Supporting Information

Selective Photooxidation of Methane to Methanol with Oxygen over Dual-Cocatalysts Modified Titanium Dioxide

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Table S1 Physicochemical properties of TiO_2-based photocatalysts.

Catalyst	Noble metal loading (wt%)	Cobalt loading (wt%)
Pt/TiO_2	1.01	-
Pd/TiO_2	0.97	-
Au/TiO_2	1.02	-
Ag/TiO_2	0.95	-
$Pt\text{-}CoO_x/TiO_2$	0.97	0.93
$Pd\text{-}CoO_x/TiO_2$	0.95	0.95
$Au\text{-}CoO_x/TiO_2$	0.97	0.96
$Ag\text{-}CoO_x/TiO_2$	0.95	0.92

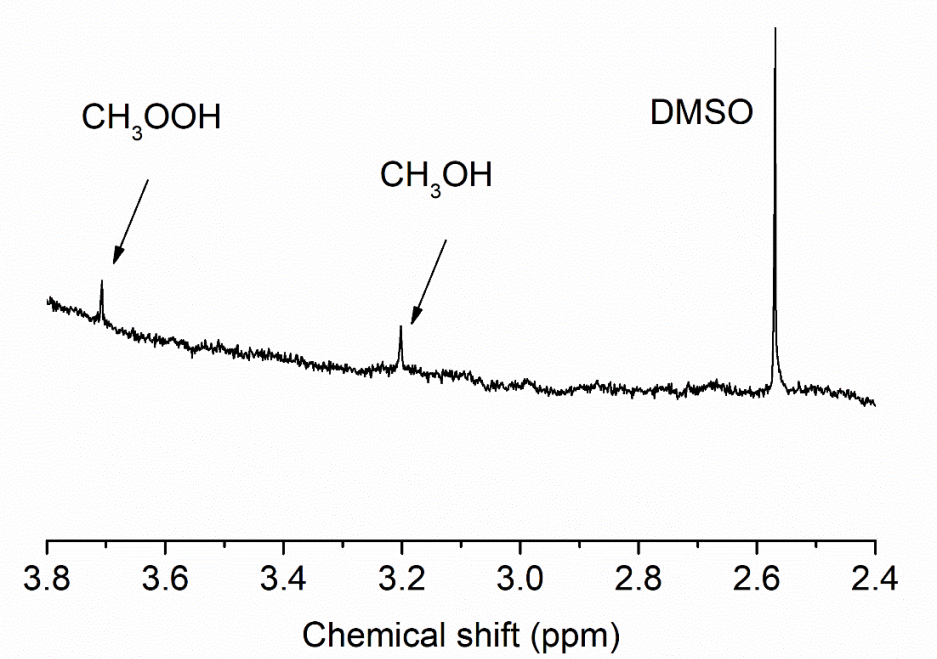

Figure S1. ^{1}H NMR spectrum of the liquid product obtained from photocatalytic methane oxidation over Au/TiO_2. (CH_3OOH, δ= 3.71 ppm; CH_3OH, δ= 3.20 ppm; DMSO, δ= 2.57 ppm)

Table S2. The amount of formed CH_3OOH and CH_3OH molecules and the number of incident photons in photocatalytic CH_4 oxidation over Au-CoO_x/TiO_2, as well as the measurement of AQE.

Wavelength (nm)	Photon number*	Amount of product (μmol)		AQE (%)§
		CH_3OOH	CH_3OH	
368 ($\lambda_{1/2}$=23.8 nm)	2.38×10^{21}	9.8	11.6	1.2

*Light intensity: 0.0039 W/cm^2, irradiation area: 15.2 cm^2, irradiation time: 6 h.
§AQE = [*N*(CH_3OOH) + *N*(CH_3OH)×3]×100%/*N*(Photons), where *N*(CH_3OOH), *N*(CH_3OH) and *N*(Photons) represent the number of formed CH_3OOH, CH_3OH molecules and incident photons, respectively. Therefore, AQE = $(9.8+11.6\times3)\times10^{-6}\times6.02\times10^{23}\times100/2.38\times10^{21}$ = 1.2%..

