

## Supporting information

# Thermo-photo catalytic CO<sub>2</sub> hydrogenation over Ru/TiO<sub>2</sub>

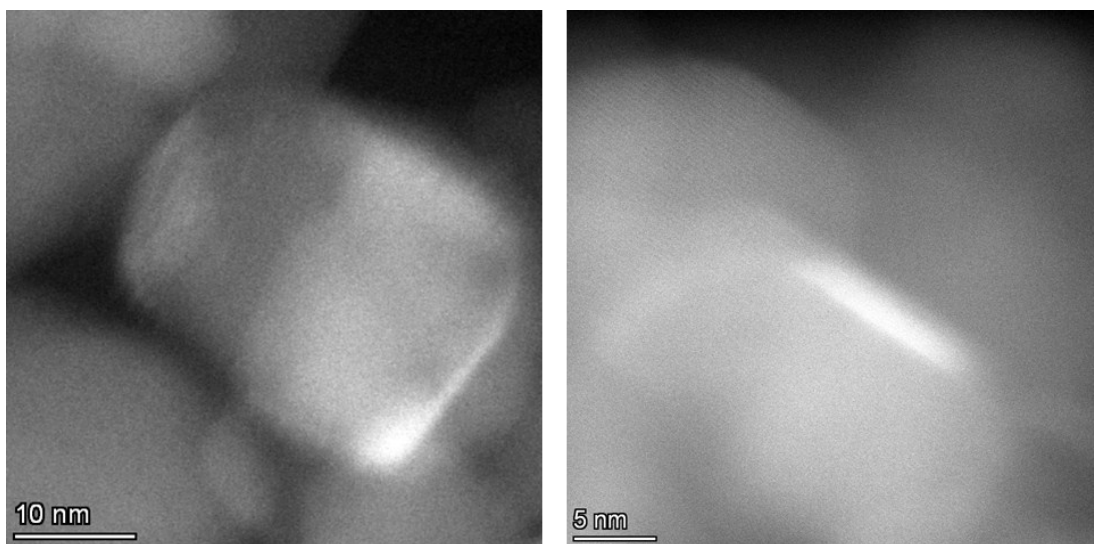
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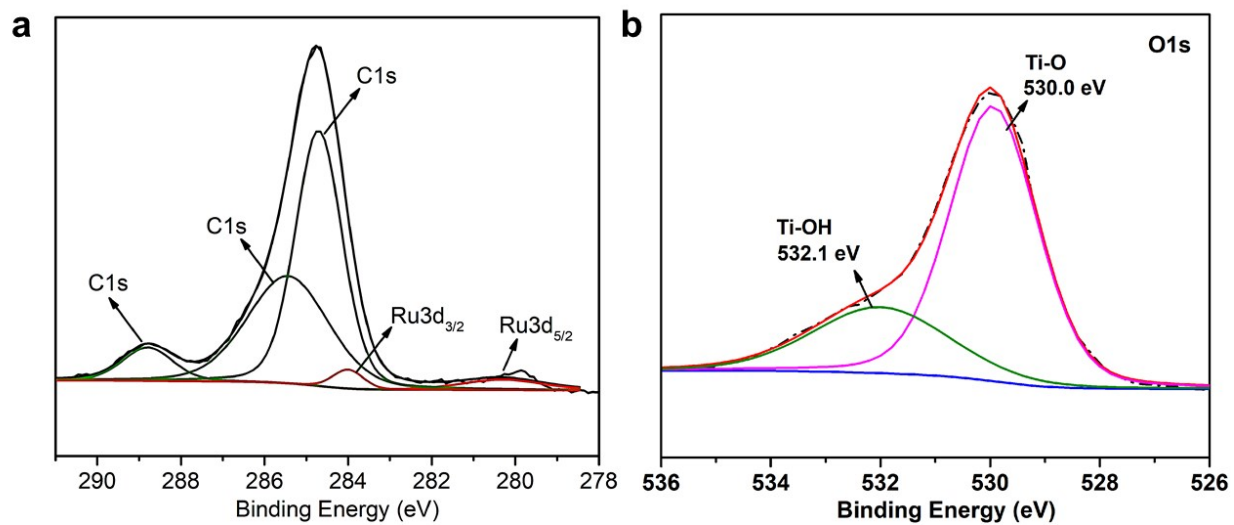
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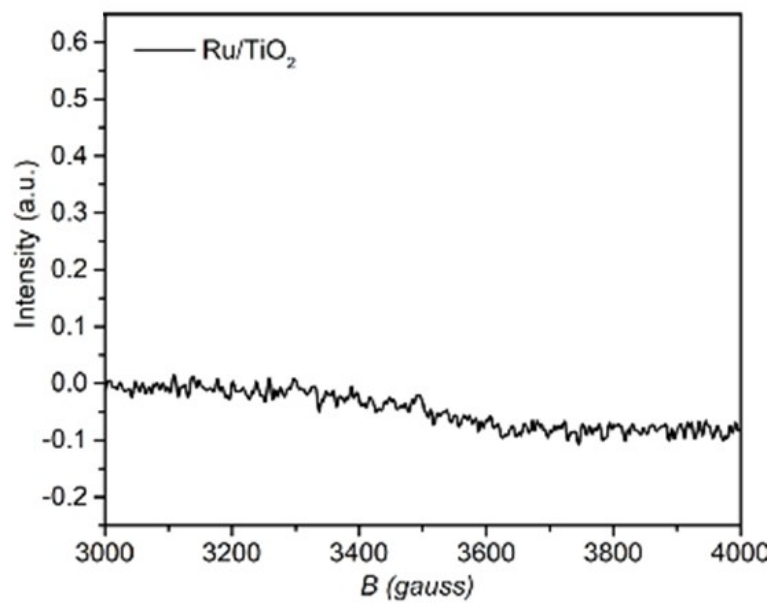
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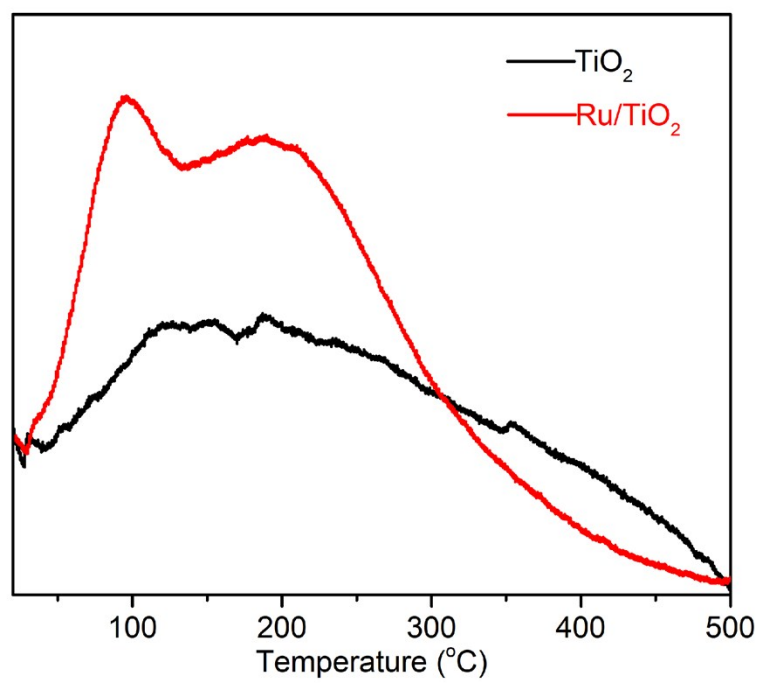
**Figure S1.** HAADF-STEM images of Ru/TiO<sub>2</sub>



