Electronic Supplementary Information (ESI)

Synthesis of monodisperse organosilica nanoparticles with hollow interiors and porous shells using silica nanospheres as templates

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Preparation of silica nanospheres (SNSs)

SNSs with different diameters were synthesized by the oil–water biphasic method established by us. First, SNSs ca. 14 nm in diameter were synthesized as seed by stirring a biphasic mixture of deionized water (35 g), L-arginine (Arg, 0.04 g), and TEOS (2.6 g) at 60 °C for 1 day under stirring at 500 rpm. The molar composition of the reactants was $160H_2O$: 0.02Arg: 1TEOS. Then, to synthesize SNSs ca. 40 nm in diameter, 40 g of deionized water, 0.05 g of Arg, and 13 g of TEOS ($160H_2O$: 0.02Arg: 4.5TEOS) were added to 10 g of the above dispersion of 14 nm SNSs, and the mixture was stirred for 2 days under the same conditions. In the same way, SNSs ca. 60 nm in diameter were obtained by adding 20 g of deionized water, 0.03 g of Arg, and 6 g of TEOS ($160H_2O$: 0.02Arg: 4.5TEOS) to the dispersion of the 40 nm SNSs (10 g) followed by stirring for 2 days under the same conditions.

Characterization

Field-emissoin scanning electron microscopy (FE-SEM) images were obtained with a Hitachi S-900 at an accelerating voltage of 6 kV. Samples for SEM observation were prepared by spin-coating of the dispersions of nanoparticles onto silicon substrates followed by sputter deposition of Pt for 15 s in an argon atmosphere with a Hitachi E-1030 ion sputter. Transmission electron microscopy (TEM) observations of nanoparticles on carbon-coated copper grids were carried out on JEOL JEM 2000EXII operated at 200 kV. Solid-state ^{29}Si MAS NMR spectra were obtained on a Chemagnetics CMS-300 spectrometer at 59.7 MHz with a pulse width of 2.0 μs and a recycle delay of 80 s. Nitrogen adsorption and desorption isotherms were obtained at 77 K using Autosorb-iQ2-MP (Quantachrome Instruments). Before measurements, samples were degassed at 150 °C for 6 h. The Brunauer–Emmett–Teller (BET) specific surface areas of samples were calculated from adsorption data at a relative pressure range of 0.05–0.2. The total pore volumes were evaluated from the adsorbed amount of nitrogen at a relative pressure of 0.99. The pore size distributions were obtained with the adsorption branches of the isotherms by the Barrett–Joyner–Halenda (BJH) method. Powder samples for solid-state NMR and nitrogen sorption analyses were obtained by evaporation of solvents from the dispersions at 60 °C under vacuum. Fourier transform infrared (FT-IR) spectra were obtained on a JASCO FT/IR-6100 spectrometer with a nominal resolution of 0.5 cm^{-1} by the KBr pellet technique. Dynamic light scattering and Zeta potential measurements were performed with a Malvern Zetasizer Nano ZS90 instrument at 25 °C. The zeta potentials of SNSs were calculated from the electrophoretic mobility using the Helmholtz-Smoluchowski equation.

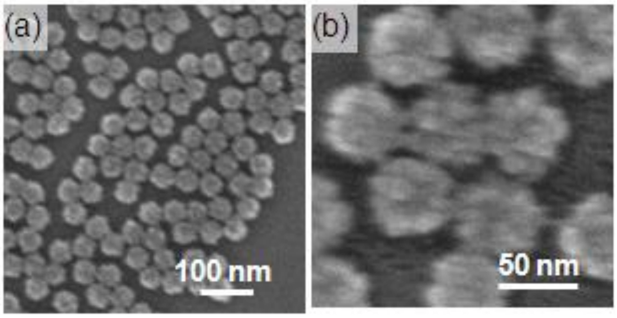

Fig. S1 FE-SEM images of the hollow organosilica nanoparticles after sonication at 42 Hz, 130 W for 30 min using Branson ultrasonic bath 3510J.

