

*Electronic Supplementary Information for*

**Hexagonal CeO<sub>2</sub> plate@Au catalysts for the selective oxidation of 1,3-propanediol to a polymer platform, 3-hydroxypropionic acid at room temperature**

Yoon Kee Kim,<sup>a</sup> Sang Lim Park,<sup>a</sup> Jong Doo Lee,<sup>a</sup> and Seung Uk Son<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

E-mail: sson@skku.edu

**Experimental Section**

**General:** Solution state <sup>1</sup>H and <sup>13</sup>C spectra were obtained using a Bruker Ascend 500 MHz spectrometer at the Chiral Material Core Facility Center of Sungkyunkwan University. A high resolution mass (HR-MS) spectrum was obtained using a Xevo G2-XS-UPC2 spectrometer. SEM images were obtained using JSM-7100F and JSM-7800F instruments at the Chiral Material Core Facility Center of Sungkyunkwan University. TEM, HR-TEM, and EDS based elemental mapping images were obtained using a JEM2100F equipment. N<sub>2</sub> adsorption-desorption isotherm curves (77 K) were obtained using a Micromeritics ASAP2020. Pore size distribution diagrams were obtained by the nonlocal-density functional theory (NL-DFT) method. PXRD patterns were obtained using a Rigaku MAX-2200 equipment. IR spectra were obtained using a Bruker VERTEX70 spectrometer. A solid state <sup>13</sup>C NMR spectrum was obtained using at cross polarization/total sideband suppression (CP/TOSS) mode using a 500 MHz Bruker ADVANCE III HD spectrometer in NCIRF (National Center for Inter-University Research Facilities, Seoul National University, Republic of Korea). XPS spectra were obtained using a Thermo VG Spectrometer. ICP-AES analysis was conducted using an OPTIMA8300 equipment. XANES and EXAFS spectra were obtained using the 7D (XAFS) beamline of the Pohang Light Source (PLS-II, Korea) under 3.0 GeV operation with a ring current of 250 mA.

**Synthesis of Co(OH)<sub>2</sub> plates**

Tetramethylammonium bromide (0.52 g, 3.4 mmol) and degassed distilled water (200 mL) were added to a flame-dried 250 mL two-necked Schlenk flask under argon. The solution was degassed under vacuum. After charging the flask with argon, the solution was further degassed through argon bubbling using a needle connected to an argon gas tank. After 2 M NaOH solution (1.6 mL, 3.2 mmol) was added, CoCl<sub>2</sub> hexahydrate (0.95 g, 4.0 mmol) dissolved in degassed water (1.5 mL) was added quickly. The reaction mixture was stirred at 60 °C for 1 h. After cooling in an ice bath, the mixture was transferred to four 50 mL Falcon tubes. The pink precipitates (Co(OH)<sub>2</sub> plates) were separated by centrifugation, washed with a mixture of ethanol (40 mL) and water (10 mL) two times and ethanol (50 mL) once, and dried under vacuum.

**Synthesis of H-MOP, H-CeO<sub>2</sub>, and control N-CeO<sub>2</sub>**

Co(OH)<sub>2</sub> plates (0.20 g), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (28 mg, 40 μmol), CuI (7.6 mg, 40 μmol), and triethylamine (40 mL) were added to a flame-dried 100 mL two necked Schlenk flask under argon. The mixture was sonicated for 30 min at room temperature. After tetra(4-ethynylphenyl)methane (42 mg, 0.10 mmol) and 1,4-diiodobenzene (66 mg, 0.20 mmol) dissolved in distilled toluene (20 mL) were added, the reaction mixture was stirred at 80 °C for 18 h. After cooling to room temperature, the precipitates (Co(OH)<sub>2</sub>@MOP) were

separated by centrifugation, washed with a mixture of methylene chloride (10 mL) and methanol (40 mL) three times.

After  $\text{Co(OH)}_2\text{@MOP}$  (0.25 g) was added to a Falcon tube, hydrochloric acid (9.0 mL, 35.0~37.0 %) and acetone (40 mL) were added. The reaction mixture was stirred at room temperature for 1 h. The precipitates (H-MOP) were separated by centrifugation, washed with a mixture of acetone (40 mL) and water (10 mL) until the pH reached a neutral state, and dried under vacuum. After H-MOP (50 mg) was added to a two-necked 20 mL Schlenk flask, aqua regia (10 mL) was added. After the reaction mixture was stirred at room temperature for 12 h to remove the Pd and Cu residues in MOP networks, the precipitates were separated by centrifugation, washed with a mixture of methanol (45 mL) and water (5 mL) until the pH reached neutral, and dried under vacuum.

H-MOP (25 mg) and ethanol (10 mL) were added to a flame-dried 50 mL two-necked Schlenk flask under argon. The reaction mixture was sonicated for 30 min at room temperature. After cerium acetate (0.30 g, 0.95 mmol) was added to water (20 mL), the mixture was sonicated for 30 min at room temperature. After the cerium acetate solution was added to a two-necked Schlenk flask containing H-MOP, the reaction mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the precipitates (H-MOP@ $\text{CeO}_2$ ) were separated by centrifugation, washed with a mixture of ethanol (40 mL) and water (10 mL) five times, and dried under vacuum. After H-MOP@ $\text{CeO}_2$  was calcined at 500 °C for 4 h under air in a furnace, the pale yellow powder (H- $\text{CeO}_2$ ) was obtained. The control N- $\text{CeO}_2$  was prepared by the same synthetic procedures of H- $\text{CeO}_2$  in the absence of H-MOP template.

### ***Synthesis of H-CeO<sub>2</sub>@Au-1, H-CeO<sub>2</sub>@Au-2, H-CeO<sub>2</sub>@Au-3, and control N-CeO<sub>2</sub>@Au-2***

For the preparation of H- $\text{CeO}_2\text{@Au-1}$ , after H- $\text{CeO}_2$  (0.10 g) and water (5 mL) were added to a 50 mL two-necked Schlenk flask, the suspension was sonicated at room temperature for 5 min. After  $(\text{NH}_4)_2\text{CO}_3$  (1 M, 2.5 mL) was added,  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$  (6.0 mg, 15  $\mu\text{mol}$ ) in water (2.5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h. After the reaction mixture was transferred to a vial, the precipitates were separated by centrifugation, washed with water (10 mL) five times. After drying at 70 °C for 4 h, the powders were calcined at 400 °C for 4 h under air to form H- $\text{CeO}_2\text{@Au-1}$ .

