Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Activating Molecular Oxygen by Au/ZnO to Selectively Oxidize Glycerol to Dihydroxyacetone

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Chemicals

Glycerol (purity ≥ 99.0%), $HAuCl_4\cdot 4H_2O$ (Au containing ≥ 47.8%), Urea (AR, purity ≥ 99.0%) and oxalic acid (AR, purity ≥ 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. ZnO (99.9%), Al_2O_3 (γ phase, 99.9%) and CeO_2 (99.95%) were purchased from Aladdin Chemistry Co., Ltd. Dihydroxyacetone (purity ≥ 98%), glycolic acid (purity ≥ 99.0%) and glyceraldehyde (purity ≥ 90%) were purchased from J&K Chemical. MgO (99.9%) and Tiron (AR) were purchase from Shanghai Macklin Biochemical Co., Ltd. Glyceric acid (20% in water) was purchased from TCI Shanghai.TiO_2 (rutile, 99.5%) was purchased from Sigma-Aldrich Chemicals. All the chemicals were used without further purification.

Characterizations

TEM images were recorded on a Hitachi JEM-2100F operated at 200 kV. Wide-angle XRD patterns were recorded on a Bruker D8 diffractometer using CuKα radiation. Electron paramagnetic resonance (EPR) signals were recorded on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3514.16 G; sweep width, 100 G; microwave frequency, 9.85 G; modulation frequency, 100 kHz; power, 6.41 mW; conversion time, 20 msec. The spin trapping experiments were performed as follows: in water system, 200 μL of 0.05 M Sodium 4,5-dihydroxybenzene-1,3-disulfonate (tiron) aqueous solution and 200 μL of catalyst suspension was mixed and quickly injected into a glass capillary tube, and was then tested by EPR spectroscopy at room temperature. In glycerol system, 200 μL tiron was mixed with 400 μL post-reaction mixture in glove box (O_2 < 0.1 ppm). The mixture was quickly injected into a glass capillary tube, sealed with lotime, and tested by EPR spectroscopy at room temperature.

Materials synthesis

Au/MO_x (M = Zn, Cu, Ti, Si, Mg, Al) catalysts were prepared by a deposition-precipitation method. In a typical preparation, 500 mg of metal oxide nanoparticles were dispersed in 25 mL of deionized (D.I.) water, followed by the addition of 1.22 g of urea and 1.045 mL of $HAuCl_4$ solution (0.024 M). Subsequently, the mixture was placed in an 80 ^{o}C oil bath under vigorously stirring for 6 h followed by aging for 12 h at room temperature. Suspension was then filtered and washed intensively with D.I. water to remove Cl^-. The solid was dried at 110 ^oC and then calcined at 200 ^oC in air for 4 h.

Experimental details for glycerol oxidation and product analysis

Catalytic glycerol oxidation was carried out in a 30 mL autoclave with 24 mg catalyst dispersed in 12 mL of 0.1 M GL. The autoclave was purged with pure oxygen for 3 times before pressuring with oxygen to 1 MPa. Stirring (650 rpm) was turned on after the inside temperature reaching 80 ^oC. A water bath was used to cool down the autoclave as soon as the reaction stopped. Reaction products, after filtered, were analyzed by high performance liquid chromatography (HPLC) equipped with a BP-OA 2000-0 column (Benson Polymeric Inc., USA) with UV (270 nm) and refractive index detection. The standard curves of the observed substances were determined first and were shown in Fig. S9. CO_2 was identified as the only gas phase product during reaction. It was collected in a gas collecting bag after reaction and detected on a GC-TCD detector equipped with a Porapak Q column. The carbon balance of the catalytic reactions was within 100 ± 2%.

NMR analysis was conducted on a Bruker AVANCE ||| 500 spectrometer, with 5 mm PABBO BB-1H/D Z-GRD probe. Deuterium oxide was used as solvent in standard sample and reaction product detection.

H_2O_2 was identified by a colorimetric method.[1] Typically, 2 mL of filtered reaction sample was acidified with 2 mL of 0.5 M H_2SO_4 and 200 μL of $TiO(SO_4)$ (15 % in 2 M H_2SO_4) solution. Absorbance at 405 nm was recorded by a UV-vis spectroscopy to quantify the formed H_2O_2. Standard curve of H_2O_2 concentration is shown in Fig. S15. Besides, H_2O_2 decomposition in different systems were also studied (Table S6).

Calculation methods

DFT calculations were carried out using a plane wave based program, Castep.[2, 3] The Perdew-Burke-Ernzerhof (PBE) functional[4, 5] was used together with the ultrasoft-core potentials.[6] The calculation models were different between oxidation of glycerol on the Au slab and O_2 adsorption onto the oxide supported Au slab.

In the former calculation, two and three layer FCC (111) oriented slab consisting of Au_{32} and Au_{48} atoms was used. The bottom layer of slab was fixed to the crystalline structure. The lattice constants were a = 11.535 Å, b = 9.980 Å, c = 30 and 40 Å (including the vacuum region, amd depending on layers), and $\alpha = \beta = \gamma = 90°$. The basis set cutoff energy was set to 300 eV for geometry optimization and 340 eV for post energy calculation. The Monkhorst-Pack method[7] was used for k-point sampling, and the number of k-points were two and three, respectively.

