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Supporting Information

A novel self-templating strategy for facile fabrication of monodisperse polymeric microporous capsules with tunable hollow structure

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Experimental Section

Materials

Styrene (St, analytical grade), divinylbenzene (DVB, Aldrich, 80% grade) and 4-vinylpyridine (4VP, Aladdin, 98%) were purified by sodium hydroxide solution (3 times) and stored at 4 °C. Potassium persulfate ($K_2S_2O_8$, Fisher) was recrystallized from deionized water then dried under reduced pressure at room temperature. Sodium dodecyl sulfate (SDS), 1,2-dichloroethane (DCE), anhydrous ferric chloride ($FeCl_3$), 4-nitrophenol (4NP), sodium borohydride ($NaBH_4$) methanol, ethanol, tetrahydrofuran (THF) and hexane of analytical grade were obtained from National Medicines Corporation Ltd. of China, and used without further purification. Dimethoxymethane/formaldehyde dimethyl acetal (FDA, 98%) and iodine (99.8%) was purchased from Aladdin company and used as received. Chloroauric acid ($HAuCl_4 \cdot 4H_2O$) of analytic grade was purchased from Shanghai Chemicals Company and used as reserved.

Synthesis of self-templating hollow capsule precursor

The hollow capsule precursor was prepared in a two-step process, including the formation of core-shell spheres by emulsion polymerization and their selective etching of inner core. In a typical experiment, 0.1 g SDS emulsifier was dissolved in 140 mL ethanol/water mixture (volume ratio was changed from 40:100 to 50:90 and 60:80 to adjust the particle size) and transferred to a 250 mL three-necked round bottom flask. Then, 10 mL styrene as organic phase was added into the mixture under 300 rpm mechanical stirring to form the emulsion. The emulsion was heated to 70 °C afterwards under N_2 protection, followed by the addition of 0.1 g $K_2S_2O_8$ initiator. After a certain period (0.5 h, 2 h and 3.5 h to adjust the hollow structure), 0.25 mL DVB monomer as pre-crosslinker was added to form a core-shell structure. The whole reaction was kept for 5 h and quenched in ice bath, then the emulsion was centrifuged at 11000 rpm, washed with ethanol to get the dense sphere. The inner PS core was selective etched by THF Soxhlet extraction (for 24 h) and the obtained hollow capsule precursor was dried under vacuum at 60 °C.

Synthesis of microporous hollow capsules (SMHCs)

The hypercrosslinking of hollow capsule precursors was conducted by applying the external knitting strategy. Firstly, 1.0 g hollow capsule precursor was swollen in 20 mL DCE for 5 h. Then, 1.73 mL FDA external crosslinker was added to the mixture as well as 3.11 g anhydrous

$FeCl_3$ catalyst. The Friedel-Crafts reaction was carried out at 45 ºC for 5 h and 80 ºC for 19 h. After cooling to room temperature, the resulting product was filtered and the residual was washed 3 times with methanol followed by methanol extraction in a Soxhlet for 24 h, dried in vacuum oven at 60 °C for 24 h.

Iodine uptake and release by SMHCs-317nm

The iodine capture was investigated by iodine vapor uptake as well as iodine adsorption in hexane solution. For the vapor uptake, 50 mg of SMHCs-317nm was placed into an open glass vessel kept in another sealed container with iodine. Then, the device was put into the oven at 75 °C under ambient pressure. At certain time period, the device was taken out and cooled down to room temperature. Afterwards, the sample was weighed to calculate the uptake capacity using the following equation;

$$C = \frac{m1 - m0}{m0} \times 100\%$$

where m1 and m0 represent the mass of SMHCs-317nm after and before iodine uptake. The release of iodine was realized by placing the iodine loaded hollow capsules in an open system and heated at 125 ℃. The release rate was also recorded through the gravimetric analysis.

