

Supporting Information for
An Unusual Chemoselective Hydrogenation of Quinoline Compounds Using
Supported Gold Catalysts

Dong Ren, Lin He, Lei Yu, Ran-Sheng Ding, Yong-Mei Liu, Yong Cao,* He-Yong He, and
Kang-Nian Fan

*Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative
Materials, Fudan University, Shanghai 200433, P. R. China*

Table of contents

1. Materials	S2
1.1- General	
1.2- Catalyst preparation	
2. Catalytic activity measurements	S4
2.1- General procedure for catalytic hydrogenation of quinolines	
2.2- Recovery and reuse of Au/HSA-TiO ₂	
2.3- Au/HSA-TiO ₂ -catalyzed 100 mmol-scale hydrogenation of quinoline	
2.4- Isotope H ₂ -D ₂ exchange reaction	
2.5- Catalytic results obtained with different gold catalysts	
3. Characterization of catalysts	S6
3.1- Elemental analysis	
3.2- Brunauer–Emmett–Teller (BET) analysis	
3.3- X-ray diffraction (XRD) analysis	
3.4- Transmission electron microscopy (TEM)	
3.5- High resolution transmission electron microscopy (HRTEM)	
3.7- X-ray photoelectron spectroscopy (XPS)	
3.7- Diffuse reflectance Infrared Fourier transform (DRIFT) measurements	
4. Mechanistic/Reactivity studies	S12
5. Time-conversion plot of typical representative catalysts	S13
6. Reference	S14

1. Materials

1.1 General

Commercially available organic and inorganic compounds were used without further purification. 1-(2-methylquinolin-6-yl) ethanone and 2-methyl-7-vinylquinoline (Table 2, entry 11, 12) were synthesized according to our previously reported procedure.^{S1} 6-chloro-1,2-dihydroquinoline (Figure S7, 2') can be synthesized conveniently by the reaction of quinoline with methyl lithium according to literature.^{S2}

Gold catalysts including 1.5 wt% Au/TiO₂ (type A, lot no. Au/TiO₂ no. 02-1) was supplied by the World Gold Council (WGC). 1 wt% Au/TiO₂ (catalogue number 79-0165), 1 wt% Au/Al₂O₃ (catalogue number 79-0160) and 1 wt% Au/ZnO (catalogue number 79-0170) were supplied by Mintek. 5 wt% Pd/C (stock # 38300), 5 wt% Pt/C (stock # 38321), 5 wt% Ru/Al₂O₃ (stock # 11749) were provided by Alfa Aesar.

1.2 Catalyst preparation

Preparation of high surface area TiO₂ (HSA-TiO₂) support: High surface area nanocrystalline TiO₂ powders predominantly in the anatase phase were prepared by the hydrolysis of tetrabutyl titanate [TTBT, Ti(OBu)₄]. Typically, 17.2 g Ti(OBu)₄ was dropwise added to 800 mL water under vigorous stirring at room temperature, and then the mixture was further stirred for 2 h. The precipitate obtained was filtered and washed with water. The resultant powder was dried at 100 °C for 12 h and then calcined in a tubular oven at 400 °C in air for 4 h. The BET surface area of the resultant material was 124 m²·g⁻¹.

Preparation of Au/HSA-TiO₂: 0.5 wt% Au/HSA-TiO₂ catalyst was prepared by a routine deposition precipitation (DP) method as developed by Haruta et al.^{S3} An appropriate amount of aqueous solutions of chloroauric acid (HAuCl₄) was heated to 80 °C under vigorous stirring. The pH was adjusted to 8.0 by dropwise addition of NaOH (0.2 M), and then 1.0 g of HSA-TiO₂ was dispersed in the solution. The mixture was stirred 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 calcined in air at 250 °C for 2 h. The mean gold particle size of Au/HSA-TiO₂ catalyst obtained was 2 nm. To prepare Au/HSA-TiO₂ catalyst with the mean gold particle size about 3.5 nm, the sample was calcined in air at 350 °C instead of 250 °C for 2 h, and denoted as a reference (ref.) catalyst Au/HSA-TiO₂-ref..

Preparation of Au/TiO₂ (P25)-ref: 0.5 wt% Au/TiO₂ (P25)-ref. was prepared by DP method. An appropriate amount of aqueous solutions of HAuCl₄ was heated to 80 °C under vigorous stirring.

The pH was adjusted to 8.0 by dropwise addition of NaOH (0.2 M), and then 1.0 g of TiO₂ (Degussa P25, specific surface area: 45 m² g⁻¹) was dispersed in the solution. The mixture was stirred 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 calcined in air at 250 °C for 2 h.

Preparation of Au/CeO₂: 0.5 wt% Au/CeO₂ catalyst was prepared by DP method. An appropriate amount of aqueous solutions of chloroauric acid (HAuCl₄) was heated to 80 °C under vigorous stirring. The pH was adjusted to 9.0 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO₂ (Degussa, Adnano 50, specific surface area: 50 m² g⁻¹) was dispersed in the solution. The mixture was stirred 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 calcined in air at 250 °C for 2 h. The mean gold particle size of Au/CeO₂ catalyst obtained was 2.1 nm.

