Supporting Information

Efficient photocatalytic oxidation of CH_4 over Ag-modified ZnO nanorods

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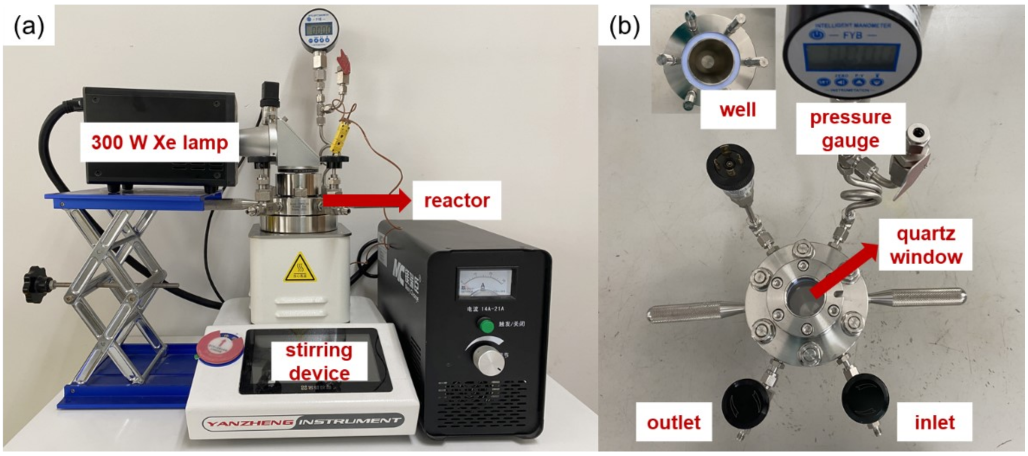

Fig. S1 Device diagram of photocatalytic conversion of methane experiments. (a) The simple indication of the light source, reactor, and stirring device; (b) Detail structure of the used reactor.

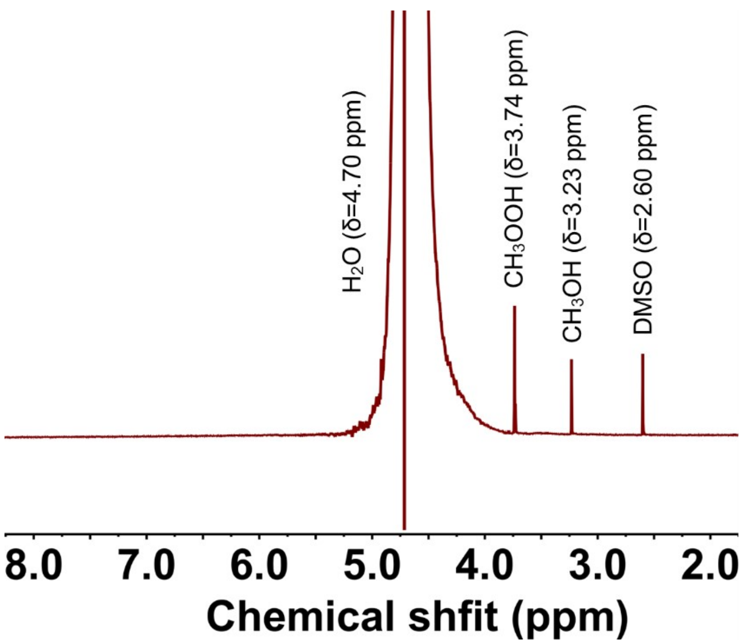

Fig. S2 [1]H NMR spectrum of the liquid product obtained from photocatalytic methane oxidation over 5.0Ag/r-ZnO. Reaction conditions: 1 mg catalyst, 75 mL H_2O, 2 MPa CH_4, 1 MPa O_2, 8 h reaction time, 300 W Xe lamp. DMSO was adopted as an internal standard in the NMR test.

