Supplementary Materials

A new approach for methane oxidation: photocatalytic ozonation over noble metal decorated zinc oxide nanocatalysts

Haiyuan Zhang[1], Yun Wang[1], Jiahua Zhu[1], Xiaohua Lu[1], Yang Bai[2], Wei Li[2,*], Liwen Mu[1,*]

[1]State Key Laboratory of Materials-oriented Chemical Engineering College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, Jiangsu, China.
[2]Institute for Materials and Processes School of Engineering, The University of Edinburgh, Edinburgh EH9 3FB, Scotland, UK.

[*]**Correspondence to:** Prof. Liwen Mu, State Key Laboratory of Materials-oriented Chemical Engineering College of Chemical Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing 210009, Jiangsu, China. E-mail: lwmu@njtech.edu.cn; Prof. Wei Li, Institute for Materials and Processes, School of Engineering, The University of Edinburgh, Robert Stevenson Road, Edinburgh EH9 3FB, Scotland, UK. E-mail: wei.li@ed.ac.uk

Iodometric determination of ozone concentration

Potassium iodide solution (20%): 20 g of potassium iodide was dissolved in 100 mL of boiling, cooled distilled water and stored in a brown bottle in the refrigerator for at least one day before use. (1 + 5) Sulfuric acid solution: Concentrated sulfuric acid was measured in 5 times the volume of distilled water. 0.01 $mol \cdot L^{-1}$ sodium thiosulfate standard solution: 0.24817 g of sodium thiosulfate was weight and dissolved in 100 mL of distilled water cooled after boiling in the brown bottle of volumetric flask. Starch solution: 1 g of soluble starch was mixed into suspension with cold water, boiling distilled water was added while stirring, diluted to 100 mL, boiled again for 2 min, then left to settle overnight and the supernatant was taken for use.

Measured 20 mL of potassium iodide solution, poured into a stoppered triangular flask, after the ozone generator had been running stably, took a sample at the outlet of gas chromatography, when the gas had passed through the amount of a certain value, stopped taking samples and immediately added 5 mL of (1 + 5) sulfuric acid solution, mixed and left it to stand for 5 min away from light. Titrated with 0.01 $mol \cdot L^{-1}$ sodium thiosulfate standard solution, added 1 mL of starch solution when it was light yellow. Continued to titrate carefully and rapidly until the color disappears. Recorded the amount of sodium thiosulfate standard solution.

The proportionality between O_3 and $Na_2S_2O_3$ was established by the two reaction equations：

$$O_3 + 2\ KI + H_2O \rightarrow O_2 + I_2 + 2\ KOH \quad (1)$$

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6 \quad (2)$$

The ozone concentration was calculated as follows:

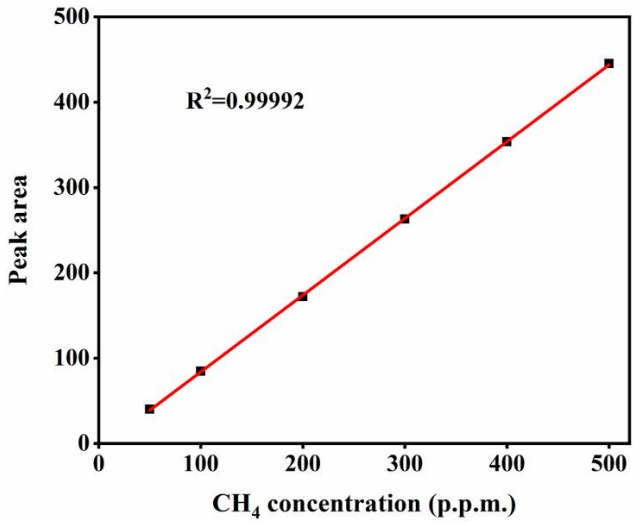
$$C_{O_3} = V_{Na} \times C_{Na} \times \frac{24000}{V_{O_3}} (mg / L) \quad (3)$$