In the latter part of calculation, two-layer Au slabs were employed for metal oxide supports, i.e., ZnO, TiO_2 (anatase), MgO, CuO, Al_2O_3, and SiO_2. The number of Au atoms and size of unit cells depend on individual oxides, and are summarized in Table S1. The most stable and common surfaces were adopted for the support slab: TiO_2 (anatase) (101), MgO (001), and CuO (001). For ZnO, wurtzite (0001) surface was selected since both (Au and ZnO) surfaces have the hexagonal symmetry and the atomic spacing is rather similar (Au-Au: 2.884 Å and Zn-Zn: 3.225 Å). For Al_2O_3, rhombohedral structure of alumina was converted to rectangular unit cell, and cleaved at (001) surface. For SiO_2, high-temperature cristobalite structure was employed to prepare the slab. The support slab was built by cleaving at the (001) surface and adding H and OH to O and Si atoms at the bottom layer.

The basis set cutoff energies were dependent on individual unit cells, and as general case, set to 300 eV for geometry optimization and 340 eV for the energy re-evaluation.

The electron configurations of the atoms were H: $1s^1$, C: $2s^22p^2$, O: $2s^22p^4$, Mg: $2p^63s^2$, Al: $3s^23p^1$, Si: $3s^23p^2$, Ti: $3s^23p^63d^24s^2$, Cu: $3d^{10}4s^1$, Zn: $3d^{10}4s^2$, and Au $5d^{10}6s^1$.

TOF calculations

TOF values are defined as the amount of glycerol reacted per hour per surface Au site.

$$TOF = \frac{GL(mol)}{Au(mol) \times D \times t(h)} \times \frac{conv.(\%)}{100}$$

$$D = \frac{1.3}{Au\ average\ diameter(nm)}$$

D is the dispersion of Au nanoparticle on ZnO support. This method is proposed by Overbury et al.[9]

Table S1. Attributes of six unit cells of oxide support.

Oxide	Atomic composition including Au	*a*	*b*	*c*	α	β	γ
ZnO	$(ZnO)_{36}/Au_{36}$	9.7644	11.2750	30	90	90	90
CuO	$(CuO)_{36}/Au_{24}$	9.2384	10.269	30	90	99.54	90
Anatase	$(TiO_2)_{36}/Au_{32}$	10.2099	11.328	30	90	91.01	90
Al_2O_3	$Al_{42}O_{72}/Au_{18}$	14.283	8.2463	30	90	90	90
MgO	$(MgO)_{54}/Au_{32}$	12.6336	12.6336	30	90	90	90
SiO_2	$Si_{32}O_{72}H_{16}/Au_{60}$[a]	14.32	14.32	30	90	90	90

[a] Only for $Si_{32}O_{72}H_{16}$, H atoms were added to stabilize the dangling bonds. The composition, $Si_{32}O_{72}H_{16}$, is decomposed into $(SiO_2)_{32}$ + $(H_2O)_8$. Thus the stoichiometric composition of SiO_2 and the equal number of OH (bonded to Ti atom) and H (bonded to O atom) avoid artificial changes in electron density.

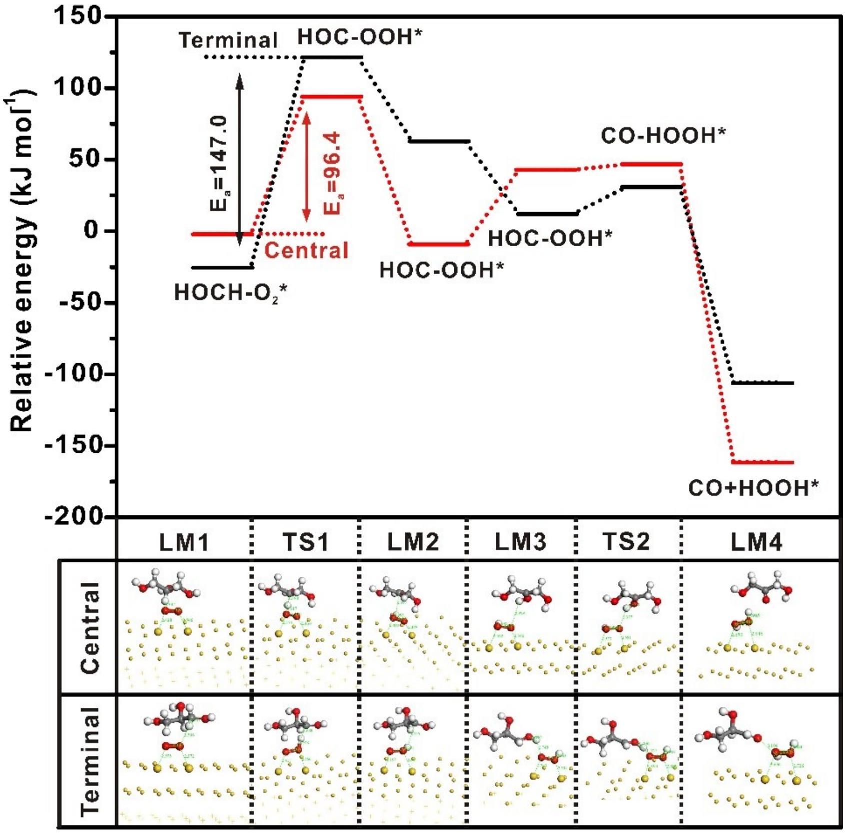

Fig. S1 Energy changes of two different reaction path-ways on a 3-layer Au model for oxidation of central OH (red line) and terminal groups (black line) of glycerol, respectively. The configurations of local minimums (LM) and transition states (TS) are listed in the bottom.