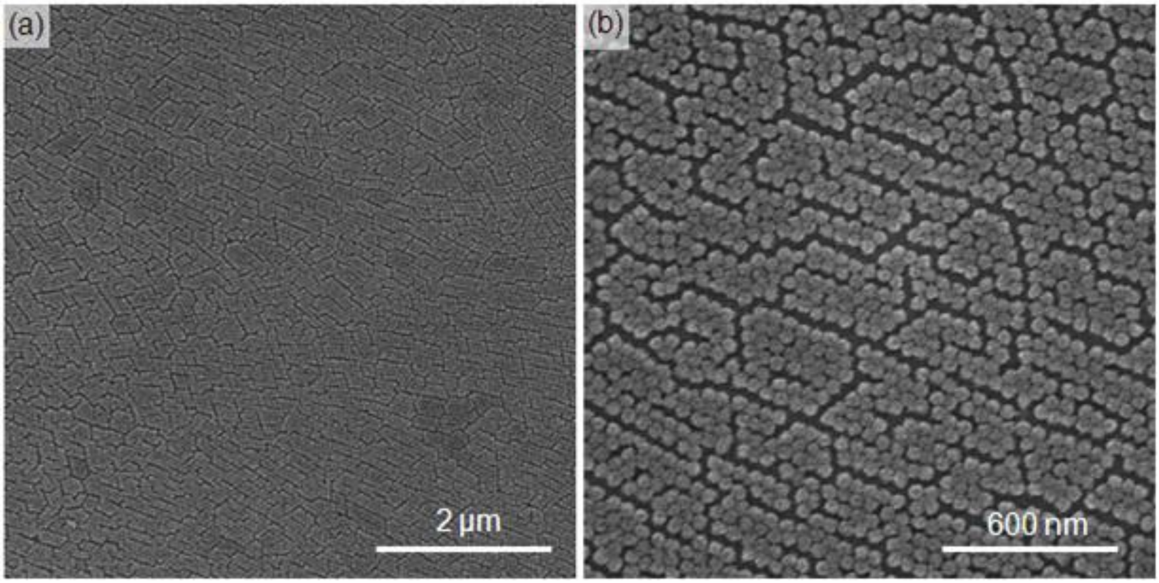

Fig. S2 FE-SEM images of the monolayer of hollow organosilica nanoparticles on a silicon substrate. A small amount of arginie (0.1wt%) was added to the dispersion before spin-coating at 1500 rpm. We have recently reported that ordered assembly of silica nanoparticles can be achieved by adding basic amino acid (see J. Wang, A. Sugawara-Narutaki, M. Fukao, T. Yokoi, A. Shimojima and T. Okubo, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1538).

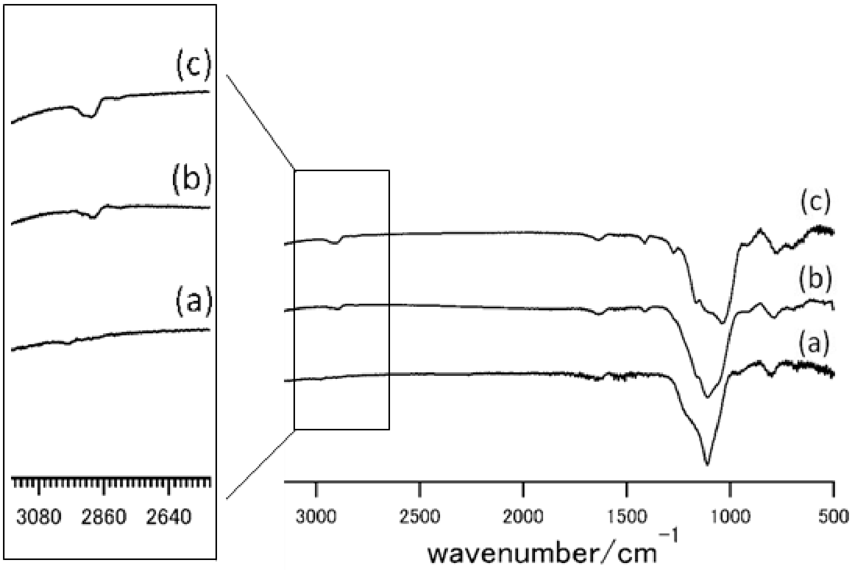

Fig. S3 FT-IR spectra of (a) silica nanospheres (SNSs), (b) core-shell nanoparticles and (c) hollow organosilica nanoparticles. The spectra of the C-H stretching region before and after the core removal are similar, confirming that no cleavage of the Si-$(CH_2)_2$-Si linkages proceeded to form Si-CH_3 groups.

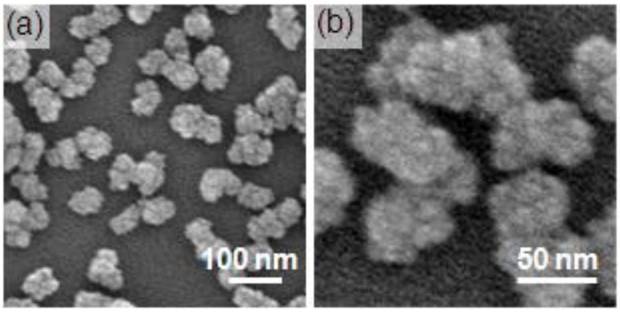

Fig. S4 FE-SEM images of organosilica nanoparticles prepared in the absence of SNSs. The mixture of BTEE, H_2O and Arg (molar ratio of 0.5:160:0.02) was stirred at 60 °C for 20 days under stirring at 500 rpm.

