

Supporting Information

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**Efficient and Selective Room-Temperature Gold-Catalyzed Reduction of Nitro Compounds with CO and H<sub>2</sub>O as the Hydrogen Source\*\***

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## Experimental Details

### I. Catalytic materials

Gold catalysts including 1.5 wt % Au/TiO<sub>2</sub> (type A, lot no. Au/TiO<sub>2</sub> no. 02-1) and 4.5 wt % Au/Fe<sub>2</sub>O<sub>3</sub> (type C, lot no. Au/Fe<sub>2</sub>O<sub>3</sub> no. 02-5) were supplied by the World Gold Council (WGC). 5 wt % Pd/C (stock # 38300), 5 wt % Ru/Al<sub>2</sub>O<sub>3</sub> (stock # 11749) were provided by Alfa Aesar.

**Preparation of Au/TiO<sub>2</sub>-VS catalysts:** A modified deposition-precipitation procedure<sup>[S1]</sup> has been employed to prepare the Au/TiO<sub>2</sub>-VS sample. TiO<sub>2</sub> (1.0 g, Degussa P25, specific surface area: 45 m<sup>2</sup>/g nonporous, 70 % anatase and 30 % rutile, purity > 99.5 %) was added to 100 mL of an appropriate amounts of aqueous solution of [Au(en)<sub>2</sub>]Cl<sub>3</sub> at a fixed pH = 9.4 adjusting with 0.2 M NaOH at 40 °C. The mixture was aged for 2 h, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and then reduced in 5 % H<sub>2</sub>/Ar (30 mL/min) at 300 °C for 2 h. The as-prepared Au/TiO<sub>2</sub> with very small Au nanoparticles (*ca.* 1.9 nm, see TEM data in Fig. S1) was denoted as Au/TiO<sub>2</sub>-VS. Elemental analysis results revealed that the real gold loading was 0.98 wt % in Au/TiO<sub>2</sub>-VS.

**Preparation of Au/CeO<sub>2</sub> catalysts:** 1 wt % Au/CeO<sub>2</sub> catalysts were prepared by a routine deposition precipitation method.<sup>[S2]</sup> An appropriate amount of aqueous solutions of chloroauric acid (HAuCl<sub>4</sub>) was heated to 80 °C under vigorous stirring. The pH was adjusted to 10 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO<sub>2</sub> (Degussa, Adnano 90, specific surface area: 90 m<sup>2</sup>/g) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and reduced in 5 % H<sub>2</sub>/Ar at 300 °C.

**Preparation of Pt/TiO<sub>2</sub> catalysts:** 1 wt % Pt/TiO<sub>2</sub> catalysts were prepared by incipient wetness technique. TiO<sub>2</sub> (1.0 g Degussa P25, specific surface area: 45 m<sup>2</sup>/g nonporous, 70 % anatase and 30 % rutile, purity > 99.5 %) was added to 10 mL of an aqueous solution containing appropriate amounts of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. After a perfect mixing of the corresponding slurries, samples were under vacuum at room temperature for 12 h and then reduced in 5 % H<sub>2</sub>/Ar at 300 °C for 2 h.

## II. Catalytic activity measurements

**Procedure for reduction of nitrobenzene by CO/H<sub>2</sub>O under 1 atm of CO:** A mixture of nitrobenzene (1 mmol), supported metal catalysts (metal: 1 mol%), and ethanol (10 mL), water (5 mL) was put into a flask (100 mL) fitted with a gas inlet tube for introducing CO by bubbling (10 mL/min). The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. No variation in reduction rate was observed over a range of stirrer speeds (800-1500 rpm) indicating the absence of mass transfer control. The conversion and product selectivity were periodically determined by GC analysis (Shimadzu GC-17A equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID)) using *n*-decane as an internal standard. The value of kinetic isotope effect ( $k_H/k_D$ ) for Au/TiO<sub>2</sub>-VS was calculated as 1.54 ± 0.02 based on the initial rate of reaction when H<sub>2</sub>O was switched to D<sub>2</sub>O under otherwise identical conditions.

