Supporting Information

High light-to-fuel efficiency and CO_2 reduction rate achieved on a unique nanocomposite of Co/Co doped Al_2O_3 nanosheets with UV-Vis-IR irradiation

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Experimental.

Preparation. The sample of Co nanoparticles supported on Co doped Al_2O_3 nanosheets was prepared in accordance to the following procedure. 15.005 g $Al(NO_3)_3$❿$9H_2O$，1.151 g $Co(NO_3)_2$❿$6H_2O$， and 4.221g $CO(NH_2)_2$ were dissolved into 50 mL deionized water under magnetic stirring. The molar ratio of Co/(Co+Al) in the reactants is 0.09. The mixture solution was transferred to a 100 mL Teflon bottle. The Teflon bottle was sealed in stainless autoclave, and heated at 150 ^oC for 24 h in an electric oven. The resultant precipitate was filtered, washed with deionized water, dried at 120 ^oC for 12 h, and calcined at 500 ^oC for 8h in a muffle furnace. The obtained powder was labeled as CoO/Co-Al_2O_3. 0.050 g of CoO/Co-Al_2O_3 was put in a quartz tubular reactor and pre-reduced by 5 vol% H_2/Ar with 40 mL min^{-1} flow rate at 700 ^oC for 1 h. The obtained sample was labeled as Co/Co-Al_2O_3.

The Co doped Al_2O_3 sample (labeled as Co-Al_2O_3) was prepared by the same procedure as that of Co/Co doped Al_2O_3 except for reducing the amount of $Co(NO_3)_2$❿$6H_2O$ in the reactants from 1.151 g to 0.613 g. The molar ratio of Co/(Co+Al) in the reactants is 0.05.

The pure Al_2O_3 sample was prepared in accordance to the following procedure. 15.005 g $Al(NO_3)_3$❿$9H_2O$ and 3.96 g $CO(NH_2)_2$ were dissolved into 50 mL deionized water under magnetic stirring. The mixture solution was transferred to a 100 mL Teflon bottle. The Teflon bottle was sealed in stainless autoclave, and heated at 150 ^oC for 24 h in an electric oven. The resultant Al_2O_3❿nH_2O precipitate was filtered, washed with deionized water, dried at 120 ^oC for 12 h, finally calcined at 500 ^oC for 8 h in a muffle furnace.

The sample of Co nanoparticles supported on Al_2O_3 nanosheets (labeled as Co/Al_2O_3) was prepared in accordance to the following procedure. The Al_2O_3❿nH_2O precipitate, prepared by the same procedure as that of the pure Al_2O_3 sample mentioned above, was mixed with 50 mL deionized water. The mixture was intensively magnetically stirred until it became uniform slurry. 1.151g

$Co(NO_3)_2$❿$6H_2O$ was dissolved in 10 mL deionized water. Ammonia aqueous solution, obtained by diluting concentrated ammonia solution (25.0~28.0 wt%) with deionized water according to the volume ratio of 1:5, was dropped in the $Co(NO_3)_2$ solution under magnetic stirring until the pH value is 7~8. The resultant $Co(OH)_2$ suspension was mixed with the $Al_2O_3.nH_2O$ slurry, and intensively magnetically stirred for about 20 min. The obtained mixture was filtered, washed with deionized water, dried at 120 ^oC for 12h, and calcined at 240 ^oC for 8 h in a muffle furnace. The obtained powder was labeled as CoO/Al_2O_3. 0.050 g of CoO/Al_2O_3 was put in a quartz tubular reactor and pre-reduced by 5 vol% H_2/Ar with 40 mL min^{-1} flow rate at 700 ^oC for 1 h.

Characterization. A RigakuDmax X-ray diffractometer was used to obtain XRD patterns of the samples. A JEM-ARM200F electron microscope was used to obtain their TEM images and EDX mappings. An inductively coupled plasma/optical emission spectroscopy (ICP-OES, Optima 4300DV, PerkinElmer) was used to analyze their compositions. XPS spectra were recorded on an X-ray photoelectron spectrometer (ESCALAB 250Xi) using Mg Kα radiation to determine the element valence state of the samples. An ASAP2020 physisorption instrument was used to measure their BET surface area and pore volume by N_2 adsorption. A STA449F3 thermal analyser linked with a QMS403 mass spectrometer was used to make thermogravimetric/mass spectrometry (TG-MS) analysis. A Lambda 750S spectrophotometer was used to obtain their diffuse reflectance absorption spectra. A Raman microscope (Renishaw inVia) with 633 nm excitation was used to obtain their spectra.

Photothermocatalytic or photocatalytic tests. The photothermocatalytic or photocatalytic CO_2 reduction by CH_4 on the samples with the focused irradiation from a 500 W Xe lamp was conducted on a home-made stainless steel reactor with a quartz window as schematically illustrated in Scheme 1.[46] A stream of 30.0/29.3/40.7 vol% $CH_4/CO_2/Ar$, adjusted by a mass flow meter (S49-31/MT), constantly flowed at a flow rate of 89.2 mL min^{-1} into the reactor with 0.0200 g of the samples. To conduct the photothermocatalytic CO_2 reduction by CH_4 on $Co/Co-Al_2O_3$ with the focused visible-IR irradiation, $\lambda >$ 420, 560, and 690 nm long-wave pass filters were placed in the front of the reactor quartz window. The power of the focused UV-Vis-IR irradiation was 6949.7 mW. The spot diameter of the focused irradiation was 5 mm. Thus, the intensity of the focused UV-Vis-IR irradiation was 353.9 kW m^{-2} (corresponding to a solar flux concentration ratio of 353.9). The power values of the $\lambda >$ 420, 560, and 690 nm focused Vis-IR irradiation were 6228.4, 5398.6, and 4288.2 mW, respectively. A GC-9560 gas chromatograph (GC) was utilized to measure the concentration of the reactants and products. The procedures of photothermocatalytic tests, the focused irradiation power measurement, ligh-to-fuel efficiency calculation, and GC analysis were described in details in the previous publications.[46]

For conducting photocatalytic CO_2 reduction by CH_4 on Co/Co-Al_2O_3 with the focused UV-Vis-IR irradiation, the reactor was placed in an ice-water bath to maintain the photocatalytic reaction at near room temperature .

The η values on the basis of the standard molar Gibbs formation energy were also calculated:[46]

$$\eta = (r_{H2} \times \Delta_f G^0_{H2} + r_{CO} \times \Delta_f G^0_{CO} - r_{CH4} \times \Delta_f G^0_{CH4} - r_{CO2} \times \Delta_f G^0_{CO2})/P_{irradiation}$$

The values of $\Delta_f G^0_{H2}$, $\Delta_f G^0_{CO}$, $\Delta_f G^0_{CH4}$, and $\Delta_f G^0_{CO2}$ are 0, -137.2, -50.5, and -394.4 kJ mol^{-1}, respectively. The η value of Co/Co-Al_2O_3 with the focused UV-Vis-IR irradiation is 19.7%. The η values of Co/Co-Al_2O_3 with the $\lambda > 420$, 560, and 690 nm focused Vis-IR irradiation are 20.6%, 20.6%, and 21.4%, respectively.

The η values on the basis of $\Delta_f G^0$ less than the corresponding values on the basis of $\Delta_c H^0$ are attributed to the following reason. As the reaction is an entropy enhancement reaction (ΔS_{298} =256.6 J K^{-1} mol^{-1}), the reaction ΔG_{298} (170.5 kJ mol^{-1}) is less than its ΔH_{298} (247 kJ mol^{-1}) according to the Gibbs free energy equation ($\Delta G = \Delta H - T \times \Delta S$).