For the adsorption kinetic study of iodine in hexane, 5 mg SMHCs-317nm was added to 3 mL 1 g/L iodine solution. After different time intervals, the supernatant was diluted and then examined by UV-Vis spectrophotometer to determine the iodine concentration. The uptake capacity was confirmed by immersing 5 mg SMHCs-317nm in excess iodine solution (10 mL) for 2 days. The iodine concentration was recorded before and after adsorption by the UV-Vis spectra to calculate the capacity.

Synthesis of functionalized microporous hollow capsules (F-SMHCs)

The synthetic procedure of F-SMHCs was similar to that of SMHCs, in which, however, the ethanol:water ratio was fix at 40:100 and the adding amount of functional monomer 4VP was 0.5 mL together with 0.25 mL DVB at 2 h in the emulsion co-polymerization. The resulting functionalized microporous hollow capsules were named as F-SMHCs.

Gold nanoparticles loading in F-SMHCs (Au@F-SMHCs)

The immobilization of gold nanoparticles in F-SMHCs was achieved by in situ $NaBH_4$ reduction of Au^{3+} ions. Typically, 10 mg F-SMHCs were well dispersed in 10 mL ethanol under

sonification. Then, 50 μL (20 mM) Au^{3+} solution was added into the system and stirred for 10 min to allow the Au^{3+} penetrates thought the capsules. After that, 1 mL aqueous solution of $NaBH_4$ (100mM) was added dropwise into the solution slowly under magnetic stirring at room temperature. The mixture was kept stirring for 1 h, filtered and washed with ethanol and water alternately for 3 times, then dried at 60 °C for 24 h resulting the Au@F-SMHCs.

Gold loaded F-SMHCs catalyst for 4NP reduction

1 mg catalyst was immersed into the 4NP aqueous solution (10 mL, 0.5 mM) at room temperature. Under magnetic stirring, 1 mL $NaBH_4$ solution (1 M) was added at once. The residual concentration of 4NP was detected with a UV-Vis spectrometer at 400 nm, which was subsequently used to calculate the catalytic reaction rate.

Characterization

The particle size as well as inner hollow morphology were investigated using a FEI Sirion 200 field emission scanning electron microscope (FE-SEM) and a Tecnai G20 transmission electron microscope (TEM). Before SEM analysis, the samples were placed on a small platform and then coated with platinum. The average particle sizes of the hollow capsules were calculated using Image J software. Specific surface areas, N_2 sorption isotherms (77 K), pore size distributions and H_2/CO_2 uptake analysis (up to 1.13 bar, 77 K/273 K, 298 K) were measured using a Micromeritics ASAP 2020M surface area and porosity analyzer. Before analysis, the SMHCs were degassed at 110 °C for 8 h under vacuum (10^{-5} bar). Thermogravimetric analysis (TGA) measurements were performed on a PerkinElmer instrument from room temperature to 900 °C with a heating rate of 10 °C/min under nitrogen flow. UV-Vis spectra were recorded by a Shimadzu UV-1601PC spectrophotometer. Raman measurements were performed with a LabRAM HR spectrometer. FTIR spectra were recorded under ambient conditions in the wave number range of 4000-400 cm^{-1} using a Bruker Equinox 55 FTIR Spectrometer. Elemental analysis (EA) was performed on a VarioMicro cube Elemental Analyser (Elementar, Germany). Solid state ^{13}C NMR measurement was carried out on a Bruker Avance II WB 400 MHz spectrometer with a contact time of 2 ms and pulse delay of 3 s.

