

Supporting Information for

**Facile Preparation of Highly Active Zirconia-Supported  
Gold Nanoparticle Catalyst**

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## Table of Contents

<b>Experimental methods</b> .....	3
<b>Table S1.</b> Catalytic activity of Au/MOs for H <sub>2</sub> O <sub>2</sub> generation .....	4
<b>Fig. S1.</b> XRD patterns of ZrO <sub>2</sub> , Au/ZrO <sub>2</sub> -DP <sub>400</sub> , and Au/ZrO <sub>2</sub> -MDP <sub>400</sub> .....	5
<b>Fig. S2.</b> TEM image (a) and Au particle size distribution (b) of Au/ZrO <sub>2</sub> -DP <sub>400</sub> .....	5
<b>Fig. S3.</b> TEM (a) and HR-TEM images of Au/ZrO <sub>2</sub> -MDP <sub>400</sub> .....	6
<b>Fig. S4.</b> Plots of the amount of H <sub>2</sub> O <sub>2</sub> generated versus the amount of CO <sub>2</sub> generated in the Au/ZrO <sub>2</sub> -MDP <sub>400</sub> system .....	6
<b>Fig. S5.</b> (a) XRD patterns of Au/ZrO <sub>2</sub> -MDP <sub>400</sub> before and after the repeated reactions. (b) TEM image of Au/ZrO <sub>2</sub> -MDP <sub>400</sub> after the repeated reactions. Au4f (c) and O1s (d)-XP spectra of Au/ZrO <sub>2</sub> -MDP <sub>400</sub> before and after the repeated reactions. ....	7
<b>Fig. S6.</b> Kubelka-Munk-transformed absorption spectra of Au <sup>3+</sup> /ZrO <sub>2</sub> -MDP calcined at various temperatures in the air. ....	7
<b>Fig. S7.</b> Zr3d-XP spectra for Au/ZrO <sub>2</sub> -MDP <sub>400</sub> , Au/ZrO <sub>2</sub> -DP <sub>400</sub> , and ZrO <sub>2</sub> . ....	8

## Experimental methods

**Materials.** Commercial monoclinic ZrO<sub>2</sub> (mean particle size = 20 nm, specific surface area = 100 m<sup>2</sup>g<sup>-1</sup>), UEP-100, Daiichi Kigenso Kagaku Kogyo Co.) was used as the support. Hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O > 99%), sodium hydroxide (NaOH >97%), and formic acid (C<sub>1</sub>H<sub>2</sub>O<sub>2</sub> 88-90%) were purchased from Kanto Chemical Co. All chemicals were used as received without further purification.

**Catalyst preparation.** ZrO<sub>2</sub> particles (5 g) were dispersed into an aqueous solution of HAuCl<sub>4</sub> (4.86 mM, 50 mL), and stirred at room temperature (25°C) for 24 h. The suspension was neutralized to pH 7.0 by using 1 M NaOH aq., and heated at 80°C for 2 h. After washing and drying in vacuo, the resulting particles were calcined at 400°C for 1 h to obtain Au/ZrO<sub>2</sub>-MDP<sub>400</sub>. Au/ZrO<sub>2</sub>-MDP<sub>450</sub> and Au/ZrO<sub>2</sub>-MDP<sub>500</sub> were prepared by the similar procedure with the calcination at 450°C and 500°C, respectively. Au/ZrO<sub>2</sub>-DP<sub>400</sub> was prepared by the similar procedure without long time stirring. ZrO<sub>2</sub> particles (5 g) were dispersed into an aqueous solution of HAuCl<sub>4</sub> (4.86 mM, 50 mL), and immediately neutralized to pH 7.0 by using 1 M NaOH aq. The suspension was heated at 80°C for 2 h, and the resulting particles were collected by the centrifugation. The sample was washed and dried at room temperature in vacuo, and calcined at 400°C for 1 h to obtain Au/ZrO<sub>2</sub>-DP<sub>400</sub>.

**Characterization.** X-ray diffraction (XRD) patterns were collected by using a Rigaku SmartLab X-ray diffractometer operated at 40 kV and 100 mA. The morphologies were characterized by using a transmission electron microscopy (TEM) operated with an applied voltage of 200 kV (JEM-2100F, JEOL). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image was obtained by means of JEM-2100F (JEOL) with an applied voltage of 200 kV. Au loading amounts were determined by using an inductively coupled plasma spectroscopy (ICPE-9820, Shimadzu). The diffuse reflectance UV-Vis-NIR absorption spectra were obtained by means of a UV-2600 spectrometer (Shimadzu) with integrating sphere unit (Shimadzu, ISR-2600Plus). BaSO<sub>4</sub> is used as a reference for the reflectance ( $R_{\infty}$ ). Kubelka-Munk function [ $F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$ ] was used for expressing the relative absorption coefficient. TG-DTA measurements were carried out by means of a simultaneous DTA-TG apparatus (Shimadzu, DTG-60). X-ray photoelectron spectra (XPS) were collected by means of a Kratos Axis Nova X-ray photoelectron spectrometer with 15 kV and 10 mA using Al K $\alpha$  as X-ray source. The peak of C1s (284.6 eV) was used as the energy reference. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained by using a Fourier transform infrared spectrophotometer (Shimadzu, FTIR-8400S) with a diffuse reflectance attachment (Shimadzu, DRS-8000).

