Electronic Supplementary Information

Highly Active and Sintering-resistant Au/FeO$_x$-hydroxyapatite Catalyst for CO Oxidation

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1. Catalysts Preparation

1.1 Synthesis of FeO$_x$

At room temperature (~25 °C), an aqueous solution of Fe^{3+} and Fe^{2+} (mole ratio was 2:1) obtained by dissolving $FeCl_3{\cdot}6H_2O$ (14.8 mmol) and $FeCl_2{\cdot}4H_2O$ (7.4 mmol) in deoxygenated water (120 ml) under Ar atmosphere was added dropwise to a 25% ammonia water (60 ml) under vigorous stirring. Black precipitates appeared instantly. After being stirred for 45 min, the resulted black suspension was heated to 90 °C and continuously stirred for 2 h, and then cooled to room temperature and aged overnight. The black precipitates were filtered, washed repeatedly with deionized water till neutrality, freeze-dried and calcined at 400 °C for 5 h. The final brownish red powder was FeO$_x$ and denoted as F in this work.

1.2 Synthesis of Hydroxyapatite

At room temperature (~25 °C), two 80 ml aqueous solutions of $Ca(NO_3)_2{\cdot}4H_2O$ (33.7 mmol) and $(NH_4)_2HPO_4$ (20 mmol), with pH being separately adjusted to 10.3, were simultaneously added dropwise to a 25% ammonia water (15 ml) under vigorous stirring. The resultant milky like suspension was heated to 90 °C immediately and stirred continuously for 2 h, and then cooled to room temperature and aged overnight. The white precipitates were filtered, washed repeatedly with deionized water till neutrality, freeze-dried and calcined at 400 °C for 5 h. The final white powder was hydroxyapatite (HAP) and denoted as H in this work.

1.3 Synthesis of FeO$_x$-HAP

At room temperature (~25 °C), an aqueous solution of Fe^{3+} and Fe^{2+} (mole ratio was 2:1) obtained by dissolving $FeCl_3·6H_2O$ (3.7 mmol) and $FeCl_2·4H_2O$ (1.85 mmol) in deoxygenated water (30 ml) under Ar atmosphere was added dropwise to a 25% ammonia water (15 ml) under vigorous stirring, as mentioned in section 1.1. After being stirred for 15 min, two 80 ml aqueous solutions of $Ca(NO_3)_2·4H_2O$ (33.7 mmol) and $(NH_4)_2HPO_4$ (20 mmol), with pH being adjusted to 10.3 as mentioned in section 1.2, were added dropwise simultaneously. The resultant grey suspension was heated to 90 °C immediately and stirred for 2 h, and then cooled to room temperature and aged overnight. The obtained red brown precipitates were filtered, washed repeatedly with deionized water till neutrality, freeze-dried and calcined at 400 °C for 5 h. The final brown powder was FeO_x modified HAP, FeO_x-HAP, which was denoted as FH.

1.4 Depositing Au on Supports

Gold was deposited onto the three supports via a deposition-precipitation method. Typically, 40 ml $HAuCl_4$ aqueous solution (1.25 mg_{Au}/ml) was taken into a beaker, and its pH value was adjusted to 9 by dropwise addition of aqueous solution of 0.1 M NaOH under vigorous stirring and monitored with a pH meter. 1.0 g supports (F, H and FH) were separately added to the solution under stirring, and the pH values of the resulted suspension were readjusted to 9 by 0.1 M NaOH aqueous solution. Then the suspension was heated to 65 °C and stirred for 1 h. The precipitates were filtered, washed with deionized water for several times and then dried at 60 °C overnight. The samples only dried at 60 °C (denoted as Au/F-60, Au/H-60 and Au/FH-60), were further calcined at 400 °C for 3 h (denoted as Au/F-400, Au/H-400 and Au/FH-400), 600 °C for 3 h (denoted as Au/F-600, Au/H-600 and Au/FH-600), respectively.