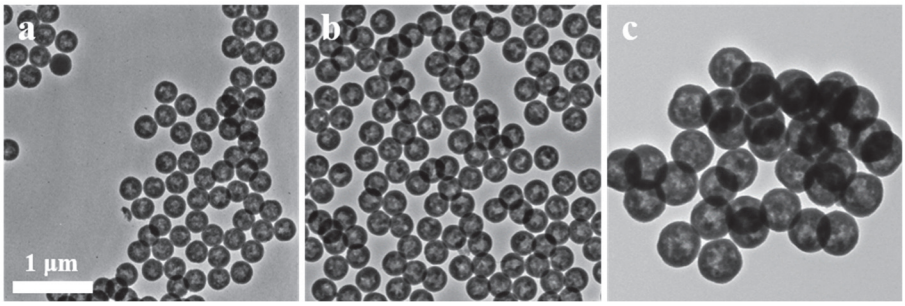

Figure S1. TEM images of the SMHCs with different particle size, (a) 317 nm, (b) 394 nm, (c) 549 nm. scale bar: 1 μm

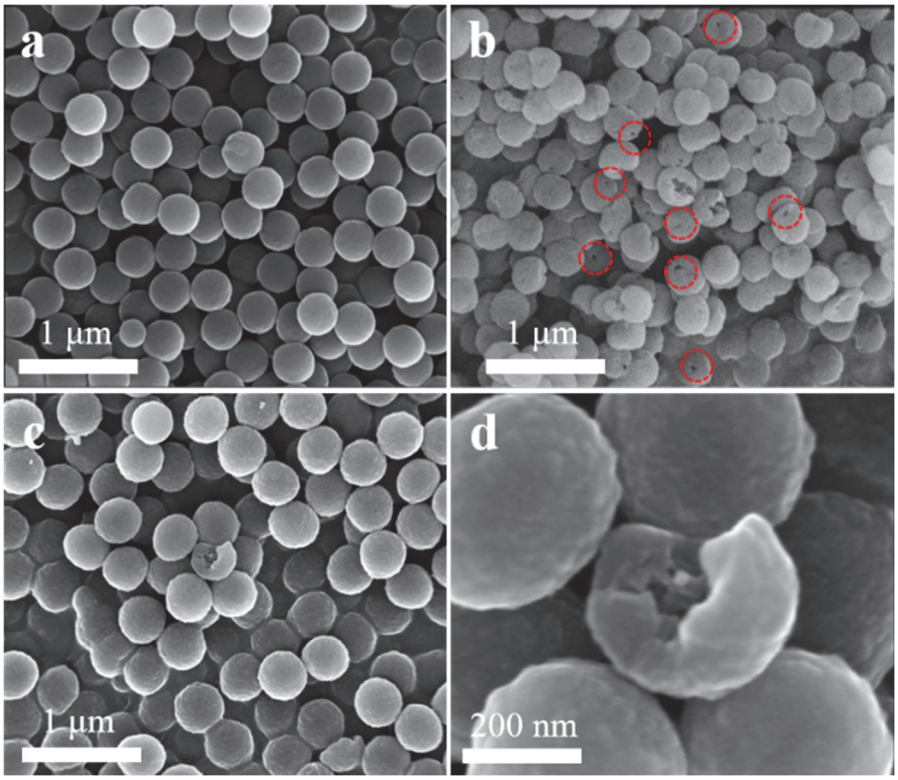

Figure S2. SEM images of (a) core-shell spheres, (b) hollow capsule precursors, (c, d) SMHCs-317nm, scale bar: 1 μm and 200 nm

