Electronic Supplementary Information

Au nanoparticles embedded into the inner wall of TiO_2 hollow spheres as nanoreactor with superb thermal stability

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Experimental Section

Au nanoparticles loading on SPS

Sulfonated-polystyrene spheres (SPS) were prepared according to Yang's method.[1] In the synthesis of Sample A, 500 mg SPS was dispersed in 200mL distilled water by ultrasound treatment. 0.2 g $SnCl_2$ was dissolved in 40 mL 0.02 M HCl solution, and then mixed with SPS suspension. After stirring for 10 min, the suspension was centrifuged and washed with distilled water for five times. The Sn^{2+}-absorbed SPS was dispersed in 100 mL distilled water again, followed by drop-wise adding of 215 μL 0.0975 M $HAuCl_4$ solution. Ten min later, 20 mL of 0.15 M sodium formate (HCOONa) solution was added and the mixture was stirred for 5 h. After centrifugation and washing with distilled water five times, the precipitate was dried at 60 ºC overnight. (The dosages of $SnCl_2$, $HAuCl_4$, HCOONa used in preparation of Sample B and Sample C were adjusted accordingly.)

Production of Au@TiO_2 nanoreactor

The Au-loading SPS was dispersed in 100 mL of tetrabutyl titanate (TBOT)/alcohol (1:1 vol/vol) mixture for 8 h to allow a saturated adsorption of TBOT. The TBOT saturated particles were separated by centrifugation, and dispersed into ethanol/water (1:1 vol/vol; 50 mL), then stirred at ambient temperature for 2 h to allow complete TBOT hydrolization. The Au/SPS@TiO_2 was centrifuged, washed and dried at 80 °C for 2 h followed by calcination in air at 500 °C for 6 h.

Characterization

TG/DTA analysis was conducted on a DSC6220 Differential scanning calorimeter under air atmosphere at heating rate of 10 ºC /min. X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using Cu Ka irradiation. EDS measurement was operated on field emission scanning electron microscopy (FE-SEM, JEOL-6701F) and transmission electron microscopy (TEM, JEOL JEM-1011 and Tecnai G2 F20 U-TWIN) were used to observe the morphology and crystalline nature. The UV-visible absorption spectra of catalysts were obtained by using a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard. IR spectra and XPS information were obtained on Nicolet iN10 MX FT-IR Microscope and ESCALab220i-XL photoelectron spectroscopy respectively. The specific surface area and pore size distribution were measured by BET on an Autosorb-1 analyzer.

Determination the loading mount of Au

10 mg catalyst was dispersed in 10 mL nitrohydrochloric acid. After overnight the supernatant was taken out and diluted, and insoluble titanium dioxide was washed several times to recover all the loading Au. Each time washing liquid was added into diluted supernatant, and the final volume was 100 mL. The concentrations of $AuCl^{-}_{4}$ of liquid samples were measured by ICPE-9000. Results were shown in Table S1.

Catalytic reaction of CO oxidation

Carbon monoxide oxidation tests were conducted using a conventional quartz tubular reactor (i.d. 6mm; length, 400 mm) at atmospheric pressure using 50 mg of catalyst (mixed with 450 mg sea sand in order to prevent excessive pressure drop and mass flow restrictions). The reactant gas mixture consisted of 1.0 % CO balanced with nitrogen and equivalent dry air. The total flow rate of the reaction mixture was 50 mL/min, which is equivalent to a weight hourly space velocity (WHSV) of 60,000 ml/(hr·g catalyst). The effluent gases were analyzed online by a gas chromatography (Agilent 6890N GC) throughout the catalyst test. The reactor residence time for each desired temperature was 30 min. After the conversion reached at 100%, the catalytic process had been run continuously for 2 h at different high temperatures. Then catalysts were cooled down to room temperature for next catalysis.

Catalytic reduction of 4-nitrophenol

20 mg catalyst was dispersed into 25 mL deionized water by ultrasound treatment in a beaker. Aqueous solutions of 4-nitrophenol (750 uL, 0.01M) and $NaBH_4$ (3 mL, 0.1M) were added to form bright yellow solution. The reaction was carried in dark to exclude the influence of light irradiation. After every 2 min, 3 ml solution was taken out to get the supernate by rapid centrifugation within 1 min. The variation of concentration of 4-nitrophenol in the supernatant was immediately recorded by a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). All catalysts were centrifuged out and collected for the recyclable catalysis. All catalysts were treated at 800° C in muffle furnace for 2h, then the catalytic reduction was operated again for these heat-treated catalysts.

Synthesis of traditional loading Au-TiO_2 catalyst

The procedure of synthesis of Au-NP traditional loading catalyst is almost same as Au-encapsulated TiO_2 hollow spheres nanoreactor, except Au loading was preceded after calcination of the PS@TiO_2.

Figure Captions

Table. S1 Elemental composition of three catalysts (wt%) by EDS analysis

Table. S2 The turnover frequencies (TOF) of Samples for CO oxidation

Fig. S1 TG/DTG/DTA curves of Au/SPS@TiO_2 (for Sample A).

Fig. S2 TEM images, particle size distribution and EDS spectra of Sample A (a), Sample B (b), and Sample C (c). The signs of Si and Pt resulted form the substrate and conductive coating

Fig. S3 TEM image of Au@TiO_2 by direct deposition–precipitation method.

Fig. S4 XRD patterns of Sample A, Sample B and Sample C.

Fig. S5 IR spectra of Sample A, Sample B and Sample C.

Fig. S6 XPS survey spectra of Sample A (a), Ti2p (b), O1s (c), and S2p scan.