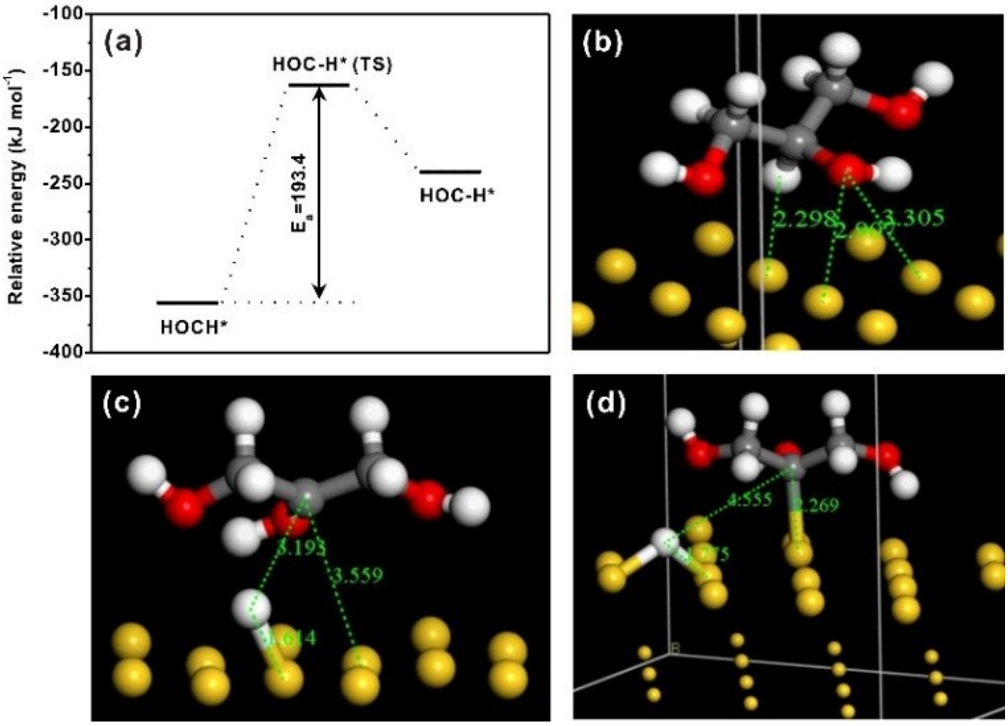

Fig. S2 Energy profile (a) and configurations (b. reactants, c. transition state and d. product) of the direct dehydrogenation of central C-H bond on Au (111). The activation energy (193.4 kJ mol^{-1}) is much higher than that of O_2 assisted dissociation of central C-H in Fig. 1 (112.3 kJ mol^{-1}).

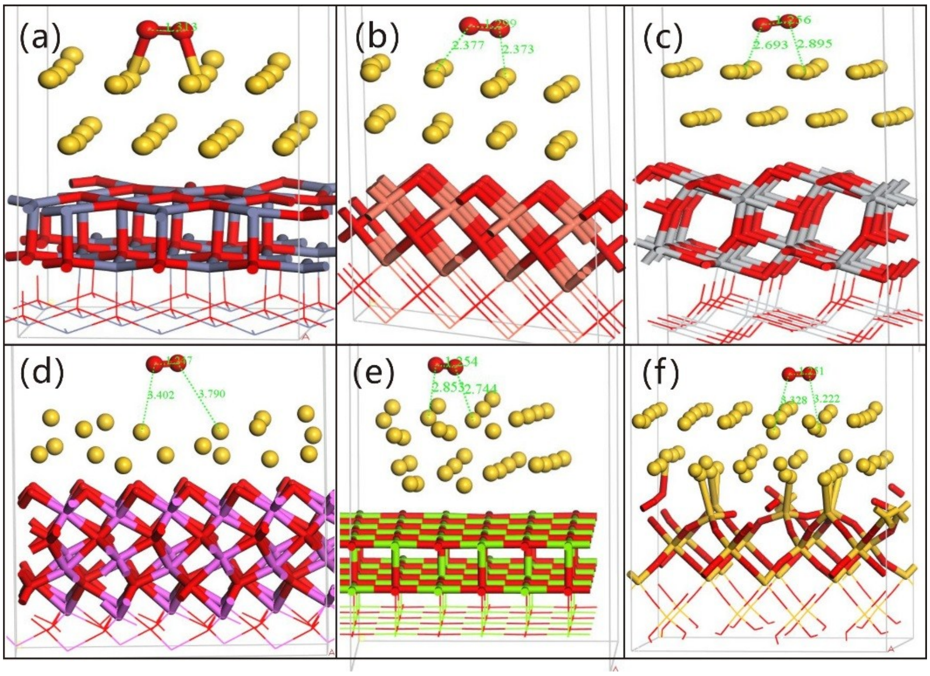

Fig. S3 (a) $(ZnO)_{36}/Au_{36}/O_2$ (O top layer) unit cell. Atoms in the bottom layers were fixed to the Zincite (Wurtzite) (0001) structure. (b) $(CuO)_{36}/Au_{24}/O_2$ (O top layer) unit cell. Atoms in the bottom layers were fixed. (c) Anatase $(TiO_2)_{36}/Au_{32}/O_2$ unit cell. Atoms in the bottom layers were fixed. (d) $Al_{42}O_{72}/Au_{18}/O_2$ unit cell. Atoms in the bottom layers were fixed. (e) $(MgO)_{54}/Au_{32}/O_2$ unit cell. Atoms in the bottom layer were fixed to the crystalline MgO (001) structure. (f) $Si_{32}O_{72}H_{16}/Au_{60}/O_2$ unit cell. Atoms in the bottom layers were fixed.