The thermodynamic maximum η_{max} value of our reaction system is determined by the solar absorption and Carnot efficiencies in accordance to the equation as follows: [46, 48]

$$\eta_{max} = [1 - \sigma \times T_H^4 / (I_{DNI} \times C)] \times [1 - T_L/T_H]$$

Where σ is Stefan–Boltzmann constant, I_{DNI} is the direct normal solar irradiation (1 kWm^{-2}), C is the concentration ratio of solar flux, T_H and T_L are the high and low temperatures of the equal Carnot heat engine.

In the present case, C is equal to 353.9. Upon the focused UV-Vis-IR irradiation, the surface temperature of Co/Co-Al_2O_3 was quickly elevated from room temperature (25 ^oC) to an equilibrium temperature (665 ^oC). T_L and T_H are 25 and 665 ^oC, respectively. The η_{max} value is calculated to be 59.8%.

Isotope labeling. Isotope labeling of photothermocatalytic $^{12}C^1H_4$ reduction by $^{12}C^{18}O_2$ (Aldich) on Co/Co-doped Al_2O_3 was conducted in the stainless steel reactor mentioned above on a home-made setup.[47] Before the isotope labeling experiment, the CoO/Co-doped Al_2O_3 sample was pre-reduced by a flow of 5 vol% H_2/Ar at 25 mL min^{-1} at 700 ^oC for 30 min with the focused UV-Vis-IR irradiation. After removing unreacted and adsorbed H_2 by a stream of high purity N_2 at room temperature, 20 mL

$^{12}C^{1}H_4$ and 10 mL $^{12}C^{18}O_2$ were introduced in the reactor. When the focused UV-Vis-IR irradiation was irradiated on the pre-reduced sample, the FTIR spectra were obtained at a known time on an infrared spectrometer (Nicolet-6700).

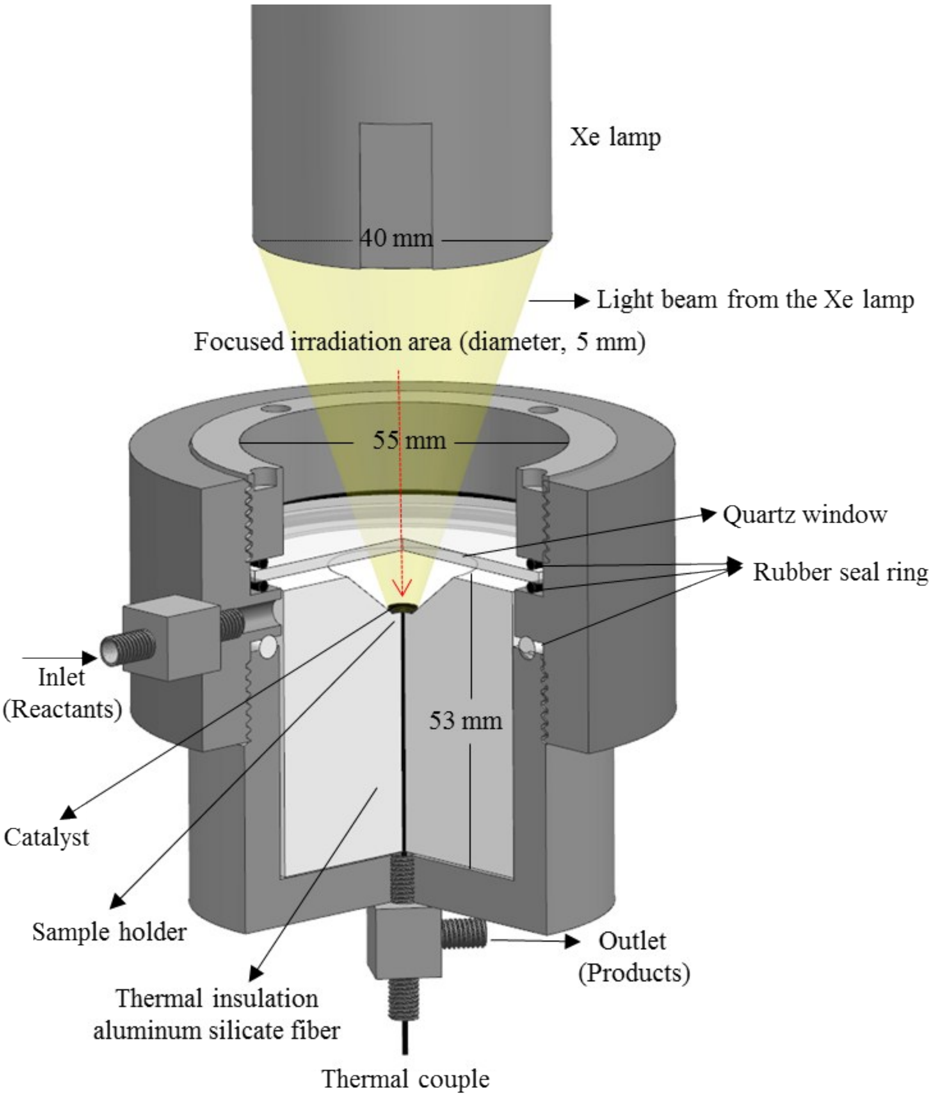
Controlled catalytic tests. The catalytic CO_2 reduction by CH_4 and CO_2 reduction by H_2 on the samples at different temperatures in the dark or with the focused irradiation was conducted on a quartz tubular reactor that was linked with a quartz window.[47] In the tests, the reaction temperature of the samples in the reactor was controlled by a tubular electric furnace.[47] 0.0050 g of CoO/Co-Al_2O_3 or CoO/Al_2O_3 was in-situ pre-reduced to Co/Co-Al_2O_3 or Co/Al_2O_3 by 5 vol% H_2/Ar with a flow rate of 50.0 mL min^{-1} at 700 ^{o}C for 1 h. After the pre-reduction, the stream of 5 vol% H_2/Ar was switched to a stream of 10.2/10.0/79.8 vol% CH_4/CO_2/Ar with a flow rate of 49.6 mL min^{-1} for the catalytic CO_2 reduction by CH_4. The procedure was described in details in the previous works.[47] For catalytic CO_2 reduction by H_2 on Co/Co-Al_2O_3, a stream of 10.0/10.0/80.0 vol% /CO_2/H_2/Ar constantly flowed at 51.6 mL min^{-1} into the reactor.

Temperature programmed reactions. Temperature programmed reactions of CO_2 decomposition (CO_2-TPD), CH_4 decomposition (CH_4-TPD), oxidation of pre-deposited CH_x by CO_2 (CH_x-TPO), and CO disproportionation (CO-TPD) on Co/Co-Al_2O_3 in the dark or with the irradiation were conducted on a multifunctional adsorption apparatus (TP-5080) by using a quartz tubular reactor that was linked with a quartz window.[47] 0.0030 g of the CoO/Co-Al_2O_3 sample was in-situ pre-reduced to Co/Co-Al_2O_3 at 700 ^{o}C for 1 h in a flow of 5 vol% H_2/Ar at 23 mL min^{-1}, and then cooled to room temperature. CH_4-TPD was conducted by heating the pre-reduced sample (Co/Co-Al_2O_3) in a flow of 10 vol% CH_4/He at 25 mL min^{-1} in the dark or with the UV-Vis-IR irradiation. CO_2-TPD was conducted by heating the Co/Co-Al_2O_3 sample in a flow of 10 vol% CO_2/He at 25 mL min^{-1} in the dark or with the UV-Vis-IR irradiation.

For conducting CH_x-TPO, 0.0500 g of the CoO/Co-Al_2O_3 sample was pre-treated by a flow of pure CH_4 at 25 mL min^{-1} in the dark at 700 ^{o}C for 10 min for the pre-reduction and pre-deposition of CH_x species, and then cooled to room temperature. 0.0030 g of the Co/Co-Al_2O_3 sample with pre-deposited CH_x species was heated in a flow of 10 vol% CO_2/He at 25 mL min^{-1} in the dark or with the UV-Vis-IR irradiation.