For the preparation of H- $\text{CeO}_2\text{@Au-2}$ , the same synthetic procedures of H- $\text{CeO}_2\text{@Au-1}$  were applied except using  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$  (15 mg, 38  $\mu\text{mol}$ ). For the preparation of H- $\text{CeO}_2\text{@Au-3}$ , the same synthetic procedures of H- $\text{CeO}_2\text{@Au-1}$  were applied except using  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$  (30 mg, 76  $\mu\text{mol}$ ). For the preparation of control N- $\text{CeO}_2\text{@Au-2}$ , the same synthetic procedures of H- $\text{CeO}_2\text{@Au-2}$  were applied except using control N- $\text{CeO}_2$  instead of H- $\text{CeO}_2$ .

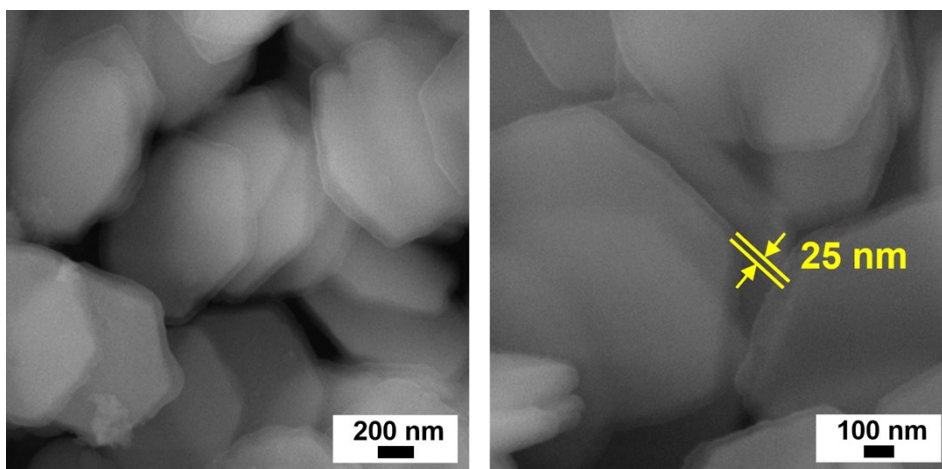
### ***Procedures of catalytic reactions***

According to the ICP-AES analysis, the contents of Au in H- $\text{CeO}_2\text{@Au-1}$ , H- $\text{CeO}_2\text{@Au-2}$ , H- $\text{CeO}_2\text{@Au-3}$ , and control N- $\text{CeO}_2\text{@Au-2}$  were analyzed to be 2.2, 5.4, 10, and 5.4 wt%, respectively, corresponding to 0.11, 0.27, 0.51, and 0.27 mmol Au/g, respectively. H- $\text{CeO}_2\text{@Au}$  or control N- $\text{CeO}_2\text{@Au-2}$  (1.0 mol% Au, 91 mg of H- $\text{CeO}_2\text{@Au-1}$ , 37 mg of H- $\text{CeO}_2\text{@Au-2}$ , 20 mg of H- $\text{CeO}_2\text{@Au-3}$ , 37 mg of N- $\text{CeO}_2\text{@Au-2}$ ), 1 M NaOH (5 mL), and 1,3-propanediol (72  $\mu\text{L}$ , 1.0 mmol) were added to a flame-dried 20 mL two-necked

Schlenk tube under argon. Using a O<sub>2</sub> balloon, Ar gas was replaced with O<sub>2</sub>. After being stirred at room temperature for 48 h, the reaction mixture was analyzed by NMR studies (D<sub>2</sub>O as NMR solvent) using maleic acid as an internal standard (IS). After reaction finished, we added the IS with the same mole (1.0 mmol) of the reactant, PD to the reaction mixture. The <sup>1</sup>H NMR peak (2H) of the alkene of the maleic acid sodium salt was observed at 5.99 ppm. The <sup>1</sup>H NMR peaks of 3HP sodium salts were observed at 3.79 ppm (2H of a methylene moiety) and 2.44 ppm (2H of another methylene moiety). The <sup>1</sup>H NMR peak (2H of a methylene moiety) of malonic acid (MA) sodium salt was observed at 3.12 ppm. The <sup>1</sup>H NMR peaks of PD were observed at 3.69 ppm (4H of two methylene moieties) and 1.80 ppm (2H of a methylene moiety). The conversions of reactant were through the comparison of the integration values of the <sup>1</sup>H NMR peak of IS at 5.99 ppm with that of PD at 1.80 ppm. The yields of products (3HP and MA) were obtained through the comparison of the integration values of the <sup>1</sup>H NMR peak of IS at 5.99 ppm with that of 3HP at 2.44 ppm and that of MA at 3.12 ppm. The neutral 3HP was isolated as follows. The catalyst was retrieved using a syringe filter. The resultant solution was quenched by adding 1 M HCl solution to reach pH 3~4. After evaporating water under vacuum, white power was obtained. After 3HP was extracted using diethylether (20 mL) three times, the solution was dried using MgSO<sub>4</sub>. After filtration, diethylether in solution was evaporated to form white powder of 3HP.

For the recyclability tests, the catalysts were separated by centrifugation, washed with water until the pH of washed solution reached neutral state, dried under vacuum, and used for the next run. Characterization data of 3-hydroxypropionic acid: an isolated yield of 83%, <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O)  $\delta$  = 2.65 (t, *J* = 6.0 Hz, 2H), 3.86 (t, *J* = 6.0 Hz, 2H) ppm, <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O)  $\delta$  = 176.5, 57.3, 36.7 ppm, HRMS (FAB): *m/z* calc. for C<sub>3</sub>H<sub>5</sub>O<sub>3</sub> [M-H] 89.0239, found, 89.0239.

**Fig. S1** SEM images of  $\text{Co}(\text{OH})_2@\text{MOP}$ .



**Fig. S2** Additional HR-TEM images of (a) H-CeO<sub>2</sub>@Au-1, (b) H-CeO<sub>2</sub>@Au-2, and (c) H-CeO<sub>2</sub>@Au-3.

