Supplementary Information

Highly selective aerobic oxidation of methane to methanol over gold

decorated zinc oxide via photocatalysis

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G 4 TD											
Sample ID: Replicates	1					1.30) mg Au	$n_{08}/Zn($		а	_
Replicate	1							J.U0		~	
IS	Analyte	Mass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			
	Au	197		1595.4		1289.641	0.1	ug/L			
Replicate	2	-									_
IS	Analyte	Mass 107	Meas.	Intensity 1650 1	Net	Intensity	Concentration	Sample Unit			_
Replicate	AU 2	197		1650.1		1344.314	0.11	ug/L			-
IS	Analyte	Mass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			-
10	Au	197	noubi	1676.1		1370. 317	0.11	ug/L			
Summary								_			
IS	Analyte	Mass	Meas.	Intens. Mean	Net	Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD H	Report Un	it
	Au	197		1640.5		1334. 8	0.11	0.003	3.09 ι	ıg/L	_
Quantitativ	e Analy	sis -	Compr	ehensive Repo	rt	1.60		/7n(h	-
Sample ID:	2					1.00		D.15/ ZIIV		D	_
Replicates	1										-
IS	Analyte	Mass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			
10	Au	197	ACCOL	3558.4		3252.662	0.26	ug/L			
Replicate	2										
IS	Analyte	Mass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			_
	Au	197		3260.4		2954.591	0.23	ug/L			_
Replicate	3						a				_
15	Analyte	Mass	Meas.	Intensity 2201 7	Net	Intensity	Concentration	Sample Unit			-
Summarry	Au	191		3321.7		3015.936	0.24	ug/L			-
IS	Analvte	Mass	Meas.	Intens. Mean	Net	Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD R	eport Un	it
10	Au	197	acto.	3380. 2		3074.4	0.24	0.012	5. 12 u	g/L	
Ouentitetir	a Analu	-i	Come	shonaine Rone						0	۲
Sample ID.	e Analy	sis -	Compr	enensive Kepo	rι	3.8	8 ma Au	~ 20/Zn	0	С	
Replicates	5							0.30			
Replicate	1										
IS	Analyte	Hass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			
	Au	197		15254.8		14949.026	1.18	ug/L			
Replicate	2										_
IS	Analyte	Mass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			_
Pauliante.	Au	197		15432.3		15126.55	1.19	ug/L			-
Replicate	Analyta	Hace	Noac	Intensity	Not	Intensity	Concentration	Sample Unit			
10	Au	197	meas.	15252. 1	Nec	14946. 357	1. 18	ug/L			
Summary				1000011							
IS	Analyte	Mass	Meas.	Intens. Mean	Net	Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD F	eport Un	it
	Au	197		15313.1		15007.3	1.18	0.008	0.69 u	ig/L	
Sample ID:	4					4.50		17.00			
Replicates						1.50	o mg Au	₇₅ /2nc)	a	
Replicate										~	
IS	1										
D 11	1 Analyte	Mass	Meas.	Intensity	Net	Intensity	Concentration	Sample Unit			
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Keplicate IS	Analyte Au 2 Analyte Au	Mass 197 Mass 197	Meas. Meas.	Intensity 14757.6 Intensity 14444.6	Net Net	Intensity 14451.838 Intensity 14138.851	Concentration 1.14 Concentration	Sample Unit ug/L Sample Unit			
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Replicate IS Replicate IS	Analyte Au 2 Analyte Au 3 Analyte	Mass 197 Mass 197 Mass	Neas. Neas. Neas.	Intensity 14757.6 Intensity 14444.6 Intensity	Net Net Net	Intensity 14451.838 Intensity 14138.851 Intensity	Concentration 1.14 Concentration 1.11 Concentration	Sample Unit ug/L Sample Unit ug/L Sample Unit			
Replicate IS Replicate IS	Analyte Au Analyte Au 3 Analyte Au	Mass 197 Mass 197 Mass 197	Meas. Meas. Meas.	Intensity 14757.6 Intensity 14444.6 Intensity 14329.2	Net Net	Intensity 14451.838 Intensity 14138.851 Intensity 14023.402	Concentration 1.14 Concentration 1.11 Concentration 1.1	Sample Unit ug/L Sample Unit ug/L Sample Unit ug/L			
Replicate IS Replicate IS Summary	Analyte Au Analyte Au Analyte Au Analyte	Mass 197 Mass 197 Mass 197 Mass 197	Neas. Neas. Neas.	Intensity 14757.6 Intensity 14444.6 Intensity 14329.2	Net Net	Intensity 14451.838 Intensity 14138.851 Intensity 14023.402	Concentration 1.14 Concentration 1.11 Concentration 1.1	Sample Unit ug/L Sample Unit ug/L Sample Unit ug/L			
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Fig. S1 ICP-OES results of the samples. (a) 1.30 mg of $Au_{0.08}/ZnO$, (b) 1.60 mg of $Au_{0.15}/ZnO$, (c) 3.88 mg of $Au_{0.3}/ZnO$, (d) 1.56 mg of $Au_{0.75}/ZnO$, (e) 2.24 mg of $Au_{1.57}/ZnO$ and (f) 3.59 mg of $Au_{1.79}/ZnO$ were dissolved in the mixed acid solutions for the concentration tests of Au species.



