It can be seen from a-b that the position of the absorption peak does not change significantly before and after illumination. There is a small peak at 2102 cm^{-1}, which is attributed to the vibrational peak of CO adsorption to Cu under dark conditions[2]. After light addition, this peak has been slightly reduced, which also implies that light promotes the dissociation of H_2 and the reaction of surface CO species.

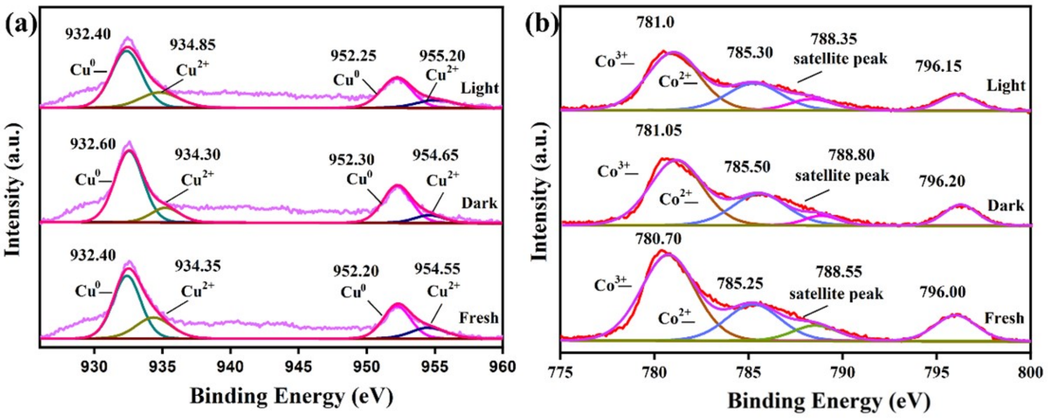

Figure S13. High-resolution XPS of Cu and Co of Co-Cu/CeO2 sample

The XPS of Cu_{2p} and Co_{2p} are tested as shown in Figure S13 a-b. Unfortunately, Co is inevitably oxidized in the XPS test. But combined with TPR, we think that Co is 0 valence in the reaction. Nevertheless, we have done an analysis of Co with two different valence states. For metal Co, the valence state of Co^{2+} and Co^{3+} was located at 783.65 eV and 779.85 eV respect. After the dark reaction, the main peak shifted to 781.12 eV, which means that the surface electron density of cobalt decreased during the reaction, which may be caused by the electron injection and adsorption of the reactant. Under light conditions, the electron binding energy of the main peak decreases, which may be due to the photogenerated electrons generated by CeO_2 being excited by light to transfer to Co, thereby increasing the electron density on the surface. Copper mainly exists in two valence states of Cu^0 and Cu^{2+} in the catalyst. The peaks at 932.40 eV and 952.20 eV are attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. After the dark reaction, the peak at 932.40 eV shifted to 932.60 eV, indicating that the Cu surface electrons were partially transferred to the reactant during the reaction. Under light conditions, the peak recovered to 932.40 eV, which may be that the plasmon effect of Cu stimulated by light accelerates H_2 overflow, thereby supplementing the electron density on the surface. It is worth mentioning that the hot electrons excited by the LSPR of Cu will be injected into CeO_2 to accelerate the reaction.

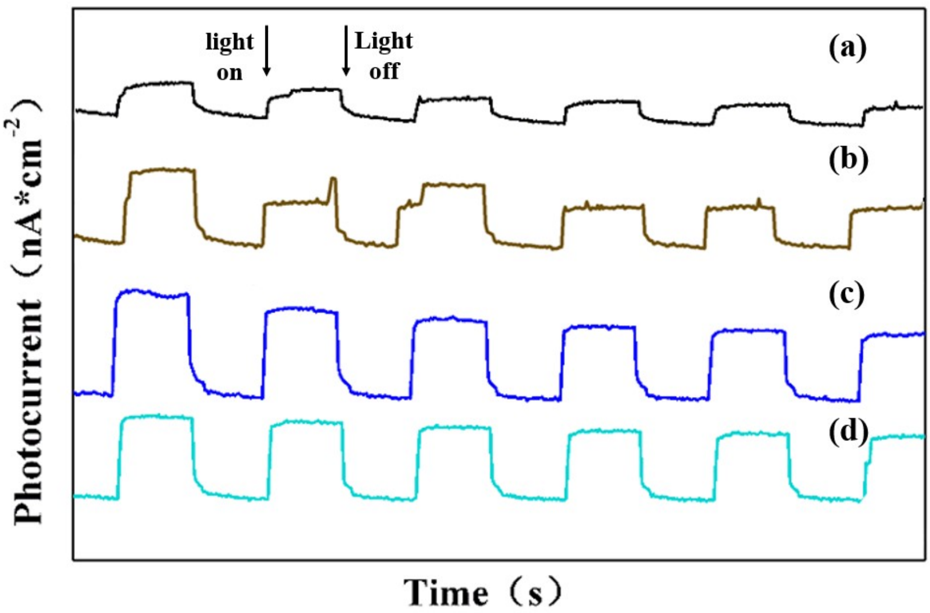

Figure S14. Transient photocurrent responses of (a) CeO_2, (b) Co/CeO_2, (c) Co-Cu/CeO_2, (d) Cu-CeO_2

1. L. Zhao, J. Duan, Q. Zhang, Y. Li and K. Fang, Preparation, Structural Characteristics, and Catalytic Performance of Cu–Co Alloy Supported on Mn–Al Oxide for Higher Alcohol Synthesis via Syngas, *Industrial & Engineering Chemistry Research*, 2018, **57**, 14957-14966.
2. J. Su, Z. Zhang, D. Fu, D. Liu, X.-C. Xu, B. Shi, X. Wang, R. Si, Z. Jiang, J. Xu and Y.-F. Han, Higher alcohols synthesis from syngas over CoCu/SiO2 catalysts: Dynamic structure and the role of Cu, *Journal of Catalysis*, 2016, **336**, 94-106.