

Supporting Information

Elucidation of Active Sites of Gold Nanoparticles on Acidic Ta₂O₅ Supports for CO Oxidation

Mingyue Lin,[†] Chihiro Mochizuki,[†] Baoxiang An,[†] Yusuke Inomata,[†] Tamao Ishida,^{†, ‡} Masatake Haruta,[†] and Toru Murayama^{*, †, #}

[†]Research Center for Gold Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

[‡]Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

[#]Yantai Key Laboratory of Gold Catalysis and Engineering, Shandong Applied Research Center of Gold Nanotechnology, School of Chemistry & Chemical Engineering, Yantai University, Yantai 264005, China

Corresponding Author

*murayama@tmu.ac.jp

1. EXPERIMENTAL SECTION

1.1 Materials. $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was purchased from Mitsuwa Chemical (Lot No. 59678). Tetraoctylammonium bromide, 1-dodecanethiol, sodium borohydride (NaBH_4), toluene, and hexane were obtained from FUJIFILM Wako Pure Chemical Corporation. Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Tanaka Kikinzoku Kogyo. All chemicals were used as received without further purification.

1.2 Catalyst Preparation. Ta_2O_5 was prepared by hydrothermal synthesis¹ from $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. The Ta precursor (3 mmol based on Ta) was added to 45 mL water and dispersed by ultrasonication for 15 min. Then the mixture was sealed in a 60 mL autoclave and put into an oven at 175°C for 72 h. The obtained mixture was thoroughly washed with deionized water and dried at 80°C overnight. The sample was calcined at 400°C and 650°C (10°C min⁻¹) for 4 h before being used as P- Ta_2O_5 (pyrochlore) and TT- Ta_2O_5 (pseudo-hexagonal), respectively. T- Ta_2O_5 (orthorhombic) was obtained from FUJIFILM Wako Pure Chemical Corporation as a commercial one. For comparison, commercial Au/TiO₂ was purchased from Haruta Gold Inc.

Thiolate-protected gold colloid was prepared according to previous reports.²⁻⁴ A mixture of tetraoctylammonium bromide (3 g in 160 mL toluene) and HAuCl_4 solution (0.9 g in 50 mL deionized water) was stirred for 10 min at room temperature. 1-Dodecanethiol (1.325 mL) was added to the separated upper organic solution and stirred at 0°C for 10 min. Then NaBH_4 solution (0.83 g in 50 mL water) was added and the mixture was vigorously stirred at 0°C for 30 min and at room temperature overnight. The organic phase was separated and evaporated. The obtained solid was dissolved in hexane and filtered. After evaporation of hexane, the solid was washed three times with ethanol. The obtained black product of thiolate-protected gold colloid was stored at 4°C before use. The thiolate-protected gold colloid was used as the gold precursor for the sol immobilization (SI) method. Firstly, the gold colloid was dissolved in 20 mL of toluene. Then the dissolved gold colloid solution was added dropwise into a solution of metal oxide dispersed in 10 mL of toluene. After stirring for 1 h at room

temperature, the solvent was evaporated at 40°C and the residue was dried under vacuum overnight. Unless stated otherwise, the calcination was conducted at 300°C for 2 h.

1.3 Sample Characterization. A high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEOL, JEM-3200FS) at 300 kV (Tokyo Metropolitan University) and FEI Titan Cubed G2 60-300 (Hokkaido University) were used to obtain high-resolution transmission electron microscopy images. AAS measurements were carried out on a Shimadzu AA-6200 to obtain the gold loading amount. The specific surface area of each sample was determined by the Brunauer-Emmett-Teller (BET) method. The measurement was performed on an auto-adsorption system (BELSORP-max, MicrotracBEL). Firstly, the samples were pretreated at 250°C for 2 h in air and evacuated under vacuum at 250°C for 1 h before N₂ adsorption (77 K).

Temperature-programmed desorption of NH₃ (NH₃-TPD) was performed on an auto-chemisorption system (MicrotracBEL). The catalyst (ca. 50 mg) was preheated under He flow (50 mL min⁻¹) at 250°C for 1 h. Then 5% NH₃ was introduced at 100°C for 30 min and followed by purging He for 30 min. The desorption profile from 100°C to 750°C was recorded with a mass spectrometer under He flow (50 mL min⁻¹). Temperature-programmed CO reduction (CO-TPR) and temperature-programmed O₂ oxidation (O₂-TPO) were carried out. The catalyst (ca. 70 mg) was pretreated under 20% O₂/He (50 mL min⁻¹) or He (50 mL min⁻¹) at 250°C for 1 h and then cooled to -100°C followed by purging He for 15 min. Then, the desorption of CO₂ from -100°C to 100°C/or 300°C in 0.5%CO/He flow (30 mL min⁻¹) was recorded by a mass spectrometer under He flow. After CO-TPR, the temperature was cooled again to -100°C under 0.5%CO/He flow. After purging He at -100°C for 15 min, the 0.5% O₂/He was flowed from -100°C to 100°C at a flow rate of 30 mL min⁻¹ to obtain the CO₂ desorption profiles. To check whether the O₂ can recover the defect sites resulting from the first CO-TPR measurement, a subsequent CO-TPR experiment was conducted from -100°C to 100°C in 0.5% CO/He after O₂-TPO measurement.

Powder X-ray diffraction (XRD) measurement was conducted on a Rigaku Smartlab with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The patterns were taken over a 2θ range from 10° to 65° at a scan rate of 2° min^{-1} . Measurements of X-ray photoelectron spectroscopy (XPS) were recorded on JPC-9010MC (JEOL) using non-monochromatic Mg K α radiation. XPS data were referenced to the adventitious C 1s signal, taken as 284.8 eV.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a JASCO FT/IR-6100 spectrometer equipped with a diffuse reflectance accessory (ST Japan Heat Chamber HC-500). CO-DRIFTS spectra were recorded by accumulating 128 scans with a resolution of 4 cm^{-1} . The catalyst was set in a sample cup and pretreated in N_2 flow (50 mL min^{-1}) at 250°C for 1 h. After cooling to -180°C under N_2 flow, the background spectrum was recorded. Then 10vol% CO/He (50 mL min^{-1}) was introduced for 30 min. The spectra were recorded after removal of residual CO under N_2 flow for 30 min. *In situ* CO oxidation on Au/TT-Ta $_2$ O $_5$ was also studied by using DRIFTS. Firstly, the catalyst was set in a sample cup and pretreated in N_2 flow (50 mL min^{-1}) at 250°C for 1 h. Then, it was cooled to -120°C and the whole system was vacuumed. The background spectrum was recorded at -120°C under vacuum condition. 30 Torr of 10% CO/He was introduced and stabilized for 15 min to obtain the CO adsorption spectrum. Then, 30 Torr of O $_2$ was introduced into the sample cup for 45 min and the spectra were recorded every 5 min.