Fig. S2 XRD patterns of Au_x/ZnO (x = 0, 0.08, 0.15, 0.30, 0.75, 1.57 and 1.79).

To investigate the influences for crystal types by Au loading amounts, XRD patterns of Au_x/ZnO (x = 0, 0.08, 0.15, 0.30, 0.75, 1.57 and 1.79) are tested as shown in Fig.S2. However, in the cases of Au_x/ZnO (x = 0.08, 0.15, 0.30, 0.75 and 1.57), merely ZnO crystal peaks with no observation of Au are detected, which may be attributed to the trace loading amounts of Au. Until enhancing the Au loading amount to 1.79 %, obvious XRD peaks on Au (111) and Au (200) emerge as convincing proofs for Au deposition. Meanwhile, ZnO also remains the intact crystal structure in the sample of $Au_{1.79}/ZnO$.



Fig. S3 (a) HAADF-STEM image and (b-d) corresponding element mapping of (b) Zn, (c) O and (d) Au over $Au_{0.75}/ZnO$. (e) EDX spectroscopy of $Au_{0.75}/ZnO$.

The successful synthesis of $Au_{0.75}/ZnO$ can also been verified by the elements distributions of Zn (Fig. S3b), O (Fig. S3c) and Au (Fig. S3d) from the element mapping by high-angle annular dark field scanning transmission electron microscope (HAADF-STEM, Fig. S3a) and energy dispersive X-ray (EDX) spectroscopy (Fig. S3e).



Fig. S4 Detailed configurations of high-pressure photocatalytic reactor for photocatalytic CH₄ oxidation.

The standard stainless-steel pressure vessel is assembled by a sample inner cup within a reactor well possessing 50 mL volume for reactant loading. A quartz window configurated is deposited in top plate to transit the external light source. Gas inlet and gas outlet are for reaction gas loading and unloading. Safety release valve is for security assurance. Electronic pressure gauge is for gas-pressure display.



Fig. S5 Detailed illustration of the photocatalytic CH₄ oxidation reaction setup.

The photocatalytic CH₄ oxidation reaction setup contains light source, high pressure reactor, reactor holder, cooling water circulation and stirring apparatus.



Fig. S6 Full light spectrum emission of Xenon lamp.



