

## Electronic Supplementary Information

# Geometric Effect of ZnO Supported Au Nanoclusters on Room Temperature CO Oxidation

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## 1 Synthesis of materials

### 1.1 Materials and reagents

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , reagent grade 98%, Sigma-Aldrich), sodium citrate tribasic dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , minimum 98%, Sigma-Aldrich), Hexamethylenetetramine (HMTA, ACS reagent  $\geq 99\%$ , Sigma-Aldrich), isopropanol (anhydrous 99.5%, Sigma-Aldrich), gold(III) chloride hydrate (99.999% trace metal basis, Sigma-Aldrich) were purchased from the corresponding vendors and used without further purification.

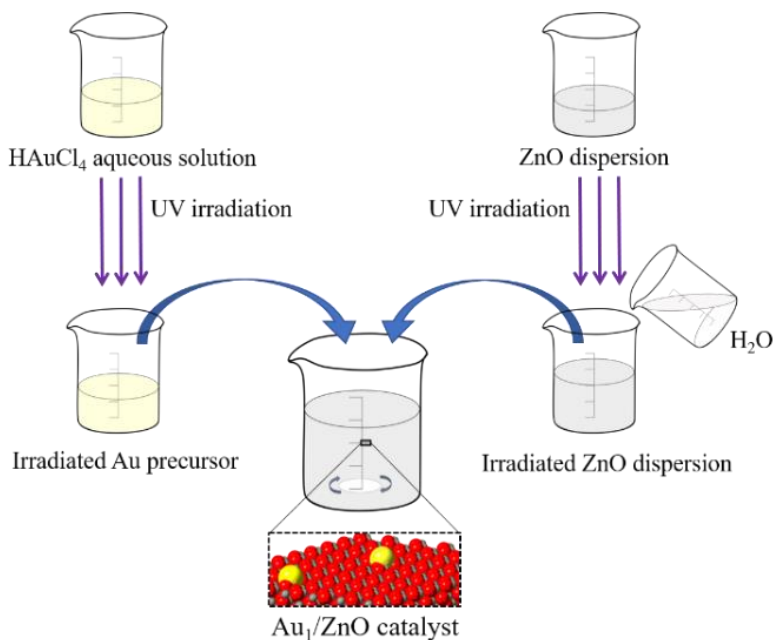
### 1.2 Synthesis of flowerlike ZnO

The flowerlike ZnO precursor was prepared by a modified hydrothermal method<sup>1</sup>. Briefly, 22.3 mg  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 8.8 mg sodium citrate and 21.0 mg HMTA were dissolved into 30 mL deionized water and stirred at room temperature for 1 hour. The resulting transparent solution was transferred to a Teflon-lined stainless-steel autoclave and hydrothermally treated at 95°C and kept at 95°C for 3 hours. After cooling down to room temperature naturally, the white color powder precipitates were collected after filtration, washing with deionized water and drying at 60°C for 12 hours. The as-prepared ZnO powders were rapidly calcined at 400°C for 15 min to make the final ZnO support.

### 1.3 Synthesis of ZnO supported Au single atom ( $\text{Au}_1/\text{ZnO}$ ) catalyst

The  $\text{Au}_1/\text{ZnO}$  catalyst was prepared by a UV-assisted photochemical method as illustrated in Scheme S1. It should be noted that Au is very sensitive to light and all the synthesis processes should be conducted in dark environment except for the UV treatment processes. In a typical synthesis, 100 mg ZnO support was dispersed by 5 ml isopropanol in a 25 ml beaker by ultrasonication, then the dispersion was irradiated under a UV light (wavelength of 365 nm power density of 40 mW/cm<sup>2</sup>) for 2 hours. The final dispersion was diluted by adding 15 ml H<sub>2</sub>O. Then

an appropriate amount of  $\text{HAuCl}_4$  aqueous solution (0.5 mmol/L) was subjected to the UV treatment described above for 15 minutes. Low concentrations of  $\text{HAuCl}_4$  was used to ensure the presence of only isolated single Au atoms on the ZnO support. The two solutions were immediately mixed together by simultaneous addition of the two separate aqueous solutions into 10 ml  $\text{H}_2\text{O}$  under vigorous stirring. After another 5 minutes of stirring, the light grey product was separated via centrifugation and further washed by DI water for 3 times, respectively. After being dried at  $60^\circ\text{C}$  in an oven for 12 hours, the product was ready for catalytic tests and characterizations. The Au loading level can be tuned by using different amounts of the  $\text{HAuCl}_4$  solution.



**Scheme S1.** Schematic diagrams illustrate the synthesis processes of  $\text{Au}_1/\text{ZnO}$  single-atom catalysts.

## 2 Materials characterization

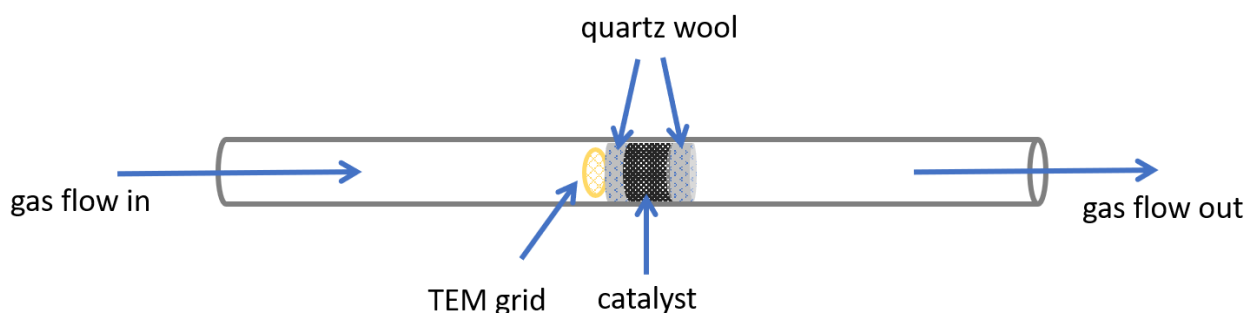
### 2.1 General instruments and characterization techniques

