Supporting information

Silica-Supported Ultra Small Gold Nanoparticles as Nanoreactors for the Etherification of Silanes

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Due to the ultra small size of gold nanoparticles, it was difficult to determine its accurate size directly. In addition, the gold nanoparticles was too small to show a SPR peak in UV-vis spectrum and diffraction peaks in XRD pattern. In order to prove the existence of Au, calcination under hydrogen and high temperature was done to aggregate gold particles. Figure S1 shows the large scale TEM images of Au-SiO_2 and the aggregated Au-SiO_2. The generation of big Au particles can be clearly observed in Figure S1b.

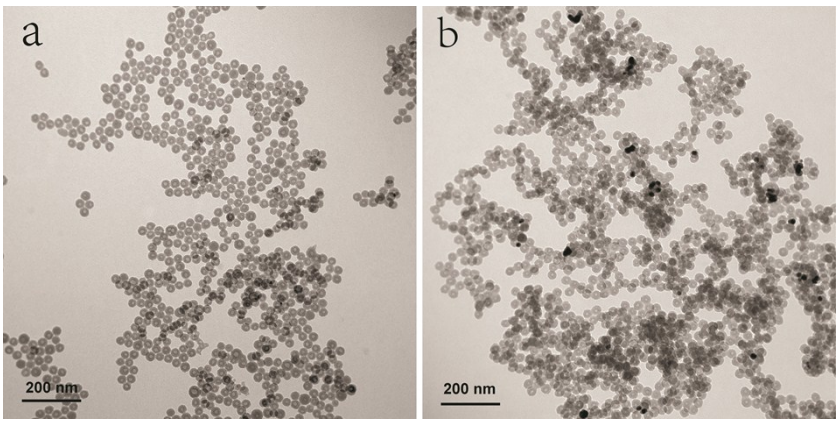


Figure S1 a) TEM image of ultra small Au-SiO_2; b) TEM image of aggregated Au-SiO_2

All the catalysts were prepared in a reverse microemulsion. The gold loading was

determined to be 0.87 wt% (Au-Al_2O_3), 1.58 wt% (Au-FeO_x) and 1.35 wt% (Au-SiO_2 4 nm) by ICP. The characterizations of catalysts can be seen in Figure S2-Figure S7.

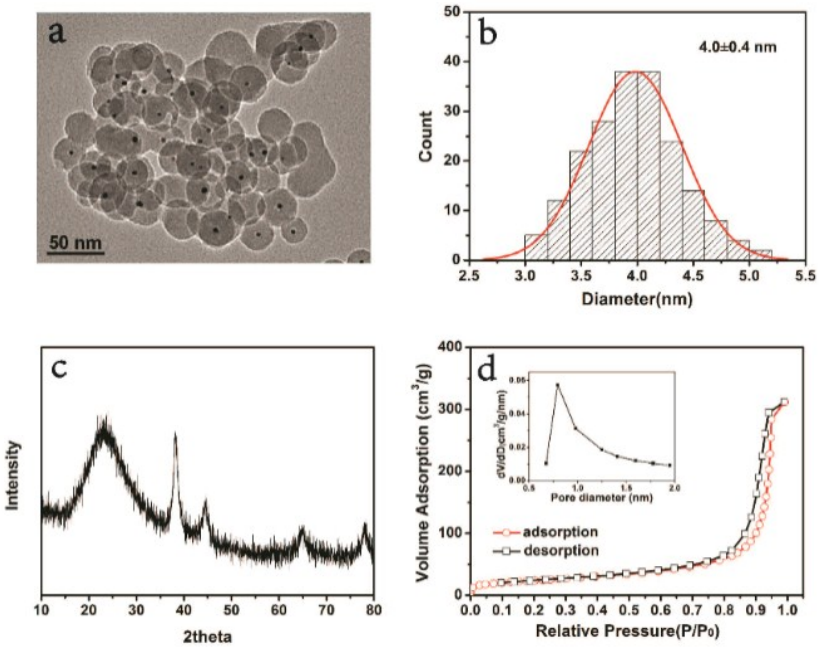


Figure S 2 a) TEM image of Au (4.0 nm)-SiO_2; b) size distribution of gold nanoparticles; c) XRD pattern of the aggregated Au-SiO_2; d) N_2 sorption isotherm of Au-SiO_2 (inset was the distribution of micropore size).