Fig. S7 (a) EIS plots of Au_x/ZnO (x= 0, 0.08, 0.15, 0.30, 0.75, 1.57 and 1.79) measured at 10 mV (vs. Ag/AgCl) in 1 M Na₂SO₄ solution under dark conditions. The semicircles of Nyquist plots have been fitted to demonstrate the accurate R_{ct} values with (b) corresponding equivalent circuit diagram. R_s, CPE and R_{ct} represent solution resistance, constant phase angle element and faraday impedance, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were conducted in 1 M NaSO₄ solution by a CHI 760E electrochemical workstation as shown in Fig. S7. In order to accurately calculate the faraday impedance (R_{ct}), the semicircles of Nyquist plots have been fitted using the ZView software (Fig. S7a) with corresponding equivalent circuit diagram (Fig. S7b) sketched. As shown in Fig. S7a, along with the increasing amount of Au, the arc radius of Au_x/ZnO (x= 0, 0.08, 0.15, 0.30, 0.75, 1.57 and 1.79 wt%) decreases continuously, indicating the enhanced conductivity. Besides, through the equivalent circuit simulations, the R_{ct} values of ZnO, Au_{0.08}/ZnO, Au_{0.15}/ZnO, Au_{0.30}/ZnO, Au_{0.75}/ZnO, Au_{1.57}/ZnO and Au_{1.79}/ZnO are demonstrated to be 14.0, 10.9, 9.8, 8.9, 8.0, 7.2 and 7.0 k Ω , respectively. Compared to pristine ZnO, the smaller R_{ct} value of Au loaded ZnO represents the faster electronic transmission characteristic, which is benefit for the separation of photo-generated carriers.



Fig. S8 ¹H NMR of CH₄ oxidation product over $Au_{0.75}/ZnO$. DMSO was added as internal standard in NMR test. ¹H NMR peak of CH₃OH is 3.28 ppm.

Only CH₃OH as product has been observed in photocatalytic CH₄ oxidation of Au_{0.75}/ZnO from ¹H NMR spectrum. The chemical shift at 3.28 ppm is ¹H NMR characteristic peak of CH₃OH, no CH₃OOH peak (3.78 ppm) is observed.



Fig. S9 Fluorescence spectra of 1 mM coumarin solution over $Au_{0.75}/ZnO$ and $Au_{0.30}/ZnO$ with the incorporation of 5 bar O₂. The fluorescence peaks are located at 456.6 nm under 332 nm excitation.



Fig. S10 GC spectra of CO₂ produced over (a) ZnO, (b) Au_{0.08}/ZnO, (c) Au_{0.15}/ZnO, (d) Au_{0.30}/ZnO, (e) Au_{0.75}/ZnO, (f) Au_{1.57}/ZnO and (g) Au_{1.79}/ZnO in photocatalytic CH₄ conversion.



Fig. S11 (a) EIS plots of $Au_{0.75}/ZnO$ before and after 500 °C calcination, which have been measured at 10 mV (vs. Ag/AgCl) in 1 M Na₂SO₄ solution under dark conditions. The semicircles of Nyquist plots have been fitted to demonstrate the accurate R_{ct} values with (b) corresponding equivalent circuit diagram. R_s, CPE and R_{ct} represent solution resistance, constant phase angle element and faraday impedance, respectively.



Fig. S12 XPS spectra of Au 4f and Zn 3p from the surface of Au_{0.75}/ZnO before and after 500 °C calcination.



Fig. S13 (a) No liquid product has been found in ¹H NMR spectrum taking Au as photocatalyst. DMSO was added as internal standard in NMR test. (b) GC spectrum of the gas phase product taking Au as photocatalyst, and only $0.2 \ \mu mol \ g^{-1}$ of CO₂ has been observed.

For photocatalytic CH_4 oxidation, 10 mg of Au sample was suspended in 10 mL deionized water under stirring. The reactor was sealed and purged with a CH_4/O_2 mixing gas with 15 and 5 bar, respectively. During the light irradiation (2h), the reaction temperature was maintained at 30 °C using a cooling water bath. After photocatalytic CH_4 reaction, the liquid and gas products were collected and tested by NMR and GC spectra, respectively. No liquid product and only 0.2 µmol g⁻¹ of CO_2 have been found as shown in Fig. S13a, b.