C_{O3} - Concentration of ozone, $mg \cdot L^{-1}$,

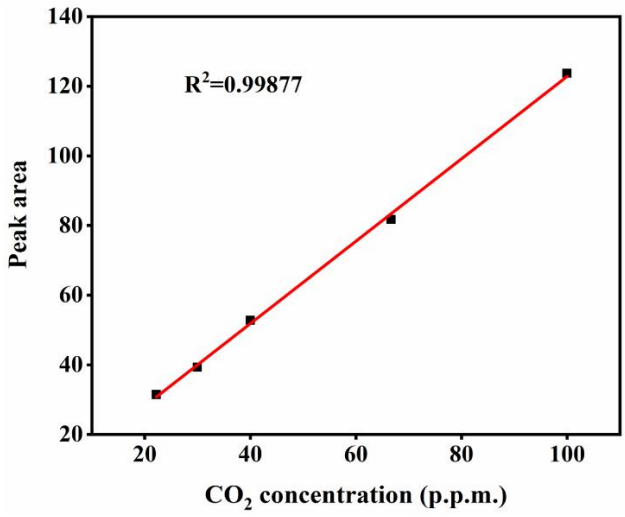
V_{Na} - Amount of sodium thiosulfate standard solution, mL,

C_{Na} - Concentration of sodium thiosulfate standard solution, $mol \cdot L^{-1}$,

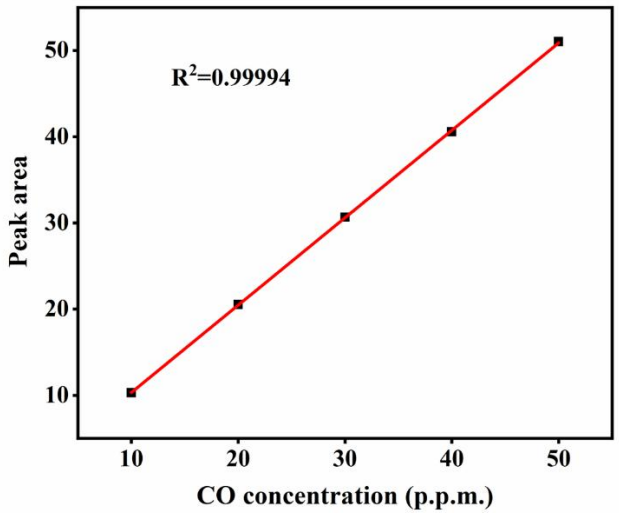
V_{O3}- Gas sampling volume, mL.



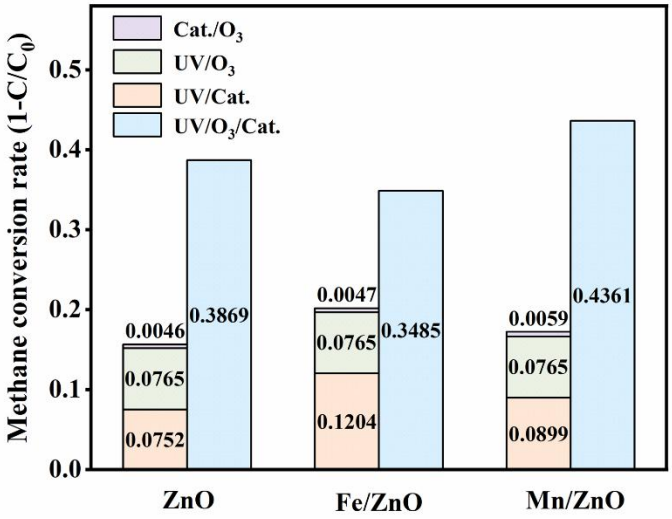
Supplementary Figure 1. Calibration curve for the quantification of CH_4 by external reference method.



