Supporting Information

Materials and characterizations:

Chloroauric acid, hexadecyl trimethyl ammonium bromide (CTAB), polyvinyl pyrrolidone (PVP-K30) and tetraethoxysilane (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. Na_2PdCl_4 and $RuCl_3$ were purchased from Aladdin. 1,2-bis-(trimethoxysilyl)-ethane was purchased from FluonoChem. All chemicals were used as received without further purification.

The high resolution scanning electron microscopy (HRSEM) was performed on Hitachi S-5500 scanning electron microscope operating at an acceleration voltage of 30 kV. The transmission electron microscopy (TEM) was undertaken using an Hitachi HT-7700 at an acceleration voltage of 100 kV. The samples were placed onto an ultrathin carbon film supported on a copper grid. The powder X-ray diffraction data were collected on a Rigaku D/Max2500PC diffractometer with Cu Kα radiation (λ=1.5418 Å) over the 2θ range of 5^o - 80^o with a scan speed of 5^o/min at room temperature. The nitrogen sorption experiments were performed at 77 K on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were degassed at 140 °C for 6 h. The reaction products were analyzed using an Agilent 7890B gas chromatography equipped with a HP-5 column.

Synthesis of PVP protected gold nanoparticles (Au-PVP):

Au-PVP was prepared according to the procedure published previously.[1] In a typical synthesis, a stock solution of Au precursor was prepared by dissolving Chloroauric acid (1 g) into deionized water and diluting it to 50 ml. PVP (K30, 556 mg) was dissolved in 49 ml deionized water and stirred in ice-water bath for over 15 min. Au precursor (1 ml) was added and the solution was stirred under ice-water bath for 30 min. Then $NaBH_4$ (10 mg in 5 ml water) was quickly added to the light yellow solution and the color instantly converted to brown and the mixture was kept stirring for another 30 min and then dialyzed overnight.

Synthesis of Au@O-SiO_2 Y-S nano-reactors:

CTAB (160 mg) and NH_3H_2O (0.5 ml) were dissolved in H_2O (30 ml) and EtOH (10 ml). After stirring at 50 ^oC for 30 min, TEOS (0.16 ml in 2 ml EtOH) was added and the mixture was stirred for another 30 min. During the period the clear solution turned milky white indicating the formation of silica. After that PVP-Au solution (10 ml) together with TEOS (0.24 ml) were added. After stirring for 3 min, BTME (0.2 ml in 2ml of EtOH) was added and the temperature was raised to 80 ^oC and the mixture was stirred at this temperature for 2h. The pink solid was filtrated and the CTAB left in the pores was removed by stirring in NH_4NO_3 ethanol solution for three times (200 mg NH_4NO_3 in 50 ml EtOH, 30 min*3 times).

Synthesis of O-SiO_2 H-S:

The synthesis of O-SiO_2 H-S was almost the same with Au@O-SiO_2 Y-S except that no PVP-Au solution was added before the second portion of TEOS was added. White powder was obtained as the product after removing CTAB in the pores by stirring in NH_4NO_3 ethanol solution.

Synthesis of Au/O-SiO_2:

The Au/O-SiO_2 catalyst was prepared via traditional impregnation method using

Chloroauric acid as the gold source. In a typical synthesis 0.052 ml Chloroauric acid solution (used in preparation of Au-PVP) was diluted in EtOH and 0.1g O-SiO_2 H-S was added. The suspension was sonicated and all solvents were removed via rotatory evaporator. The white powder obtained was heated to 120 ^{o}C (5 ^{o}C/min) in H_2 gas and kept at the temperature for 2h. Pink powder was obtained as the final product.

Synthesis of PVP-Au/SiO_2:

The Au/O-SiO_2 catalyst was prepared via impregnation method using Au-PVP as the gold source. In a typical synthesis 10 ml Au-PVP colloidal solution was diluted in EtOH and 0.25g O-SiO_2 H-S was added. The suspension was sonicated and all solvents were removed via rotatory evaporator. Pink powder was obtained as the final product after drying in vacuum under ambient temperature.