CO-TPD was conducted by heating the Co/Co-Al_2O_3 sample in a flow of 5 vol% CO/He at 23 mL min^{-1} in the dark or with the UV-Vis-IR irradiation. In accordance to the CO consumption amount, which is calibrated by the CO consumption amount of a known amount of CuO during its temperature programmed reduction, the carbon deposition rate (r_C) due to the CO disproportionation on the Co/Co-Al_2O_3 sample is calculated.

To conduct the temperature programmed reactions with focused Vis-IR irradiation, a corresponding long wave pass filters of 420 or 560 nm was used. The light intensities of UV-Vis-IR, Vis-IR irradiation of $\lambda > 420$ and 560 nm are 549.6, 461.2, and 399.8 mW cm^{-2}, respectively.



Scheme S1. Schematically illustrated home-made reactor for conducting photothermocatalytic CO_2 reduction by CH_4 on the samples under the focused irradiation from a 500 W Xe lamp without using additional electric heater.[46]

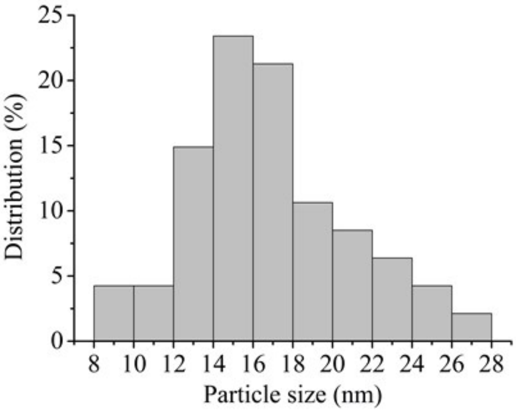


Figure S1. The size distribution of Co nanoparticles for the Co/Co-Al_2O_3 according to its TEM image (Figure 2B).

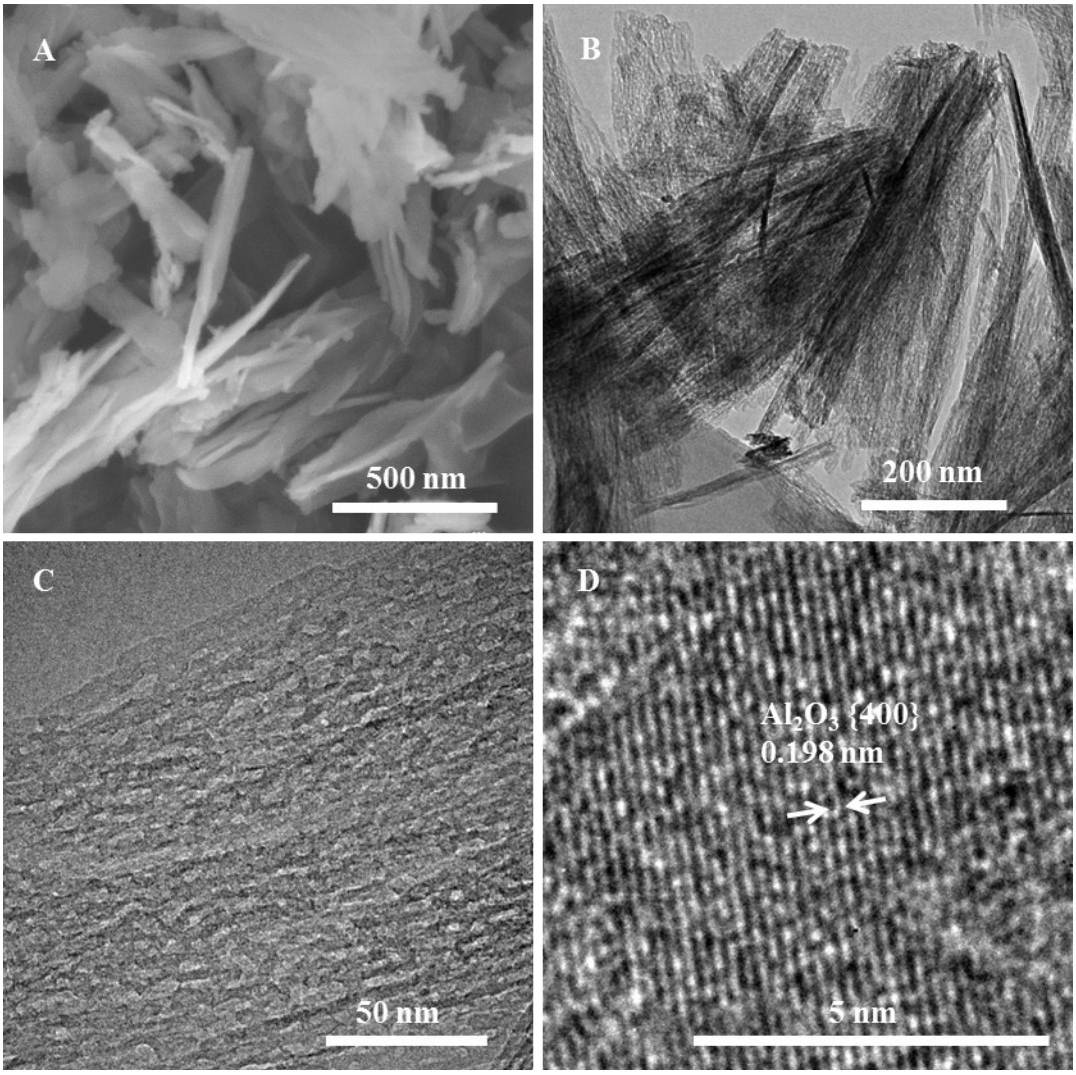


Figure S2. SEM image (A), TEM images (B, C), and HRTEM image (D) of Co-Al_2O_3.

