Supporting Materials:

Colloidal Deposition Synthesis of Supported Gold Nanocatalysts Based on Au-Fe_3O_4 Dumbbell Nanoparticles

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Experimental Section

1. Synthesis of supported Au-Fe_3O_4 dumbbell catalysts

Au-Fe_3O_4 dumbbell nanoparticles were synthesized according to a modified reference method.[S1] The resulting nanoparticles (unwashed) were washed via dispersion in hexane and precipitation in ethanol for 4 times before dispersing in hexane, with help of sonication and mixing with a solid support [CabOSil (Aldrich), P25 (Degussa), and carbopack (Supelco, Inc)] under vigorous stirring. The approximate ratio of dumbbell nanoparticles to supports is 1:6 in weight. Hexane was evaporated and the resulting powder was dried under vacuum at 60 ^{o}C overnight. The final catalyst is named as "as synthesized".

2. Synthesis of supported Au/SiO_2 catalysts.

Au/SiO_2 was synthesized according to the deposition-precipitation method in our previous work.[S2]

3. Pretreatment for stability test under HNO_3 vapor

The "as-synthesized" catalyst (80 mg) was packed into a U-shaped silica tube, and calcined at 500 ^oC, 300 ^oC, 300C ^{o} for the support CabOSil, P25, and carbopack, respectively, in 8% O_2/He mixture for 1 h. The resulting powder was exposed to concentrated HNO_3 vapor at room temperature for 12 h and used to perform CO oxidation.

3. Catalysis test: CO oxidation

To perform CO oxidation reaction test, 53 mg of a catalyst (either "as synthesized" or HNO_3 vapor treated) was packed into a U-shaped silica tube (4 mm i.d.) on an Altamira AMI 200 microreactor. The catalysts supported on CabOSil, P25, and carbopack were calcined at 500 ^oC, 300 ^oC, and 300 ^oC, respectively, in 8% O_2/He mixture for 1 h to remove possible organic residues or moisture. The catalysts were cooled down to room temperature and the gas stream was switched to 1% CO (balance air, < 4 ppm H_2O) through the catalysts at a rate of 37 cm^3/min [space velocity 41900 $cm^3/(h \cdot g_{cat})$]. A portion of the product stream was extracted periodically with an automatic sample valve, and analyzed by a dual-column GC with a thermal conductivity detector.

4. Catalyst characterization

To characterize catalysts, XRD data were collected on a Siemens D5005 diffractometer with Cu K_α radiation (λ = 1.5418 Å). Scans were performed at a rate of 0.01^o/s for TiO_2-based catalysts and 0.005^o/6s for SiO_2- and carbon-based catalysts, typically in the range of $2\theta = 20\text{-}90^o$. The average gold particle sizes were estimated from X-ray line broadening analysis applying the Debye-Scherrer equation on the (111)

diffreaction ($2\theta = 44^{o}$). All "as synthesized" catalysts have the similar gold particle sizes of 3.0±0.1 nm. The gold and iron contents were estimated by EDAX on a JOEL JSM-6060 scanning electron microscope coupled with an EDAX detector. TEM (transmission electron microscopy) images were taken on a Hitachi HD2000 STEM electron microscope operated at 200 kV.

Results

Table S1 T_{50} of Au-Fe_3O_4 dumbbell nanoparticle-based catalysts in CO oxidation

Catalyst	Au loading / wt%	Pretreatment	T_{50} / ^{o}C
Au-Fe_3O_4	6.55	1)	N/A
Au-Fe_3O_4, washed with hexane/ethanol	6.55	1)	-25
Au-Fe_3O_4/TiO_2, unwashed	1.60	1)	260
Au-Fe_3O_4/SiO_2, washed with hexane/ethanol	1.67	2)	-40
Au-Fe_3O_4/TiO_2, washed with hexane/ethanol	1.62	1)	68
Au-Fe_3O_4/C,washed with hexane/ethanol	1.52	1)	17