1.4 Catalytic Test. The catalysts were tested for CO oxidation in a fixed-bed flow reactor under atmospheric pressure. 1vol% CO in air (50 mL min^{-1}) was flowed through the catalyst (0.15 g) and the concentrations of CO and CO $_2$ (inlet and outlet) were analyzed with an online 490 Micro GC System (Agilent). The catalyst was pretreated at 250°C in 20% O $_2$ /N $_2$ (50 mL min^{-1}) for 1 h before measurement. Moisture concentration during the CO oxidation was monitored by using a dew point meter (AIR LIQUIDE Japan DPO-6), and the concentrations of water calculated were 40 ~ 140 ppm in all experiments. The catalytic activities were compared by metal time yields based on all gold used at 20°C and TOFs based on perimeter gold atom at 20°C that were obtained under conditions in

which the conversion of CO was below 15% for a differential reactor condition. The gold atoms were calculated based on the face-centered cubic (FCC) structure. The deposited gold nanoparticle was supposed to be a hemisphere. Therefore, the perimeter gold atoms could be calculated based on the diameter of gold nanoparticles.

$$V = \frac{1}{2} \times \frac{4}{3} \pi r_p^3$$

$$S = \frac{1}{2} \times 4 \pi r_p^2$$

$$P = 2 \pi r_p$$

$$V_{Au} = (2 \times 2^{1/2} r_{Au})^3 / 4$$

$$S_{Au} = 2 \times 3^{1/2} r_{Au}^2$$

$$P_{Au} = 2 r_{Au}$$

$$N(V) \approx V / V_{Au}$$

$$N(S) \approx S / S_{Au}$$

$$N(P) \approx 2 \pi (r_p - r_{Au}) / 2 r_{Au}$$

V: volume of particle

S: surface area of particle

P: perimeter length of particle

V_{Au} : volume per gold atom based on the assumption of the FCC structure for closest packing

S_{Au} : surface area per gold atom on the assumption of hexagonal packing in 2 dimensions

P_{Au} : perimeter per gold atom on the assumption of hexagonal packing in 2 dimensions

$N(V)$: number of Au atom in particle

$N(S)$: number of Au atom in the particle surface

$N(P)$: number of Au atom in the perimeter

r_p : radius of the particle, r_{Au} = radius of the Au atom (= 1.44×10^{-10} m)

2. RESULTS

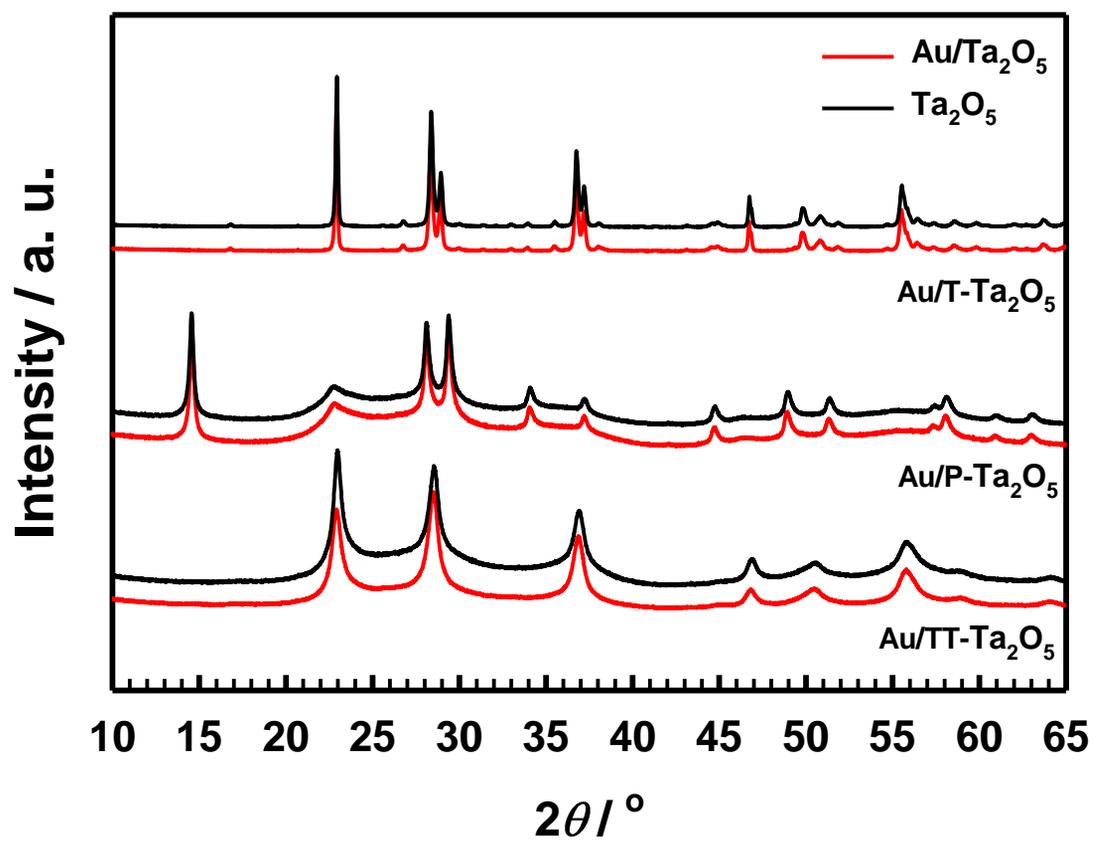


Figure S1. Comparison of XRD patterns of Ta₂O₅ and Au/Ta₂O₅ with three different crystalline structures.