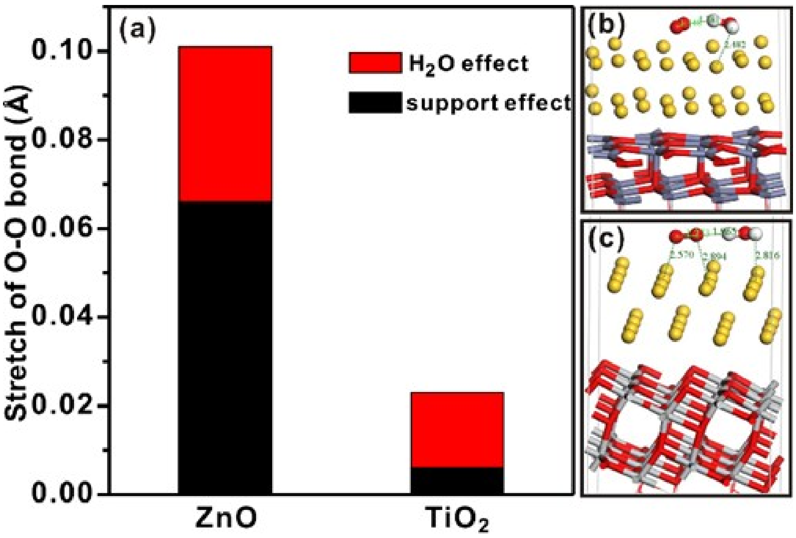

Fig. S4 (a) O-O bond stretch on Au/ZnO and Au/TiO$_2$ in the presence of water; the models for oxygen adsorption on Au/ZnO (b) and Au/TiO$_2$ (c).

Table S2. Dissolved O_2 under different O_2 partial pressure at 80 °C.

O_2 pressure (atm)	Total O_2 (mmol)	Dissolved O_2 (umol)	Converted GL (umol)[a]	GL conv. (%)
0.17	0.5	1.6	69.1	1.9
0.33	0.9	3.2	149.9	4.2
0.67	1.9	6.5	239.1	6.6
1	2.8	9.7	281.9	7.8
2	1.6	19.3	334.6	9.3
4	3.2	38.6	316	8.8
6	4.8	58	353.7	9.8
8	6.4	77.3	322.8	9
10	8	96.6	325.4	9

[a] The total amount of GL is 3.6 mmol.

The dissolved O_2 concentration at different p_{O2} is calculated according to Henry's Law:

$p_{O2} = k_H \times c$,

where k_H is a temperature-dependent constant (770 $L\cdot atm\ mol^{-1}$ for O_2 in water at 25 °C, and 1242 $L\cdot atm\ mol^{-1}$ at 80 °C), c is the concentration of the dissolved O_2 in water.

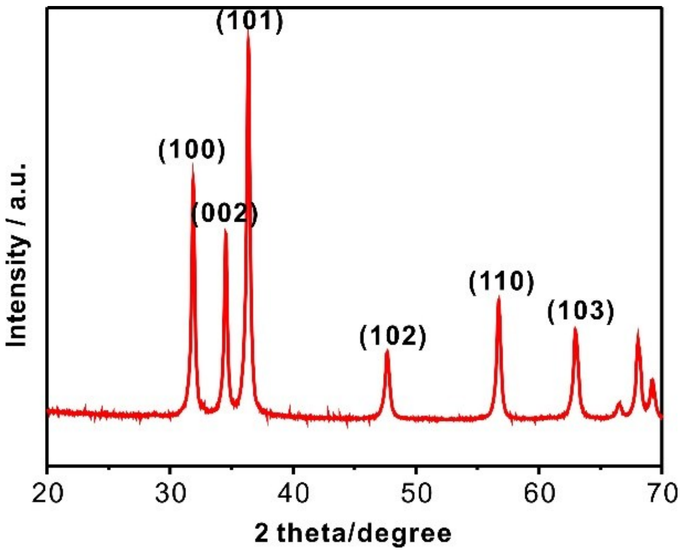

Fig. S5 XRD pattern of 1 wt.% Au/ZnO, marked peaks can be indexed to zincite ZnO.

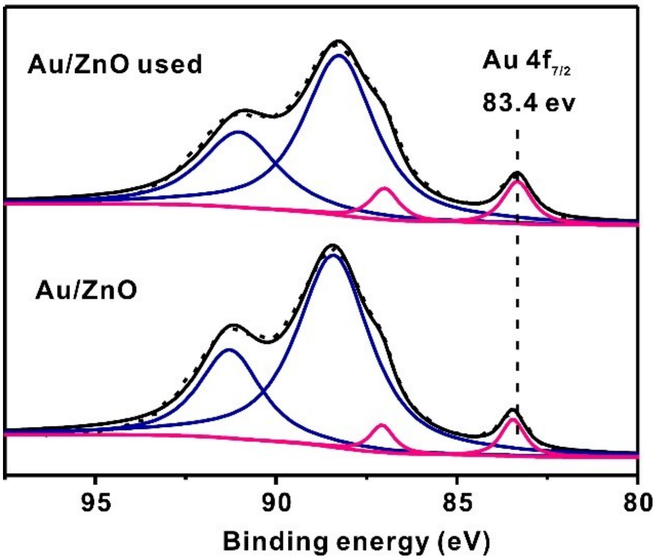

Fig. S6 XPS spectra of Au/ZnO before and after reaction.