Fig. S7 Adsorption-desorption curves and pore size distribution (inset) of Sample A (a), Sample B (b) and Sample C (c).

Fig. S8 The light-off curves of Sample A (a), Sample B (b) and Sample C (c) treated at different temperatures for 2h, and particle size distributions of Sample A (a), Sample B (b), Sample C (c) treated at 800 °C for 2h. TEM image of treated Sample A (d) and XRD pattern of all treated samples.

Fig. S9 (a) TEM image of fresh outside-loading Au-TiO_2 catalyst. (b)The light-off curves of Au-TiO_2 catalyst treated at different temperatures for 2h, and UV-Vis spectra changing for catalytic reduction of 4-nitrophenol of Au-TiO_2 before (c) and after (d) treated at 800 °C for 2h

Fig. S10 UV-Vis spectra changing with concentration of 4-nitrophenol, cycling conversions for catalytic reduction of 4-nitrophenol of three catalysts before (left) and after (right) heat treatment.

Fig. S11 The side-view TEM images of Sample A (a,b) and Au-TiO_2 (c,d) catalysts before (left) and after (right) heat treatment.

Table. S1 Elemental composition of three catalysts (wt%) by EDS analysis

	Ti	O	Au	C	S	Au[a]
Sample A	42.48	52.94	2.86	1.72	0	2.58
Sample B	46.33	49.73	1.98	1.96	0	1.74
Sample C	46.19	50.80	1.07	1.94	0	1.01

a. Results from ICP analysis.

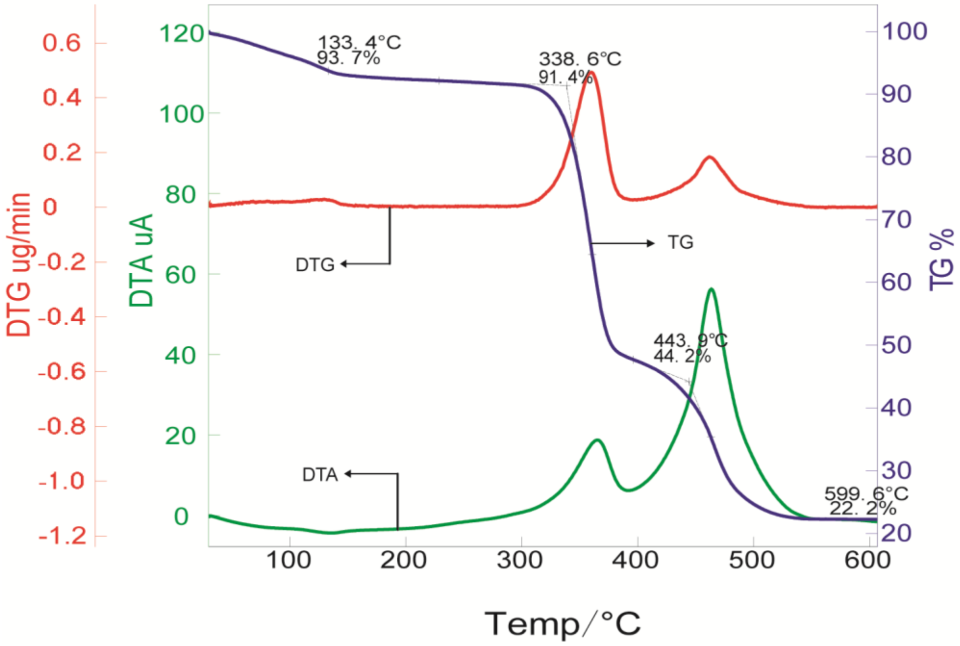
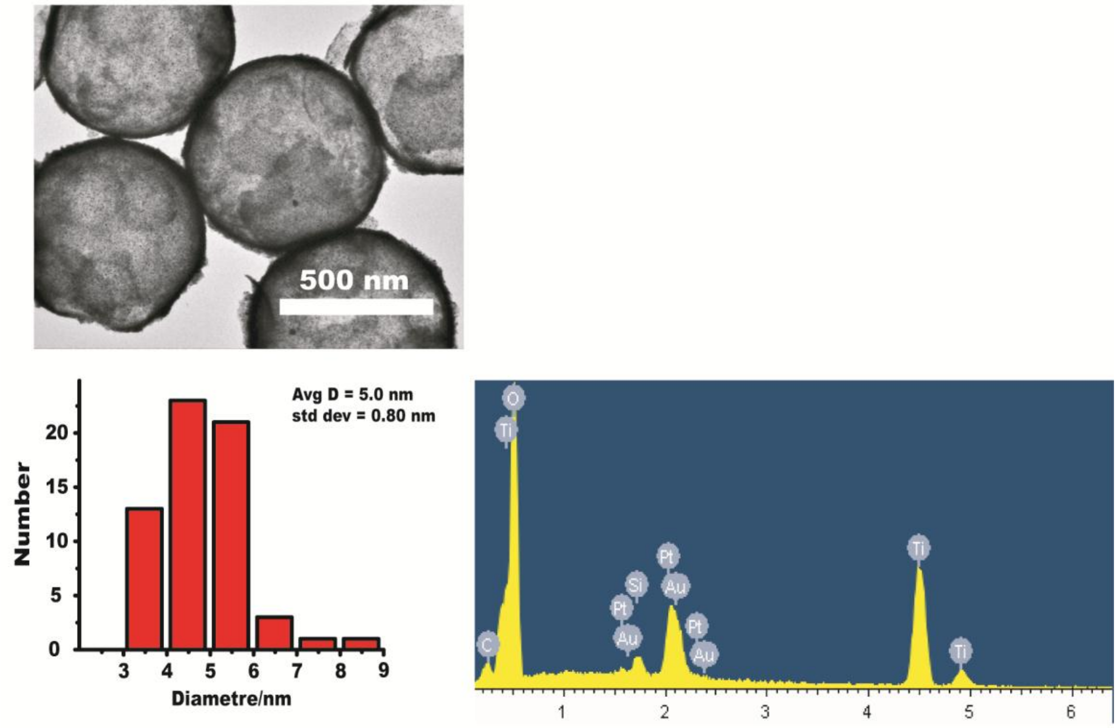


Fig. S1 TG/DTG/DTA curves of Au/SPS@TiO_2 (for Sample A).