Fig. S14 (a) Mott-Schottky curves of ZnO under frequencies of 800 and 1000 Hz. (b) UV-Vis diffuse reflectance spectrum of pristine ZnO with (c) the transformed Kubelka-Munk plot, respectively.

The band structure of ZnO has been accurately explore through Mott-Schottky plots (Fig.S14a), UV-Vis diffuse reflectance spectra (Fig.S14b) and transformed Kubelka-Munk function plots (Fig.S14c). Bandgap value of ZnO is calculated to be 3.21 V vs. NHE via Kubelka-Munk function plot in Fig. S14c, which transformed from the UV-Vis absorption spectra in Fig. S14b. Flat conduction band potential of ZnO is revealed to be -0.10 eV vs. NHE through Mott-Schottky plots at frequencies 800 Hz and 1000 Hz in Fig. S14a. Then, deriving from the values between flat conduction band and bandgap, the valence band potential of ZnO is calculated be to 3.11 V vs. NHE.



Fig. S15 (a) Time-resolved PL spectra for fresh ZnO and $Au_{0.75}/ZnO$ nanocrystals under 344 nm excitation.

Comparing to ZnO (109.9 ns), the descent of emission lifetime of $Au_{0.75}/ZnO$ (61.4 ns) is attributed to the decreased conduction electrons within ZnO, which has been transferred into adjacent Au.











Fig. S18 (a) ESR spectrum of $Au_{0.75}/ZnO$ with O₂ dissolved in methanol. DMPO has been added in solution as the radical trapping agent of 'OOH. (b) Fluorescence spectra of 1 mM coumarin solution over $Au_{0.75}/ZnO$ with or without O₂ incorporation. The fluorescence peaks are located at 456.6 nm under 332 nm excitation.

Different from the reported work that O2 was the only O-source of CH3OH, we find that H2O has provided more O-atoms than O2 for the formation of CH3OH. We think that the light source, including wavelength and light intensity, as well as the loading amount of Au should bear the most responsibility for the mechanistic differences. In our work, due to the lower energy input of light source (full light spectrum, 100 mW cm⁻², Fig. S6) than the previous report (UV irradiation, 100 mW cm⁻²)¹, O_2 can be more readily reduced to 'OH (0.695 V vs. NHE) rather than 'OOH (-0.046 V vs. NHE), as no 'OOH is observed in the ESR spectrum (Fig. S18a). Therefore, O₂ cannot engage in the formation of CH_3OH through the 'OOH path, which reduces the chance of O_2 as the O-source of CH_3OH . As mentioned above, OH plays two roles in the oxidation of CH_4 , one is to active CH_4 into 'CH₃ (step 2, Fig. 3), other is combined with 'CH₃ to form CH₃OH (step 3, Fig. 3). And the 'OH can be produced through both H₂O oxidation and O₂ reduction. Thus, the separate contributions of 'OH generation, from H₂O oxidation or O₂ reduction, have been investigated by fluorescence spectra of coumarin solution with and without O2 (Fig. S18b). From the peak intensity analysis of fluorescence spectra, we can find that O_2 offers less than 17.4 % enhancement in the formation of 'OH. This is because the consumption of electrons can accelerate the generation of holes to oxidize H₂O into OH. Thus, more than 82.6 % of OH is generated by H₂O oxidation. Therefore, the Oatom of CH₃OH mainly comes from H₂O as shown in the results of GC-MS (Fig. 6a). Since no CH_3OOH is observed in the products of $Au_{0.75}/ZnO$, we can deduce that little O_2 has engaged in the generation of CH₃OH through step 4. But step 4 is fitting for the generation of CH₃OH when the loading amount of Au less than 0.75 wt%.