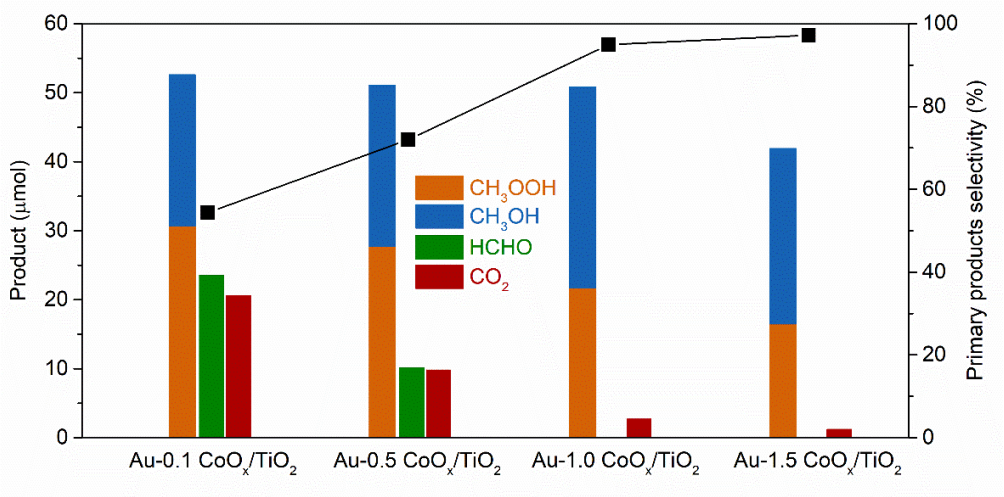

Figure S2. Product yields and primary products selectivity on Au/TiO_2 loaded with different amount of Co after 2 h reaction.

Table S3. Comparison of catalytic activity in photooxidation of methane to methanol.

Entry	Catalyst	Oxidant	Reaction condition	CH_3OH		CH_4 conversion (%)	Ref.
				Amount	Selectivity (%)		
1	Au-CoO_x/TiO_2	O_2	10 mg catalyst, 2.0 MPa CH_4, 0.1 MPa bar O_2, 25 ºC, 2 h 300 W Xe lamp, 450 mW cm^{-2}	50.8 µmol of CH_3OOH and CH_3OH	95	0.07	This work
2	Au-CoO_x/TiO_2	O_2	10 mg catalyst, 2.0 MPa CH_4, 0.1 MPa bar O_2, 25 ºC, 4 h 300 W Xe lamp, 450 mW cm^{-2}	63.7 µmol of CH_3OOH and CH_3OH	80	0.1	This work
3	Au/TiO_2	O_2	10 mg catalyst, 2.0 MPa CH_4, 0.1 MPa bar O_2, 25 ºC, 1 h 300 W Xe lamp, 450 mW cm^{-2}	29.2 µmol of CH_3OOH and CH_3OH	39	0.1	This work
4	0.1 wt% Au/ZnO	O_2	10 mg catalyst, 2.0 MPa CH_4, 0.1 MPa bar O_2, 25 ºC, 2 h 300 W Xe lamp, 100 mW cm^{-2}	164.6 µmol CH_3OOH and CH_3OH	63	0.3	1
5	$BiVO_4$	H_2O	300 mg catalyst, 20% CH_4/He, 55 ºC, 2 h 450 W immersion medium-pressure Hg lamp with UVC-visible radiation	12.48 µmol of CH_3OH	51	-	2
6	WO_3 mesoporous	H_2O + $FeCl_3$ (2 mM)	300 mg catalyst, 20% CH_4/He, 55 ºC, 2 h 450 W immersion medium-pressure Hg lamp with UVC-visible radiation	33.3 µmol of CH_3OH	37.4	0.3%	3
7	La-doped WO_3 mesoporous	H_2O	300 mg catalyst, 20% CH_4/He, 55 ºC, 2 h 450 W immersion medium-pressure Hg lamp with UVC-visible radiation	18.84 µmol of CH_3OH	47	0.17	4

Note: the CH_4 conversion in ref. 3 cannot be calculated because the amount of CH_4 was not provided.