High resolution field-emission scanning electron microscope (SEM) was used to examine the morphology of the as-synthesized ZnO. Aberration-corrected scanning transmission electron microscopy (ac-STEM) techniques, extremely useful in characterizing atomic structures of nanoscale materials especially supported metal clusters and atoms<sup>2, 3</sup>, were used to examine different Au species. The JEM-ARM200F TEM/STEM with a guaranteed resolution of 0.08 nm was used in this work. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 focus diffraction spectrometer using  $\text{Cu K}\alpha$  radiation (1.54056 Å). The operation voltage and current were 40 kV and 40 mA, respectively. The diffraction data was collected with a 2theta range from  $10^\circ$  to  $80^\circ$  with a scan rate of  $6 \text{ degrees min}^{-1}$ . The loading of Au was determined by inductively coupled plasma atomic emission spectroscopy method (ICP-AES,

Agilent). The X-ray photoelectron spectroscopy (XPS) data was collected on Thermo Fisher Scientific ESCALAB 250Xi, using a monochromated Al K $\alpha$  X-ray source. The XPS spectra of the selected elements were measured with a constant analyzer-pass energy of 30.0 eV. All binding energies (BEs) were calibrated by the C 1s peak (284.8 eV). Samples after CO oxidation for 0, 4, 8, and 60 min were kept in helium and characterized soon after the reaction test. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of CO adsorption was carried out on a Nicolet Nexus 6700 spectrometer equipped with a mercury cadmium telluride (MCT) detector. The DRIFTS reaction chamber (Harrick) with a heating component allows samples to be temperature programmed and heated. For each IR measurement, about 30 mg Au<sub>1</sub>/ZnO catalyst was pretreated at 60°C in 30 ml·min<sup>-1</sup> Ar for 30 minutes. Then a mixed gas of 1 vol.% CO, 4 vol.% O<sub>2</sub> and Ar balance, similar to that used for catalytic test, was introduced for 4, 8, 30 and 60 minutes, respectively, followed by pure Ar purging for 5 minutes to purge the residual gaseous CO and CO<sub>2</sub> from the sample chamber. CO-DRIFTS spectra were collected in Kubelka-Munk unit with a resolution of 4 cm<sup>-1</sup> and 64 scans.

## 2.2 Preparation of STEM samples

Dispersion of used catalysts in solvent (ethanol or water, etc.) for electron microscopy sampling may bring about changes to these samples. To minimize the influence of this factor, we used the gas-flow reaction setup as illustrated in Scheme S2 to investigate the structure of the used catalysts after CO oxidation for different time intervals. As-prepared Au<sub>1</sub>/ZnO single-atom catalyst was ultrasonically dispersed in water and then a drop of the solution was put onto a lacey carbon coated Cu TEM grid. Then the TEM grid was put into the reactor tube close to the catalyst bed or embedded into the catalyst bed.



**Scheme S2.** Schematic diagram illustrates the gas-flow reaction setup for preparing the relevant TEM samples for STEM examination.

To assure that the sample handling processes do not change the integrity of the catalyst structure we investigated the storage stability of the as-prepared Au<sub>1</sub>/ZnO SACs and confirmed that the as-prepared Au<sub>1</sub>/ZnO SACs were stable for at least 3 days under ambient condition. All the catalytic tests and characterizations were conducted within three days after the Au<sub>1</sub>/ZnO SACs

were synthesized. We also tested the integrity of the Au/ZnO catalysts in the reactor with flowing He with space velocities similar to those used for CO conversion reaction. All these tests showed that the Au<sub>1</sub>/ZnO SACs maintained their structural integrity, suggesting that the isolated Au single atoms on the ZnO support did not sinter under inert or oxidizing atmosphere at room temperature. After CO oxidation reaction for the designated time, flowing He was used to terminate the CO oxidation reaction and the TEM grid with the catalyst powders was removed and immediately loaded into the aberration-corrected STEM for examination.

### 3 Catalytic measurement

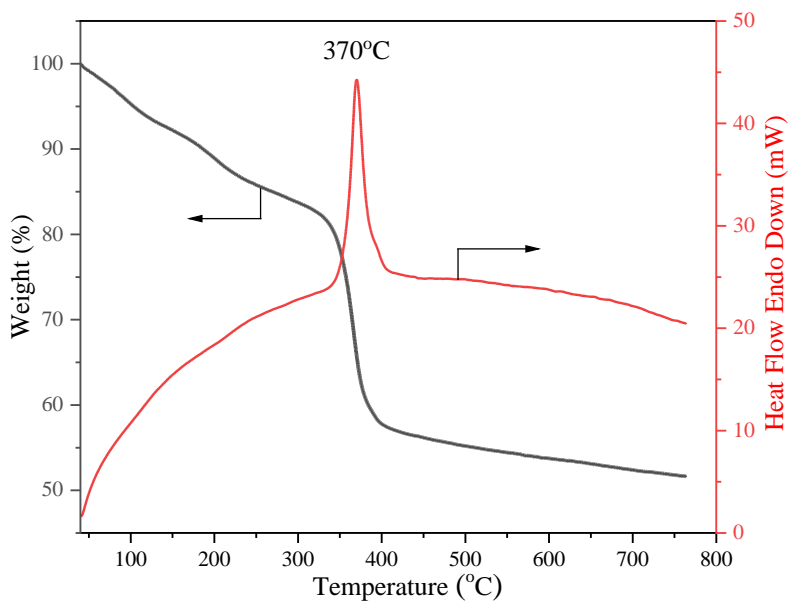
CO oxidation was conducted in a plug flow fixed-bed reactor at atmospheric pressure. Typically, 30 mg catalyst was mixed with 200 mg SiO<sub>2</sub> and then the whole mixture was immobilized by quartz wool in a quartz tube, as indicated in Scheme S2. The catalyst bed temperature was measured by a thermocouple. The feed gas was composed of 1 vol.% CO, 4 vol.% O<sub>2</sub> and He balance. The total gas flow rate was 30 ml·min<sup>-1</sup>, resulting in a space velocity (SV) of 60,000ml·g<sup>-1</sup>·h<sup>-1</sup>.