(a)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Avg D = 5.0 nm
std dev = 0.80 nm
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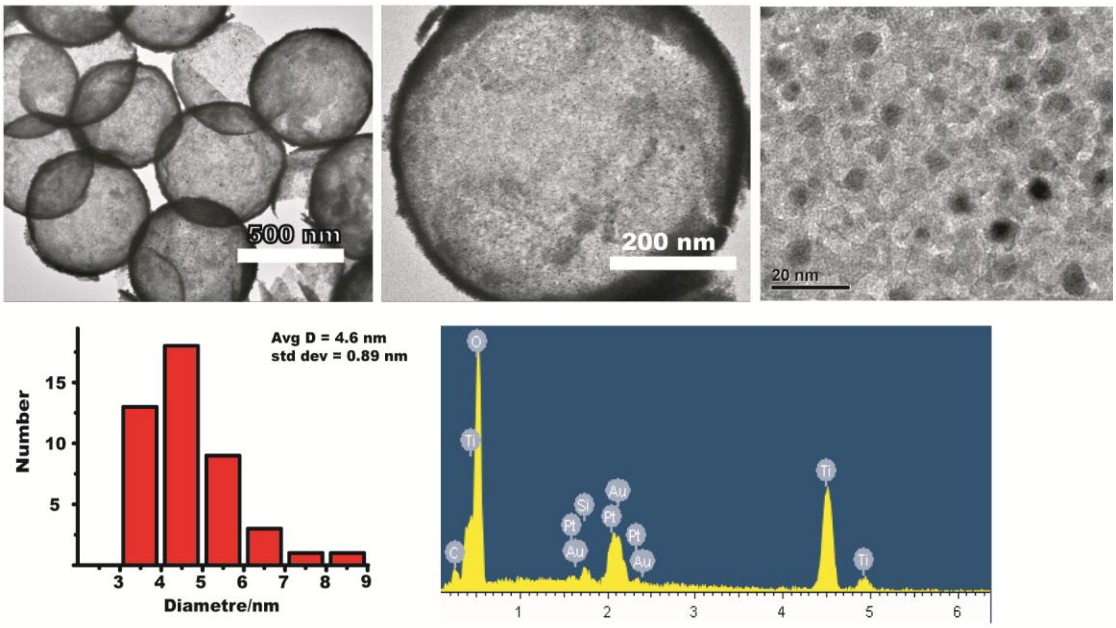
10
15
20
3
4
5
6
7
8
9
Diametre/nm
O
Ti
C
Si
Pt
Au
Pt
Au
Pt
Au
Ti
Ti
1
2
3
4
5
6

(b)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20 nm
Avg D = 4.6 nm
std dev = 0.89 nm
Number
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10
15
3
4
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6
7
8
9
Diametre/nm
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C
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Pt
Pt
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Ti
Ti
1
2
3
4
5
6