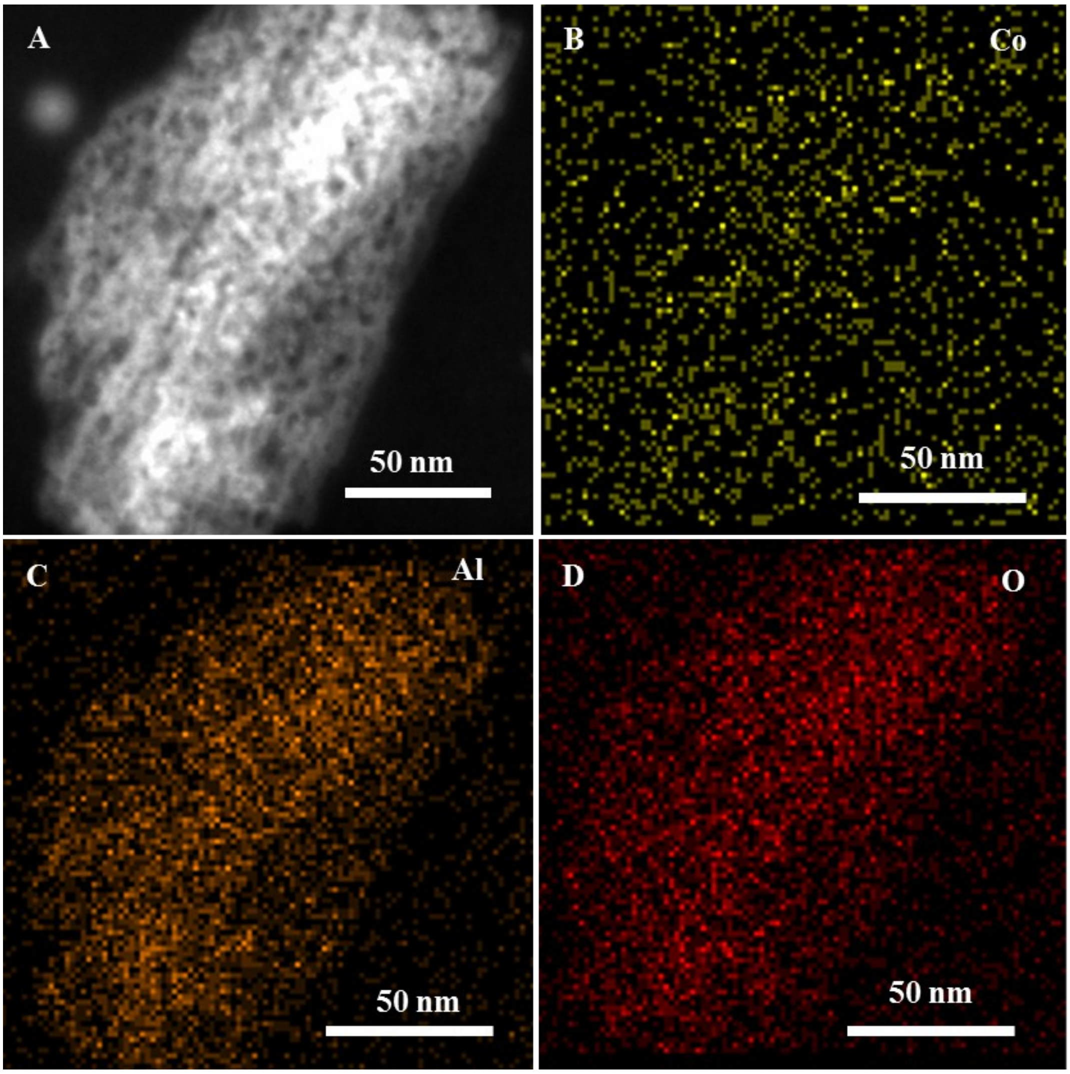


Figure S3. HAADF image (A) and the corresponding element mappings of Co (B), Al (C), and O (D) of Co-Al_2O_3.

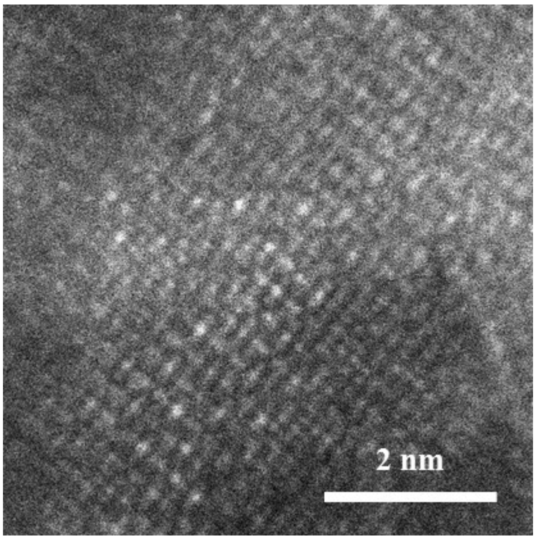


Figure S4. High-resolution HAADF-STEM image of Co-Al_2O_3

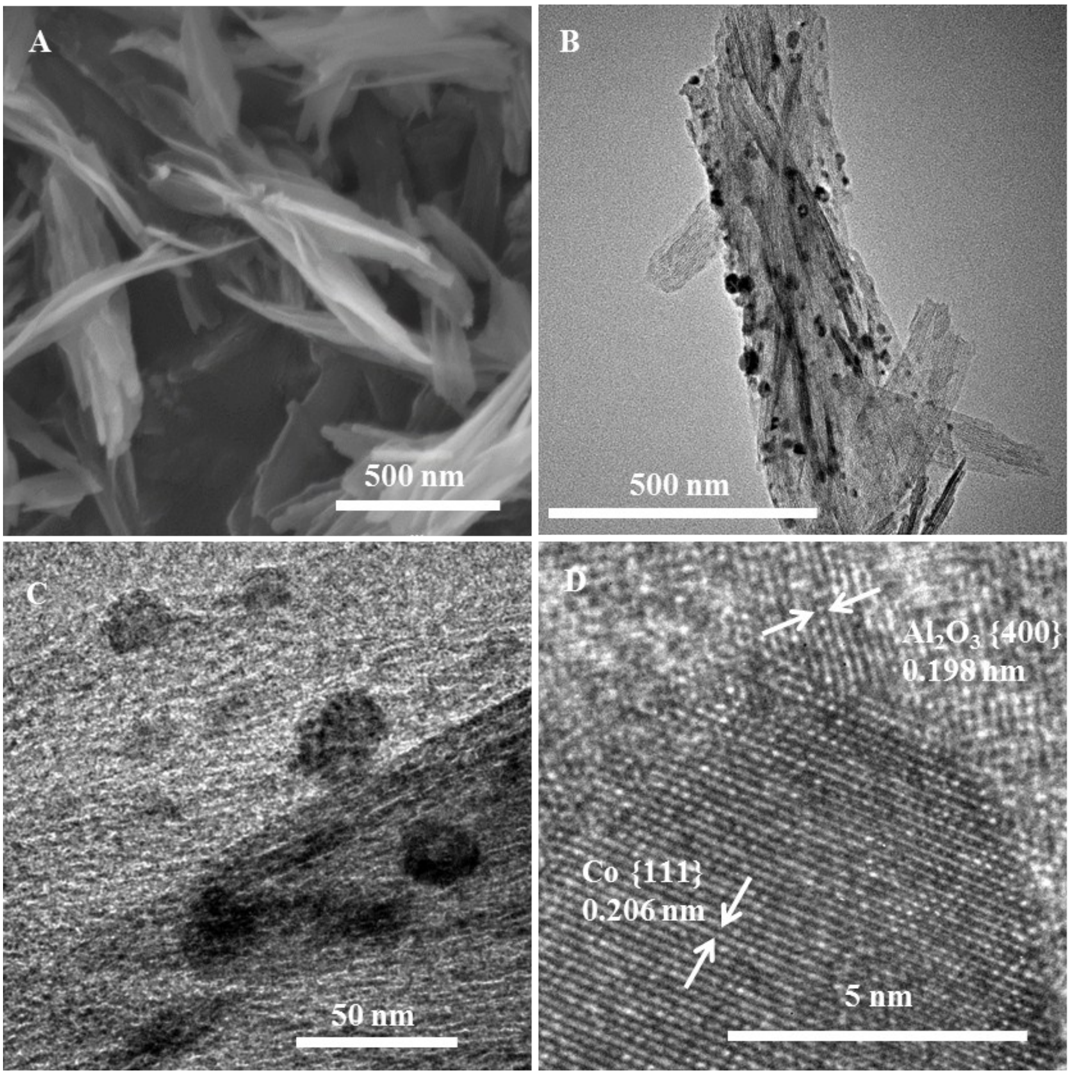


Figure S5. SEM image (A), TEM images (B, C), and HRTEM image (D) of Co/Al_2O_3.

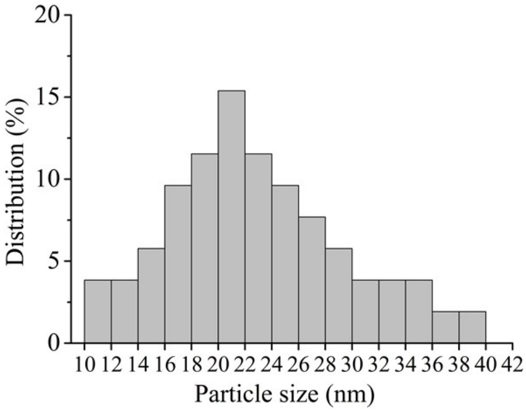


Figure S6. The size distribution of Co nanoparticles for the Co/Al_2O_3 according to its TEM image (Figure S5B).