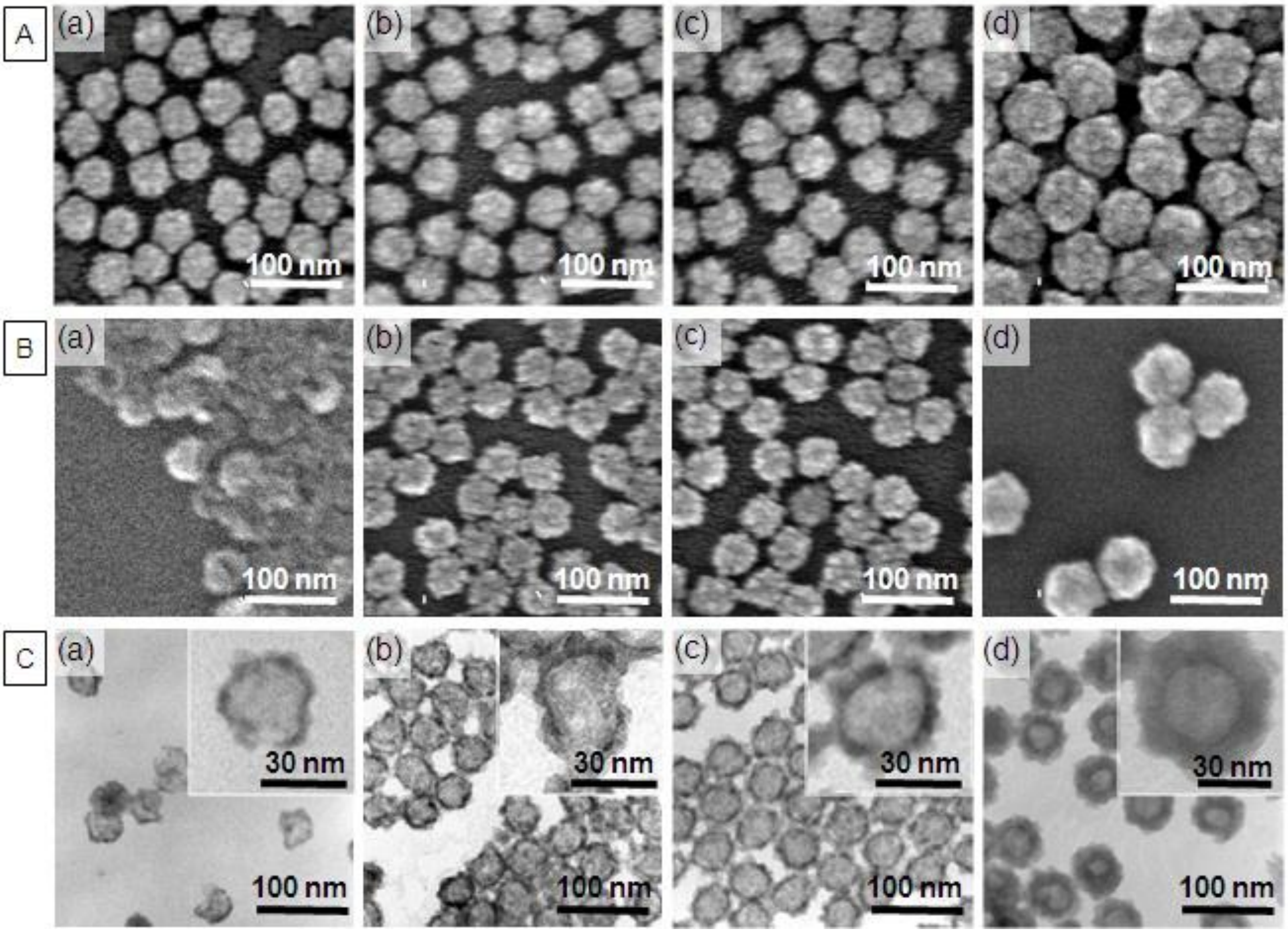

Fig. S5 (A) FE-SEM images of core-shell nanoparticles, (B) FE-SEM and (C) TEM images of the hollow organosilica nanoparticles prepred by varying the amount of BTEE ((a) 0.29 g, (b) 0.6 g, (c) 0.60 g, and (d) 2.2 g) under otherwise identical conditions.