Table S4. Controlled experiments of photocatalytic oxidation of CH_4 over Au-CoO_x/TiO_2. 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 450 mW cm^{-2}.

Entry	Catalyst	Amount of product (μmol)				All products (μmol)	Primary products sel. (%)
		CH_3OOH	CH_3OH	HCHO	CO_2		
1	-	0	0	0	0	0	-
2*	Au-CoO_x/TiO_2	0	0	0	0	0	-
3#	Au-CoO_x/TiO_2	0	0		0	0	-
4§	Au-CoO_x/TiO_2	0	0		0	0	-

*Entry 2: 2 MPa bar Ar gas was used instead of CH_4
#Entry 3: Without light irradiation
§Entry 4: Without O_2

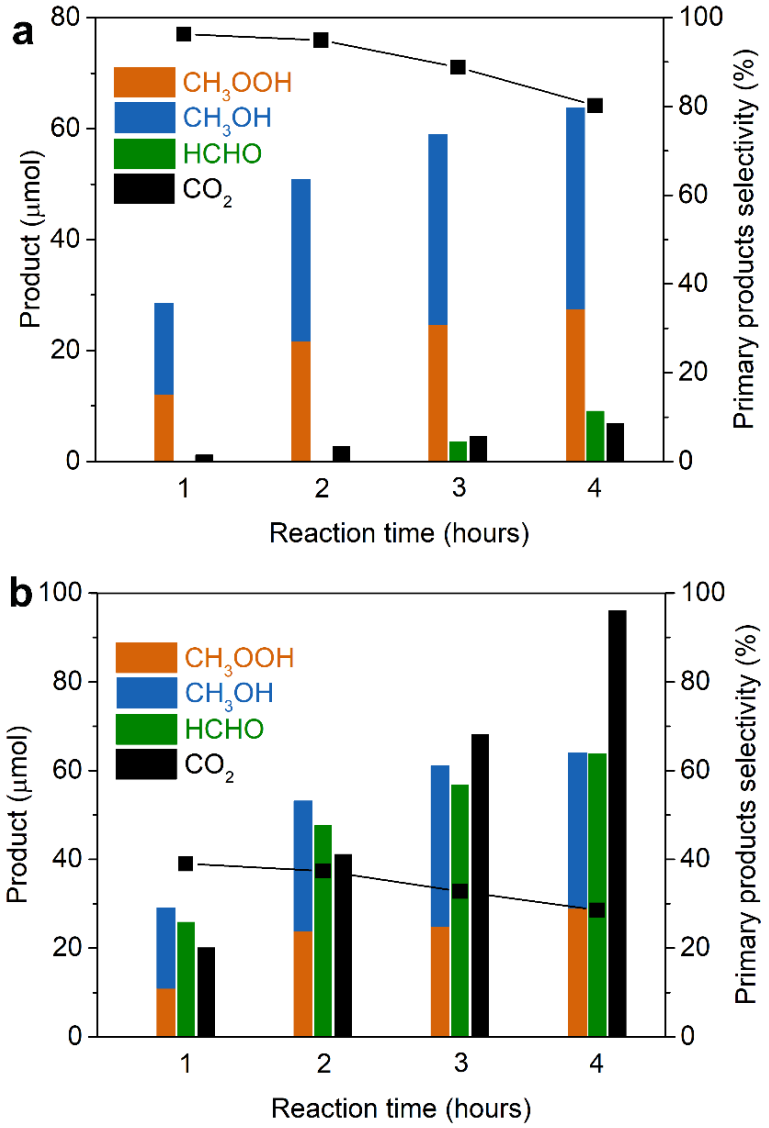

Figure S3. Time course of product yields and the primary products selectivity over Au-CoO_x/TiO_2 (a) and Au/TiO_2 (b).