Preparation of Au/C catalysts 0.5 wt% Au/C catalyst was prepared by the procedure as described elsewhere.^{S4} Typically, the poly vinyl alcohol (PVA) was added (Au/PVA = 1.5:1, wt/wt) to a aqueous solution containing appropriate amount of aqueous solutions of HAuCl₄ at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of 0.1 M NaBH₄ (Au/NaBH₄ = 1:5, mol/mol), led to formation of a dark orange-brown solution, indicating the formation of the gold sol. Activated carbon (refluxed with 2.5 wt% HNO₃ solution for 6 h) was then added to the colloidal gold solution under stirring and kept in contact until total adsorption (0.5 wt% of gold on the support) occurred. After 2 h stirring, the slurry was filtered and the resulting sample was dried at room temperature for 12 h.

Preparation of Pd/HSA-TiO₂, Pt/HSA-TiO₂, Ru/HSA-TiO₂: 0.5 wt% Pd/HSA-TiO₂, 0.5 wt% Pt/HSA-TiO₂ and 0.5 wt% Ru/HSA-TiO₂ catalysts were prepared by impregnation technique. HSA-TiO₂ (1.0 g) was added to an appropriate amount of aqueous solution containing PdCl₂, H₂PtCl₆·6H₂O or RuCl₃. After a perfect mixing of the corresponding slurries, the samples were dried under vacuum at RT for 12 h and then reduced in 5 vol% H₂/Ar at 400 °C for 2 h.

Preparation of Pd/HAP: Pd/HAP catalyst was prepared according to the previously reported procedure.^{S5}

2. Catalytic activity measurements

2.1 General procedure for catalytic hydrogenation of quinolines: A mixture of substrate (0.5 mmol), catalyst (metal: 1 mol%) and toluene (3 mL) was charged into a Parr autoclave (25 mL capacity). Then the autoclave was sealed and 2 MPa H₂ was charged into it after internal air being degassed completely. The resulting mixture was vigorously stirred (1200 r. p. m. with a magnetic stir bar) at given reaction temperature. The products were confirmed by the comparison of their GC retention time, mass, and ¹H NMR spectroscopy. The conversion and product selectivity were determined by a GC-17A gas chromatograph equipped with a HP-5 column (30 m × 0.25 mm) and a flame ionization detector (FID). The tetrahydroquinoline products can be isolated by silica gel chromatography (hexanes/ethyl acetate). Isotope effect (k_H/k_D) was 3.2 based on initial rate when H₂ was switched to D₂ in the direct hydrogenation of 6-chloroquinoline to 6-chloro-1,2,3,4-tetrahydroquinoline over Au/HSA-TiO₂ under otherwise identical conditions.

2.2 Recovery and reuse of Au/HSA-TiO₂: The reused catalyst was recovered by centrifuging the solid Au/HSA-TiO₂ from liquid phase after reaction. The recovered catalyst was washed with toluene several times. The catalyst was then dried under vacuum at room temperature for 12 h.

2.3 Au/HSA-TiO₂-catalyzed 100 mmol-scale hydrogenation of quinoline: A mixture of quinoline (100 mmol), Au/HSA-TiO₂ (0.02 mol% Au) was charged into an autoclave (100 mL capacity). After sealing the reactor and degassed internal air, H₂ was fed to the reactor via a mass flow controller, and 2 MPa H₂ was adjusted by a back-pressure regulator located on the exit line of the reactor. The flow rate of H₂ was 10 mL min⁻¹. Then, the mixture was extensively stirred (1200 r.p.m.) at 140 °C for 48 h.

2.4 Isotope H₂-D₂ exchange reaction: The H₂-D₂ exchange reaction was carried out in a fixed bed quartz reactor with an inner diameter of 4 mm at 60 °C. The feed gas containing 20 vol% H₂, 20 vol% D₂ and balancing He is at a total flow rate of 60 mL·min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 1.8×10^5 mL h⁻¹ g_{cat}⁻¹. Under these conditions, the H₂-D₂ exchange conversions were always kept below 15% to avoid mass-transfer limitations. Reaction products (H₂, HD and D₂) were analyzed with an on-line mass spectrometer (Balzers, QMS 200 Omnistar). Trace amounts of HD formed in the experimental setup without catalyst, and the product concentrations were corrected for this. Prior to catalytic test, the catalysts were heated in He flow (10 mL·min⁻¹) at 200 °C for 0.5 h, followed by cooling to the desired temperature under He flow. For the introduction of quinoline or tetrahydroquinoline to the samples, the liquid compound (25 μmol) was injected under the He flow.

2.5 Catalytic results obtained with different gold catalysts

Table S1 The hydrogenation of 6-chloroquinoline to 6-chloro-1,2,3,4-tetrahydroquinoline over different Au-based catalysts. ^a

Entry	Catalyst	Average Au particle size (nm)	t (h)	Yield by GC (%)
1	Au/TiO ₂ -M	2.7	4	100
2	Au/Al ₂ O ₃	2.9	4	31
3	Au/ZnO	2.1	4	19
4	Au/CeO ₂	2.1	4	16
5	Au/C	4.1	4	6
6	Au/HSA-TiO ₂	2.0	1.5	100
7	Au/TiO ₂ (P25)-ref.	1.9	1.5	51
8	Au/HSA-TiO ₂ -ref.	3.5	1.5	26

^a Reaction conditions: 6-chloroquinoline (0.5 mmol), toluene (3 mL), catalyst (Au: 1 mol%), 80 °C, 2 MPa H₂.