Synthesis of PVP protected Pd and Ru:

Pd-PVP was prepared according to the procedure published previously.[1] In a typical synthesis, 555 mg PVP (K-30) was dissolved in 40 ml deionized water and the solution was stirred vigorously in ice bath. 15 mg Na_2PdCl_4 in 10 ml deionized water was added and the solution was continuously stirred for another 30 min. then 5 ml $NaBH_4$ (0.1M) was poured into the clear solution and its color turned rapidly from light yellow to black. The colloidal solution was dialyzed overnight to obtain the final product of Pd-PVP.

Ru-NW-PVP was prepared according to the procedure published previously.[2] In a typical synthesis, 140 mg $RuCl_3$ and 1.2 g PVP (K-30) were dissolved into 40 ml deionized water. Then the solution was transferred into a 60 ml stainless autoclave

(Parr) with a pressure gauge. The metal salt was reduced via H_2 under 2 MPa at 170 ^oC with stirring. The resulting black solution was used after dialysis overnight.

Synthesis of Pd, Ru nano-reactors:

The synthesis of Pd@O-SiO_2 Y-S and Ru NW@O-SiO_2 Y-S were almost the same with Au@O-SiO_2 Y-S except that 10 ml Pd-PVP and 1 ml Ru NW-PVP (diluted in 10 ml deionized water) instead of 10 ml Au-PVP were used

Catalytic test:

All catalytic tests were conducted under 1 atm O_2 and the atmosphere was kept by using a rubber balloon. In a typical test 3 ml dioxane, 0.63 ml styrene and 10 μl n-decane (as internal standard) were mixed in a 10 ml Schlenk reaction tube. Catalyst containing 0.25 mg Au was added and the solution was briefly sonicated for a better dispersion. The atmosphere inside the reaction tube was replaced by flushing with oxygen gas for over 3 times using an O_2 balloon. The reaction was carried on at 100 ^oC with stirring for 15h. In the recycle test catalyst was recovered by centrifugation and washed with EtOH for 3 times after each reation and dried before performing the next run. The products were analyzed using a gas chromatography equipped with a HP-5 column.

