Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Fully Dispersed Pt Entities on Nano-Au Dramatically Enhance the Activity of Gold for Chemoselective Hydrogenation Catalysis

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Preparation of Pt_m^Au/SiO_2 catalysts:

PVA-stabilized Au nanoparticles with an averaged size of 3.0 ± 0.6 nm were prepared by reduction of $AuCl_4^-$ ($HAuCl_4 \cdot 4H_2O$, Acros) with $NaBH_4$ (99%, Sigma Aldrich) in aqueous solutions containing polyvinyl alcohol (PVA, typical repeating units 1750, AR, Beijing Chemical Reagent Company). In a typical procedure, 1 mL of 0.05 M $HAuCl_4$ solution was diluted with 130 mL of deionized water and then mixed with 50 mL of PVA solution (0.2 mg mL^{-1}) and 20 mL of ethanol. The solution was kept under vigorous stirring for 2 h, and then 5 mL of fresh 0.1 M $NaBH_4$ solution was added dropwise. The resulted wine-colored solution was kept under vigorous stirring for 2 h to ensure the formation of Au nanoparticles.

Pt_m^Au nanoparticles were obtained via a successive hydrogen reduction of $PtCl_6^{2-}$ (K_2PtCl_6, AR, Beijing Chemical Reagent Company) onto as-prepared Au nanoparticles. In the case of $Pt_{0.05}$^Au nanoparticles, 50 mL of 0.05 mM K_2PtCl_6 solution (2.5 μmol of Pt) was mixed with the as-prepared Au colloid (50 μmol of Au). The resulted solution was kept under vigorous stirring for 2 h and then transferred into a bubbling tube. After purged with N_2 for 30 min, the solution was bubbled with H_2 for 2 h and then kept airtight for 48 h at room temperature to obtain Pt_m^Au nanoparticles.

SiO_2 (Aerosil 90, Degussa) with a BET surface area of 90 m^2/g was used as an inert support for the Pt_m^Au nanoparticles. In a typical immobilization procedure, 1 g of SiO_2 was added to the as-prepared Pt_m^Au colloid (50 μmol of Au) under vigorous stirring, then pH of the suspension (initial pH = *ca.* 7.6) was adjusted to 0.5 by addition of HNO_3 solutions of different concentrations (0.2, 1.0 and 3.2 M, used in different stage to avoid any rapid drop in pH). The resulted suspensions were vigorously stirred for 2h and then filtrated. The solids were extensively washed with deionized water (500 mL for each time) for 3 times and then dried at 110 ◦C.

Characterizations:

Transmission electron microscopy (TEM) measurements were performed on a Tecnai G2 F20 U-Twin system operating at 200 kV. Inductively coupled plasma atomic emission spectrometry (ICP-AES), X-Ray photoelectron spectroscopy (XPS), UV-vis spectroscopy and electrochemical measurements were performed following the same procedure detailed in Ref. 8 and 9.

Catalytic testing:

Hydrogenation reactions were performed on a high pressure reaction set equppted with a Parr 4843 controller and a 25 mL Hastelloy autoclave. In a typical procedure, the autoclave was first loaded with 5 mL of toluene (AR, Beijing Chemical Reagent Company), certain amount of catalyst and substrate, and then purged with H_2 (0.8 MPa, in excess) for 6 times. After pressurized to the desired H_2 pressure at room temperature, the autoclave was heated to the reaction temperature (150 ◦C). Zero reaction time was taken as soon as the reaction temperature was reached and mechanical stirring (900 rpm) was started then.

Transfer hydrogenation reactions were performed on a similar high pressure reaction set equppted with a Parr 4843 controller and a 50 mL Hastelloy autoclave. In a typical procedure, the autoclave was first loaded with 10 mL of benzyl alcohol (AR, Beijing Chemical Reagent Company), 50 mg of catalyst and 0.5 mL of cinnamaldehyde (4 mmol), and then purged with

N_2 (0.8 MPa, in excess) for 6 times. Zero reaction time was taken as soon as the autoclave was heated to the reaction temperature (150 ◦C), and mechanical stirring (900 rpm) was started then.

After each reaction, the autoclave was quenched by ice-water bath. The reacted liquid was separated with catalyst by filtration and then analyzed by an HP-7890A gas chromatograph equipped with a Shimadzu HiCap CBP20 capillary column and a flame ionization detector (FID) or an HP-4890 gas chromatograph equipped with an HP-5 capillary column and an FID. Identification of products was performed on an HP-6890 gas chromatograph equipped with an HP-5 capillary column and an HP-5973 mass selective detector (MSD).