3. Characterization of catalysts

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

3.2 Brunauer–Emmett–Teller (BET) analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

3.3 X-ray diffraction (XRD) analysis: The XRD information of the samples was carried out on a German Bruker D8 Avance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 40 mA.

3.4 Transmission electron microscopy (TEM): TEM images for catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

3.5 High resolution transmission electron microscopy (HRTEM): HRTEM images for catalysts were taken with a JEM-2100F electron microscope operating at 200 kV. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

3.6 X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K α , $h\nu = 1253.6$ eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (B.E.).

3.7 Diffuse reflectance Infrared Fourier transform (DRIFT) measurements: The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out on a Nicolet Magna-IR 760 Fourier transform spectrometer (ThermoNicolet, Madison, WI) using an MCT detector. Prior to chemisorptions, the sample (typically 20 mg) was pretreated in a flow of He (35 mL min⁻¹) at 250 °C for 2 h and then cooled under He to 25 °C. Unless stated otherwise, infrared (IR) spectra were recorded against a background of the sample at the reaction temperature under flowing He. IR spectra were recorded with co-addition 64 scans in single-beam spectra or absorbance spectra, by applying a resolution of 4 cm⁻¹.

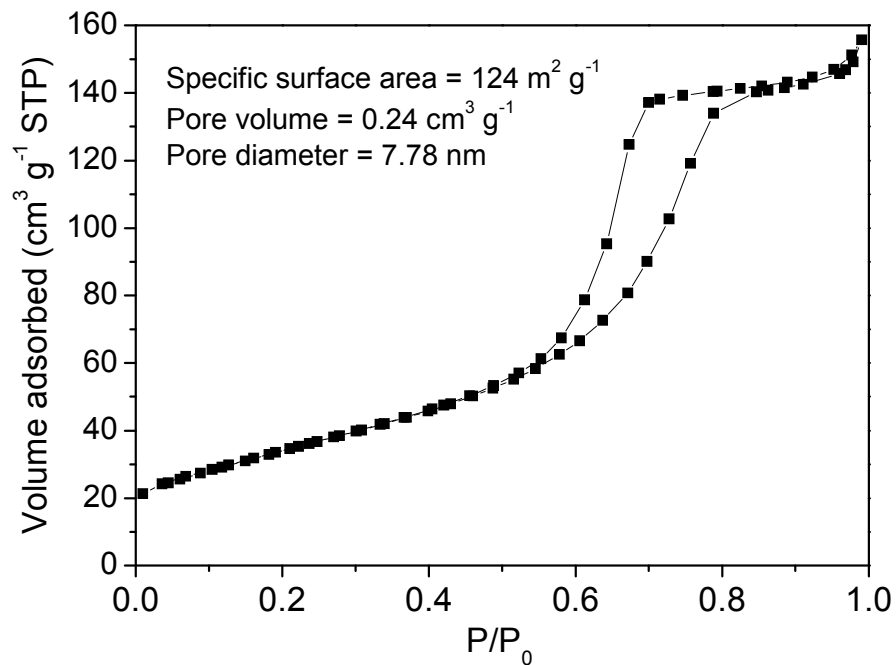


Figure S1. N₂ adsorption/desorption isotherm and pore size distribution for HSA-TiO₂.

