Electronic Supplementary Information

Silica-Based Hierarchical Porous Janus Microcapsules: Constructure and Supported Au Nano-Particles Catalyst inside

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Experiment

Materials:

Styrene (St), Potassium persulfate (KPS), Tetraethoxysilane (TEOS), Ammonium Hydroxide ($NH_3 \cdot H_2O$, 28%), Tetrahydrofuran (THF, 99.5%), and Polyvinylpyrrolidone (PVP-K30, $M_w = 30\ 000\ g \cdot mol^{-1}$) were ordered from Tianjin Guangfu Fine Chemical Research Institute. KPS, St and TEOS were respectively used with recrystallization and vacuum distillation to remove impurities and inhibitor. Hexadecyltrimethoxysilane (HETMS, ≥85%), 3-Aminopropyltriethoxysilane (APTES, 98%, AR), Trisodium citrate dehydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, AR), sodium borohydride ($NaBH_4$, 98%, AR) and 4-nitrophenol (4-NP) were purchased from Aladdin Industrial Corporation. Chloroauric Acid ($HAuCl_4 \cdot 4H_2O$) was obtained from j&k chemical. All other reagents were used as received.

Synthesis of PVP-functionalized polystyrene microspheres:

0.065 g PVP was added to 180 mL ultrapure water in four round bottom flask. 10 mL of St was dropwise added under the protection of Ar. After half-hour, 0.1 g of KPS slowly added at 70 °C. The polymerization last for 13 h under a constant stirring rate of 180 rpm. The synthesized polystyrene (PS) microspheres were collected by centrifugation and finally dried in vacuum oven for further use.

Preparation of core/shell composite microspheres:

0.1 g of freeze-dried PS microspheres was dispersed in 6 mL ethanol under ultrasonication for 30 min. After 33 μL of $NH_3 \cdot H_2O$ and 250 μL of ultrapure water were added into the above mixing dispersion within 5 min under the magnetic stirring, 300 μL of TEOS was added into the reaction system at ambient temperature for 10 h to enable the sol-gel forming silica shell. The obtained mesoporous silica-coated PS microspheres, denoted as PS@SiO_2, were separated and washed with ethanol, and then dried under vacuum for further use.

Synthesis of alkyl chains-functionalized PS@SiO_2 composite microspheres:

0.1 g of vacuum-dried PS@SiO_2 core-shell composite particle was dispersed in 10 mL of ethanol under ultrasonication for 30 min. 60 μL of HETMS was added into the above dispersion under stirring at 80 °C for 10 h. The particles were separated and washed with ethanol to obtained outer surface alkyl chains-functionalized PS@SiO_2 composite microspheres. The materials were denoted as PS@SiO_2-CH_3.

Synthesis of alkyl chains-functionalized hierarchical porous SiO_2 microcapsules with open-mouthed:

0.1 g of vacuum-dried PS@SiO_2-CH_3 composite microspheres was dispersed in 2 mL of ethanol under ultrasonication for 10 min. Then, 4 mL of ethanol/THF (1:1 v/v) mixture solution was rapidly added into the above composite dispersion under magnetic stirring at 25 °C for 20 min to obtain the anisotropic snowman-like PS@SiO_2-CH_3 composite particles. Subsequently, the particles were washed with THF for five times to remove PS template, and the obtained outer surface alkyl chains-functionalized SiO_2 microcapsules with open-mouthed was washed with ethanol to remove THF, and then dried under vacuum. The obtained particles were denoted as HPMs SiO_2-CH_3.

Synthesis of bifunctional hierarchical porous Janus SiO_2 microcapsules:

0.05 g of vacuum-dried HPMs SiO_2-CH_3 microcapsules was dispersed in 20 mL of ethanol, 120 μL of APTES was added into the above composite dispersion. The reflux reaction was held for modification at 80 °C for 10 h. Finally, the obtained silica-based bifunctional hierarchical porous Janus microcapsules with amine groups on the inner surface and alkyl chains on the outer surface, denoted as HPJMs SiO_2, were washed ethanol for further uses.