1) 8% O_2/He, 300^{o}C, 1h; 2) 8% O_2/He, 500^{o}C, 1h;

Table S2 Average gold particle sizes (nm) in supported Au-Fe_3O_4 dumbbell catalysts

Treatment method / Support	Calcination	HNO_3
SiO_2	2.9[1)]	3.0[2)]
TiO_2	3.4[3)]	3.4[4)]
carbon	3.0[3)]	4.2[4)]

1) 8% O_2/He, 500^{o}C, 1h; 2) 8% O_2/He, 500^{o}C, 1h / HNO_3 vapor, 12h / 8% O_2/He, 500^{o}C, 1h; 3) 8% O_2/He, 300^{o}C, 1h; 4) 8% O_2/He, 300^{o}C, 1h / HNO_3 vapor, 12h / 8% O_2/He, 300^{o}C, 1h.

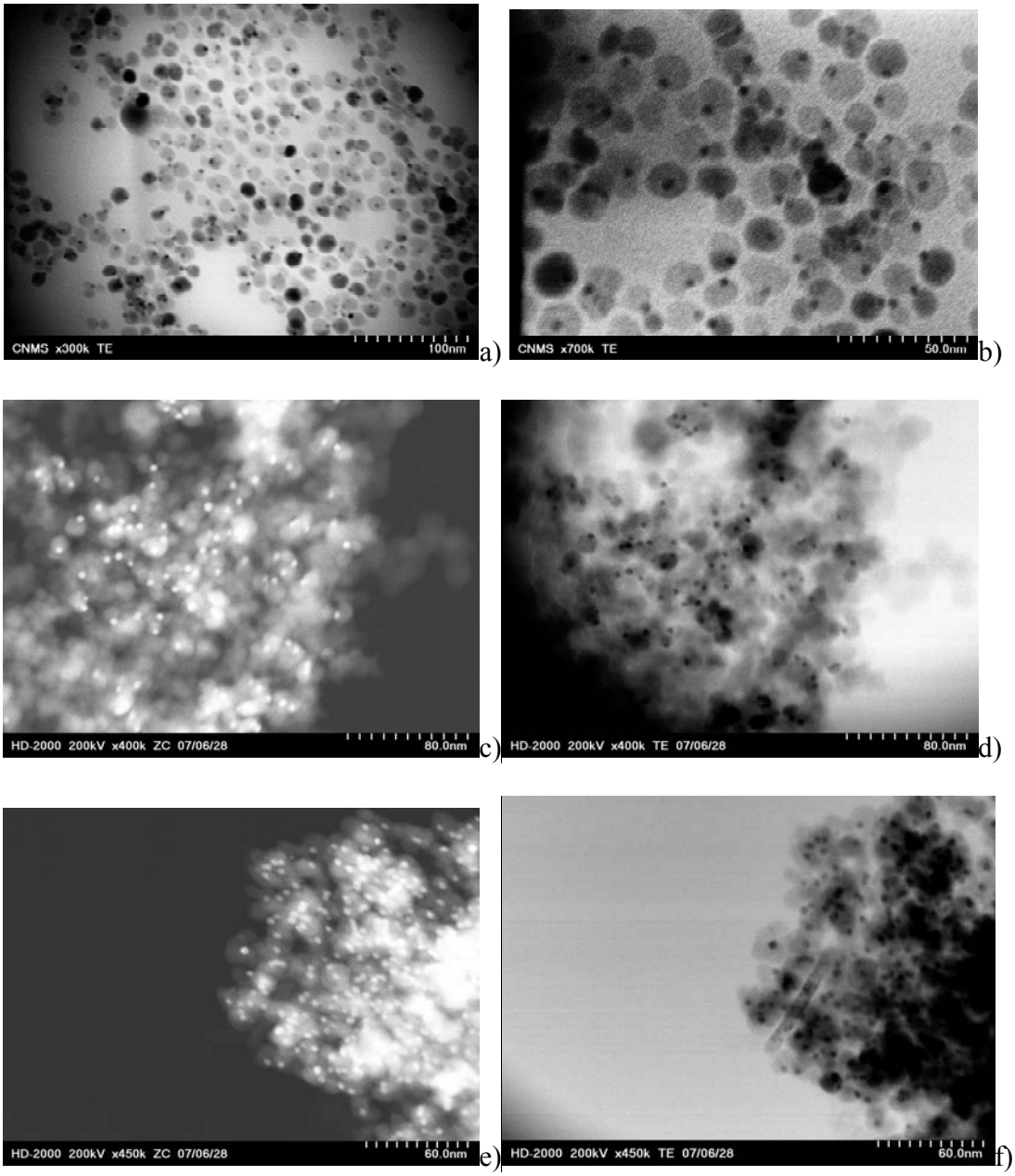