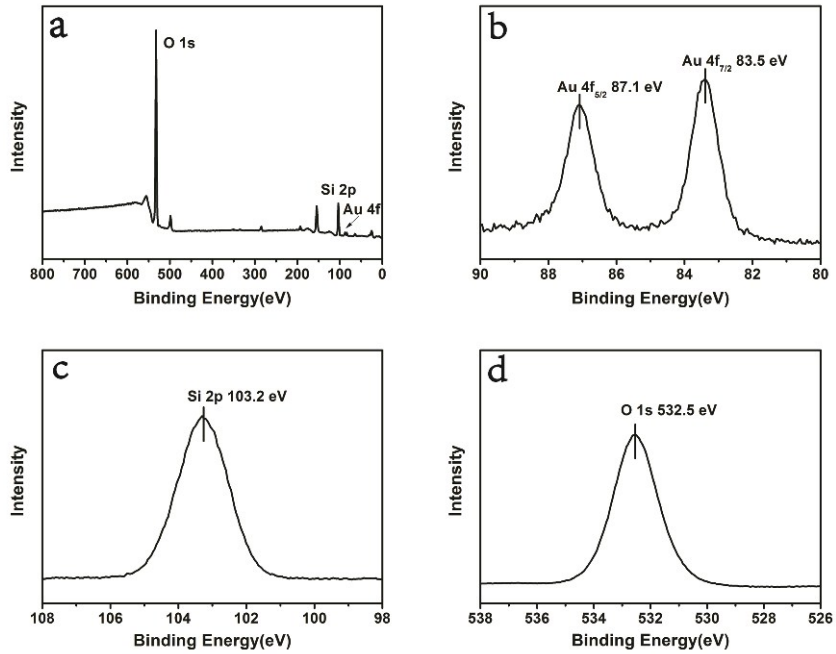


Figure S 3 a) Survey XPS spectrum of Au (4.0 nm)-SiO_2; b-d) narrow scan spectra for the elements of Au, Si and O.

