Electronic Supplementary Information

Hybrid Hollow Microspheres Templated from Double Pickering Emulsions

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1. Materials and methods

Materials

Tetraethoxysilane (TEOS) and styrene (St) were purchased from Shanghai Chem. Reagent Co. (China) and distilled in a vacuum before use. 2, 2`–Azobis(isobutyronitrile) (AIBN, Shanghai Chem. Reagent Co.) was purified by recrystallization in ethanol. γ–(trimethoxysilyl)propyl methacrylate (MPS, Aldrich), hexadecane (HD, Fluka), and ammonium hydroxide (28% by *wt*) (Shanghai Chemical Reagent Co.) were purchased in their reagent grade and used without further purification. Polystyrene (PS) was synthesized in our laboratory. Deionized water was used for all purposes.

Experimental procedures

The schematic diagram of the Pickering double emulsions were shown in Figure. 1 In a typical synthesis, 0.8 g of hexadecane and 0.2 g of AIBN were first added in a mixture of 12.0 g of St, 8.0 g of TEOS, and 2.4 g of MPS to form an oil phase. A portion of 13 g of TEA aqueous solution (1.5 g TEA in 11.5 g water) was employed as the inner water phase. The mixture of oil phase and water phase was first pre–emulsified by mechanical stirring for 0.5 h and then a portion of 200 g of the water uses as the outer water phase was added followed by high speed shearing via a Fluko FM200 homogenizer (Fluko® equipment Shanghai Co., Ltd, China) at 18000 rpm for 5 min in an ice bath. The polymerization was carried out under N_2 atmosphere at 75 ℃ for 8.0 h in a 250–ml four–neck round flask equipped with a reflux condenser and an agitator.

Table S1 Synthetic conditions of hybrid hollow microspheres.

	Oil phase						Internal water phase		External water phase
Runs	St/g	PS/g	AIBN/g	MPS/g	TEOS/g	HD/g	Water/g	TEA/g	Water/g
1	12.0	0.15	0.2	1.2	8.0	0.8	5.5	1.5	200
2	12.0	0.15	0.2	1.2	8.0	0.8	7.5	1.5	200
3	12.0	0.15	0.2	1.2	8.0	0.8	9.5	1.5	200
4	12.0	0.15	0.2	1.2	8.0	0.8	11.5	1.5	200
5	12.0	0.15	0.2	1.2	8.0	0.8	15.5	1.5	200
6	12.0	0.15	0.2	0.4	8.0	0.8	11.5	1.5	200
7	12.0	0.15	0.2	0.8	8.0	0.8	11.5	1.5	200
8	12.0	0.15	0.2	1.2	8.0	0.8	11.5	1.5	200
9	12.0	0.15	0.2	2.4	8.0	0.8	11.5	1.5	200
10	16.0	0.15	0.2	1.2	4.0	0.8	11.5	1.5	200
11*	10.0	0.15	0.2	1.2	4.0	0.8	11.5	1.5	200

* 6.0 g heptane was added with St.

Instrumentation

Samples of transmission electron microscopy (TEM) were prepared by drying a drop of the dilute hybrid hollow microspheres dispersion onto a carbon–coated copper grid. Analysis was conducted using a Hitachi H–800 electron microscope operating at 100 kV. The surface and cross section images of hollow microspheres were studied by scanning electron microscopy (SEM, Hitachi S–4800) operating at 20 kV. Elemental analysis of the sample was conducted using an energy–dispersive X–ray (EDX) detector attached to the SEM to check the composition of the as–prepared hybrid hollow microspheres. Samples of FT–IR characterization were dried at 60 °C under vacuum for 24 h and measured in the wavenumber range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} using a Nicolet Nexus–870 FT–IR spectrophotometer. Digital photographs showing the amphiphilic properties of silica particles in water and water/toluene were pictured by optical microscopy (Olympus, BX41). The average particle size and size distribution of the Pickering double emulsions were determined using light scattering equipment (Zetasizer 3000 HSA, Malvern Company). The samples were previously diluted in water without filtration. Thermogravimetric analysis (TGA) was conducted using a Perkin–Elmer Pyris1 TGA instrument. Samples dried at 70 °C were heated in air to 800 °C at a heating rate of 10 °C min^{-1}.