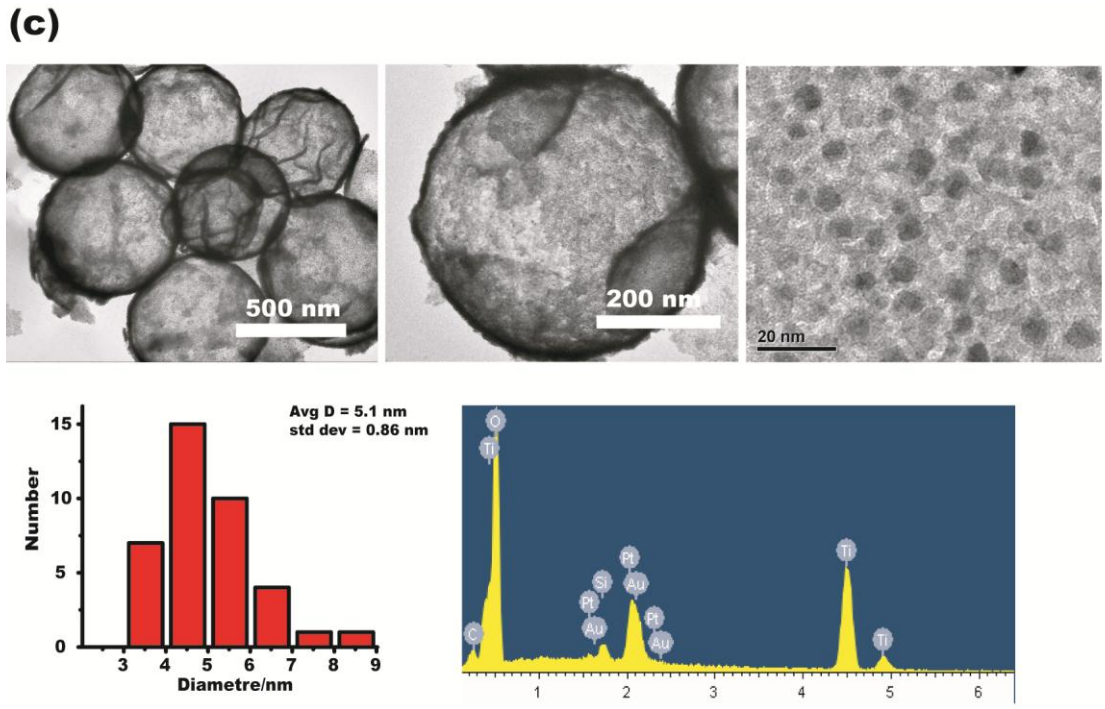


Fig. S2 TEM images, particle size distribution and EDS spectra of Sample A (a), Sample B (b), and Sample C (c). The signs of Si and Pt resulted form the substrate and conductive coating

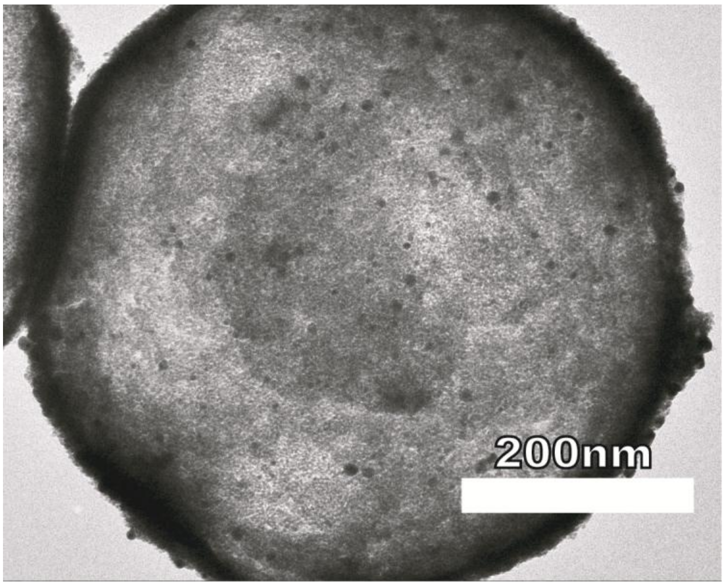


Fig. S3 TEM image of Au@TiO_2 by direct deposition–precipitation method.

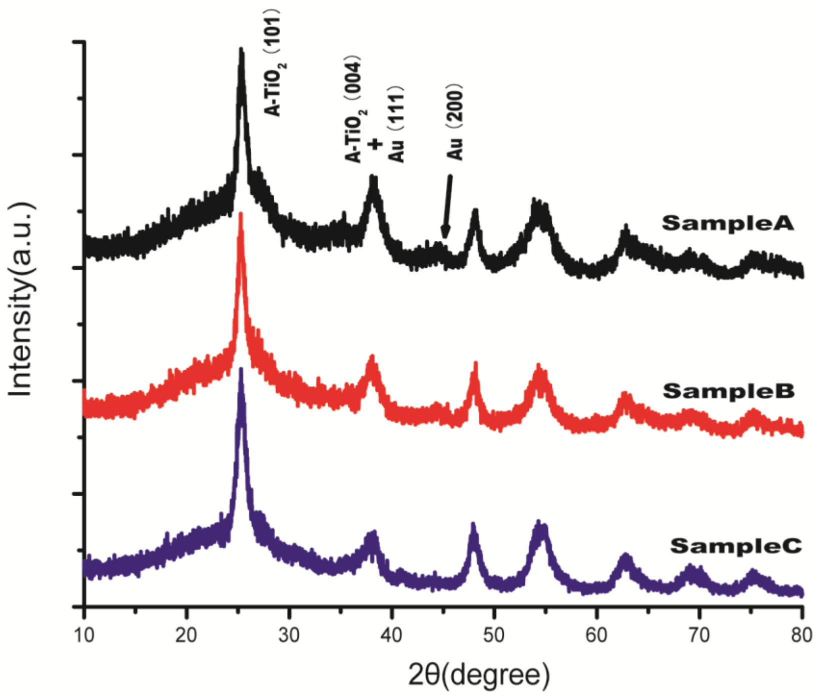


Fig. S4 XRD patterns of Sample A, Sample B and Sample C.