2. Measurement of Catalytic Activity

The catalytic performances of the prepared samples for CO oxidation were evaluated in a fixed-bed reactor. 100 mg of the catalyst powder diluted with about 130 mg SiC was loaded in a U-shape quartz reactor (with length of 200 mm and inner diameter of 8 mm) and was purged with He for 30 min. The resultant height of catalyst bed was about 4~5 mm. Then, the feed gas containing 1 vol% CO, 1 vol% O_2 and balance He was allowed to pass through the reactor at a flow rate of 33.3 ml/min (corresponding to a space velocity of ~20,000 $\mathrm{ml\,g_{cat}^{-1}\,h^{-1}}$). The effluent gas compositions were on line analyzed by a gas chromatograph (HP 6890) equipped with a TDX-01 column and a thermal conductivity detector using He as carrier gas. As a reference, a 4.4 wt% Au/Fe_2O_3 standard catalyst (type C, provided by World Gold Council (WGC), denoted as Au/F-WGC) was also evaluated for comparison. The durability measurements under reaction conditions were performed at 24 °C and 50 mg catalysts were used to avoid reaching 100% CO conversion, resulting in a space velocity of 40,000 $\mathrm{ml\,g_{cat}^{-1}\,h^{-1}}$. The CO conversion was calculated based on the difference between inlet and outlet concentrations.

For measuring the specific reaction rate, the catalytic CO oxidation reaction was conducted at a differential mode where the CO conversion was controlled below 20 %. For this purpose, certain amounts of the sample (3 ~ 167 mg) with a size of 200 mesh was diluted with SiC (300 ~ 400 mg, size was also around 200 mesh). The resultant height of catalyst bed was about ~8 mm. For each run at a specified reaction temperature (24 ^{o}C), the CO conversions at 20, 40, and 60 min were averaged and used for calculation of the specific rate. The turnover frequency (TOF) was then calculated based on the specific rate and the dispersion of Au nanoparticles, which was roughly estimated according to the relationship between the dispersion and particle size, i.e. $D = 0.9/d_{\mathrm{Au}}$, where d_{Au} means average diameter of Au nanoparticles.

3. Characterization Techniques

The actual Au and Fe loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The Brunauer-Emmett-Teller (BET) specific surface areas were measured by nitrogen adsorption at -196 ^{o}C on a Micromeritics ASAP 2010 apparatus.

The binding energy of the surface Au species was determined by X-ray photoelectron spectra (XPS) on an ESCALAB250 X-ray photoelectron spectrometer with contaminated C as internal standard (C_{1s}=284.5 eV).

The morphologies of the prepared samples were observed with transmission electron microscopy (TEM) using a JEOL JEM-2000EX microscope operated at 120 kV. Before the TEM experiments, the samples were ultrasonically dispersed in ethanol and then a drop of the solution was put onto a copper grid coated with a thin holey carbon film.

X-ray diffraction (XRD) patterns were collected at a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm), operating at 40 kV and 40 mA. A continuous mode was used for data collecting in the 2θ range from 10 to 80 ^{o}.

The ^{57}Fe Mössbauer spectra of the prepared samples were recorded on a Topologic 500A spectrometer and a proportional counter at room temperature. ^{57}Co(Rh) moving in a constant acceleration mode was used as radioactive source.

Table S1 Reaction rate and turnover frequency (TOF) of supported Au catalysts

	Diameter of Au[a] (nm)	Diameter of FeO_x[b] (nm)	B. E. of $Au_{4f7/2}$ (eV)	Specific rate×10^2 ($mol_{CO}/g_{Au}/h$)	TOF×10^3 (s^{-1})[c]	Reaction temperature[d] (°C)
Au/F-60	U.D.[e]	10	84.1	378.0	230.0	24
Au/F-400	2.7	14	83.4	16.1	26.4	24
Au/F-600	7.7 (9[b])	26	83.4	0.9	4.3	24
Au/H-60	U.D.[e]	--	84.7	24.6	15.0	24
Au/H-400	2.4	--	83.6	15.5	22.6	24
Au/H-600	4.5	--	83.7	3.8	10.3	24
Au/FH-60	U.D.[e]	5	84.3	174.0	106.0	24
Au/FH-400	2.2	5	83.6	63.0	84.3	24
Au/FH-600	4.5	7	83.8	7.1	19.4	24
Au/F-WGC	4.0	--	--	18.5	44.9	24
Au/F-WGC-600	10.0[b]	--	--	1.1	6.4	24