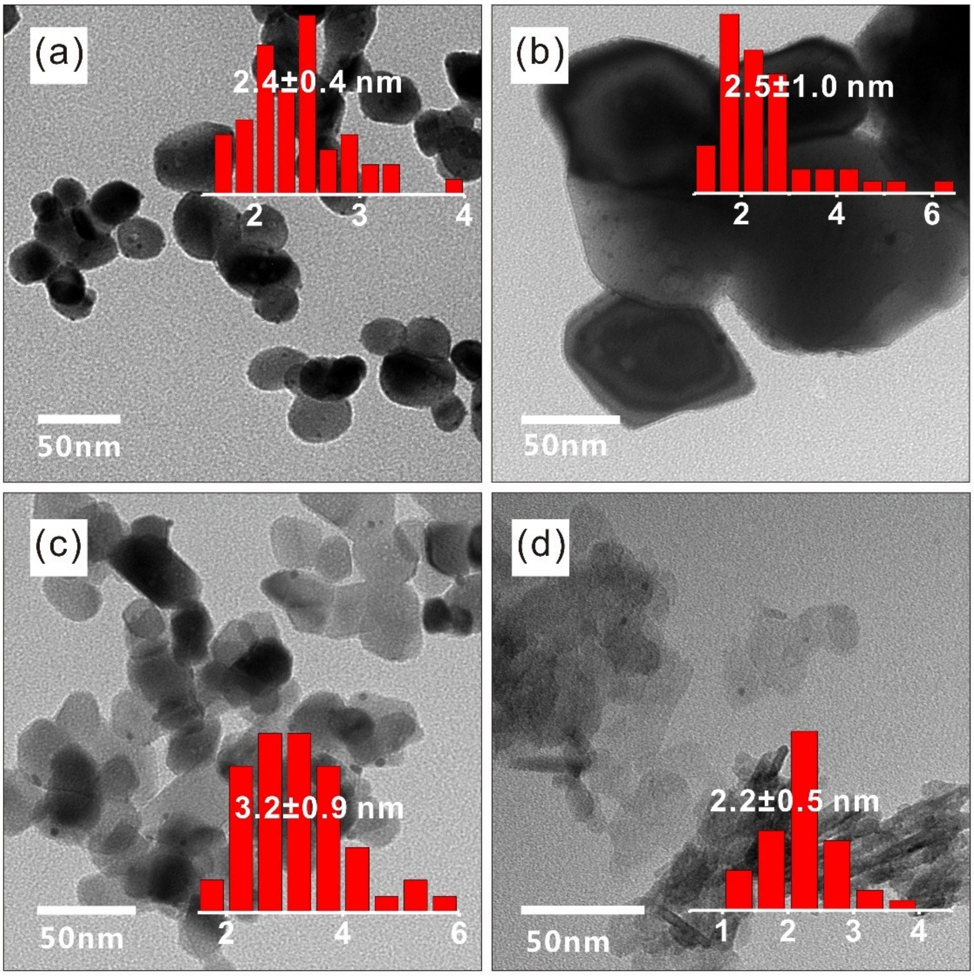

Fig. S7 AuNPs supported on different metal oxides, (a) CuO, (b) CeO_2, (c) TiO_2, (d) Al_2O_3. The size distribution is based on the statistics of 50 nanoparticles.

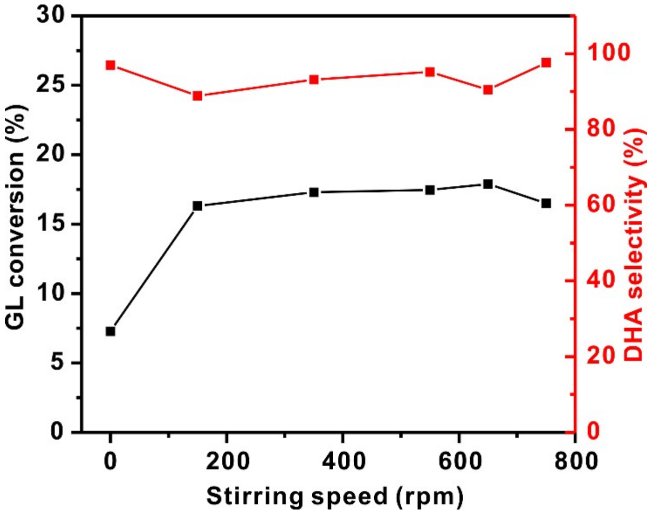

Fig. S8 The conversion of glycerol as a function of stirring speed. Experimental conditions: 12 mL of 0.1 M GL, 24 mg of 1 wt.% Au/ZnO catalyst (GL/Au = 1000 mol/mol), reaction temperature = 80 °C, P_{O2} = 1 MPa, reaction time = 1 h.

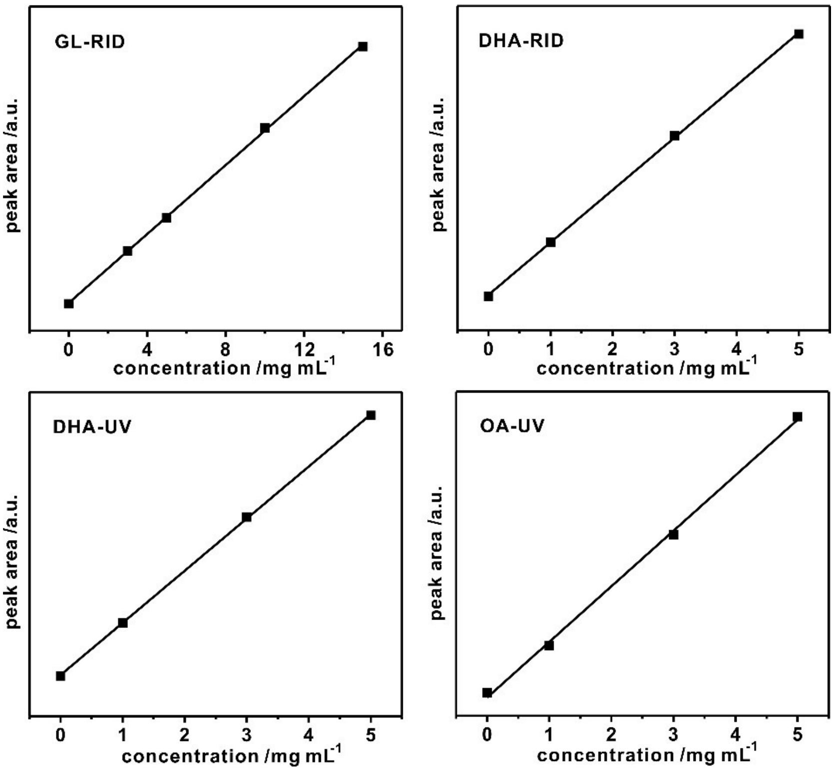

Fig. S9 HPLC quantitative analysis standard curves of GL (RID detector), DHA (RID and UV detector) and OA (UV detector).

