Supporting Information

Direct and Selective Photocatalytic Oxidation of CH_4 to Oxygenates with O_2 on cocatalysts/ZnO at Room Temperature in Water

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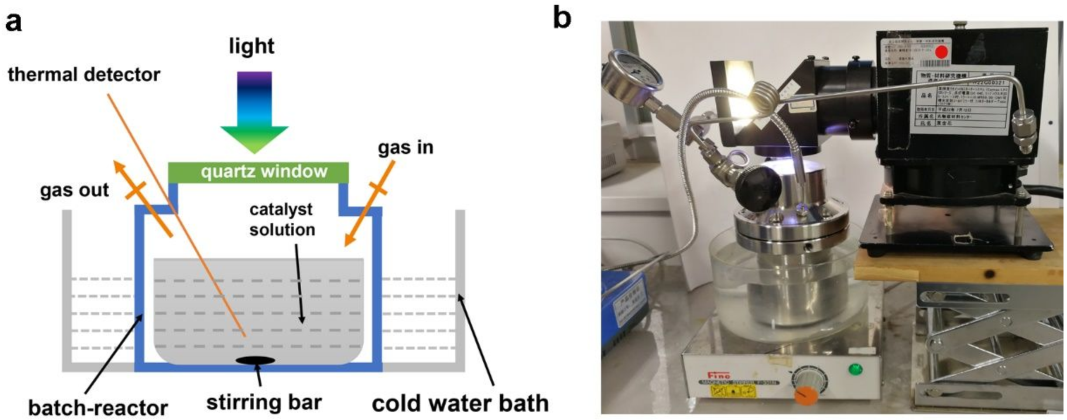

Figure S1. Schematic diagram (a) and picture (b) of batch-reactor system.

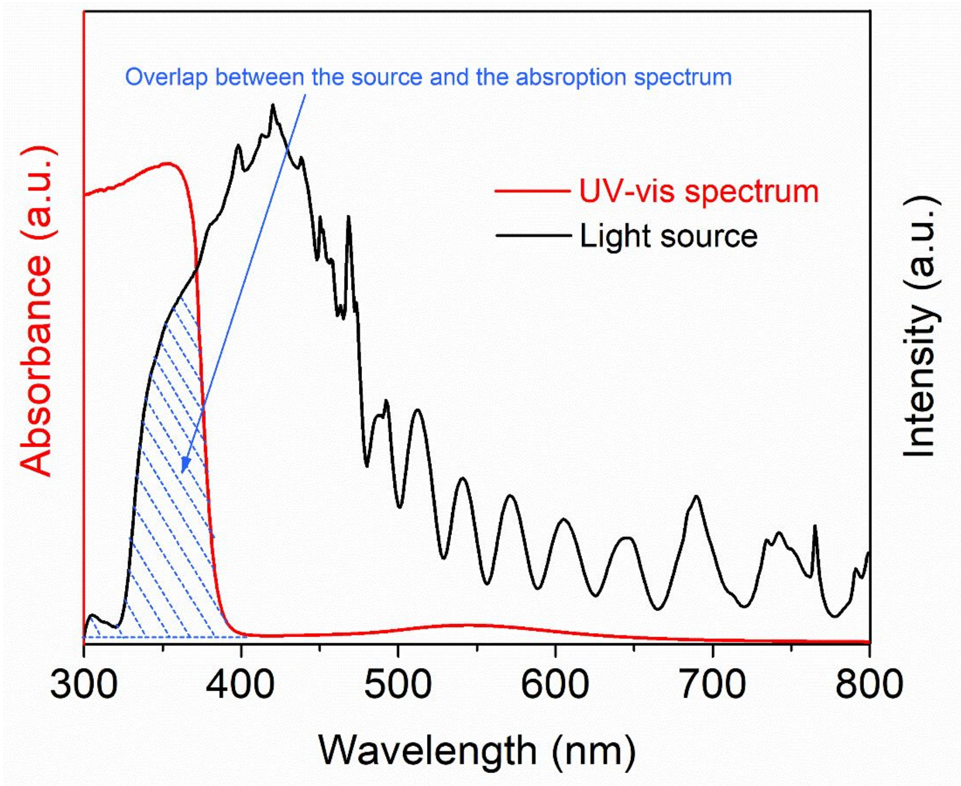

Figure S2. The spectrum of the incident light source and UV-vis spectrum of 0.1wt% Au/ZnO.

CH_3OOH formation:

$$CH_4 \xrightarrow[\text{photochemical reaction}]{-(e^- + H^+)} {}^{\bullet}CH_3$$

$$O_2 \xrightarrow[\text{photochemical reaction}]{+(e^- + H^+)} {}^{\bullet}OOH$$

(Note: O_2 reduction process may also undergo 2 e^- or 4 e^- reduction reaction)

$$ {}^{\bullet}CH_3 + {}^{\bullet}OOH \xrightarrow[\text{chemical reaction}]{} CH_3OOH$$

CH_3OH & HCHO formation:

$$CH_3OOH \xrightarrow[\text{photochemical reaction}]{+2(e^- + H^+)} CH_3OH + H_2O$$

$$H_2O \xrightarrow[\text{photochemical reaction}]{-(e^- + H^+)} {}^{\bullet}OH$$

$$CH_3OH \xrightarrow[\text{photochemical reaction}]{-2(e^- + H^+)} HCHO$$

Figure S3. The processes of electron and proton transfer in the formation of CH_3OOH, CH_3OH and HCHO in photocatalytic CH_4 oxidation with O_2.

