Electronic Supplementary Information

Fabrication of Colloidal Crystals Composed of Pore-Expanded Mesoporous Silica Nanoparticles Prepared by a Controlled Growth Method

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Preparation of pore expanded colloidal mesostructured silica nanoparticles.

All colloidal solutions of TIPB-x-as (x=0, 0.4, 1, and 2) were clouded because of the presence of surfactant micelles and TIPB emulsions, though there are no precipitations (Figure S1, ESI). The hydrodynamic diameter distributions calculated from DLS showed only one peak at ca. 110 nm for all the samples (Figure S2, ESI). The TEM images of TIPB-x-as (x = 0, 0.4, 1, and 2) showed that the nanoparticles had uniform spherical shape (Figure S3, ESI). Moreover, the mean diameters of the nanoparticles were 92 nm, 96 nm, 98 nm, and 97 nm, respectively. These indicate that prepared nanoparticles were stably dispersed as primary nanoparticles. Furthermore, the standard deviations of the diameters were calculated to be 5.6 nm, 5.7 nm, 8.7 nm, and 8.7 nm for TIPB-x-as (x=0, 0.4, 1, and 2), respectively. These standard deviations were almost same as that of TIPB-0-seed (Figure S4, ESI).

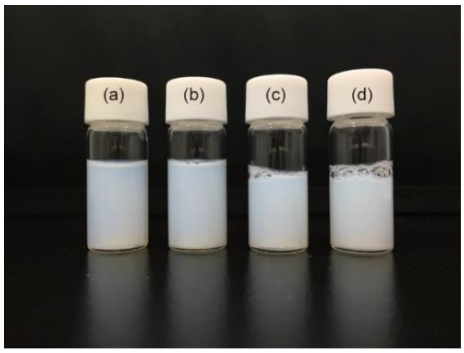

Figure S1 Appearances of TIPB-x-as ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

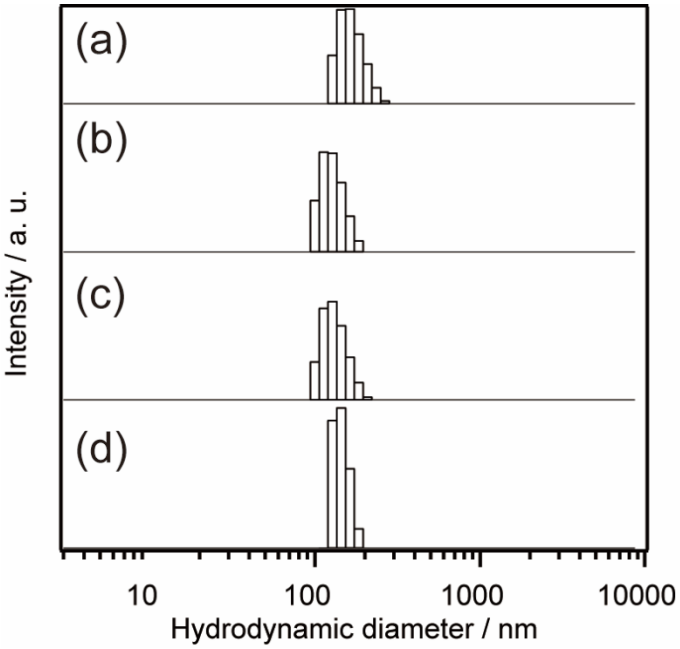

Figure S2 Hydrodynamic diameter distributions of TIPB-x-as ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

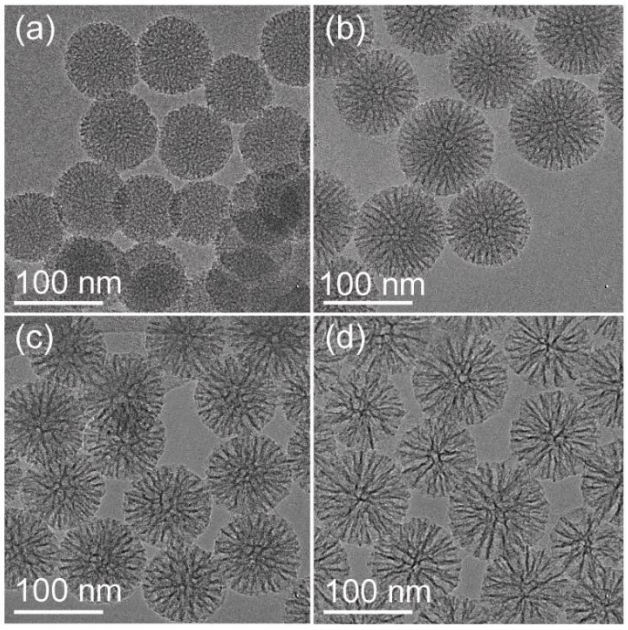

Figure S3 TEM images of TIPB-x-as ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

