Supplementary Material (ESI) for Chemical Communications

Supporting Information

Janus Hollow Spheres by Emulsion Interfacial Self-Assembled Sol-Gel Process

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1. Experimental

1.1 Materials:

Amido-propyltrimethoxysilane (APTMS) and phenyl-triethoxysilane (PTES) were purchased from Acros. Tetraethyl orthosilicate (TEOS), sodium dodecyl sulfate (SDS), polysorbate-80 (Tween-80), sorbitan monooleate (Span-80) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (SCRC). Hydrolyzed styrene-maleic anhydride (HSMA) copolymer was synthesized (S1). Unless specified otherwise, all reagents were used as received.

1.2 Preparation of the Janus hollow spheres:

15 mL of 10 wt.-% hydrolyzed styrene-maleic anhydride (HSMA) copolymer solution was dissolved in 75 mL of water. PH of the mixture was adjusted to 2.5 with 2 M aqueous hydrochloric acid and the solution was heated to 70 ^{o}C. At 70 ^{o}C, 25.0 g of paraffin (Tm 52-54 ^{o}C) was mixed with 5.2 g of TEOS, 0.92 g of APTMS and 1.2 g of PTES under stirring. The oil mixture was dispersed into the aqueous solution with a homogenizer at a speed of 12000 rpm for 5 min forming an oil-in-water emulsion. The emulsion stood at 70 ^{o}C for varied time for the sol-gel process. After the resultant emulsion was cooled down to ambient temperature, the core/shell spheres with a frozen paraffin core were obtained by a sequential filtration and wash with water. Afterwards, the spheres were immersed in hexane to dissolve the paraffin core under ultrasonication, forming Janus hollow spheres.

1.3 Labeling Janus hollow spheres with sulfonated PS nanoparticles:

0.1 g of the dried Janus hollow spheres was dispersed in water. A small amount of sulfonated PS nanoparticles (30 nm in diameter) was added to the dispersion under stirring for 5 min. The spheres were centrifugated and washed with water.

1.4 Preparation of the Janus hollow porous spheres:

After a given amount of Tween-80 was dissolved in 10 mL of water as aqueous phase, pH of the solution was adjusted to about 2.5 with 2 M aqueous hydrochloric acid. 60 g of toluene was mixed with 6 g of Span-80, 5.2 g of TEOS, 0.92 g of APTMS and 1.2 g of PTES as the oil phase. The aqueous phase was dispersed into the oil mixture with a homogenizer at a speed of 12000 rpm for 5 min forming a water-in-oil emulsion. The emulsion stood at 70 ^{o}C for 12 h for the sol-gel process. After the resultant emulsion was cooled down to ambient temperature, the spheres were obtained by a sequential filtration and wash with ethanol.

1.5 Janus performance of the Janus hollow spheres:

A trace amount of organic dye 1, 1' -dioctadecyl -3, 3, 3', 3', -tetramethylindo - carbocyanine perchlorate was introduced into 1 mL of toluene, which was emulsified using 0.05 g of SDS in 5 mL of water with a homogenizer at a speed of 12000 rpm for 5 min forming an oil-in-water emulsion. 0.2 g of the Janus hollow sphere was added into the mixture under stirring. Toluene was absorbed into the oleophilic internal cavities of the Janus hollow spheres. Toluene contained Janus spheres settled onto the bottom after cessation of stirring. The emulsion composed of 10 mL of toluene, 50 mL of water, and 0.5 g of SDS was added into the chromatograph stacked with 2 g of the Janus hollow spheres. Toluene was adsorbed into the cavities of the Janus hollow spheres, while water eluted.

1.6 Characterization:

Very dilute dispersions of the samples in ethanol were dropped onto carbon coated copper grids for transmission electron microscopy (TEM) characterization (JEOL 100CX operating at 100 kV). Scanning electron microscopy (SEM) measurements were performed with a HITACHI S-4800 apparatus operated at an accelerating voltage of 15 kV. The samples were ambient dried and vacuum sputtered with Pt. AFM images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating at a tapping mode. Polarizing optical micrograph images were performed with an Olympus optical microscopy. Particle size and size distribution were measured by a Malvern Master-Sizer 2000 Particle Size Analyzer.