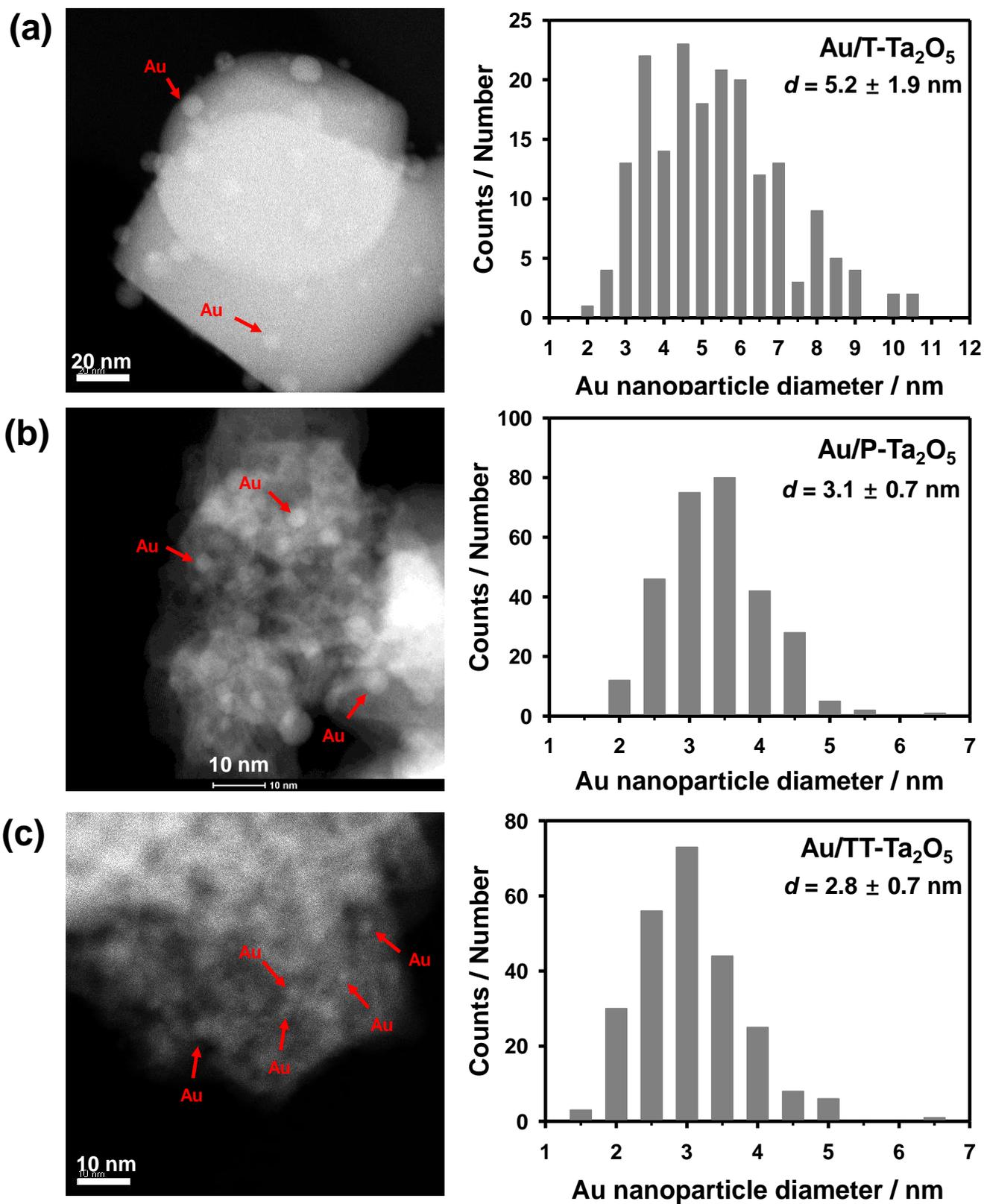


Figure S2. HAADF-STEM images and Au size distributions of (a) Au/T-Ta₂O₅, (b) Au/P-Ta₂O₅, (c) Au/TT-Ta₂O₅.

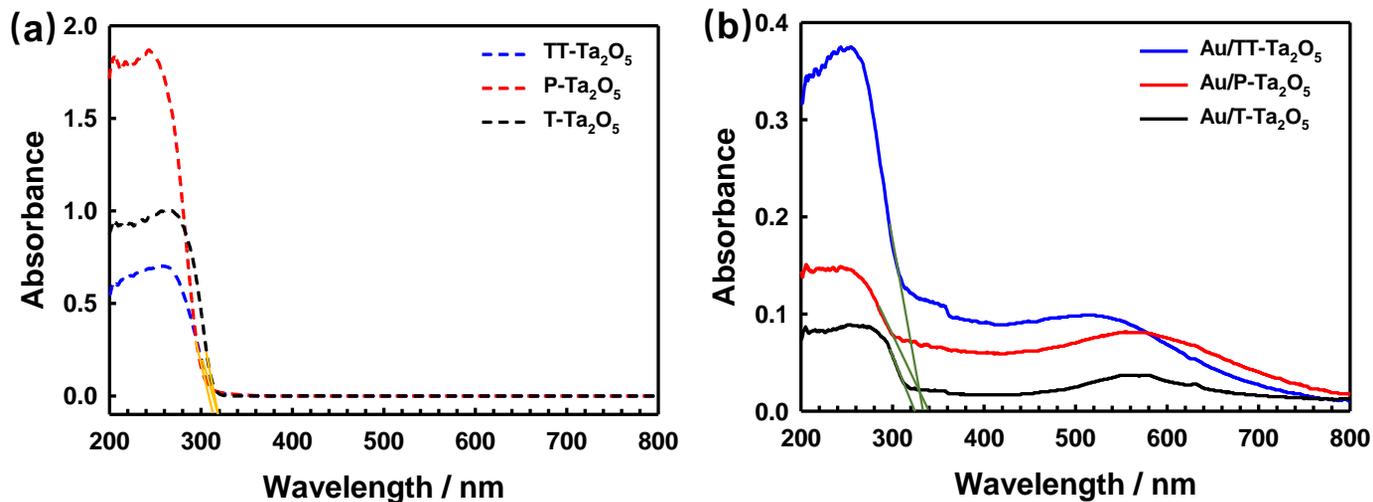


Figure S3. Comparison of UV-vis spectra of (a) bare Ta₂O₅ supports (TT-Ta₂O₅, P-Ta₂O₅, and T-Ta₂O₅), (b) gold loaded Ta₂O₅ (Au/TT-Ta₂O₅, Au/P-Ta₂O₅, and Au/T-Ta₂O₅).