[a] measured by TEM, [b] measured by XRD, [c] dispersion was calculated according to the formula $D = 0.9/d_{Au}$, where *d* means diameter, [d] controlled by water bath. [e] undetected

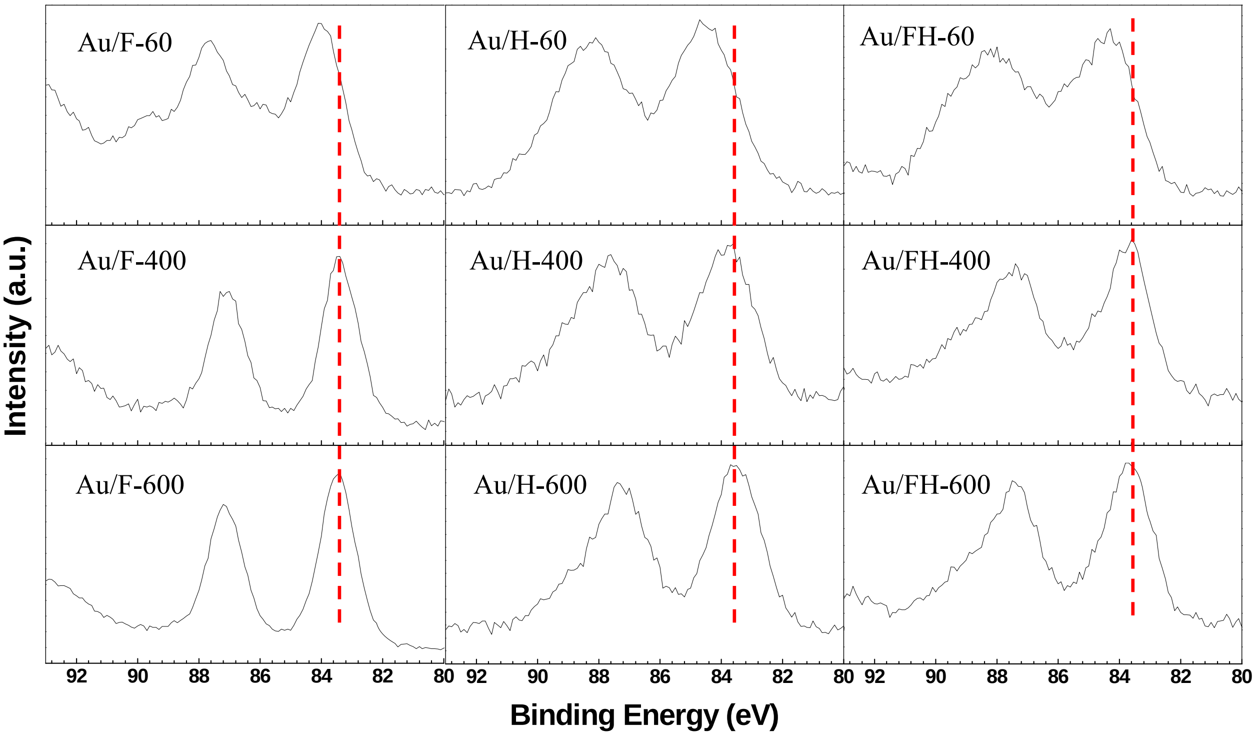

Fig. S1 XPS spectra of Au/F, Au/H and Au/FH calcined at different temperatures

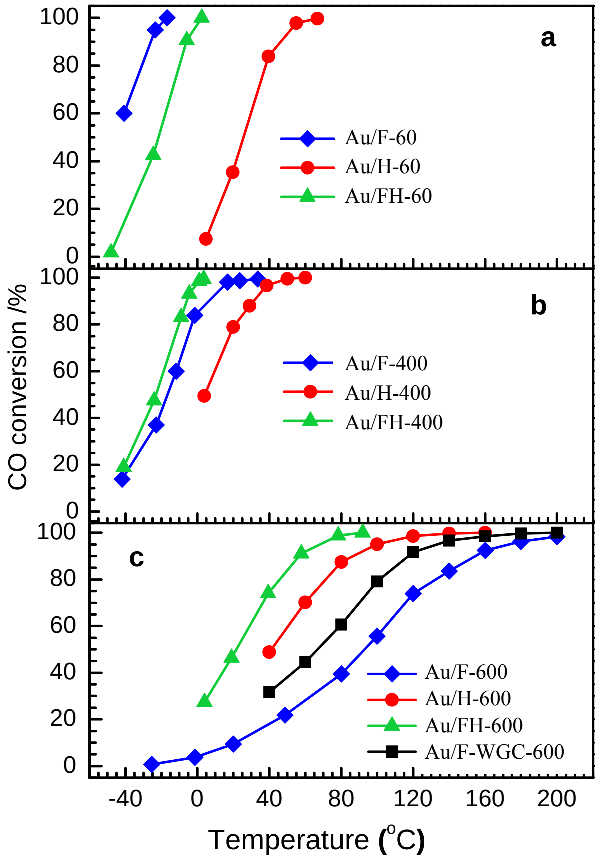

Fig. S2 CO conversion as a function of temperature over Au/F (diamond), Au/H (cycle), Au/FH (triangle) with