SUPPORTING INFORMATION

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Highly Efficient Photocatalytic CO_2 Methanation over Ru-Doped TiO_2 with Tunable Oxygen Vacancies

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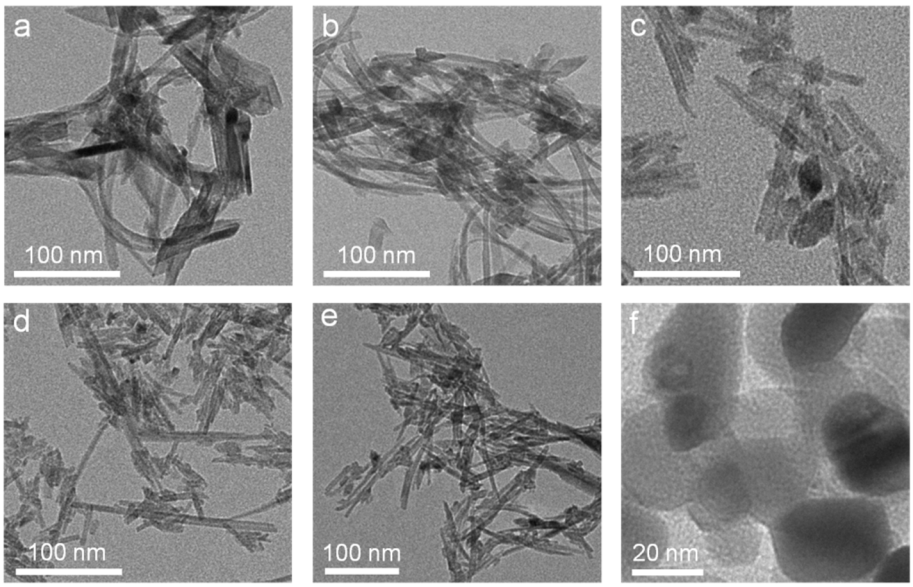

Figure S1. TEM images of **a** TiO_2-OV-0, **b** TiO_2-OV-25, **c** TiO_2-OV-50, **d** TiO_2-OV-75, **e** TiO_2-OV-100 and **f** commercial TiO_2 samples.

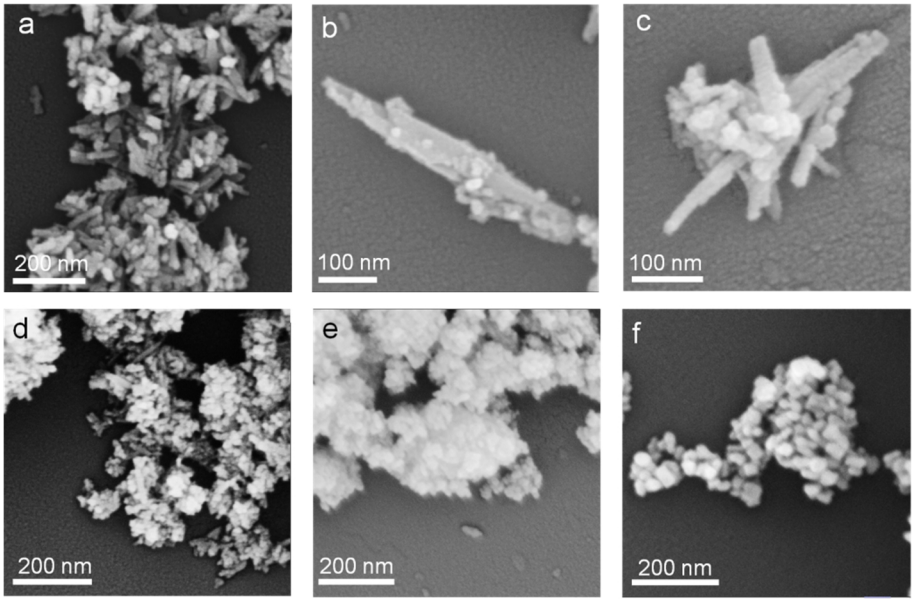

Figure S2. SEM images of **a** Ru/TiO_2-OV-0, **b** Ru/TiO_2-OV-25, **c** Ru/TiO_2-OV-50, **d** Ru/TiO_2-OV-75, **e** Ru/TiO_2-OV-100 and **f** Ru/TiO_2 samples.