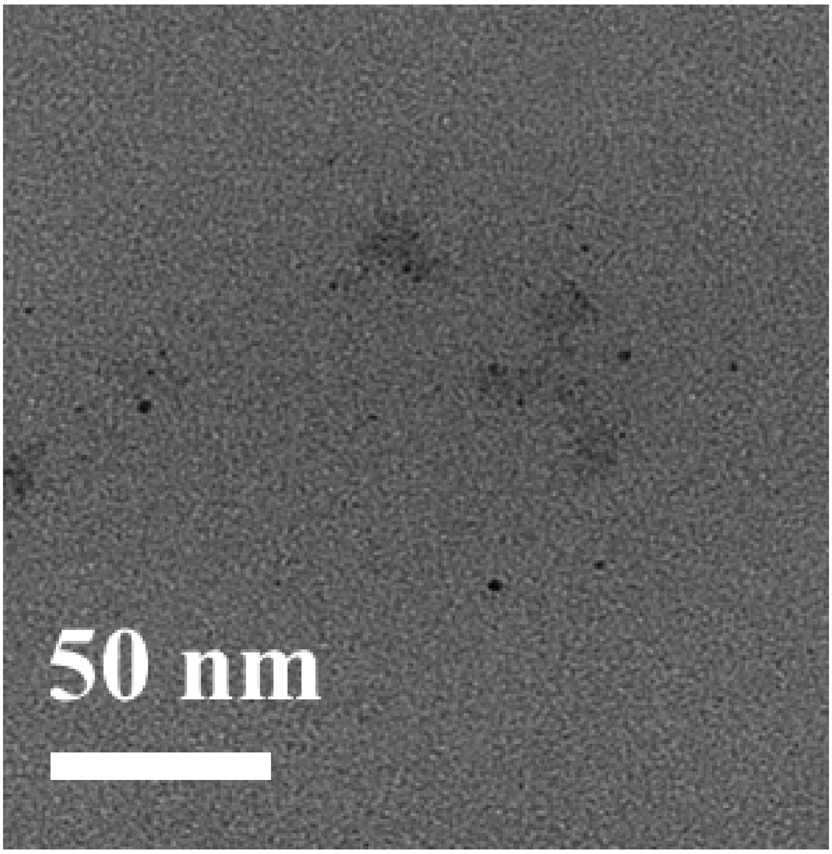

Figure S1. TEM image of Au-PVP

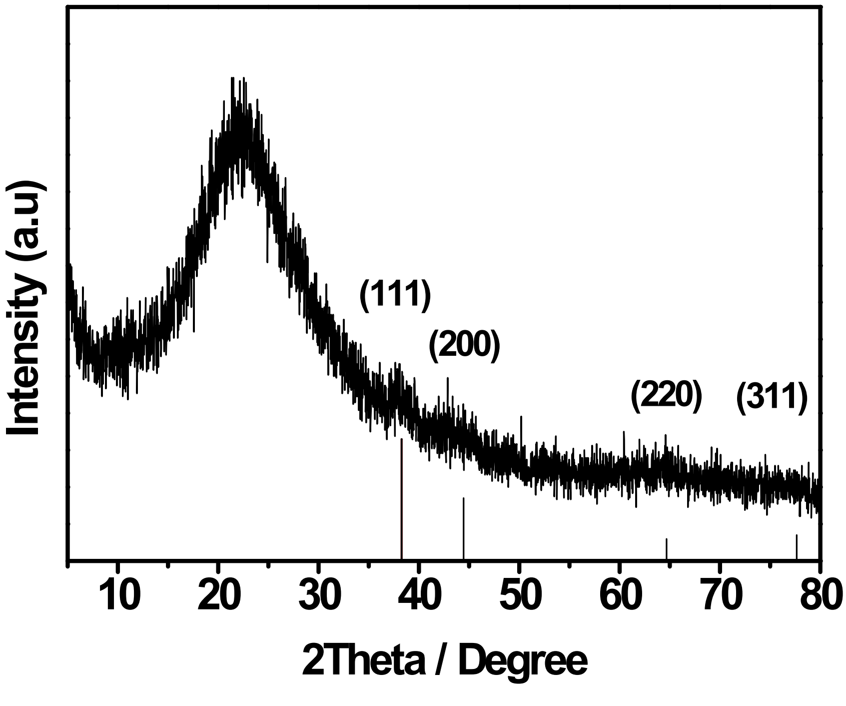

Figure S2. XRD diffraction pattern of Au@O-SiO$_2$ Y-S

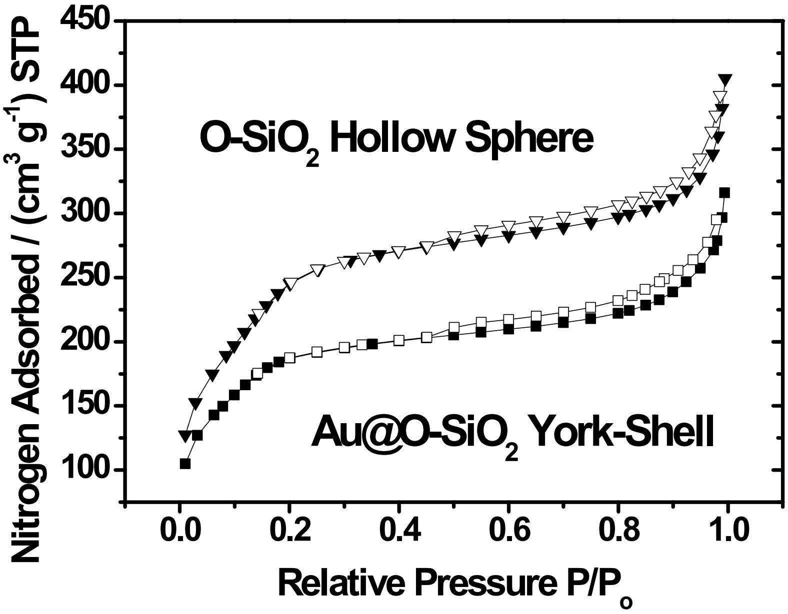

Figure S3. Nitrogen adsorption/desorption isotherm curve of Au@O-SiO$_2$ Y-S and O-SiO$_2$ H-S