2. Characterization

FT–IR characterization showing the structure of MPS modified silica particles

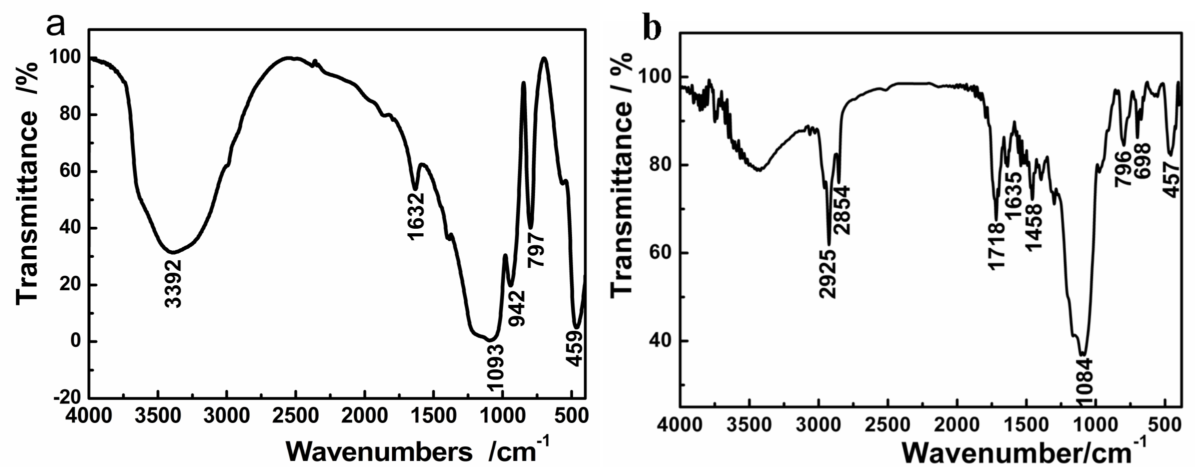


Fig. S1 FT–IR spectroscopy of bare (a) and MPS modified (b) silica nanoparticles.

The FT–IR spectroscopy of bare silica nanoparticles was obtained without MPS in the oil phase before the polymerization of organic monomer. The peaks at 464, 797, 942, 1094, 1632 cm^{-1} in Figure S1a are the typical peaks demonstrating the formation of SiO_2. The FT–IR spectroscopy of MPS modified silica nanoparticles was obtained before the polymerization of organic monomer. Figure S1b shows an absorption band characteristic for the Si–O–C group (1084 cm^{-1}) and absorptions at 2925, 1718, and 1635 cm^{-1}, corresponding to the stretching vibration of the $–CH_3$, C=O, and C=C groups of MPS.[1] Because the redundant MPS was eliminated by rinsing three times with hot ethanol, the result indicated that there existed chemical interaction between MPS and SiO_2 nanoparticles, not single physical absorption.