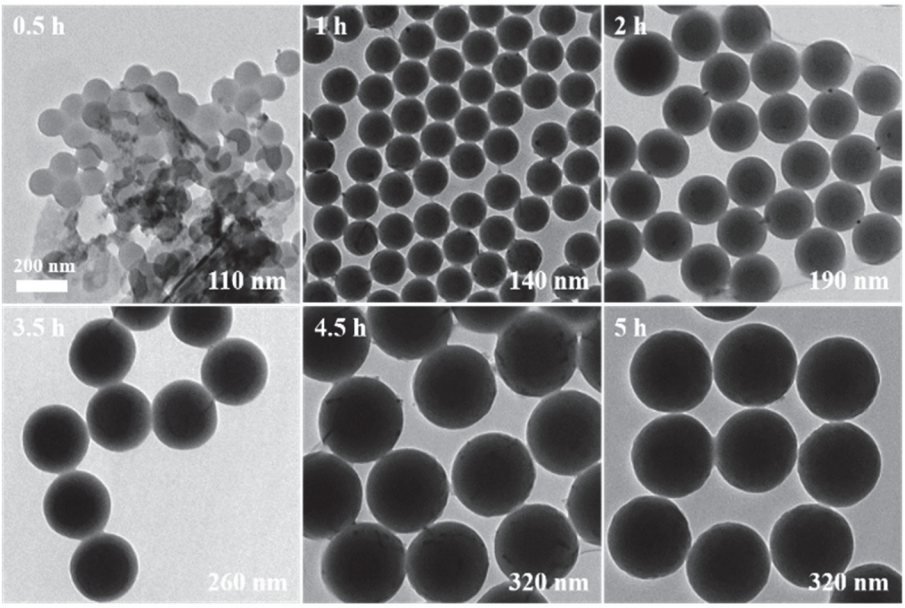

Figure S3. Particle size growth with different polymerization time, scale bar: 200 nm

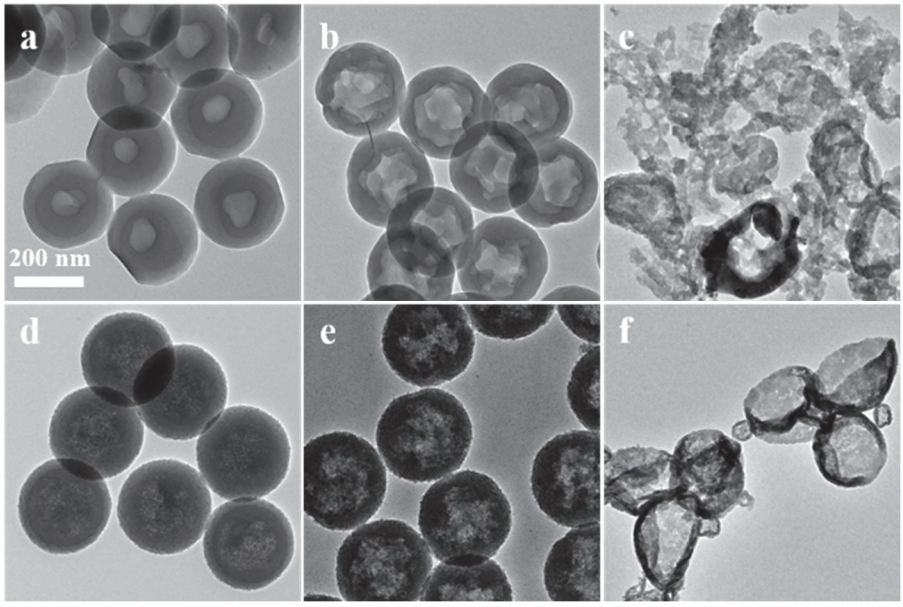

Figure S4. TEM images of hollow capsule precursors (a-c) and SMHCs (d-f) with different DVB adding time, (a,d) 0.5 h, (b,e) 2 h, (c,f) 3.5 h. scale bar: 200 nm