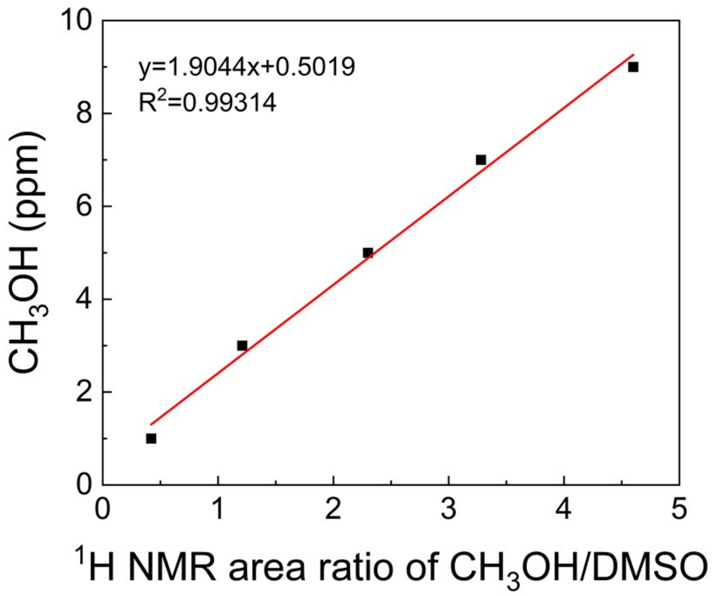

Fig. S3 Calibration curve for the quantification of CH_3OH by ^1H NMR. There is no commercial product for CH_3OOH. As the number of protons of methyl in CH_3OH and CH_3OOH molecules is the same, the quantification of CH_3OOH is calibrated by the same curve as that of CH_3OH, which is the usual way of quantifying CH_3OOH.

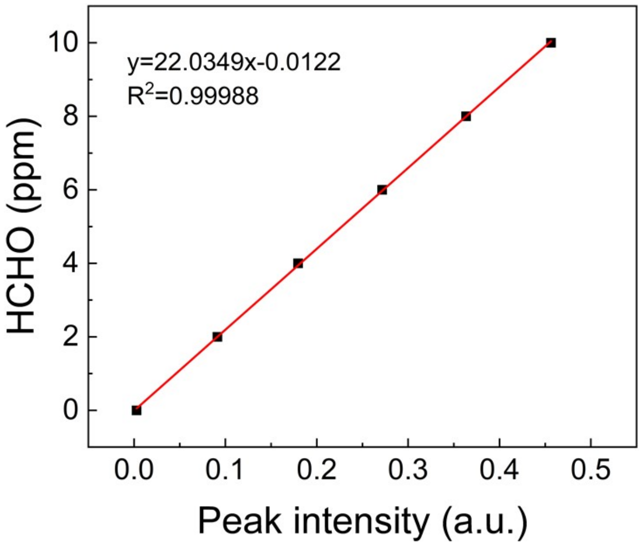

Fig. S4 Calibration curve for the quantification of HCHO by colorimetric method.

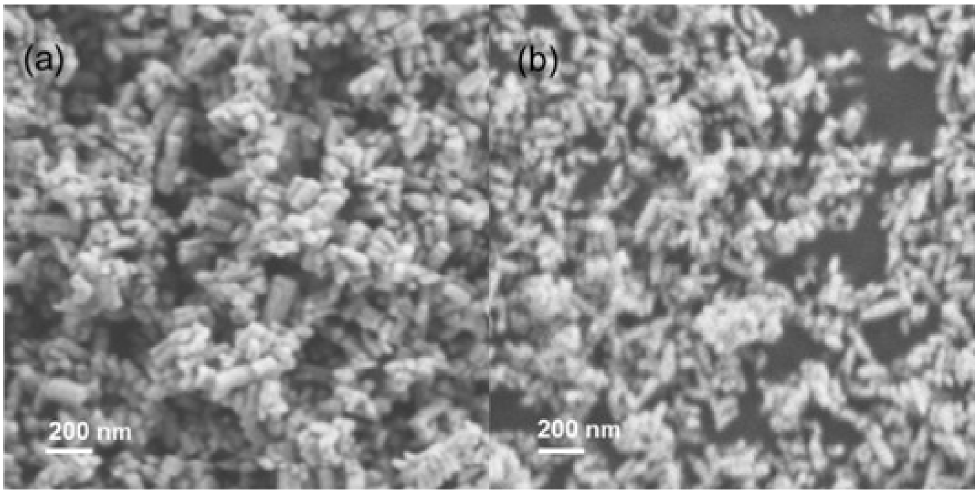

Fig. S5 FE-SEM images of r-ZnO.

