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Supporting information

Rattle-type microspheres as support of tiny sized gold nanoparticles for high efficient catalysis

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Experimental

Synthesis of MPS modified SiO₂ particles

MPS modified SiO₂ particles were prepared through a sol-gel process. About 2.6 mL of TEOS was added to a mixture of 108 mL of ethanol, 5 mL of deionized water, and 5 mL of ammonium hydroxide aqueous solution (25 wt%). The mixture was vigorously stirred at room temperature for 12 h. Then 0.5 mL MPS was added for stirring another 24 h. The product was collected by centrifugation and purified through extraction with ethanol for five times, and finally dried at vacuum oven till constant weight.

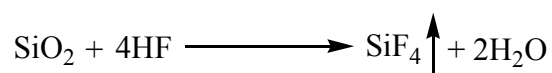
Synthesis of SiO₂@P(EGDMA) core-shell microspheres

SiO₂@P(EGDMA) core-shell microspheres were prepared through distillation-precipitation polymerization of EGDMA in the presence of MPS modified silica particles as seeds. The details as follows: 0.2 g MPS modified silica particles, 0.8 mL of EGDMA monomer and 0.016 g BPO initiator were dissolved in 80 mL acetonitrile in a 100 mL flask. The flask attaching with a fractionating condenser and receiver was submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 15 min and the reaction system was kept under refluxing state for further 15 min. The polymerization was further carried out with distilling the solvent out of the reaction system and the reaction was ended after 40 mL of acetonitrile was distilled off the reaction mixture within 90 min. After the polymerization, the resultant SiO₂@P(EGDMA) microspheres were purified by repeated centrifugation, decantation, and resuspension in ethanol for three times. The

products were dried in a vacuum oven at room temperature till constant weight.

Preparation of SiO₂/P(EGDMA) rattle-type microspheres

SiO₂/P(EGDMA) Rattle type microspheres were obtained through the quantitatively etching of silica with 1 wt% HF aqueous solution. The driving force for the etching process was as the following equation:



The resultant of the SiO₂@P(EGDMA) microspheres were suspended in 10 mL ethanol and then 6 mL 1 wt% HF aqueous solution was added to quantitatively remove the silica core. After the reaction was lasted for 30 min, the rattle-type microspheres were characterized by TEM and another 6 mL 1 wt% HF aqueous solution was added for further etching. Until the addition of three times of 6 mL 1 wt% HF aqueous solution, a small part of the rattle type microspheres was immersed into the excessive HF aqueous solution to completely remove the silica core and the other rattle type microspheres were purified by repeating centrifugation, decantation, and resuspension in ethanol three times. The final SiO₂/P(EGDMA) rattle-type microspheres were dried in a vacuum oven at room temperature till constant weight.

APS modification of the silica core of the rattle-type microspheres

0.1 g of the rattle-type microspheres, 1mL NH₃·H₂O (25 wt%), 5mL H₂O and 25mL ethanol were dissolved in 100 mL flask and submerged to 50 °C water bath under the magnetic stir. Then, 0.05 mL APS was added for stirring another 48 h. The APS modified rattle-type microspheres were purified by repeating centrifugation, decantation, and resuspension in ethanol for five times and dried in a vacuum oven at

room temperature till constant weight.

Loading of Au nanoparticles

0.05 g APS modified or unmodified SiO₂/P(EGDMA) rattle-type microspheres was dispersed in 1 mL HAuCl₄ aqueous solution (0.1M) and incubated for 24 h at room temperature. Then, the rattle-type microspheres were centrifugated from the solution and washed with water through repeating centrifugation, decantation, and resuspension for 5 times. The color of the APS modified SiO₂/P(EGDMA) rattle-type microspheres was changed from yellow to white while the unmodified SiO₂/P(EGDMA) rattle-type microspheres still retained the initial white. At last, the rattle-type microspheres were suspended in 5 mL de-ionized water in ice bath. 1 mL of NaBH₄ aqueous solution (0.1M) was added. The deep purple color was appeared for APS modified SiO₂/P(EGDMA) rattle-type microspheres while very light red color was observed for unmodified SiO₂/P(EGDMA) rattle-type microspheres. The final products were purified by repeated centrifugation, decantation, and resuspension in water for three times and dried in a vacuum oven at room temperature till constant weight.