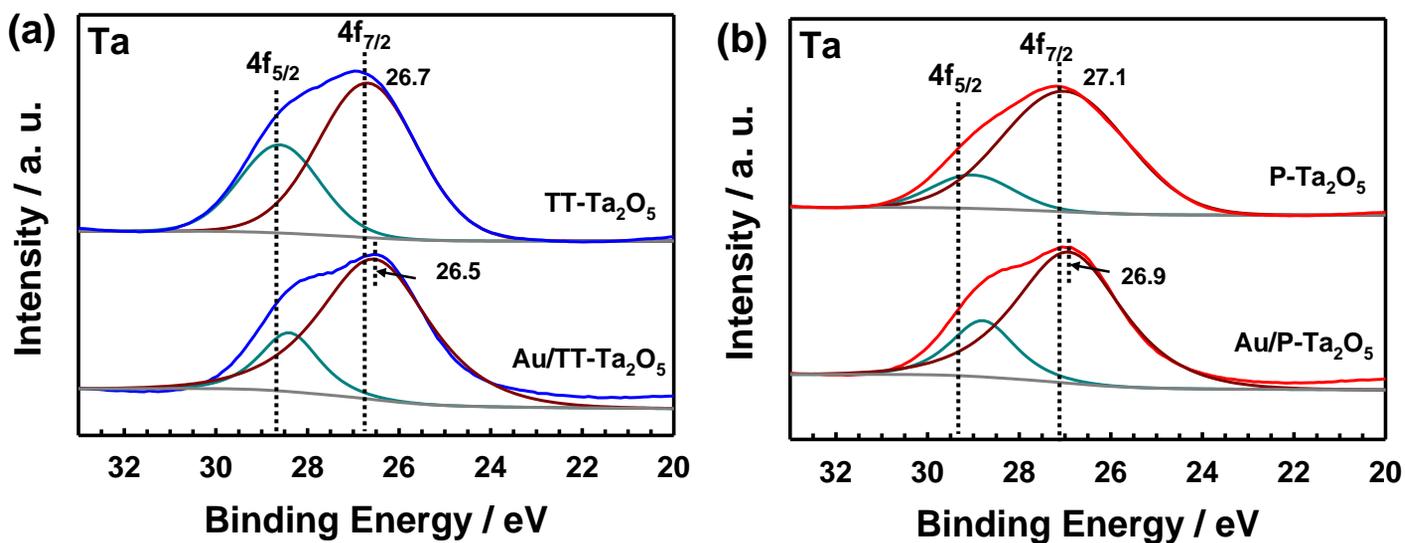


Figure S4. Comparison of Ta 4f XPS spectra of (a) TT-Ta₂O₅ and Au/TT-Ta₂O₅, and (b) P-Ta₂O₅ and Au/P-Ta₂O₅.

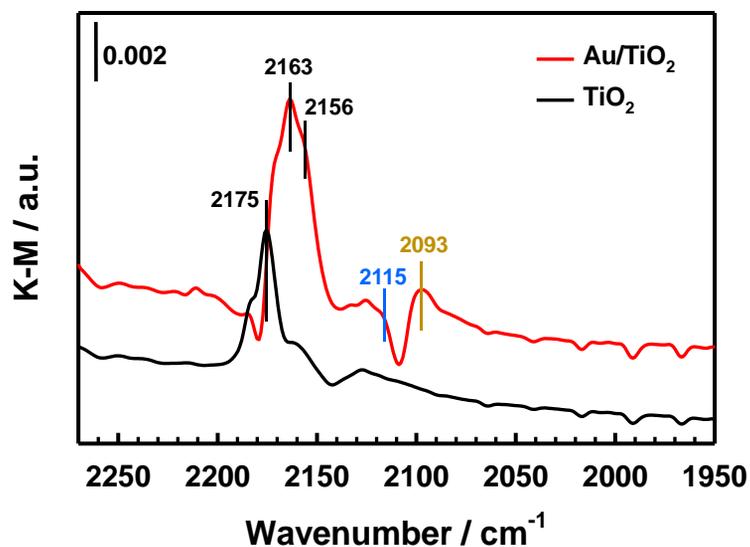


Figure S5. DRIFTs of CO adsorption at -180°C on Au/TiO_2 and TiO_2 after purging with N_2 for 30 min to fully exclude the band from gas-phase CO.