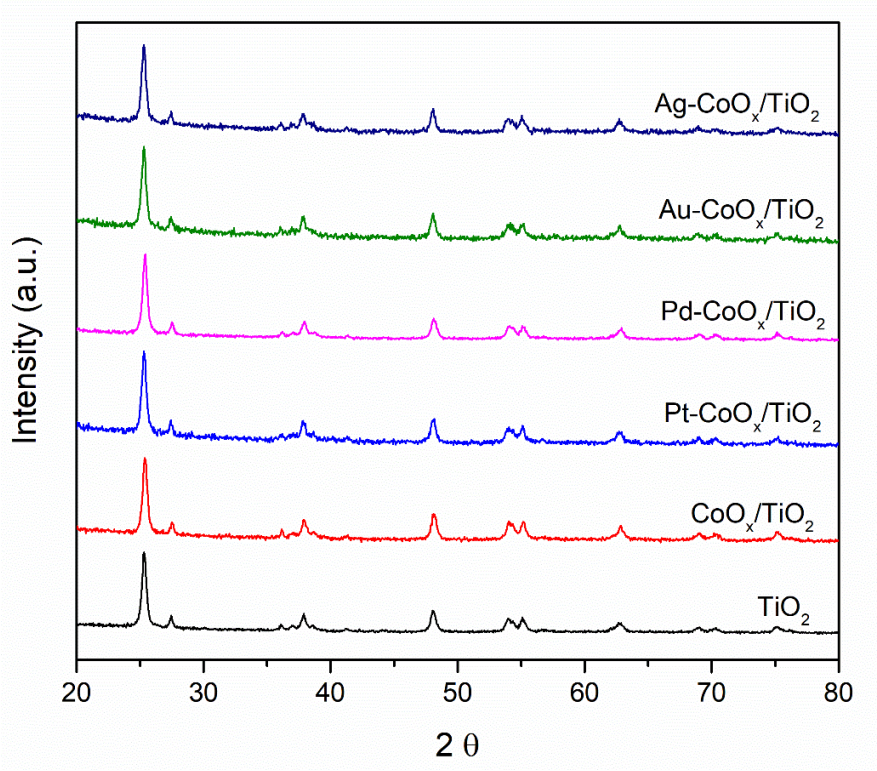

Figure S4. X-ray diffraction (XRD) pattern of photocatalysts

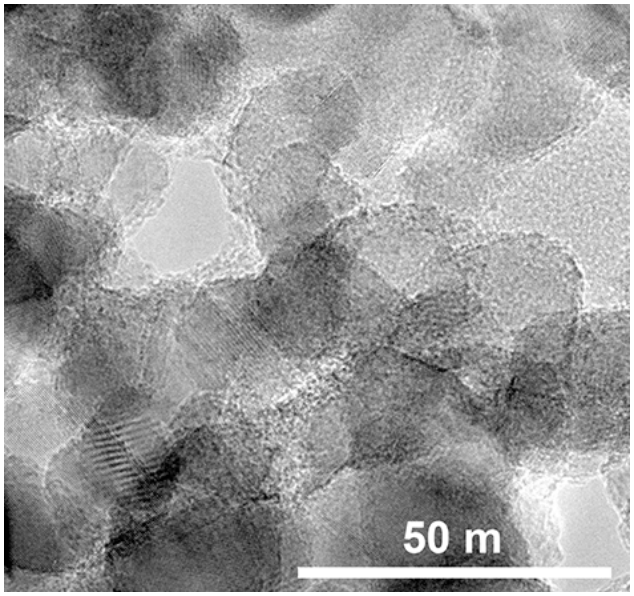

Figure S5. TEM image of CoO_x/TiO_2.