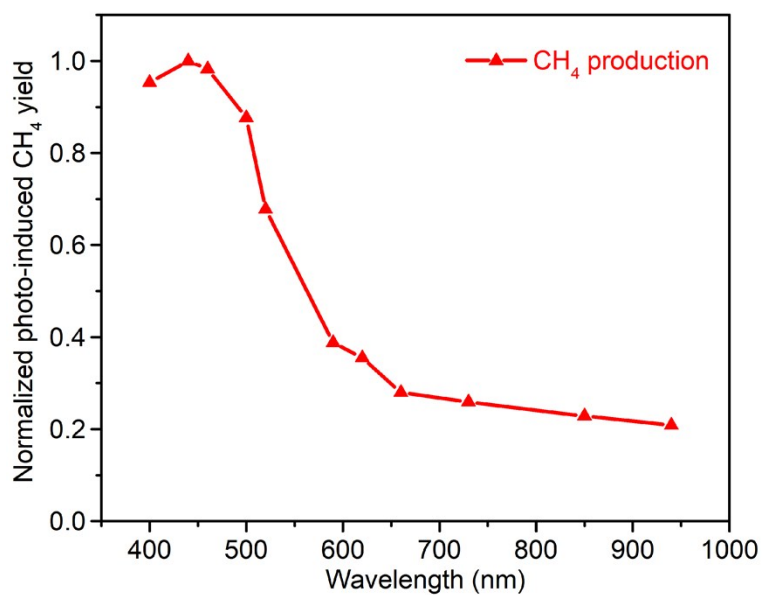
**Figure S2.** XPS spectra of (a) C1s and Ru3d and (b) O1s for Ru/TiO<sub>2</sub> sample.