Amphiphilic properties of silica particles

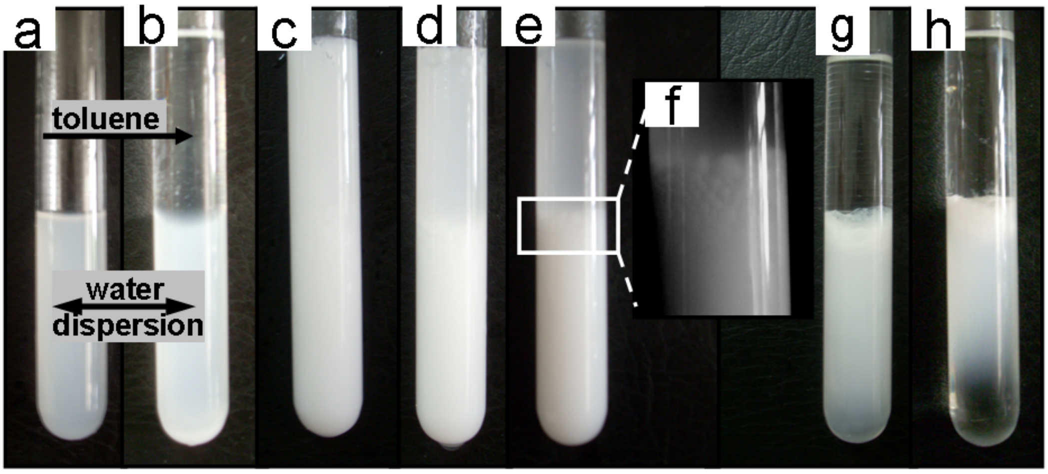


Fig. S2 Optical pictures showing the amphiphilic properties of the in situ formed silica particles. Locations of MPS modified silica particles were investigated and pictured in water/toluene medium by the following successive process. (a) Sonification for 15 min after adding water and then removal of precipitated silica particles. (b), Toluene added to the test–tube. (c) After 15 min sonification. (d) After standing for 10 min. (e) After standing for 30 min. (f) Magnified local picture in (e). (g), (h) After standing for 1 and 3 days, respectively. The in–situ formed silica particles were withdrawn from step b in Fig. 1.

Dispersion behavior of the unmodified and fully modified silica nanoparticles in a dual-solvent system

In our experiment, the unmodified silica nanoparticles were obtained without the addition of MPS in the oil phase of the step a of Scheme 1 and withdrawn in the step b of Scheme 1 before the further polymerization of monomers. And the fully modified silica nanoparticles were prepared by adding TEA into the oil phase of St, MPS, HD, and TEOS without the addition of internal water phase (without the formation of water-in-oil emulsions). The locations of silica nanoparticles fullly modified by MPS and unmodified silica nanoparticles was investigated and pictured in a water/toluene medium. Optical pictures showing their dispersibility in a dual-solvent system were displayed in **Fig. S2a** and **S2b**.

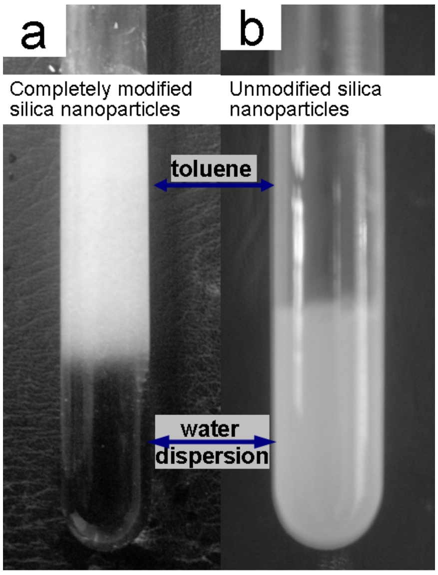


Fig. S3 Optical pictures showing the locations of MPS fullly modified silica nanoparticles (a) and unmodified silica nanoparticles (b) in a water/toluene medium.

Optical pictures showing the stabilities of the as–prepared double emulsions by using the amphiphilic silica particles as emulsifier alone

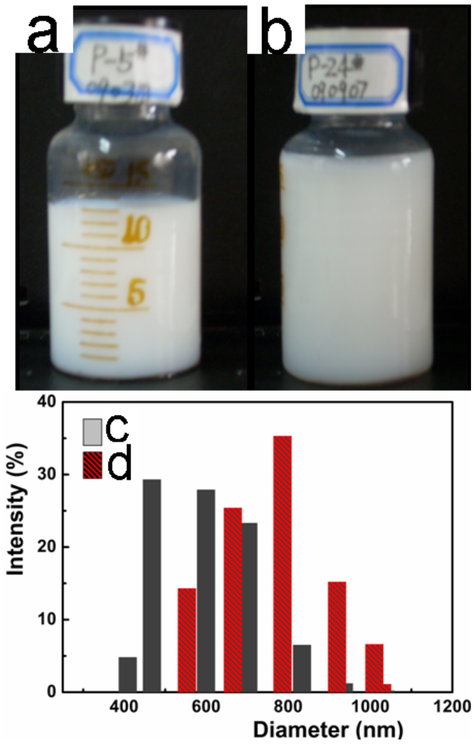
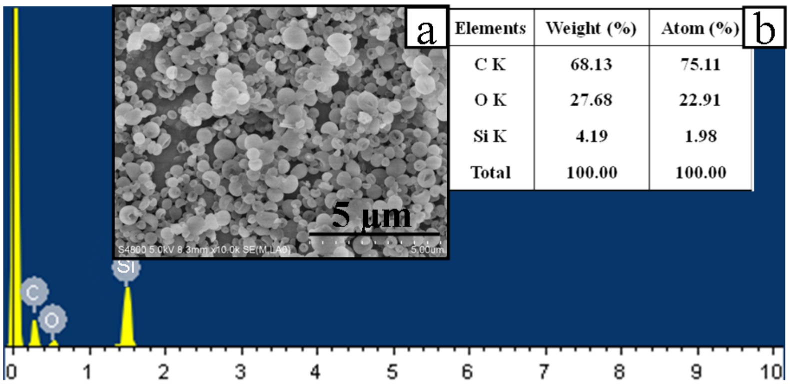