		produ	ctivity (µmol	g-1)	CH ₃ OH	CH3OH	
entry	photocatalyst	CH ₃ OH	СН3ОН СН3ООН		selectivity in liquid products (%)	selectivity in all products (%)	
1	ZnO	178	135	0.5	56.9	56.8	
2	Au _{0.08} /ZnO	343	297	0.8	53.6	53.5	
3	Au _{0.15} /ZnO	951	1082	11.7	46.8	46.5	
4	Au _{0.30} /ZnO	1996	407	12.2	83.1	82.7	
5	Au _{0.75} /ZnO	1371	0	12.3	100	99.1	
6	Au _{1.57} /ZnO	1197	0	13.2	100	98.9	
7	Au _{1.79} /ZnO	1173	0	14.7	100	98.8	

Table S1. Comparisons of photocatalytic activities of ZnO and Au_x/ZnO (x= 0.08, 0.15, 0.30, 0.75, 1.57 and 1.79) for CH₄ conversion.

Reaction conditions: 10 mg catalyst, 10 mL H₂O, 5 bar O₂ and 15 bar CH₄, 30 °C reaction temperature, 2 h reaction time, light source: Xenon full light irradiation, light intensity 100 mW cm⁻². CH₃OH selectivity in liquid products (%) = productivity of CH₃OH × 100 / (productivity of CH₃OOH + productivity of CH₃OH). CH₃OH selectivity in all products (%) = productivity of CH₃OH × 100 / (productivity of CH₃OH) × 100 / (productivity of CH₃OH).

		reaction condition		CH3OH productivity (µmol g ⁻¹)	STY of CH ₃ OH (μmol g ⁻¹ h ⁻¹)	CH ₃ OH selectivity (%)	ref.
catalyst	reactants	T (°C)	light				
Au _{0.75} /ZnO	$P_{CH_4} = 15$ bar; $P_{O_2} = 5$ bar; Cat.: 10 mg	30	300 nm < λ < 1200 nm; light intensity 100 mW cm ⁻²	1371	685.5	99.1	My work
0.1 wt % Au/ZnO	$P_{CH_4} = 20$ bar; $P_{O_2} = 1$ bar; Cat.: 10 mg	25 ± 2	$300 \text{ nm} < \lambda < 500 \text{ nm}; \text{ light}$ intensity 100 mW cm ⁻²	4120	2060	15.7	J. Am. Chem. Soc. 2019, 141 , 20507- 20515
Cu-0.5/ PCN	$P_{CH_4} = 1$ bar; Cat.: 20 mg	room temperature	visible light	24.5	24.5	18.8	Nat. Commun. 2019, 10 , 506
0.33 metal wt.% FeO _x / TiO ₂	$P_{CH_4} = 1$ bar; $V_{H_2O_2} = 4$ mL; Cat.: 10 mg	25	$300 \text{ nm} < \lambda < 710 \text{ nm}$	1056	352	90	Nat. Catal. 2018, 1 , 889–896
WO ₃ /La	$P_{CH_4} = 1$ bar; Cat.: 0.3 g	55	medium-pressure Hg lamp	~ 64.7	~32.3	~47.1	Appl. Catal. B- Environ. 2016, 187 , 30-36
Ag–ZnO	78.9% N ₂ , 21.1% O ₂ and 100 p.p.m. CH ₄ ; <i>Cat</i> .: 0.5 g	0 or 80	300 nm < λ < 1200 nm; light intensity 200 mW cm ⁻²	none	none	none	Nat. Commun. 2016, 7, 12273- 12280

Table S2. The comparisons of CH₃OH selectivities over Au_{0.75}/ZnO with other reported photocatalysts.

STY: a space-time yield is a vital benchmark for CH_3OH yield assessment taken reaction time into consideration. Though lower productivity of CH_3OH is obtained in our work compared to that of *J. Am. Chem. Soc.* 2019, **141**, 20507-20515, the selectivity is highest with 99.11 %, and the reaction conditions are much milder with low CH_4 pressure and applicable light irradiation range.

References

1. H. Song, X. Meng, S. Wang, W. Zhou, X. Wang, T. Kako and J. Ye, *J. Am. Chem. Soc.*, 2019, **141**, 20507-20515.