Figure S1 TEM of Au-Fe_3O_4 : a), b) Au-Fe_3O_4 dispersed in hexane, Au nanoparticle size 2.5 ~ 3.5 nm, Fe_3O_4 nanoparticle size 15 ~ 20 nm; c), d) Au-Fe_3O_4 deposited on TiO_2 (P25): c) dark field, d) bright field; e), f) Au-Fe_3O_4 deposited on carbon (carbopack): e) dark field, f) bright field.

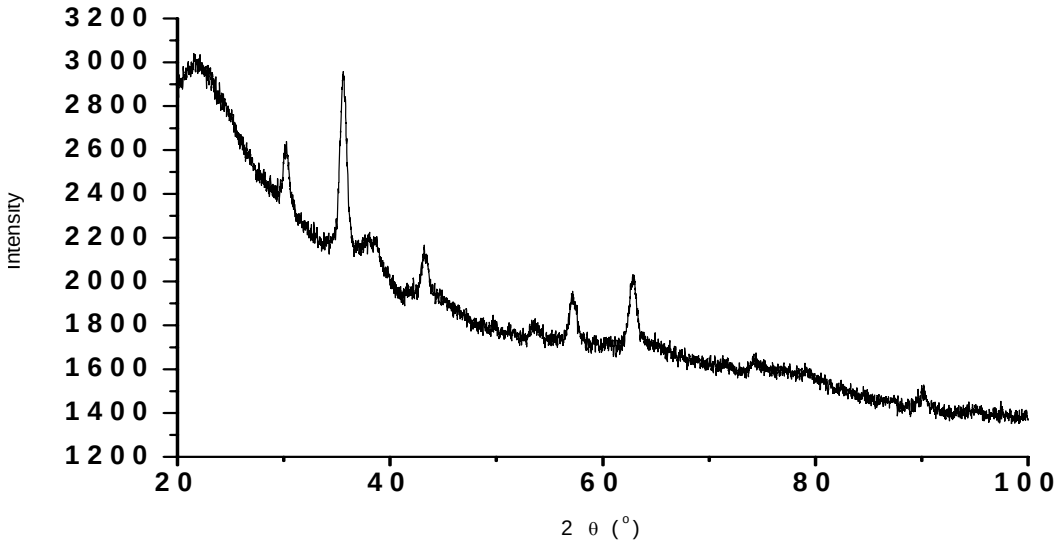

Figure S2 XRD pattern of as-synthesized Au-Fe_3O_4 dumbbell nanoparticles. Average gold particle sizes were estimated to be 2.9 nm from X-ray line broadening analysis applying the Debye-Scherrer equation on the (111) diffreaction ($2\theta = 44^o$).