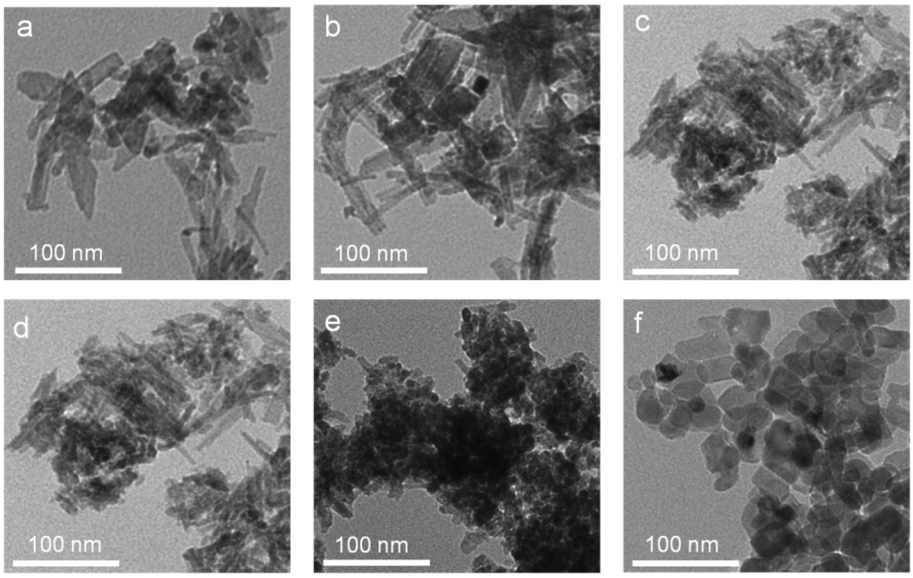

Figure S3. TEM images of **a** Ru/TiO_2-OV-0, **b** Ru/TiO_2-OV-25, **c** Ru/TiO_2-OV-50, **d** Ru/TiO_2-OV-75, **e** Ru/TiO_2-OV-100 and **f** Ru/TiO_2 samples.

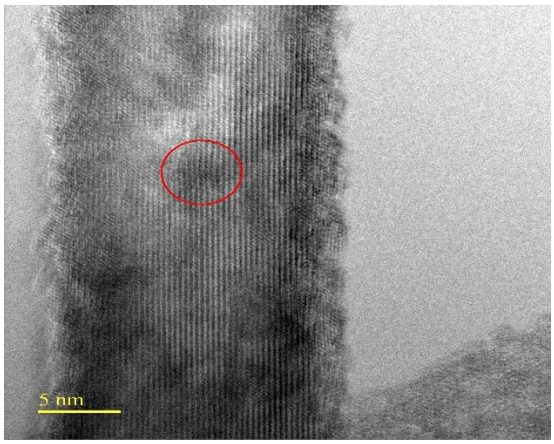

Figure S4. HRTEM image of Ru/TiO_2-OV-50 catalyst.

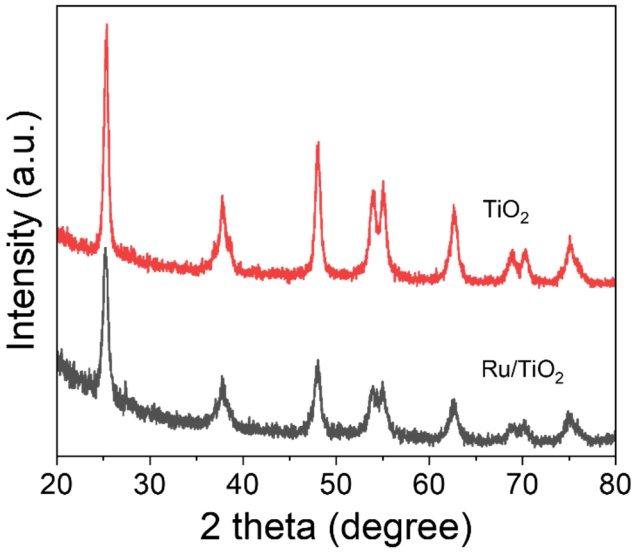

Figure S5. XRD patterns of commercial TiO_2 and Ru/TiO_2 samples.