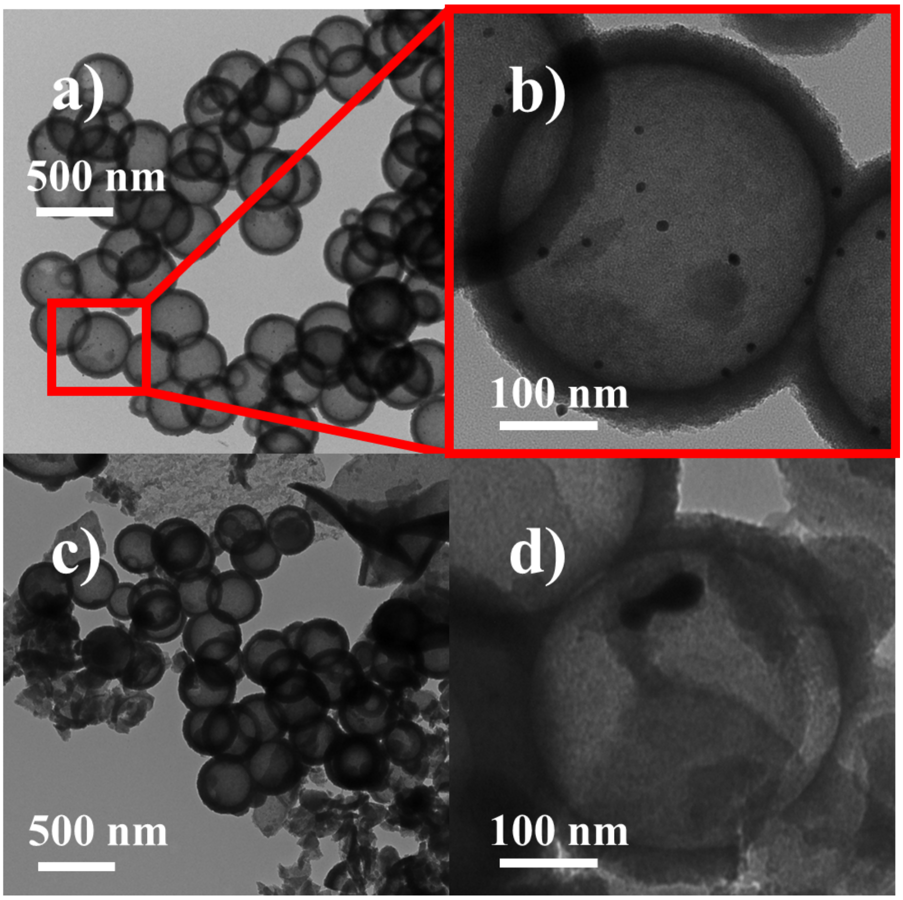

Figure S4. TEM pictures of Au/O-SiO$_2$ catalyst before (a, b) and after (c, d) 4th cycle.