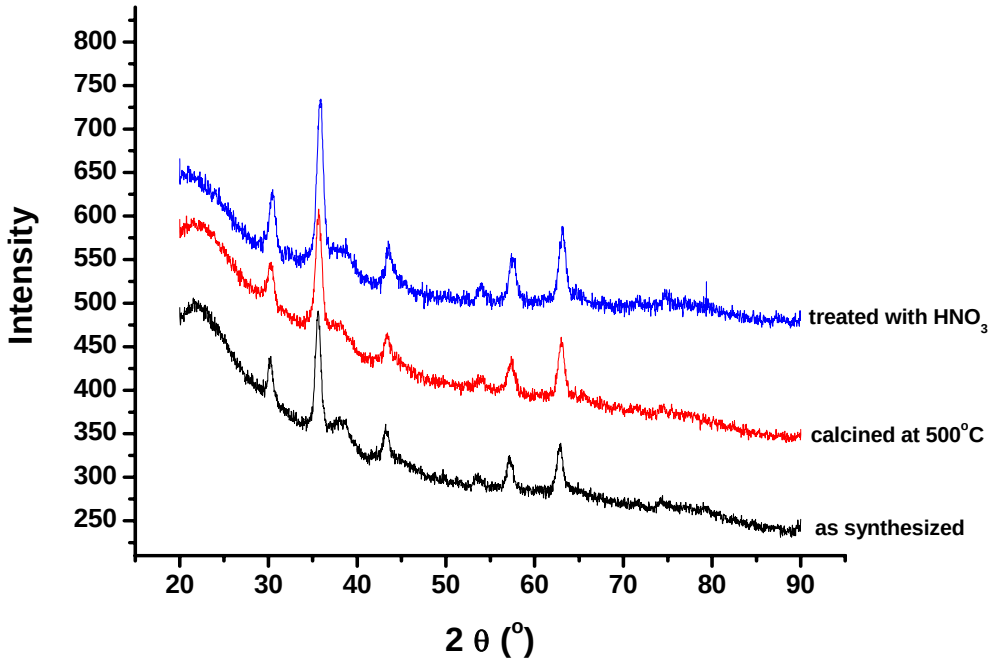

Figure S3 XRD pattern of Au-Fe_3O_4 dumbbell catalysts deposited on SiO_2 (CabOSil).

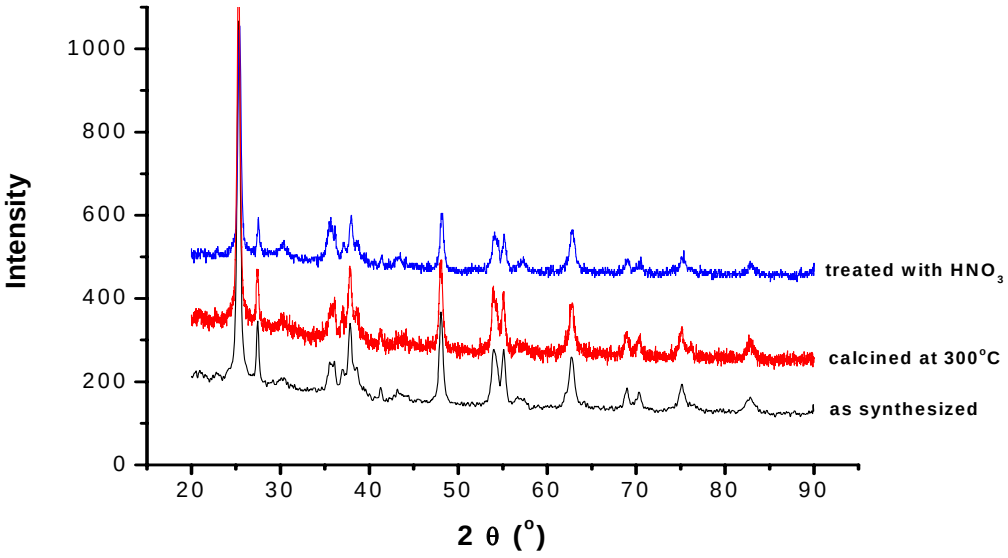

Figure S4 XRD pattern of Au-Fe_3O_4 dumbbell catalysts deposited on TiO_2 (P25).