The conversion of CO was measured by an on-line gas chromatograph (Agilent GC 7890A). The CO conversion ( $X_{CO}$ ) was calculated according to:

$$X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\%$$

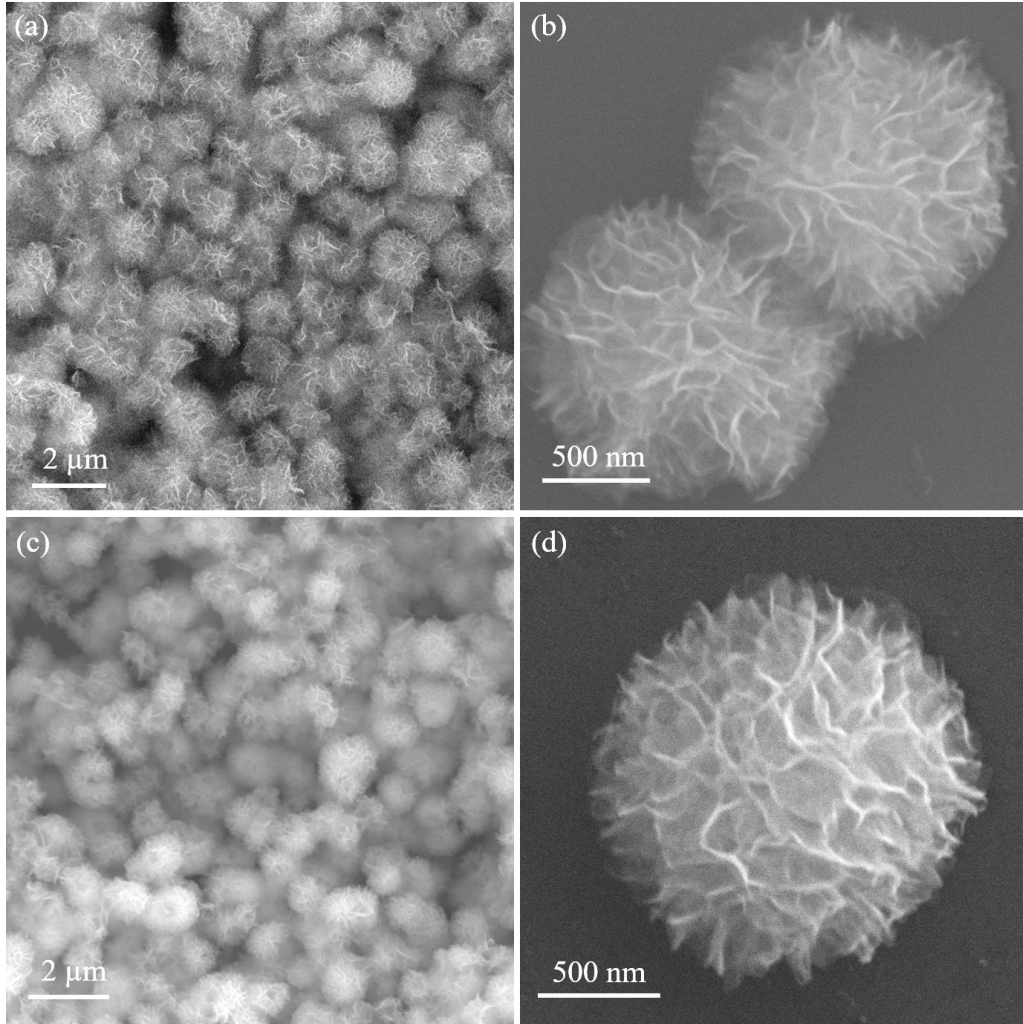
wherein  $[CO]_{in}$  and  $[CO]_{out}$  refer to the concentration of CO in the gas flow before and after the reactant gas mixture goes through the catalyst bed at the targeted reaction temperature, respectively. An on-line mass spectrometer (ICP 400, INFICON, Co.Ltd.) was used to monitor the concentration of CO and CO<sub>2</sub> concentrations.