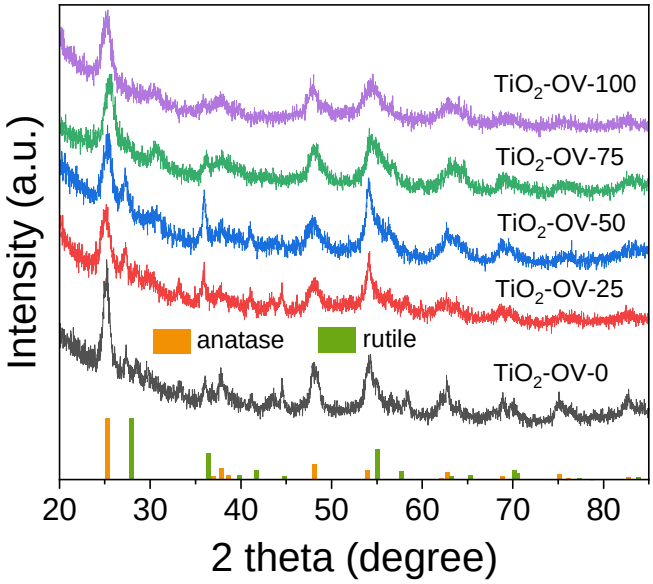

Figure S6. XRD patterns of TiO_2-OV-x samples.

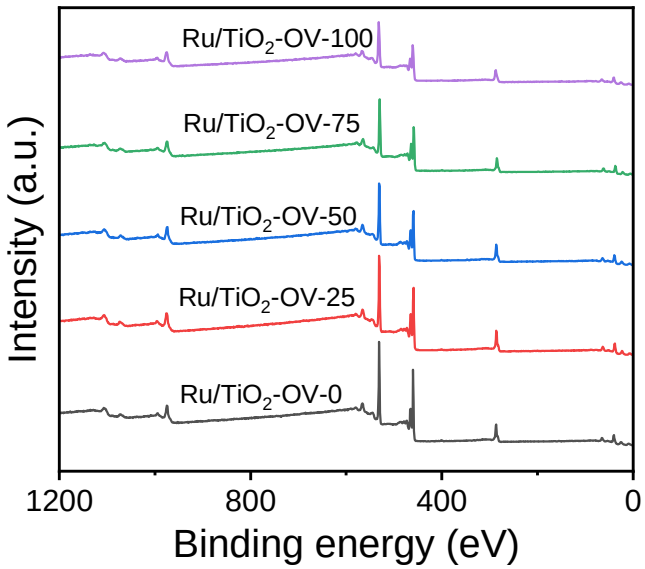

Figure S7. XPS survey spectra of Ru/TiO_2-OV-x samples.

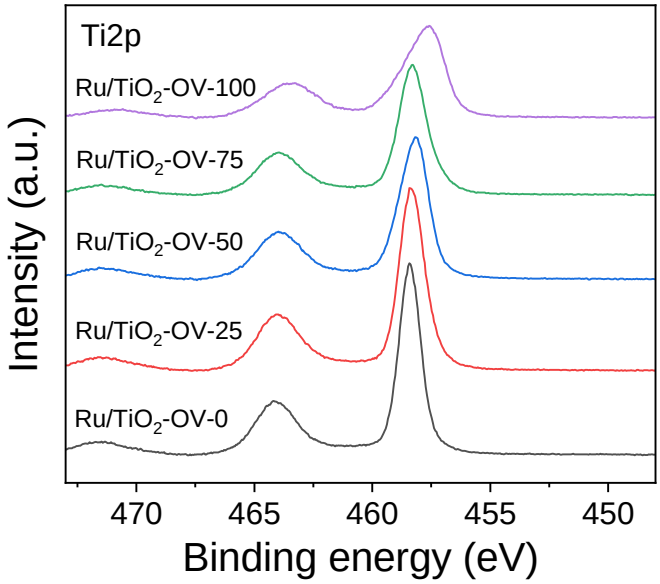

Figure S8. High resolution Ti 2p spectra of Ru/TiO_2-OV-x samples.