**Catalytic H<sub>2</sub>O<sub>2</sub> production.** Au/ZrO<sub>2</sub> or ZrO<sub>2</sub> (50 mg) was dispersed into an aqueous solution of HCOOH (1.06 M, 50 mL), and stirred at 25°C in the dark under aerobic conditions. The solution temperature was controlled by using a double jacket type cell with circulating thermostatted water through an outer jacket around the cell. The H<sub>2</sub>O<sub>2</sub> concentration was quantified by iodometric titration.<sup>S1</sup> The amount of CO<sub>2</sub> generated was measured by using gas chromatography (GC-2010Plus with BID-detector, Shimadzu, column = Micropacked ST, Shinwa Chemical Industries, He flow rate = 10 mL min<sup>-1</sup>). The number of the surface Au atoms was estimated from the Au loading amount, the  $d_{Au}$  value, and the dispersion by assuming that every Au NP is hemispherical.<sup>S2</sup> The turnover frequency (TOF) is calculated by the number of the H<sub>2</sub>O<sub>2</sub> molecule generated during unit time / the number of Au surface atoms.

## References

- S1. R. Cai, Y. Kubota and A. Fujishima, *J. Catal.* **2003**, *219*, 214–218.
- S2. G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, John Wiley & Sons, New York, **1994**.

**Table S1.** Catalytic activity of Au/MOs for H<sub>2</sub>O<sub>2</sub> generation

catalyst	Au loading amount (wt%)	Au particle size (nm)	v ( mM h <sup>-1</sup> )	TOF (h <sup>-1</sup> )	Selectivity (%)
Au/ZrO <sub>2</sub> -MDP	0.67	3.6±0.5	0.803 ± 0.003	102 ± 0.41	97.0 ± 4.8
Au/ZrO <sub>2</sub> -DP	0.69	4.6±0.7	0.192 ± 0.015	29.1 ± 2.2	---
Au/SrTiO <sub>3</sub>	0.67	4.2±1.4	0.445 ± 0.033	64.6 ± 4.7	89.2 ± 6.5
Au/CaTiO <sub>3</sub>	0.51	3.7±0.7	0.567 ± 0.034	73.9 ± 4.4	94.8 ± 4.8
Au/BaTiO <sub>3</sub>	0.67	3.8±0.9	0.467 ± 0.025	81.8 ± 4.4	94.9 ± 2.6
Au/TiO <sub>2</sub>	0.42	5.2±1.2	0.179 ± 0.046	49.5 ± 1.5	---
Au/BiVO <sub>4</sub>	0.30	16.1±3.9	0.025 ± 0.008	19.9 ± 6.4	---
Au/WO <sub>3</sub>	1.25	11.1±2.8	0.167 ± 0.009	29.2 ± 1.5	---

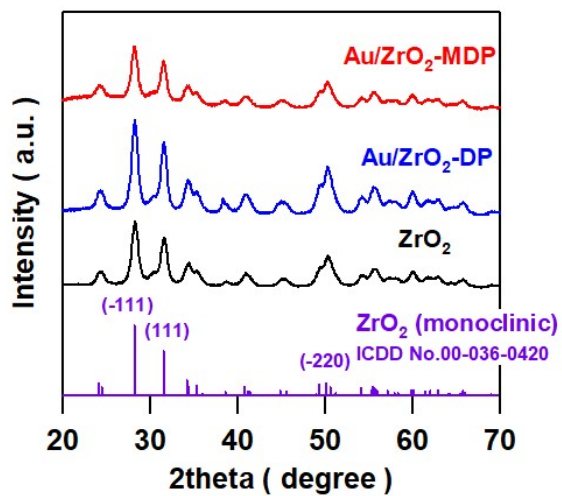
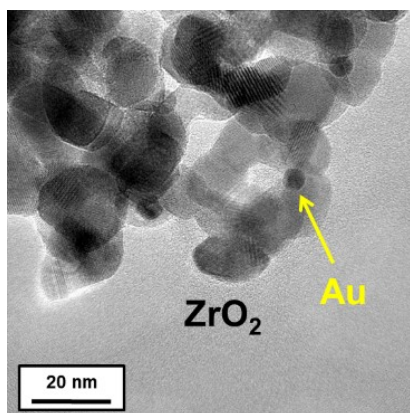