2. Result and discussion

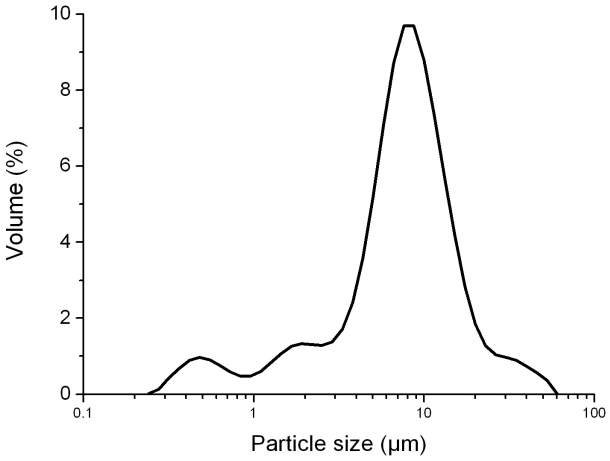


Fig. S1 Particle size and distribution of the as-synthesized core/shell spheres.

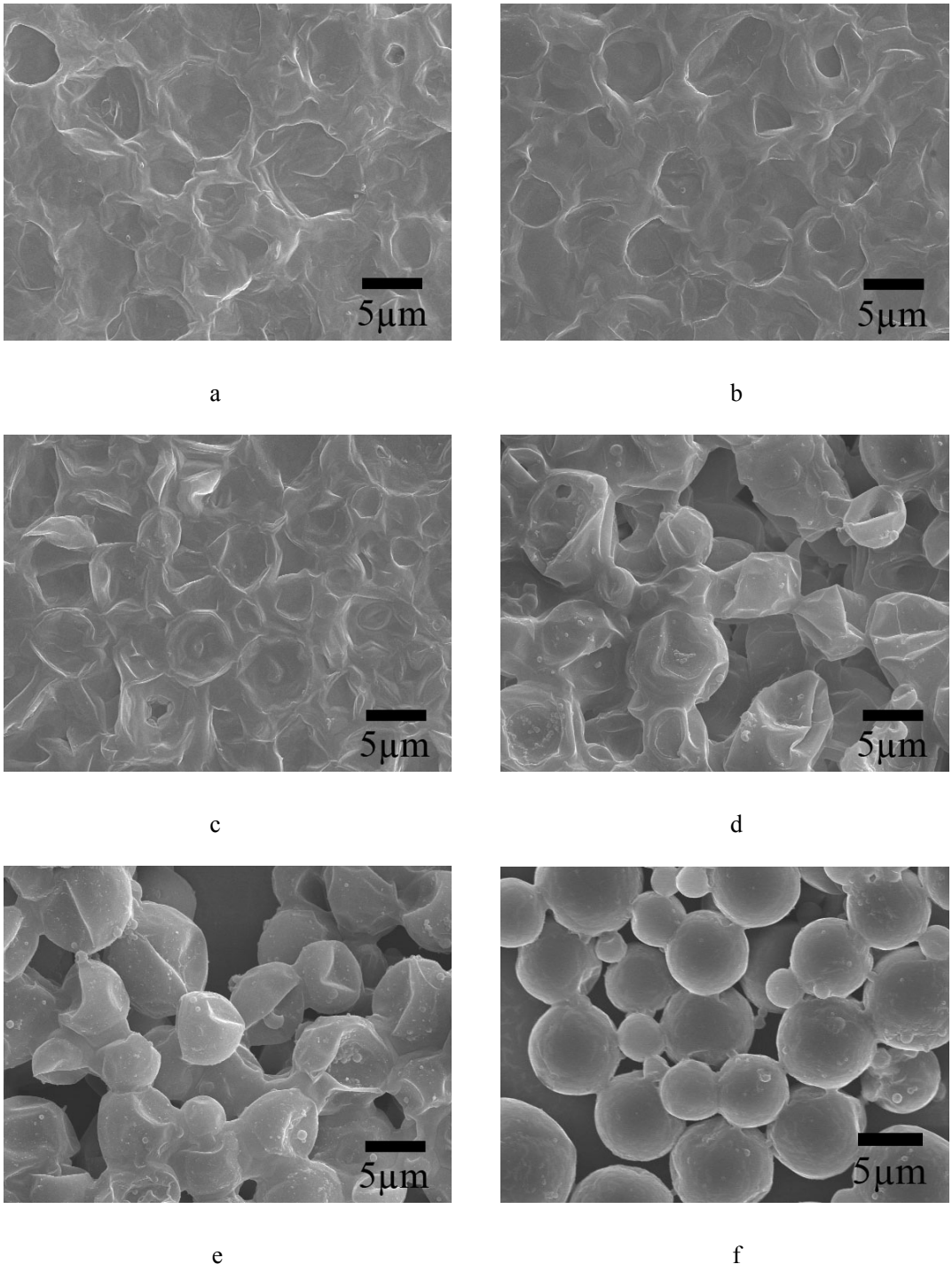


Fig. S2 Morphological evolution of the core/shell structure with increased sol-gel process time (min): a) 5; b) 15; c) 30; d) 60; e) 120; f) 720.