As shown in Figure S3, formation of one CH_3OOH molecule only needs the oxidation of CH_4 by one photo-generated hole. Then, two electron transfers are required for reduction of one CH_3OOH molecule into one CH_3OH molecule. A further two-charge transfer process should be involved for oxidation of one CH_3OH molecule into one HCHO molecule. Therefore, the AQY = Number of reacted electrons×100%/Number of incident photons = [N(CH_3OOH) ×1+N(CH_3OH)×3+N(HCHO)×5]/N(Photons), where N(CH_3OOH), N(CH_3OH) and N(HCHO) represent the number of formed CH_3OOH, CH_3OH and HCHO molecules, respectively, and N(Photons) represents the number of incident photons.

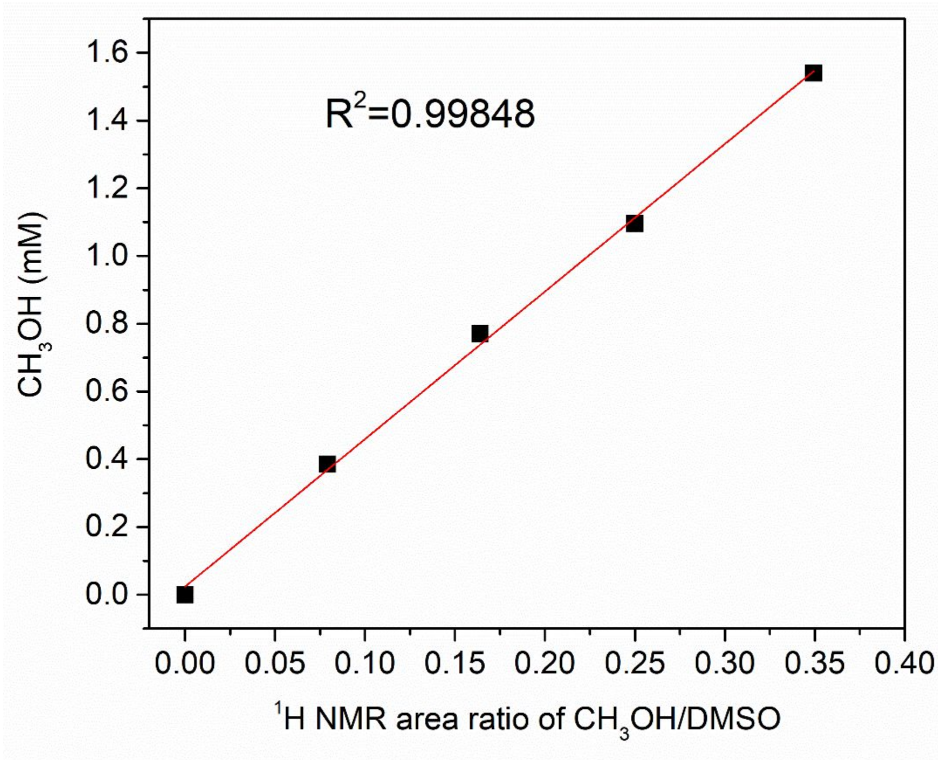

Figure S4. Calibration curve for the quantification of CH_3OH by ^{1}H NMR. As the number of protons of methyl in CH_3OH and CH_3OOH molecules is same, quantification of CH_3OOH is calibrated by the same curve as that of CH_3OH.

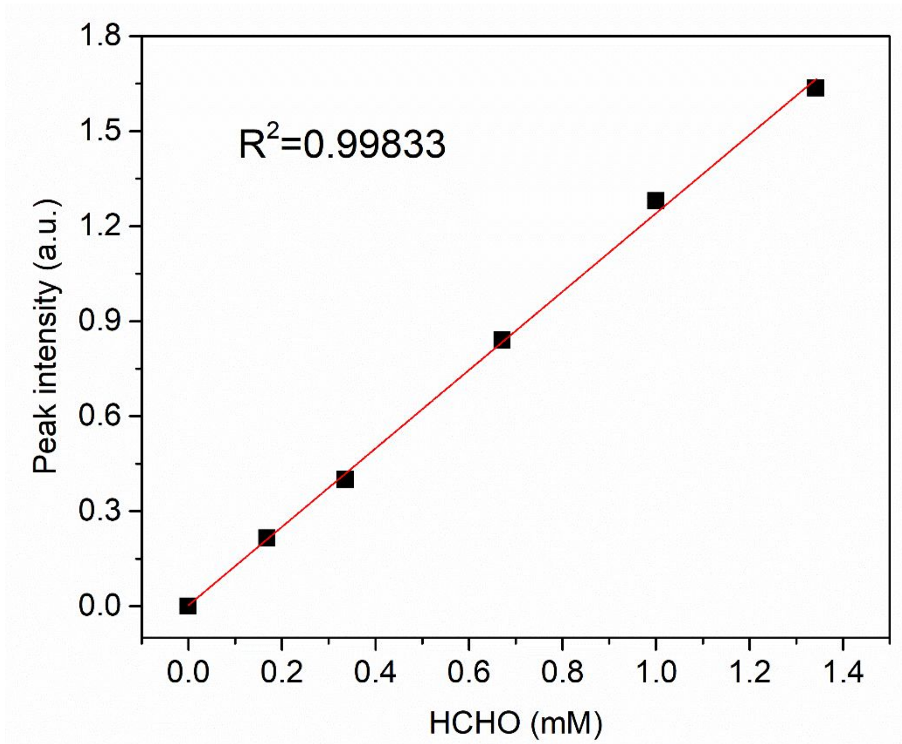

Figure S5. Calibration curve for the quantification of HCHO by colorimetric method.