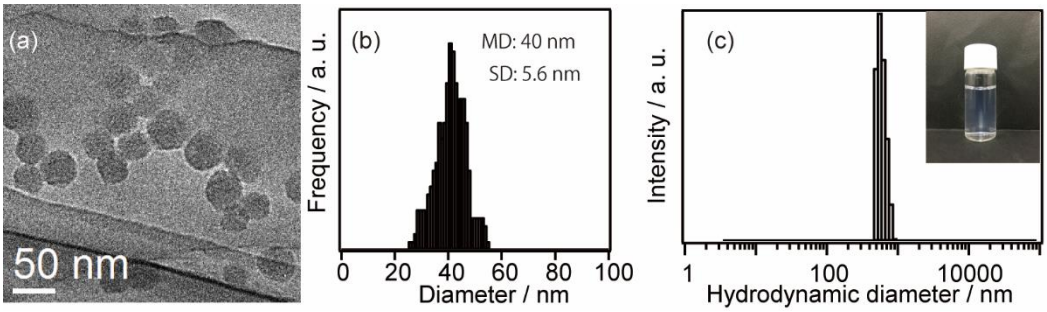

Figure S4 (a) TEM image, (b) particle size distribution calculated by TEM images, and (c) hydrodynamic diameter distribution of TIPB-0-seed.

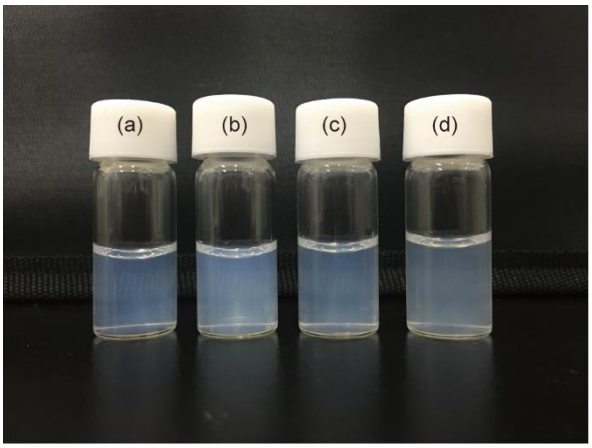

Figure S5 Appearances of TIPB-x-DI ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

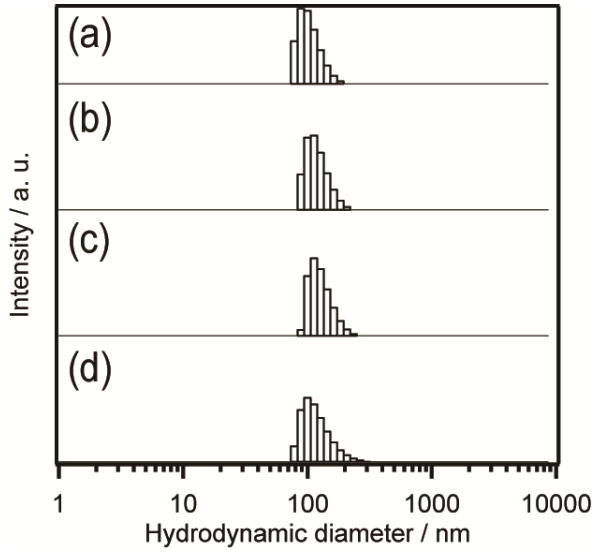

Figure S6 Hydrodynamic diameter distributions of TIPB-x-DI ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

Preparation of pore-expanded mesostructured silica nanoparticles prepared by varying the number of times of seed growth. (Experimental and description on Table S1 and Figures S7-S9)