Supported of Au NPs onto the inner surface of HPJMs SiO_2:

0.012 g of $HAucl_4$ was dispersed in 120 mL of ultrapure water, 0.0085 g of $Na_3C_6H_5O_7$ was added into the above dispersion under powerful mechanical stirring for 1 h. Subsequently, 1.44 mL of $NaBH_4$ aqueous solution (0.38 Wt %) was added into the above reaction system. After further mechanical stirring for 2 h, the solution containing Au NPs were obtained. The obtained HPJMs SiO_2 was dispersed in the excess Au NPs solution to load Au NPs. The dispersion was subjected to ultrasonication for 2 h. And the obtained Au@HPJMs SiO_2 particles were washed with water for 3 times for further use.

Catalytic reduction of 4-NP with Au@HPJMs SiO_2:

4-NP (3 mL, 0.1 mM) was added in a quartz cuvette with $NaBH_4$ (0.002 g). The Au@HPJMs SiO_2 catalysts suspension (0.1 mL, 0.4g/L) was rapidly injected into the above solution. The mixture was in situ recorded every 1 min to monitor the successive reaction progress.

To investigate the reusability of Au@HPJMs SiO_2 catalysts, the catalysts were separated and washed with water for 3 times and keep the equal catalytic procedure.

The catalyst was reused for more 5 recycles under the same reaction procedure.

Hierarchical porous SiO_2 microcapsules with open-mouthed:

0.1 g of vacuum-dried PS@SiO_2 core/shell composite microspheres was dispersed in 2 mL of ethanol under ultrasonication for 10 min. Then, 4 mL of ethanol/THF (1:1 v/v) mixture solution was rapidly added into the above composite dispersion under magnetic stirring at 25 °C for 20 min to obtain the anisotropic snowman-like PS@SiO_2 composite particles. Subsequently, the particles were washed with THF for five times to remove PS template, and the obtained SiO_2 microcapsules with open-mouthed was washed with ethanol to remove THF, and then dried under vacuum, denoted as HPMs SiO_2.

Characterization:

Diameter of particles measurement was carried out in water using a Malvern NanoZS90 Zetasizer. FT-IR spectra were obtained on a Fourier transformed infrared spectrometer (Bruker VECTOR-22) using KBr pellets. Scanning electron microscopy (SEM) images were recorded on a field-emissiona scanning electron microscopy (FEI Nova NanoSEM450, USA) with energy-dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) images were performed on a transmission electron microscope (JEM-1400). Nitrogen adsorption−desorption isotherms were performed at 77 k on a surface area and porosity analyzer (ASAP 2020M+C). The pore volume and pore size and the specific surface area were respectively computed by using the Barrett-Joyner-Halenda (BJH) model and the Brunauer-Emmett-Teller (BET) method. Water contact angle (WCA) images were recorded on a contact angle analyzer (KRÜSS DAS30). Thermal gravimetric analysis (TGA) was obtained using thermal gravimetric instrument (TA SDT/Q600) from room temperature to 800 °C at a heating speed of 5 °C /min under nitrogen atmosphere. The metal element content was determined on an inductively coupled plasma optical emission spectrometer (ICP-OES Agilent 725). X-ray photoelectron spectroscopy patterns were collected on an X-Ray photoelectron spectrometer (XPS, Thermo ESCALAB-250Xi, USA). X-ray diffraction (XRD) pattern was measured on an X-ray diffractometer

(Bruker D8-Davinci) with Cu Kα radiation (40 KV, 150 mA) at the rate of 1°/min. The reduction of 4-Nitrophenol was monitored using a UV-vis spectrophotometer (VARIAN CARY300) at room temperature.