Table S1. Photocatalytic activity of catalysts for direct oxidation of CH_4 using O_2 as the oxidant in water. Reaction conditions: 10 mg catalyst, 2 MPa CH_4, 0.1 MPa O_2, 100 mL water, 25±2 °C reaction temperature, 2 h reaction time, light source: 300 W Xe lamp, $300 < \lambda < 500$ nm, light intensity 100 mW cm^{-2}.

Entry	Catalyst	Amount of product (μmol)					Liquid products (μmol)	All products (μmol)	Liquid product selectivity (%)#
		CH_3OOH	CH_3OH	HCHO	CO	CO_2			
1	ZnO	0	0	25.2	0.04	1.2	25.2	26.4	95.3
2	TiO_2 (P25)	0	0	43.0	0.06	6.5	43.0	49.6	86.7
3	TiO_2 (anatase)	0	0	8.8	0	1.6	8.8	10.4	84.6
4	TiO_2 (rutile)	0	0	3.5	0	0.8	3.5	4.3	81.4
5	$SrTiO_3$	0	0	0	0	0.2	0.2	0.2	-
6	WO_3	0	0	0	0	0.2	0.2	0.2	-
7	$BiVO_4$	0	0	0	0	0	0	0	-
8	BiOCl	0	0	0	0	0	0	0	-
9	CdS	0	0	0	0	0	0	0	-
10	C_3N_4	0	0	0	0	0	0	0	-

#Liquid product selectivity (%) = mol of (CH_3OOH + CH_3OH + HCHO) ×100 / total mol of products.

Table S2. Physicochemical properties of ZnO- and TiO_2-based photocatalysts.

Catalyst	S_{BET} (m^2 g^{-1})	Metal loading (wt%)
ZnO	28.5	-
TiO_2 (P25)	56..8	-
0.1 wt% Pt/ZnO	27.5	0.12
0.1 wt% Pd/ZnO	27.1	0.11
0.1% wt Au/ZnO	27.7	0.12
0.1 wt% Ag/ZnO	27.3	0.10
0.1 wt% Pt/TiO_2 (P25)	55.8	0.12
0.1 wt% Pd/TiO_2 (P25)	56.2	0.11
0.1 wt% Au/TiO_2 (P25)	56.1	0.12
0.1 wt% Ag/TiO_2 (P25)	55.9	0.10

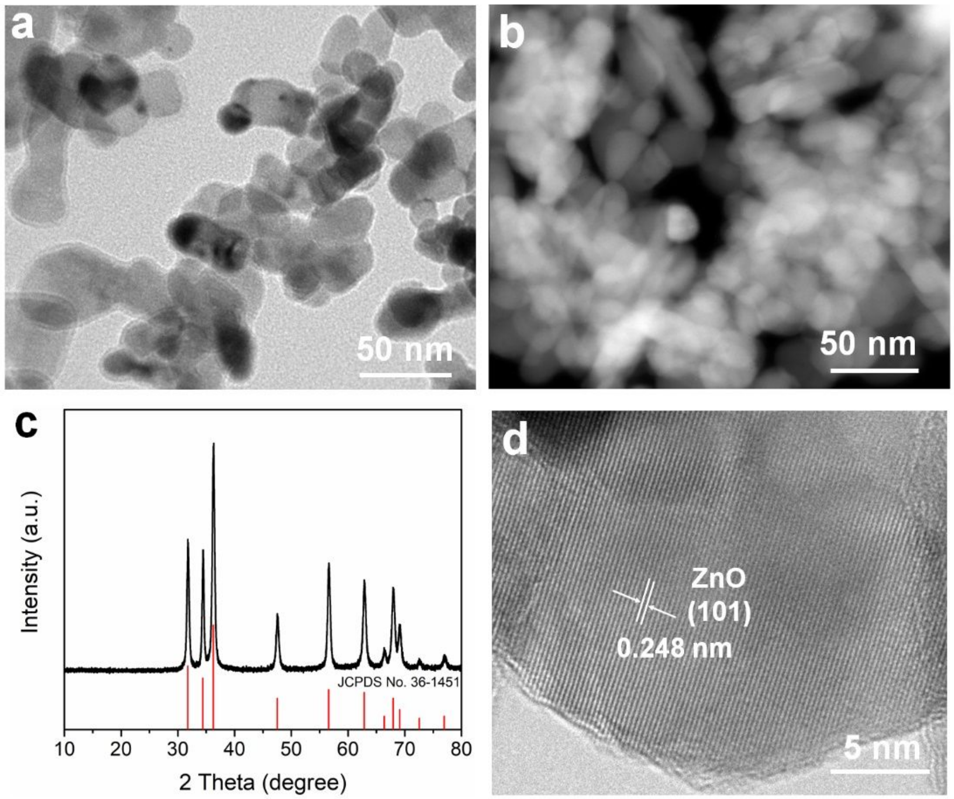

Figure S6. (a) Transmission electron microscopy (TEM) image, (b) scanning TEM (STEM) image, (c) X-ray diffraction (XRD) pattern and (d) high resolution TEM (HRTEM) image of ZnO nanoparticles.

The transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images of ZnO showed that the particle size of ZnO is in the range of 15-50 nm. The X-ray diffraction (XRD) pattern and high resolution TEM (HRTEM) image of ZnO showed that they were highly crystalline with wurtzite phase (JCPDS No. 36-1451).

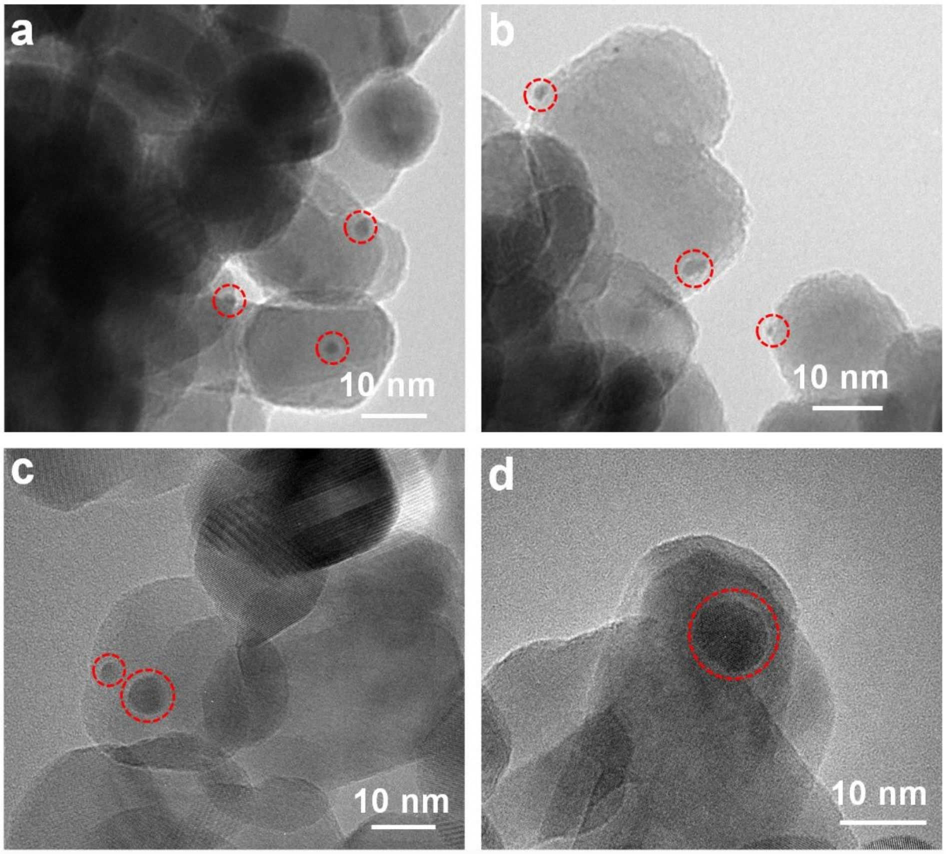

Figure S7. TEM images of 0.1 wt% Pt/ZnO (A), 0.1 wt% Pd/ZnO (B), 0.1 wt% Au/ZnO (C), and 0.1 wt% Ag/ZnO (D). Metal nanoparticles are marked with red circles.

As shown in Figure S4, the average size of Pt, Pd, Au, and Ag nanoparticles is around 2 nm, 3 nm, 5 nm, and 10 nm, respectively.