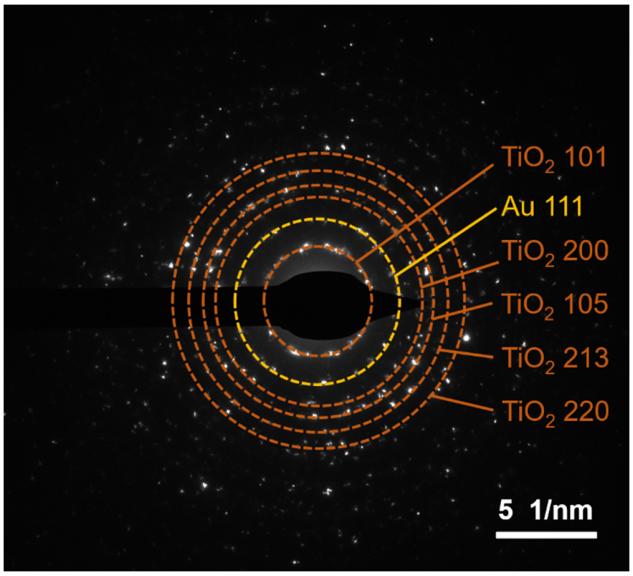

Figure S6. SAED pattern of Au-CoO_x/TiO_2.

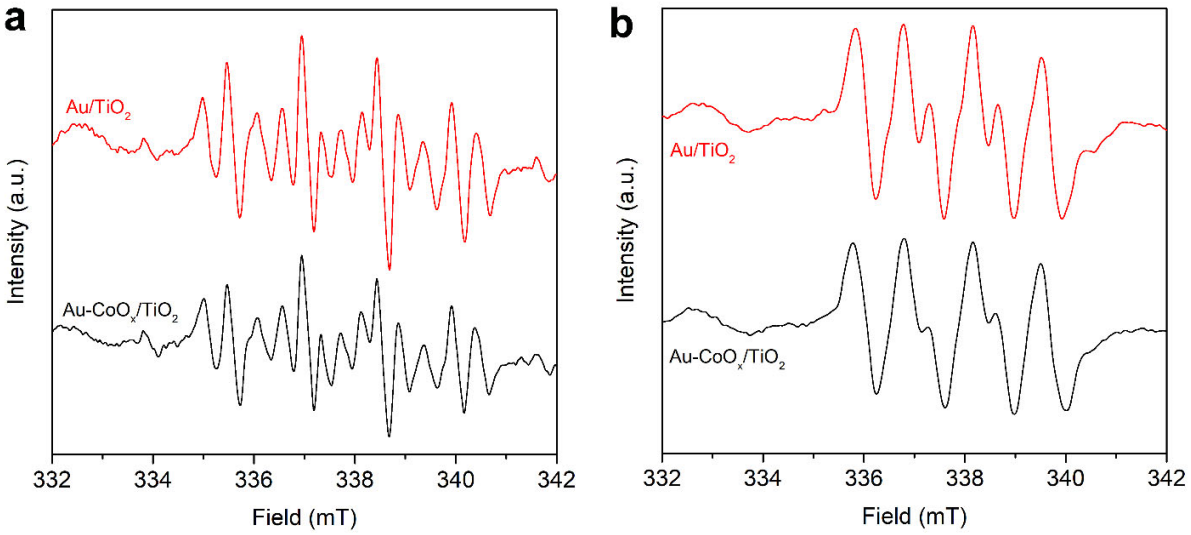

Figure S7. (a) In situ EPR spectra of Au/TiO_2 and $Au\text{-}CoO_x/TiO_2$ recorded in the presence of CH_4 and O_2 under 15 min of light irradiation. (b) In situ EPR spectra of Au/TiO_2 and $Au\text{-}CoO_x/TiO_2$ recorded in the presence of O_2 and CH_3OH (as $^{\bullet}OH$ scavenger) under 5 min of light irradiation.