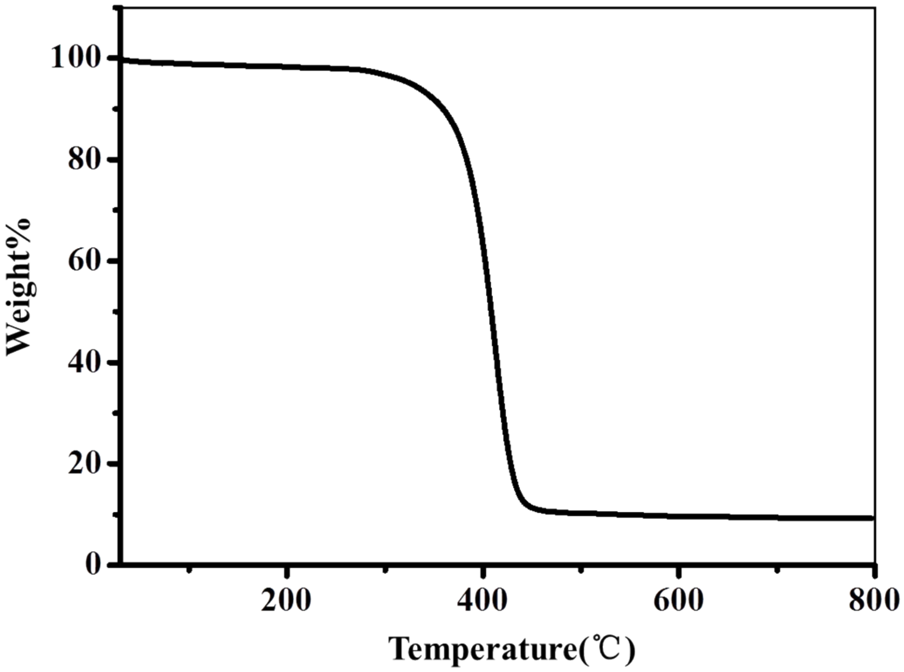

Fig. S1 The TG analysis of $PS@SiO_2$ core/shell composite microspheres

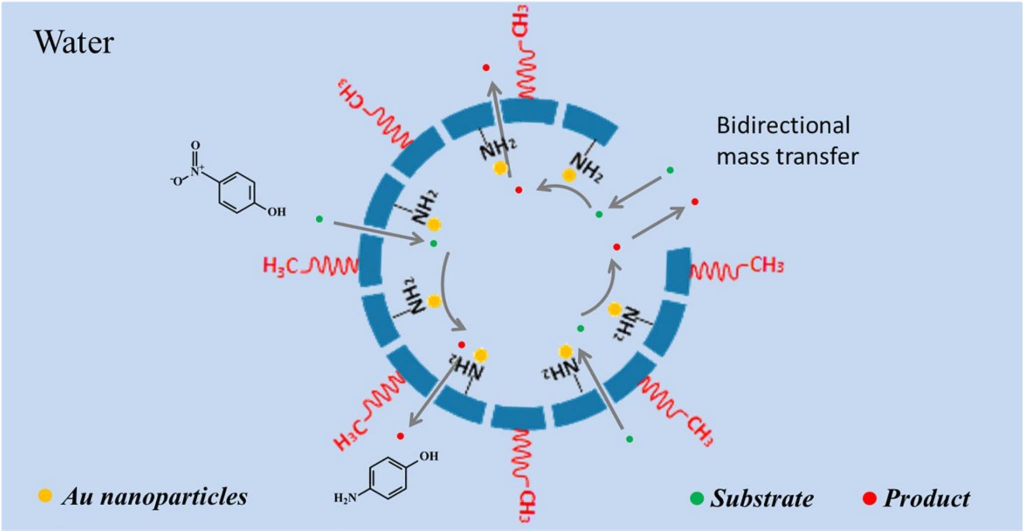

Fig. S2 Schematic illustration of catalytic 4-NP reaction within the microreacter of Au NPs immobilized the inner surface of HPJMs SiO_2 in aqueous phase.

