Electronic Supplementary Information (ESI)

Surfactant-free synthesis of hollow mesoporous organosilica

nanoparticles with controllable particle sizes and diversified organic

moieties

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Synthesis of monodisperse silica nanoparticles

Silica nanoparticles (SNs) with different diameters of 12, 44, 60, 88, and 170 nm were prepared as the hard templates for the synthesis of hollow organosilica nanoparticles. The SNs were prepared according to the oil-water biphasic method developed in our group with modifications.¹ First, SNs with a diameter of 12 nm were prepared by adding L-arginine (L-Arg, 0.04 g) and TEOS (2.6 g) to deionized water (35 g) and stirring the biphasic mixture at 500 rpm and 60 °C for 1 day.

To synthesize SNs with a diameter of 44 nm, 40 g of deionized water, 0.05 g of L-Arg, and 13 g of TEOS were added to 10 g of the above dispersion of 12 nm SNs, and the mixture was stirred for 2 days under the same conditions. In the same way, 60 nm SNs were obtained by adding 20 g of deionized water, 0.03 g of L-Arg, and 6 g of TEOS to the dispersion of the 44 nm SNs (10 g), followed by stirring for 2 days under the same conditions. SNs with a diameter of 88 nm were also obtained by using the 44 nm SNSs as seeds, but with increasing amounts of reactants (40 g of deionized water, 0.06 g of L-Arg, and 13.2 g of TEOS) added to the dispersion of 44 nm SNs (10 g). To obtain SNs with a diameter of 170 nm, the dispersion of the 88 nm SNs (10 g) was mixed with 40 g of deionized water, 0.05 g of L-Arg, and 13 g of TEOS and then stirred for 2 days under the same conditions. The silica concentrations of the obtained SN dispersions calculated from the TEOS amount used in the procedure are summarized in Table S1.

Particle diameter / nm	Silica concentration / wt%
12	2.01
44	6.27
60	6.54
88	6.94
170	7.05

 Table S1
 Silica concentrations of the synthesized SN templates

(1) Yokoi, T.; Wakabayashi, J.; Otsuka, Y.; Fan, W.; Iwama, M.; Watanabe, R.; Aramaki, K.; Shimojima, A.; Tatsumi, T.; Okubo, T. Mechanism of Formation of Uniform-Sized Silica Nanospheres Catalyzed by Basic Amino Acids. *Chem. Mater.* **2009**, *21*, 3719–3729.



Fig. S1 FE-SEM images of the silica nanoparticles (SNs) used as templates with diameters of (a) 12, (b) 44, (c) 60, (d) 88 and (e) 170 nm.



Fig. S2 Solid-state ²⁹Si MAS NMR spectra of (a) silica/organosilica core/shell nanoparticles (CS-SN44-1.25) and (b) the corresponding hollow organosilica nanoparticle after the core removal (H-SN44-1.25).



Fig. S3 FT-IR spectra of (a) silica nanoparticle templates (SN 44 nm), (b) silica/organosilica core/shell nanoparticles (CS-SN44-1.25), and (c) hollow organosilica nanoparticles (H-SN44-1.25).



Fig. S4 (a) Dynamic light scattering curves of the dispersions of (i) silica nanoparticle templates (SN 44 nm), (ii) silica/organosilica core/shell nanoparticles (CS-SN44-1.25), and (iii) hollow organosilica nanoparticles (H-SN44-1.25). (b) Photograph of H-SN44-1.25 after 2 years since its synthesis.



Fig. S5 FE-SEM images of (a) H- SN88-6.71, (b) H- SN88-6.71' and (c) TEM images of H- SN88-6.71'. The amounts of BTEE used in the syntheses of H- SN88-6.71 and H- SN88-6.71' were 0.88 and 2.3 g, respectively.



Fig. S6 (a) Argon (at -186 °C) and nitrogen (at -196 °C) adsorption–desorption isotherms and (b) their corresponding NLDFT pore size distributions of H-SN88-6.71'.



Fig. S7 FT-IR spectra of (i) silica nanoparticle templates (SN 44 nm), and the corresponding (ii) silica/organosilica core/shell nanoparticles and (iii) hollow organosilica nanoparticles after the core removal when (a) BTEM and (b) BTEB were used as organosilica sources.