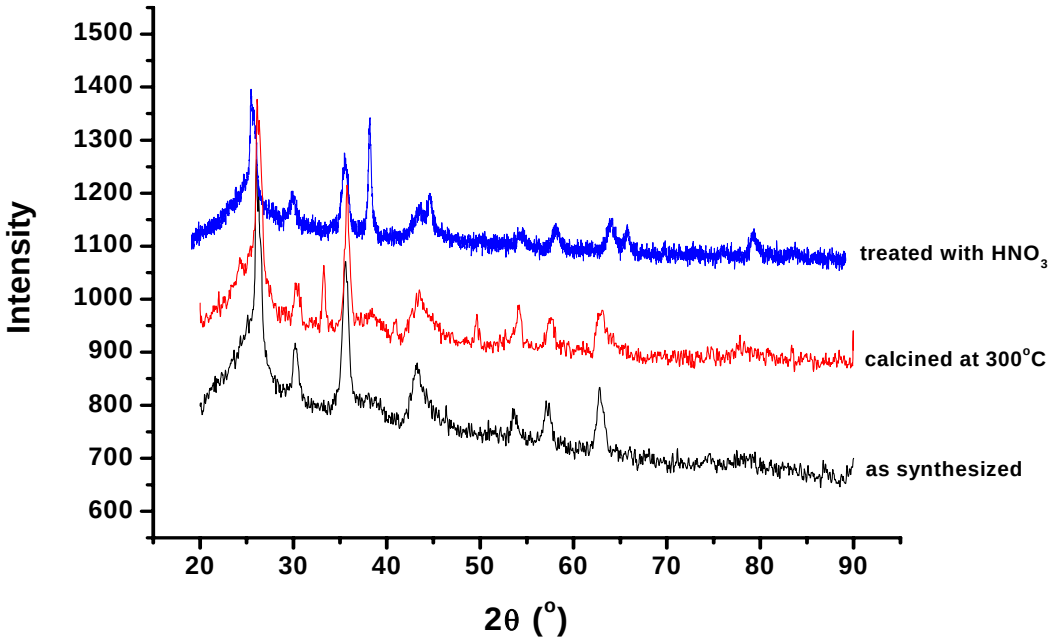

Figure S5 XRD pattern of Au-Fe_3O_4 dumbbell catalysts deposited on carbon (carbopack).

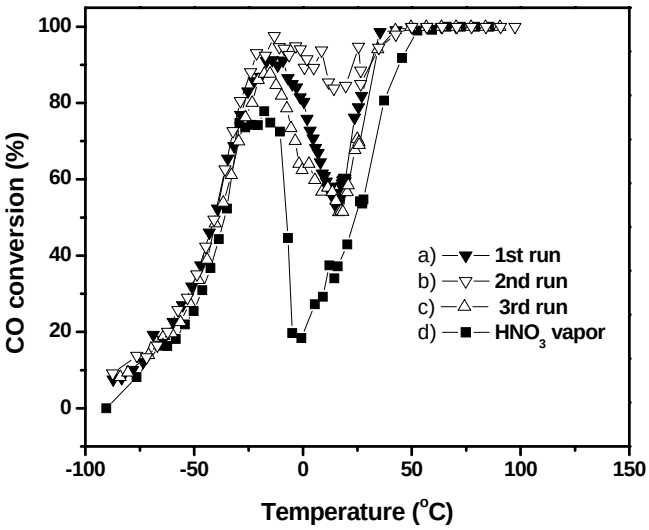

Figure S6 Light-off curves of CO oxidation with Au-Fe_3O_4/SiO_2. a), b), c): calcined at 500°C for 1 h for 1, 2, and 3 times; d): first calcined at 500°C for 1 h, then exposed to HNO_3 vapor for 12 h, then calcined at 500°C for 1 h.