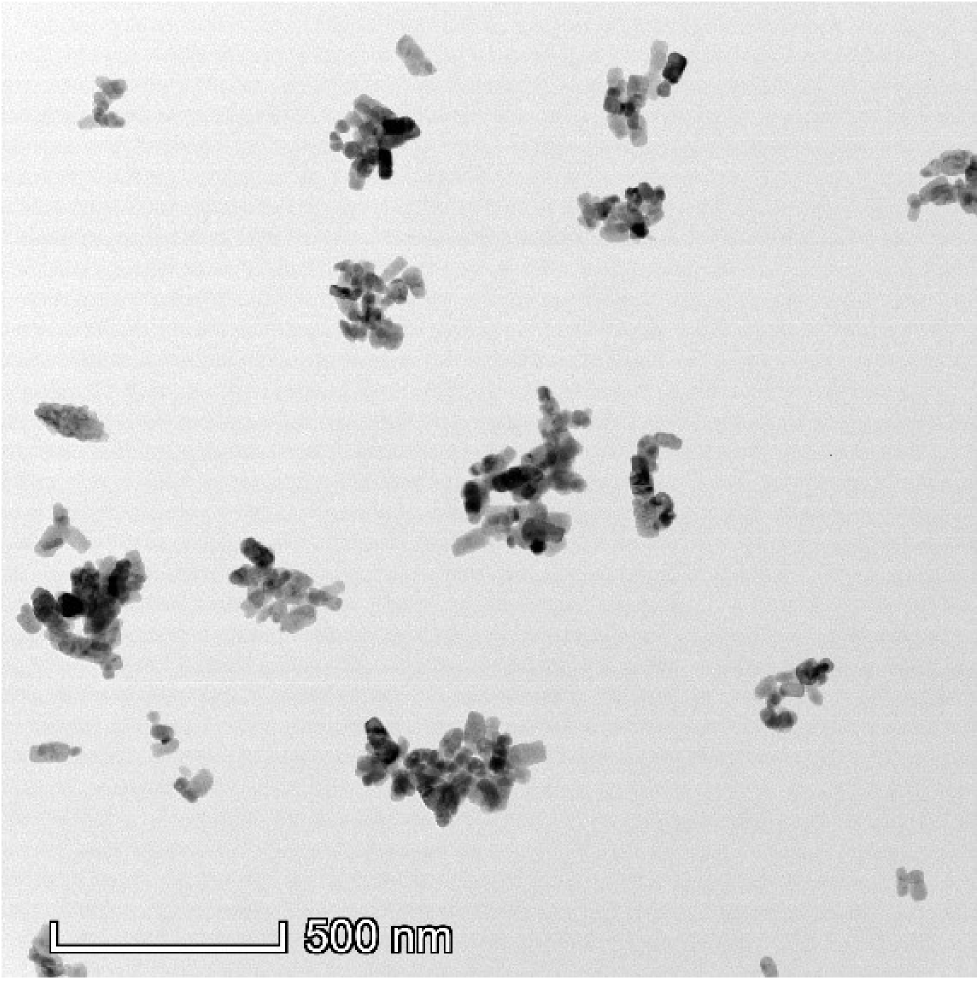

Fig. S6 TEM images of r-ZnO.

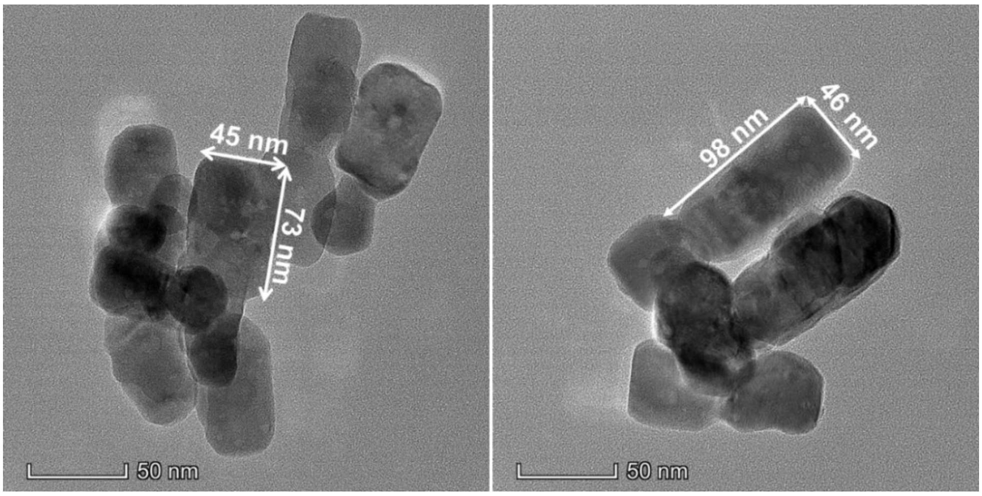

Fig. S7 TEM images of r-ZnO.