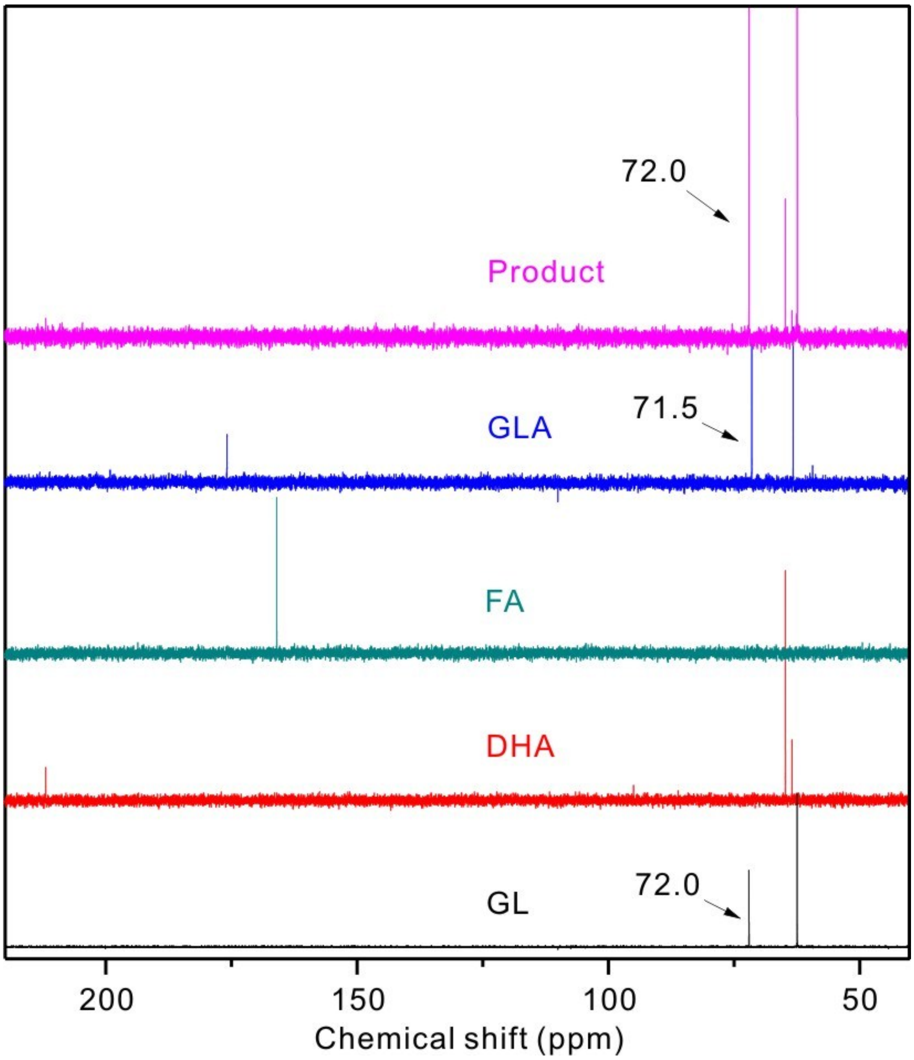

Fig. S10 NMR spectra of GL, DHA, FA, GLA standard sample and catalytic reaction product using Au/ZnO as catalyst in base-free conditions. As is well-known, there is a difficulty in product analysis in glycerol oxidation, especially for dihydroxyacetone and formic acid.[8] To this end, NMR was utilized as a tool to verify the result obtained from HPLC. Clearly, the main product is DHA, consistent with HPLC analysis. No NMR peak was detected at 166 ppm , excluding the production of formic acid.