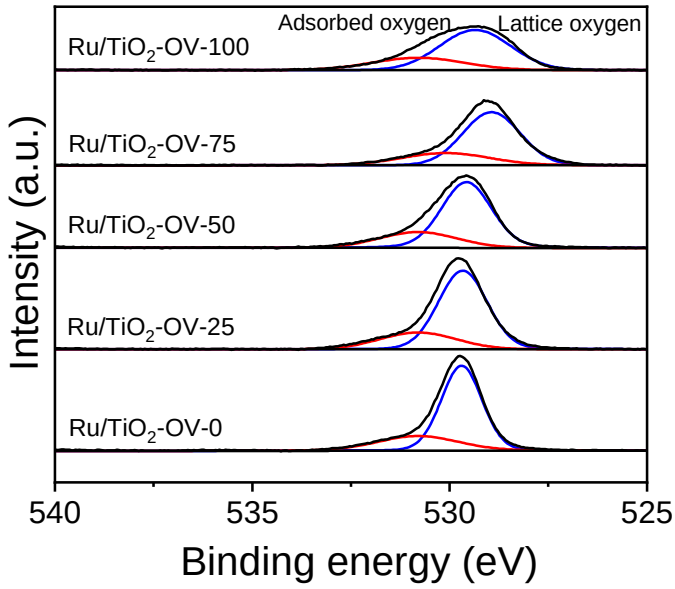

Figure S9. High-resolution O 1s XPS spectra of Ru/TiO_2-OV-x samples.

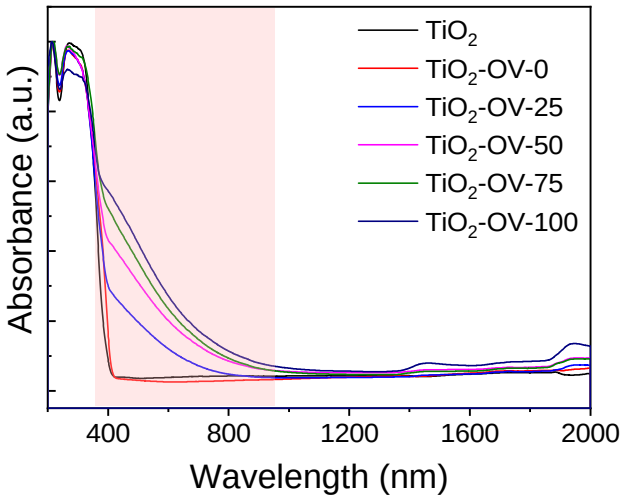

Figure S10. UV-vis absorption spectra of TiO_2-OV-x samples.