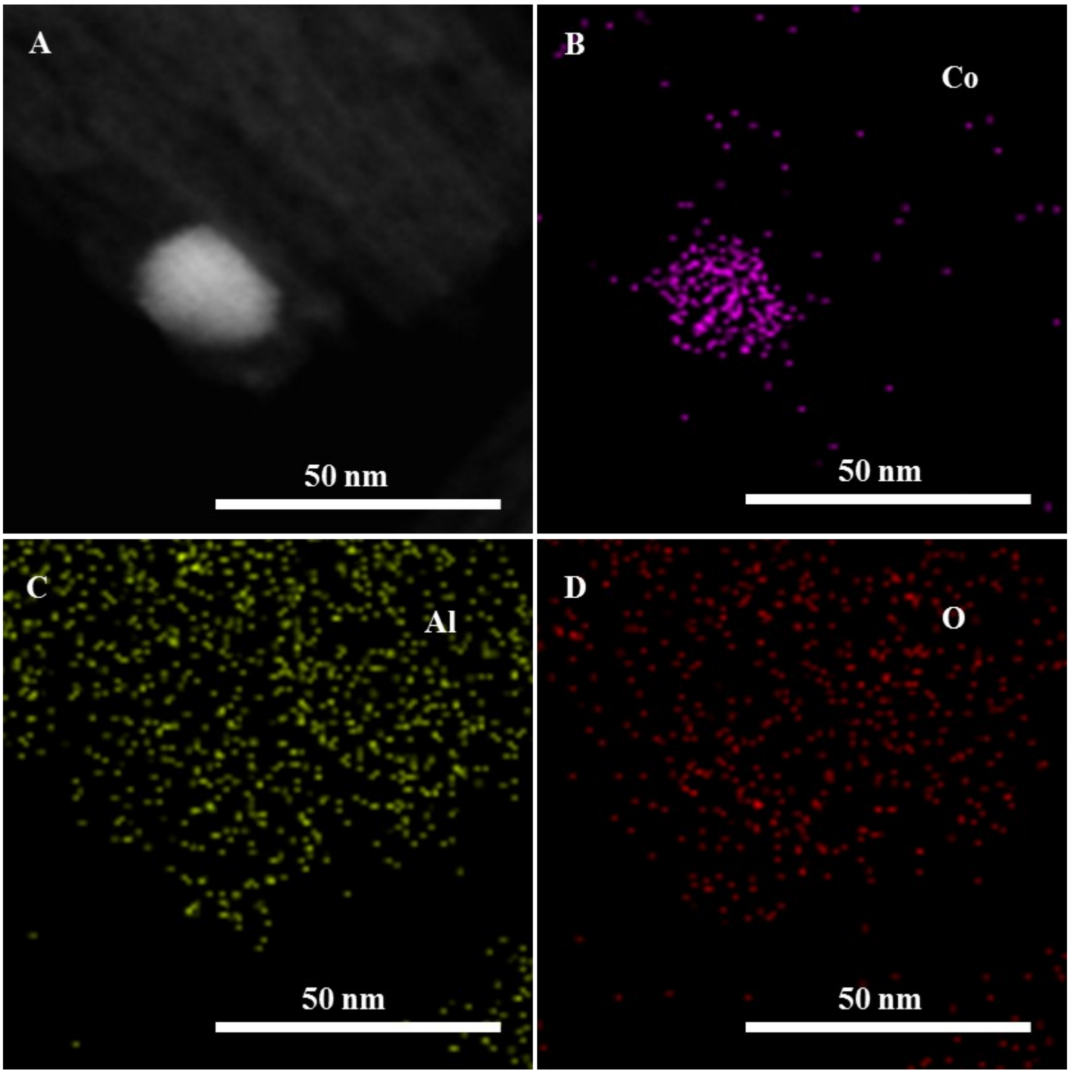


Figure S7. HAADF image (A) and the corresponding element mappings of Co (B), Al (C), and O (D) of Co/Al_2O_3.

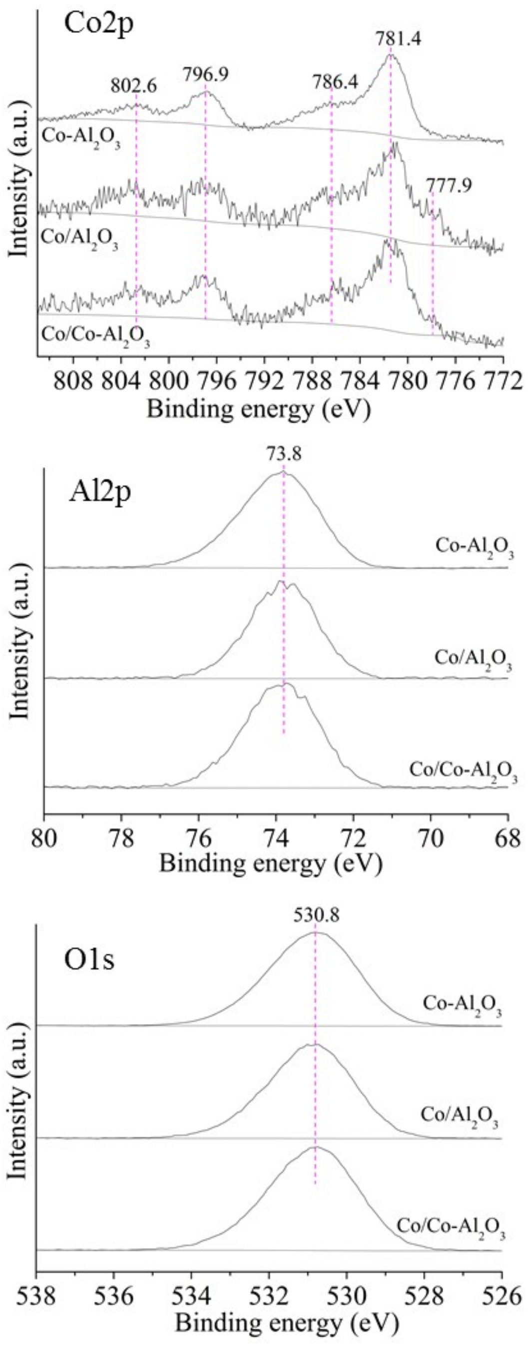


Figure S8. XPS spectra of Co2p, Al1s, and O1s in Co-Al_2O_3, Co/Co-Al_2O_3 and Co/Al_2O_3. In Figure S8A, two strong peaks around 781.4 and 796.9 eV are assigned to the Co 2p3/2 and Co 2p1/2 of Co^{2+}, respectively, as the binding energy values are the same as the corresponding those of Co^{2+} in $CoAl_2O_4$.[S1] Two broad peaks around 786.4 and 802.6 eV are assigned to the satellite peaks of Co 2p3/2 and Co 2p1/2 of Co^{2+}, respectively. [S1] The small shoulder peak around 779.9 eV for Co/Co-Al_2O_3 and Co/Al_2O_3 is assigned to Co 2p3/2 of metallic Co.[S1] In Figure S8B, the strong peak around 73.8 eV is assigned to Al 2p of Al^{3+}. [S1] In Figure S8C, the strong peak around 530.8 eV is assigned to O 1s of O^{2-}.[S1]

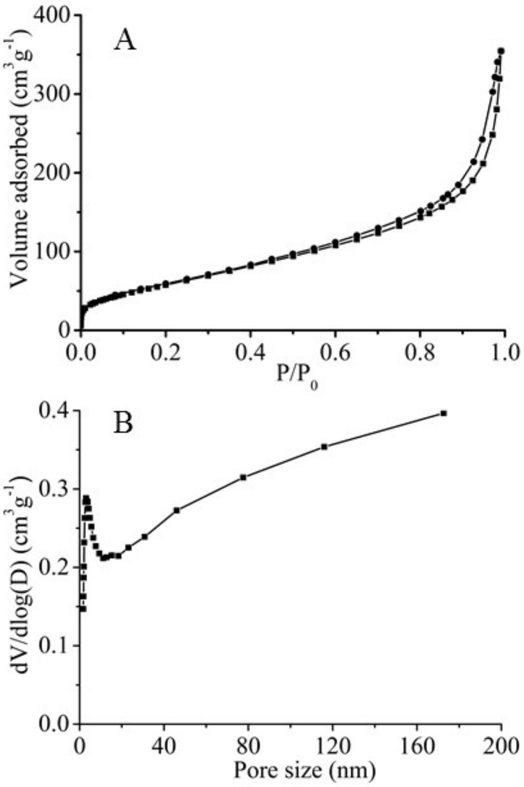


Figure S9. N_2 adsorption and desorption (A) and BJH adsorption pore size distribution (B) of Co-Al_2O_3.