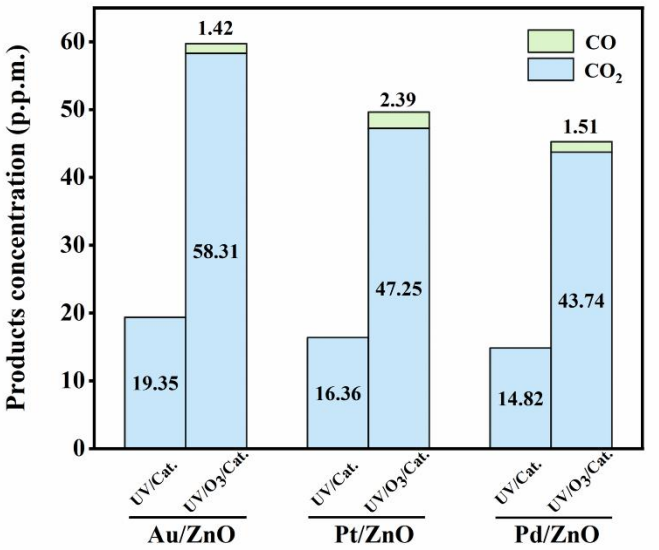
Supplementary Figure 2. Calibration curve for the quantification of CO_2 by external reference method.



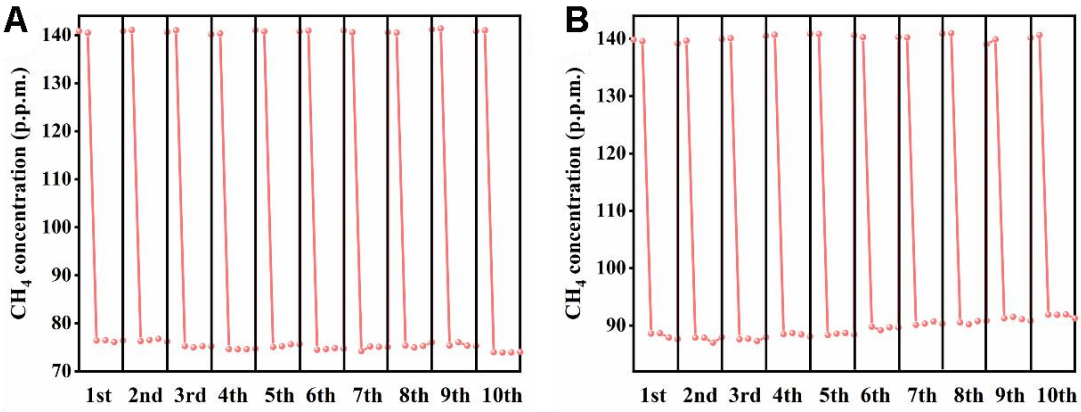
Supplementary Figure 3. Calibration curve for the quantification of CO by external reference method.



Supplementary Figure 4. Methane conversion of different catalysts under different oxidation processes. (Reaction condition: 0.5 g photocatalyst, reaction temperature of 25± 2°C, light intensity: 16 W 254 nm UV*2, gas flow rate: 200 mL·min^{-1}, ozone concentration: 0, 300 ppm).



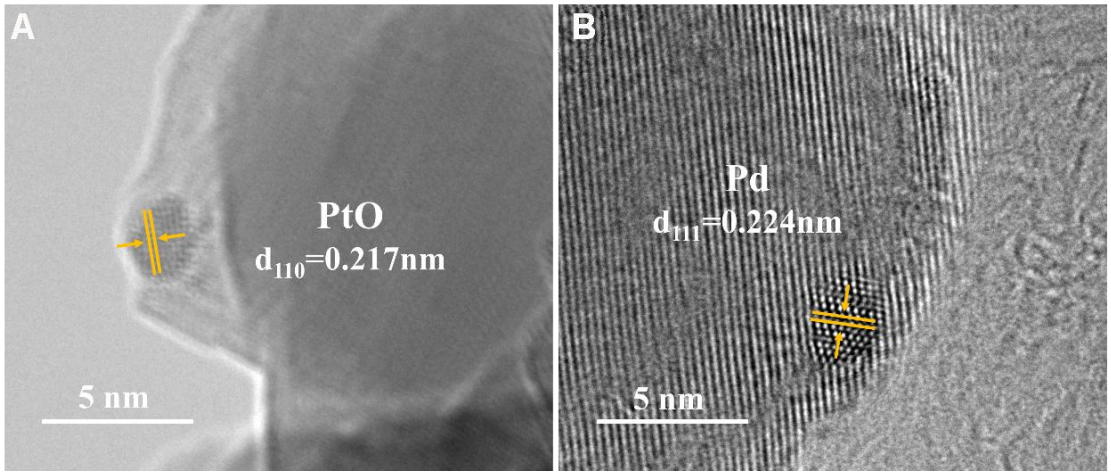
Supplementary Figure 5. Photocatalysis and photocatalytic ozonation product concentration of noble metal modified ZnO (Reaction condition: 0.5 g photocatalyst, reaction temperature of 25± 2°C, light intensity: 16 W 254 nm UV*2, gas flow rate: 200 mL·min^{-1}, ozone concentration: 0, 300 ppm).