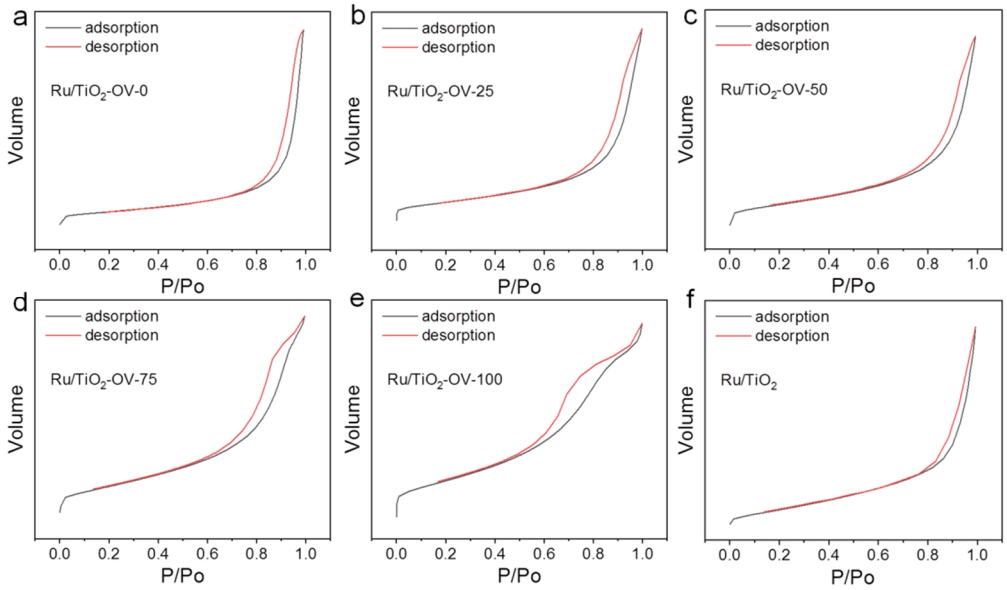

Figure S11. Nitrogen adsorption and desorption isotherms of Ru/TiO_2-OV-x and Ru/TiO_2 samples.

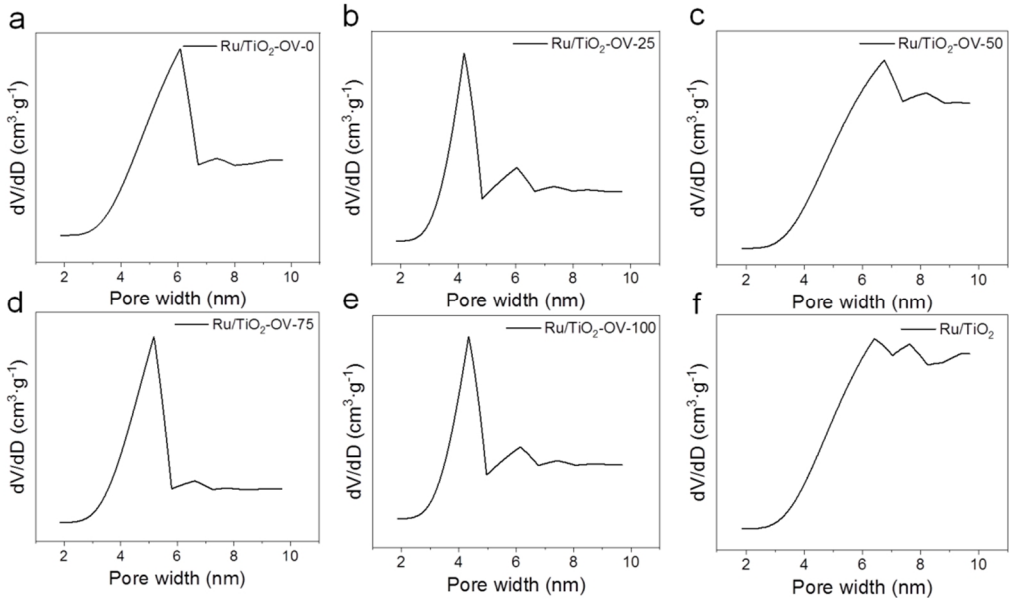

Figure S12. Pore width distributions of Ru/TiO_2-OV-x and Ru/TiO_2 samples.