Experimental

Seed nanoparticles were prepared by the following process. TEA (0.7 g) and 3.33 g of C_{16}TMABr were dissolved in 400 mL of deionized water in a round-bottomed flask (500 mL). The mixture was stirred for 1 h at 80 °C by using a magnetic stirrer with a football-typed stirring bar. Then, 0.78 mL of TEOS was added into the solution with stirring at 900 rpm and 80 °C. The obtained colloidal solution was cooled to room temperature slowly. The colloidal solution was denoted as TIPB-0-seed. The seed nanoparticles were grown by the following seed-growth method. TIPB-0-seed (50 mL) was added into a round-bottomed flask, and TIPB (0.109 mL, 0.272 mL, or 0.544 mL) was added in the solution. Then, 0.29 mL of TPOS was added. The colloidal solution was stirred for 2 d at room temperature. The process of the addition of TPOS was repeated up to 4 times for the controlled particle growth. The samples denoted as TIPB-x-z-as (x means the amount of TIPB: 0.4, 1, and 2, z means the number of times of seed growth)

Description on Table S1 and Figures S7-S9.

The particle sizes of TIPB-x-z-as estimated by TEM images and their standard deviations were summarized in Table S1. The particles sizes did not depend on the amount of TIPB. Furthermore, the standard deviations of all the samples were almost same as that of TIPB-0-as. These results indicate that the particles sizes and pore sizes of MSNs can be tuned independently with retaining their monodispersity. Unfortunately, only small differences of standard deviations were observed when large amounts of TIPB were added. Such a slight difference of standard deviation may be due to the Ostwald ripening or generation of spontaneous nuclei.

Table S1 Particles size of mesostructured nanoparticles prepared under different seed growth times.

sample	Added number of times of TPOS addition			
	1	2	3	4
TIPB-0.4-as	MD: 66 nm SD: 4.8 nm	MD: 78 nm SD: 5.0 nm	MD: 85 nm SD: 5.8 nm	MD: 96 nm SD: 5.7 nm
TIPB-1-as	MD: 65 nm SD: 6.2 nm	MD: 82 nm SD: 6.5 nm	MD: 91 nm SD: 6.8 nm	MD: 98 nm SD: 8.7 nm
TIPB-2-as	MD: 63 nm SD: 5.6 nm	MD: 81 nm SD: 7.4 nm	MD: 92 nm SD: 8.2 nm	MD: 97 nm SD: 8.7 nm

MD: Mean Diameter

SD: Standard Deviation

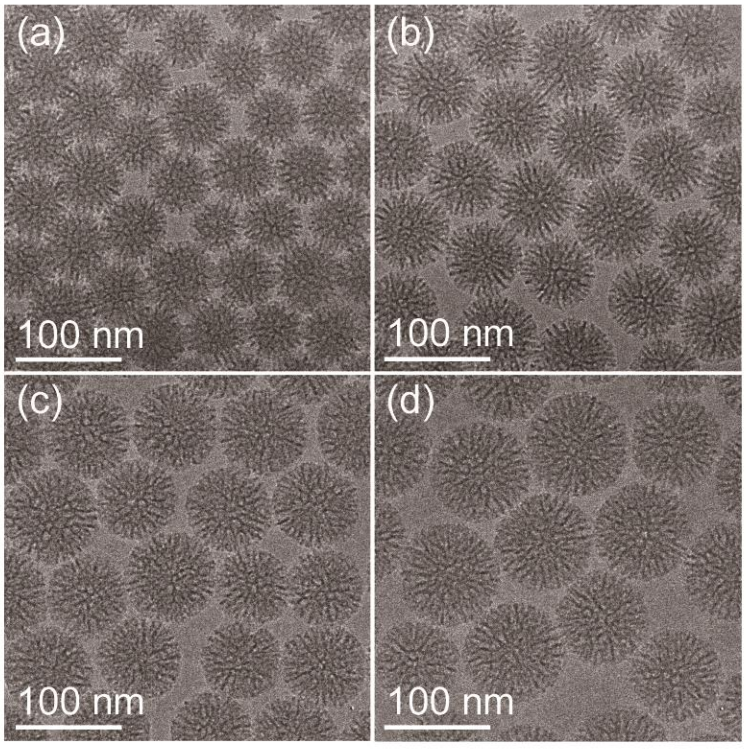

Figure S7 TEM images of TIPB-0.4-z-as, prepared by varying the number of times of seed growth (z), ((a) z = 1, (b) z = 2, (c) z = 3, and (d) z = 4).