## Supporting figures

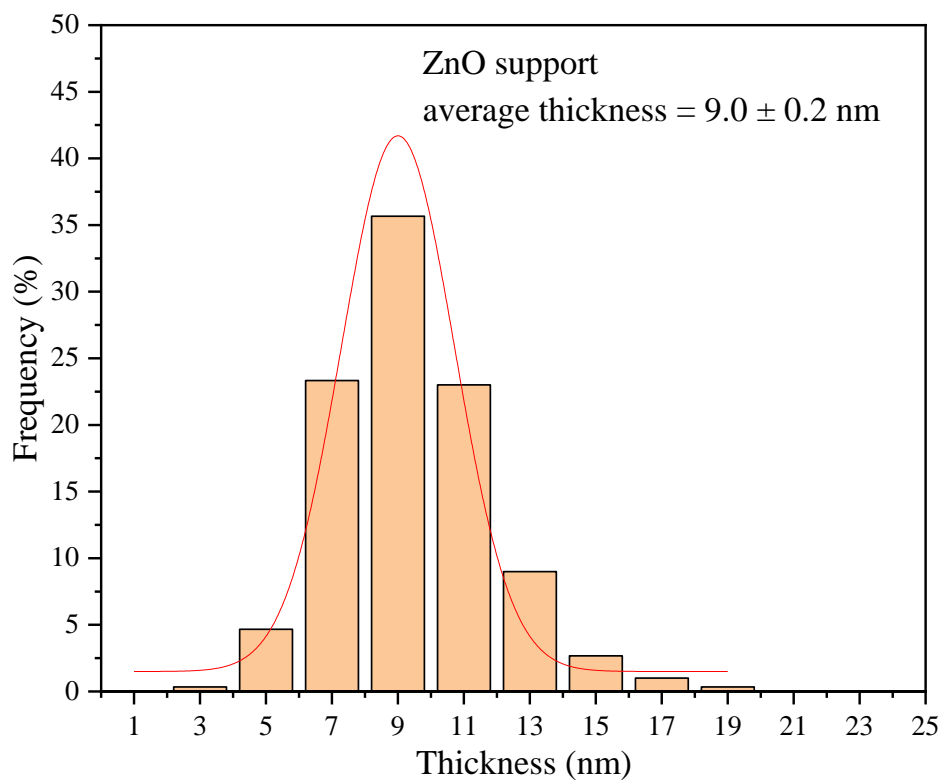


**Fig. S1** Thermogravimetry-Differential Thermal Analysis (TG-DTA) curve of pure ZnO support.

The TG curve showed a weight loss of about 15 wt.% between 40°C to 200°C, due to the release of physically adsorbed water and hydroxyl species. Another dramatic weight loss of about 30% between 200°C to 400°C was attributed to the combustion of organic compounds within the hydrothermally synthesized ZnO. Large amount of heat was released during the combustion process as indicated by the sharp exothermic peak centered at ~370°C in the DTA curve. We selected to calcine our ZnO at 400°C for 15 min in order to eliminate all the organic residues from the as-synthesized ZnO.

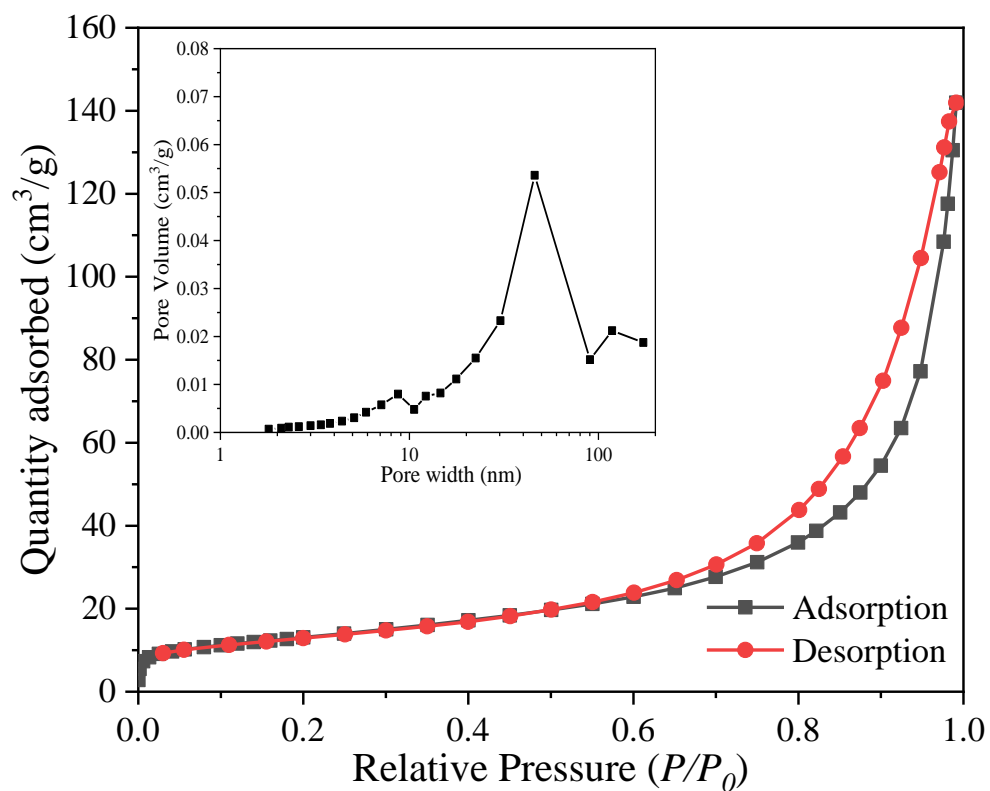


**Fig. S2.** Representative SEM images of flower-like ZnO before (a-b) and after calcination at 400°C for 15 minutes (c-d).