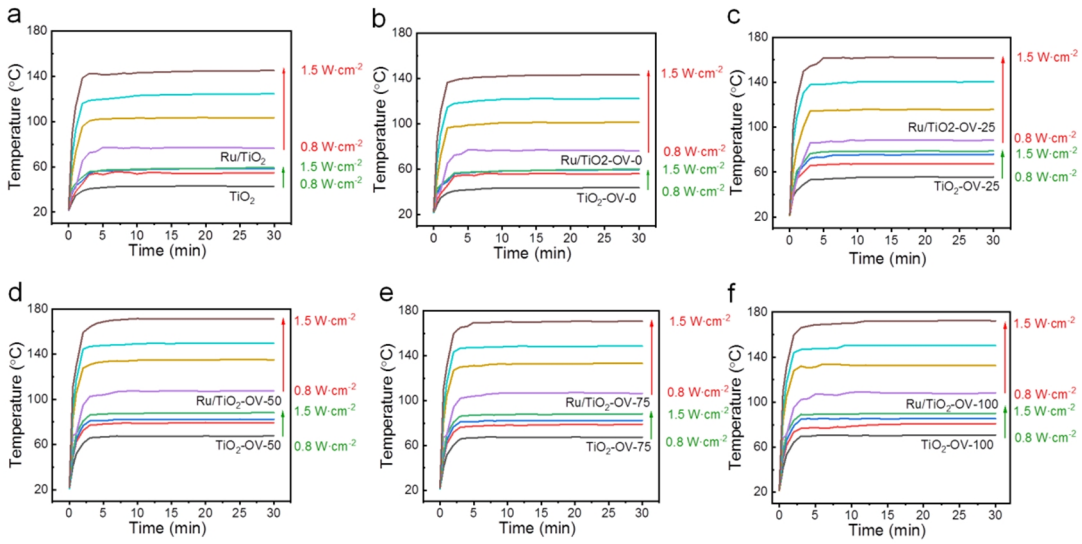

Figure S13. Photothermal temperature monitoring of catalysts under different light intensities.

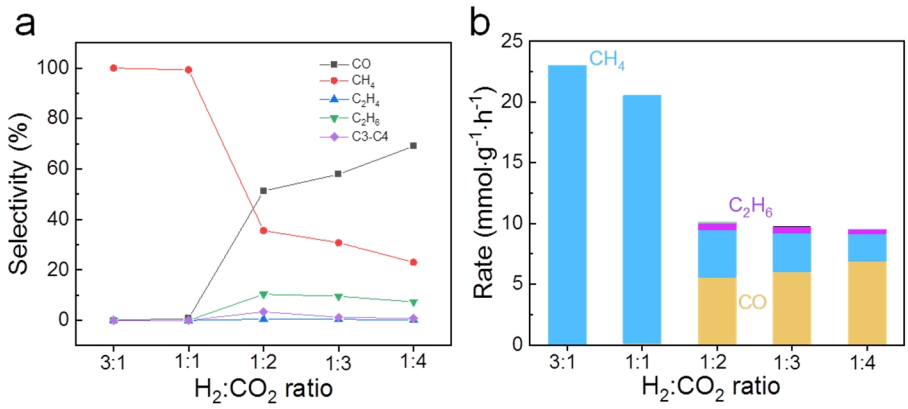

Figure S14. Photocatalytic CO_2 methanation over Ru/TiO_2-OV-50 under different H_2:CO_2 ratios at an irradiation intensity of 1.0 W·cm^{-2}.

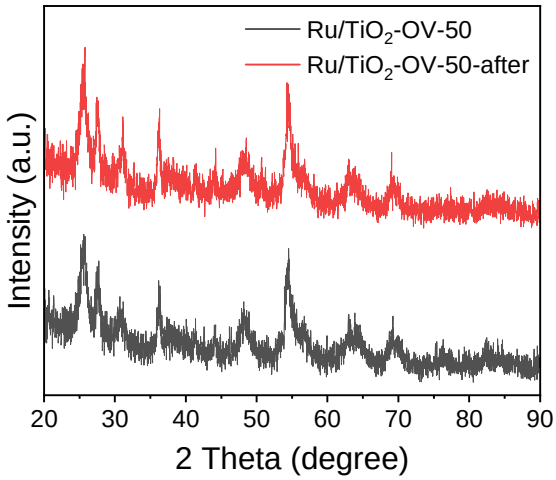

Figure S15. XRD patterns of Ru/TiO_2-OV-50 before and after 5 cycles.