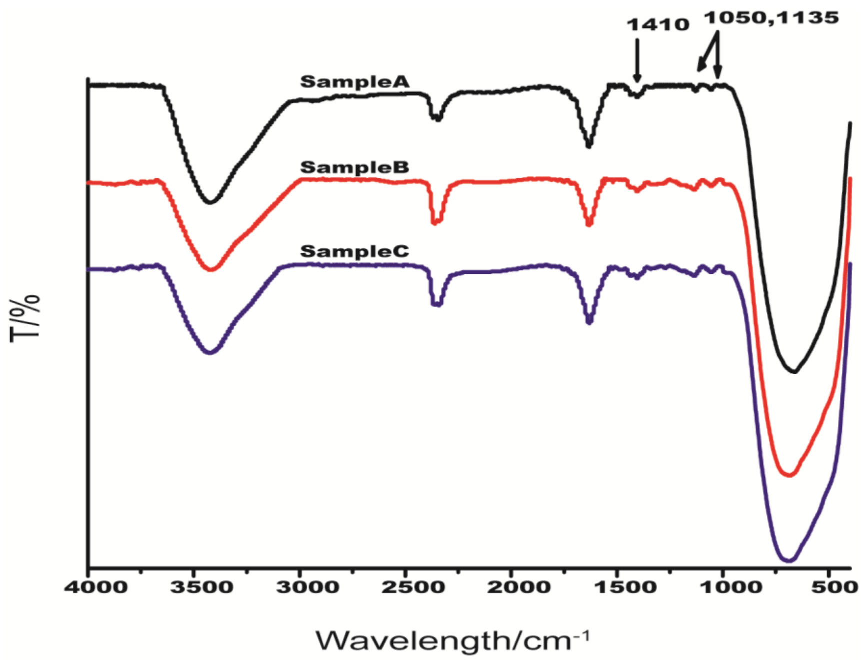
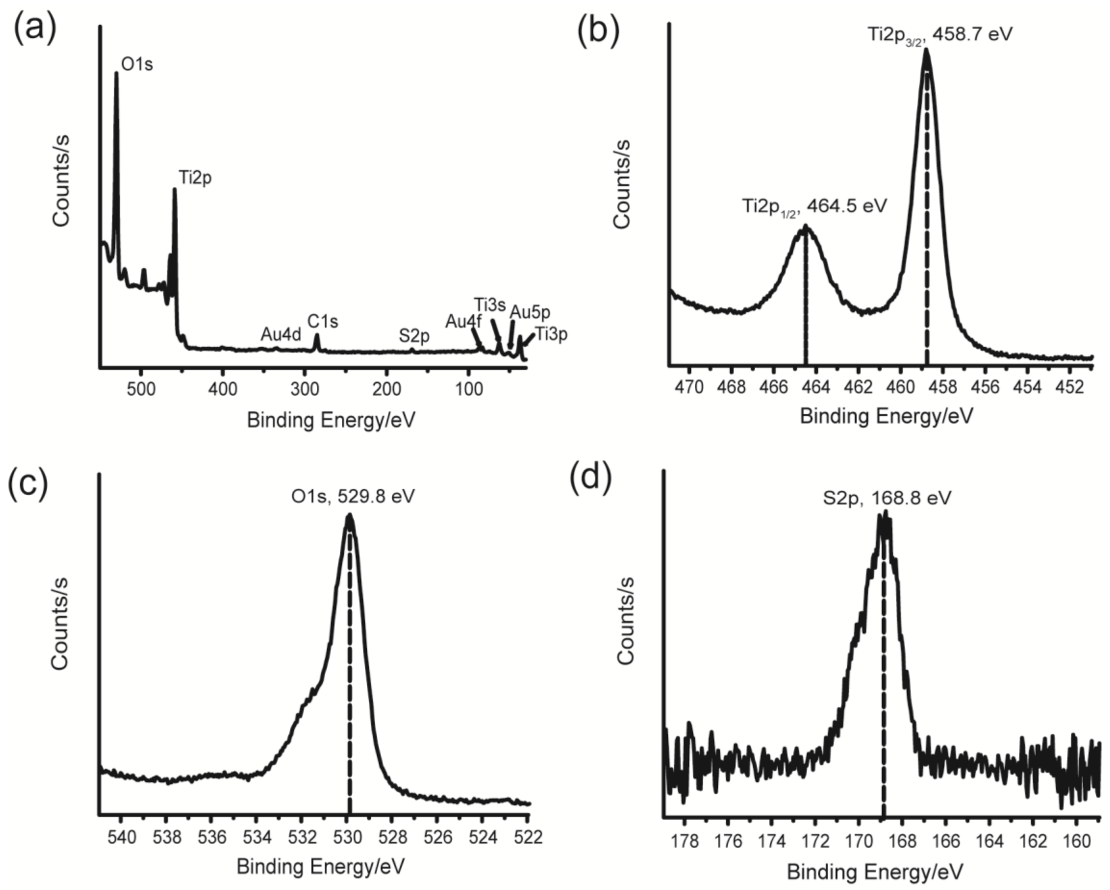


Fig. S5 IR spectra of Sample A, Sample B and Sample C.