**General procedure for reduction of nitro compounds under elevated pressure of CO:** A mixture of substrate (1 mmol), Au/TiO<sub>2</sub>-VS (Au: 1 mol%), and ethanol (10 mL), water (5 mL) was put into a batch autoclave reactor (100 mL). After sealing the reactor, CO (10 mL/min) was fed to the reactor via a mass flow controller, and the pressure (3-15 atm) was adjusted by a back-pressure regulator located at the exit line of the reactor. The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. The conversion and product selectivity were periodically determined by GC analysis using *n*-decane as an internal standard. All products were known and available. The products were confirmed by the comparison of their GC retention time, mass, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy with those of authentic samples.

**Procedure for reduction of nitrobenzene by CO in neat water:** A mixture of nitrobenzene (1 mmol), Au/TiO<sub>2</sub>-VS (Au: 1 mol%), and water (15 mL) was put into a batch reactor (100 mL). After sealing the reactor, CO (10 mL/min) was fed to the reactor via a mass flow controller, and the pressure (5 atm) was adjusted by a back-pressure regulator located at the exit line of the reactor. Then the mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. The conversion and product selectivity were periodically determined by GC analysis using *n*-decane as an internal standard.

**Procedure for 250-mmol scale reduction of nitrobenzene:** A mixture of nitrobenzene (250 mmol), Au/TiO<sub>2</sub>-VS (Au: 0.01 mol%), ethanol (500 mL) and water (100 mL) was put into a batch reactor (2 L). After sealing the reactor, CO (60 mL/min) was fed to the reactor via a mass flow controller, and the pressure (15 atm) was adjusted by a back-pressure regulator located at the exit line of the reactor. The reaction mixture was vigorously stirred (1200 rpm with a magnetic coupled stirrer) at 100 °C

for 2.5 h. The resultant mixture was extracted with Et<sub>2</sub>O for 3 times and passed through a short silica gel column before GC analysis. For isolation, the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by silica gel column chromatography. Aniline (>97 %) was obtained as a colorless, oily liquid.

**Recovery and reuse of Au/TiO<sub>2</sub>-VS under 250-mmol scale:** The reused catalyst was recovered by filtering the solid Au/TiO<sub>2</sub>-VS from liquid phase after the reaction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried at 100 °C for 12 h. In the three successive cycles, the conversion of nitrobenzene (250 mmol) was >99 %, 92 %, and 90 % (GC yield).

**Procedure for reduction of nitrobenzene by CO in anhydrous ethanol in the absence of water:** A mixture of nitrobenzene (1 mmol), Au/TiO<sub>2</sub>-VS (Au: 1 mol%), and anhydrous ethanol (15 mL) was put into a batch reactor (100 mL). After sealing the reactor, CO (10 mL/min) was fed to the reactor via a mass flow controller, and the pressure (5 atm) was adjusted by a back-pressure regulator located at the exit line of the reactor. The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. Under these conditions, no conversion of nitrobenzene was observed up to 3 h of contact time.

**Procedure for reduction of nitrobenzene with 1 atm H<sub>2</sub>:** A mixture of nitrobenzene (1 mmol), Au/TiO<sub>2</sub>-VS (Au: 1 mol%), ethanol (10 mL), and water (5 mL) was put into a flask (100 mL) fitted with a gas inlet tube for introducing H<sub>2</sub> by bubbling (10 mL/min). The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. Under these conditions, the reduction practically did not occur up to 3 h of contact time thus indicating that the reaction does not proceed by the reduction of nitro compounds with hydrogen gas generated from the WGS reaction.

### III. Characterization

**Elemental analysis:** The Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

**Transmission electron microscopy (TEM):** TEM images for supported gold catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

**X-ray photoelectron spectroscopy (XPS):** XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg K $\alpha$  ( $h\nu = 1253.6$  eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C1s peak at 284.6 eV. Prior to the measurements, the sample was pretreated in 30 mL/min of H<sub>2</sub>/Ar at 300 °C for 2 h and then cooled under He to 25 °C.