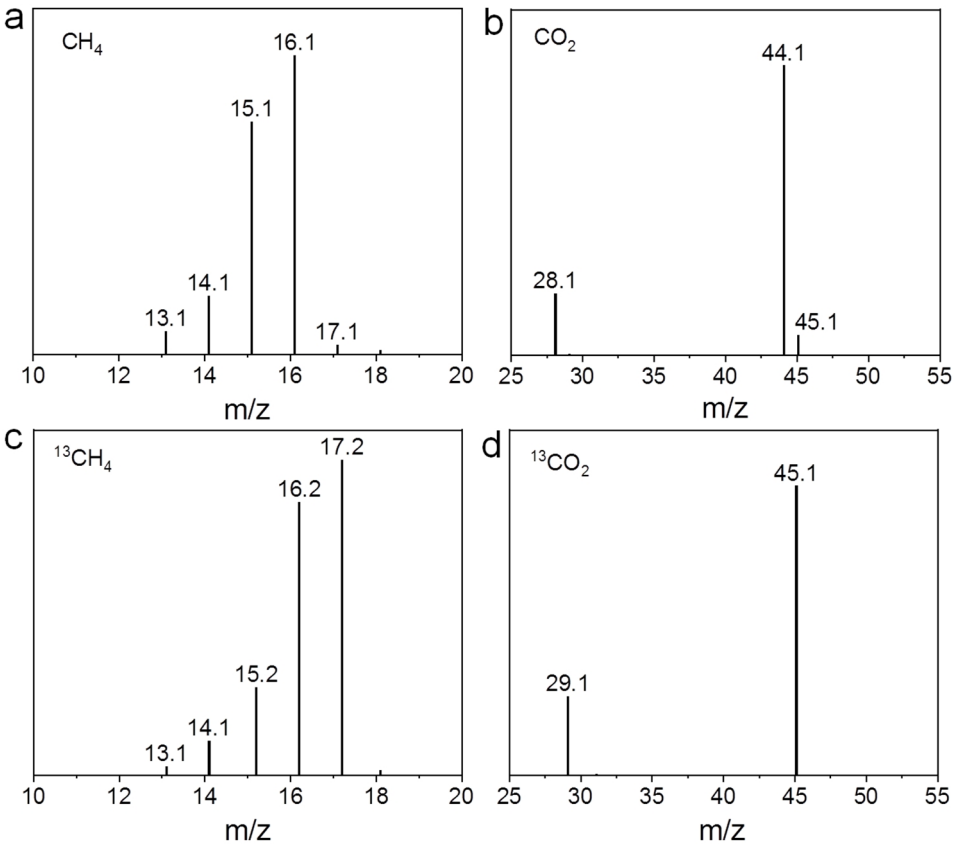

Figure S16. Mass spectra fragments of isotope labelling experiments. **a** CH_4; **b** CO_2; **c** $^{13}CH_4$; **d** $^{13}CO_2$.

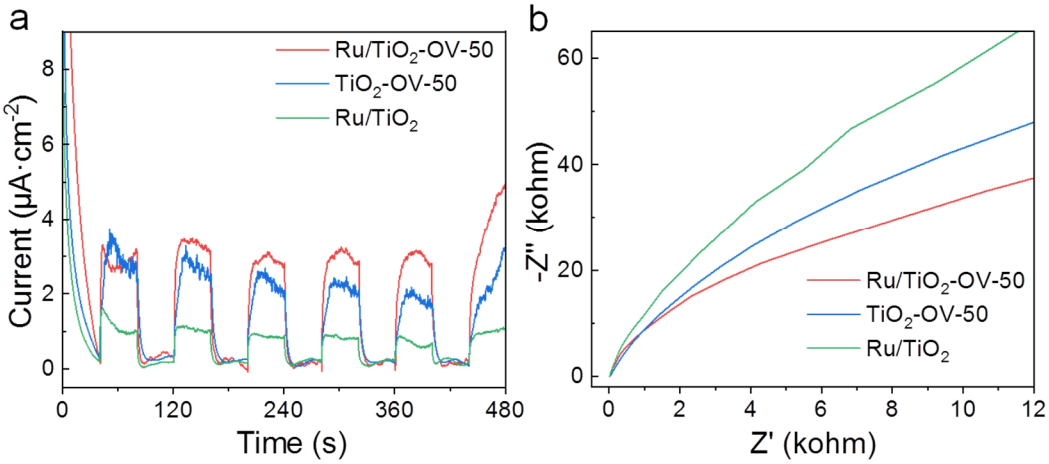

Figure S17. a Photocurrent curves and **b** Nyquist plots of as-synthesized samples.

