

Supporting Information

**Catalyst-free photochemical CO₂ hydrogenation to CO and CH₄
conversion to C₂H₆**

Experimental Procedures

Chemicals

H₂SO₄ (AR) and CH₃COOH (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium acetate (99.99%) was obtained from Aladdin Chemical Reagent, Ltd. Acetylacetone (99.5%) was provided by Alfa Aesar Chemical Co. Ltd. CO₂ (99.995%), CH₄ (99.995%) and Ar (99.9995%) were provided by Air Liquid Houlding Co., Ltd., China. H₂ (99.99%) was obtained from Shanghai Chemistry Industrial Zone Pujiang Special Type Gas Co., Ltd. Deionized (DI) water was used in the all the experiments.

Performance test

The photochemical reaction was conducted in a home-made quartz reactor (220 mL) at standard room temperature, and a 172 nm-140 W Xe₂ excimer lamp was employed as the light source (ZIBOR UV. Co., Ltd.) without any extra energies.

For CO₂ hydrogenation, in a typical process, prior to illumination reaction, the reactor was evacuated by a vacuum pump, and then filled with Ar gas to attain atmospheric pressure. This evacuation-filling operation was repeated three times. Subsequently, 100 mL of CO₂/H₂ mixture with known volume ratio was introduced into the reactor. Throughout the experiment, the reactor was enveloped with aluminum foil to avoid any external light interference. The reaction was stopped after desired time. H₂O-promoted CH₄ conversion was conducted via nearly the same procedure; and the major difference was the feedstock employed.

The gaseous products such as CO, C₂H₆, H₂ and CH₄ were analyzed by a gas chromatograph (Agilent GC-8860) equipped with a thermal conductivity detector (TCD), flame ionization detector (FID) and a methanizer which contains Ni catalyst and calibrated with a standard gas mixture. The amount of H₂ was quantified on the TCD using a Molsieve 5Å column. The amount of C₂H₆ was measured on the FID using a Hayesep Q column. The amount of CO and CH₄ was quantified on the FID using a Molsieve 5Å column. The role of methanizer is to convert CO to CH₄ for FID analysis. Meanwhile, hydrocarbons such as C₃H₈ were analyzed by a gas chromatograph (Agilent GC-7890A) equipped with a TCD and FID and calibrated with a standard gas mixture. The amount of hydrocarbons such as C₃H₈ was determined on the FID using a HP-AL/S column. Meanwhile, to detect liquid products, 10 mL of H₂O was injected into the system after the reaction. Possible liquid products such as methanol, ethanol, acetic acid, and acetaldehyde were measured using an Agilent Technology 7890B gas chromatography system with a flame ionization detector using an DB-WAX-UI column. The possible product of formic acid was analyzed by HPLC (Waters 2695) equipped with Aminex HPX-87H column, UV/visible detector (WATER2489), and using 5 mM sulfuric acid as the mobile phase with a flow rate of 0.7 mL/min. The amount of HCHO was analyzed by using the acetylacetone colour-development method. Specifically, 1 mL of the as-prepared acetylacetone solution was mixed with 4 mL of the aqueous solution with product in a glass bottle, and heated for 5 min in boiling water, then the yellow colour of the mixed solution could be investigated. Afterwards, desired amount of solution was taken out and measured by using a

Shimadzu UV-2700 spectrophotometer. Through the absorbance intensity at 413 nm, the HCHO concentration was obtained. Typically, 100 mL of acetylacetone solution was first prepared by dissolving 15 g of ammonium acetate, 0.3 mL of acetic acid, and 0.2 mL of acetylacetone in water, and was stored in refrigerator with 2-6 °C.