**Fig. S3** Thickness distribution of the 2D ZnO nanosheets.

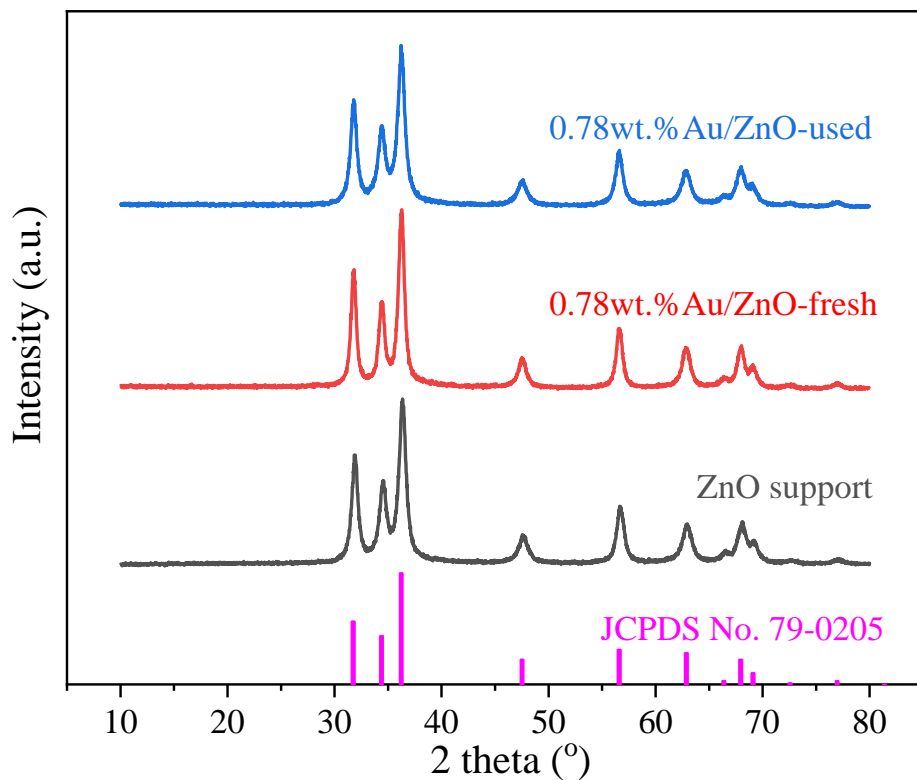
The histogram was obtained by counting more than 300 individual ZnO flakes. The thicknesses of the ZnO support ranges from 3 to 19 nm with an average thickness of 9 nm after the 400°C calcination.



**Fig. S4** N<sub>2</sub> adsorption and desorption isotherms of the 0.78 wt.% Au<sub>1</sub>/ZnO obtained at 77.35 K.

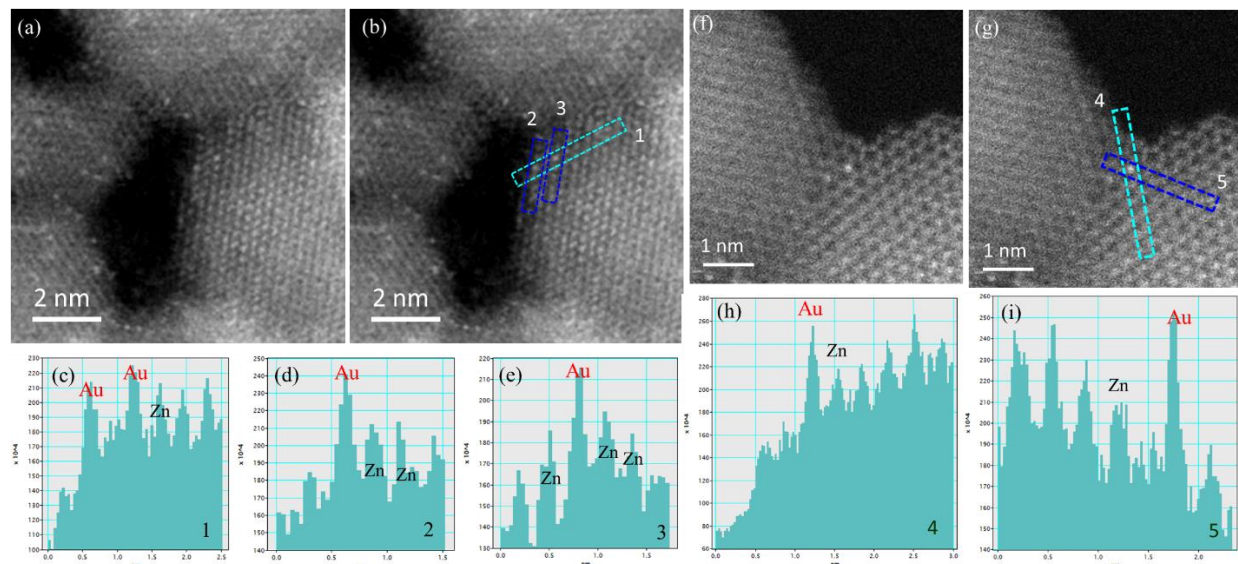
The specific surface area was calculated to be 46.6 m<sup>2</sup>·g<sup>-1</sup> according to the Brunauer-Emmett-Teller (BET) method by the N<sub>2</sub> adsorption isotherm. The pore size distribution (inset) was calculated by using the Barrett-Joyner-Halenda (BJH) formula. Most of the pores are meso-pores with sizes ranging from 5 nm to ~100 nm, consistent with STEM imaging results.