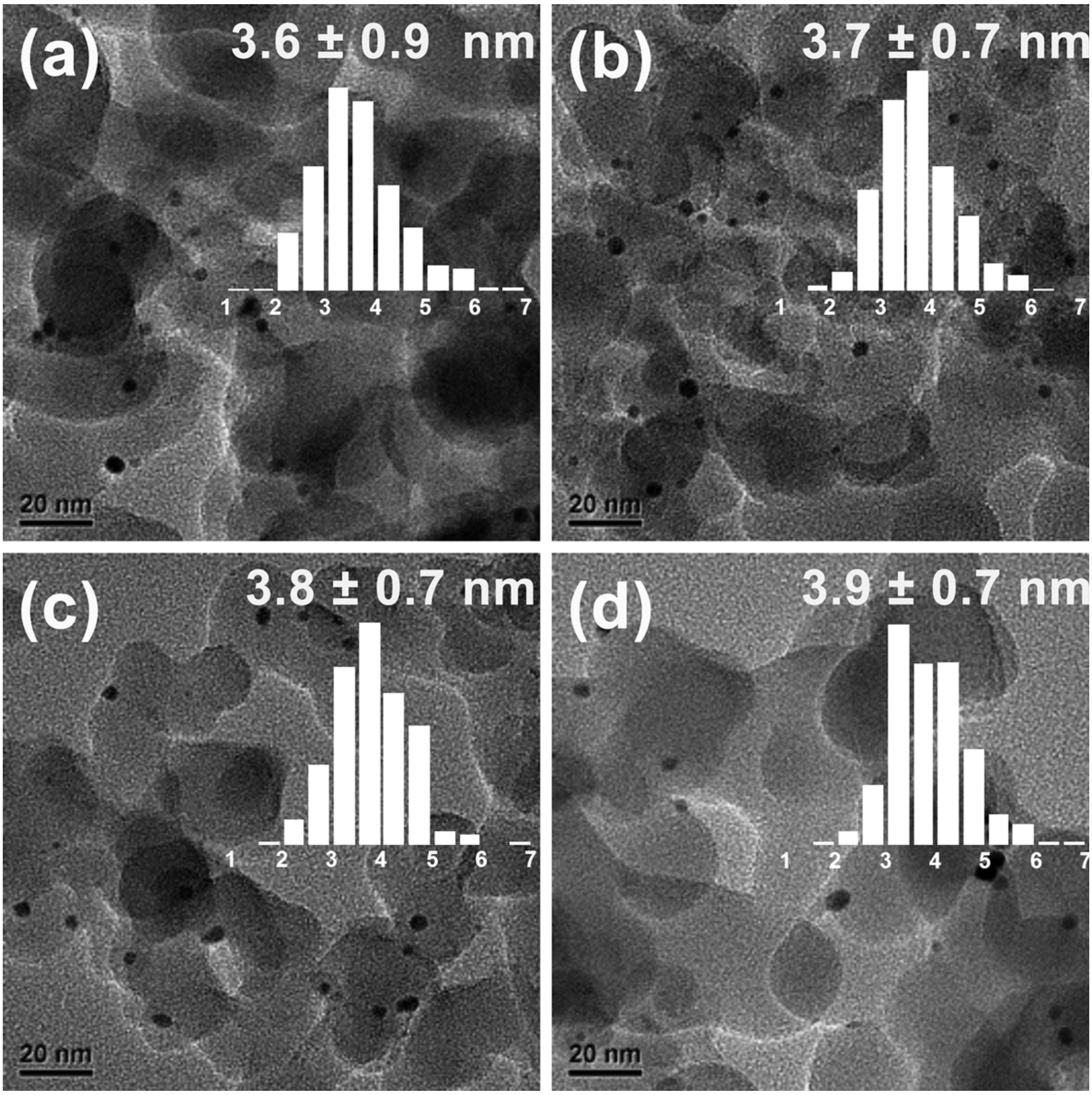
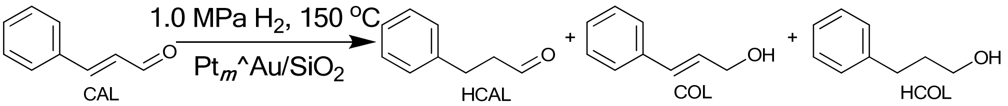


Fig. S1 Representative TEM images of $Pt_{\boldsymbol{m}}$^Au/SiO_2 samples: (a) $\boldsymbol{m} = 0$; (b) $\boldsymbol{m} = 0.01$; (c) $\boldsymbol{m} = 0.05$; (d) $\boldsymbol{m} = 0.1$; the accompanying bar graphs give the size distributions of the immobilized $Pt_{\boldsymbol{m}}$^Au nanoparticles.