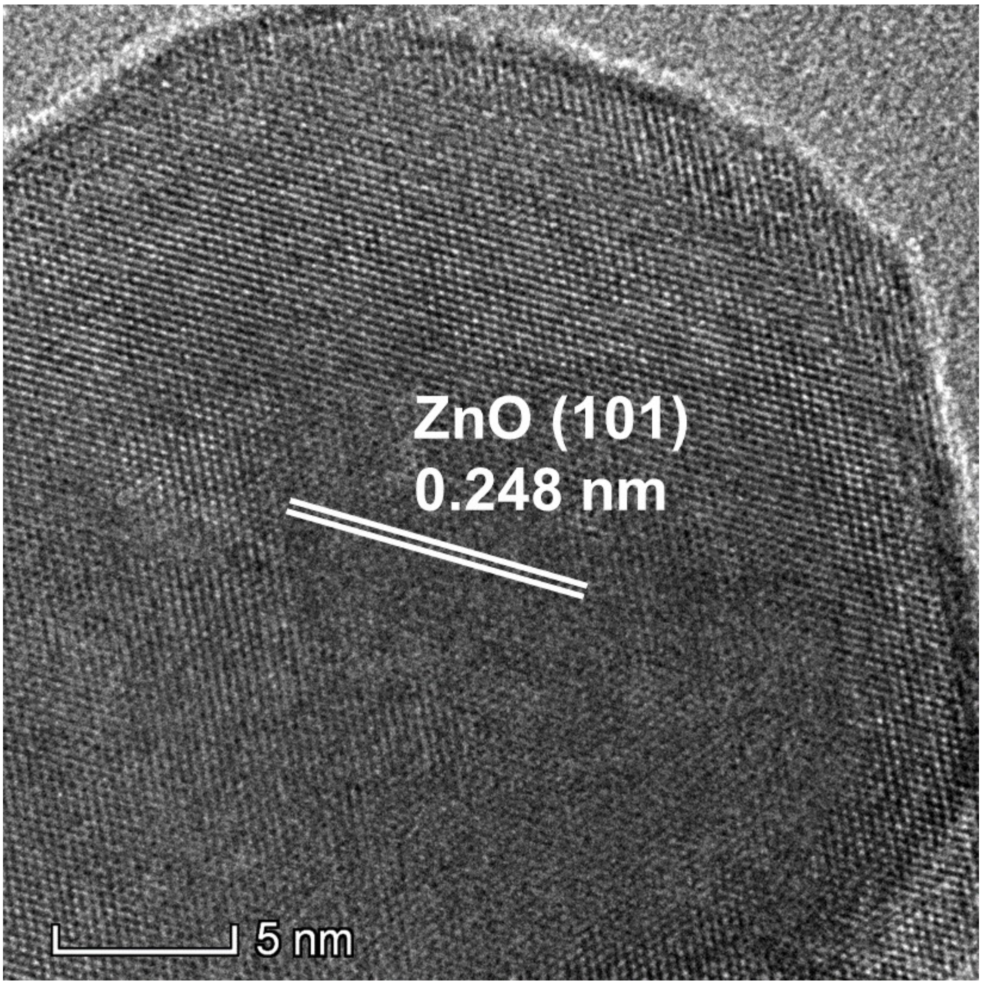

Fig. S8 HR-TEM images of r-ZnO.