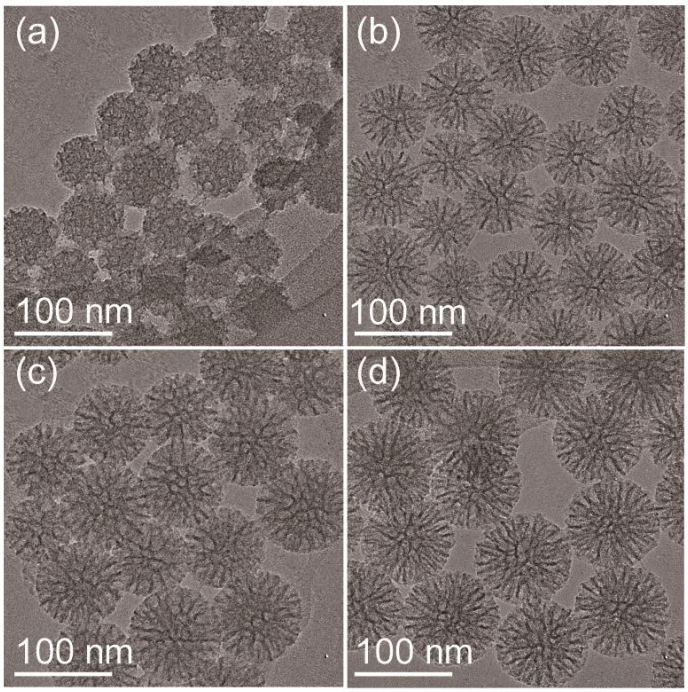

Figure S8 TEM images of TIPB-1-z-as, prepared by varying the number of times of seed growth (z), ((a) z = 1, (b) z = 2, (c) z = 3, and (d) z = 4).

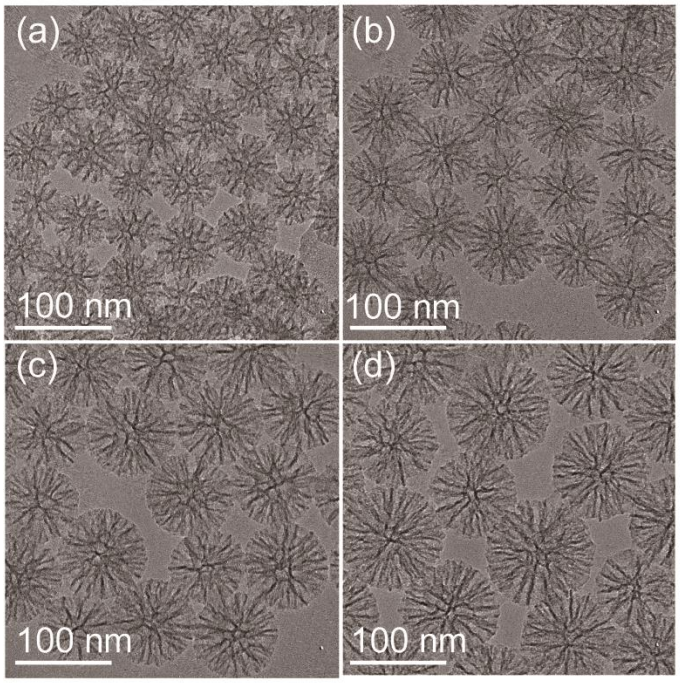

Figure S9 TEM images of TIPB-2-z-as, prepared by varying the number of times of seed growth (z), ((a) z = 1, (b) z = 2, (c) z = 3, and (d) z = 4).

Preparation of pore expanded colloidal mesostructured silica nanoparticles *as a seed* by the addition of pore expanding agents (Experimental and description on Figures S10 and S11).

Experimental

Seed nanoparticles with expanded pore size were prepared for comparison by the following processes. TEA (0.7 g) and 3.33 g of C_{16}TMABr were dissolved in 400 mL of deionized water in a 500 mL of a round-bottomed flask. TIPB (0.87 mL, 2.18 mL, or 4.35 mL) was added in the solution, and the mixture was stirred for 1 h at 80 °C by using a magnetic stirrer. Then, 0.78 mL of TEOS was added in the solution with stirring at 900 rpm and 80 °C for 1 h. The obtained colloidal solutions were cooled to room temperature slowly. The molar ratio of the solution is Si:C_{16}TMABr:TEA:H_2O:TIPB = 1:2.3:1.8:5600:3.2x. The colloidal solutions were denoted as TIPB-x-seed (x means the additive amount of TIPB: 0, 0.4, 1, or 2). The core nanoparticles (TIPB-0.4-seed) were grown by the seed-growth method without adding extra TIPB.