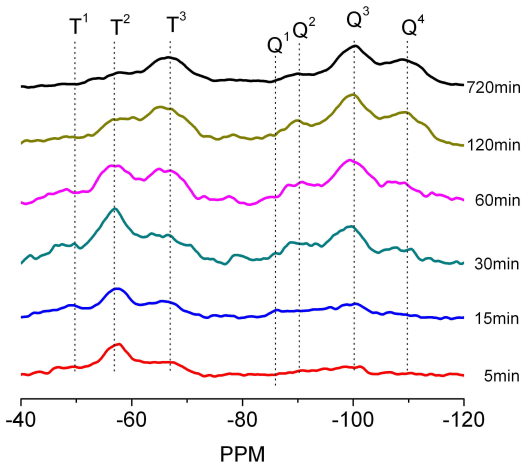


Fig. S3 ^{29}Si MAS NMR spectra of the core/shell structure with increased sol-gel process time (min): 5; 15; 30; 60; 120; 720.

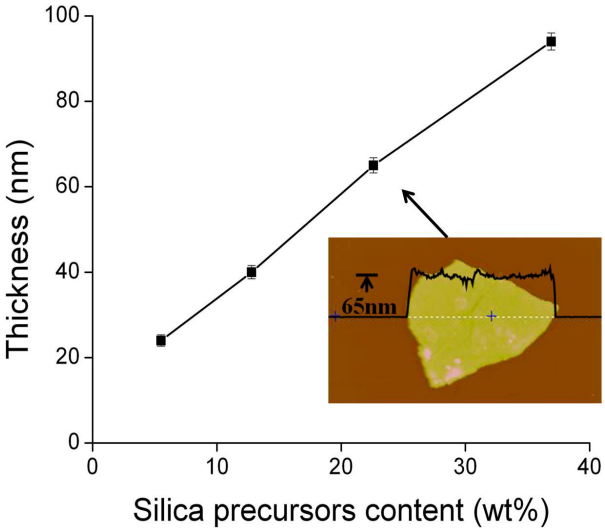
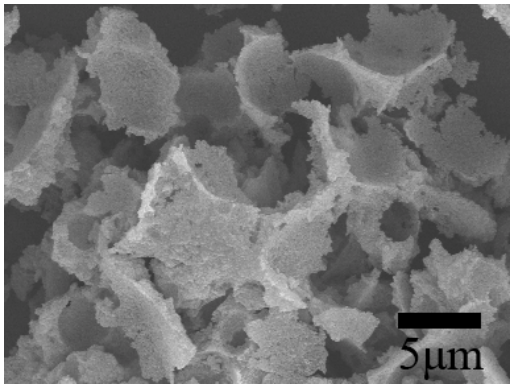
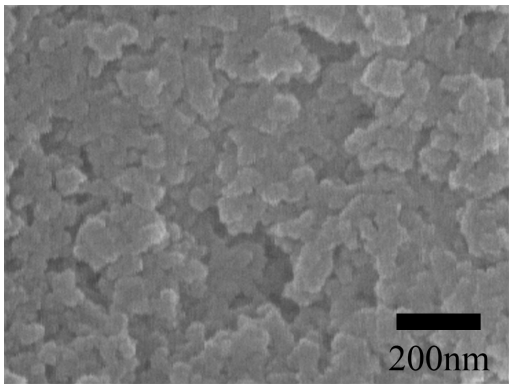