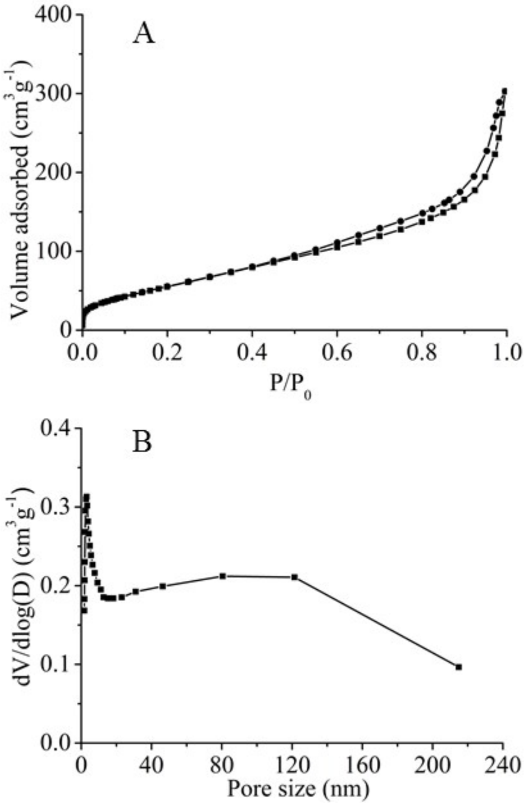


Figure S10. N_2 adsorption and desorption (A) and BJH adsorption pore size distribution (B) of Co/Co-Al_2O_3.

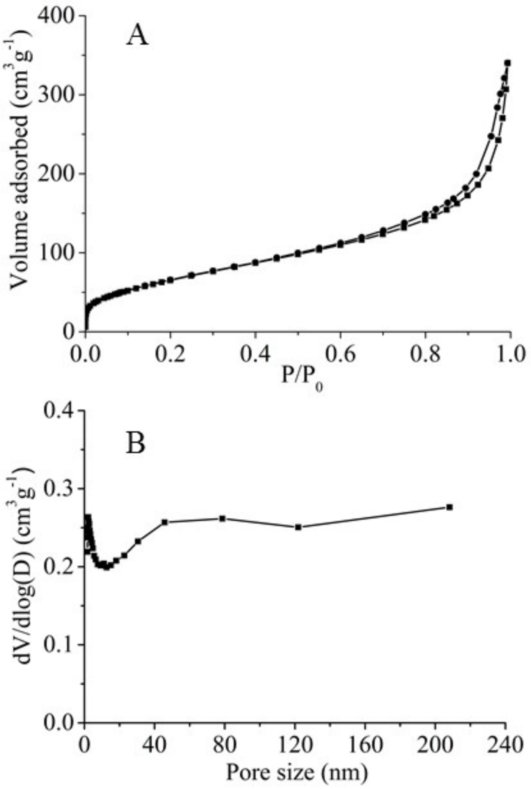


Figure S11. N_2 adsorption and desorption (A) and BJH adsorption pore size distribution (B) of Co/Al_2O_3.

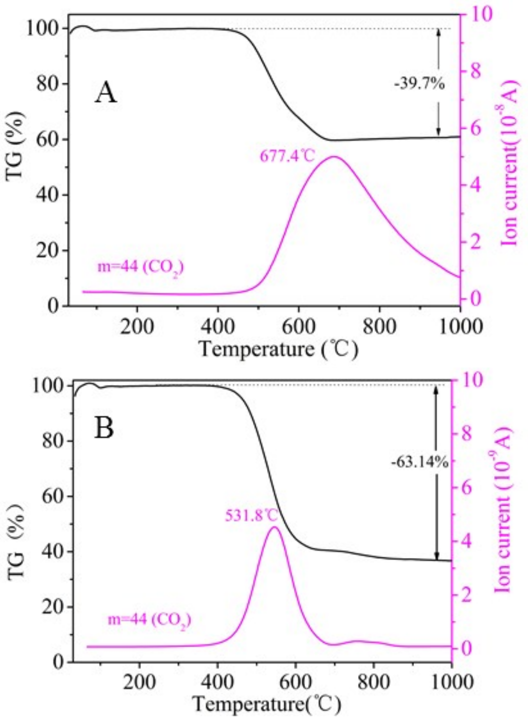


Figure S12. TG-MS profiles of the used Co/Al_2O_3 catalyst after 4 h photothermocatalytic durability test (A) and the used Co/Co-Al_2O_3 catalyst after 70 h photothermocatalytic durability test (B).

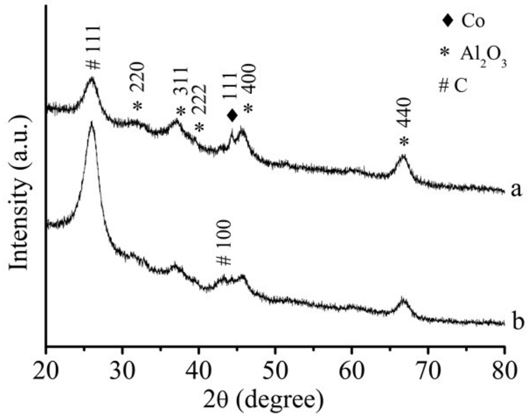


Figure S13. XRD patterns of the used Co/Al_2O_3 catalyst after 4 h photothermocatalytic durability test (a) and the used Co/Co-Al_2O_3 catalyst after 70 h photothermocatalytic durability test (b).

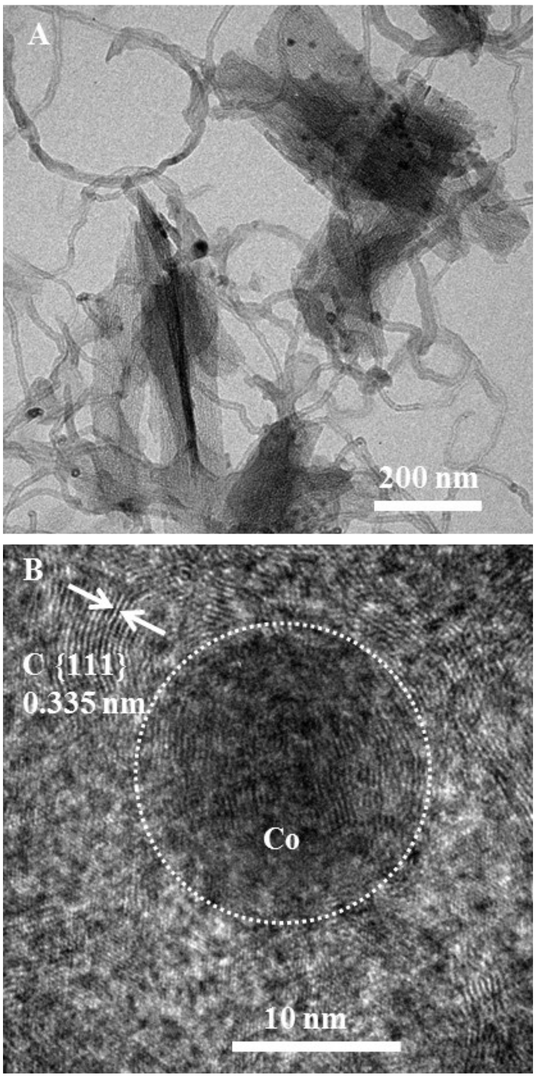


Figure S14. TEM image (A) and HRTEM image (B) of the used Co/Al_2O_3 catalyst after 4 h photothermocatalytic durability test.