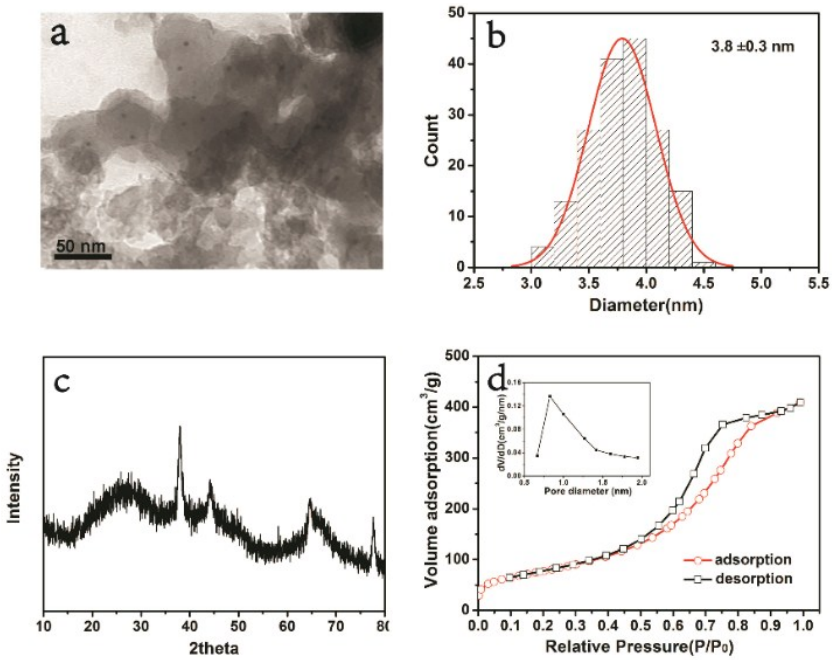


Figure S 4 a) TEM image of Au-Al_2O_3 (3.8 nm); b) size distribution of gold nanoparticles; c) XRD pattern of Au-Al_2O_3; d) N_2 sorption isotherm of Au-Al_2O_3 (inset was the distribution of micropore size).

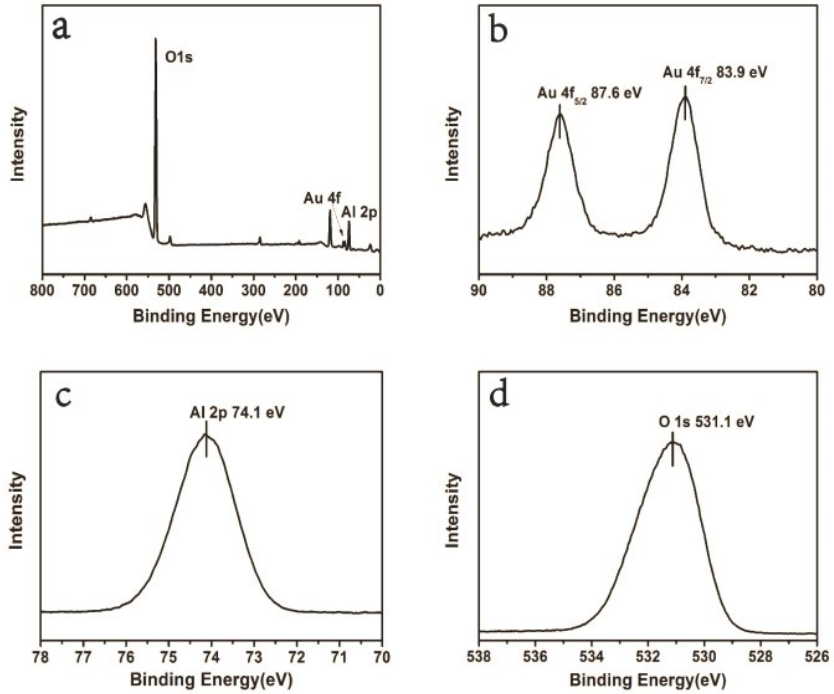


Figure S 5 a) Survey XPS spectrum of Au-Al_2O_3; b-d) narrow scan spectra for the elements of Au, Al and O.