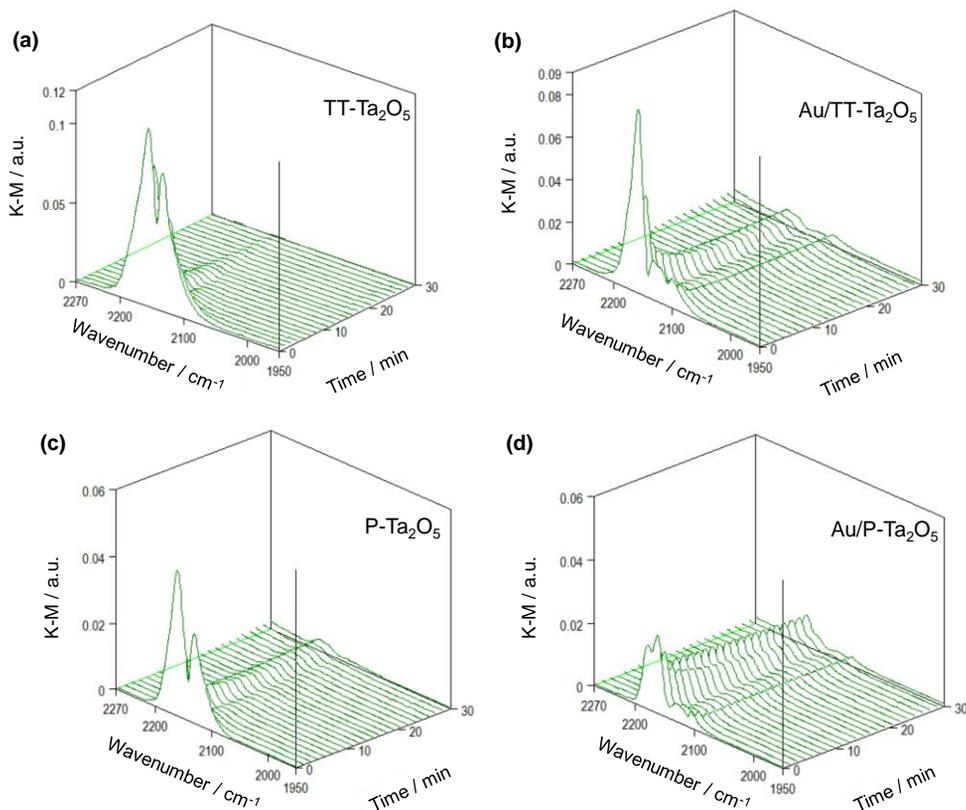


Figure S6. Time courses of CO-DRIFTs at -180°C in N_2 flow after CO adsorption. (a) $\text{TT-Ta}_2\text{O}_5$, (b) $\text{Au}/\text{TT-Ta}_2\text{O}_5$, (c) $\text{P-Ta}_2\text{O}_5$, and (d) $\text{Au}/\text{P-Ta}_2\text{O}_5$.

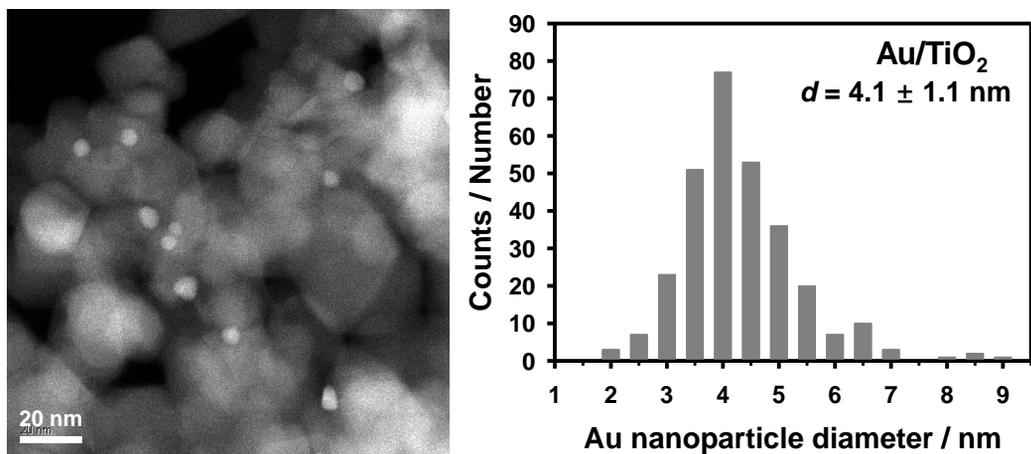


Figure S7. HAADF-STEM image and Au size distribution of Au/TiO₂.