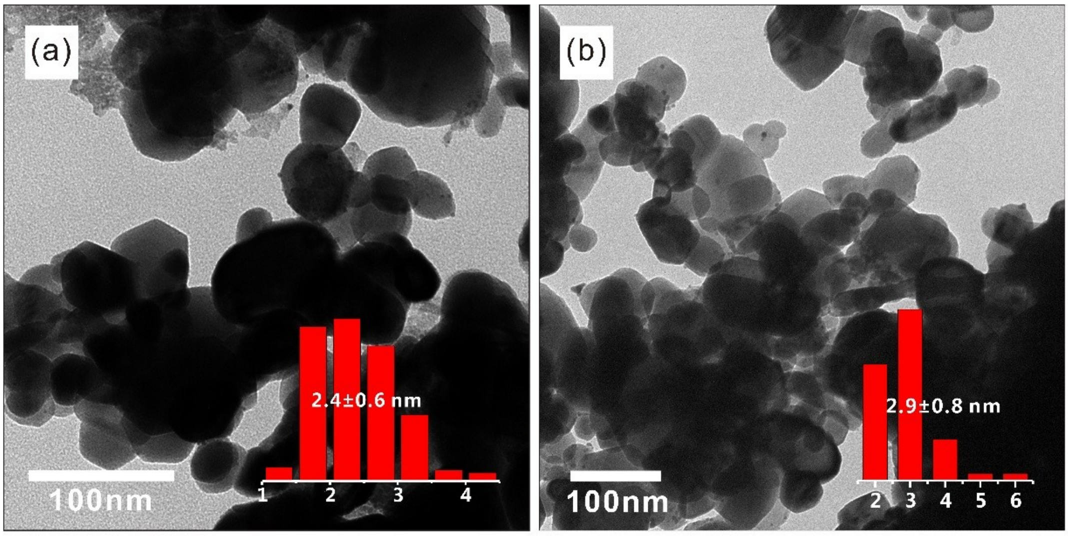

Fig. S11 Au/ZnO (a) before and (b) after reaction. Everage size of Au nanoparticle increased from 2.4 nm to 2.9 nm, indicating a slight agglomeration of Au during reaction. ZnO nanoparticle showed the same morphology before and after reaction.

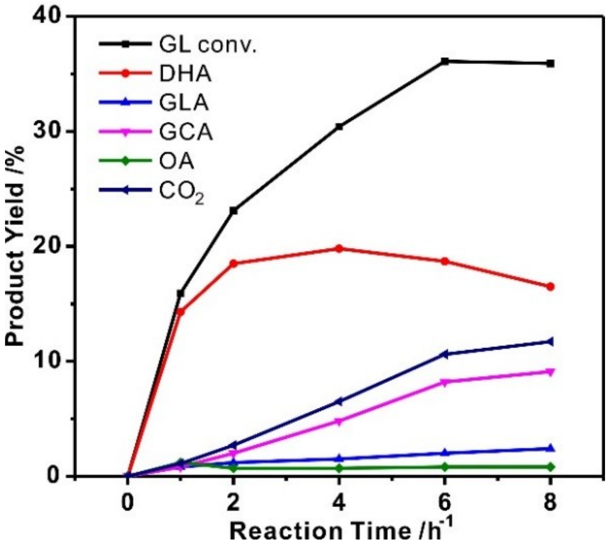

Fig. S12 Glycerol conversion and product yield at prolonged reaction time. 1 wt.% Au/ZnO catalyst was used (GL/Au = 1000 mol/mol).

Table S3. Catalytic Oxidation of DHA.

Catalyst	**Product sel. (Carbon %)**			**DHA conv. (%)**
	GLA	GCA	OA	
Au/ZnO	66.5	5.9	27.6	15.4

Reaction conditions: 12 mL of 0.1 M DHA, 24 mg of 1 wt.% supported Au catalyst (DHA/Au = 1000 mol/mol), reaction temperature = 80 ^{o}C, P_{O2} = 1 MPa, stirring speed = 650 rpm, reaction time = 2 h.

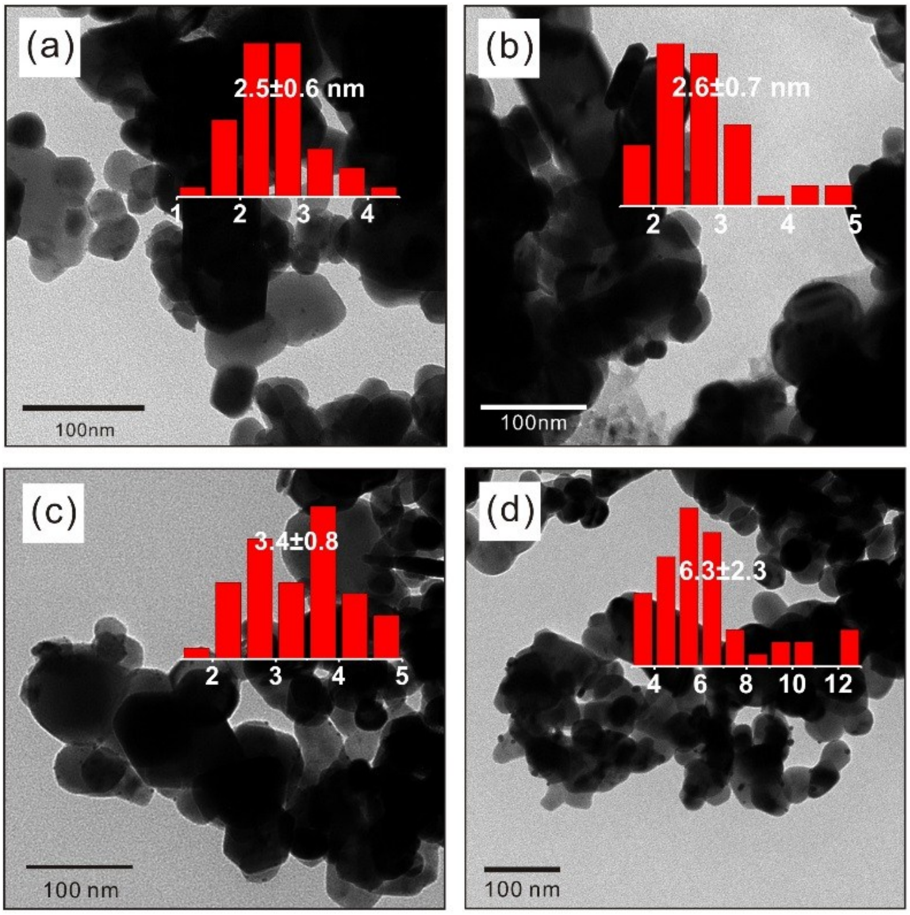

Fig. S13 Au/ZnO catalysts with different Au NPs average sizes (a) 2.5 nm, (b) 2.6 nm, (c) 3.4 nm and (d) 6.3 nm.