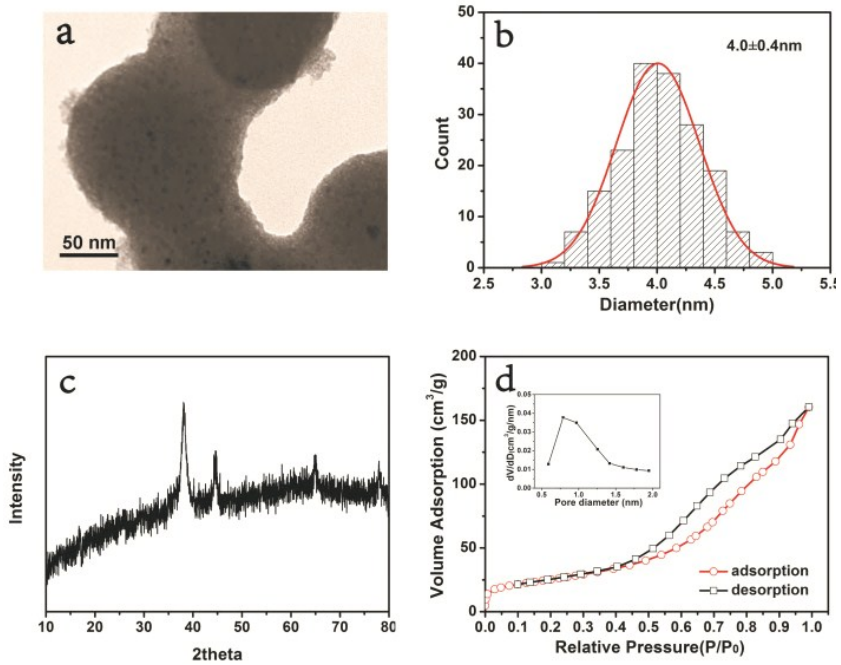


Figure S 6 a) TEM image of Au-FeO_x (4.0 nm); b) size distribution of gold nanoparticles; c) XRD pattern of Au-FeO_x; d) N_2 sorption isotherm of Au-FeO_x (inset was the distribution of micropore size).

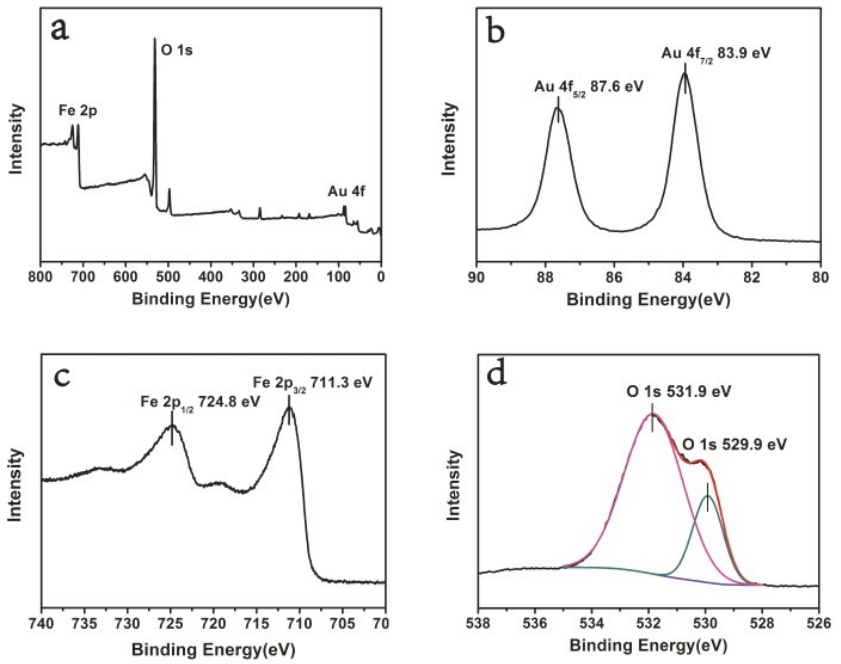


Figure S 7 a) Survey XPS spectrum of Au-FeO_x, b-d) narrow scan spectra for the elements of Au, Fe and O.

Adsorption ability of Au-SiO_2, Au-Al_2O_3 and Au-Fe_2O_3 for the substrates, shown in Table S1.

Table S 1 The adsorption amount of substrate over catalysts.

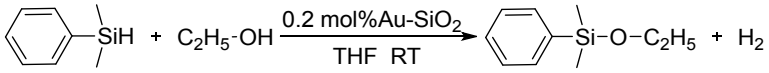
Catalysts	$PhMe_2SiH$	Ethanol

	Before (mol/L)	After (mol/L)	Adsorption amount (mmol/g)	Before (mol/L)	After (mol/L)	Adsorption amount (mmol/g)
Au-SiO_2	0.126	0.110	1.55	0.105	0.094	1.11
Au-Al_2O_3	0.108	0.107	0.07	0.118	0.115	0.28
Au-Fe_2O_3	0.104	0.103	0.11	0.098	0.096	0.14

Reaction conditions: $PhMe_2SiH$ (0.1 mL) or C_2H_5OH (0.05 mL), THF (6.0 mL), catalysts (20 mg). The reactions were performed at room temperature under air and the adsorption amount was calculated by GC with internal standard.