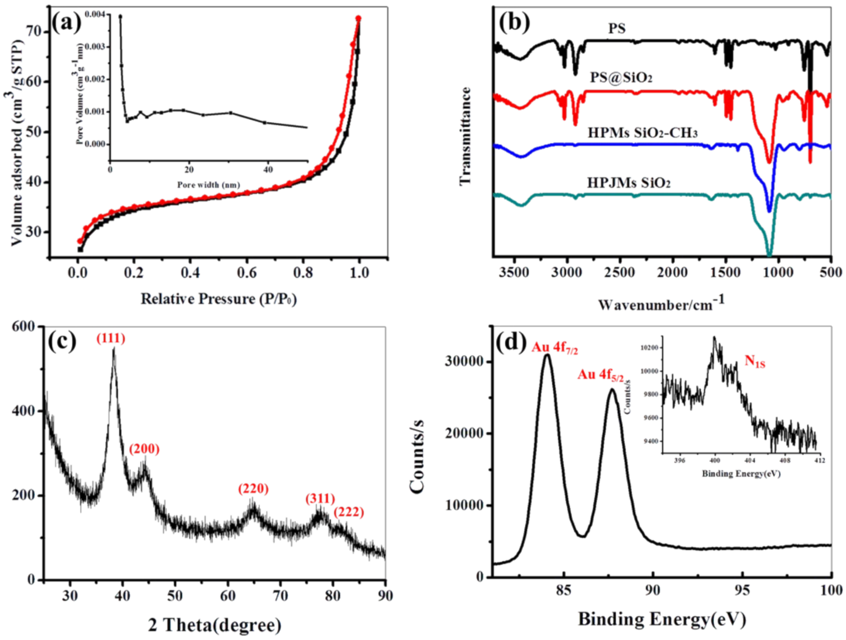

Fig. S3 (a) The nitrogen adsorption–desorption isotherms and pore size distribution (inset) of the HPJMs SiO_2; (b) FT-IR spectra of the PS microsphere template, PS@SiO_2 core/shell composite microspheres, HPMs SiO_2–CH_3, and HPJMs SiO_2; (c) XRD patterns of the Au@HPJMs SiO_2; (d) the high-resolution XPS pattern of Au 4f (inset is the spectrum of N 1s).

As shown in Fig. S3b, the FT-IR spectrum of the PS@SiO_2 composite microspheres showed that the intense absorption band at 1095 cm^{-1} was assigned to the stretching vibration of the Si–O–Si groups, suggesting the formation of the silica shell.

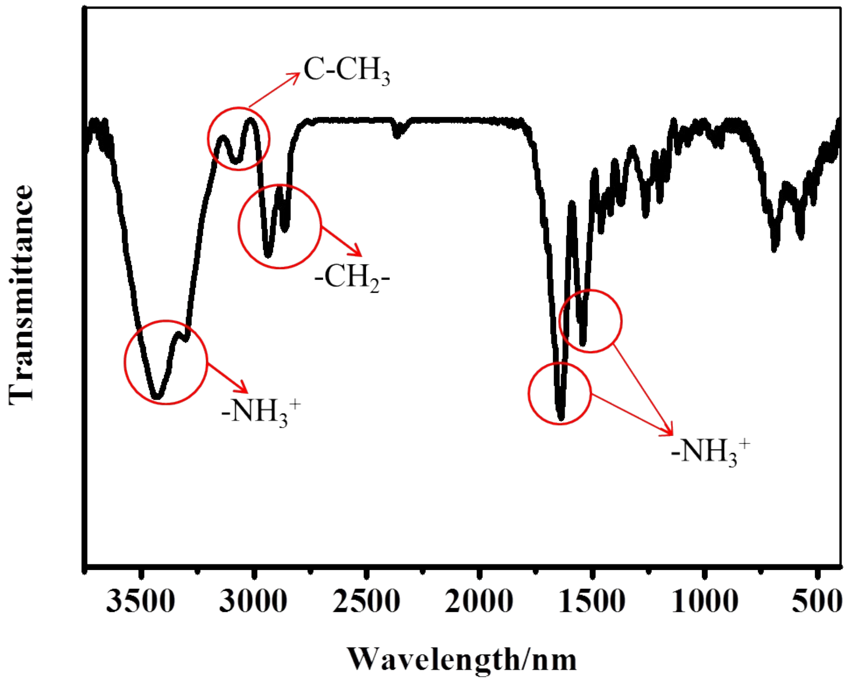

Fig. S4 The FT-IR of the residues after etching the silica shell of HPJMs SiO_2 with HF.

The stretching vibration bands at 3424 cm^{-1} and 3295 cm^{-1} and the deformation vibration bands at 1637 cm^{-1} and 1541 cm^{-1} were attributed to the resulting $–NH^{3+}$. Strong stretching vibration peaks at 2937 cm^{-1} and 2864 cm^{-1} and 3081 cm^{-1} were assigned to $–CH_2–$ and $C–CH_3$, respectively.