different heat treatment: (a), dried at 60 °C, (b), calcined at 400 °C and (c), calcined at 600 °C and over Au/F-WGC calcined at 600 °C (square). Reaction condition: CO : O_2 : He = 1 : 1 : 98, GHSV = 20,000 $\mathrm{ml\,g_{cat}^{-1}\,h^{-1}}$

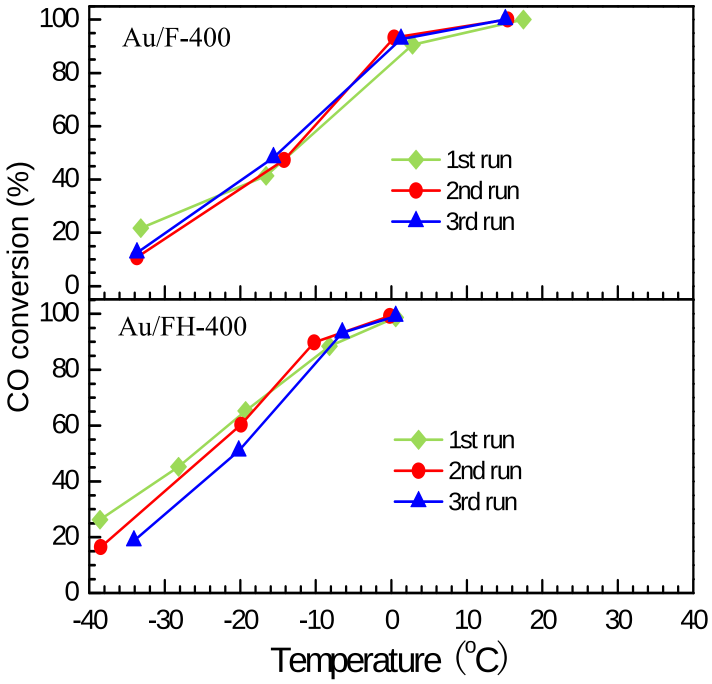

Fig. S3 CO oxidation curves of Au/F-400 and Au/FH-400 catalysts for cycle use. CO : O_2 : He = 1 : 1 : 98, GHSV = 20,000 $\mathrm{ml\,g_{cat}^{-1}\,h^{-1}}$