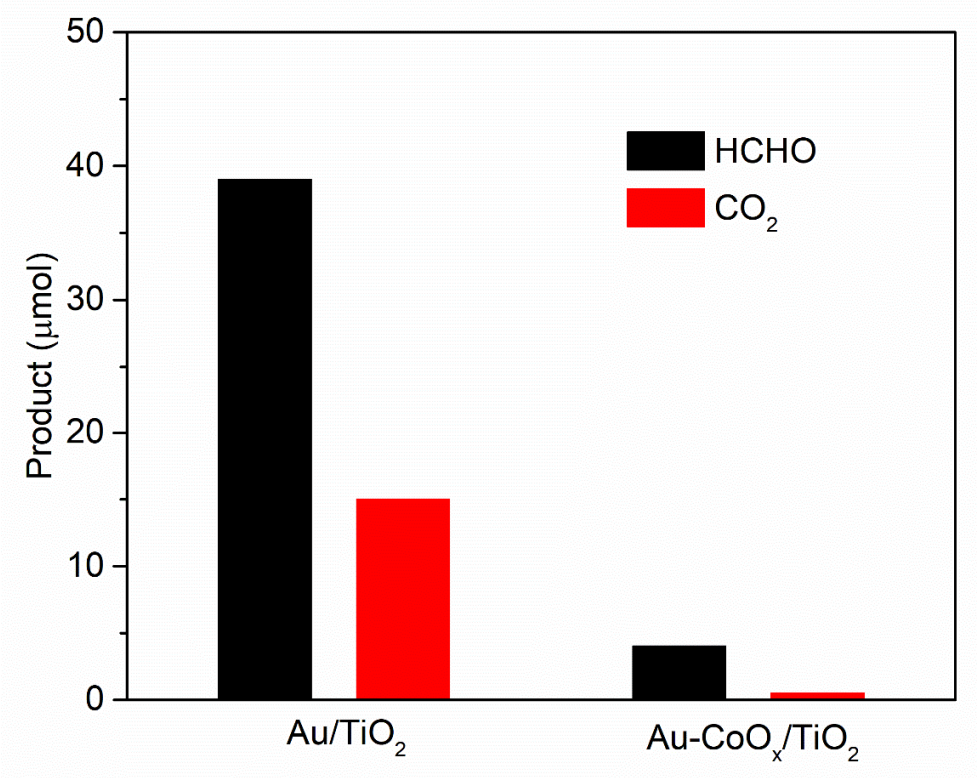

Figure S8. Product yields in photocatalytic oxidation of methanol over Au/TiO_2 and $Au\text{-}CoO_x/TiO_2$. Reaction conditions: 10 mg catalyst, 0.1 MPa O_2, 100 mL of 50 mM CH_3OH, 25±2 °C reaction temperature, 0.5 h reaction time.