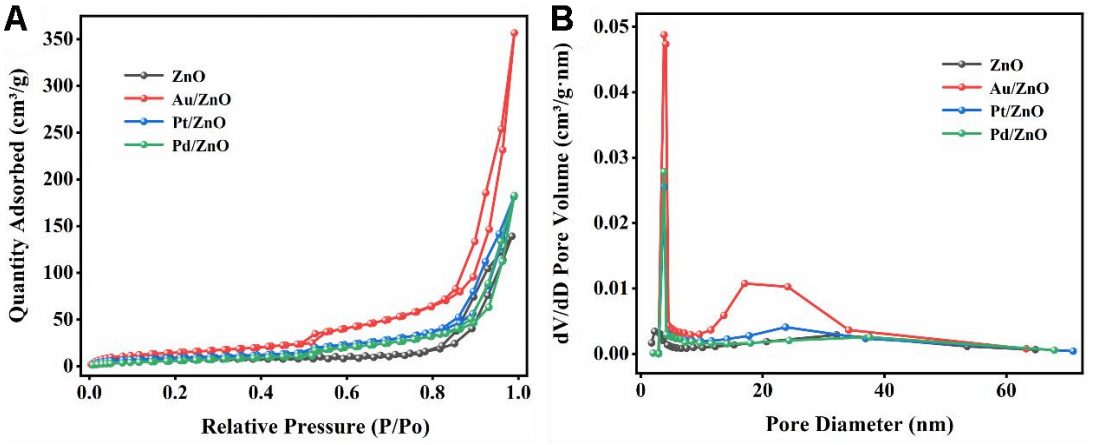
Supplementary Figure 6. Cyclic tests of photocatalytic ozonation over the (A) Pt/ZnO, (B) Pd/ZnO (Reaction condition: 0.5 g photocatalyst, reaction temperature of 25± 2°C, light intensity: 16 W 254 nm UV*2, gas flow rate: 200 mL·min^{-1}, ozone concentration: 300 ppm, One cycle: 4 h; ten cycles: 40 h).

Supplementary Table 1. Ozone concentration before and after photocatalytic ozonation (calculated by the iodometric method)

	Before / p.p.m.	After - 5 min / p.p.m.	After - 30 min / p.p.m.
Au/ZnO	297.012	72.852	72.852
Pt/ZnO	302.616	78.456	78.456
Pd/ZnO	297.012	72.852	72.852



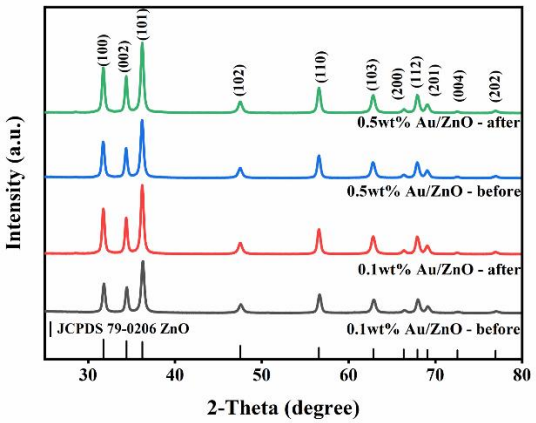
Supplementary Figure 7. HR-TEM images of (A) 0.1 wt% Pt/ZnO; (B) 0.1 wt% Pd/ZnO.