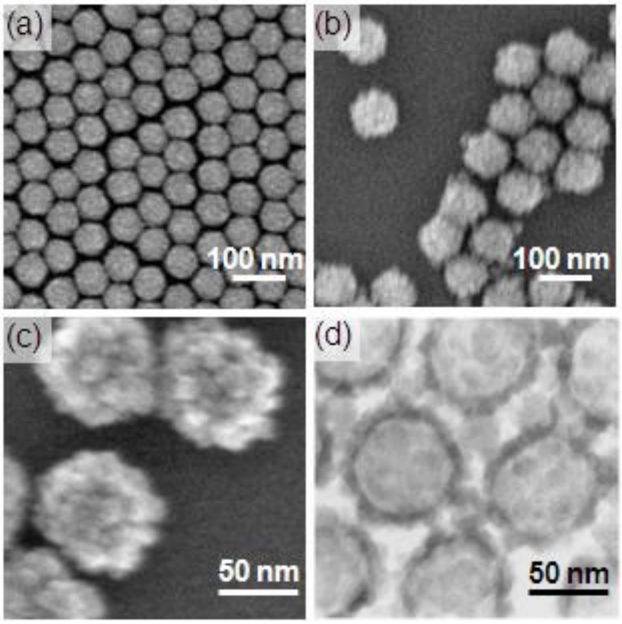

Fig. S6 FE-SEM images of (a) silica nanospheres (SNSs) ca. 60 nm in diameter, (b) SNS core-organosilica shell nanoparticles, and (c) hollow organosilica nanoparticles. (d) TEM image of hollow organosilica nanoparticles. To the dispersion of SNSs ca. 60 nm in diameter (ca. 6.5 wt% SiO_2, 5 mL), deionized water (20 mL), arginine (0.02 g), and BTEE (0.9 g) were added, and the biphasic mixture was stirred at 60 °C until the upper oil (BTEE) phase disappeared. Then, the SNS core was removed by adjusting the pH to 13, followed by dialysis against deionized water.

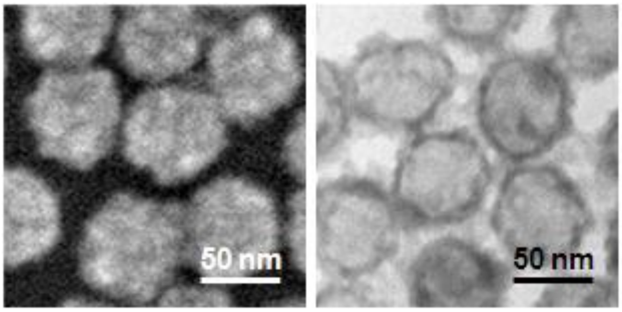

Fig. S7 FE-SEM (left) and TEM (right) images of hollow nanoparticles of phenylene-bridged silsesquioxane. To the dispersion of SNSs ca. 50 nm in diameter (ca. 6.3 wt% SiO_2, 5 mL), water (20 mL), 0.1 N NaOH solution (0. 2 g), and 1,2-bis(triethoxysilyl)benzene (BTEB, 0.33 g) were added, and the biphasic mixture was stirred at 60 °C until the upper oil (BTEB) phase disappeared. Then the core SNS was removed at pH 13 followed by dialysis against deionize water.