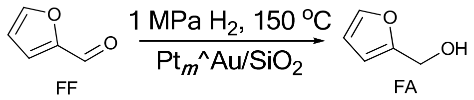
Table S1 Detailed catalytic data for CAL hydrogenation [a]



Catalyst	Rxn. time (min)	CAL conv. (%)	Sel. (%)		
			HCAL	COL	HCOL
Au/SiO_2	720	11	73	23	4
$Pt_{0.005}$^Au/SiO_2	240	20	77	15	8
$Pt_{0.01}$^Au/SiO_2	240	19	79	17	4
$Pt_{0.05}$^Au/SiO_2	15	15	72	19	9
$Pt_{0.1}$^Au/SiO_2	15	16	71	21	8
$Pt_{0.2}$^Au/SiO_2	15	15	75	19	6
$Pt_{0.05}$^Au/SiO_2	240	63	78	10	12
$Pt_{0.05}$^Au/SiO_2	120	44	78	13	9
$Pt_{0.05}$^Au/SiO_2	60	33	74	18	8
$Pt_{0.05}$^Au/SiO_2	30	23	79	14	7
$Pt_{0.1}$^Au/SiO_2	120	45	74	15	11
$Pt_{0.1}$^Au/SiO_2	30	23	76	16	8
$Pt_{0.2}$^Au/SiO_2	240	47	79	11	10
$Pt_{0.2}$^Au/SiO_2	120	33	78	12	10
$Pt_{0.2}$^Au/SiO_2	60	25	79	12	9
$Pt_{0.2}$^Au/SiO_2	30	21	74	19	7

[a] Reaction conditions: 0.5 mL CAL dissolved and 50 mg of catalyst dispersed in 5 mL toluene.

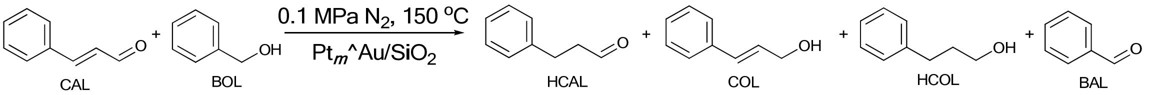
Table S2 Detailed catalytic data for furfural hydrogenation [a]



Catalyst	Rxn. time (min)	FF conv. (%)	Sel. of FA (%)	MSA_{Au} ($mol/h/g_{Au}$)	MSA_{Pt} ($mol/h/g_{Pt}$)
SiO_2	240	0	-	-	-
Au/SiO_2	240	1	> 99	0.02	
$Pt_{0.005}$^Au/SiO_2	240	4	> 99	0.08	15.9
$Pt_{0.01}$^Au/SiO_2	240	5	> 99	0.10	9.94
$Pt_{0.05}$^Au/SiO_2	240	10	> 99	0.20	3.98
$Pt_{0.1}$^Au/SiO_2	240	18	> 99	0.36	3.58
$Pt_{0.2}$^Au/SiO_2	240	11	> 99	0.22	1.09
5 wt% Pt/SiO_2	60	6	> 99	-	0.10

[a] Reaction conditions: 0.33 mL furfural dissolved and 50 mg of catalyst dispersed in 5 mL toluene; stirring speed = 900 rpm·

Table S3 Detailed catalytic data for CAL transfer hydrogenation [a]



Catalyst	CAL conv. (%)	$BAL/CAL_{con.}$ [b]	Sel. (%)		
			HCAL	COL	HCOL
SiO_2	0	-	-	-	-
Au/SiO_2	7	1.3	33	63	4
$Pt_{0.005}$^Au/SiO_2	14	1.2	67	25	9
$Pt_{0.05}$^Au/SiO_2	12	1.2	66	29	5
$Pt_{0.2}$^Au/SiO_2	8	1.3	56	38	7

[a] Reaction conditions: 0.5 mL CAL dissolved and 50 mg of catalyst dispersed in 10 mL BOL; rxn. time = 240 min; stirring speed = 900 rpm; [b] Mole ratio of BAL produced and CAL converted, indicating hydrogen produced in BOL dehydrogenation was not fully consumed.