Fig. S4 Shell thickness of the Janus hollow spheres prepared at varied silica precursor content and inset AFM height image of presentative sample at a silica precursor content of 22.6 wt.-%.



a



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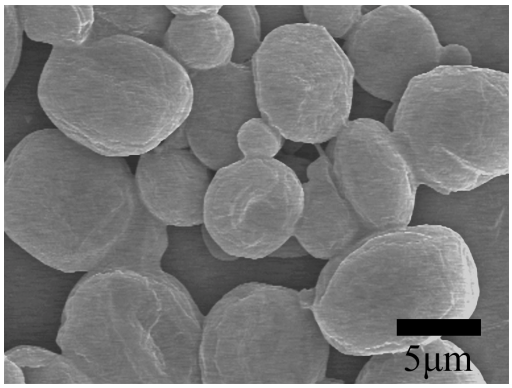
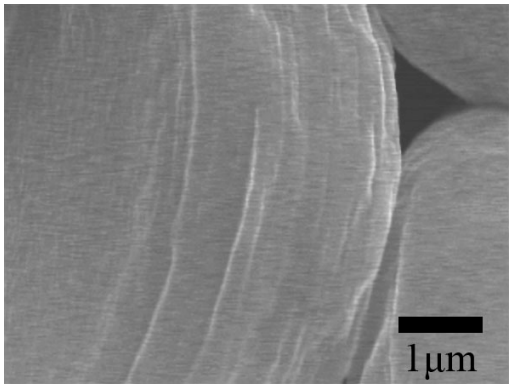


c



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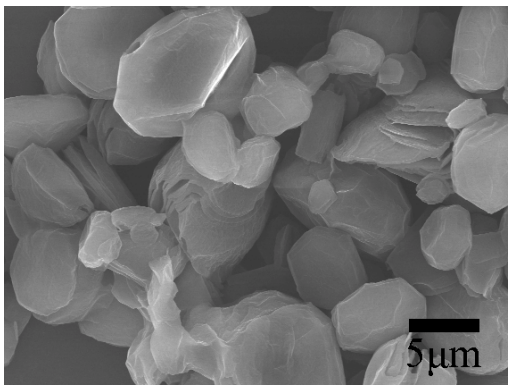

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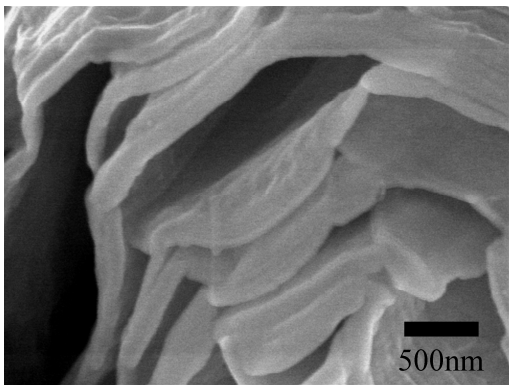

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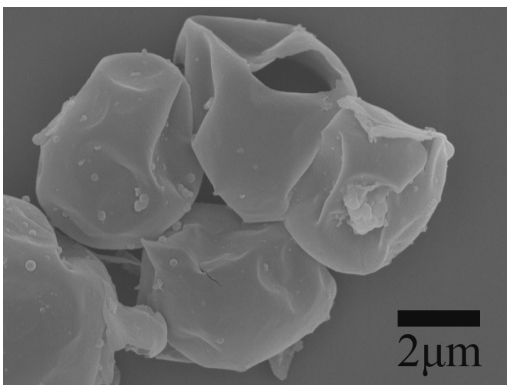