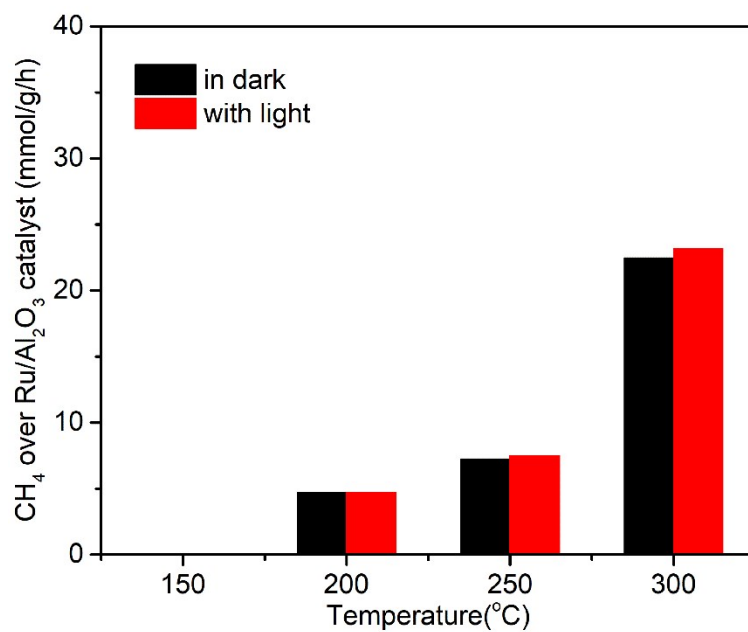
**Figure S3.** Electron paramagnetic resonance (EPR) spectra of Ru/TiO<sub>2</sub>.



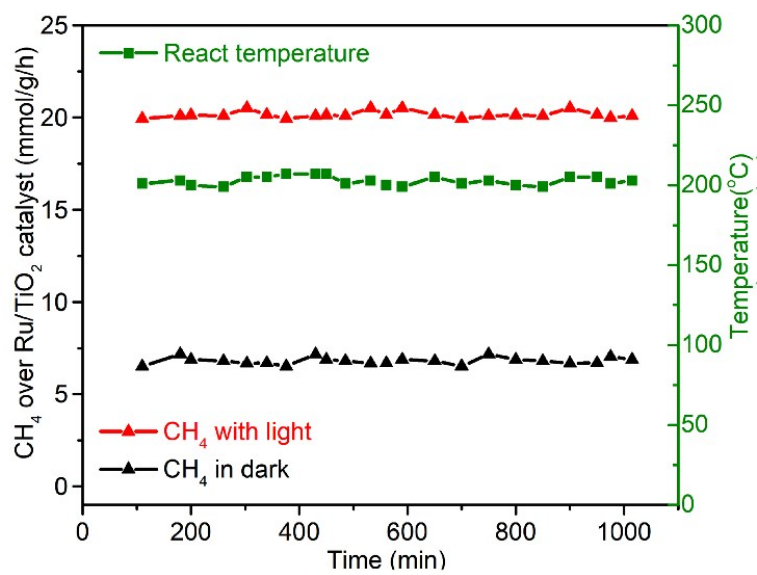
**Figure S4.** CO<sub>2</sub>-TPD for TiO<sub>2</sub> and Ru/TiO<sub>2</sub>



**Figure S5.** Normalized photo-induced CH<sub>4</sub> yield vs. wavelength of incident light for CO<sub>2</sub> hydrogenation (single-wavelength LED lights were used; temperature: 300 °C; CO<sub>2</sub>/H<sub>2</sub> = 1:3, flow rate 10ml/min; and 15 mg catalyst).