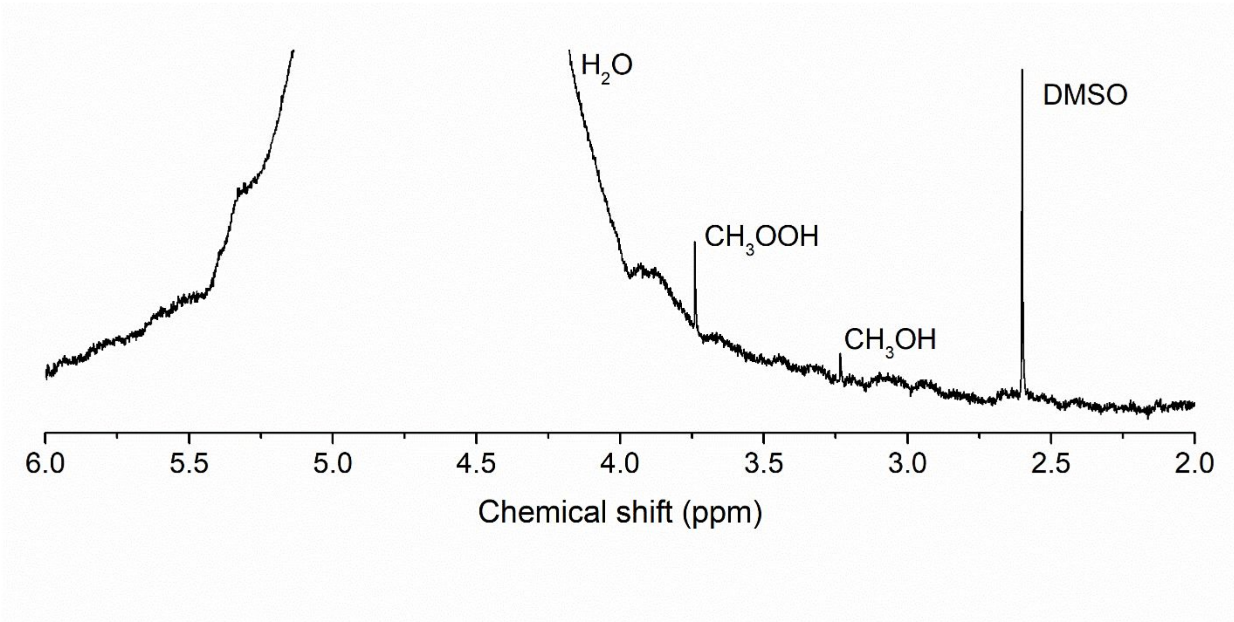

Figure S8. ^{1}H NMR spectrum of the liquid product obtained from photocatalytic methane oxidation over 0.1 wt% Au/ZnO. Reaction conditions: 10 mg 0.1 wt% Au/ZnO, 100 mL water, 2 MPa CH_4, 0.1 MPa O_2, 2 h reaction time, 25±2 °C reaction temperature, light source: 300 W Xe lamp, $300 < \lambda < 500$ nm, light intensity 100 mW cm^{-2}. (CH_3OOH, δ= 3.74 ppm; CH_3OH, δ= 3.23 ppm; DMSO, δ= 2.60ppm)

Table S3. Comparison of catalytic activity in oxidation of methane to liquid oxygenates.

Catalyst	Oxidant	Reaction condition	Liquid oxygenates		Ref.
			Product	Selectivity (%)	
0.1 wt% Au/ZnO	O_2	Photocatalysis 10 mg catalyst, 2.0 MPa CH_4, 0.1 MPa bar O_2, 25 ºC, 2h	Total: 251 µmol $CH_3OOH + CH_3OH + HCHO$	95	This work
0.33 wt% FeO_x/TiO_2	H_2O_2	Photocatalysis 10 mg catalyst, 70 µmol CH_4, 8 µmol H_2O_2, 25 ºC, 3h	Total: 11.4 µmol $CH_3OH + CH_3CH_2OH$	97	*Nat. Catal.* 2018, *1*, 889-896.
Au-Pd colloids	$O_2 + H_2O_2$	Thermocatalysis 6.6 µmol of metal, 30 bar CH_4, 5 bar O_2, 50 µmol H_2O_2, 23 ºC, 0.5h	Total: 5.2 µmol. $CH_3OOH + CH_3OH$	96	*Science* 2017, *358* (6360), 223-227
0.6 wt% Rh-TiO_2	$CO + O_2$	Thermocatalysis 20 mg catalyst, 20 bar CH_4, 2 bar O_2, 5 bar CO, 150 ºC, 3h	Total: 4.6 µmol CH_3OH	100	*Nature* 2017, *551*, 605-608
0.3 wt% Rh/ ZrO_2	H_2O_2	Thermocatalysis 30 mg catalyst, 30 bar 95% CH_4/He, 5 mmol H_2O_2, 70 ºC, 0.5h	Total: 1.1 µmol $CH_3OOH + CH_3OH$	78	*J. Am. Chem. Soc.* 2017, *139* (48), 17694-17699.
FeN_4/GN	H_2O_2	Thermocatalysis 50 mg catalyst, 20 bar CH_4, 49.5 mmol H_2O_2, 25 ºC, 10 h	Total: 118 µmol $CH_3OH + CH_3OOH + HCOOH$	94	*Chem* 2018, *4* (8), 1902-1910.

Table S4. The amount of formed liquid oxygenates molecules and the number of incident photons in photocatalytic CH_4 oxidation over 0.1 wt% Au/ZnO for 6 h, as well as the measurement of AQY.

Wavelength (nm)	Photon number*	Amount of product (μmol)			AQY (%)§
		CH_3OOH	CH_3OH	HCHO	
368 ($\lambda_{1/2}$=23.8 nm)	1.95×10^{21}	41.5	24.8	52.6	11.7

*Light intensity: 0.0032 W/cm^2, irradiation area: 15.2 cm^2, irradiation time: 6 h.
§AQY = $(41.5+24.8\times3+52.6\times5)\times10^{-6}\times6.02\times10^{23}\times100/1.95\times10^{21}$.

Table S5. Photocatalytic activity of 0.1 wt% Pt, Pd, Au or Ag/ZnO catalysts for oxidation of methane using O_2 as oxidant. Reaction conditions: 10 mg catalyst, 2 MPa CH_4, 0.1 MPa O_2, 100 mL water, 25±2 °C reaction temperature, 4 h reaction time; light source, 300 W Xe lamp, 300 < λ < 500 nm, light intensity 100 mW cm^{-2}.