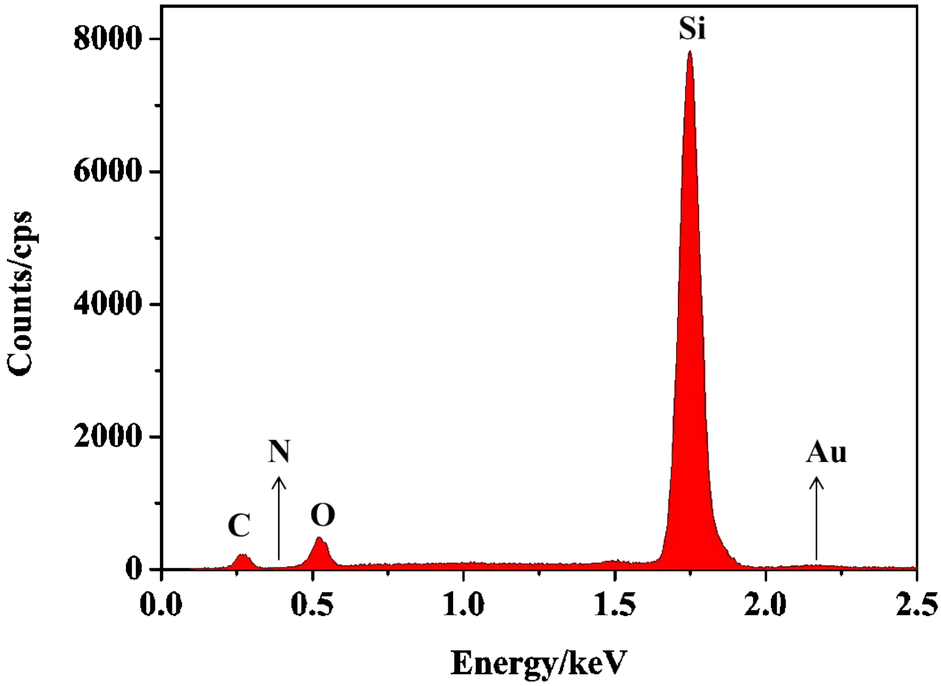

Fig. S5 The EDX pattern of Au@HPJMs SiO_2.

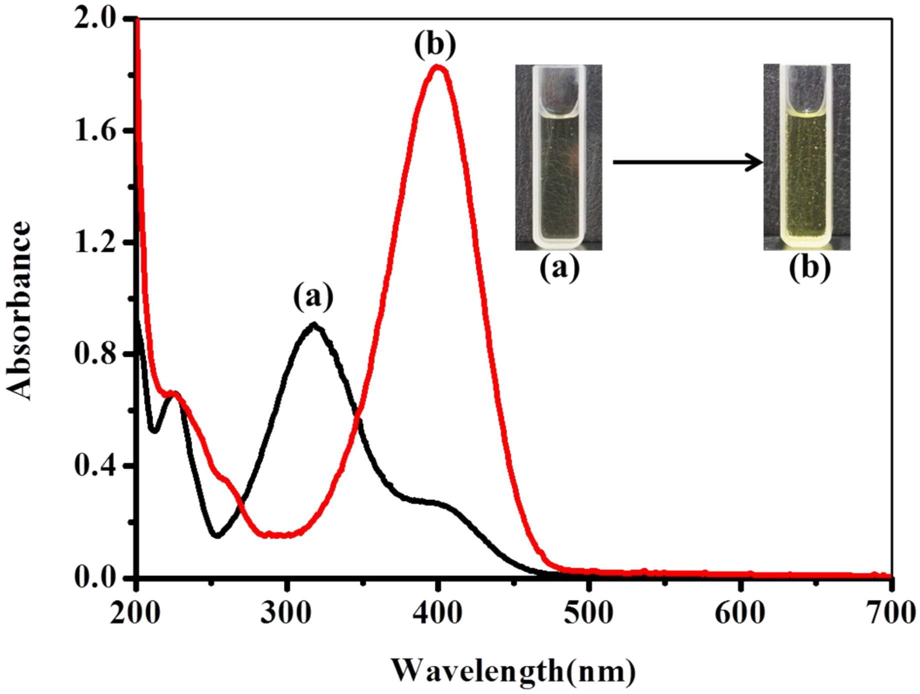

Fig. S6 The UV-vis absorption spectra of (a) 4-NP; (b) the mixture solutions of 4-NP and $NaBH_4$.