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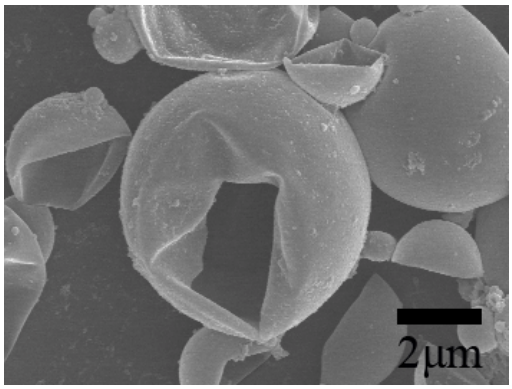
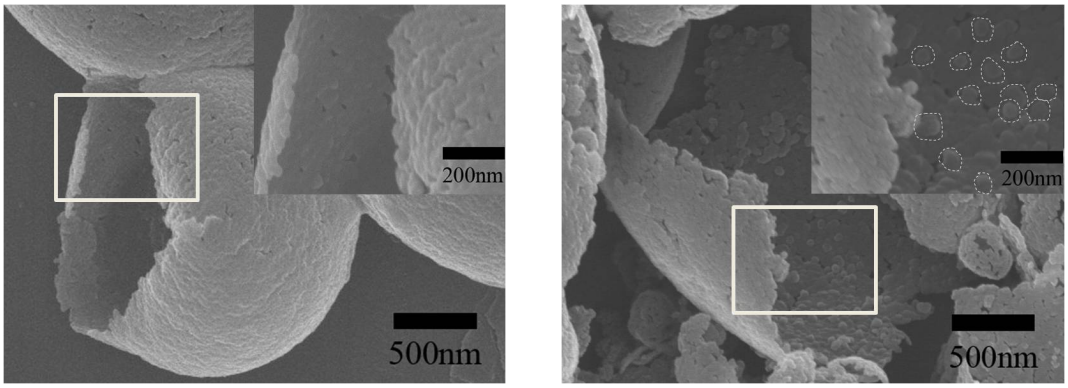


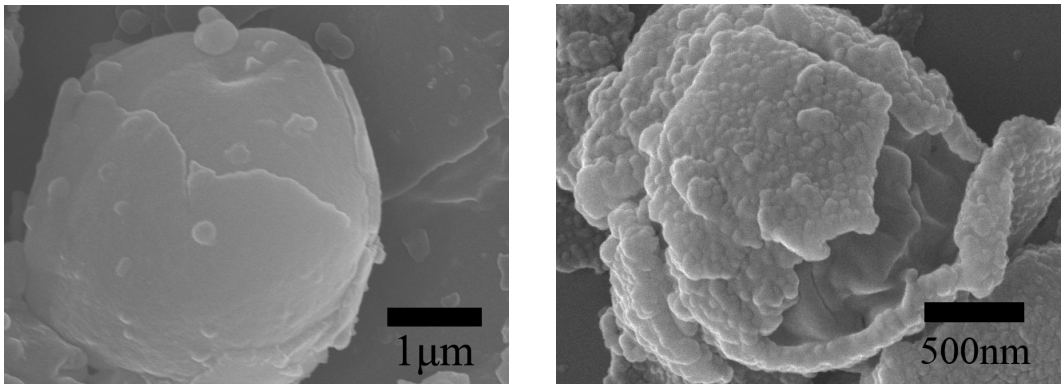
h

Fig. S5 SEM images of the samples synthesized with different precursors. a, b) SEM images of the particles prepared from TEOS/PTES mixture in the absence of APTMS, the paraffin was dissolved; c, d) SEM images of the paraffin/silica particles prepared from TEOS; e, f) SEM images of the silica particles after paraffin was dissolved; g) SEM image of the hollow spheres prepared from APTMS/TEOS mixture; h) SEM image of the Janus hollow spheres prepared from APTMS/PTES mixture.



a b

Fig. S6 a) SEM image of the Janus hollow porous spheres and magnified image (inset) of the marked region within the frame; b) SEM image of the Janus hollow porous spheres with sulfonated PS (sPS) nanoparticles (30 nm) labeled and magnified image (inset) of the marked region within the frame.



a b

Fig. S7 a) SEM image of the Janus hollow sphere with paraffin preferentially absorbed inside the cavity; b) the same sample but with sulfonated PS nanoparticles labeled onto the exterior surface.

Reference:

S1. Z. G. Jin, Y. D. Wang, J. G. Liu, Z. Z. Yang, *Polymer* 2008, **49**, 2903.