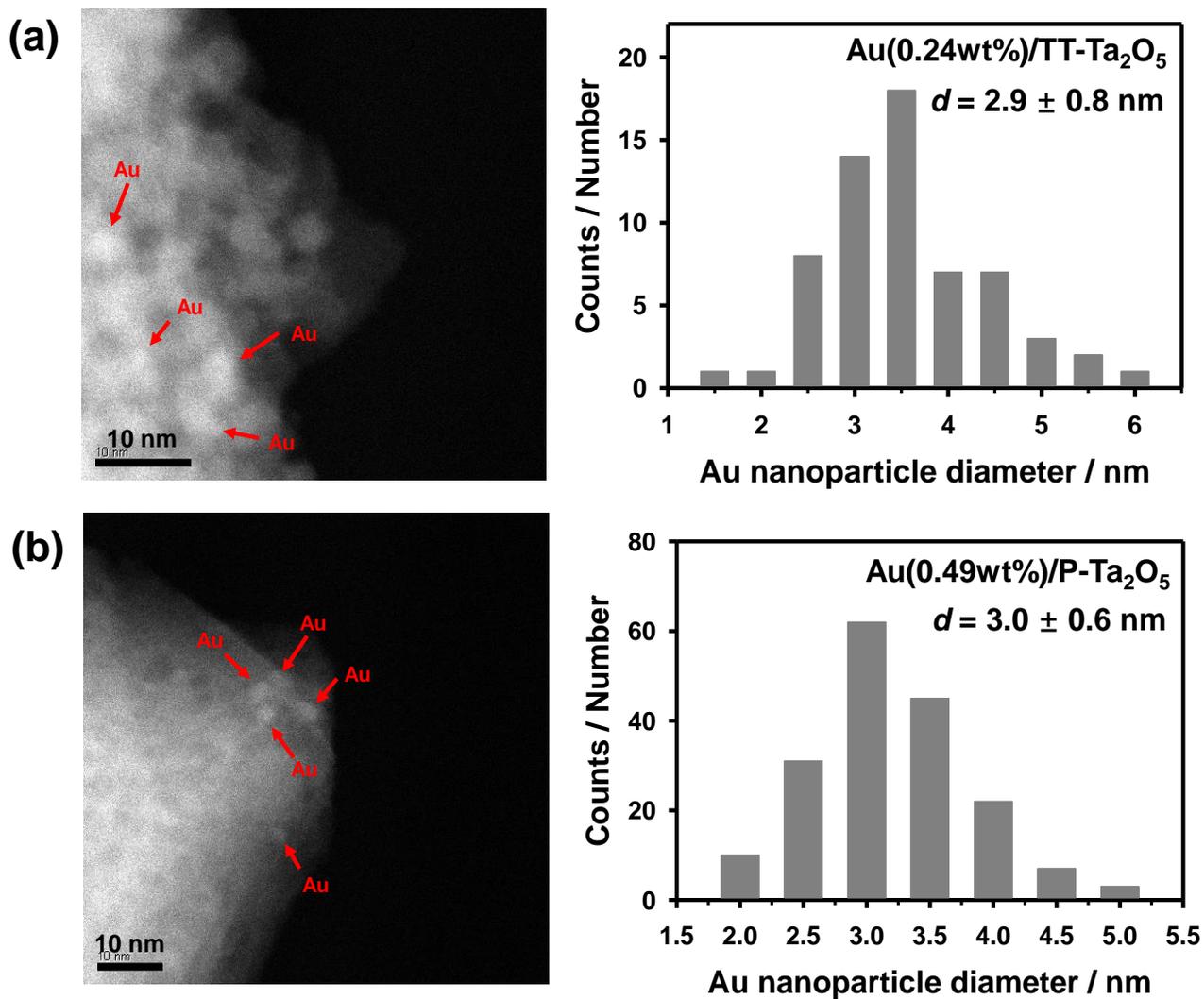


Figure S8. HAADF-STEM images and Au size distributions of (a) Au(0.24wt%)/TT-Ta₂O₅, (b) Au(0.49wt%)/P-Ta₂O₅.

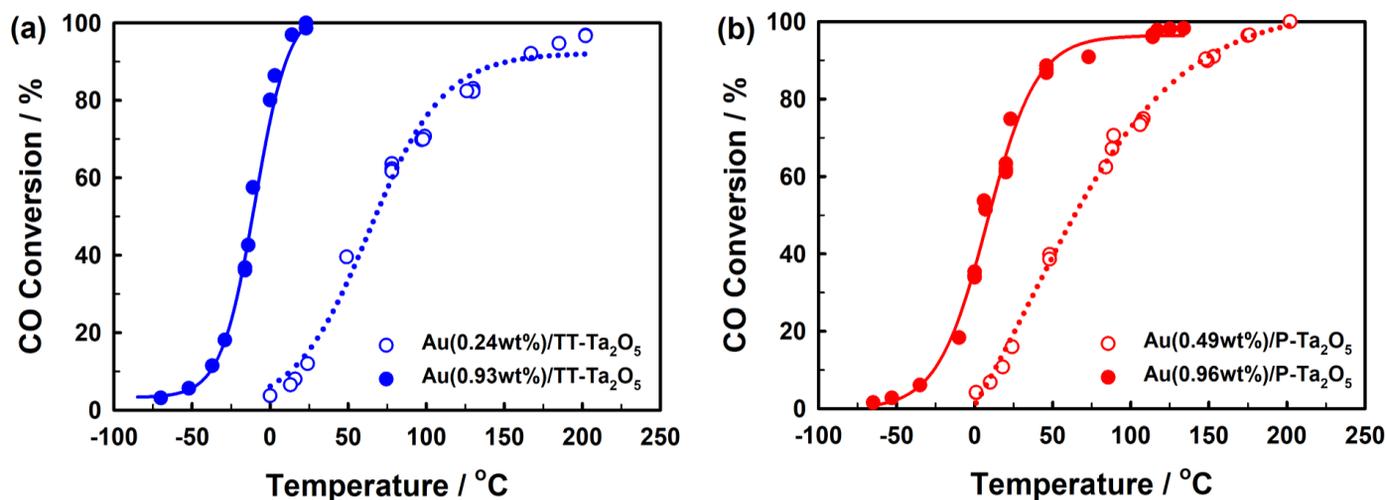


Figure S9. Comparison of catalytic activities for CO oxidation over (a) Au/TT-Ta₂O₅ and (b) Au/P-Ta₂O₅ with different gold loading amounts. Reaction conditions: catalyst, 0.15 g; 1 vol% CO in air (50 mL min⁻¹); SV, 20000 mL h⁻¹ g_{cat}⁻¹.

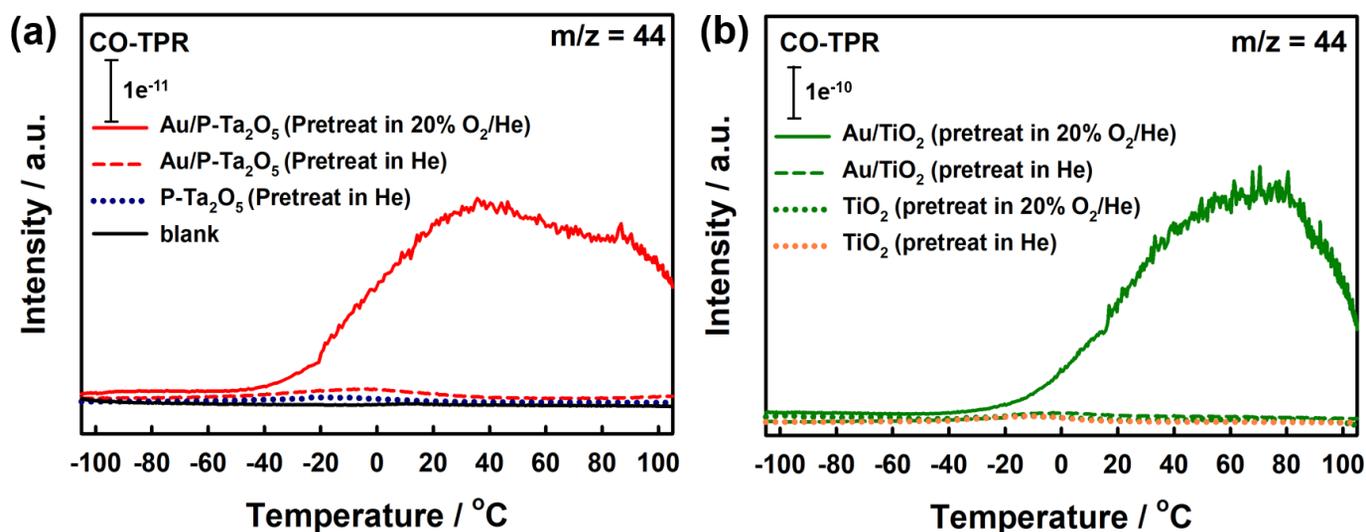


Figure S10. CO-TPR profiles of (a) Au/P-Ta₂O₅ and P-Ta₂O₅, and (b) Au/TiO₂ and TiO₂ with different pretreatment processes. An empty quartz cell was used as the blank comparison. Pretreatment occurred in 20% O₂/He or He carrier gas at 250°C for 1 h. CO-TPR measurement conditions: catalyst, ca. 70 mg; 0.5% CO/He flow, 30 mL min⁻¹.