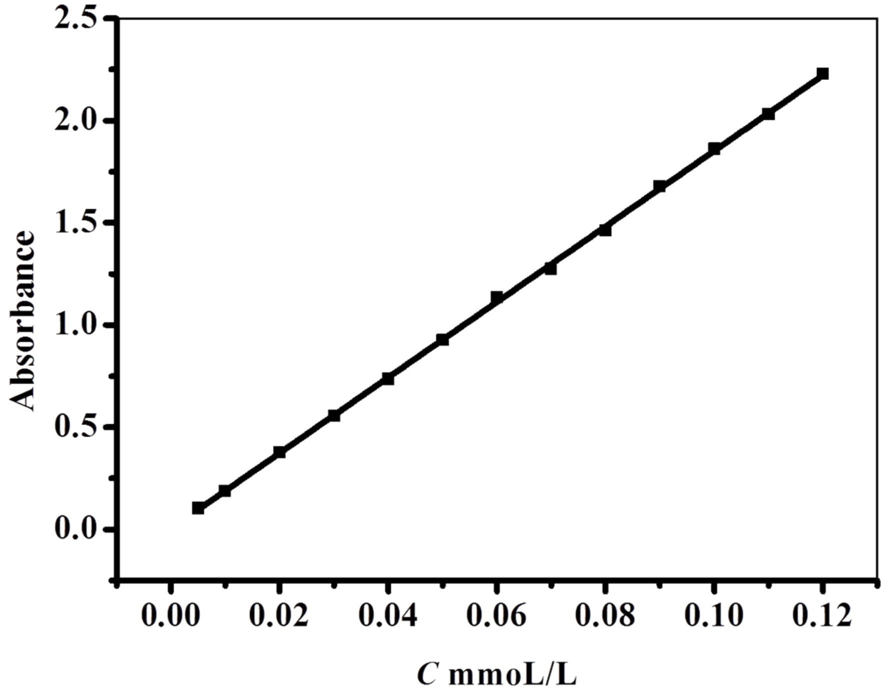

Fig. S7 The calibration curve 4-nitrophenolate ion in certain concentrations of 4-NP.

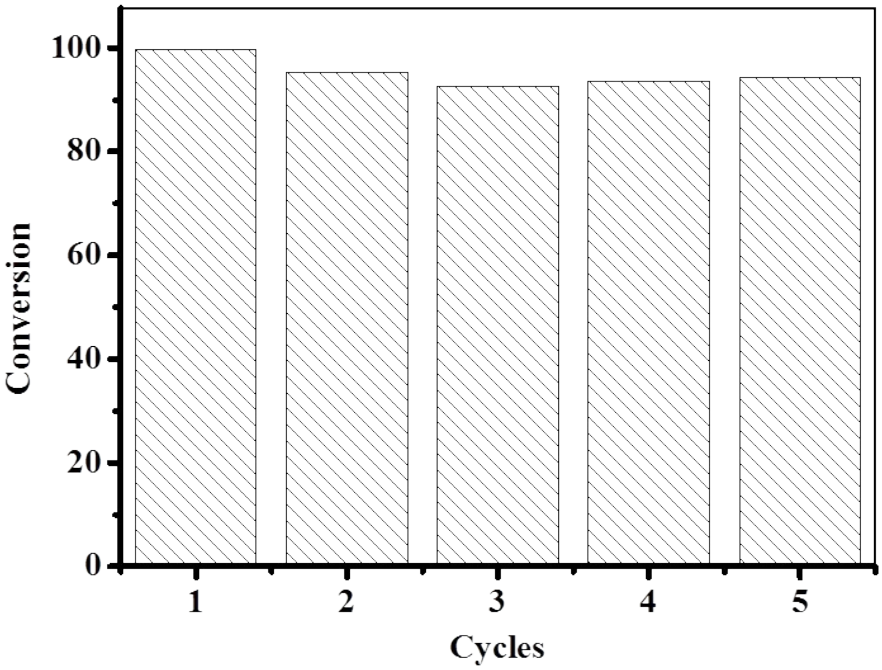

Fig. S8 The reusability of Au@HPJMs SiO_2 as a catalyst for the reduction of 4-NP with $NaBH_4$.

