Electronic Supplementary Information

Preparation of Periodic Mesoporous Organosilica with Large Mesopores Using Silica Colloidal Crystals as Templates

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Contents

Additional experimental details

Hydrolysis behavior of BTEE1

The mixture of BTEE1 (150 μL), EtOH (71.8 μL), H_2O (84.6 μL), and 0.1 M HCl (4.10 μL) (molar ratio of 1 BTEE1:3 EtOH:12 H_2O:0.001 HCl) was stirred at room temperature for 15 min. For ^{1}H NMR and ^{29}Si NMR measurements, 200 μL of this mixture, 400 μL of THF-d8, 50 μL of TMS, and a small amount of $Cr(acac)_3$ (acac: acetylacetonate) were mixed in an NMR sample tube (5 mm φ). The measurement was started from ^{1}H NMR (accumulation number of 16 with a recycle delay of 5 s), followed by ^{29}Si NMR (accumulation number of 64 with a recycle delay of 10 s).

Treatment of SCC43-organosiloxane composite with NaOH aq. for varied durations.

Five sample bottles (volume 15 mL) were put on a hot plate placed within a filtration bell. SCC43 was added to each sample bottle and vacuum dried at 120 °C for 3 h. BTEE1 was partially hydrolyzed by stirring a mixture of BTEE1 2000 μL, EtOH 957 μL, H_2O 1128 μL, and 0.1 M HCl 54.7 μL (molar ratio of 1 BTEE1:3 EtOH:12 H_2O:0.001 HCl) at room temperature for 15 min. This hydrolyzed BTEE1 solution (190 μL) was added to each sample bottle containing dried SCC43 (1.00 g). After the evacuation at room temperature for 3 min, the same amount of hydrolyzed BTEE1 solution was added and vacuum dried for 1 h. The hydrolyzed solution of BTEE1 was prepared again and the same procedures for filling and drying were repeated. Subsequently, 13.3 mL of 1 M NaOH aq. (molar ratio of NaOH to SiO_2 in the template was 0.8:1.0) was added and the mixtures were heated at 80 °C for *y* hour(s) (*y* = 1, 8, 24, 96, and 167 h) in an oven. The samples were recovered by filtration and white solids were finally obtained.

Preparation of PMO43_BTEE1 (extended hydrolysis time of BTEE1)

BTEE1 was hydrolyzed by stirring a mixture of BTEE1 (380 μL), EtOH (182 μL), pure water (214 μL), and 0.1 M HCl (10.4 μL) (molar ratio of 1 BTEE1:3 EtOH:12 H_2O:0.001 HCl) at room temperature for 4 h. 197 μL (1/4 of the total amount) of this hydrolyzed solution was added to the dried SCC43 under a nitrogen atmosphere and was infiltrated and vacuum dried in the voids of the colloidal crystals for 3 min at room temperature. Then 197 μL of the same hydrolyzed solution was subsequently infiltrated and vacuum dried for 1 h. The same procedures for filling and drying were repeated using the rest of the hydrolyzed solution of BTEE1 (5 h after starting the hydrolysis reaction). Other procedures and conditions were same as those used for preparing PMO43_BTEE1.

Calculation of residual ratio of silica and organosiloxane

The mass ratio of organosiloxane and silica is calculated to be organosiloxane:silica = 1.00:1.01 on the basis of the integration ratio of T:Q = 1.00:1.11.
(Assuming that all added BTEE and Q species derived from silica colloidal crystals were hydrolyzed and polycondensed)

●Organosiloxane

・ Mass of organosiloxane in the obtained sample (0.3408 g)

$$0.3408\ g \times \frac{1.00}{1.00 + 1.01} = 0.1696\ g$$

・ Residual ratio of Si species of organosiloxane

$$\frac{0.1696\ g \times \dfrac{354.59}{132.22}}{0.566\ g\ (Added\ BTEE1)} \times 100 = 80\ \%$$

●Silica

・ Mass of the silica in the obtained sample (0.3408 g)

$$0.3408\ g \times \frac{1.01}{1.00 + 1.01} = 0.1712\ g$$

・ Residual ratio of Si species of silica

$$\frac{0.1712\ g}{1.5359\ g\ (Added\ Silica\ colloidal\ crystals)} \times 100 = 11.1\ \%$$