Description on Figures S10 and S11.

Although TIPB-*x*-seed (*x*=0, 0.4) were nearly transparent in the visible light region and no precipitates were observed, TIPB-*x*-seed (*x*=1, 2) get slightly clouded. The hydrodynamic diameter distributions of TIPB-*x*-seed (*x*=0 and 0.4) calculated from DLS showed only one peak at ca. 86 nm and ca. 106 nm, respectively (Figure S10, ESI). While the hydrodynamic diameters of TIPB-*x*-seed (*x*=1 and 2) could not be obtained correctly owing to their aggregation. The TEM images of TIPB-*x*-seed (x=0, 0.4, 1, and 2) showed that the mean diameters of the nanoparticles were 40 nm, 79 nm, 54 nm, and 62 nm, respectively (Figure S11, ESI). In addition, TEM images showed that TIPB-*x*-seed (x=0 and 0.4) had a mesoscale periodicity of ca. 4 nm and ca. 8 nm, respectively, which means that TIPB acted as pore expanding agents. These indicate that prepared TIPB-*x*-seed (x=0 and 0.4) were stably dispersed as primary nanoparticles. Furthermore, the standard deviations of the diameters were calculated to be 5.6 nm, 14.1 nm, 7.9 nm, and 9.3 nm for TIPB-*x*-seed (x=0, 0.4, 1, and 2), respectively, by the TEM images. Although TIPB-1-seed and TIPB-2-seed seem to be monodisperse, TIPB-x-seed (x=1 and 2) had a lot of strongly aggregated nanoparticles and irregular shaped silica. Therefore, the addition of pore expanding agents in the seed formation period should not be suitable for obtaining monodispersed MSNs. In fact, MSNs grown by using TIPB-0.4-seed as seed nanoparticles cannot form colloidal crystals because they have insufficient monodispersity to form an ordered structure.

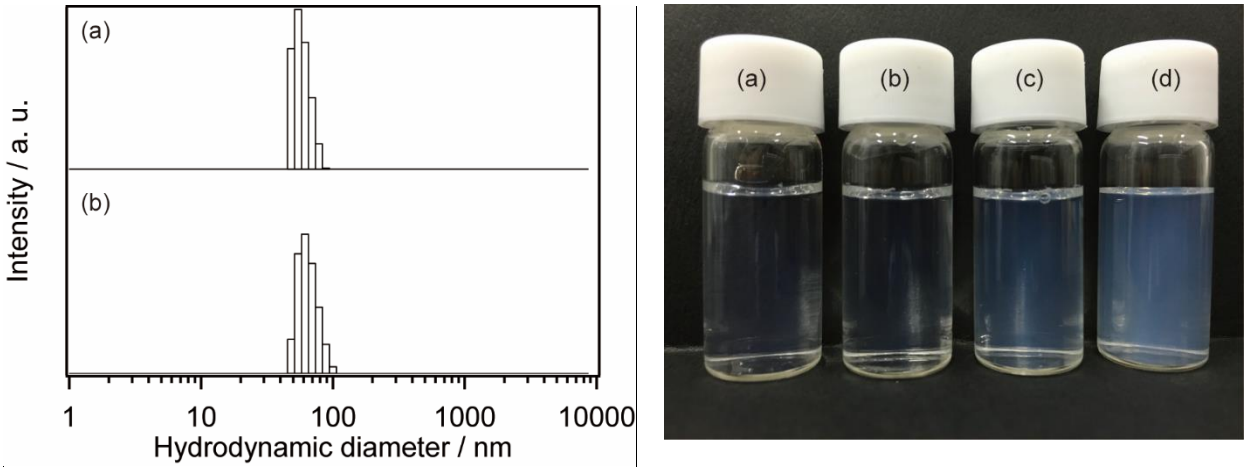

Figure S10 Hydrodynamic diameters and appearances of TIPB-x-seed ((a) x=0 and (b) x=0.4 (c) x =1, and (d) x =2).