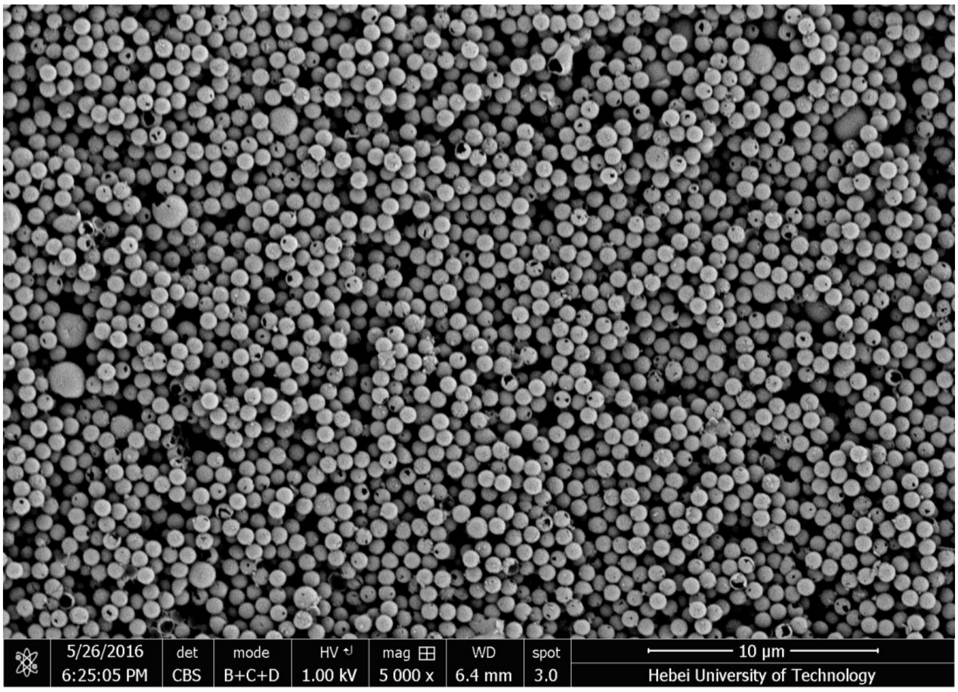

Fig. S9 The SEM image of Au@HPJMs SiO_2 after 5 cycles.

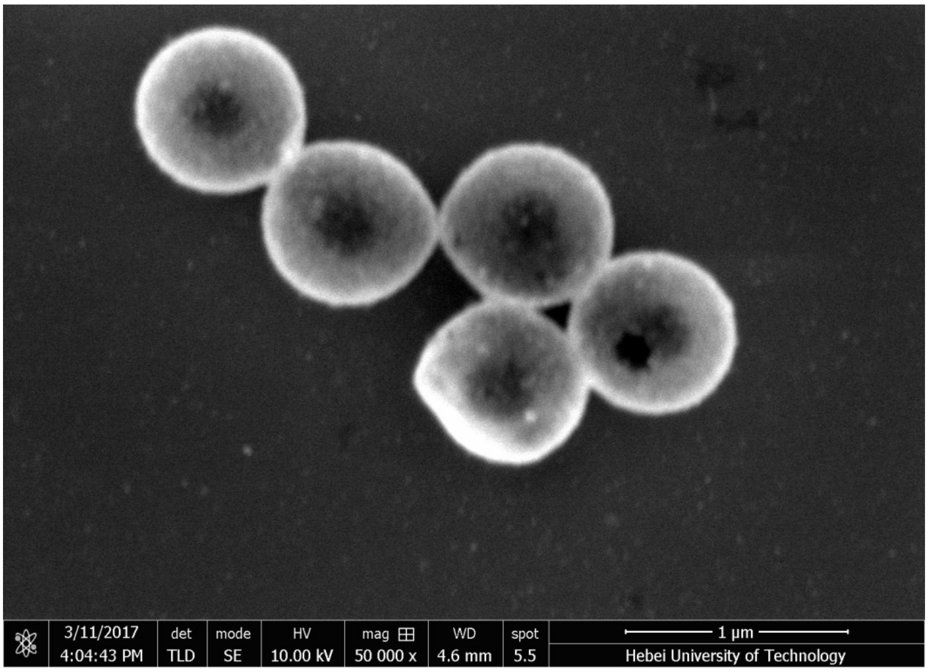

Fig. S10 The STEM image of Au@HPJMs SiO_2 after 5 cycles.