Quantum efficiency (QE) calculation

The QE for CO evolution for CO₂ hydrogenation and C₂H₆ evolution for H₂O-promote CH₄ conversion was measured using the standard experimental setup. The system was irradiated by a 172 nm-140 W Xe₂ excimer lamp for 24 h. The average intensity of irradiation (I) was 0.9 mW cm², which was determined by a UIT-250(USHIO) unimeter. The irradiation area (S) was measured to be 19.63 cm². E_λ is given by hc/λ ($\lambda = 172$ nm). The QE was calculated by the following equation.

$$QE(CO) = \frac{2 \times \text{the number of evolved CO molecules}}{I (W/cm^2) \times S(cm^2) \times t(s)/E_\lambda(J)} \times 100\%$$

$$QE(C_2H_6) = \frac{2 \times \text{the number of evolved C}_2\text{H}_6 \text{ molecules}}{I (W/cm^2) \times S(cm^2) \times t(s)/E_\lambda(J)} \times 100\%$$

Characterization

The temperature was recorded by an infrared thermal imaging camera (Fotrpic 315, Shanghai Thermal Imaging Technology Co., Ltd.). *In-situ* FT-IR spectra were recorded using a NICOLET iS50 FT-IR spectrometer (Thermo SCIENTIFIC, USA) equipped with a high-temperature reaction chamber and a mercury cadmium telluride (MCT) detector at a resolution of 4 cm⁻¹ and 32 scans per spectrum.

For CO₂ hydrogenation, the background spectrum was recorded after the introduction of the gas mixture (66%CO₂/33%H₂).

Similarly, for H₂O-promoted CH₄ conversion, the background spectrum was collected after introducing moist CH₄ gas into the testing chamber.

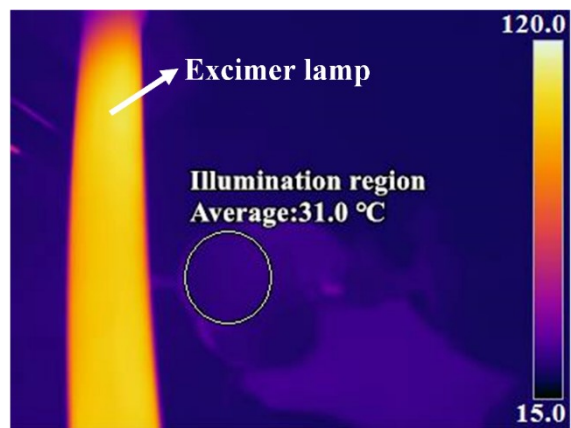


Figure S1 Infrared thermal images captured for the illumination region of the reactor.

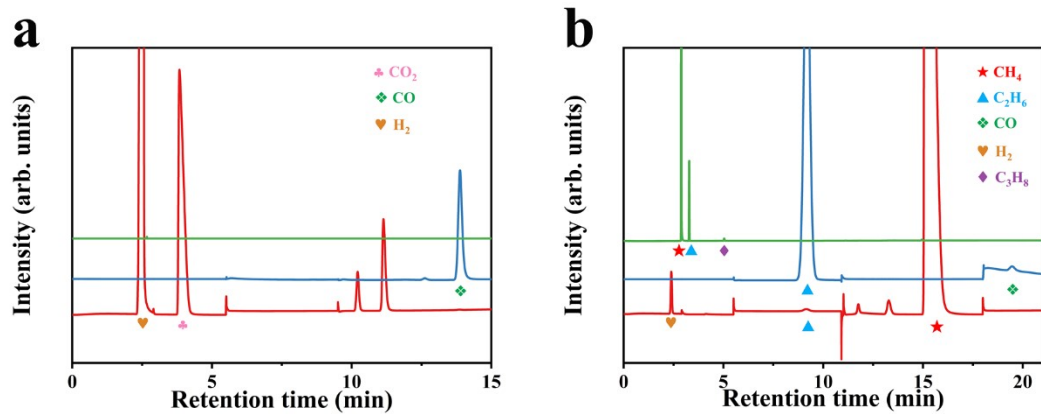


Figure S2 Typical GC curve of the sample: (a) CO₂ hydrogenation and (b) H₂O-promoted CH₄ conversion. Reaction conditions: 172 nm-140 W Xe₂ excimer lamp, irradiation time 24 hours, ambient temperature; total volume of reaction gas 100 mL and volume ratio (CO₂/ H₂ =2/1) for Figure S2a; volume of reaction gas 220 mL and volume of water (1 mL) for Figure S2b.