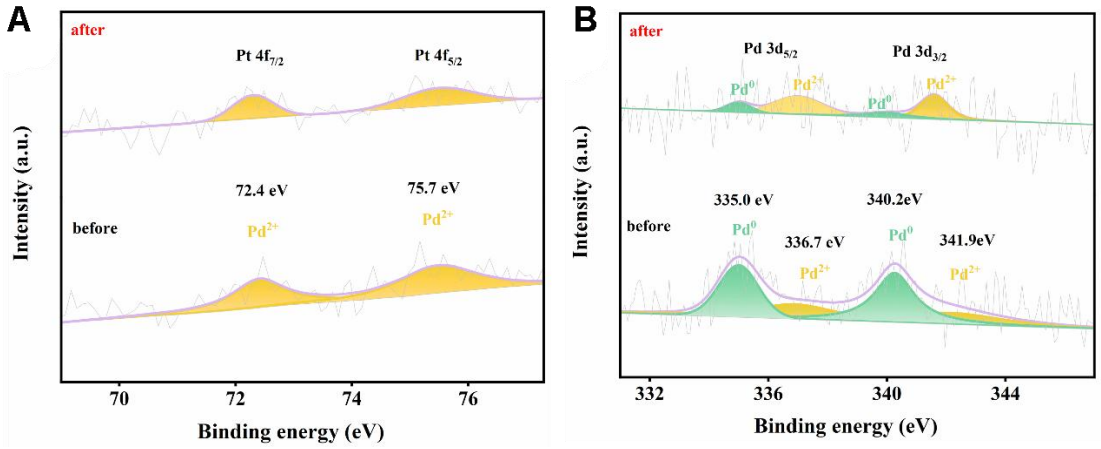
Supplementary Figure 8. (A) Argon adsorption-desorption isotherms (Test temperature: 77.4 K); (B) Pore size distribution profiles of ZnO and its composite catalysts.

Supplementary Table 2. BET surface area of ZnO and its composite catalysts.

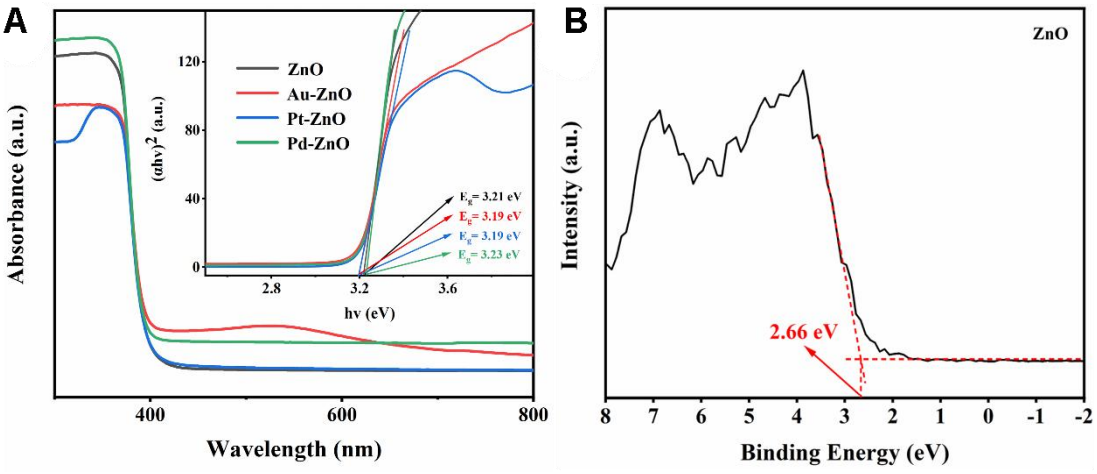
	Surface Area $m^2\ g^{-1}$	Pore Volume $cm^3\ g^{-1}$	Pore Size nm
ZnO	27.5315	0.178759	21.1255
0.1 wt% Au/ZnO	48.3863	0.433399	22.1956
0.1 wt% Pt/ZnO	29.2644	0.219577	20.2269
0.1 wt% Pd/ZnO	23.2760	0.223614	22.2027



Supplementary Figure 9. PXRD patterns of 0.1 wt%, 0.5 wt% Au/ZnO before and after photocatalytic ozonation reactions.



Supplementary Figure 10. XPS spectrum of (A) Pt 4f; (B) Pd 3d.



Supplementary Figure 11. (A) Ultraviolet-visible diffusive reflectance spectra, Tauc plots of the samples; (B) XPS-VB spectrum for ZnO.