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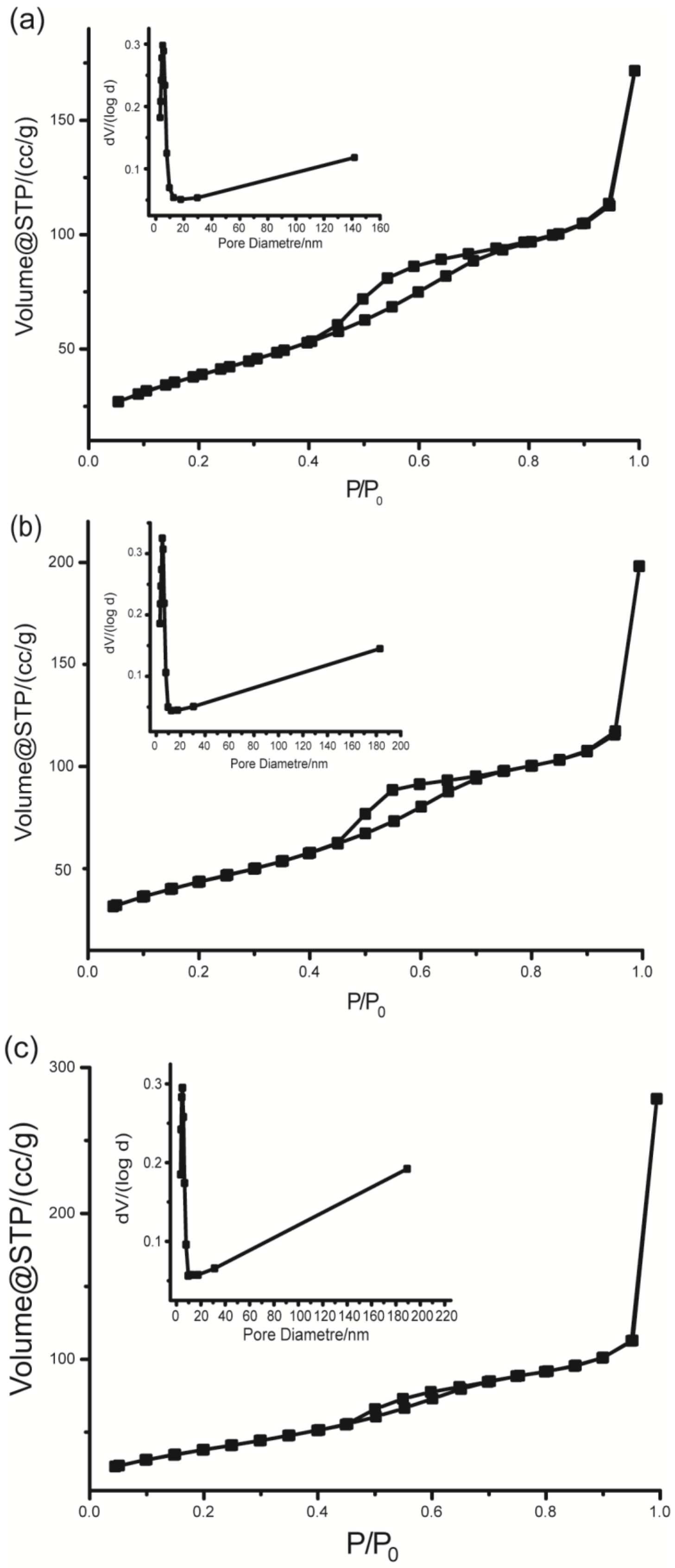

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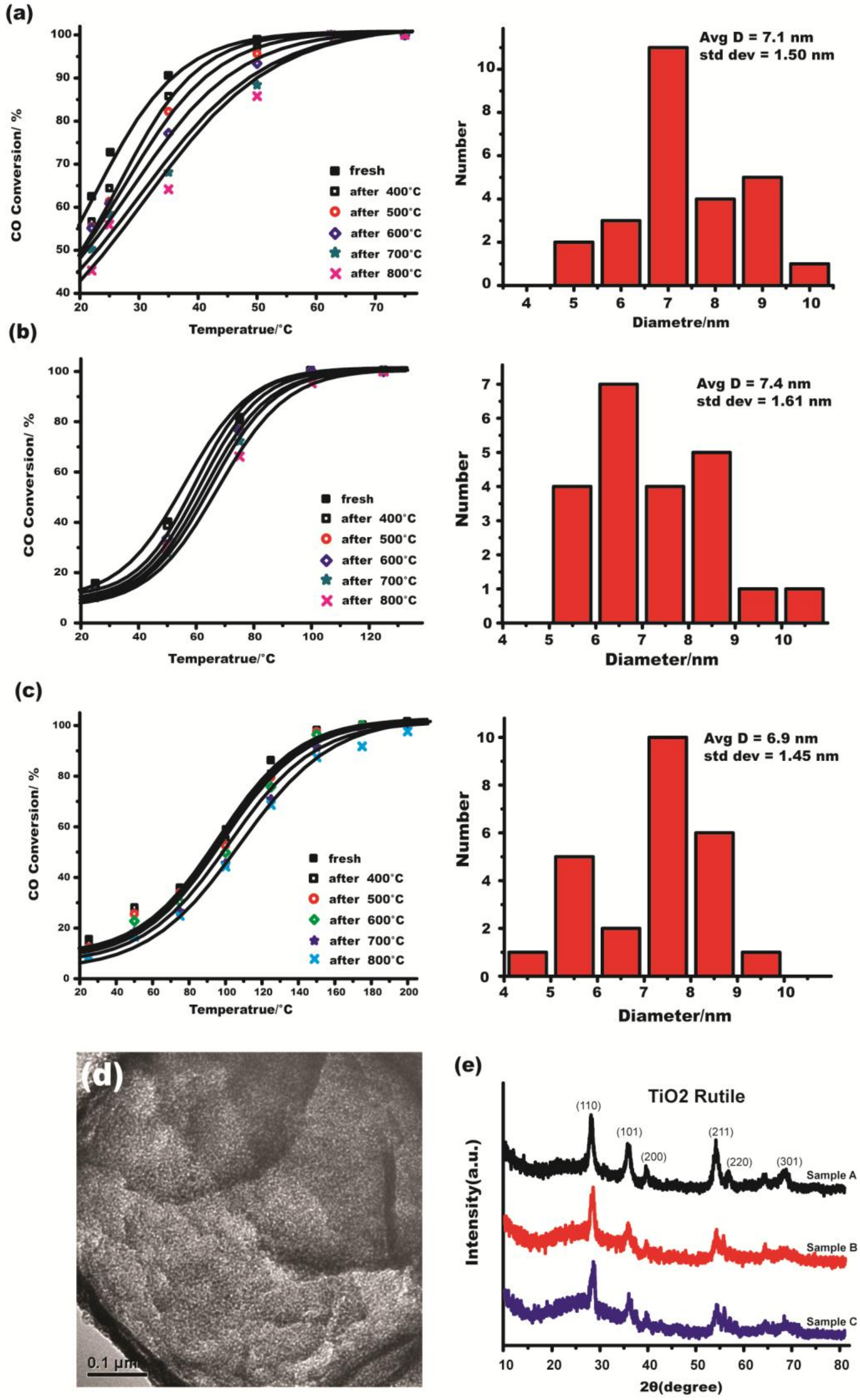