Catalytic reduction of 4-nitrophenol to 4-aminophenol in an aqueous medium

Catalytic properties of SiO₂@Au/P(EGDMA) rattle-type microspheres were investigated via the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AnP) with NaBH₄ as the reductant under ambient temperature in aqueous solution as a model reaction. A typical experiment was carried out as follows: 1 mL of 4-NP aqueous solution (0.1 mM, 1×10⁻⁷ mol) and 2 mL of NaBH₄ (0.1 M, 2×10⁻⁴ mol) aqueous

solution mixed in colorimetric tube. 10 μL of $\text{SiO}_2@\text{Au}/\text{P}(\text{EGDMA})$ rattle-type microspheres suspension (1 mg/mL, 1×10^{-5} g) was introduced into the mixture with gentle shaking. The bright yellow solution faded gradually as the catalytic reaction proceeded. The catalytic activity was determined by a UV-vis spectrophotometer with a decrease at 400 nm in UV-vis absorption and a simultaneous increase in absorption at 300 nm, indicating the formation of 4-AnP.

To determine the catalytic recycling properties of $\text{SiO}_2@\text{Au}/\text{P}(\text{EGDMA})$ rattle-type microspheres within several minutes, both the concentration of 4-NP and catalyst were increased by 20 times compared with the above typical reduction. After complete reduction of 4-NP, the catalysts were separated by centrifugation (1.2×10^4 rpm for 10 min) and redispersed in a new reaction system. The recovery of the catalyst was proven further by recycling it nine times.

Characterization

The morphology of the resultant nanoparticles was determined by transmission electron microscopy (TEM) using a Technai G2 20-S-TWIN microscope. The samples for TEM characterization were dispersed in ethanol and a drop of the dispersion was dropped onto the surface of a copper grid coated with a carbon membrane and then dried under vacuum state at room temperature. All the size and size distribution reflect the averages about 100 particles each, which are calculated according to the following formula:

$$U = D_w / D_n \quad D_n = \sum_{i=1}^k n_i D_i / \sum_{i=1}^k n_i \quad D_w = \sum_{i=1}^k n_i D_i^4 / \sum_{i=1}^k n_i D_i^3$$

where, U is the polydispersity index, D_n is the number average diameter, D_w is the

weight-average diameter, D_i is the diameter of the determined microspheres. The thickness of the shell-layer is calculated as half of the difference between the average diameter of the core-shell particles and that of the cores.

The crystalline structure of the sample was analyzed on a D/max 2500V X-ray diffractometer using Cu K α ($\lambda=0.15406$ nm) radiation at 40 kV and 100 mA.

UV-vis spectroscopy was performed on a JASCO V-570 spectrometer.

The loading capacity of the Au nanoparticles on the rattle-type microspheres was determined by inductively coupled plasma (ICP) on an ICP-9000(N+M) (Thermo Jarrell –Ash Corp, USA).

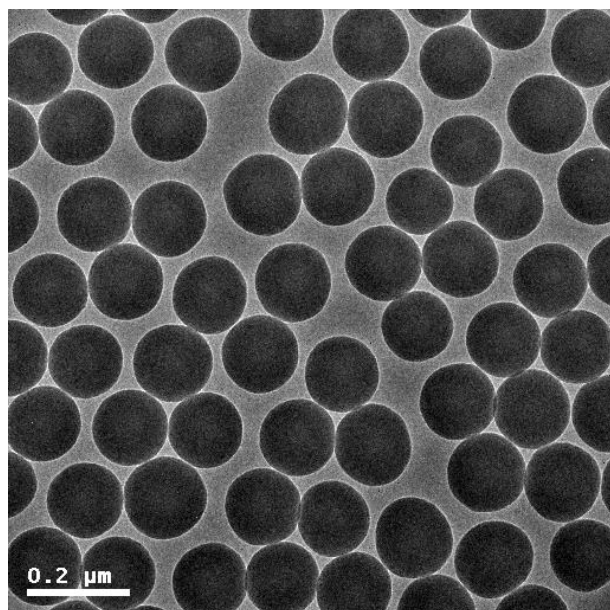


Figure S1. TEM image of MPS modified SiO₂ particles.