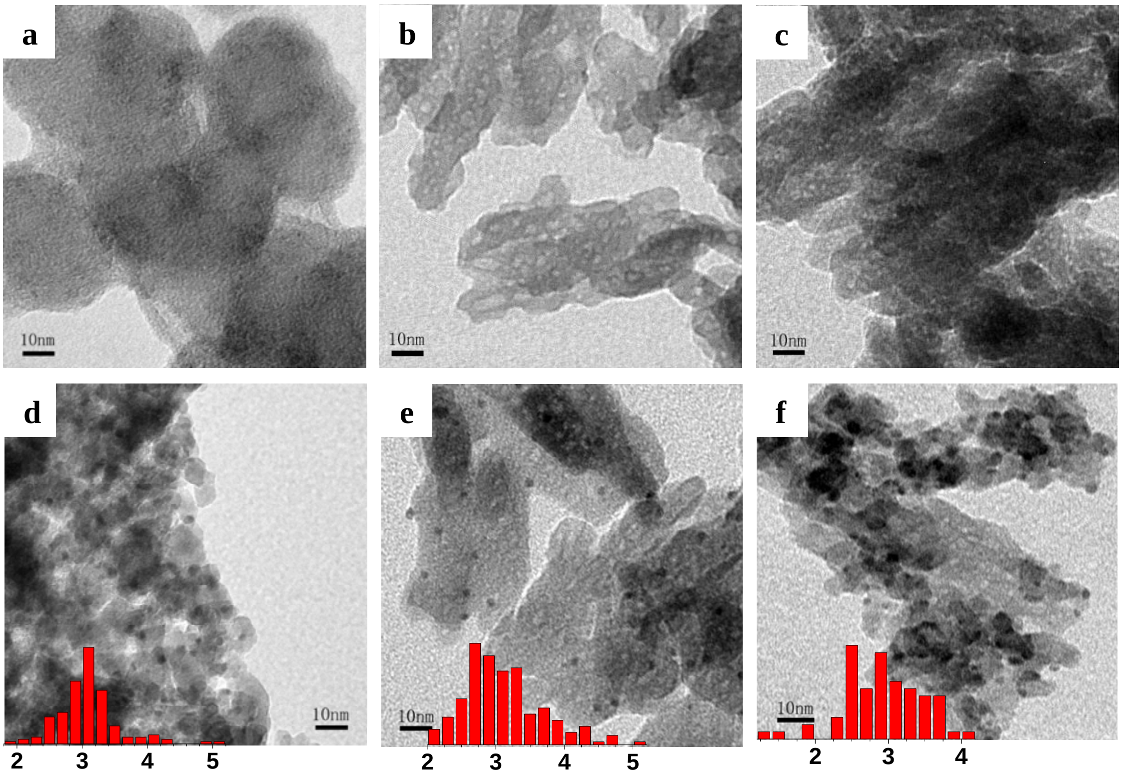

Fig. S4 TEM images of as synthesized Au/F-60 (a), Au/H-60 (b), Au/FH-60 (c) and Au/F-400 (d), Au/H-400 (e), Au/FH-400 (f) after stability tests, all the scale bars correspond to 10 nm.