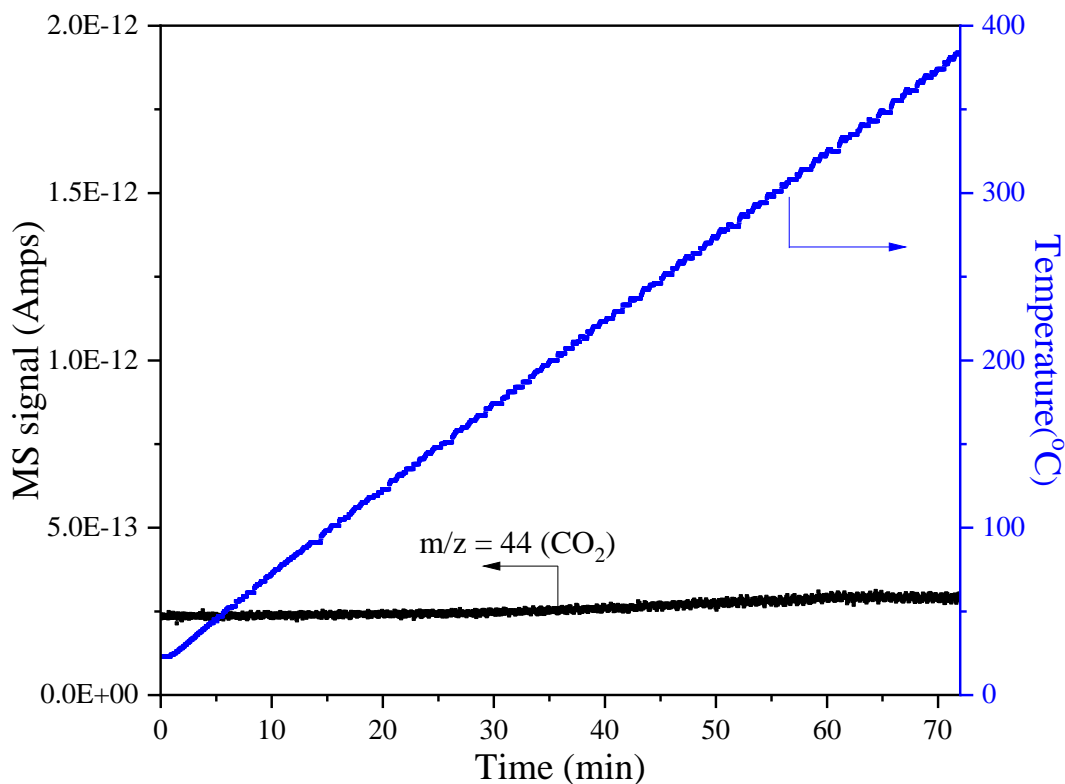
**Fig. S5** Powder XRD patterns of fresh and used Au<sub>1</sub>/ZnO catalyst and the ZnO support.

The XRD pattern of the ZnO support is in good agreement with ZnO JCPDS No. 79-0205. The fresh and used Au<sub>1</sub>/ZnO did not show any Au diffraction peaks because the sizes of the Au species are too small. It should be noted that there was no observable changes in the diffraction patterns which indicate that the crystal structure of the ZnO support was maintained during the CO oxidation reaction.



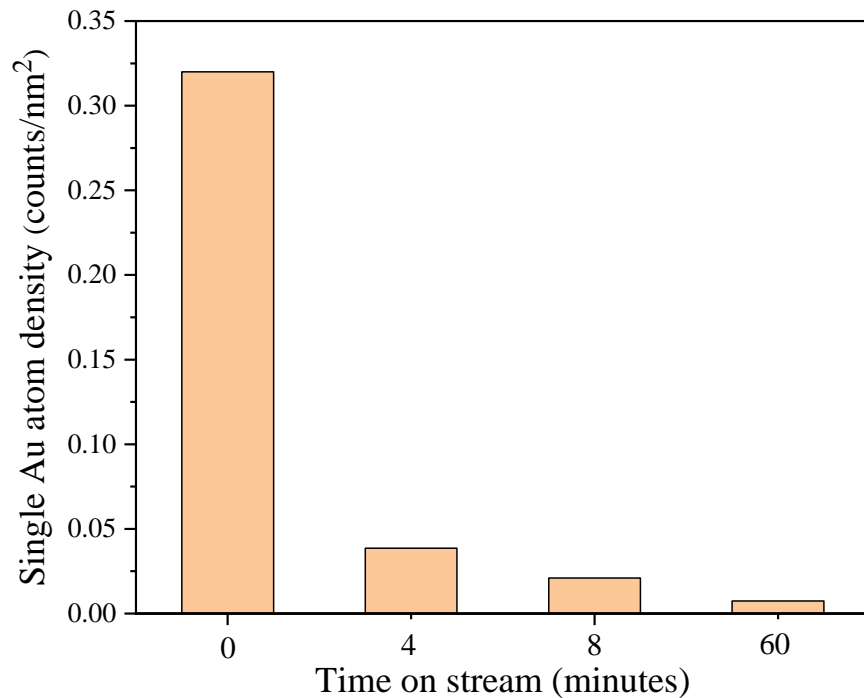
**Fig. S6** Representative STEM images and corresponding intensity profiles of single atom Au on ZnO. (a, b, f, g) HAADF-STEM images of Au<sub>1</sub>/ZnO; (c-e) intensity profiles along the rectangles shown in (b); (h,i) intensity profiles along the rectangles shown in (g).

The above intensity profiles of Au<sub>1</sub>/ZnO clearly show that single Au atoms occupy the positions of the Zn cations. After careful examination of many regions of the as-prepared Au<sub>1</sub>/ZnO samples, we unambiguously confirmed that the isolated Au single atoms primarily occupied the positions of the Zn cations in the ZnO nanoparticles.