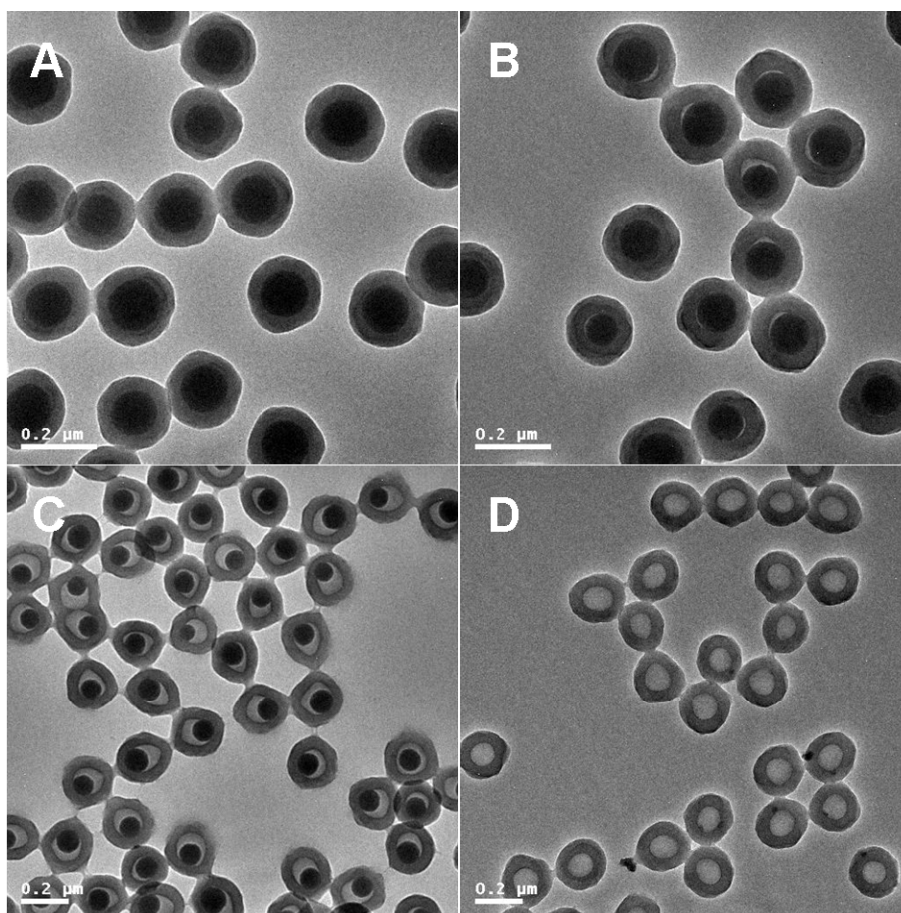


Figure S2. TEM images of $\text{SiO}_2@\text{P}(\text{EGDMA})$ microspheres being etched with different volume of 1 wt% HF aqueous solution: A) 6 mL, B) 12 mL, C) 18 mL, D) excessive amount. The diameter of the silica core was gradually reduced from 148 nm to 120nm, 104nm, 88nm and 0 nm when the volume of 1 wt% HF aqueous solution were 0 mL, 6 mL, 12 mL, 18 mL and excessive respectively. The hollow structure after being etched with 6 mL HF 1 wt% aqueous solution cannot be seen in the TEM micrograph. That was because the shrink of the polymer shell in the dry state. The content of the silica being etched can be calculated as follows. The volume of a sphere: $V_x = 4\pi r_x^3/3$, x stands for the volume of the 1 wt% HF aqueous solution for etching. So, the percent of residue silica was $V_x/V_0 = (r_x/r_0)^3$, while the percent of the etched part was $1-(r_x/r_0)^3$. From the formula, the etched parts were 46.7%, 65.3%, 79% and 100% when the volume of 1 wt% HF aqueous solution was 6 mL, 12 mL, 18 mL and excessive as shown in Figure 1A, 1B, 1C and 1D respectively.

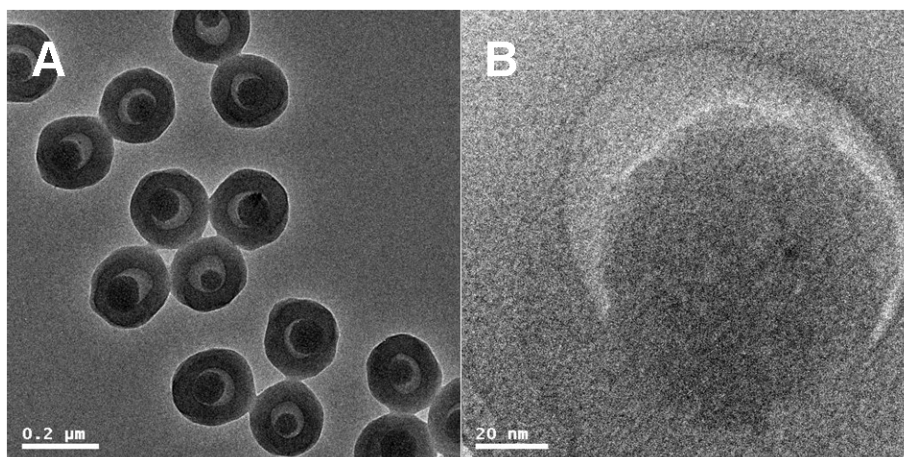


Figure S3. TEM images of unmodified rattle-type microspheres for loading Au nanoparticles with different magnifications..