Fig. S4 The stabilities of the as-prepared double emulsions by using the amphiphilic silica particles as an emulsifier alone. Optical photographs were pictured shortly after the preparation (a) and about 6 months ago (b), respectively. Sizes and size distributions of the double Pickering emulsions were determined shortly after the preparation (c) and about 6 months ago (d), respectively.

Elemental analysis (EDX) of the sample showing the composition of the as–prepared hybrid hollow microspheres



Elements	Weight (%)	Atom (%)
C K	68.13	75.11
O K	27.68	22.91
Si K	4.19	1.98
Total	100.00	100.00

Fig. S5 Elemental analysis (EDX) of the sample showing the composition of the as–prepared hybrid hollow microspheres. The inset a showed the SEM image of the sample and the result of element analysis was shown in inset b.

TGA analysis confirming the silica content of hybrid hollow microspheres

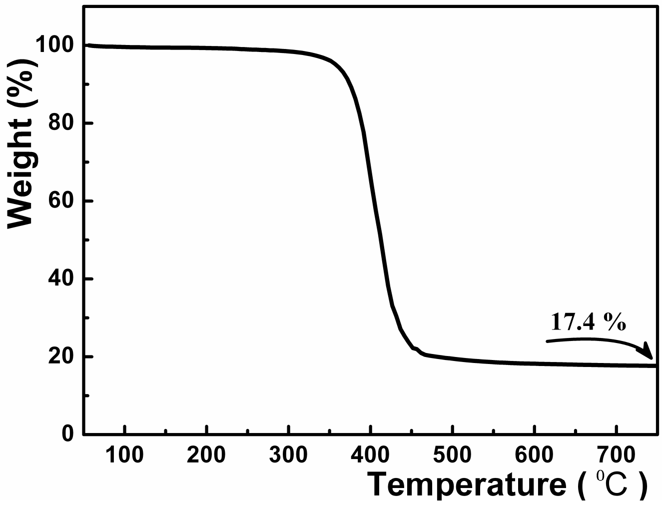


Fig. S6 TGA curve of SiO_2/PS hybrid hollow microspheres.

Size and size distribution of hybrid hollow microspheres

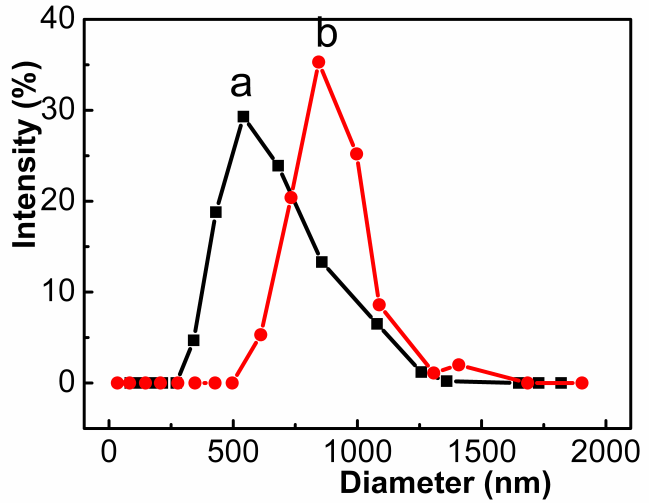


Fig. S7 Sizes and size distributions of the hybrid hollow microspheres double prepared with volume ratio of oil/water phase = 10/15 and different ratio of St/TEOS/MPS: (a) St/TEOS/MPS = 16/4/1.2, (b) St/TEOS/MPS = 12/8/2.4.

Reference

1 K. Zhang, H. T. Chen, X. Chen, Z. M. Chen, Z. C. Cui and B. Yang, *Macromol. Mater. Eng.,* 2003, **288**, 380.

2 T. Nisisako, S. Okushima and T. Torii, *Soft Matter,* 2005, **1**, *23*.