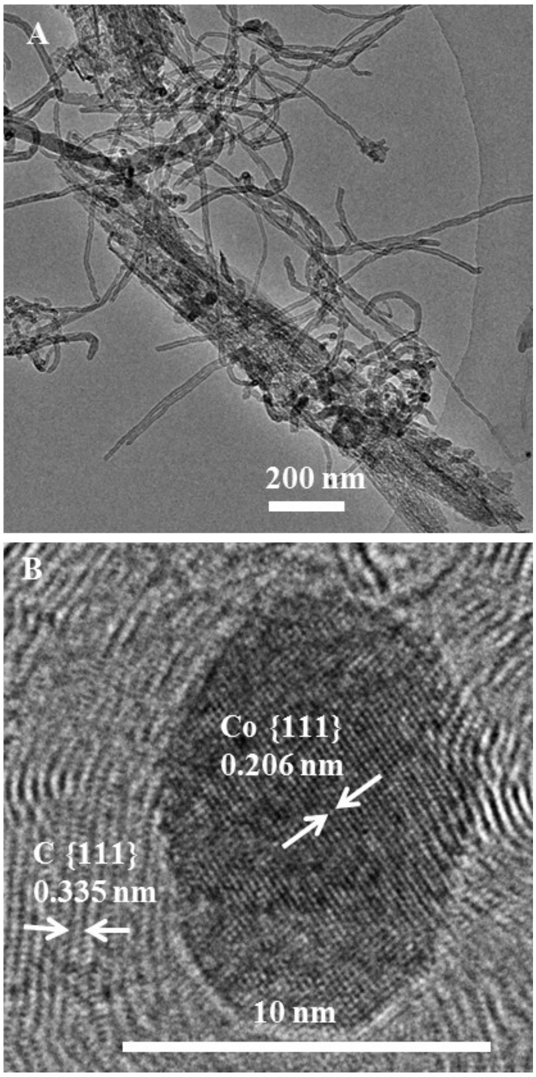


Figure S15. TEM image (A) and HRTEM image (B) of the used Co/Co-Al_2O_3 catalyst after 70 h photothermocatalytic durability test.

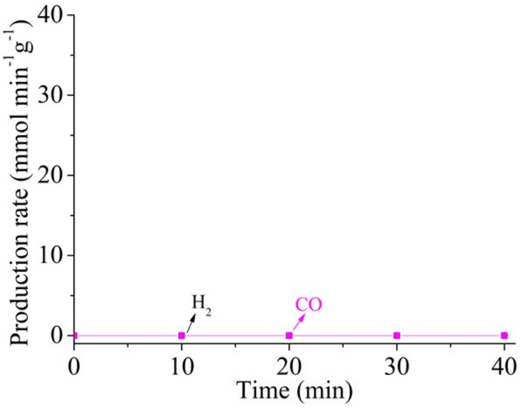


Figure S16. Time course of CO and H_2 production rates for photocatalytic CO_2 reduction by CH_4 on Co/Co-Al_2O_3 at near room temperature with the UV-Vis-IR irradiation.

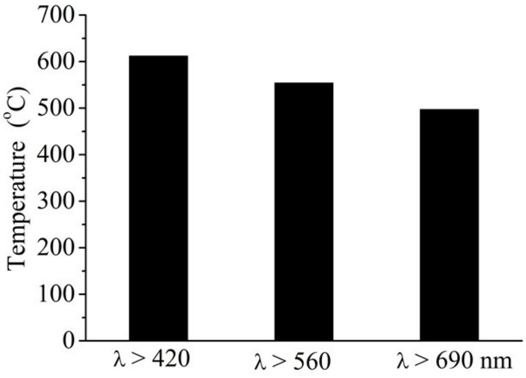


Figure S17. The equilibrium temperatures of Co/Co-Al_2O_3 with the focused Vis-IR irradiation.

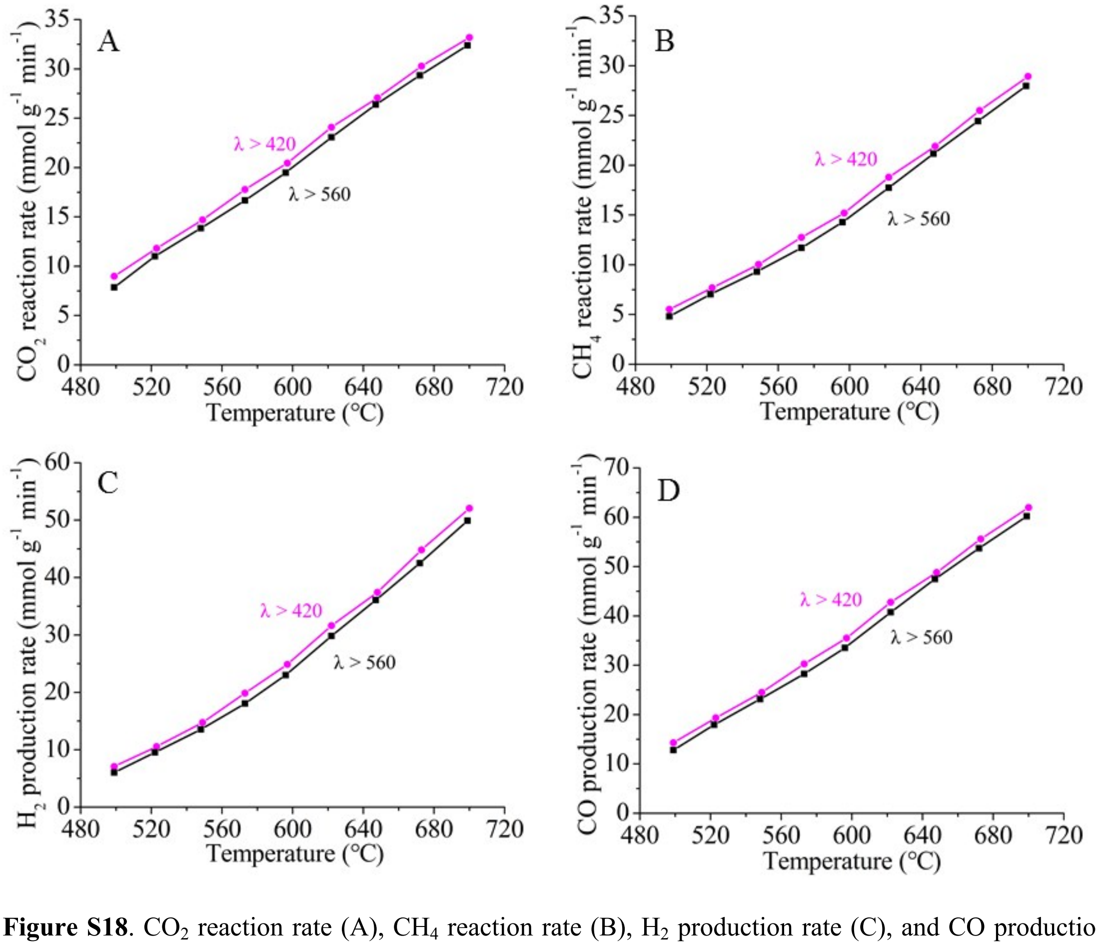


Figure S18. CO_2 reaction rate (A), CH_4 reaction rate (B), H_2 production rate (C), and CO production rate (D) *vs T* for CO_2 reduction by CH_4 on Co/Co-Al_2O_3 with the focused Vis-IR irradiation of λ > 420 nm and 560 nm.