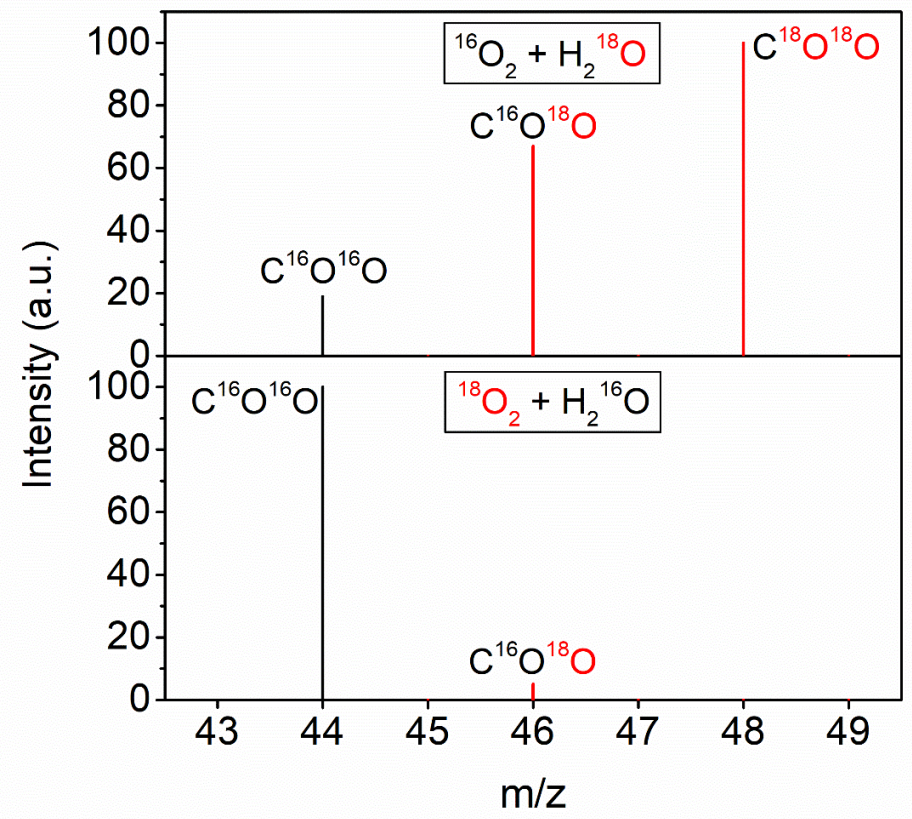

Figure S9. GC-MS spectra of CO_2 generated with $^{18}O_2 + H_2{}^{16}O$ or $^{16}O_2 + H_2{}^{18}O$ in photocatalytic CH_4 oxidation over Au/TiO_2.

As shown in Figure S9, when $^{18}O_2$ and $H_2{}^{16}O$ was used, a trace of $C^{16}O^{18}O$ (m/z=46) (4%) was generated, and most of the product was $C^{16}O^{16}O$ (m/z=44) (96%). When the reactants were replaced with $^{16}O_2$ and $H_2{}^{18}O$, the amount of $C^{16}O^{16}O$ (m/z=44), $C^{16}O^{18}O$ (m/z=46) and $C^{18}O^{18}O$ (m/z=48) accounted for 10%, 37% and 53%, respectively.