Fig. S1. XRD patterns of  $ZrO_2$ ,  $Au/ZrO_2$ -DP<sub>400</sub>, and  $Au/ZrO_2$ -MDP<sub>400</sub>.

a)



b)

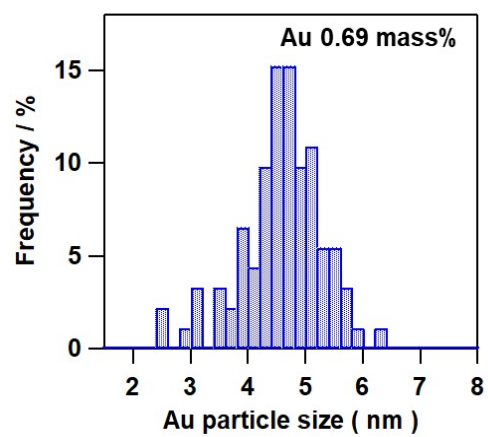
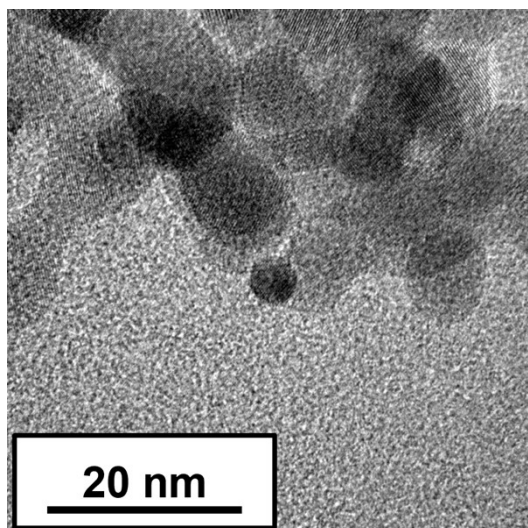


Fig. S2. TEM image (a) and Au particle size distribution (b) of  $Au/ZrO_2$ -DP<sub>400</sub>.

a)



b)

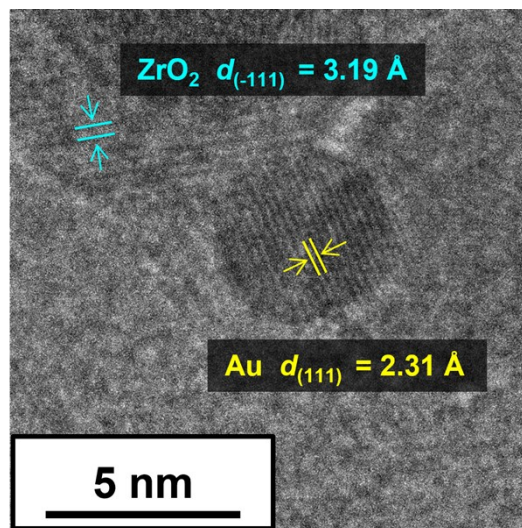


Fig. S3. TEM (a) and HR-TEM images of Au/ZrO<sub>2</sub>-MDP<sub>400</sub>.