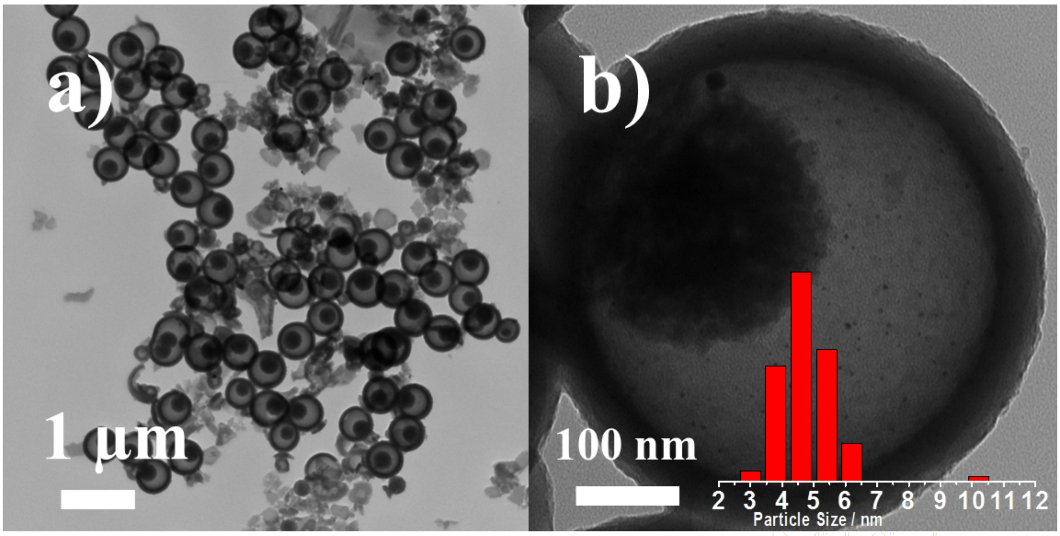

Figure S5. TEM pictures of Au@O-SiO$_2$ Y-S nano-reactors after 8th cycle and the size distribution of Au nano-particles (insert).