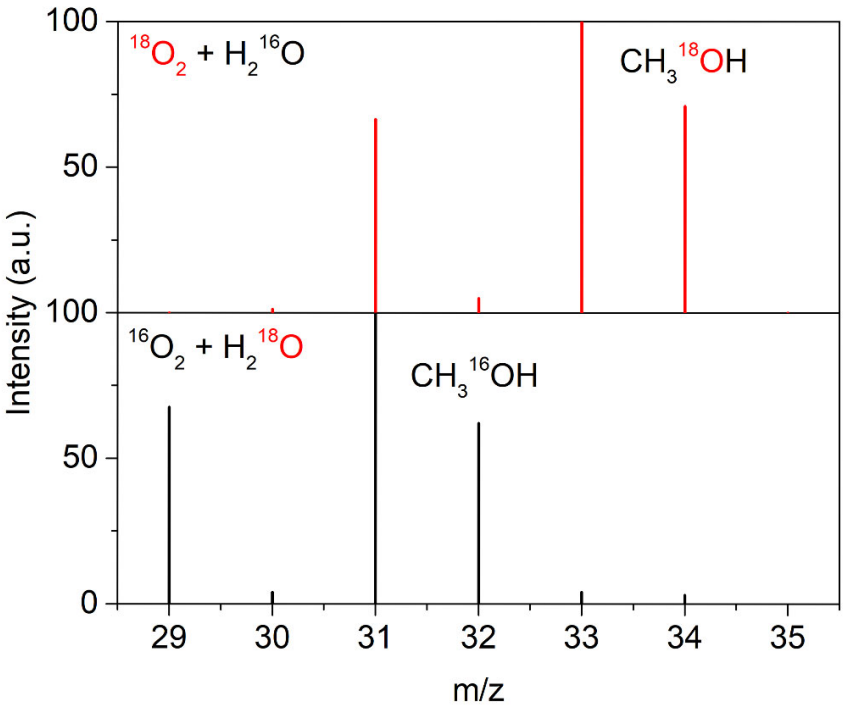

Figure S10. GC-MS spectra of CH_3OH generated with $^{18}O_2$ + $H_2{}^{16}O$ or $^{16}O_2$ + $H_2{}^{18}O$ in photocatalytic CH_4 oxidation.

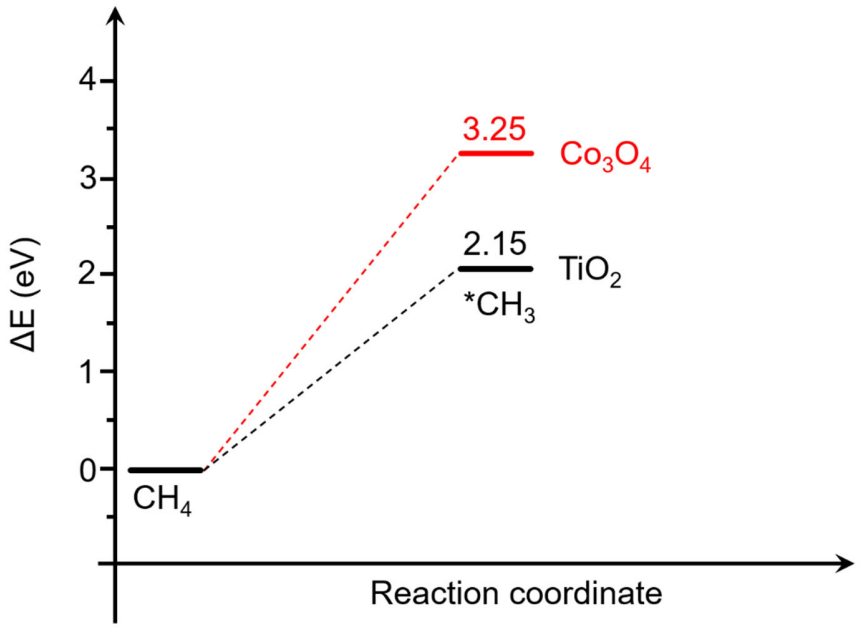

Figure S11. DFT results for the formation of $*CH_3$ from CH_4 on Co_3O_4 (311) and TiO_2 (101). The value (2.15 eV) of ΔE ($CH_4 \rightarrow *CH_3$) on TiO_2 (101) is referenced from our previous work.[1]

Reference

(1) Song, H.; Meng, X.; Wang, S.; Zhou, W.; Wang, X.; Kako, T.; Ye, J. Direct and Selective Photocatalytic Oxidation of CH_4 to Oxygenates with O_2 on Cocatalysts/ZnO at Room Temperature in Water. *J. Am. Chem.Soc.* **2019**, *141*, 20507-20515.

(2) Murcia-López, S.; Villa, K.; Andreu, T.; Morante, J. R.; Partial Oxidation of Methane to Methanol Using Bismuth-Based Photocatalysts. *ACS Catal.* **2014**, *4*, 3013-3019.

(3) Villa, K.; Murcia-López, S.; Andreu, T.; Morante, J. R.; Mesoporous WO_3 photocatalyst for the partial oxidation of methane to methanol using electron scavengers. *Appl.Catal. B* **2015**, *163* 150-155.

(4) Villa, K.; Murcia-López, S.; Morante, J. R.; Andreu, T. An insight on the role of La in mesoporous WO_3 for the photocatalytic conversion of methane into methanol. *Appl.Catal. B* **2016**, *187*, 30-36.