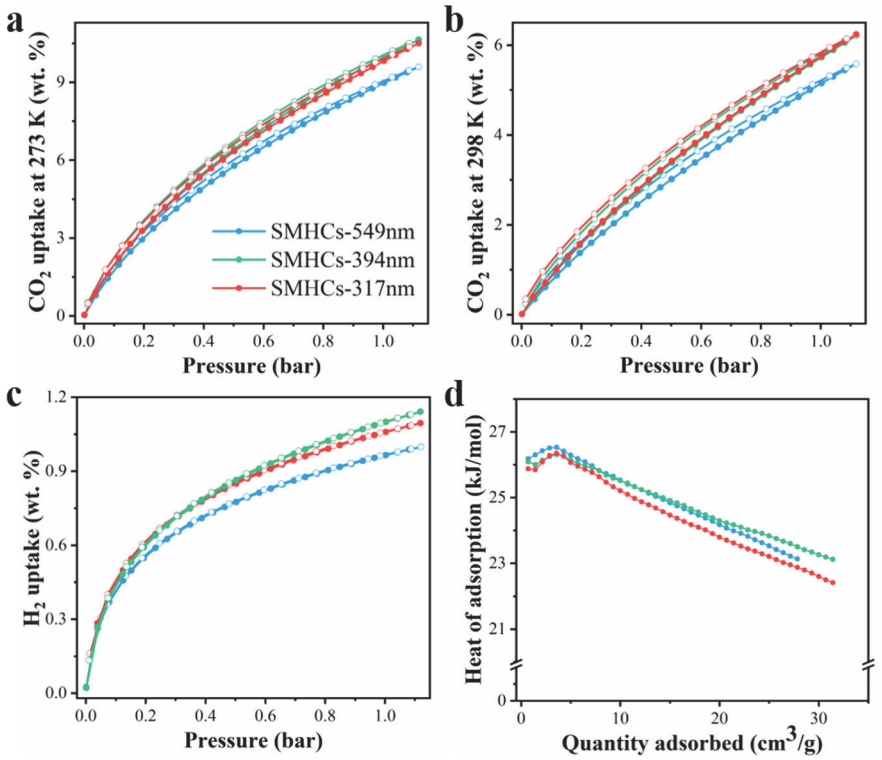

Figure S5. CO_2 sorption isotherm at 273 K (a)/298 K (b), (c) H_2 sorption isotherm at 77 K and (d) CO_2 heat of adsorption isotherm of the SMHCs