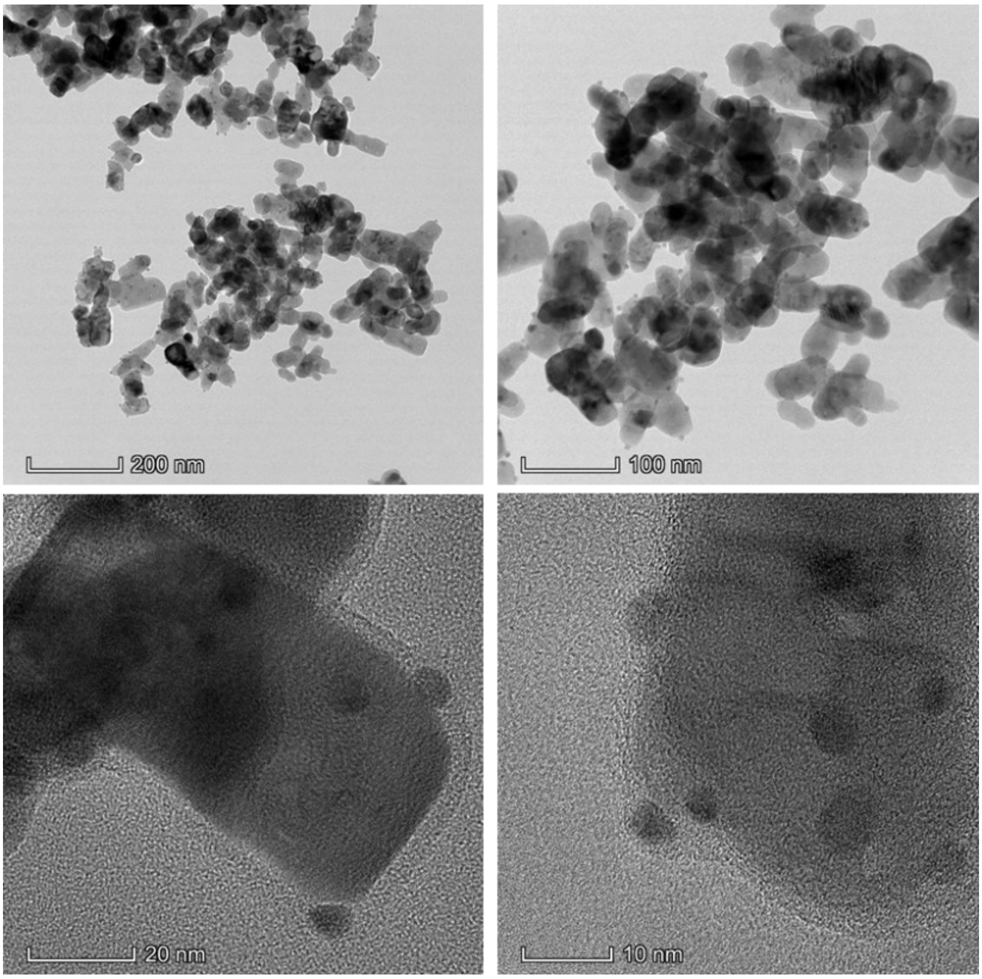

Fig. S9 TEM images of 5.0Ag/r-ZnO.

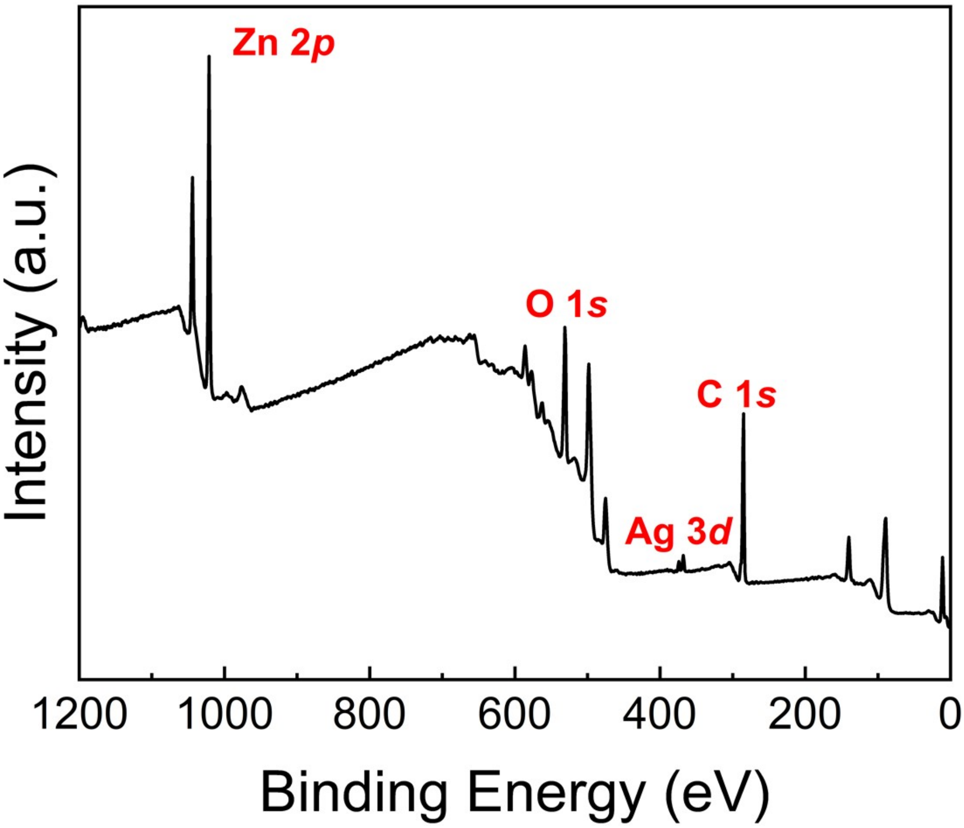

Fig. S10 XPS full survey spectra of 5.0Ag/r-ZnO.