Table S4. Glycerol Oxidation over Au/ZnO with different Au NPs sizes.

size (nm)	GL conv. (%)	Product sel. (%)					TOF (h^{-1})
		DHA	OA	GLA	GCA	CO_2*	
2.5	27.0	82.2	3.0	2.6	3.2	NA	256
2.6	26.7	81.6	1.7	3.4	3.2	NA	263
3.4	18.7	84.0	3.6	3.7	/	NA	241
6.3	10.6	91.5	3.8	7.5	/	NA	253

Reaction conditions: 12 mL of 0.1 M GL, 24 mg of 1 wt.% supported Au catalyst (GL/Au = 1000 mol/mol), reaction temperature = 80 ^{o}C, P_{O2} = 1 MPa, stirring speed = 650 rpm, reaction time = 2 h. *The gas phase product (CO_2) was not analyzed. TOF values are defined as glycerol reacted per hour per surface Au site. The TOF are roughly the same for different-sized Au nanoparticles, excluding the obvious size effect.

Table S5. Catalytic Glycerol Oxidation over Au supported on ZnO of different morphologies.

ZnO morphologies	Product sel. (Carbon %)					GL conv. (%)	TOF (h^{-1})
	DHA	OA	GLA	GCA	CO_2		
nanoparticle	81.9	1.9	3.7	2.8	2.9	21.6	205
nanorod	88.8	6.0	2.7	/	NA	22.3	211
bulk	88.6	5.6	4.8	/	NA	16.7	158

Reaction conditions: 12 mL of 0.1 M GL, 24 mg of 1 wt.% supported Au catalyst (GL/Au = 1000 mol/mol), reaction temperature = 80 ^{o}C, P_{O2} = 1 MPa, stirring speed = 650 rpm, reaction time = 2 h.

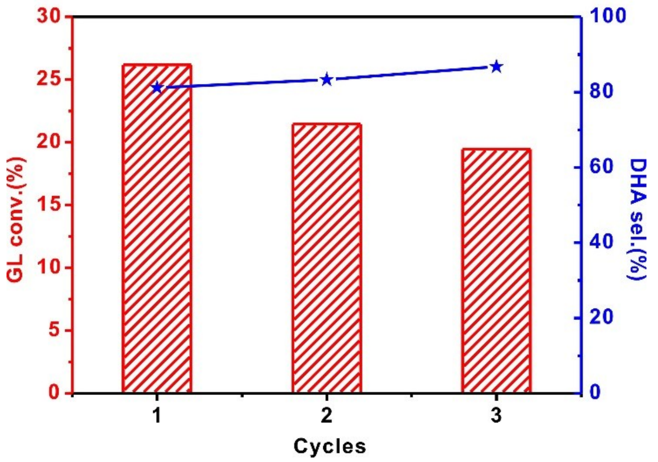

Fig. S14 Recycle tests for glycerol oxidation on Au/ZnO catalyst. Experimental conditions: 12 mL 0.1 M GL, 24 mg 1 wt.% Au/ZnO catalyst (GL/Au = 1000 mol/mol), reaction temperature = 80 ^{o}C, P_{O2} = 1 MPa, stirring speed = 650 rpm, reaction time = 2 h.

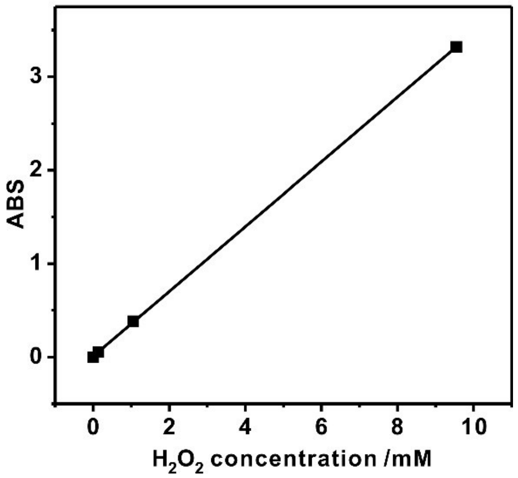

Fig. S15 Standard curve of H_2O_2 concentration.

Table S6. H_2O_2 decomposition in different reaction systems.

Substrates	H_2O_2 concentration (mM)		H_2O_2 decomposition (%)	GL conversion (%)	DHA selectivity (%)
	Before reaction	After reaction			
H_2O	50	35.4	29	/	/
H_2O+Au/ZnO	50	0	100	/	/
0.1M GL	50	17.1	66	0	0
0.1M GL+Au/ZnO	50	0.37	99	25.9	80.7

Reaction conditions：0.05 M of H_2O_2, 12 mL of H_2O/0.1 M GL, 24 mg of 1 wt.% Au/ZnO, 80 ^{o}C, P_{O2} = 1 MPa, stirring speed = 650 rpm, reaction time = 2 h.

Table S7. H_2O_2 concentration detected after reaction.

	H_2O_2 concentration (mM)	Theoretical H_2O_2 concentration (mM)	H_2O_2 decomposition (%)
Au/ZnO	0.47	24.1	98.0
Au/TiO_2	0.20	1.3	84.6
Au/Al_2O_3	0.13	3.9	96.7
Au/ZnO*	0	/	/

Reaction conditions: 12 mL 0.1 M GL, 24 mg 1 wt.% Au/MO_x catalyst (GL/Au = 1000 mol/mol), reaction temperature = 80 ^{o}C, P_{O2} = 1 MPa, stirring speed = 650 rpm, reaction time = 2 h.

*12 mL H_2O without glycerol.

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