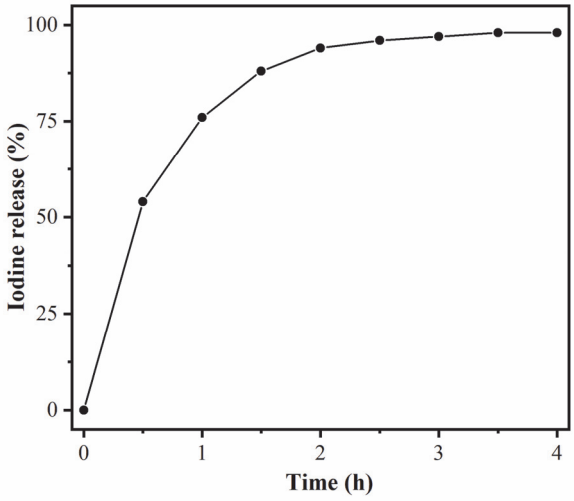

Figure S6. Iodine release of I_2@SMHCs-317nm at 125 ℃

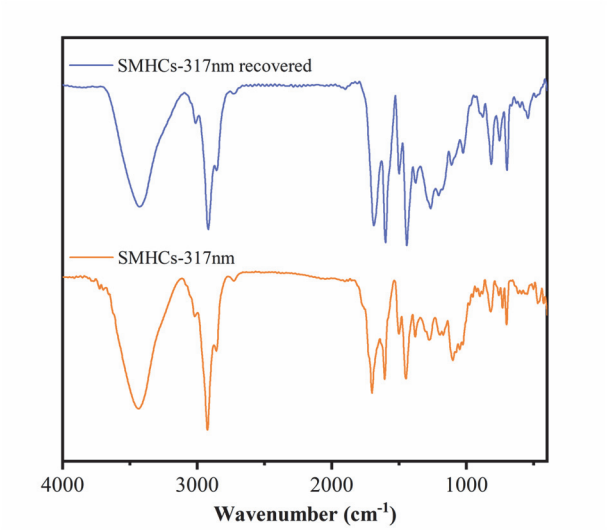

Figure S7. FTIR spectra of original SMHCs-317nm and recovered SMHCs-317nm

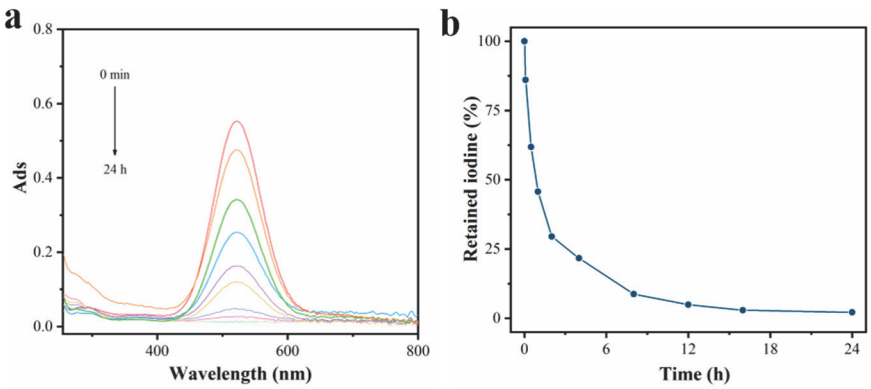

Figure S8. (a) UV-Vis spectrum of iodine uptake and (b) retained iodine in hexane by SMHCs-317nm

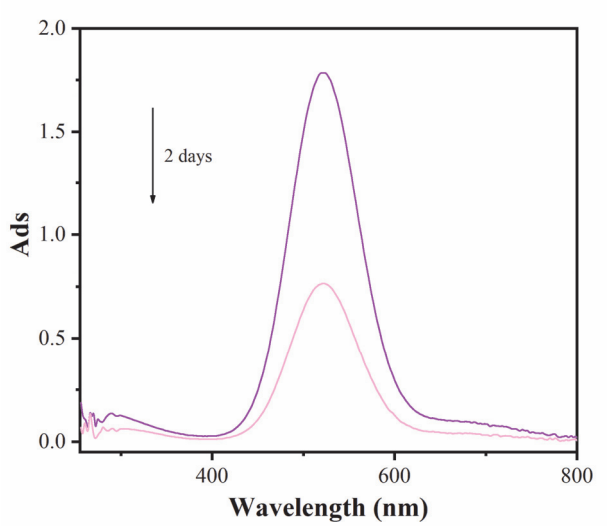

Figure S9. UV-Vis spectrum of iodine solution before and after saturated uptake by SMHCs-

317nm

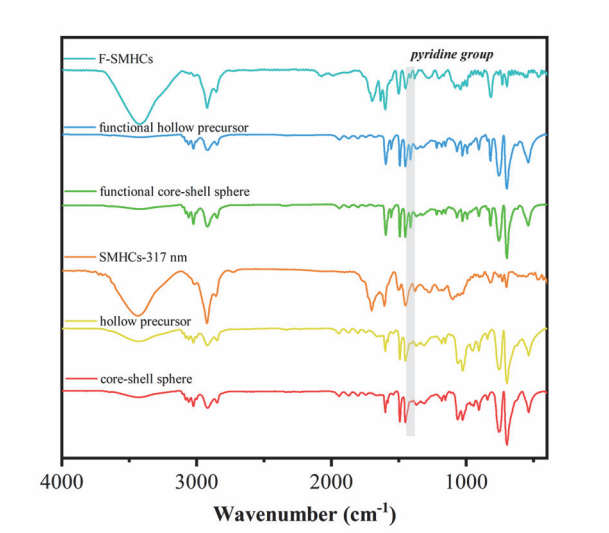

Figure 10. FTIR spectra of the core-shell sphere, hollow precursor, SMHCs-317nm and F-SMHCs