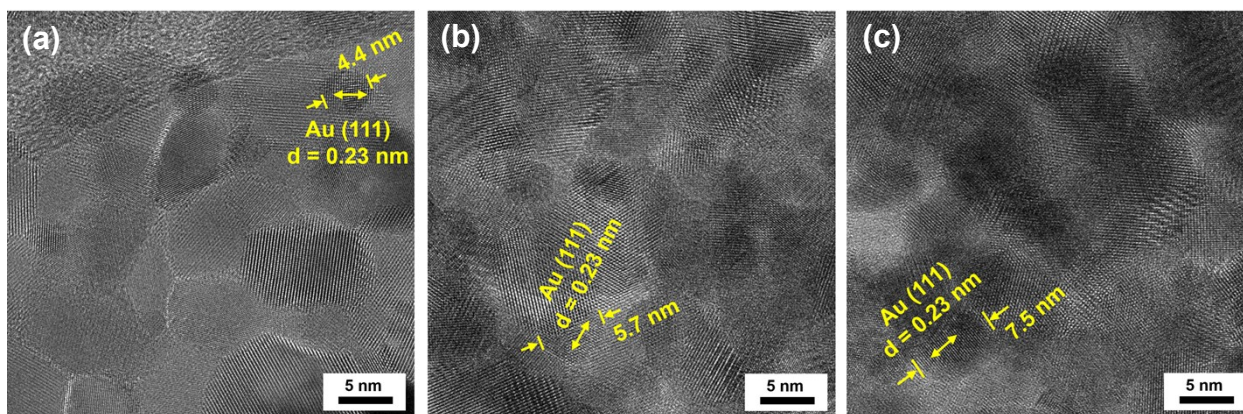
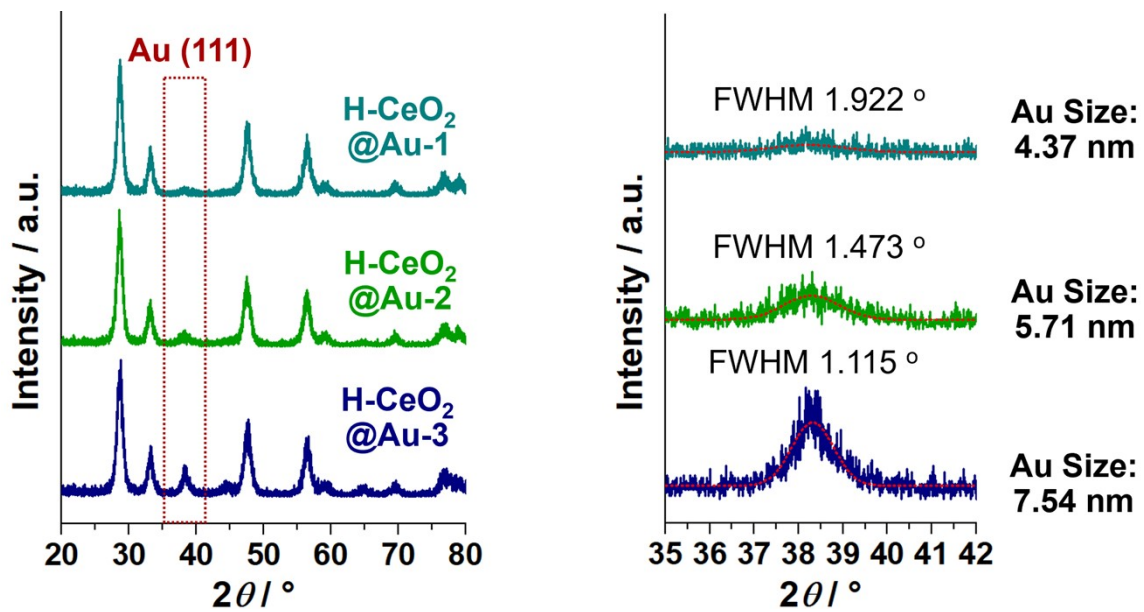
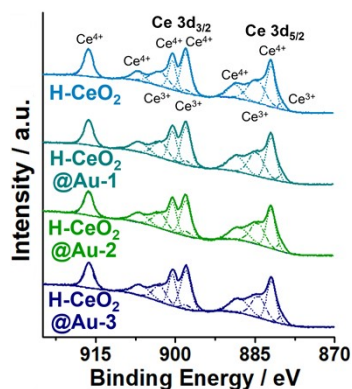


Fig. S3 Analysis of Au (111) PXR peaks based on the Scherrer equation.



**Fig. S4** Analysis of XPS Ce 3d orbital spectra of H-CeO<sub>2</sub>, H-CeO<sub>2</sub>@Au-1, H-CeO<sub>2</sub>@Au-2, and H-CeO<sub>2</sub>@Au-3.



H-CeO <sub>2</sub>	Peak	p1	p2	p3	p4	p5	p6	p7	p8	p9	p10
	Position (eV)	879.95	881.98	884.76	888.72	898.06	898.06	900.55	903.01	907.18	916.40
	FWHM	1.34	1.99	3.82	3.07	1.68	2.20	1.80	3.86	2.98	2.16
	Area (%)	2.00	16.1	17.2	7.94	1.27	17.6	10.4	11.0	5.08	11.4
r <sup>2</sup>	0.9968										

**Ce<sup>3+</sup>: Ce<sup>4+</sup> = 31.4: 68.6**

H-CeO <sub>2</sub> @Au-1	Peak	p1	p2	p3	p4	p5	p6	p7	p8	p9	p10
	Position (eV)	879.85	881.98	884.79	888.55	897.96	897.99	900.48	902.81	906.70	916.33
	FWHM	1.61	2.18	3.37	3.69	1.89	2.16	1.96	3.33	3.79	2.18
	Area (%)	2.39	17.1	15.2	10.6	1.62	15.4	11.1	9.72	6.85	9.96
r <sup>2</sup>	0.9973										

**Ce<sup>3+</sup>: Ce<sup>4+</sup> = 28.9: 71.1**

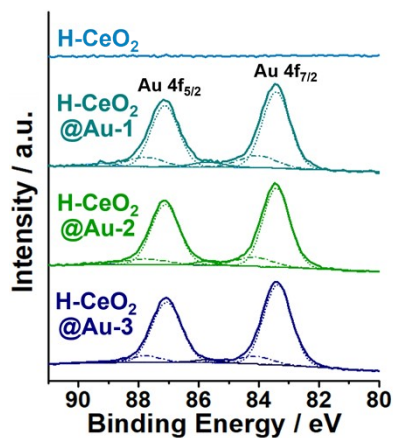
H-CeO <sub>2</sub> @Au-2	Peak	p1	p2	p3	p4	p5	p6	p7	p8	p9	p10
	Position (eV)	880.05	881.98	884.55	888.07	897.96	898.05	900.53	902.95	906.60	916.35
	FWHM	1.66	2.03	3.17	4.04	1.87	2.23	1.85	3.00	3.67	2.26
	Area (%)	2.94	16.4	13.9	10.3	1.98	16.2	11.3	9.36	6.97	10.8
r <sup>2</sup>	0.9960										

**Ce<sup>3+</sup>: Ce<sup>4+</sup> = 28.2: 71.8**

H-CeO <sub>2</sub> @Au-3	Peak	p1	p2	p3	p4	p5	p6	p7	p8	p9	p10
	Position (eV)	879.92	881.89	884.39	887.99	897.99	898.02	900.54	902.95	906.44	916.28
	FWHM	1.78	2.09	3.13	4.24	1.93	2.37	1.79	2.85	4.03	2.39
	Area (%)	2.90	15.9	12.7	11.4	1.83	17.3	10.6	8.61	7.67	11.1
r <sup>2</sup>	0.9943										

**Ce<sup>3+</sup>: Ce<sup>4+</sup> = 26.1: 73.9**

Fig. S5 Analysis of XPS Au 4f orbital spectra of H-CeO<sub>2</sub>, H-CeO<sub>2</sub>@Au-1, H-CeO<sub>2</sub>@Au-2, and H-CeO<sub>2</sub>@Au-3.