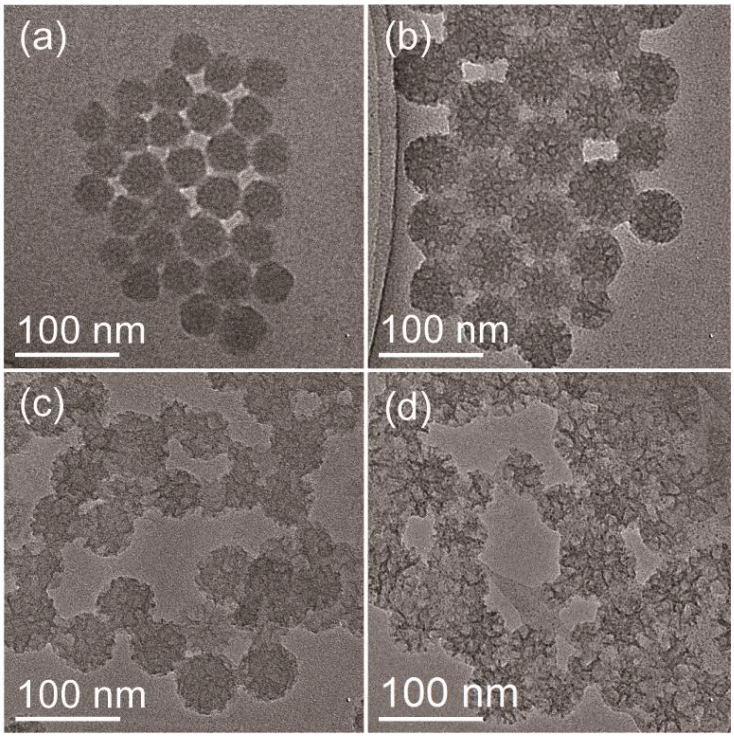

Figure S11 TEM images of TIPB-x-seed ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

Removal of surfactants

The nitrogen content of TIPB-x-Crystals was under the detection limit of CHN. The TG curve of TIPB-x-Crystals displayed two weight losses at 25-150 °C and higher than 150 °C, which corresponded to the desorption of water and gradual dehydration of silanol groups, respectively. These results suggested that almost all surfactants were removed during dialysis.

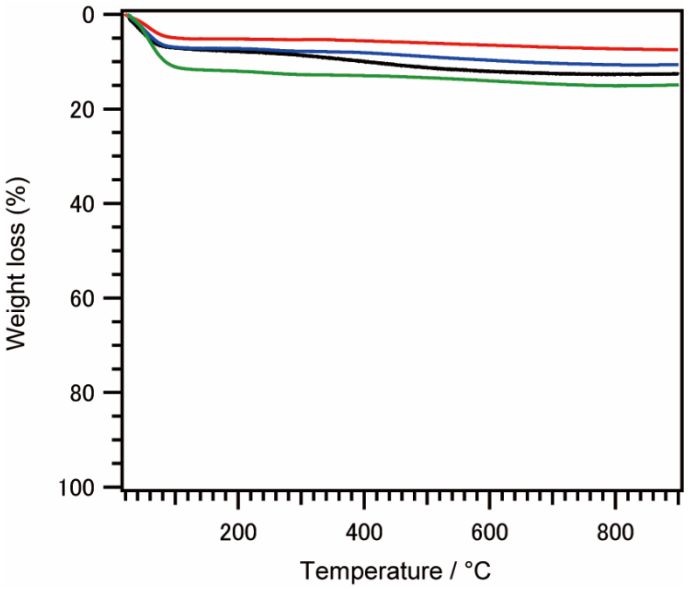

Figure S12 TG curves of TIPB-x-Crystals ((red) x = 0, (black) x = 0.4, (blue) x = 1, and (green) x = 2).

Table S2 Carbon and nitrogen contents of TIPB-x-Crystals.

Sample	C/ wt%	N/ wt%
TIPB-0-Crystal	0.7	0.1
TIPB-0.4-Crystal	0.5	0.1
TIPB-1-Crystal	0.3	0.03
TIPB-2-Crystal	0.4	0.03