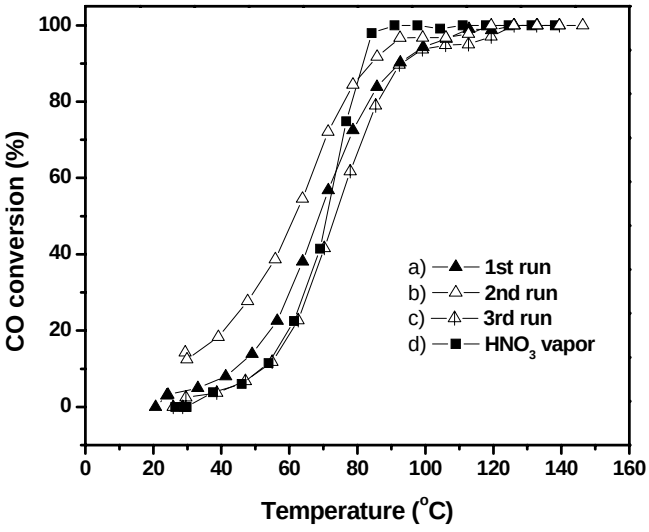

Figure S7 Light-off curves of CO oxidation with Au-Fe_3O_4/TiO_2. a), b), c): calcined at 300°C for 1 h for 1, 2, and 3 times; d): first calcined at 300°C for 1 h, subsequently exposed to HNO_3 vapor for 12 h, then calcined at 300°C for 1 h.

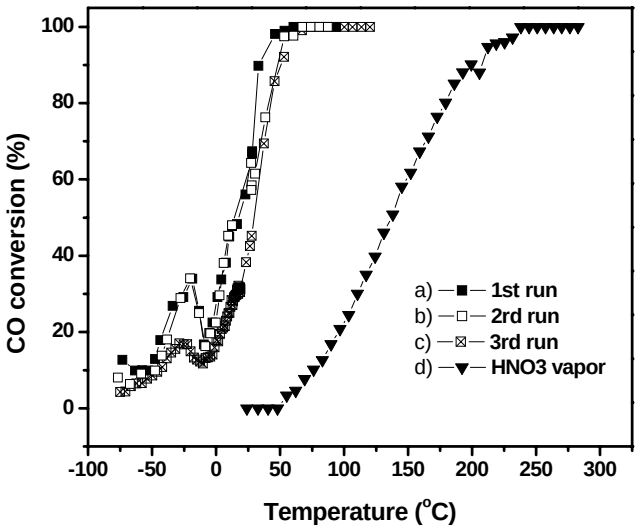

Figure S8 Light-off curves of CO oxidation with Au-Fe_3O_4/carbon. a), b), c): calcined at 300°C for 1 h for 1, 2, and 3 times; d): first calcined at 300°C for 1 h, then exposed to HNO_3 vapor for 12 h, then calcined at 300°C for 1 h.

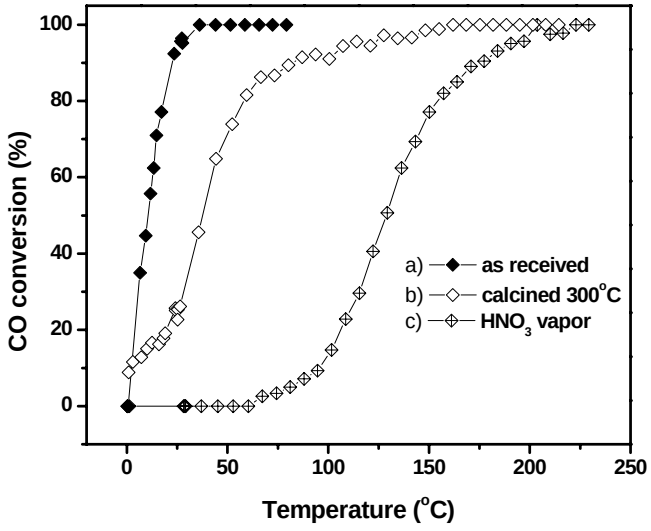

Figure S9 Light-off curves of CO oxidation with commercialized Au-Fe_2O_3 catalyst.