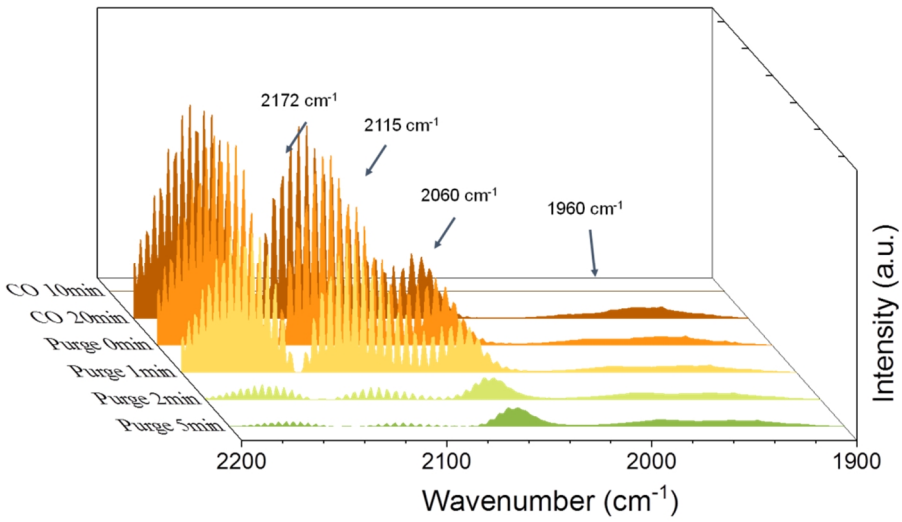

Figure S18. The CO-DRIFTS spectra over Ru/TiO_2-OV-50 catalyst.

Table S1. Fitting Results of Ru *K*-Edge EXAFS Data[a]

sample	scattering path	CN	R(Å)	σ^2 (Å)
Ru foil	Ru-Ru	12 (fixed)	2.67 +/- 0.04	0.00226
RuO_2	Ru-O	6 (fixed)	1.99 +/- 0.01	0.00460
Ru/TiO_2-OV-50	Ru-O	3.95 +/- 0.32	1.99 +/- 0.01	0.00808
	Ru-Ru	1.41 +/- 0.36	2.69 +/- 0.04	0.00300

[a] CN, the coordination numbers; R, the bonding distance; σ^2, the Debye-Waller factor.

Table S2. Reported Catalytic Performance over Various Catalysts

catalysts	rate (mmol·h^{-1}·g_{cat}^{-1})	light intensity (mw·cm^{-2})
$RuO_2/SrTiO_3$[1]	14.6	108 (150 °C external heat)
Ru/CeO_2[2]	4.9	1100
Ru/i-Si-O[3]	2.8	2470
$Ru/Mg(OH)_2$[4]	500 (mmol·h^{-1}·g_{Ru}^{-1})	heat up to 150 °C by light
Ru(002)/G[5]	113.9	135 (150 °C external heat)
$Na\text{-}BiTiO_3$[6]	103.7	293
Ru/TiO_2[7]	69.5	100 (300 °C external heat)
this work	81.7	1500

Table S3. Catalytic Reaction Rate under Irradiation with Different Wavelengths[a]

entry	temperature (°C)	wavelength (nm)	rate (mmol·g^{-1}·h^{-1})
1	--	--	--
2	--	< 400	0.02
3	--	> 420	40.45
4	--	> 440	39.19
5	--	> 600	8.96
6	--	320~780	45.60
7	160	--	0.86
8	160	< 400	1.05
9	170	--	2.08
10	170	< 400	2.37

[a] The reactions were conducted under the irradiation of a 300 W Xenon lamp (Beijing Perfectlight, PLS-SXE300D) and corresponding filters. The light intensity was 1.2 W cm^{-2}.

Table S4. Catalytic Rate under Irradiation with Different Wavelengths[a]

entry	temperature (°C)	wavelength (nm)	rate (mmol·g^{-1}·h^{-1})
1	--	--	--
2	--	< 400	0.03
3	--	> 420	78.52
4	--	> 440	76.98
5	--	> 600	20.54
6	--	320~780	81.70
7	160	--	0.86
8	160	< 400	1.22
9	170	--	2.08
10	170	< 400	2.51

[a] The reactions were conducted under the irradiation of a 300 W Xenon lamp (Beijing Perfectlight, PLS-SXE300D) and corresponding filters. The light intensity was 1.5 W cm^{-2}.

n REFERENCE

(1) Mateo, D.; Albero, J.; García, H. Titanium-perovskite-supported RuO_2 nanoparticles for photocatalytic CO_2 methanation. *Joule* **2019**, 3, 1949-1962.

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