H-CeO <sub>2</sub> @Au-1	Peak	p1	p2	p3	p4	p5	p6
	Position (eV)	83.42	84.04	85.69	87.12	87.77	89.32
	FWHM	1.08	1.48	1.23	1.08	1.38	1.32
	Area (%)	43.3	9.35	3.10	34.7	7.18	2.34
	r <sup>2</sup>	0.9969					

**Au(0): Au(I): Au(III) = 1 : 0.21 : 0.070**

H-CeO <sub>2</sub> @Au-2	Peak	p1	p2	p3	p4	p5	p6
	Position (eV)	83.41	84.16	85.78	87.11	87.80	89.41
	FWHM	1.05	1.45	0.868	1.10	1.80	1.31
	Area (%)	46.6	7.49	1.74	37.2	5.70	1.27
	r <sup>2</sup>	0.9983					

**Au(0): Au(I): Au(III) = 1 : 0.15 : 0.035**

H-CeO <sub>2</sub> @Au-3	Peak	p1	p2	p3	p4	p5	p6
	Position (eV)	83.37	84.14	85.75	87.06	87.79	89.41
	FWHM	1.10	1.37	0.982	1.15	1.23	1.23
	Area (%)	48.9	5.81	1.43	38.4	4.37	1.08
	r <sup>2</sup>	0.9980					

**Au(0): Au(I): Au(III) = 1 : 0.12 : 0.029**



**Fig. S6** A  $^1\text{H}$  NMR spectrum (NMR solvent:  $\text{D}_2\text{O}$ ) of the crude products formed through the selective oxidation of PD to 3HP and MA (Note that the compounds existed as sodium salt forms due to the excess NaOH in the reaction mixture).

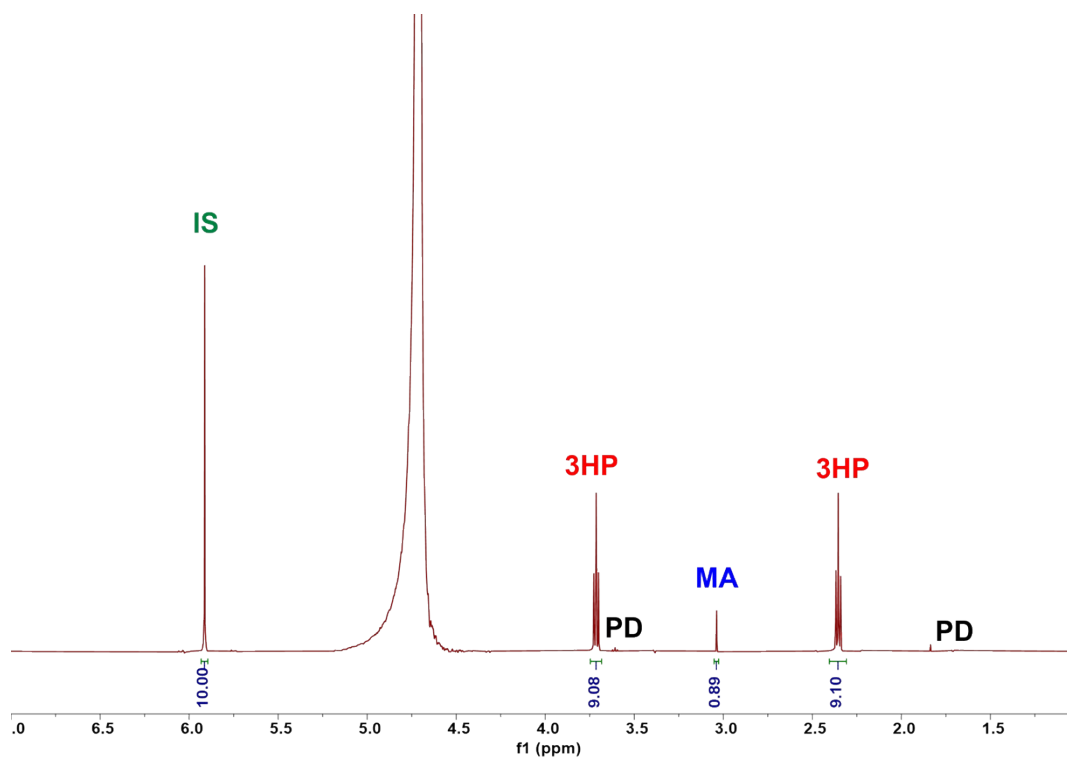
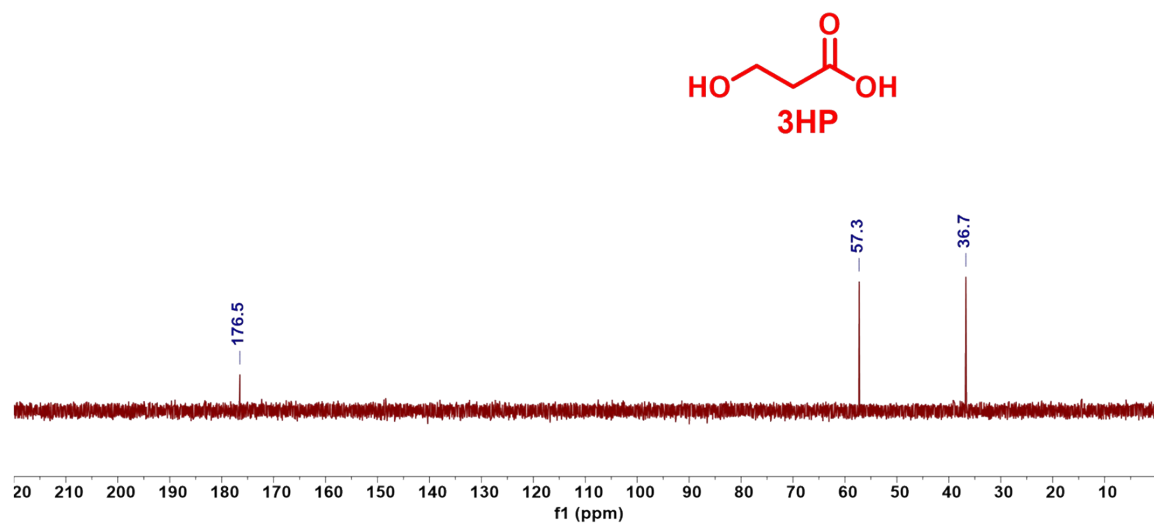
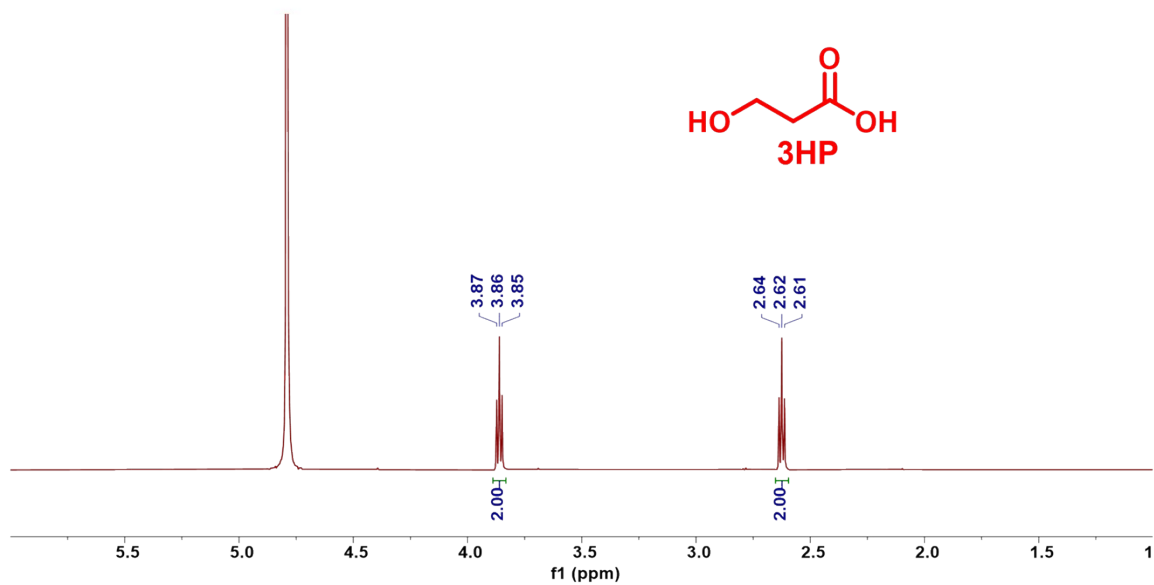