**Table S1:** The influence of solvent on the reduction of nitrobenzene by CO/H<sub>2</sub>O.

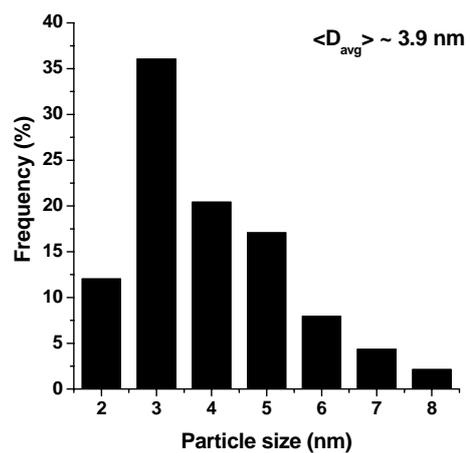
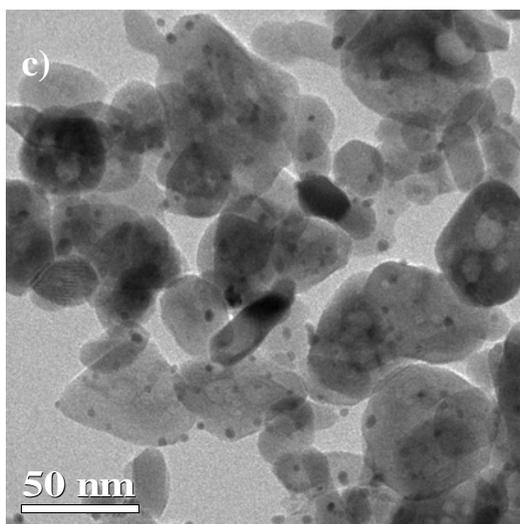
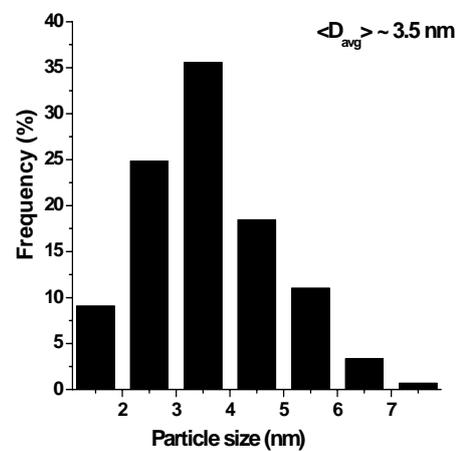
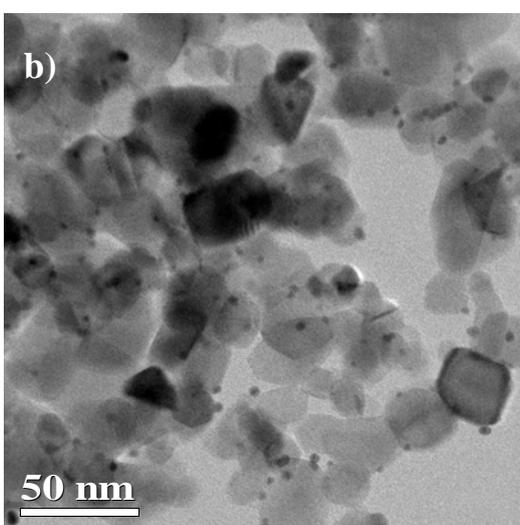
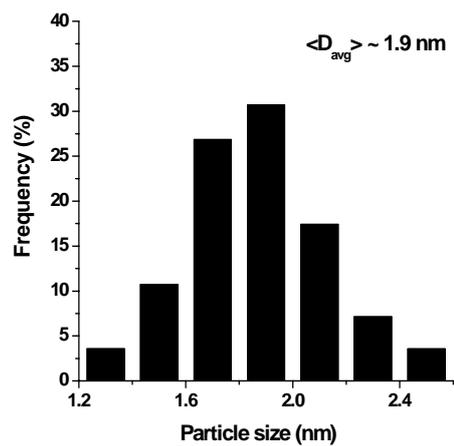
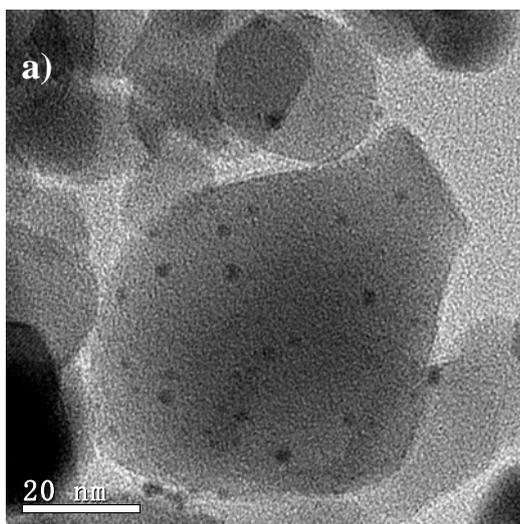
Entry	Solvent	The amount of solvent (mL)	The amount of water (mL)	t (h)	Yield (%)
1	Ethanol	10	5	1	>99
2	THF	10	5	1	65
3	DMF	10	5	1	52
4	Acetone	10	5	1	39