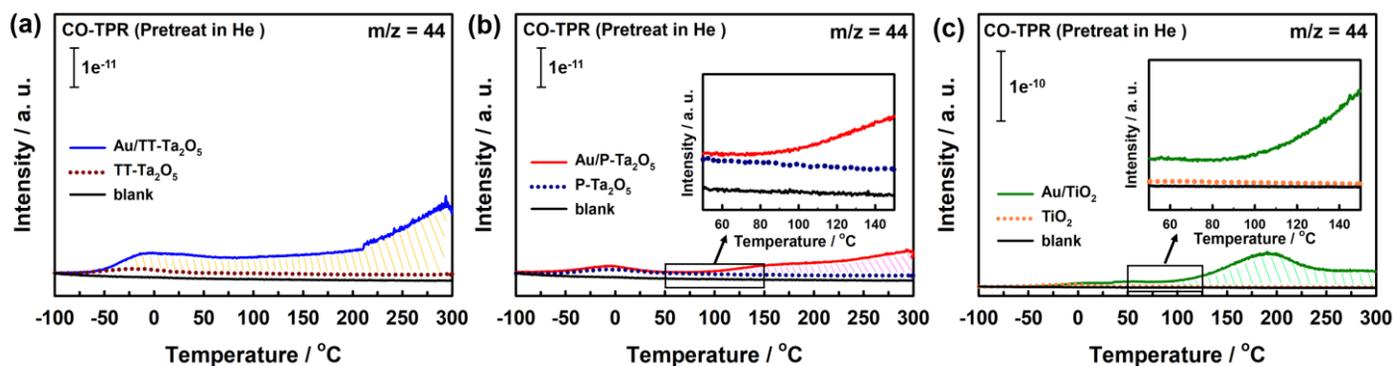


Figure S11. CO-TPR profiles of (a) Au/TT-Ta₂O₅ and TT-Ta₂O₅, (b) Au/P-Ta₂O₅ and P-Ta₂O₅, and (c) Au/TiO₂ and TiO₂. An empty quartz cell was used as the blank comparison. Pretreatment occurred in He flow at 250°C for 1 h. CO-TPR measurement conditions: catalyst, ca. 70 mg; 0.5% CO/He flow, 30 mL min⁻¹.

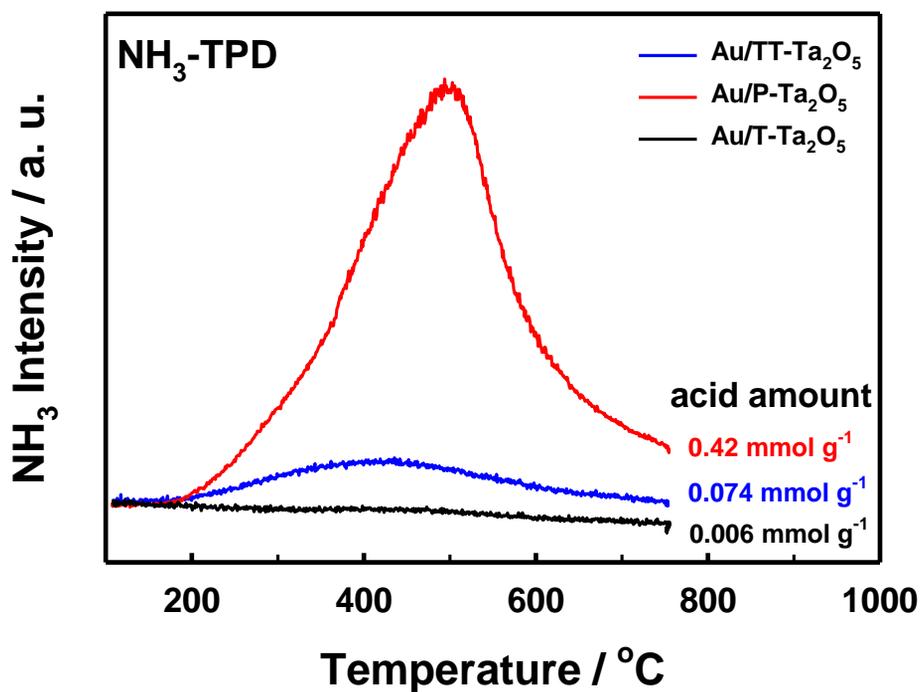


Figure S12. NH₃-TPD profiles and calculated acid amounts of Au/TT-Ta₂O₅, Au/P-Ta₂O₅, and Au/T-Ta₂O₅.