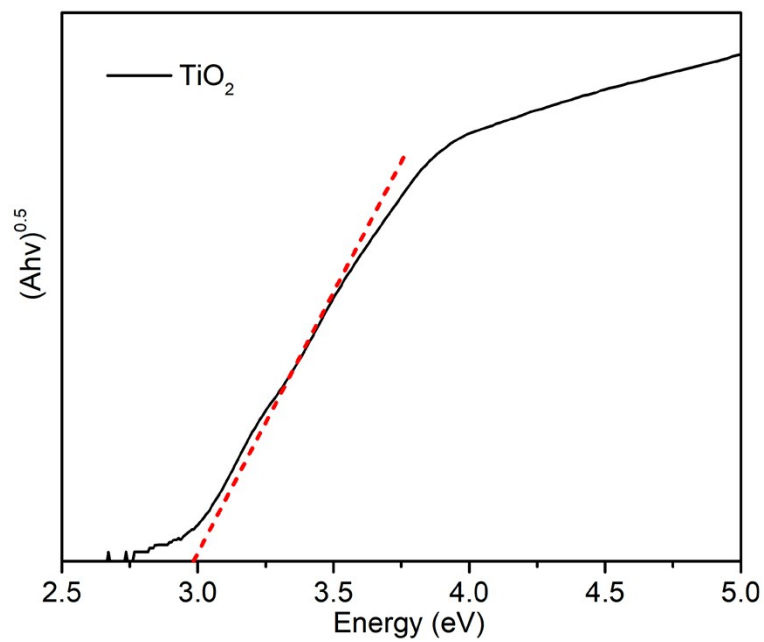


**Figure S6.** Thermo-catalytic (black bar) and thermo-photo catalytic (red bar) over Ru/Al<sub>2</sub>O<sub>3</sub> catalyst for CO<sub>2</sub> reduction with H<sub>2</sub> at various temperatures

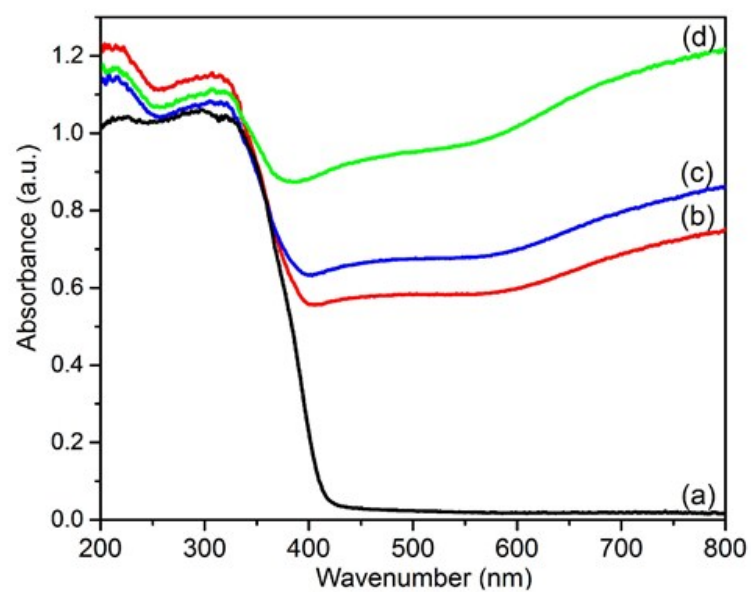


**Figure S7.** Time-resolved  $\text{CH}_4$  production over Ru/TiO<sub>2</sub> catalyst at 200°C in dark (black line) and under simulated AM 1.5G sunlight irradiation (red line)