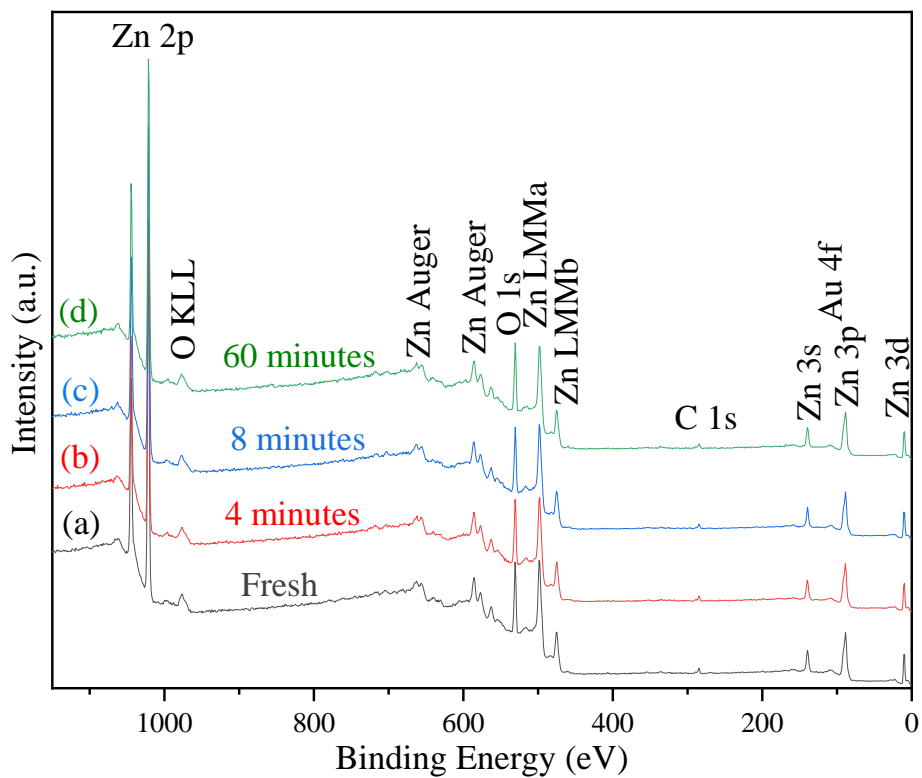
**Fig. S7** Temperature programmed desorption (TPD) of CO<sub>2</sub> after CO oxidation for 60 minutes over the 0.78 wt.% Au<sub>1</sub>/ZnO catalyst.

This experiment was conducted immediately after room temperature CO oxidation. Prior to the TPD experiment the sample was purged with He until the CO<sub>2</sub> signal ( $m/z = 44$ ) falls to the baseline. Then the temperature ramped at a rate of 10°C/min from room temperature to 380°C. The TPD of CO<sub>2</sub> showed that there was little residual CO<sub>2</sub>/carbonates on the catalyst, suggesting that the decrease in activity with time was not caused by accumulation of surface carbonaceous species.



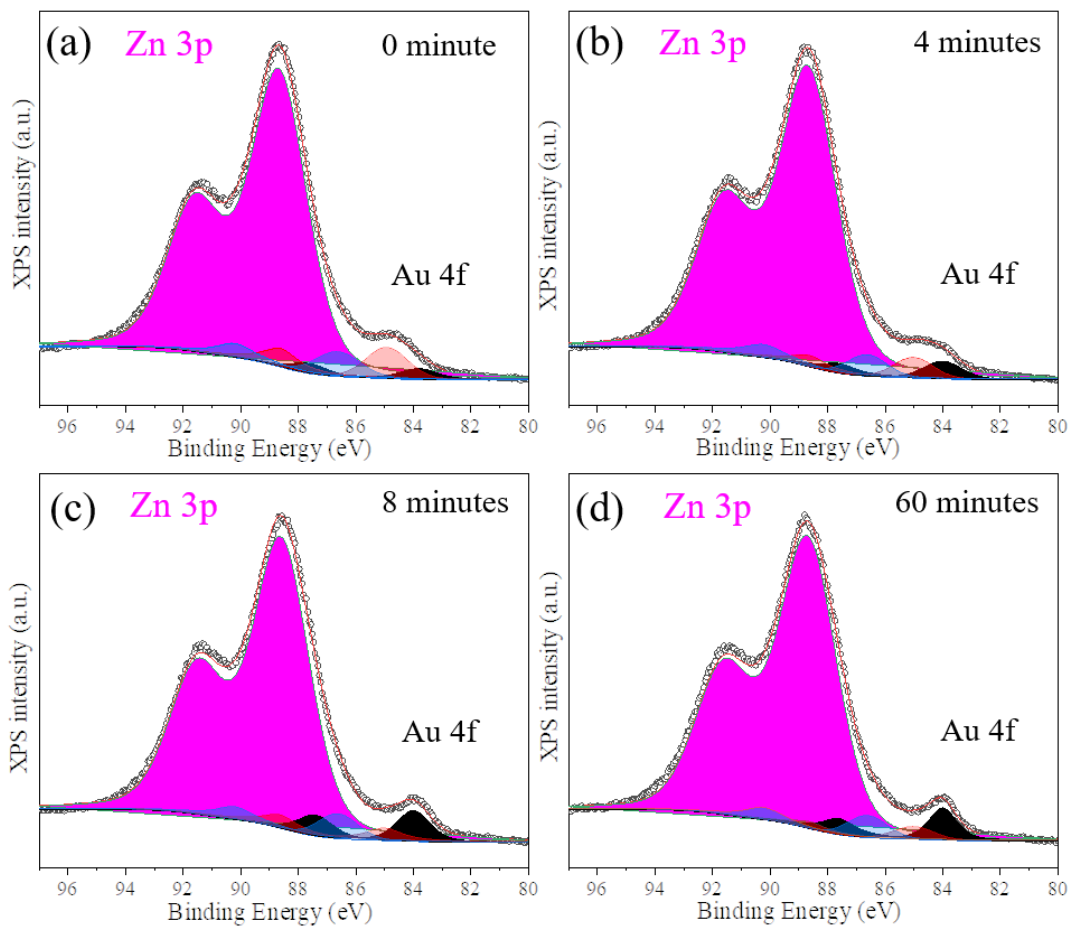
**Fig. S8** Histogram of estimated single Au atom density on ZnO after CO oxidation for 0, 4, 8, and 60 minutes.