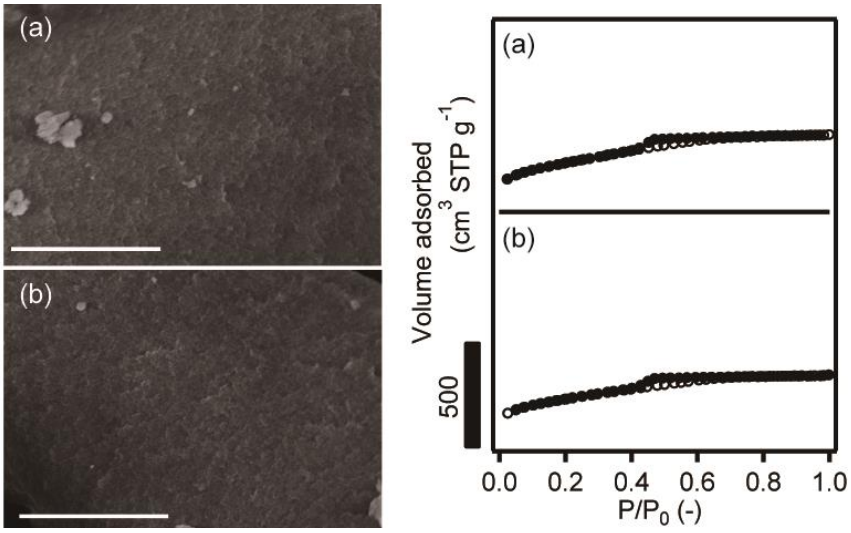

Figure S13 SEM images of TIPB-x-Crystals with low magnification and nitrogen adsorption desorption isotherms ((a) x= 1, (b) x=2). Scale bar indicates 1 μm.

Explanation of Equation S1.

We hypothesized that the ideal neck size is nearly same as the diameter of inscribed sphere in the three coordination site. The diameter (R') can be calculated by using the diameter of component nanoparticle (R).

Equation S1: $R' = 0.155 \times R$

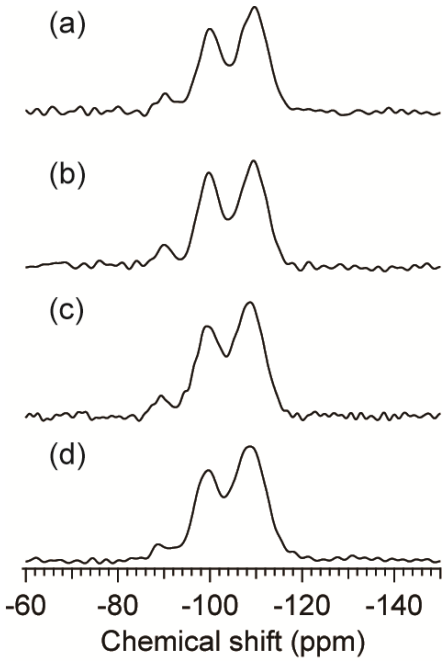

Figure S14 NMR spectra of TIPB-x-Crystals ((a) x=0, (b) x=0.4, (c) x=1, and (d) x=2).

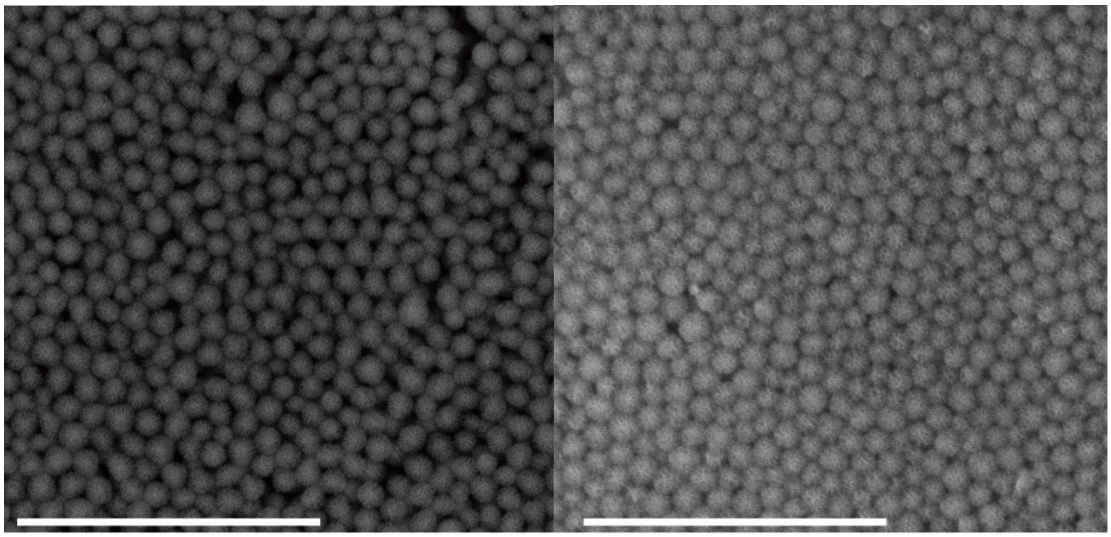

Figure S15 SEM images of TIPB-x-DI drying on silicon substrates without any pulverization process ((left) TIPB-1-DI and (right) TIPB-2-DI). Scale bar indicates 1 μm.