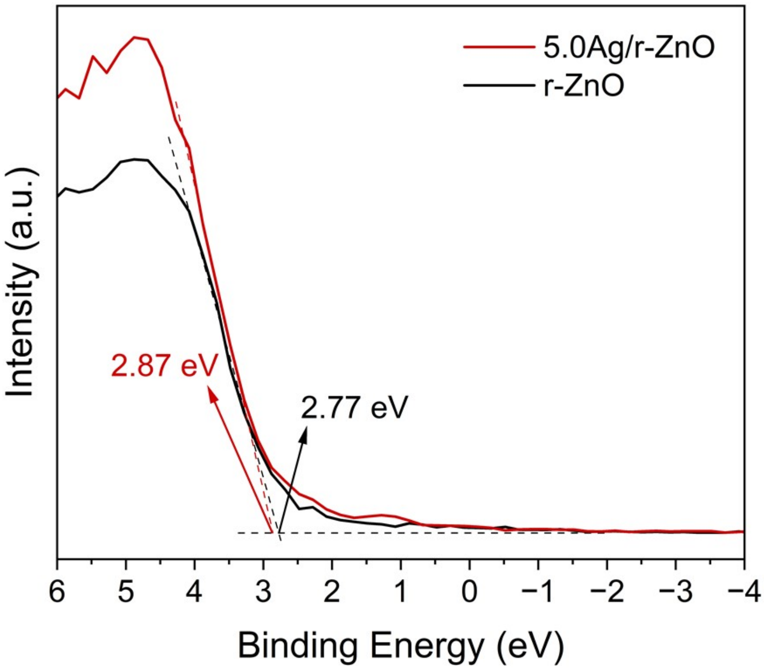

Fig. S11 XPS spectra at valence band regions of r-ZnO and 5.0Ag/r-ZnO.

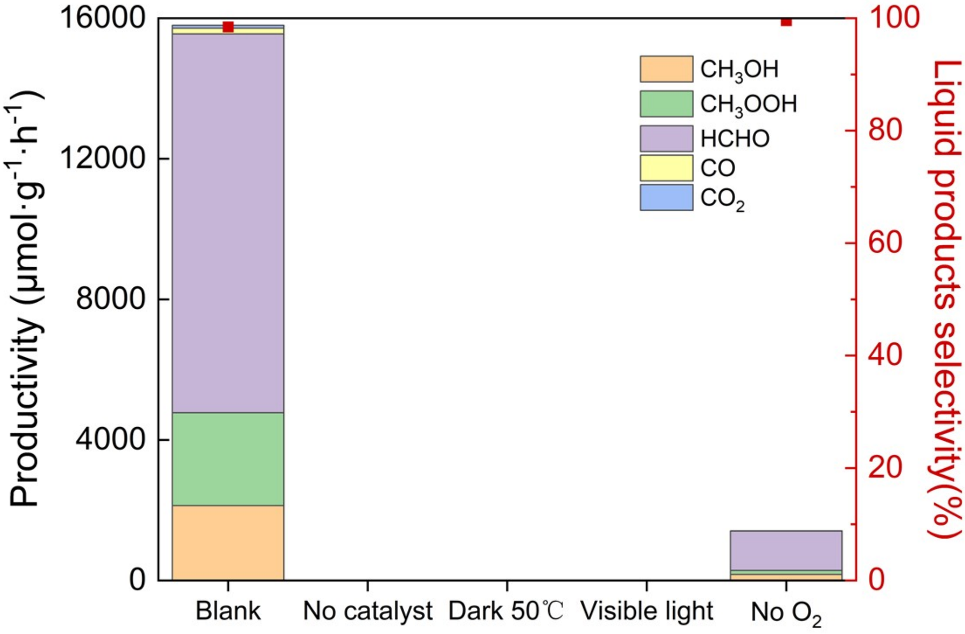

Fig. S12 Direct photocatalytic CH_4 oxidation to liquid products (Control).