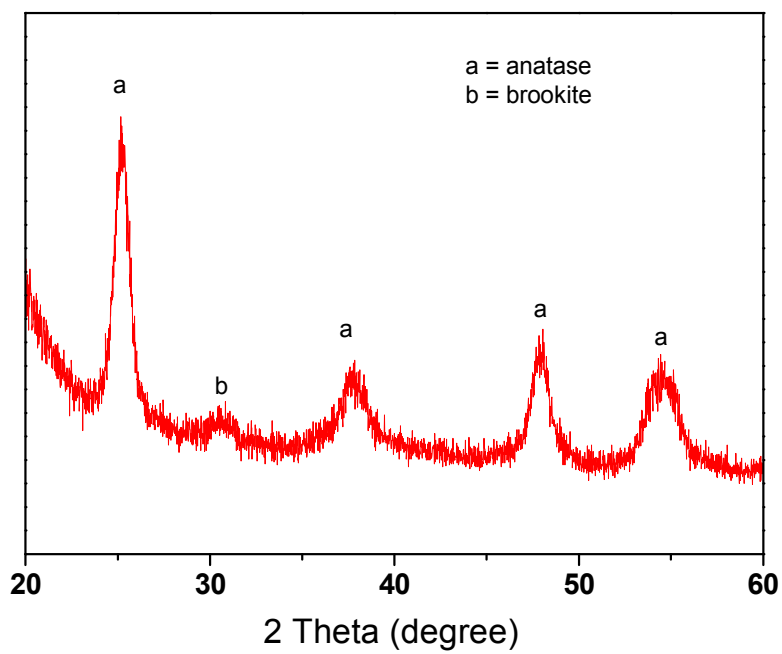
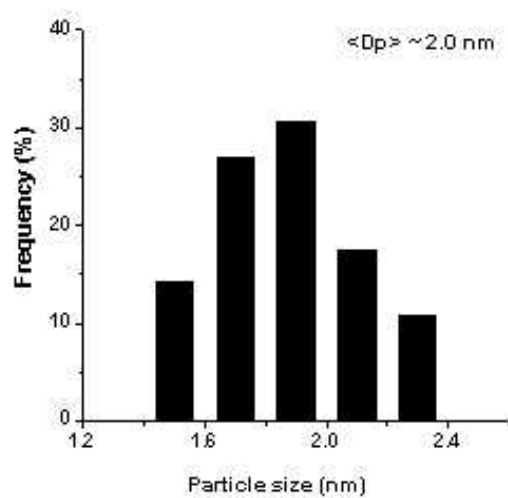
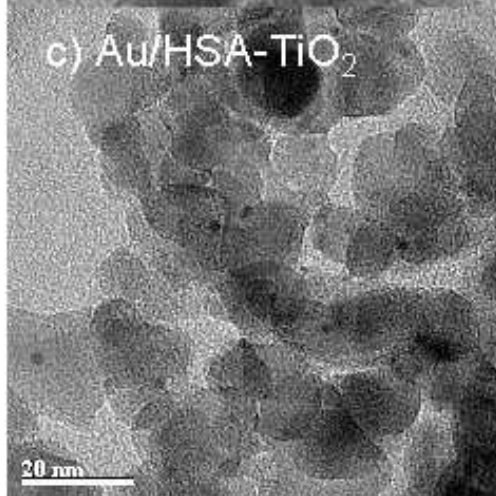
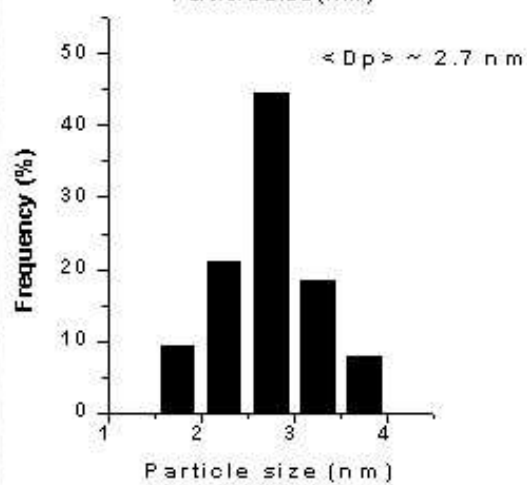
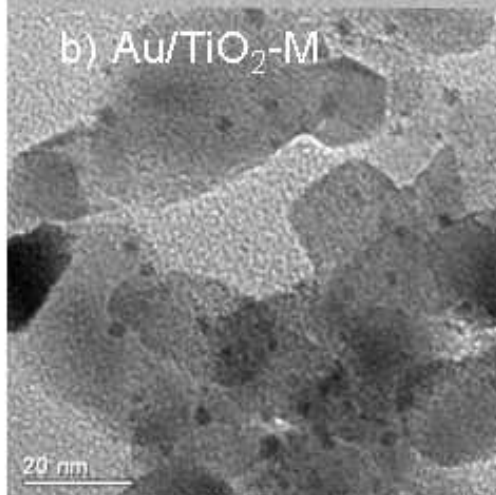
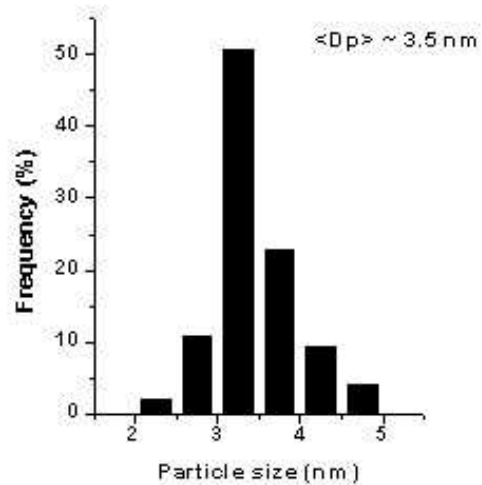
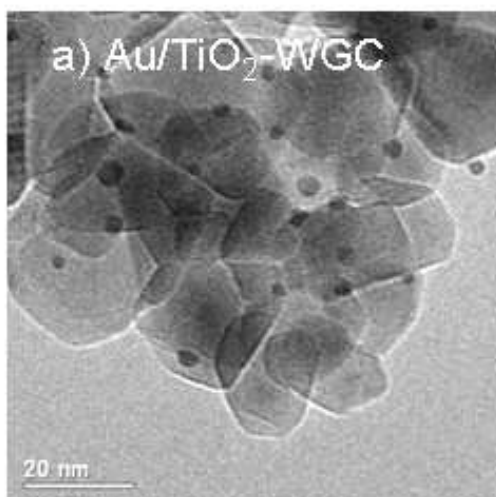