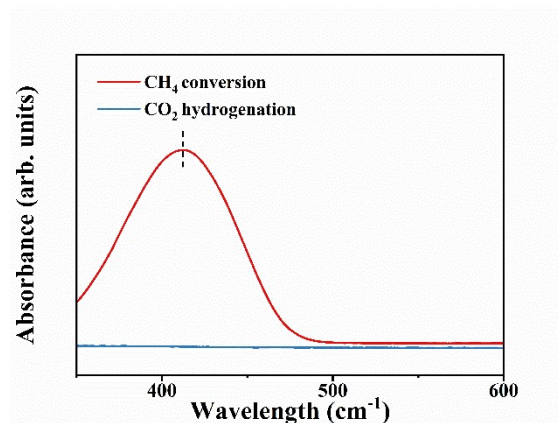


Figure S3 Ultraviolet-visible absorption spectrum of the reaction mixture from CO₂ hydrogenation (light blue) and H₂O-promoted CH₄ conversion (red). Reaction conditions: 172 nm-140 W Xe₂ excimer lamp, irradiation time 24 hours, ambient temperature; volume of reaction gas 100 mL and volume ratio (CO₂/ H₂ =2/1) for CO₂ hydrogenation; volume of reaction gas 220 mL and volume of water (1 mL) for CH₄ conversion.

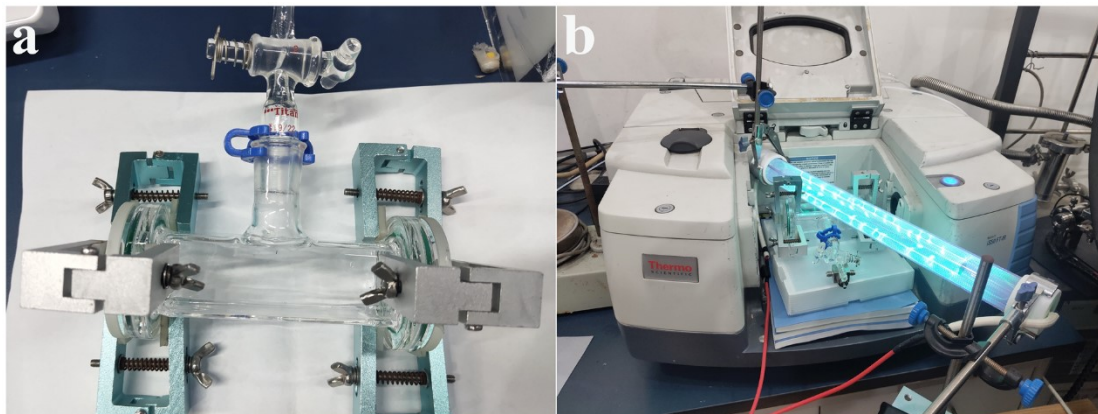


Figure S4 (a) Photograph of the *in-situ* FT-IR reactor. (b) Photograph of the *in-situ* FT-IR analysis apparatus in VUV photochemistry system.