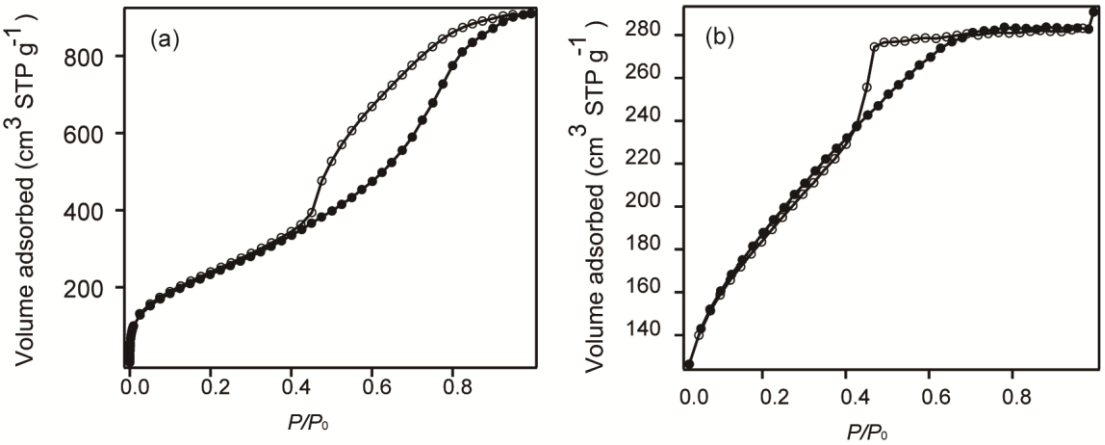

Figure S16 N_2 adsorption desorption isotherms of TIPB-x-DI dried without any pulverization process ((a) TIPB-1-DI and (b) TIPB-2-DI).

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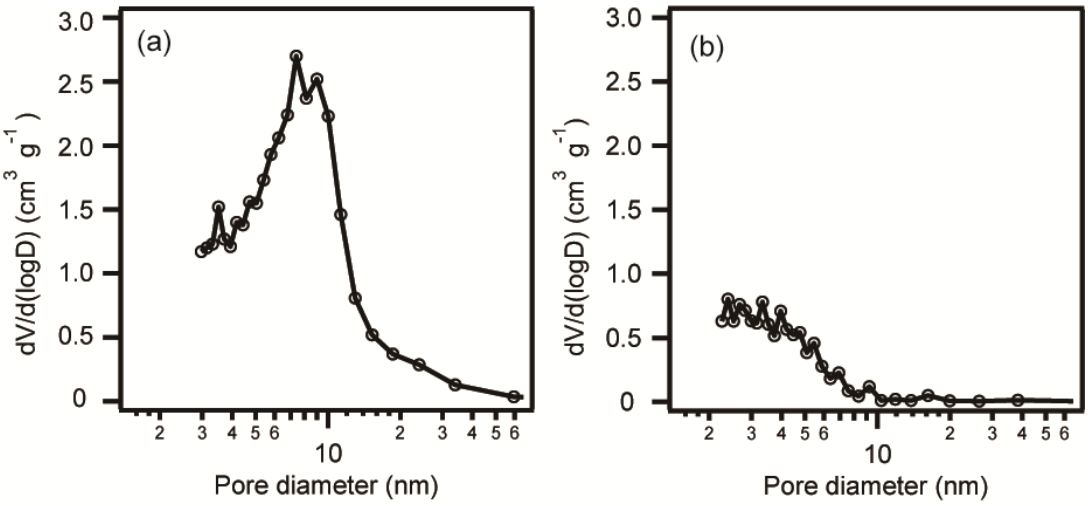

Figure S17 Pore size distributions of TIPB-x-DI dried without any pulverization process ((a) TIPB-1-DI and (b) TIPB-2-DI).