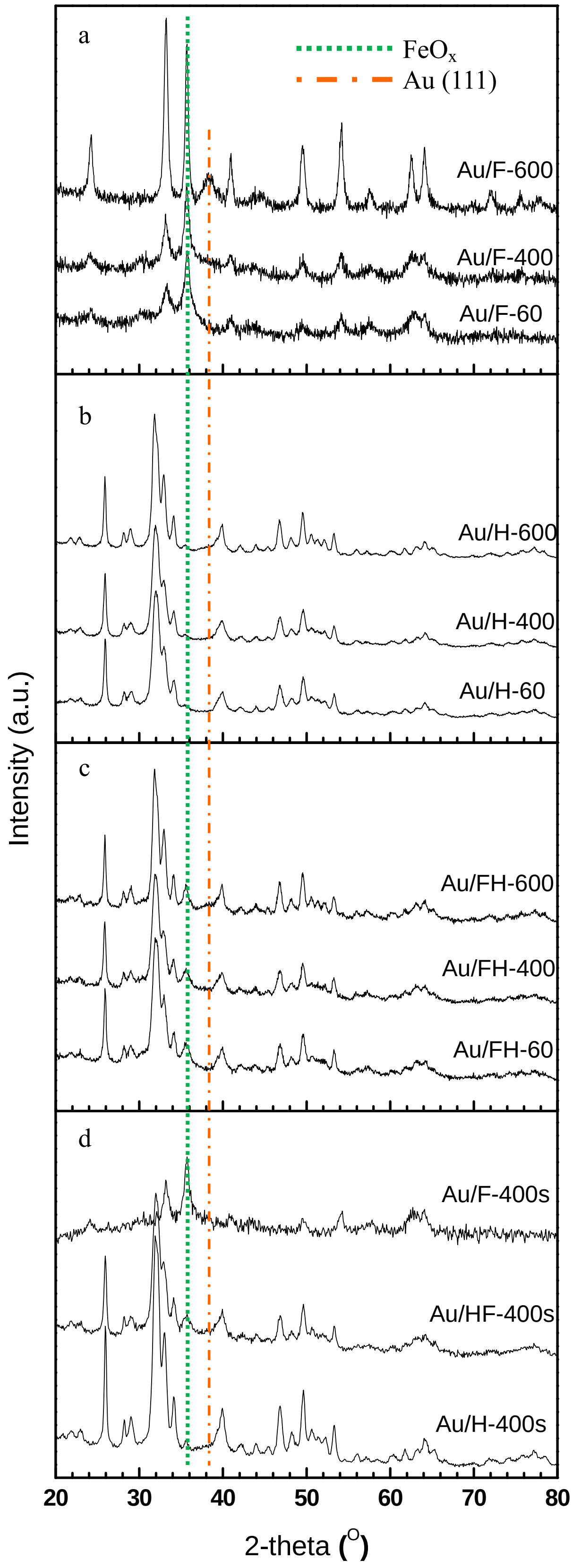

Fig. S5 XRD patterns of (a) Au/F, (b) Au/H, (c) Au/FH after different heat treatment and (d) Au/F-400, Au/H-400, Au/FH-400 after reaction at 24 °C for 120 hours.

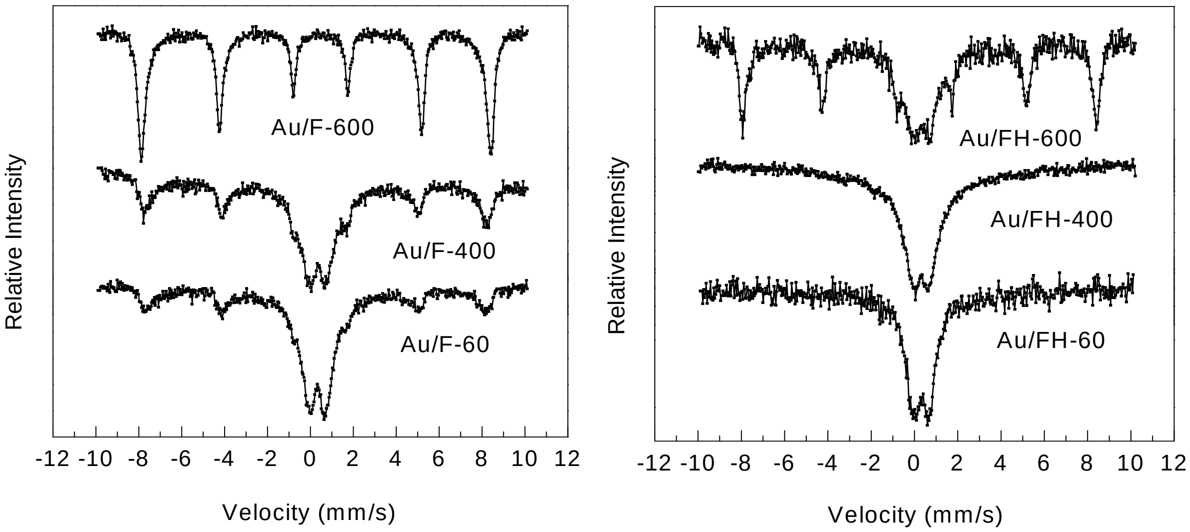

Fig. S6 Room temperature ^{57}Fe Mössbauer spectra for Au/F and Au/FH treated at different temperatures