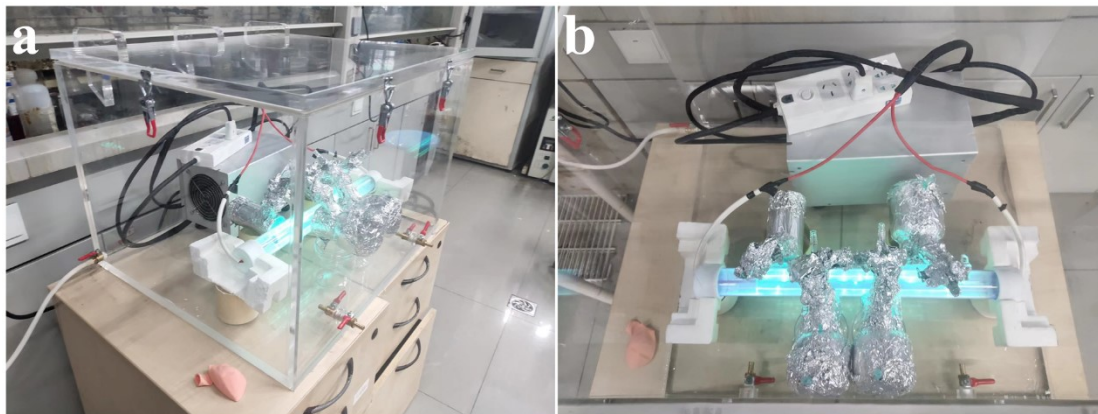


Figure S5 Photograph of the VUV photochemistry setup in Ar atmosphere.

Table S1 Representative studies on the CO₂ hydrogenation and CH₄ transformation.

Catalysts	Reaction condition	Reactant	Production	Time	Reference
None	140 W Xe ₂ excimer lamp	CO ₂ +H ₂	CO: 4.8 μmol	24 h	This work
None	140 W Xe ₂ excimer lamp	CH ₄	C ₂ H ₆ : 10.8 μmol	24 h	This work
None	140 W Xe ₂ excimer lamp	CH ₄ +H ₂ O	C ₂ H ₆ : 21.6 μmol	24 h	This work
None	140 W Xe ₂ excimer lamp + oxygen-free environment	CO ₂ +H ₂	CO: 8.6 μmol	24 h	This work
None	140 W Xe ₂ excimer lamp + oxygen-free environment	CH ₄ +H ₂ O	C ₂ H ₆ : 40.78 μmol	24 h	This work
Bismuthine (20 mg)	300 W Xe lamp	CO ₂ +H ₂ O	CO: 1.432 μmol	5 h	1
Ti ₃ C ₂ dots (1 mg)	150 W Xe lamp +300 °C	CO ₂ +H ₂	CO: 0.143 μmol h ⁻¹	/	2
rh-In ₂ O _{3-x} (OH) _y	130 W Xe lamp +270 °C	CO ₂ +H ₂	CO: 22 μmol h ⁻¹	/	3
Au-ZnO (15 mg)	5.5 ns pulsed 532 nm laser	CO ₂ +H ₂	CO: 0.015 μmol	5 h	4
Pt/B ₄ C/C ₃ N ₄ (6 mg)	300 W Xe lamp	CO ₂ +H ₂	CH ₄ : 0.04 μmol	8 h	5
Ru/MnO _x	300 W Xe lamp +200 °C	CO ₂ +H ₂	CH ₄ : 10 mmol	4 h	6
Graphdiyne/In ₂ O ₃ (5 mg)	150 W Xe lamp (20 sun)	CO ₂ +H ₂	CO: 72 μmol	4 h	7
Bi ₂ WO ₆ (300 mg)	450 W Hg lamp + 55 °C	CH ₄ +H ₂ O	C ₂ H ₆ : 0.75 μmol	0.5 h	8
Pt/TiO ₂ (75 mg)	UV light	CH ₄ +H ₂ O	C ₂ H ₆ : 23.67 μmol	6 h	9
Pd/TiO ₂ (75 mg)	UV light	CH ₄ +H ₂ O	C ₂ H ₆ : 12.38 μmol	6 h	10
BiVO ₄ bipyramids (205 mg)	350 W Xe lamp	CH ₄ +H ₂ O	CH ₃ OH: 22.94 μmol	1 h	11
Ga ³⁺ -modified microporous titanosilicate (200 mg)	150 W high pressure Hg lamp	CH ₄	C ₂ H ₆ : 20.9 μmol	5 h	12
Ag-HPW/TiO ₂ (100 mg)	400 W Xe lamp	CH ₄	C ₂ H ₆ : 14.4 μmol	7 h	13

Supplementary References

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