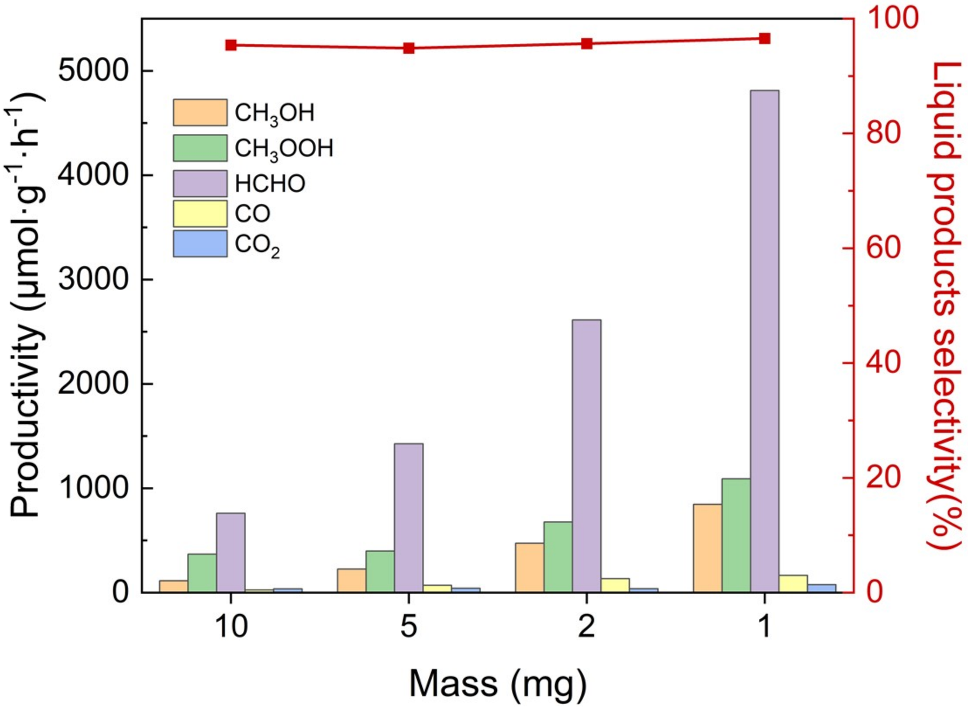

Fig. S13 Effect of catalyst mass on direct photocatalytic CH_4 oxidation.

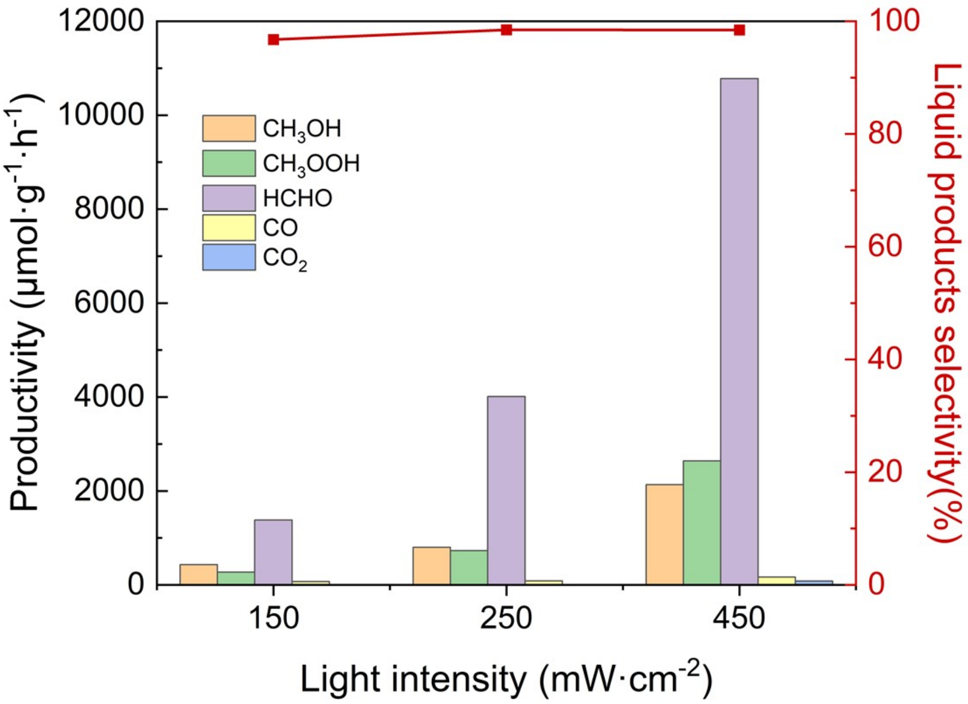

Fig. S14 Effect of light intensity on direct photocatalytic CH_4 oxidation.