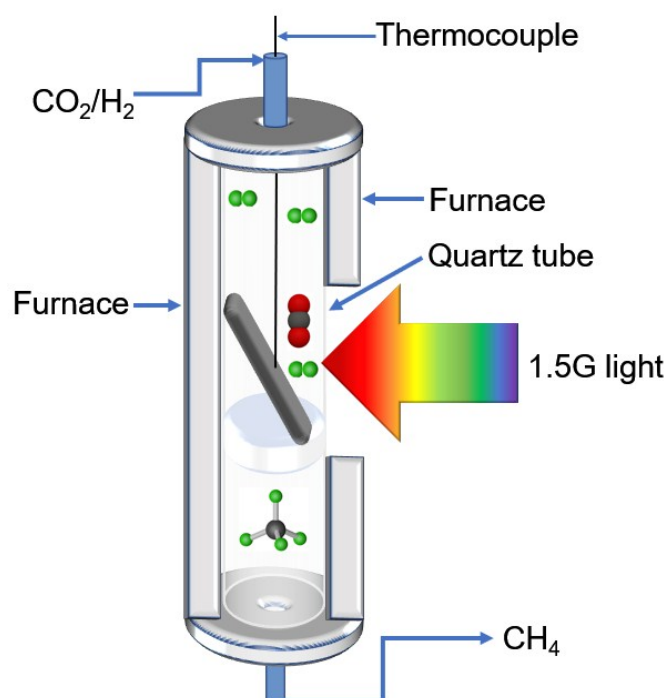




**Figure S8.** The band gap of  $\text{TiO}_2$  estimated via the Kubelka-Munk equation



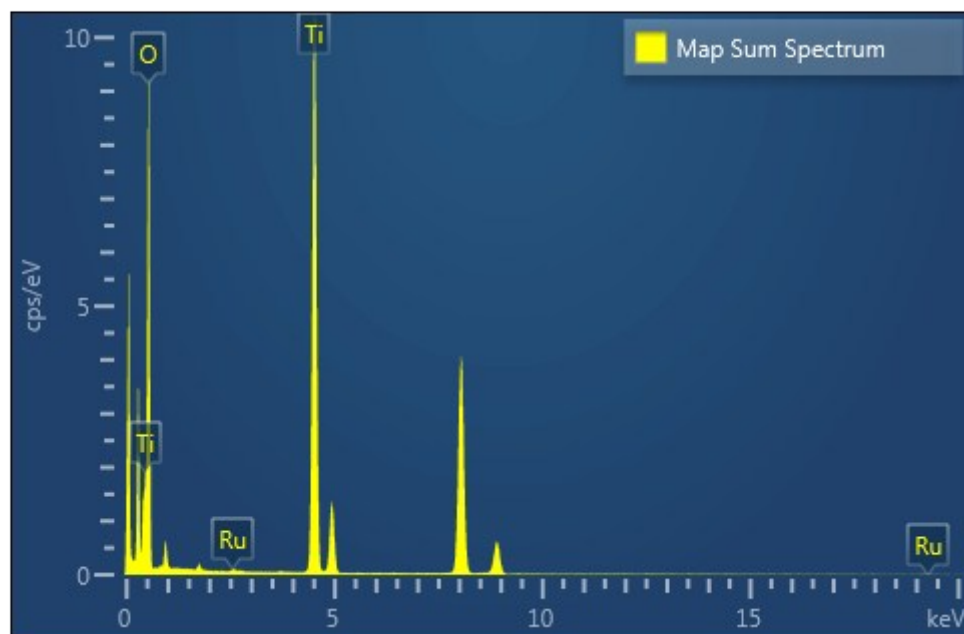
**Figure S9.** Diffuse reflectance UV-visible absorption spectra of fresh samples of (a) TiO<sub>2</sub>; (b) 0.2Ru/TiO<sub>2</sub>; (c) 1Ru/TiO<sub>2</sub>; (d) 4Ru/TiO<sub>2</sub>.



**Figure S10.** Scheme of the fixed bed reactor for photocatalytic reaction.

**Table S1** Elemental statistics according to EDS analysis for Ru/TiO<sub>2</sub> catalyst.

Element	Line Type	k Factor	k Factor type	Absorption Correction	Wt%	Wt% Sigma	Atomic %
O	K series	1.165		1.00	44.65	0.19	70.80
Ti	K series	0.635		1.00	54.92	0.19	29.09
Ru	L series	1.052		1.00	0.42	0.09	0.11
Total:					100.00		100.00



**Figure S11.** Elemental statistics according to EDS analysis for Ru/TiO<sub>2</sub> catalyst.