Entry	Catalyst	Amount of product (μmol)					Liquid products (μmol)	All products (μmol)	Liquid product selectivity (%)
		CH_3OOH	CH_3OH	HCHO	CO	CO_2			
1	0.1 wt% Pt/ZnO	117.6	85.3	113.2	1.3	35.7	316.1	353.1	89.5
2	0.1 wt% Pd/ZnO	35.5	108.2	122.5	0.1	35.5	266.2	301.8	88.2
3	0.1 wt% Au/ZnO	170.1	58.6	104.9	1.25	28.4	333.6	363.3	91.8
4	0.1 wt% Ag/ZnO	48.7	23.0	140.0	1.4	12.9	211.7	226.0	93.6

Table S6. Photocatalytic activity of 1.0 wt% Pt, Pd, Au or Ag/ZnO catalysts for oxidation of methane using O_2 as oxidant. Reaction conditions: 10 mg catalyst, 2 MPa CH_4, 0.1 MPa O_2, 100 mL water, 25±2 °C reaction temperature, 2 h reaction time; light source, 300 W Xe lamp, 300 < λ < 500 nm, light intensity 100 mW cm^{-2}.

Entry	Catalyst	Amount of product (μmol)					Liquid products (μmol)	All products (μmol)	Liquid product selectivity (%)
		CH_3OOH	CH_3OH	HCHO	CO	CO_2			
1	1.0 wt% Pt/ZnO	52.3	77.2	82.9	0.2	32.9	212.4	245.5	86.5
2	1.0 wt% Pd/ZnO	33.6	114.1	79.7	0.1	30.9	227.4	258.4	88.0
3	1.0 wt% Au/ZnO	107.2	85.3	64	0.1	13.2	256.5	269.8	95.1
4	1.0 wt% Ag/ZnO	45.3	30.3	113.8	0.4	8.2	189.4	198.0	95.7

Table S7. Conversion of CH_4 over 0.1 wt% Au/ZnO for 2 and 4 hours. Reaction conditions: 10 mg catalyst, 2 MPa CH_4, 0.1 MPa O_2, 100 mL water, 25±2 °C reaction temperature; light source, 300 W Xe lamp, $300 < \lambda < 500$ nm, light intensity 100 mW cm^{-2}.

Reaction time (h)	2	4
Total amount of all products (μmol)*	262.9	363.3
CH_4 conversion (%)#	0.3	0.4

*The products include CH_3OOH, CH_3OH, HCHO, CO and CO_2.
#CH_4 conversion = total amount of all products × 100% / amount of CH_4 introduced. The working volume of reactor is 100 mL, so the amount of CH_4 = 81.6 mmol.

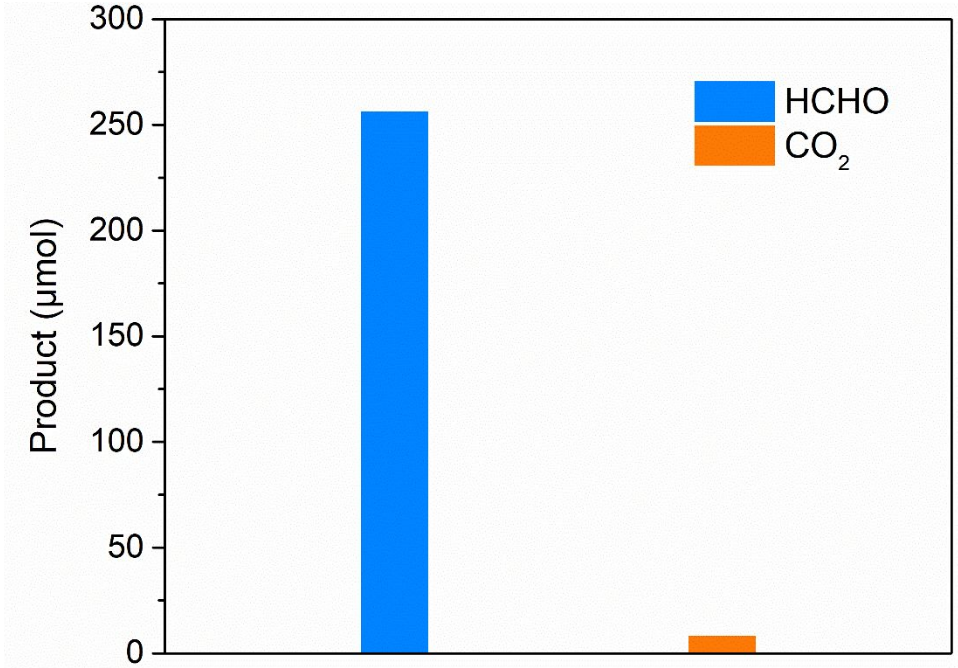

Figure S9. Product yields in photocatalytic oxidation of methanol. Reaction conditions: 10 mg 0.1 wt% Au/ZnO, 0.1 MPa O_2, 100 mL of 100 mM CH_3OH, 25±2 °C reaction temperature, 1 h reaction time; light source, 300 W Xe lamp, 300 < λ < 500 nm, light intensity 100 mW cm^{-2}.