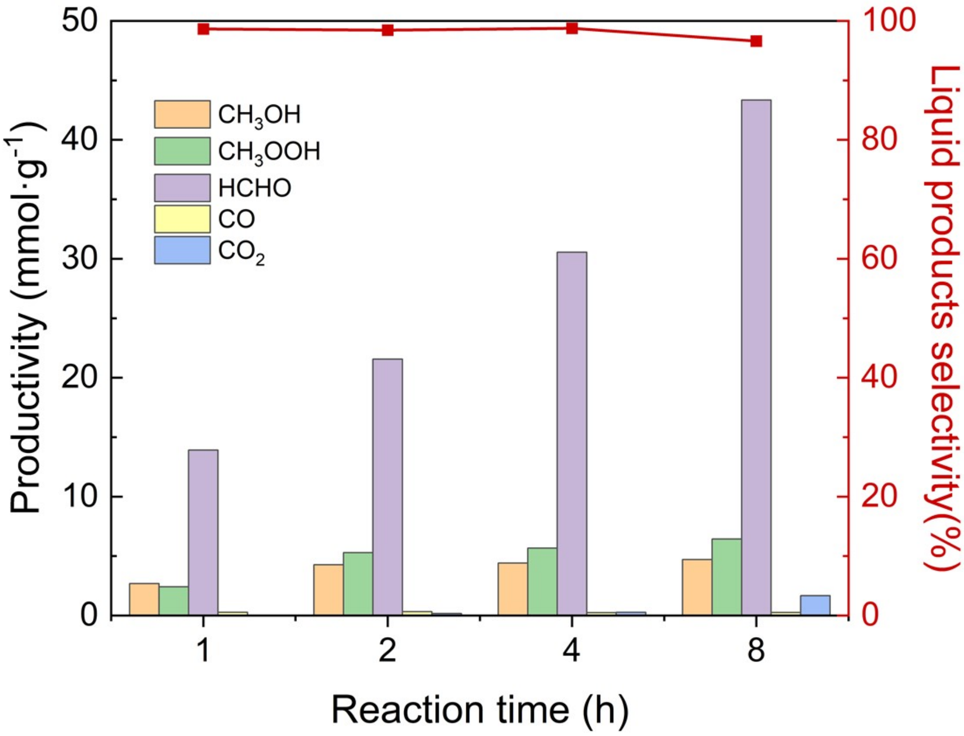

Fig. S15 Effect of reaction time on direct photocatalytic CH_4 oxidation.

Table S1 Comparison of photocatalytic performance of catalysts for CH_4 conversion to liquid oxygenates.

Catalyst	Condition	Oxidant	Major Products	Productivity	Selectively	Reference
5.0Ag/r-ZnO	Photocatalysis, 1 mg catalyst, 2 MPa CH_4, 75 mL H_2O, RT, 300 W Xe lamp, 2 h	O_2	HCHO	10778.92 $\mu mol\cdot g^{-1}\cdot h^{-1}$	68.23%	This work
TiO_2	Photocatalysis, 5 mg catalyst, 1.9 MPa CH_4, 10 mL H_2O, RT, 300 W Xe lamp, 1 h	O_2	HCHO	3.16 mmol g^{-1} h^{-1}	81.2%	[1]
AuFe-ZnO	Photocatalysis, 40 mg catalyst, 18 bar CH_4, 20 mL H_2O, 20 °C, 300 W Xe lamp, 1 h	O_2	CH_3OH	1365 $\mu mol\cdot g^{-1}\cdot h^{-1}$	90.7%	[2]
Pd/ZnO	Photocatalysis, 10 mg catalyst, 2 MPa CH_4, 100 mL H_2O, 300 W Xe lamp, 25 ± 2 °C, 2 h,	O_2	HCHO	5515 $\mu mol\cdot g^{-1}\cdot h^{-1}$	47.52%	[3]
AuCu-ZnO	Photocatalysis, 20 mg catalyst, 19 bar CH_4, 100 mL H_2O, 25 °C, 300 W Xe lamp, 2 h,	O_2	CH_3OH CH_3OOH	11224.9 $\mu mol\cdot g^{-1}\cdot h^{-1}$	79.18%	[4]
Pd/H-TiO_2	Photocatalysis, 10 mg catalyst, 2.0 MPa CH_4, 60 mL H_2O, 300 W Xe lamp, 45 °C, 2 h	O_2	CH_3OH	4.5 mmol g^{-1} h^{-1}	70%	[5]
Pd/WO_3	Photocatalysis, 20 mg catalyst, 1.9 MPa CH_4, 100 mL H_2O, 300 W Xe lamp, 25 ± 2 °C, 2 h	O_2	CH_3OH CH_3OOH	7018 $\mu mol\cdot g^{-1}\cdot h^{-1}$	81%	[6]

Ag/TiO$_2$	Photocatalysis, 10 mg catalyst, 2 MPa CH_4, 100 mL H_2O, 300 W Xe lamp, 25 °C, 2 h	O_2	CH_3OH	4.8 mmol g^{-1} h^{-1}	80%	[7]
Au-CoO$_x$/TiO$_2$	Photocatalysis, 10 mg catalyst, 2 MPa CH_4, 100 mL H_2O, 300 W Xe lamp, 25 ± 2 °C, 2 h	O_2	CH_3OH CH_3OOH	2540 μmol·g^{-1}·h^{-1}	95%	[8]

Reference

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