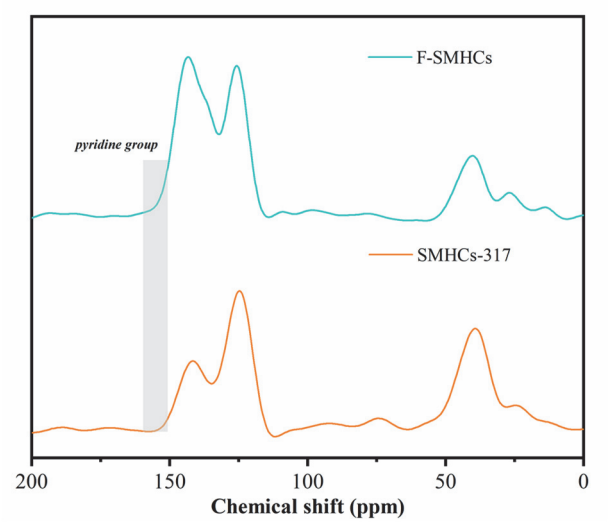

Figure S11. Solid state ^{13}C NMR of the SMHCs-317nm and F-SMHCs

Table S1. Elemental analysis results of SMHCs-317nm and F-SMHCs

Sample	C %	H %	N %	N% (theoretical value)
SMHCs-317nm	91.02	7.63	0.02	0
F-SMHCs	88.81	7.71	0.57	0.61

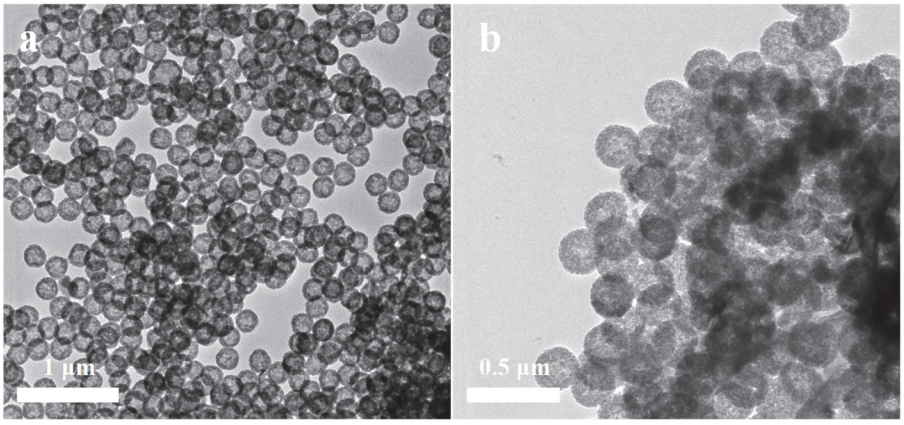

Figure 12. TEM images of (a) functionalized hollow capsule precursors and (b) F-SMHCs, scale bar: 1μm and 0.5 μm

Table S2. Catalysis performance of different catalysts for 4NP reduction

Entry	Catalyst	Chemical structure	k (s^{-1})	Reference
1	IO-Pd-1	Pd loaded Fe_3O_4 nanoparticle	7.5×10^{-3}	1
2	IO-Pd-1		4.5×10^{-3}	
3	AOBC-1	Bacterial cellulose supported Au nanoparticle	2.1×10^{-3}	2
4	AOBC-2		3.7×10^{-3}	
5	AOBC-3		4.5×10^{-3}	
6	AuNPs	TMA stabilized Au nanoparticle	4.2×10^{-3}	3
7	Complex1	Pyridine-based SNS ligands stabilized Au nanoparticle	2.6×10^{-3}	4
8	Complex2		2.7×10^{-3}	
9	Complex3		5.1×10^{-3}	
10	Au@F-SMHCs	Hollow capsule supported Au nanoparticle	1.0×10^{-2}	This work

Reference

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