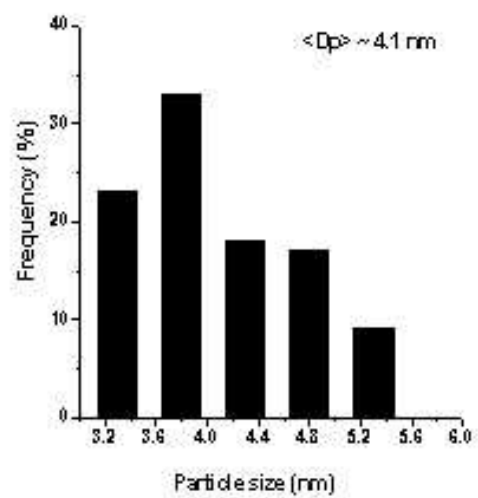
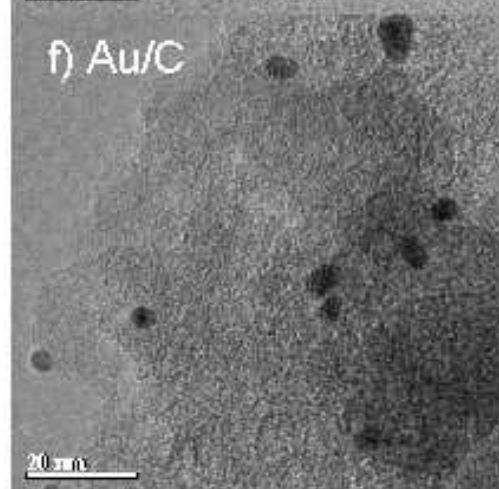
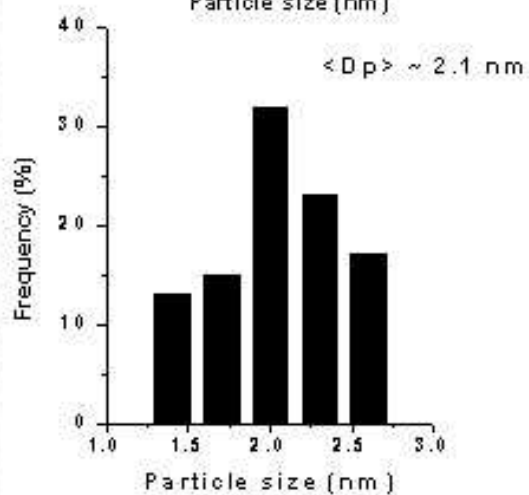
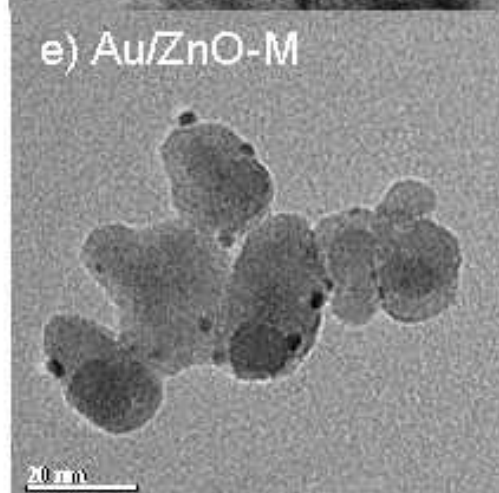
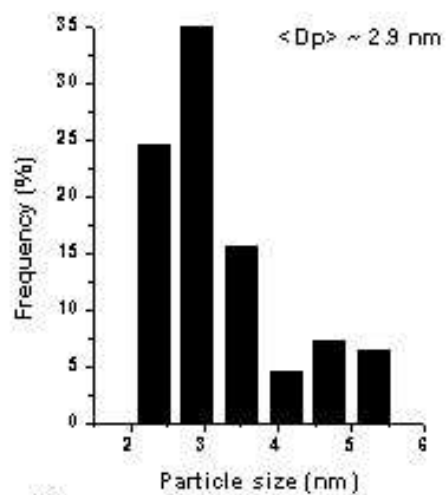
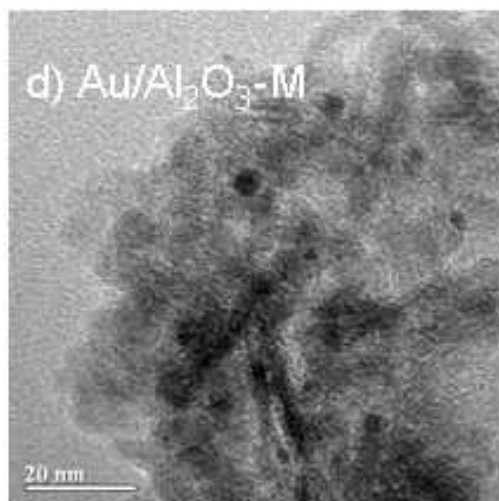