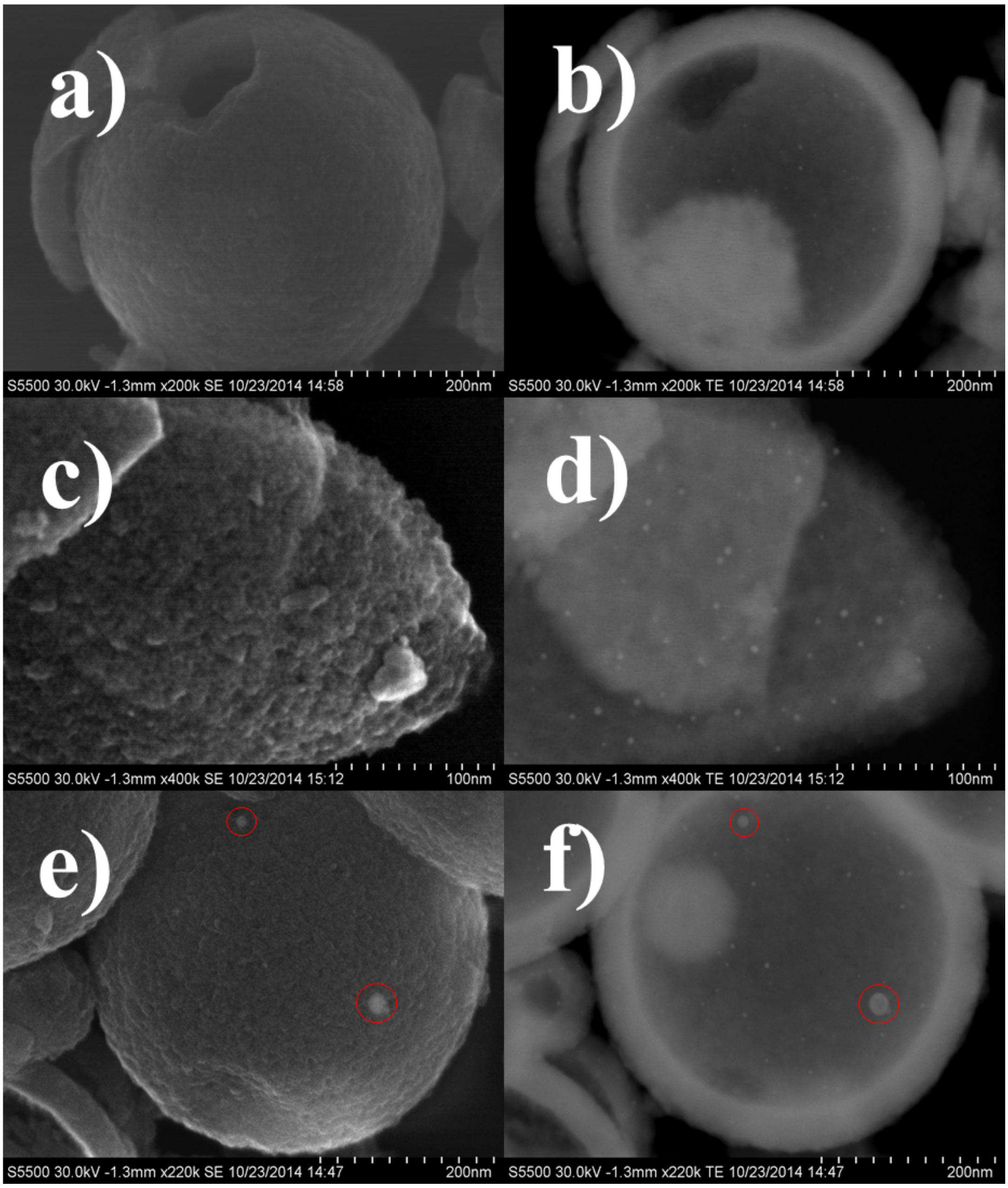

Figure S6. SEM pictures of Au@O-SiO$_2$ Y-S nano-reactors after 8th cycle. Images in the left and right are the same location with different working mode (left: scanning; right: transmitting). (a-b) show no light spots on scanning mode but gold particles under transmitting mode; (c-d) were pictures taken from inside of broken nano-reactors and still no particles observed from scanning mode; (e-f) shows large particles outside the nano-reactor.

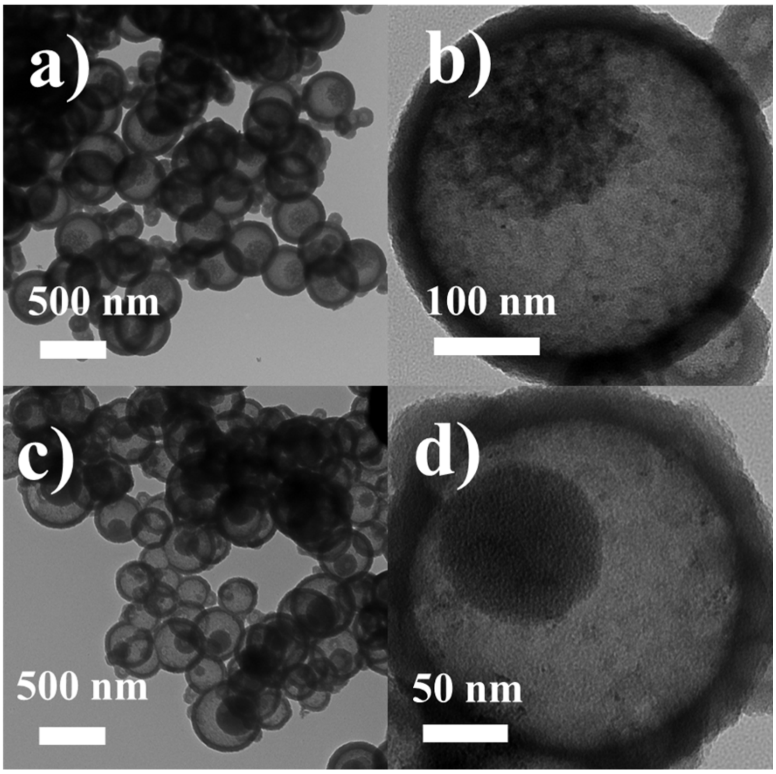

Figure S7. TEM pictures of (a- b) Pd@O-SiO_2 Y-S and (c-d) Ru@O-SiO_2 Y-S

1. H. Tsunoyama, H. Sakurai, Y. Negishi and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 9374-9375.
2. C.-x. Xiao, Z.-p. Cai, T. Wang, Y. Kou and N. Yan, *Angew. Chem. Int. Ed.*, 2008, **47**, 746-749.