Reaction conditions: 1 mmol nitrobenzene, Au/TiO<sub>2</sub>-VS (Au: 1 mol%), CO 5 atm, 25 °C. The possibility that ethanol acts as a hydrogen source leading to improved activity with respect to other solvents can be ruled out, as none of the ethanol-involved intermediates (ethyl acetate, acetic acid, etc.) could be detected under such mild conditions.

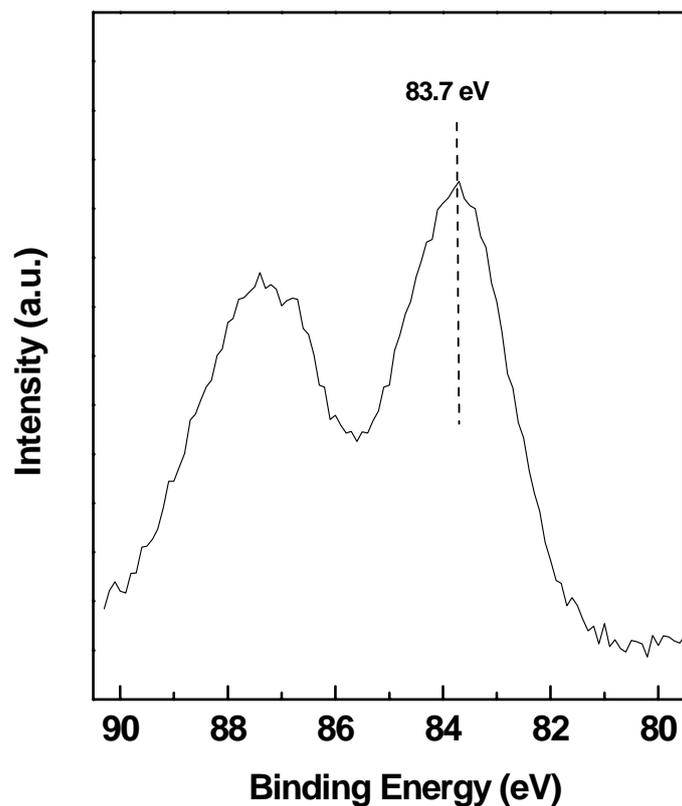
**Table S2:** Reduction of nitrobenzene and other unsaturated substrates by CO/H<sub>2</sub>O.