Figure S2. XRD patterns of HSA-TiO₂





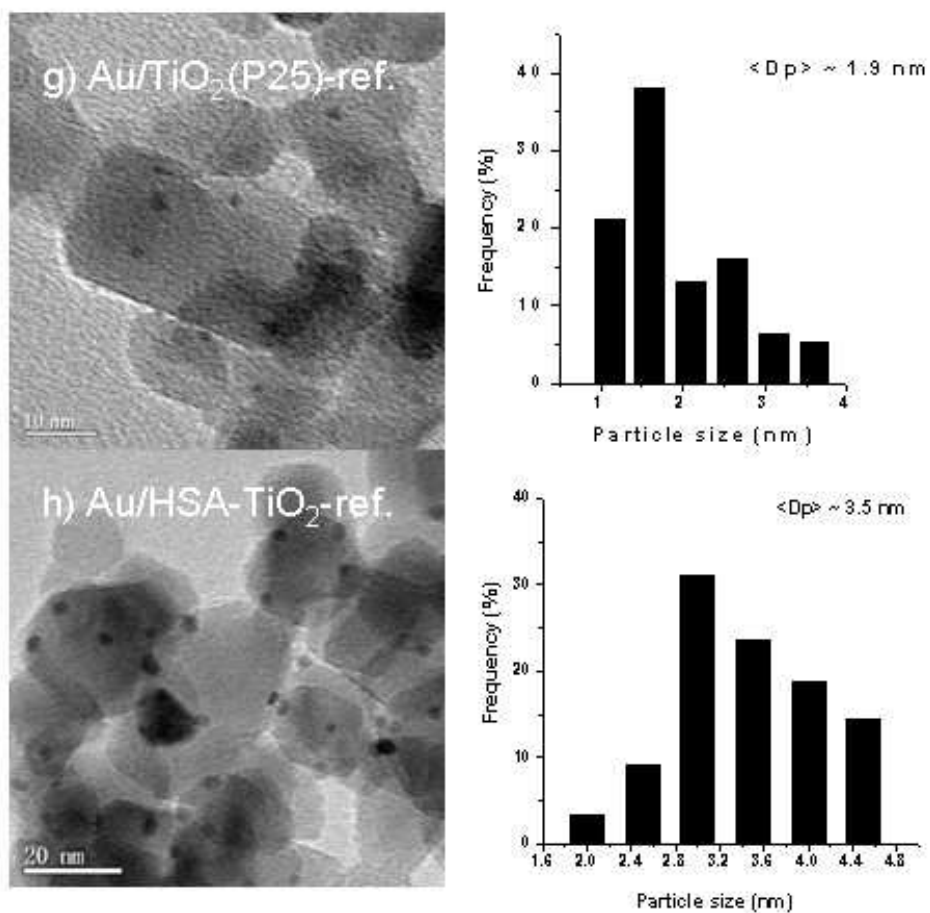


Figure S3. Representative TEM image and size distribution of a) 1.5 wt% Au/TiO₂-WGC; b) 1 wt% Au/TiO₂-M; c) 0.5 wt% Au/HSA-TiO₂; d) 1 wt% Au/Al₂O₃-M; e) 1 wt% Au/ZnO -M; f) 0.5 wt% Au/C; g) 0.5 wt% Au/TiO₂(P25)-ref.; h) 0.5 wt% Au/HAS-TiO₂-ref.

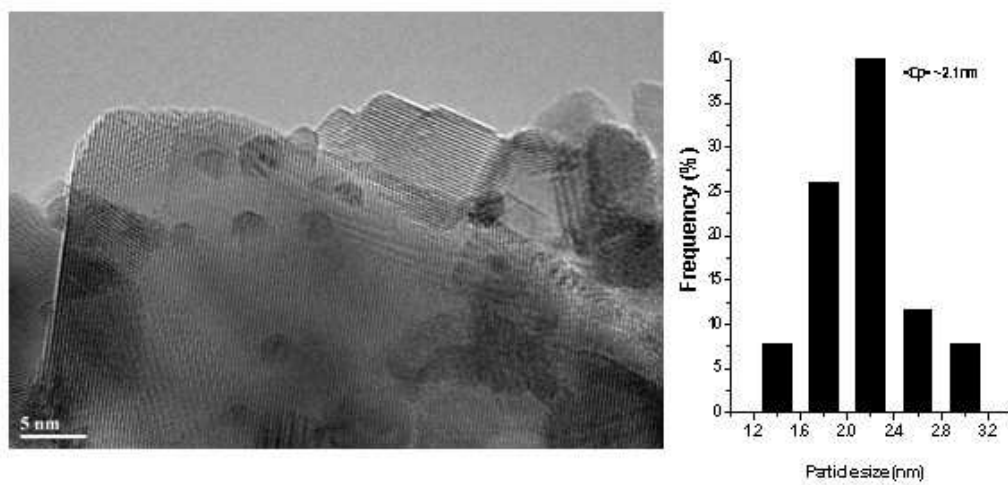


Figure S4. Representative HRTEM image and size distribution of of 0.5 wt% Au/CeO₂.

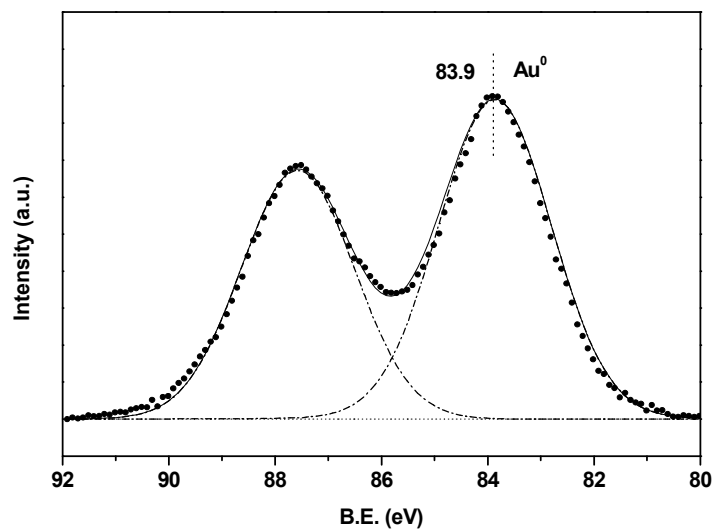


Figure S5. The binding energy of Au for Au/HSA-TiO₂.