Fig. S7  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (NMR solvent:  $\text{D}_2\text{O}$ ) of isolated 3HP.



**Fig. S8** Characterization data of control N-CeO<sub>2</sub> and N-CeO<sub>2</sub>@Au-2 catalyst: (a) TEM images, (b) N<sub>2</sub> adsorption-desorption isotherm curves obtained at 77 K, and (c) PXRD patterns.

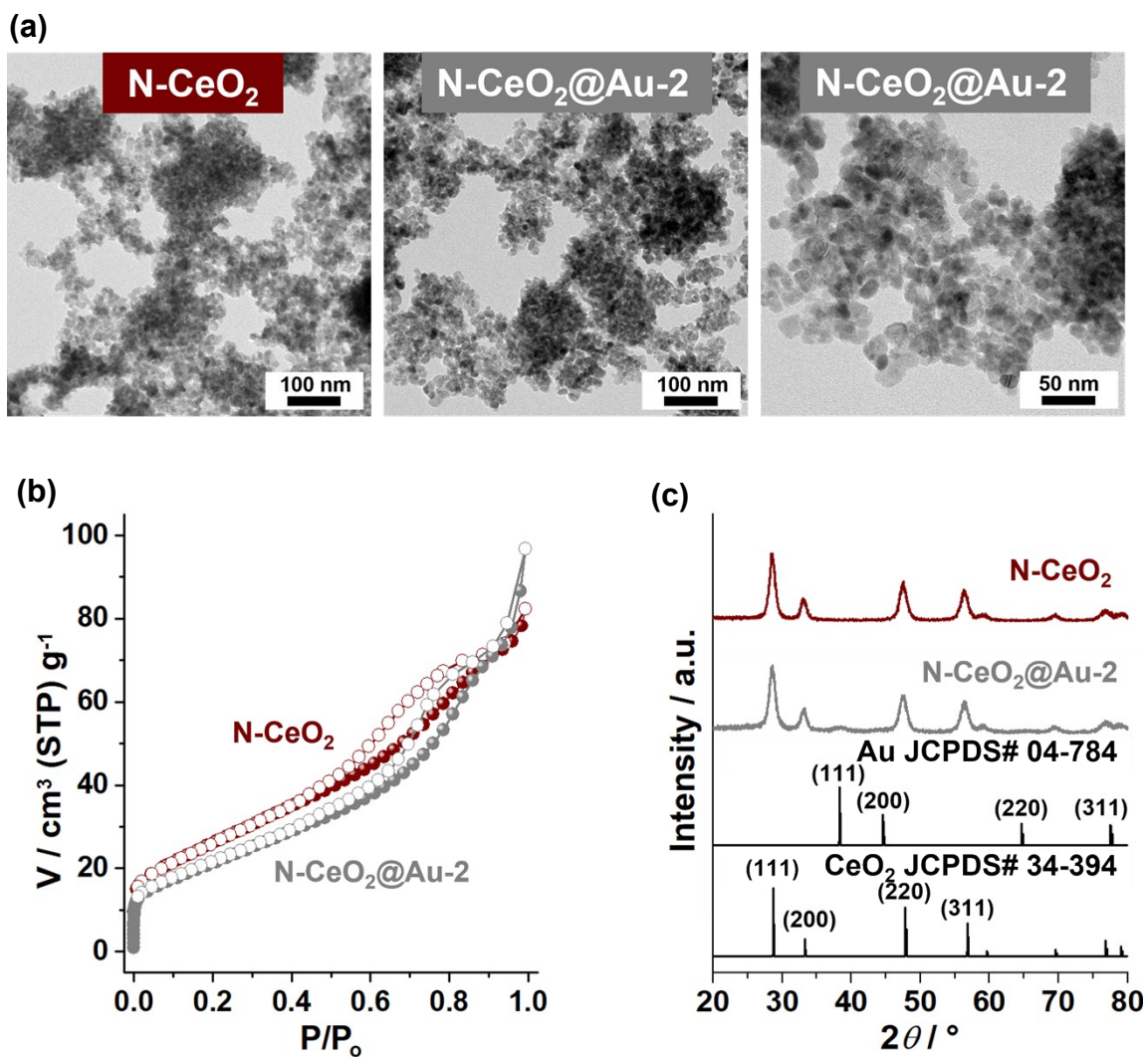
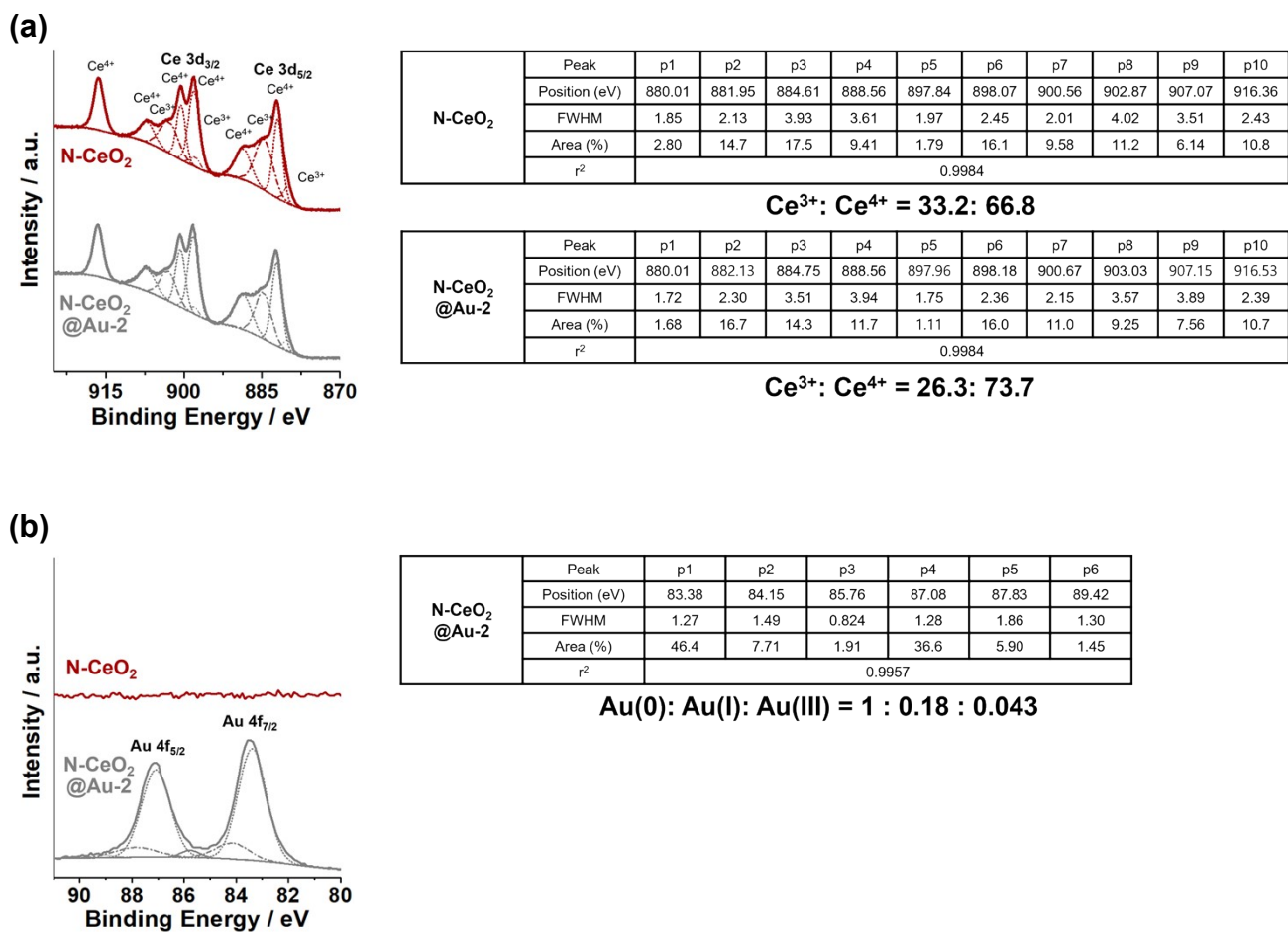
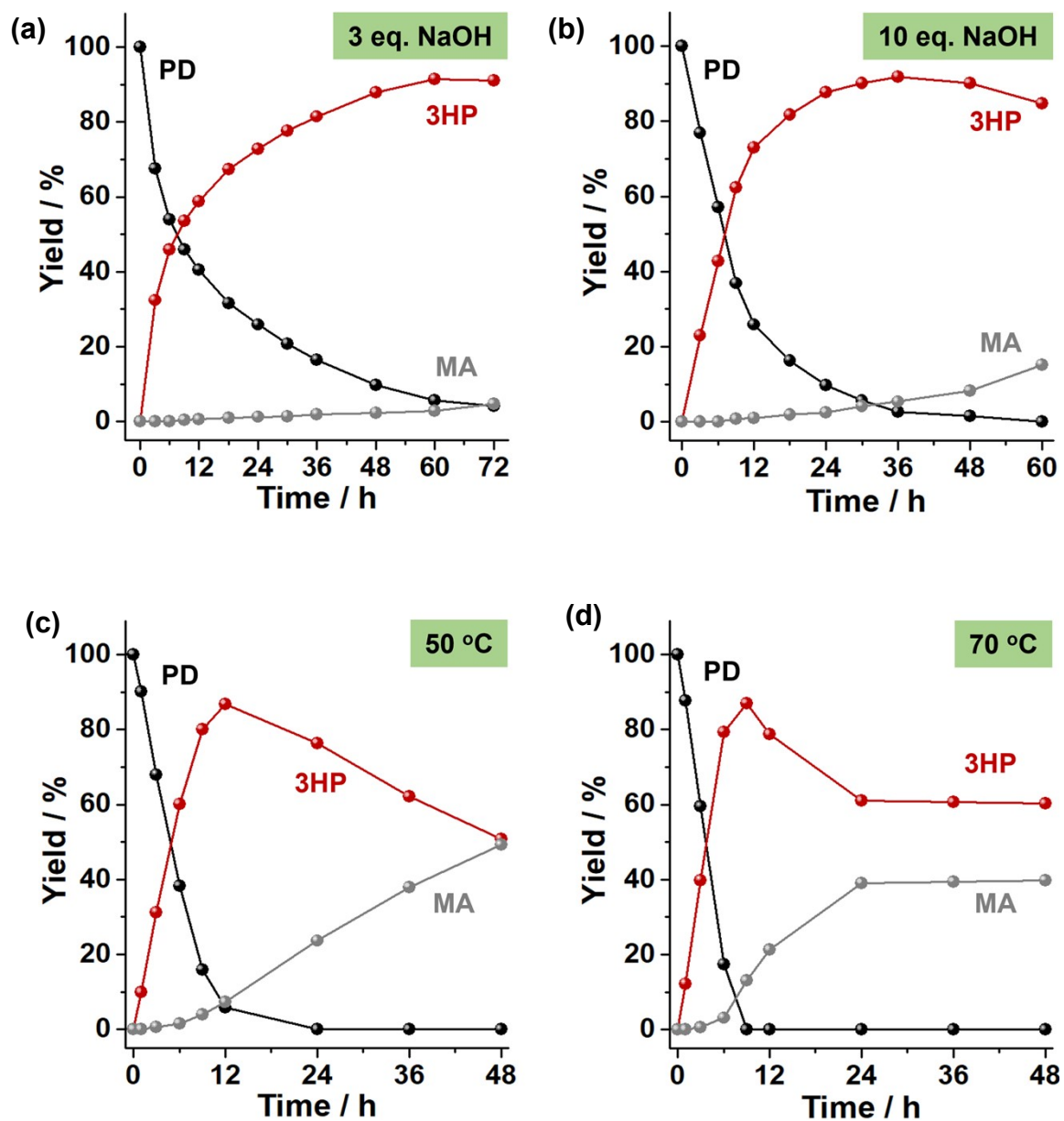