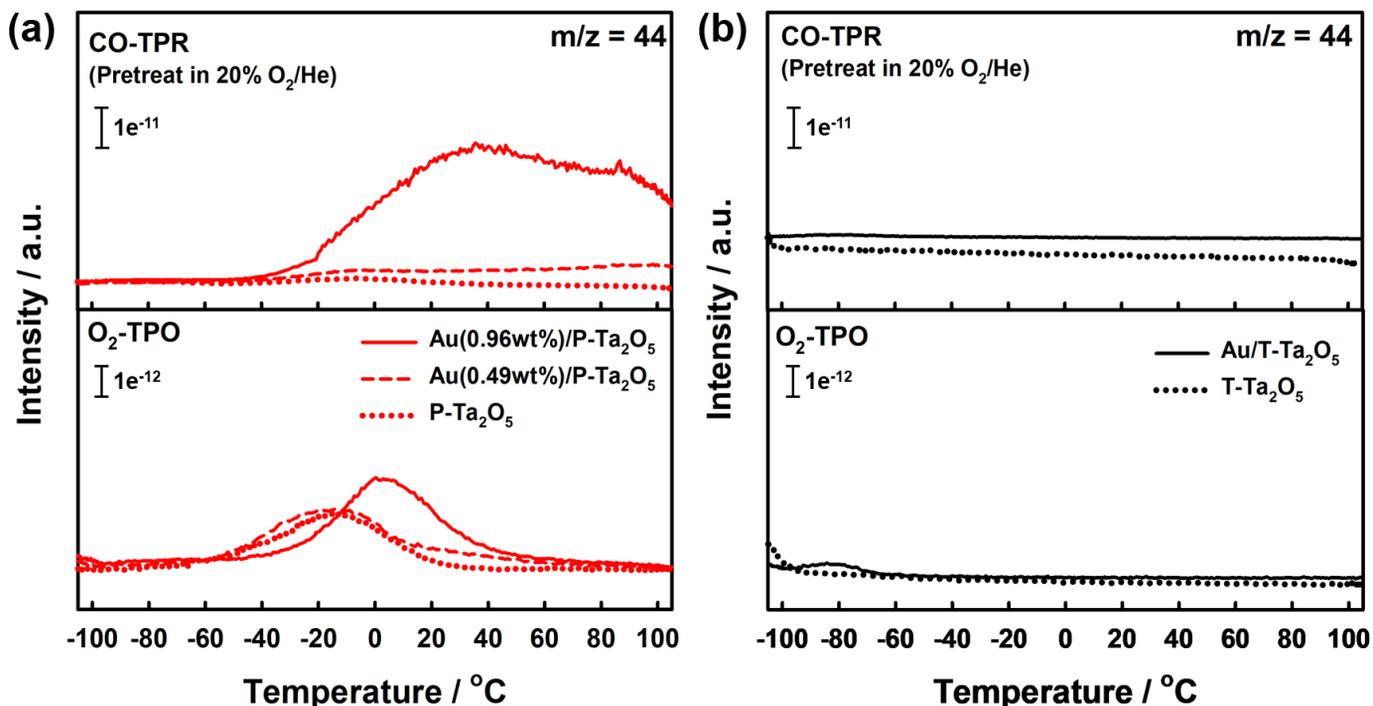


Figure S13. Comparison of CO-TPR profiles and O₂-TPO profiles of (a) Au/P-Ta₂O₅ with different gold loading amounts (0.96wt%, 0.49wt%) and bare P-Ta₂O₅, and (b) Au/T-Ta₂O₅ and bare T-Ta₂O₅. Reaction conditions: catalyst, ca. 70 mg; pretreated in 20% O₂/He at 250°C for 1 h; 0.5% CO/He flow, 30 mL min⁻¹; 0.5% O₂/He flow, 30 mL min⁻¹.

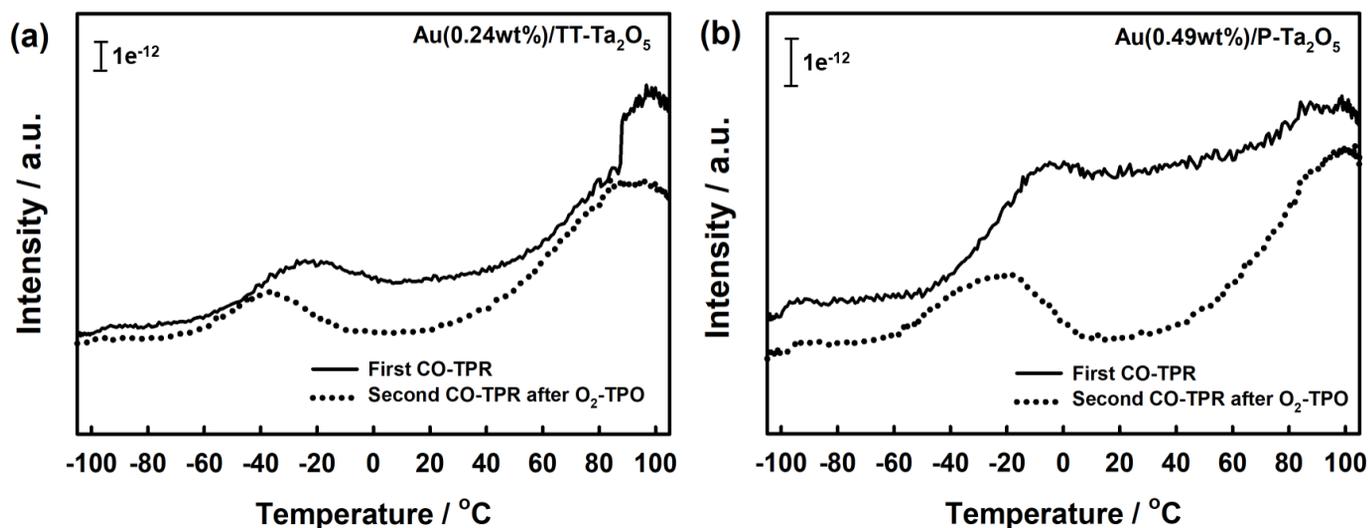


Figure S14. Comparison of the first CO-TPR profiles and the second CO-TPR profiles after O₂-TPO measurement of (a) Au(0.24wt%)/TT-Ta₂O₅ and (b) Au(0.49wt%)/P-Ta₂O₅.

Table S1. Physical properties of the supported gold catalysts and their catalytic activities for CO oxidation.

Catalyst	Au amount (wt%) ^[a]	Au size (nm) ^[b]	$T_{1/2}$ (°C) ^[c]	Metal time yield (mol _(CO) mol _(Au) ⁻¹ s ⁻¹) ^[d]	TOF (s ⁻¹) ^[e]	E_a (kJ mol ⁻¹) ^[f]
Au/P-Ta ₂ O ₅	0.49	3.0 ± 0.6	64	0.021	0.34	34.1
Au/TT-Ta ₂ O ₅	0.24	2.9 ± 0.8	64	0.032	0.48	30.4

^[a] Determined by AAS. ^[b] Measured by HAADF-STEM. ^[c] $T_{1/2}$: the temperature for 50% CO conversion. ^[d] Based on all gold used at 20°C. ^[e] Turnover frequency based on perimeter gold atom at 20°C. ^[f] Activation energy was calculated based on all gold used at the temperature ranges that the CO conversions were less than 15%. Reaction conditions: catalyst, 0.15 g; 1vol% CO in air (50 mL min⁻¹); SV, 20000 mL h⁻¹ g_{cat}⁻¹. Reaction rates for ^[d] and ^[e] were calculated by adjusting the amount of catalyst to keep CO conversion less than 15%.

References

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