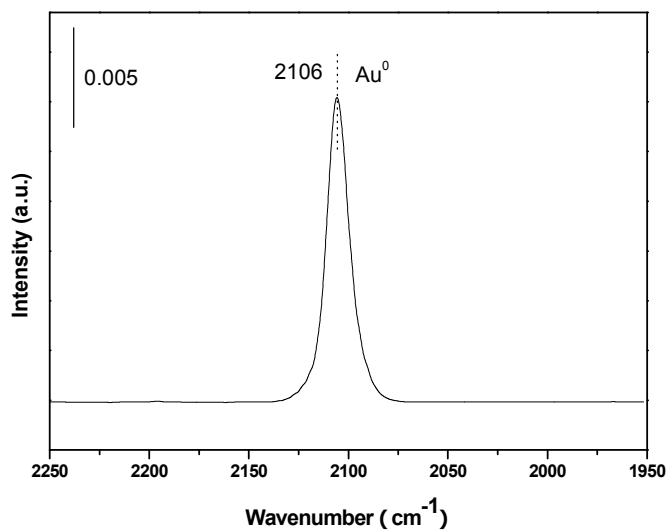


Figure S6. DRIFT spectrum of CO adsorption over Au/HSA-TiO₂ catalyst after CO adsorption for 5 min at 25 °C. Noted that there is only single peak of CO adsorption on gold catalysts at 2106 cm⁻¹ attributed to the vibration of CO adsorbed on Au⁰ species.^{S7}

4. Mechanistic/Reactivity studies

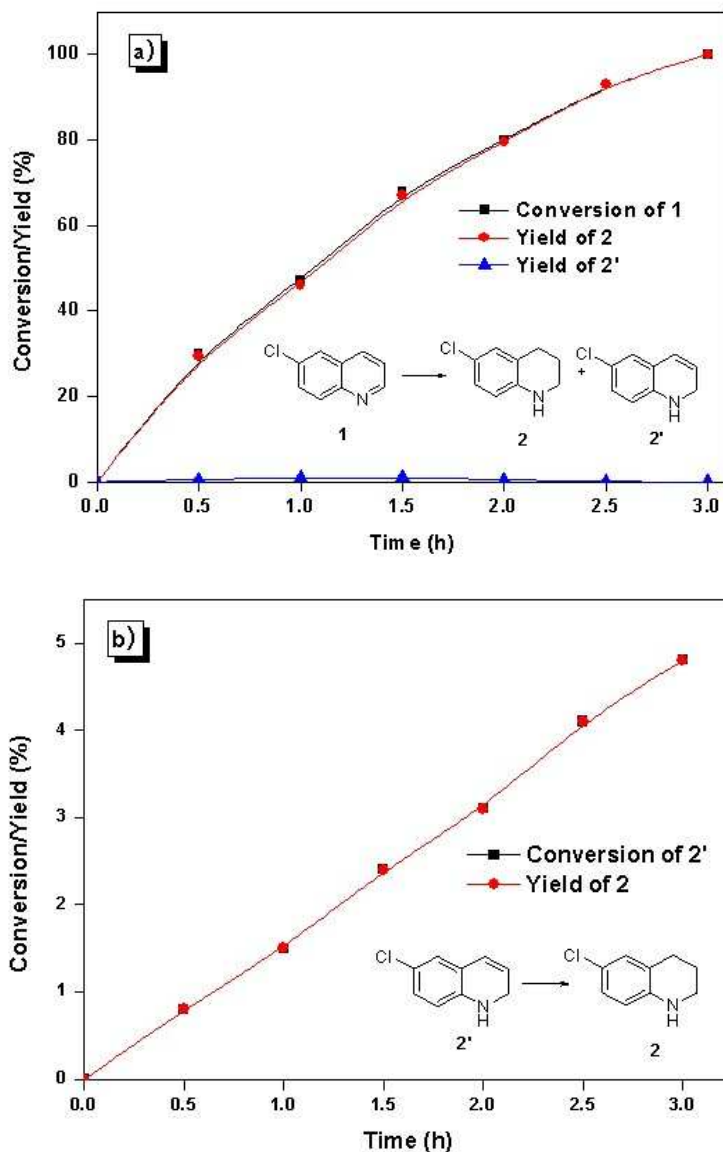


Figure S7. a) The hydrogenation of 6-chloroquinoline (1) over Au/HSA-TiO₂. b) The hydrogenation of 6-chloro-1,2-dihydroquinoline (2') over Au/HSA-TiO₂. Reaction conditions: 6-chloroquinoline or 6-chloro-1,2-dihydroquinoline (0.5 mmol), toluene (3 mL), Au/HSA-TiO₂ (Au: 1 mol%), 2 MPa H₂, 60 °C. Note that a trace amount of 2' (maximum 1% yield) has been identified as a sole by-product during the hydrogenation of 1. Based on the fact that the reaction of 2' instead of 1 proceeds very sluggishly (gave target 2 product in < 5% yield) under otherwise identical conditions, the overall reduction may occur mainly in 1,4-mode rather than through the intermediate formation of 2' via an initial 1,2-hydride addition pathway.