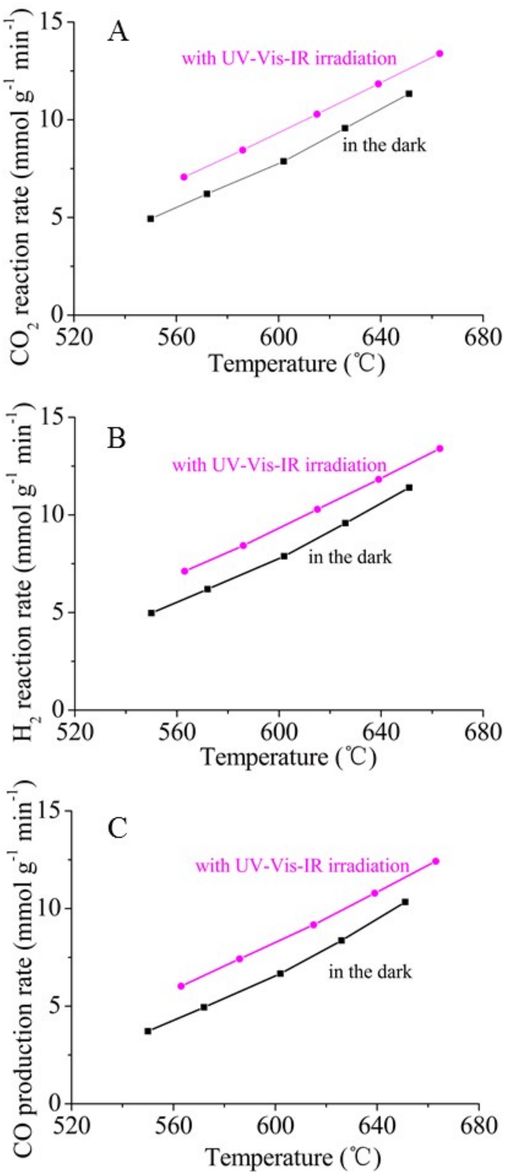


Figure S19. CO_2 reduction rate (A), H_2 reduction rate (B), and CO production rate (C) vs T for CO_2 reduction by H_2 on Co/Co-Al_2O_3 in the dark and with the focused UV-Vis-IR irradiation. As aforementioned in Section 2.2, the H_2/CO molar ratio less than the stoichiometric ratio (1:1) of the reaction ($CO_2 + CH_4 = 2CO + 2H_2$) is due to the side-reaction of reverse water–gas shift ($H_2 + CO_2 = H_2O + CO$). To demonstrate if the focused UV-Vis-IR irradiation affects the side reaction, CO_2 reduction of by H_2 on Co/Co-Al_2O_3 in the dark and with the focused UV-Vis-IR irradiation was also conducted. At the same temperature larger than 550 ^{o}C, compared with the corresponding those in the dark, the focused UV-Vis-IR irradiation also raises the values of r_{CO2}, r_{H2}, and r_{CO}. But the enhancement factors in r_{H2} and r_{CO} are less than the corresponding those for CO_2 reduction by CH_4 (Figure 9C and 9D). This leads to the H_2/CO molar ratio for CO_2 reduction by CH_4 being enhanced by the focused UV-Vis-IR irradiation (Figure 9E).

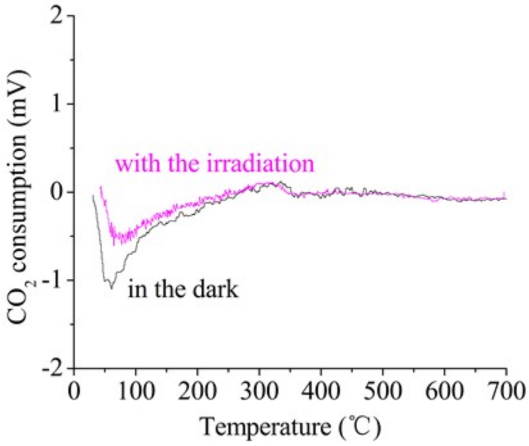


Figure S20. The CO_2-TPD profiles of Co/Co-Al_2O_3 with the UV-Vis-IR irradiation.

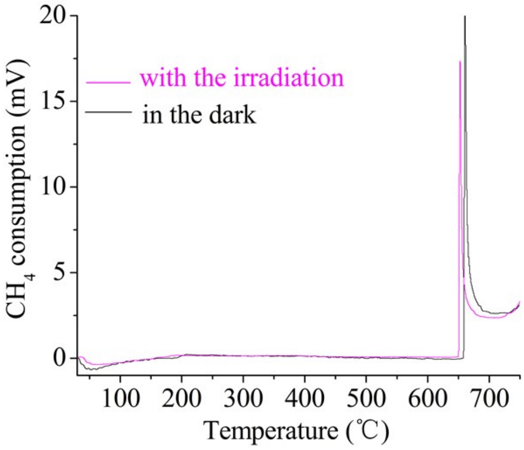


Figure S21. The CH_4-TPD profiles of Co/Co-Al_2O_3 with the UV-Vis-IR irradiation.

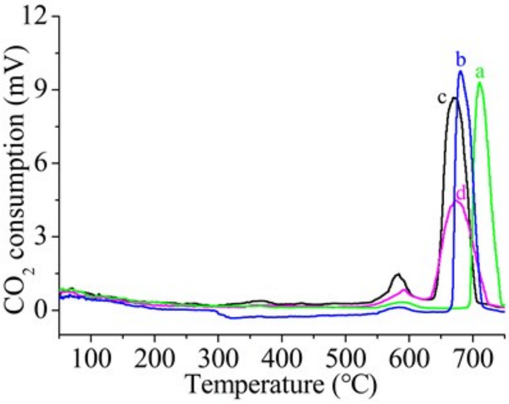


Figure S22. The profiles of oxidation of pre-deposited CH_x by CO_2 on Co/Co-Al_2O_3 in the dark (a), with the UV-Vis-IR irradiation (b), and with the Vis-IR irradiation of λ > 420 nm (c) and λ > 560 nm (d).. Compared to the CH_x-TPO profile in the dark, the strong CO_2 consumption peak considerably shifts to lower temperature upon the irradiation. This indicates that the irradiation significantly promotes the oxidation of pre-deposited CH_x* species.

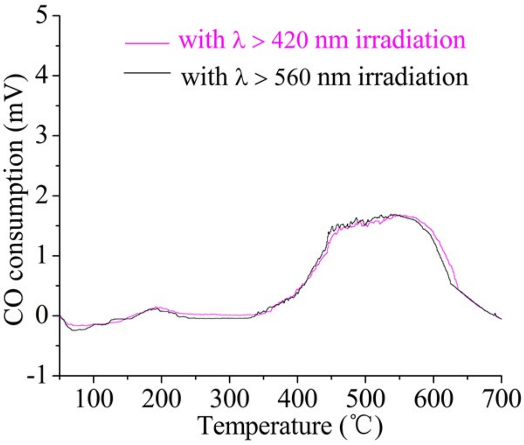


Figure S23. The CO-TPD profiles of Co/Co-Al_2O_3 with the focused Vis-IR irradiation of λ > 420 and 560 nm.

Reference

S1. C.D. Wagner, W.M. Riggs, L.E. Davis, Handbook of X-ray Photoelectron Spectroscopy, PerkinElmer, Waltham, MA, 1979.