After careful examination of many areas of each sample by STEM imaging we can conclude that single Au atoms sintered to form Au clusters during the CO oxidation process. The number density of the single Au atoms decreased rapidly from  $\sim 0.32/\text{nm}^2$  to  $\sim 0.03/\text{nm}^2$  within the first 4 minutes and then further decreased to  $\sim 0.02/\text{nm}^2$  after 8 minutes of CO oxidation. Single Au atoms were barely observable on the ZnO surfaces after 60 minutes of CO oxidation.

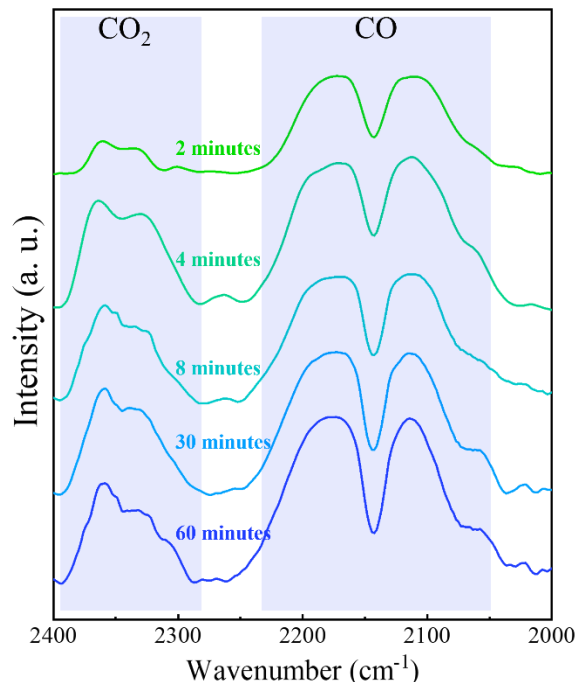


**Fig. S9** XPS scan spectra of the 0.78 wt.% Au/ZnO at different stages: (a) fresh, (b) time on stream for 4 minutes, (c) time on stream for 8 minutes, and (d) time on stream for 60 minutes.

Except the presence of a small amount of C the full XPS spectra showed that the as-prepared and used Au/ZnO samples consisted of Zn, O and Au without the presence of other detectable impurities.

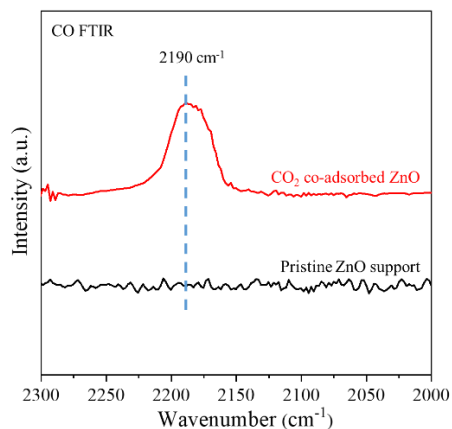


**Fig. S10** XPS spectra of Zn 3p (purple color) and Au 4f obtained from the Au/ZnO samples after CO oxidation for different time intervals: (a) fresh Au<sub>1</sub>/ZnO; (b) 4 minutes; (c) 8 minutes; (d) 60 minutes. The Au 4f peaks partially overlap with the Zn 3p peaks.



**Fig. S11** *In situ* DRIFTS spectra of Au/ZnO catalysts under CO oxidation condition (1 vol.% CO, 4 vol.% O<sub>2</sub>, Ar balance, 30 ml·min<sup>-1</sup>) at room temperature for different time intervals (2, 4, 8, 30 and 60 minutes, respectively).

The bands at 2300 – 2400 cm<sup>-1</sup> are associated with gaseous CO<sub>2</sub>, and the bands at 2050 – 2250 cm<sup>-1</sup> are associated with CO absorption. The CO<sub>2</sub> intensity was very low at 2 minutes into the CO oxidation reaction. It then increased significantly at 4 minutes. The relative peak intensity of CO<sub>2</sub> to CO increased until ~8 minutes then slowly decreased. This *in situ* CO-DRIFTS study verified that the catalytic activity increased dramatically at the early stage and then decreased slowly with prolonged reaction time.



**Fig. S12** FTIR spectroscopy of CO adsorption on pristine ZnO support and CO<sub>2</sub> co-adsorbed ZnO support.

No CO absorption band was observed after Ar purge when CO FTIR was conducted on pure ZnO at room temperature. However, after 300°C Ar treatment of the ZnO and introduction of CO<sub>2</sub> together with CO (mimicking the reaction environment), a broad CO adsorption band centered at 2190 cm<sup>-1</sup> was observed. This band can be assigned to CO and CO<sub>2</sub> co-adsorption on the exposed Zn<sup>2+</sup> sites<sup>5-7</sup>. The broad peak may reflect the structural differences of the various exposed facets of the ZnO support.



## Supporting references

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