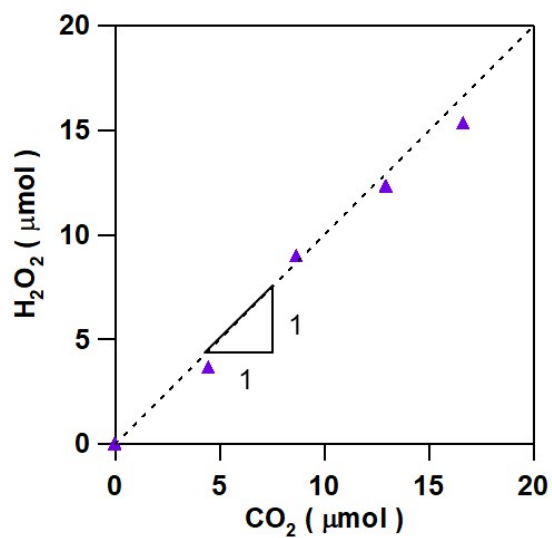
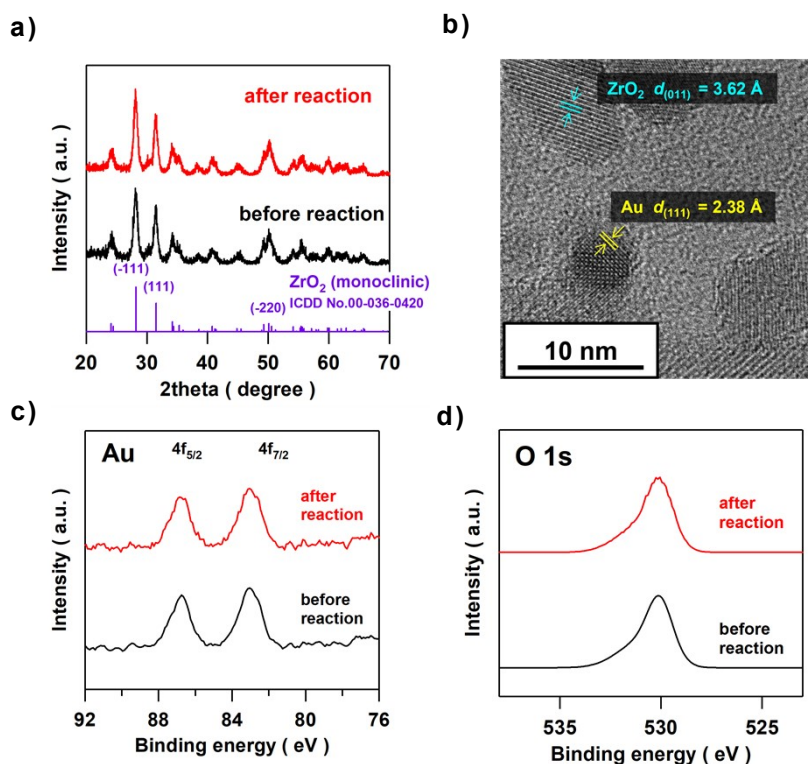
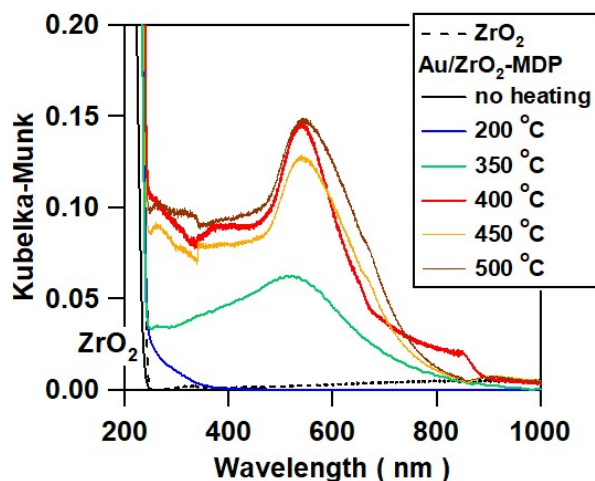


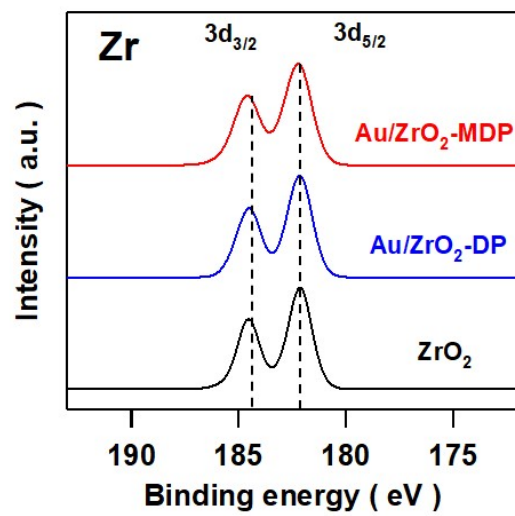
Fig. S4. Plots of the amount of H<sub>2</sub>O<sub>2</sub> generated versus the amount of CO<sub>2</sub> generated in the Au/ZrO<sub>2</sub>-MDP<sub>400</sub> system.



**Fig. S5.** (a) XRD patterns of Au/ZrO<sub>2</sub>-MDP<sub>400</sub> before and after the repeated reactions. (b) TEM image of Au/ZrO<sub>2</sub>-MDP<sub>400</sub> after the repeated reactions. Au4f (c) and O1s (d)-XPS spectra of Au/ZrO<sub>2</sub>-MDP<sub>400</sub> before and after the repeated reactions.



**Fig. S6.** Kubelka-Munk-transformed absorption spectra of Au<sup>3+</sup>/ZrO<sub>2</sub>-MDP calcined at various temperatures in the air.



**Fig. S7.** Zr3d-XPS spectra for Au/ZrO<sub>2</sub>-MDP<sub>400</sub>, Au/ZrO<sub>2</sub>-DP<sub>400</sub>, and ZrO<sub>2</sub>.