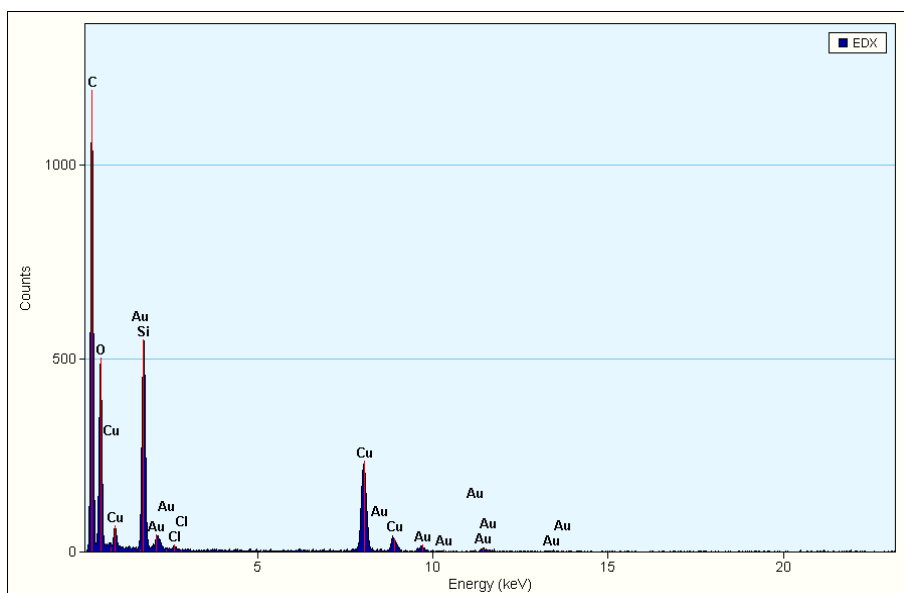


Figure S4. EDX spectrum of $\text{SiO}_2@Au/P(EGDMA)$ rattle-type microspheres. The $\text{SiO}_2@Au/P(EGDMA)$ rattle-type microspheres contained Au, Si and a very little Cl. The presence of Cl may attribute that some Cl^- was absorbed in this microspheres after the reduction of the HAuCl_4 by NaBH_4 .