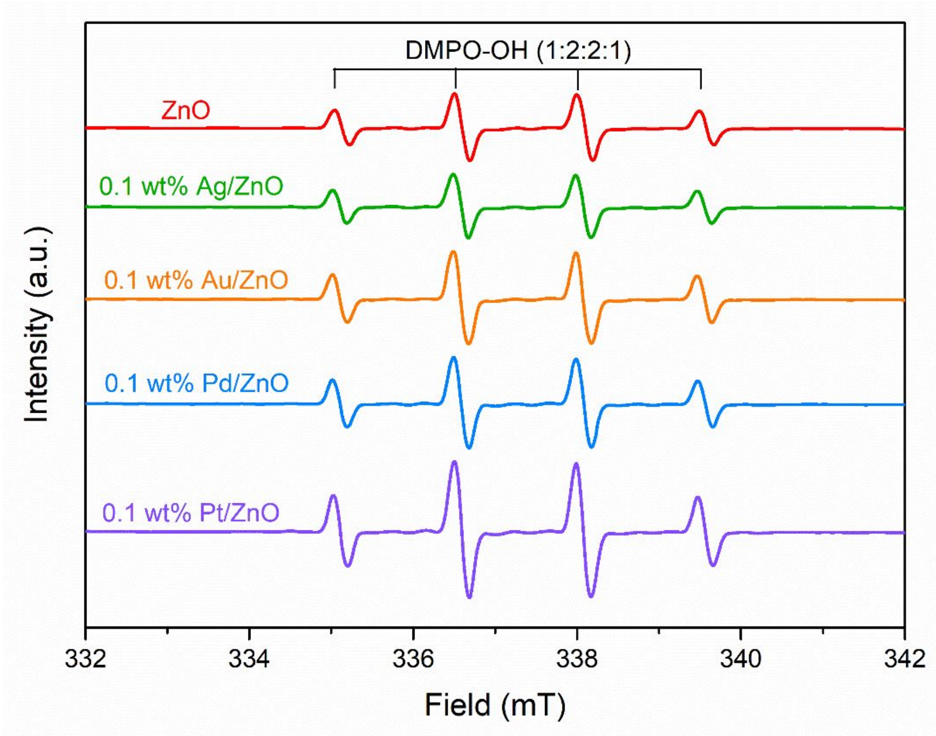

Figure S10. EPR spectra of cocatalysts/ZnO under light irradiation for 10 min in aqueous solution. DMPO was added into the reaction mixture as the radical trapping agent.

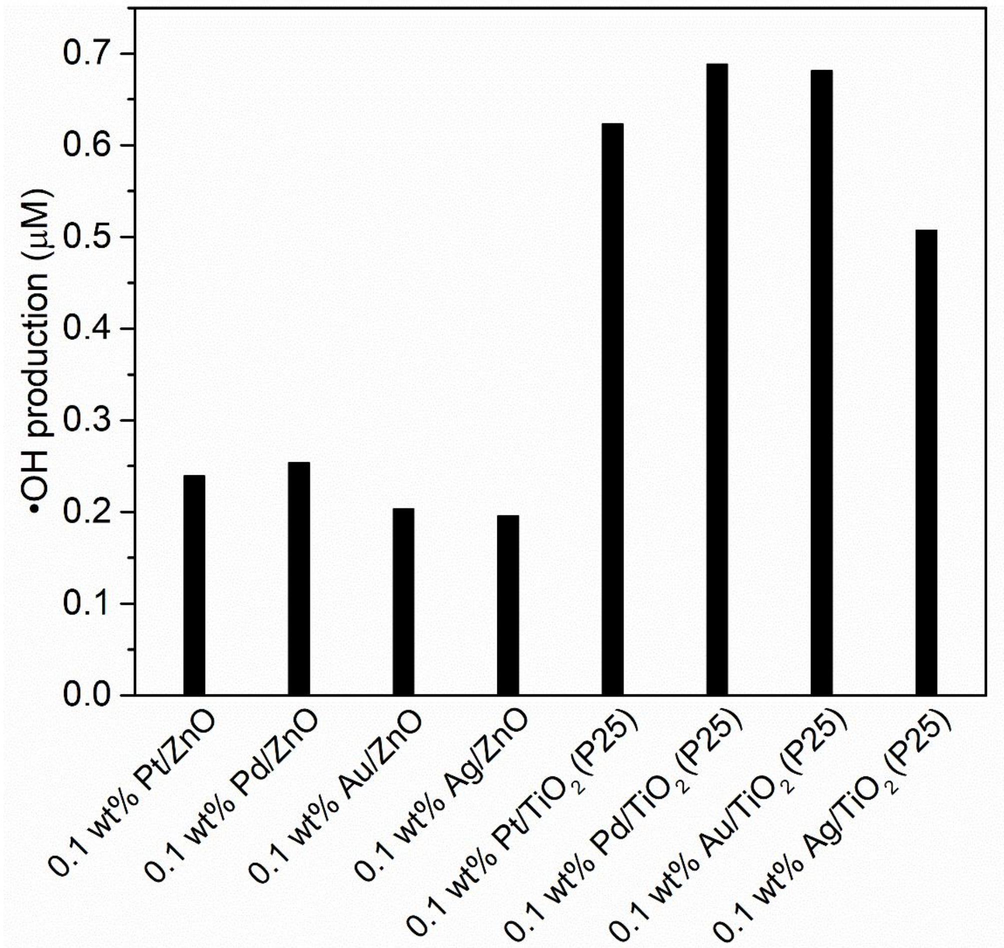

Figure S11. •OH production of cocatalyst/ZnO and cocatalyst/TiO_2 (P25) photocatalysts.