Entry	Substrate	T (°C)	P <sub>CO</sub> (atm)	t (h)	Yield (%)
1	nitrobenzene	25	5	1	>99
2	styrene	25	5	1	–
3	acetophenone	25	5	1	–
4	benzonitrile	25	5	1	–
5	benzaldehyde	25	5	1	–

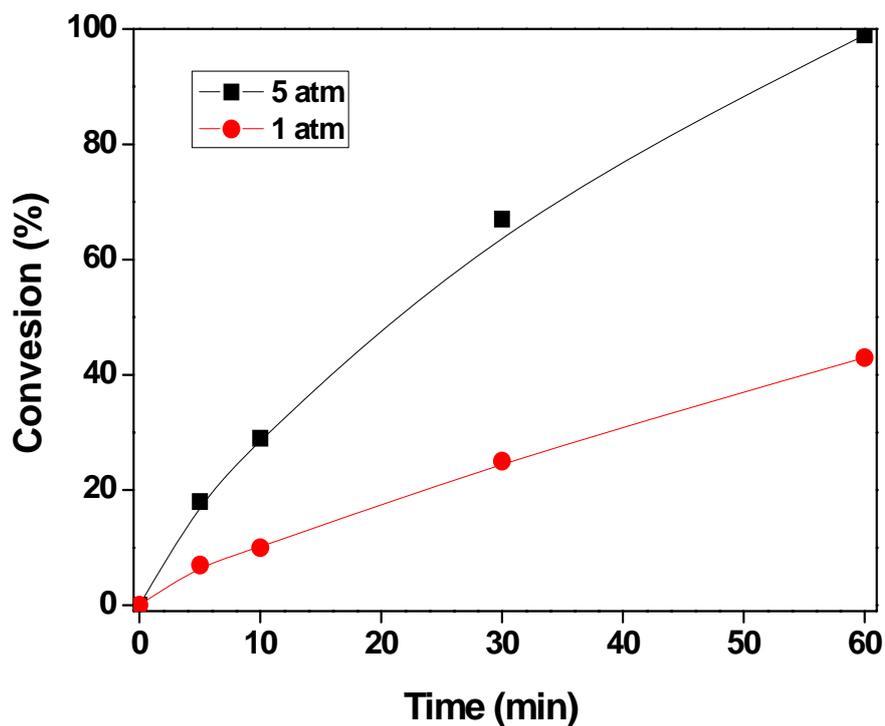
Reaction conditions: 1 mmol substrate, Au/TiO<sub>2</sub>-VS (Au: 1 mol%), EtOH/H<sub>2</sub>O (15 mL, 2:1 v/v).



**Figure S1.** TEM image and gold particle size distribution of a) 0.98 wt % Au/TiO<sub>2</sub>-VS; b) 1.5 wt % Au/TiO<sub>2</sub> (WGC); c) 4.5 wt % Au/FeO<sub>3</sub> (WGC).



**Figure S2.** XP spectra of Au/TiO<sub>2</sub>-VS. The binding energy of Au 4f<sub>7/2</sub> for Au/TiO<sub>2</sub>-VS is ca. 83.7 eV, which is 0.3 eV lower than the standard binding energy of metallic Au (84.0 eV). Note that it has been very difficult to make a solid interpretation of the oxidation state of Au because of the broad spectral feature and that final-state screening is highly dependent on the size of metal particles supported on oxide supports.<sup>[S3]</sup>



**Figure S3.** Reduction of nitrobenzene by CO/H<sub>2</sub>O under different CO pressure (5 atm and 1 atm). Reaction conditions: 1 mmol nitrobenzene, Au/TiO<sub>2</sub>-VS (Au: 1 mol%), EtOH/H<sub>2</sub>O (15 mL, 2:1 v/v), 25 °C.

## References

- [S1] R. Zanella, A. Sandoval, P. Santiago, V. A. Basiuk, J. M. Saniger, *J. Phys. Chem. B* **2006**, *110*, 8559-8565.
- [S2] M. Haruta, *Catal. Today* **1997**, *36*, 153-166.
- [S3] H.-J. Freund, *Angew. Chem. Int. Ed.* **1997**, *48*, 452-475.