To verify the reusability of Au-SiO_2, 10 consecutive runs were performed. All the runs could be finished in 2 hours with almost 99% conversion, as shown in Table S2.

Table S 2 The reusability of Au-SiO_2.



Reuse	Conversion (%)	Selection (%)
1	>99	>99
2	>99	>99
3	>99	>99
4	98.9	>99
5	>99	>99
6	98.5	>99
7	>99	>99
8	>99	>99
9	>99	>99
10	>99	>99

Reaction conditions: $PhMe_2SiH$ (0.1 mL, 0.65 mmol), C_2H_5OH (0.2 mL), THF (6.0 mL), Au-SiO_2 (20 mg, 0.2 mol%). The reactions were performed at room temperature under air and the conversion was obtained after 2 hours by GC with internal standard.

The TEM image analysis before and after the 10 consecutive runs. There is no alteration of the catalyst morphology and no aggregation of gold nanoparticles.

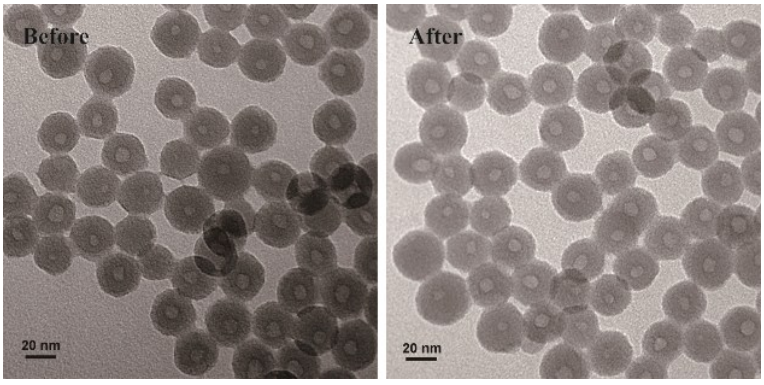


Figure S 8 TEM images of the catalyst before and after the runs.

The comparison between our work and the recently reported literatures show in Table S 3, the result indicate ultra small Au-SiO_2 was an active and effective catalyst.

Table S 3 The comparison between this work and the literatures

catalyst	**Silane**	**Alcohol**	**TOF(h^{-1})**	**ref**
Au-SiO_2	$PhMe_2SiH$	methanol	568 (25 °C)	This work
Au-SiO_2	$PhMe_2SiH$	ethanol	234 (25 °C)	This work
Au-SiO_2	$PhMe_2SiH$	*n*-butanol	94 (50 °C)	This work
Au/Al_2O_3	$PhMe_2SiH$	*n*-butanol	667(100 °C)	1
Au/HAP_{nano}	$PhMe_2SiH$	methanol	660 (25 °C)	2
Au/HAP_{nano}	$PhMe_2SiH$	ethanol	660 (25 °C)	2
Ag nanoparticles	$PhMe_2SiH$	methanol	5 (25 °C)	3
Ag nanoparticles	$PhMe_2SiH$	ethanol	5 (25 °C)	3
Pd nanoparticles	$PhMe_2SiH$	methanol	1.12(25 °C)	4
Pd nanoparticles	$PhMe_2SiH$	ethanol	1.12(25 °C)	4

References

1. P. Raffa, C. Evangelisti, G. Vitulli and P. Salvadori, *Tetrahedron Lett.*, 2008, **49**, 3221-3224.
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4. Z. Li, S. Lin, L. Ji, Z. Zhang, X. Zhang and Y. Ding, *Catal. Sci. Technol.*, 2014, **4**, 1734.