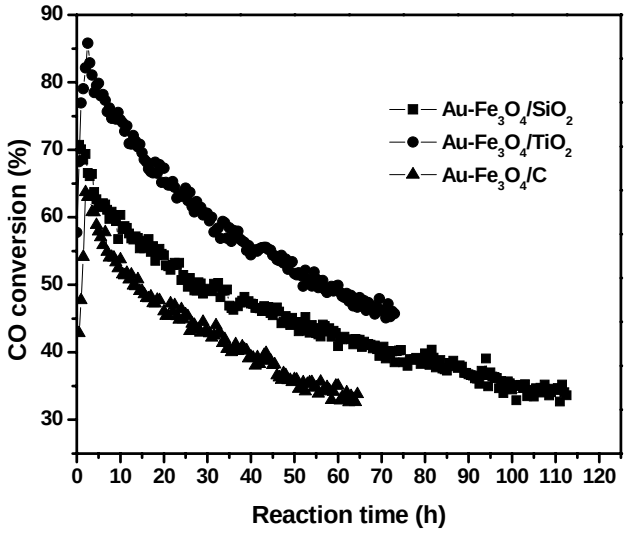

Figure S10 Catalyst durability (long-life) test for Au-Fe_3O_4 dumbbell nanoparticles supported on SiO_2, TiO_2 and Carbon.

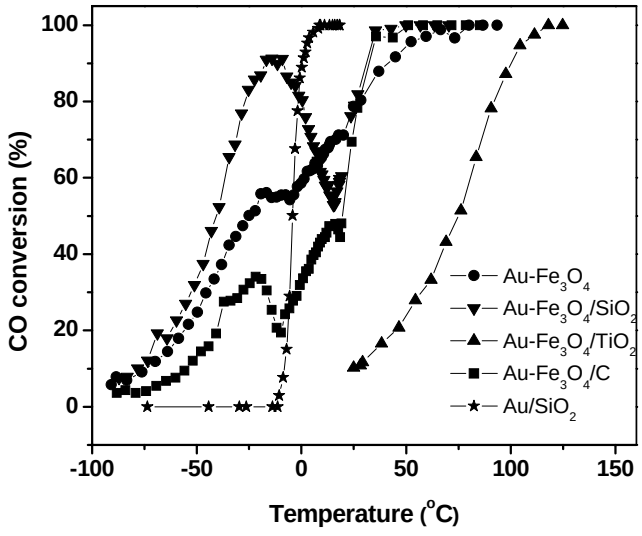

Figure S11 CO oxidation conversion light-off curves of catalysts: Au/SiO_2, Au-Fe_3O_4 deposited on SiO_2, TiO_2 and carbon: Au-Fe_3O_4: Au-Fe_3O_4 nanoparticles calcined at 300 ^oC for 1h; Au-Fe_3O_4/SiO_2: Au-Fe_3O_4 deposited on SiO_2 was calcined at 500 ^oC for 1h; Au-Fe_3O_4/TiO_2: Au-Fe_3O_4 deposited on TiO_2 was calcined at 300 ^oC for 1h; Au-Fe_3O_4/C: Au-Fe_3O_4 deposited on carbon was calcined at 300 ^oC for 1h; Au/SiO_2 (Au: 2%), calcined at 500^oC for 1h.

Reference

S1. H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. H. Sun, *Nano Letters*, 2005, **5**, 379-382.
S2. H. Zhu, Z. Ma, J. C. Clark, Z. Pan, S. H. Overbury and S. Dai, *Applied Catalysis A: General*, 2007, **326**, 89-99.