5. Time-conversion plot of typical representative catalysts.

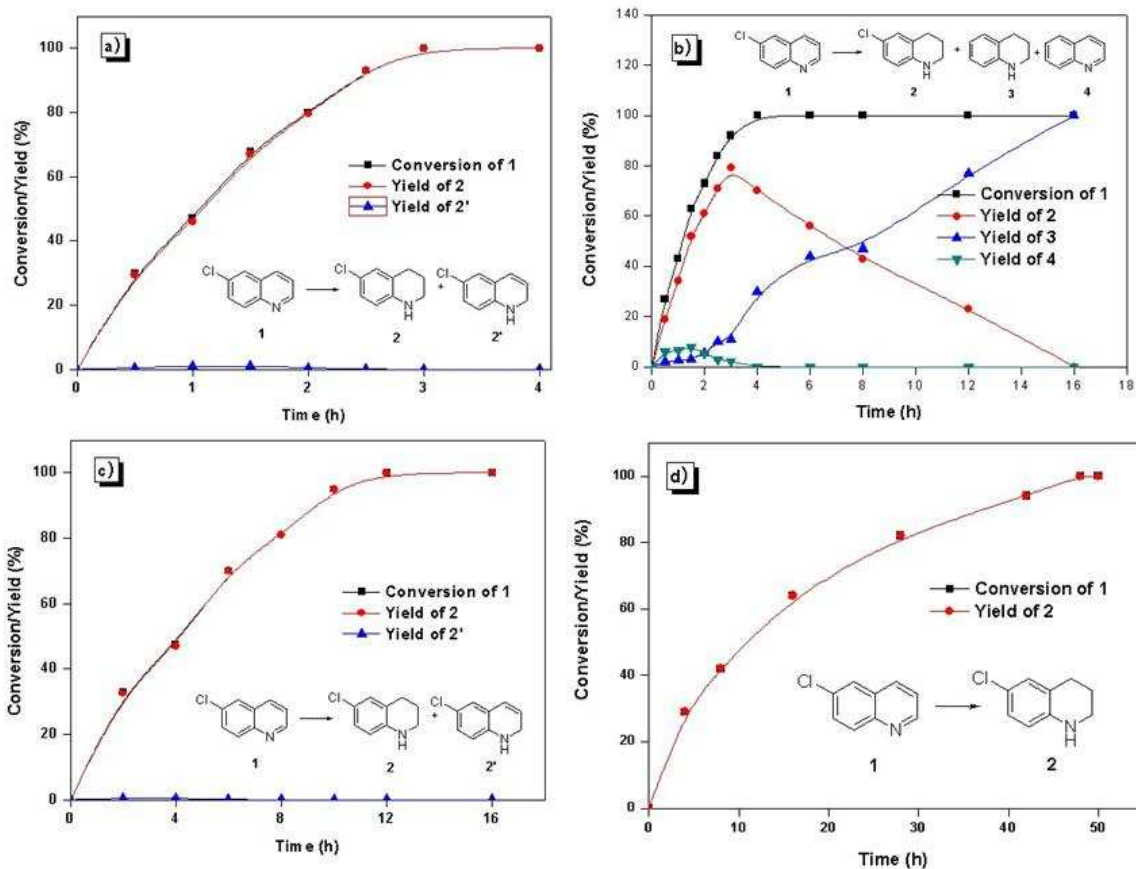


Figure S8. Time-conversion plot of typical representative catalysts. a) Au/HSA-TiO₂; b) Pd/HSA-TiO₂; c) Au/HSA-TiO₂-ref.; d) Au/CeO₂. Reaction conditions: 6-chloroquinoline (0.5 mmol), toluene (3 mL), catalyst (metal: 1 mol%), 2 MPa H₂, 60 °C.

6. References

- (S1) He, L.; Wang, J. Q.; Gong, Y.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. *Angew. Chem. Int. Edit.* **2011**, *50*, 10216.
- (S2) Forrest, T. P.; Dauphinee, G. A.; Deraniyagala, S. A. *Can. J. Chem.* **1985**, *63*, 412.
- (S3) Haruta, M. *Catal. Today* **1997**, *36*, 153.
- (S3) Porta, F.; Prati, L.; Rossi, M.; Coluccia, S.; Martra, G. *Catal. Today* **2000**, *61*, 165.
- (S5) Hashimoto, N.; Takahashi, Y.; Hara, T.; Shimazu, S.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda K. *Chem. Lett.* **2010**, *39*, 832.
- (S5) Bus, E.; Miller, J.T.; van Bokhoven, J.A. *J. Phys. Chem. B.* **2005**, *109*, 14581.
- (S6) Ravel, B.; Newville. M. *J. Synchrotron Rad.* **2005**, *12*, 537.
- (S7) Li, M.; Wu, Z.; Ma, Z.; Schwartz, V.; Mullins, D. R.; Dai, S.; Overbury, S. H. *J. Catal.* **2009**, *266*, 98.