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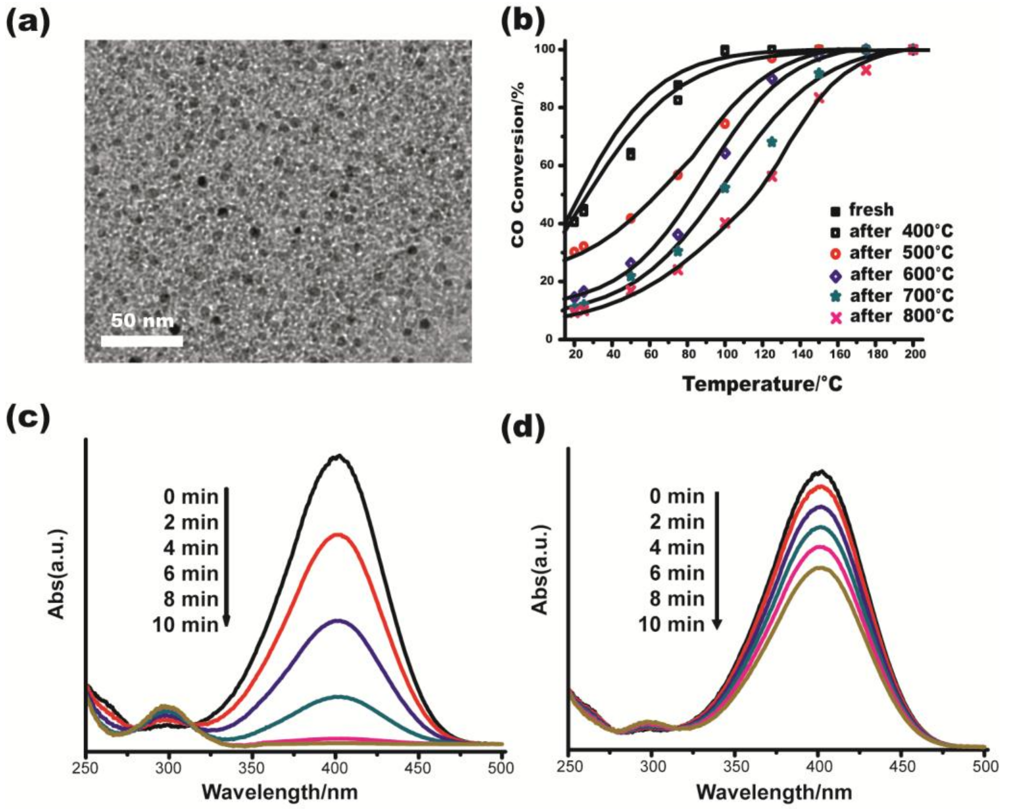

Fig. S9 (a) TEM image of fresh outside-loading Au-TiO_2 catalyst. (b)The light-off curves of Au-TiO_2 catalyst treated at different temperatures for 2h, and UV-Vis spectra changing for catalytic reduction of 4-nitrophenol of Au-TiO_2 before (c) and after (d) treated at 800 °C for 2h.

Table. S2 The turnover frequencies (TOF) of Samples for CO oxidation

	Fresh samples at 298 K	**Treated samples at 298 K**	**Fresh samples at $T_{100\%}$**[a]	**Treated samples at $T_{100\%}$**
Sample A	0.067	0.059	0.109	0.125
Sample B	0.036	0.036	0.136	0.189
Sample C	0.038	0.045	0.207	0.313
	TOF	Au Size (nm)	Method	**Ref**
	0.02	3.8	DP[b]	**2**
	0.06	1.4	CVD	
	0.10	2.1	DP	**3**

a. The temperatures of complete conversion for Sample A, B, C and Au-TiO_2 were 63 ºC, 100 ºC, 150 ºC, and 100 ºC. For calculation of the numbers of exposed Au atoms, spherical particles model was assumed.

b. DP: deposition–precipitation. CVD: chemical vapor deposition. All the measure temperature in the ref were 273K.