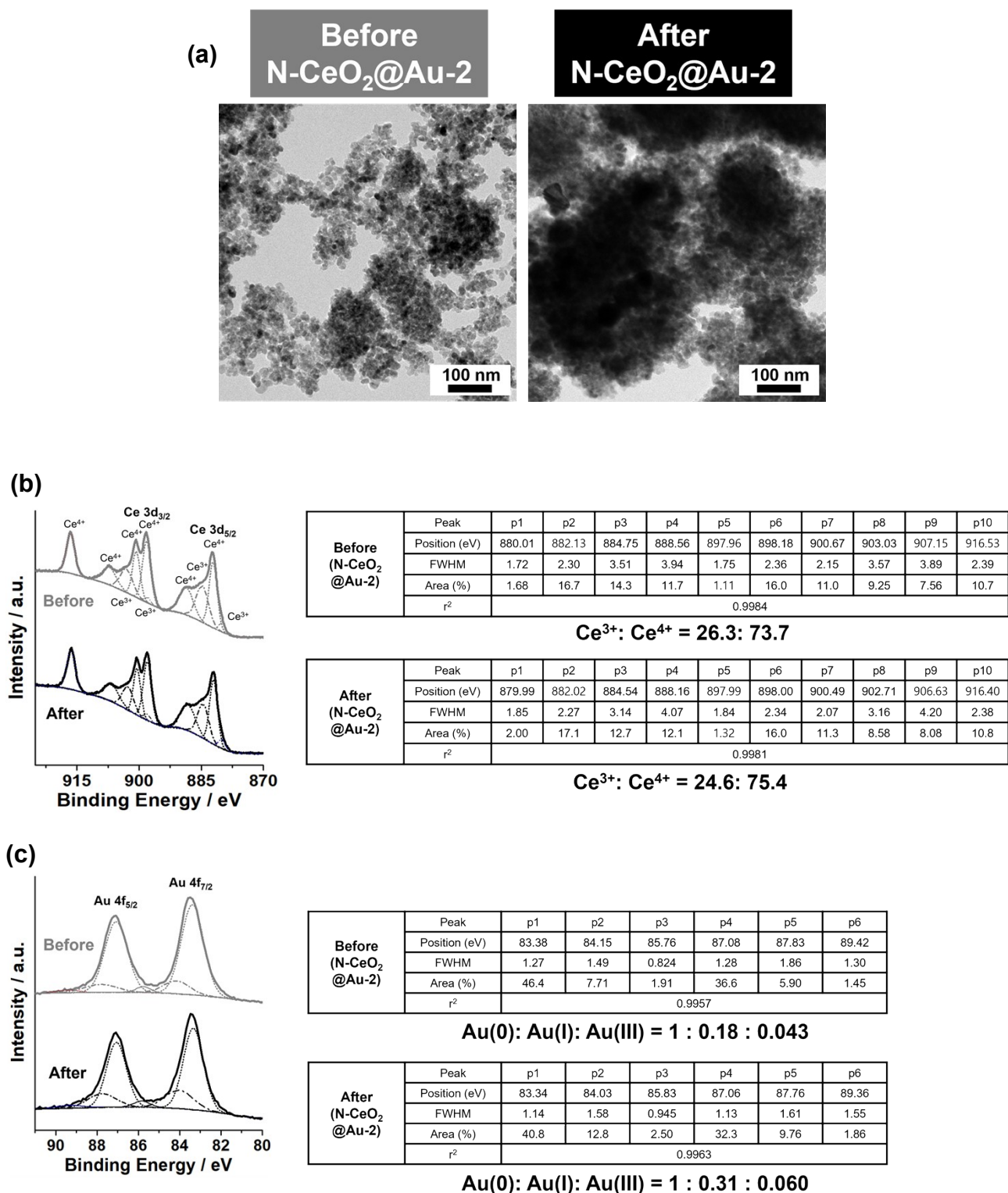
Fig. S9 Analysis of XPS (a) Ce 3d orbital and (b) Au 4f orbital spectra of N-CeO<sub>2</sub> and N-CeO<sub>2</sub>@Au-2.



**Fig. S10** (a, b) NaOH amount dependent oxidation of 1,3-propanediol (PD) to 3-hydroxypropionic acid (3HP) against malonic acid (MA) catalyzed by H-CeO<sub>2</sub>@Au-2 (1.0 mol% Au). Reaction conditions: PD (1.0 mmol), NaOH, O<sub>2</sub> (1 atm), H<sub>2</sub>O (5 mL), and room temperature. (c, d) Reaction temperature dependent oxidation of PD to 3HP catalyzed by H-CeO<sub>2</sub>@Au-2 (1.0 mol% Au). Reaction conditions: PD (1.0 mmol), NaOH (5.0 mmol), O<sub>2</sub> (1 atm), and H<sub>2</sub>O (5 mL).