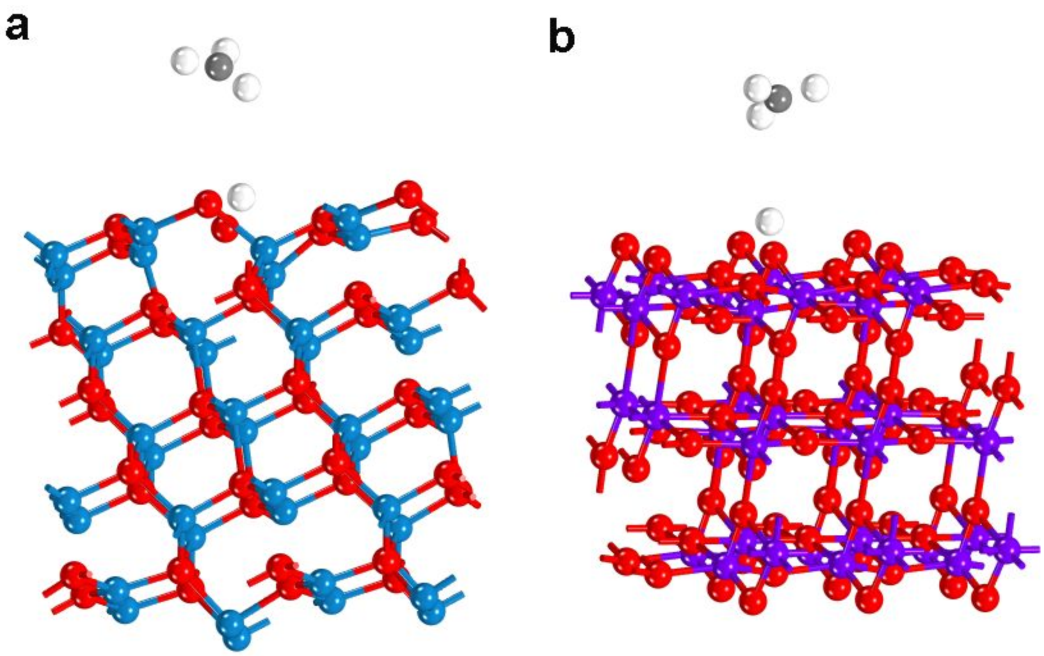

Figure S12. Calculation models. The diagram of CH_4 dissociation on the surface of (a) ZnO (101) and (b) TiO_2 (101). Zn, Ti, O, H and C atoms are shown in blue, purple, red, white and gray, respectively.

According to the surface configurations, the reaction sites of oxygen atom at surface lost one to third coordination number with cations in TiO_2 (101) models, while one half coordination number was remained for surface oxygen atoms in ZnO (101) models. Thus, the more unsaturation of surface oxygen atom as reaction site provides stronger interaction with hydrogen to lower the energy barrier of CH_4 dissociation.

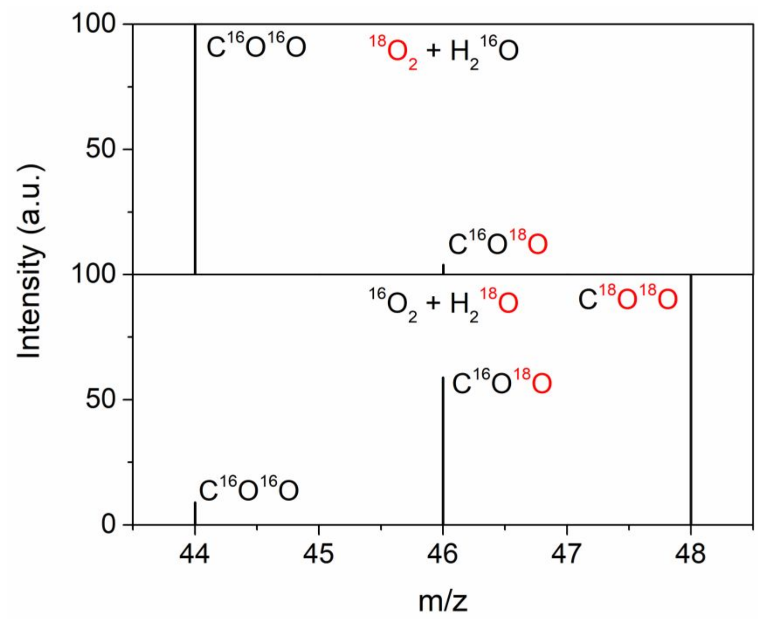

Figure S13. GC-MS spectra of CO_2 generated over 0.1 wt% Au/ZnO with $^{18}O_2 + H_2{}^{16}O$ or $^{16}O_2 + H_2{}^{18}O$ in photocatalytic CH_4 oxidation.

As shown in Figure S13, when $^{18}O_2$ and $H_2{}^{16}O$ was used as the reactants, the products $C^{16}O^{16}O$ (m/z=44) and $C^{16}O^{18}O$ (m/z=46) accounted for 96% and 4%, respectively, while no product $C^{18}O^{18}O$ (m/z=48) was detected. When $^{16}O_2$ and $H_2{}^{18}O$ was used as the reactants, the products $C^{16}O^{16}O$ (m/z=44), $C^{16}O^{18}O$ (m/z=46) and $C^{18}O^{18}O$ (m/z=48) accounted for 5%, 35% and 60%, respectively. These results demonstrate that the O atoms of CO_2 were mainly from H_2O. Thus, the overoxidation of liquid oxygenates to CO_2 was mainly dominated by $^{\bullet}OH$ derived from photooxidation of H_2O.