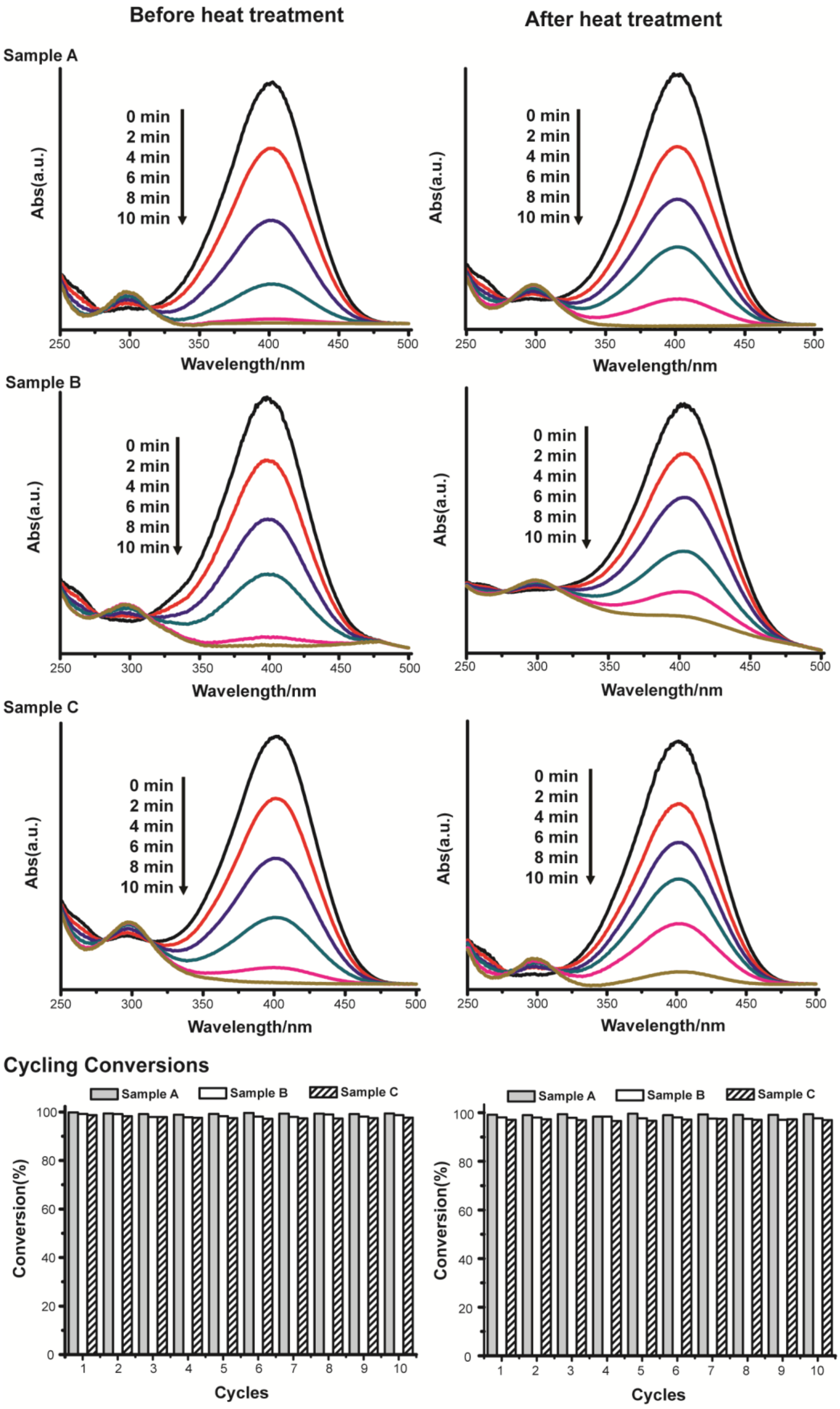

Fig. S10 UV-Vis spectra changing with concentration of 4-nitrophenol, cycling conversions for catalytic reduction of 4-nitrophenol of three catalysts before (left) and after (right) heat treatment.

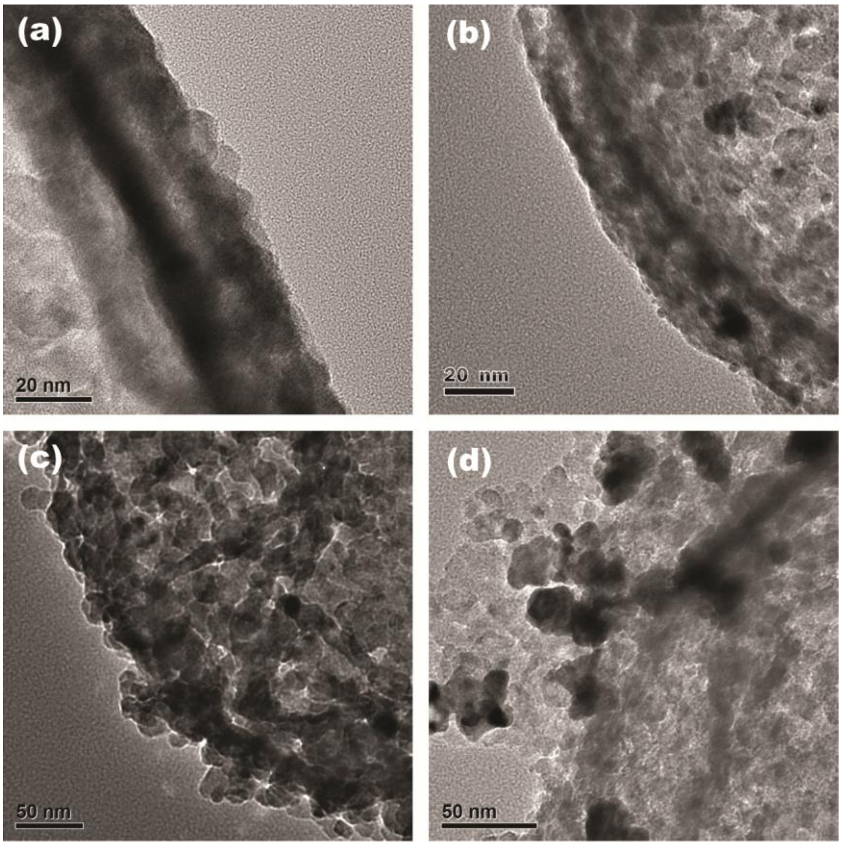

Fig. S11 The side-view TEM images of Sample A (a,b) and Au-TiO_2 (c,d) catalysts before (left) and after (right) heat treatment.

References

1. Z. Z. Yang, Z. W. Niu, Y. F. Lu, Z. B. Hu and C. C. Han, *Angew. Chem., Int. Ed.*, 2003, **42**, 1943-1945.
2. M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.*, 1998, **51**, 53–58.
3. T. Janssens, A. Carlsson, A. Puig-Molina and B.S. Clausen, *J. Catal.*, 2006, **240**, 108-113.