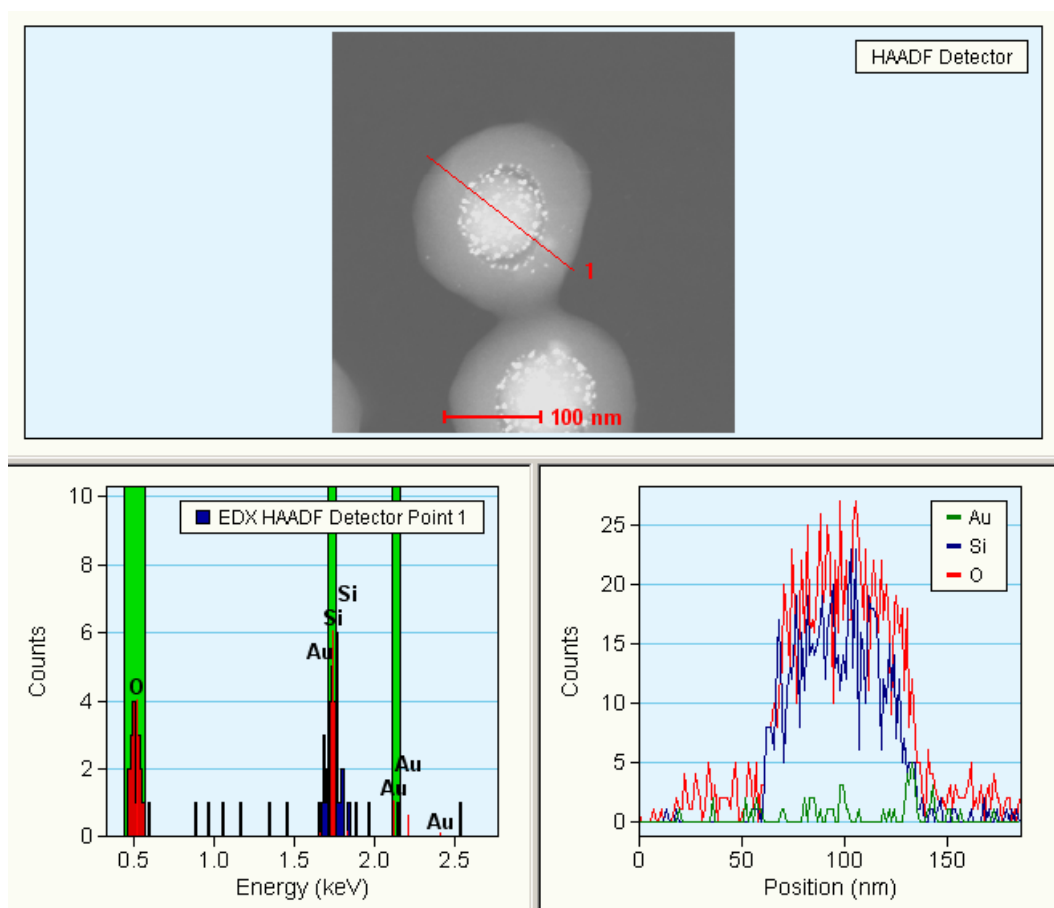


Figure S5. EDX line profiling of SiO₂@Au/P(EGDMA) rattle-type microspheres.

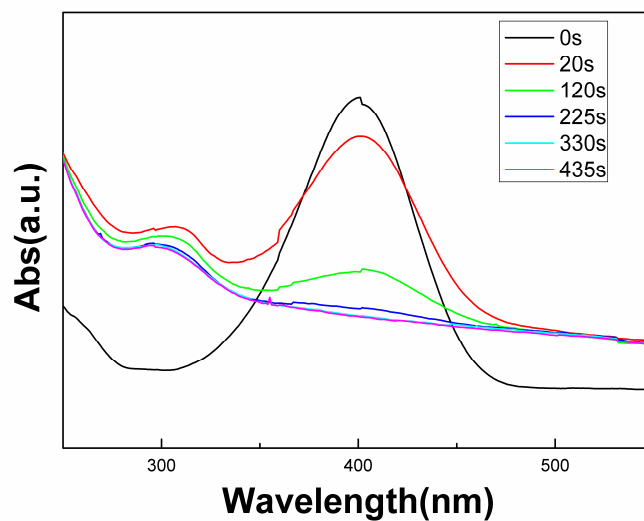


Figure S6. UV-vis spectra of the catalytic reduction of 4-nitrophenol to 4-aminophenol developed by different reaction times. Catalyst: 0.1 mL (1 mg/mL), NaBH₄: 2 mL (0.1 M), 4-nitrophenol: 1 mL (0.1 mM).

Table S1. The reaction time for complete disappearance of the peak at 400 nm in UV-vis spectrum of 4-NP after the catalyst was recycled.

Recycled time	Time for complete reaction (s)
0	92
1	127
2	261
3	374
4	424
5	562
6	664
7	720
8	755

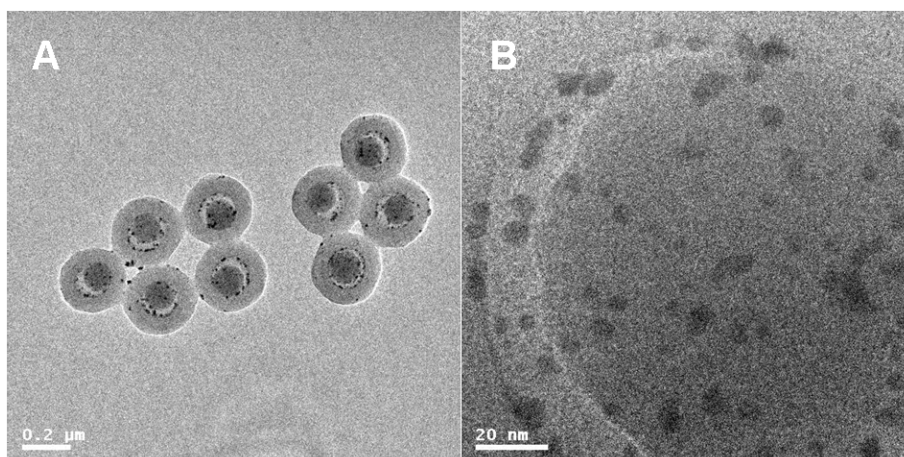


Figure S7. TEM images of SiO₂@Au/P(EGDMA) rattle-type microspheres after the catalysis for 9 times with different magnifications.