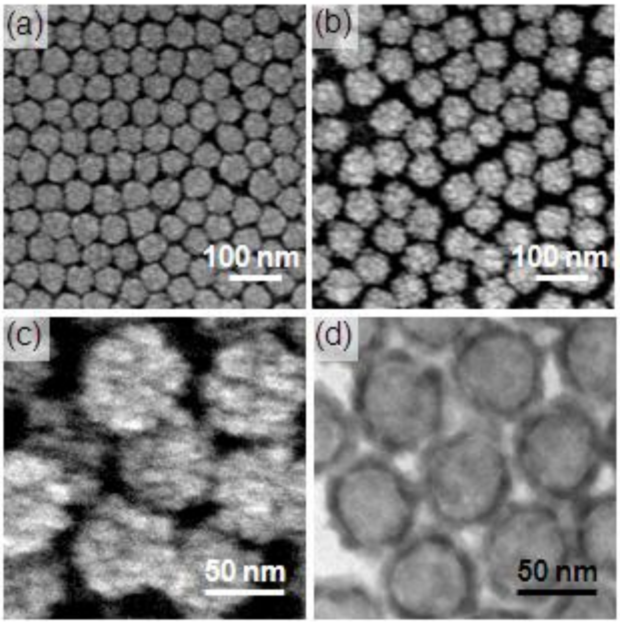

Fig. S8 FE-SEM images of (a) silica nanospheres (SNSs) ca. 50 nm in diameter prepared by the reaction of TEOS in an aqueous NaOH solution at pH~10.5, (b) core-shell nanoparticles, (c) hollow organosilica nanoparticles. (d) TEM image of hollow organosilica nanoparticles. The SNS was synthesized by the similar procedure to that described above except that arginine was replaced with NaOH. Seed SNSs ca. 15 nm in diameter were synthesized by stirring a biphasic mixture of deionized water (35 g), 0.1 N NaOH (0.3g), and TEOS (2.6 g) at 60 °C for 1 day under stirring at 500 rpm. Then, deionized water (40 g), 0.1 N NaOH (0.4 g), and TEOS (13 g) were added, and the mixture was stirred at 60 °C for 2 days. To the dispersion of SNSs ca. 50 nm (ca. 6.3 wt% SiO_2, 5 mL), additional water (20 mL), 0.1 N NaOH solution (0. 2 g), and BTEE (0.6 g) were added, and the biphasic mixture was stirred at 60 °C until the upper oil (BTEE) phase disappeared. Finally, the SNS core was removed by adjusting the pH to 13, followed by dialysis against deionized water.

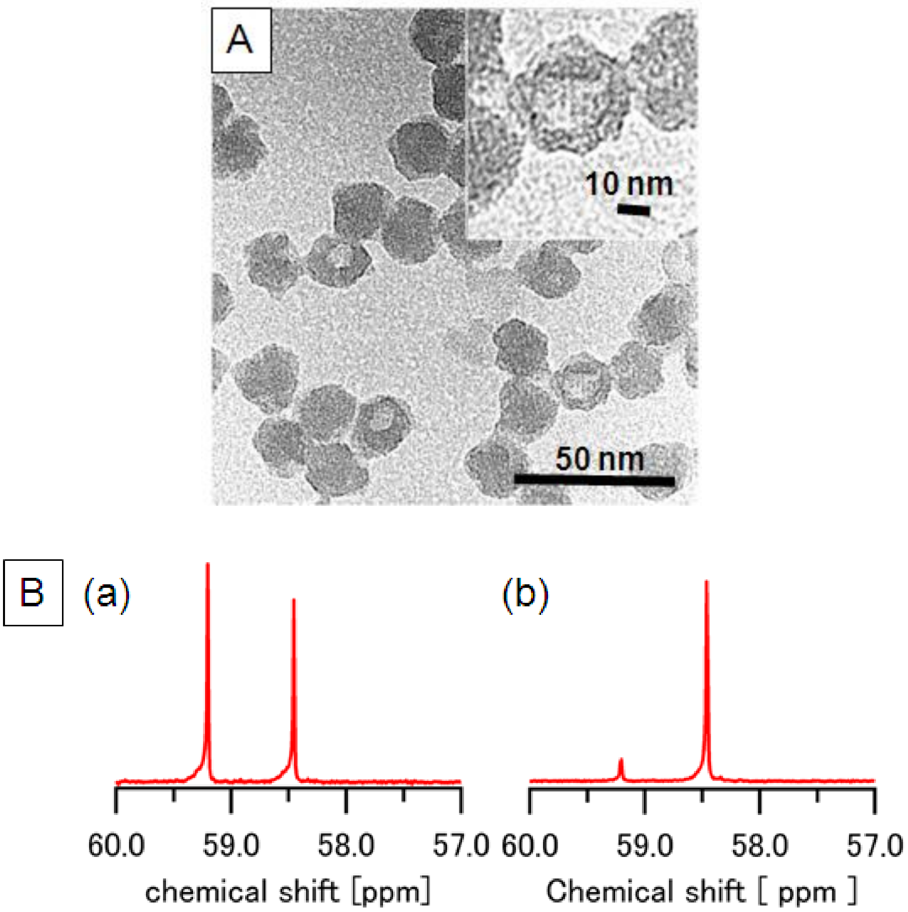

Fig. S9 (A) TEM images of nanoparticles synthesized by one-step method. The biphasic mixture of BTEE (0.9 g), TEOS (2.1 g), H_2O (29 g), and Arg (0.03 g) was stirred (500 rpm) at 60 °C for 10 days, followed by stirring at pH 13 and dialysis against deionized water. (B) Liquid-state ^{13}C NMR spectra of the oil phase of the biphasic mixtures: (a) before and (b) after 1 day of reaction. The signals at 58.45 ppm and 59.25 ppm correspond to $-CH_2Si(O\underline{\mathbf{C}}H_2CH_3)_3$ and $Si(O\underline{\mathbf{C}}H_2CH_3)_4$, respectively.