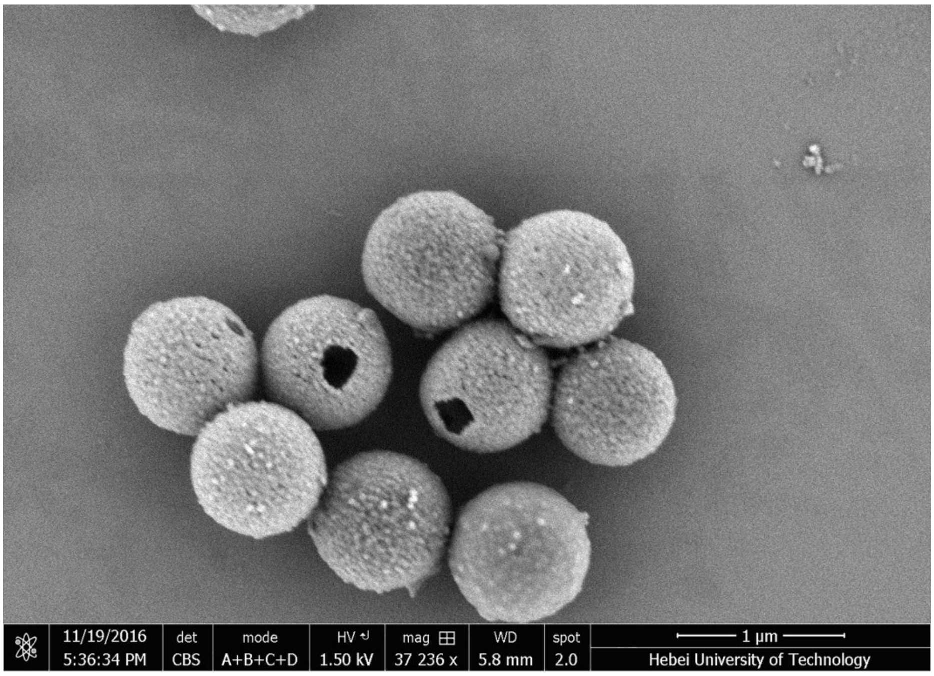

Fig. S11 The SEM image of HPMs SiO_2.

Table S1 Performance comparison of HPMs SiO_2 and HPJMs SiO_2 to enrich organic compounds in aqueous phase

Parameter	HPMs SiO_2	HPJMs SiO_2
C_0 (mmoL/L)	0.1	0.1
C_e (mmoL/L)	0.0655	0.0574
Q_e (mmoL/g)	0.0103	0.0129

Note: the volume of the 4-NP is 3 mL; the amount of HPMs SiO_2 or HPJMs SiO_2 is 0.01 g;

The adsorbing capacity (Q_e) was calculated with the following equation:

$$Q_e = \frac{(C_0 - C_e) \times V}{m}$$

Q_e: The amount of adsorption when saturated adsorption is reached, mmoL/L;

C_0: The initial concentration of the solution, mmoL/L;

C_e: The solution concentration when saturated adsorption is reached, mmoL/L;

V: The volume of the 4-nitrophenol, L;
m: The amount of SiO_2 microcapsules or HPJMs SiO_2, g.

S1 Turn over frequency (TOF) calculation of Au@HPJMs SiO_2 catalyst active sites

The per-active site's TOF (in 4 min, min^{-1}) was calculated according to the following equation:

$$TOF = \frac{n_1 \times C\%}{n_2 \times t}$$

n_1: The molar amount of reactant, mol;

n_2: The molar amount of Au, mol;

$C\%$: The conversion rate of reactant;
t: The reaction time, min.