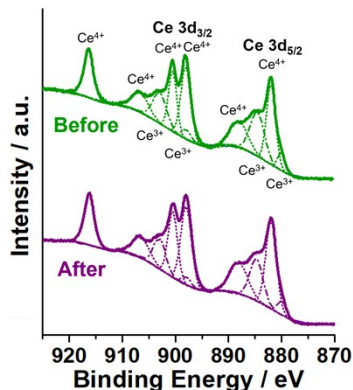


**Fig. S11** (a) TEM images and XPS (b) Ce 3d orbital and (c) Au 4f orbital spectra of control N-CeO<sub>2</sub>@Au-2 before and after five successive reactions.



**Fig. S12** Analysis of XPS (a) Ce 3d orbital and (b) Au 4f orbital spectra of H-CeO<sub>2</sub>@Au-2 before and after five successive reactions.

(a)



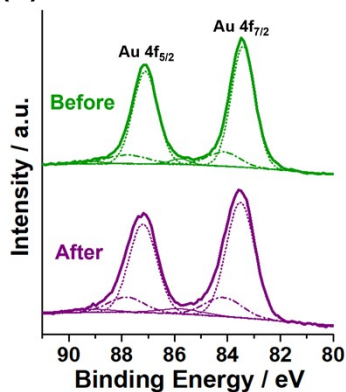
Before	Peak	p1	p2	p3	p4	p5	p6	p7	p8	p9	p10
	Position (eV)	880.05	881.98	884.55	888.07	897.96	898.05	900.53	902.95	906.60	916.35
	FWHM	1.66	2.03	3.17	4.04	1.87	2.23	1.85	3.00	3.67	2.26
	Area (%)	2.94	16.4	13.9	10.3	1.98	16.2	11.3	9.36	6.97	10.8
$r^2$	0.9960										

**Ce<sup>3+</sup>: Ce<sup>4+</sup> = 28.2: 71.8**

After	Peak	p1	p2	p3	p4	p5	p6	p7	p8	p9	p10
	Position (eV)	879.98	881.97	884.73	888.02	897.95	897.99	900.50	902.99	906.53	916.24
	FWHM	1.82	2.38	2.90	3.88	1.90	2.39	2.12	2.70	3.79	2.43
	Area (%)	2.32	18.8	11.1	10.8	1.53	17.1	12.7	7.53	6.83	11.2
$r^2$	0.9963										

**Ce<sup>3+</sup>: Ce<sup>4+</sup> = 22.5: 77.5**

(b)



Before	Peak	p1	p2	p3	p4	p5	p6
	Position (eV)	83.41	84.16	85.78	87.11	87.80	89.41
	FWHM	1.05	1.45	0.868	1.10	1.80	1.31
	Area (%)	46.6	7.49	1.74	37.2	5.70	1.27
$r^2$	0.9983						

**Au(0): Au(I): Au(III) = 1 : 0.15 : 0.035**

After	Peak	p1	p2	p3	p4	p5	p6
	Position (eV)	83.51	84.16	85.77	87.20	87.84	89.42
	FWHM	1.27	1.67	1.86	1.24	1.57	2.36
	Area (%)	44.8	9.62	2.75	33.6	7.25	2.04
$r^2$	0.9985						

**Au(0): Au(I): Au(III) = 1 : 0.21 : 0.061**

**Table S1** Catalytic performance of heterogeneous catalysts reported in the literature for the selective oxidation of 1,3-propanediol (PD) to 3-hydroxypropionic acid (3HP) or methyl ester of 3HP.

Entry	Cat	Au (mol %)	O <sub>2</sub> (bar)	Products	Temp (°C)	Time (h)	Conv. <sup>a</sup> (%)	Yield <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)	Ref
1	Au-Pb-Al <sub>2</sub> O <sub>3</sub>	-	-	Methy ester of 3HP	90	3	36	30.6	85	S1
2	Au/TiO <sub>2</sub>	0.90	21	Methy ester of 3HP	100	21	94	84.6	90	S2
3	Au <sub>0.5</sub> -Pd <sub>0.5</sub> /TiO <sub>2</sub>	0.05	10	3HP	60	1	62	58.8	94.9	S3
4	Au/CeO <sub>2</sub>	0.88	21	Methy ester of 3HP	125	8	98.1	70.2	78.8	S4
5	Au/TiO <sub>2</sub>	0.20	3	Methy ester of 3HP	80	24	39	32	82	S5
6	Au/TiO <sub>2</sub>	0.20	3	3HP	80	24	39	7	17	S5
7	Au <sub>0.8</sub> -Pd <sub>0.2</sub> -PVP/HT	0.41	flow	3HP	70	12	58	42	73	S6
8	Au/Al <sub>2</sub> O <sub>3</sub>	1.32	20	Methy ester of 3HP	100	4	92	81	88.5	S7
9	H-CeO <sub>2</sub> @Au-2	1.0	1	3HP	R.T.	48	98	91	93	This work

<sup>a</sup> Conversion yields of PD. <sup>b</sup> Yields of products. <sup>c</sup> Selectivity of 3HP or its methyl ester.

S1 T. Hayashi, T. Inagaki, N. Itayama and H. Baba, *Catal. Today*, 2006, **117**, 210-213.

S2 E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, *Green Chem.*, 2008, **10**, 408-414.

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**Table S2** Physical parameters of Co(OH)<sub>2</sub>, H-MOP, H-CeO<sub>2</sub>, H-CeO<sub>2</sub>@Au-1, H-CeO<sub>2</sub>@Au-2, H-CeO<sub>2</sub>@Au-3, control N-CeO<sub>2</sub>, and control N-CeO<sub>2</sub>@Au-2.

Materials	S <sub>BET</sub> <sup>a</sup> (m <sup>2</sup> /g)	V <sub>mic</sub> <sup>b</sup> (cm <sup>3</sup> /g)	V <sub>t</sub> <sup>c</sup> (cm <sup>3</sup> /g)
Co(OH) <sub>2</sub>	14	0	0.02
H-MOP	362	0.083	0.24
H-CeO <sub>2</sub>	50	0	0.071
H-CeO <sub>2</sub> @Au-1	49	0	0.065
H-CeO <sub>2</sub> @Au-2	46	0	0.069
H-CeO <sub>2</sub> @Au-3	45	0	0.059
Control N-CeO <sub>2</sub>	96	0	0.11
Control N-CeO <sub>2</sub> @Au-2	75	0	0.12

<sup>a</sup> Surface area obtained by a BET plot. <sup>b</sup> Micropore volume obtained by a t-plot. <sup>c</sup> Total pore volume.