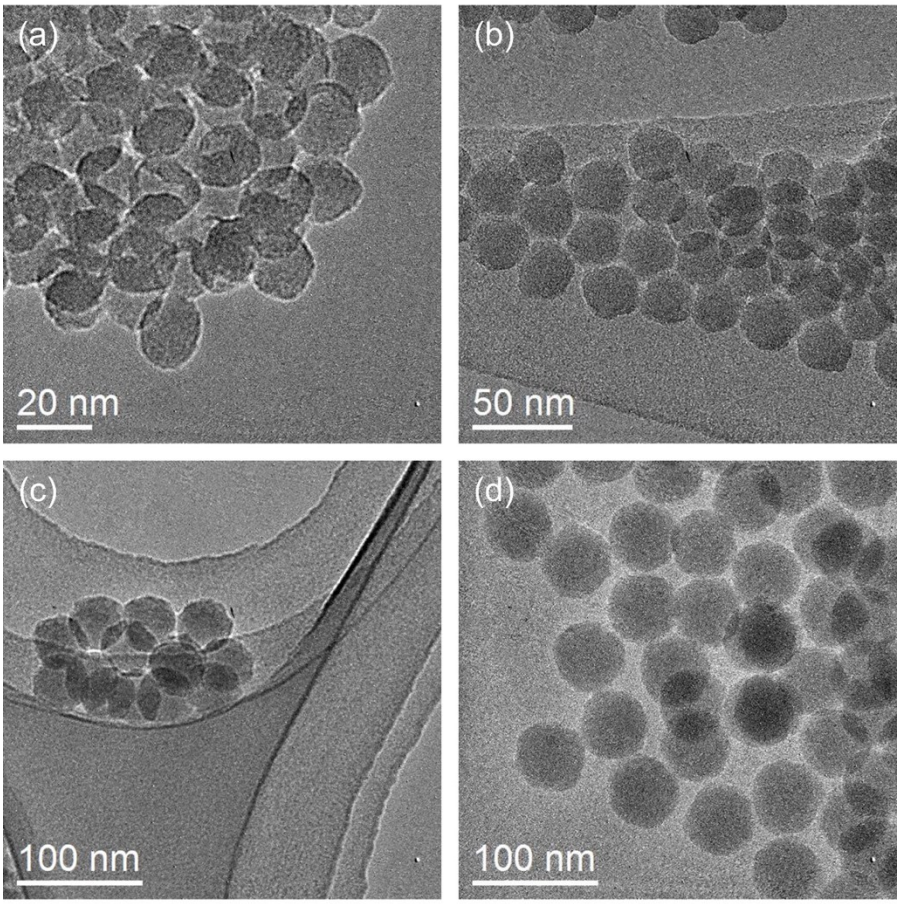

Figure S1 TEM images of silica nanospheres with average diameters of (a) 18 nm, (b) 28 nm, (c) 43 nm, and (d) 57 nm.

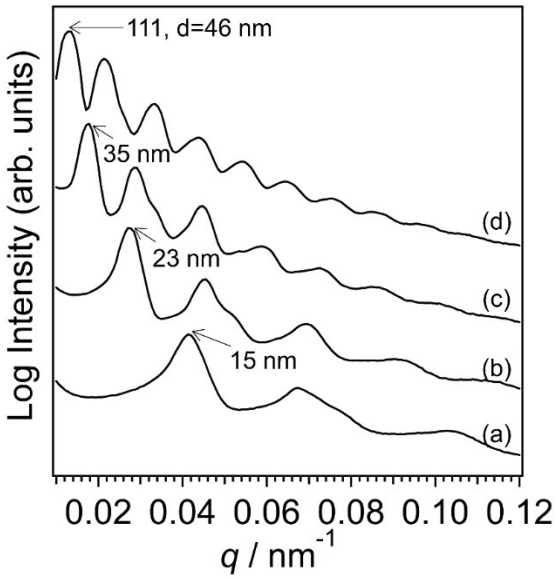

Figure S2 SAXS patterns of (a) SCC18, (b) SCC28, (c) SCC43, and (d) SCC57.

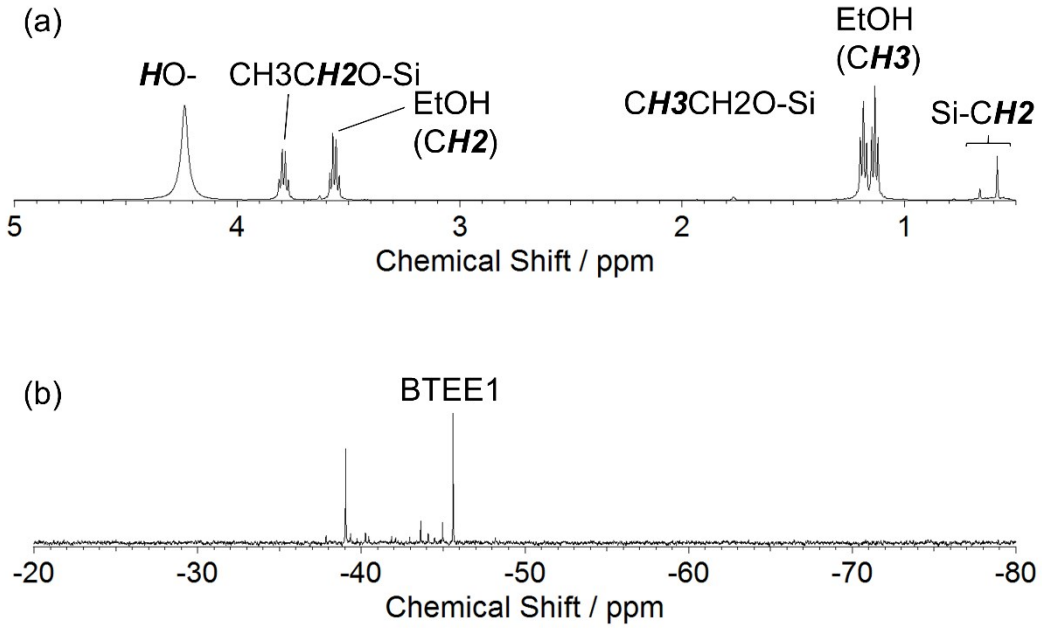

Figure S3 Liquid-state (a) ^{1}H and (b) ^{29}Si NMR spectra of BTEE1 after hydrolysis.

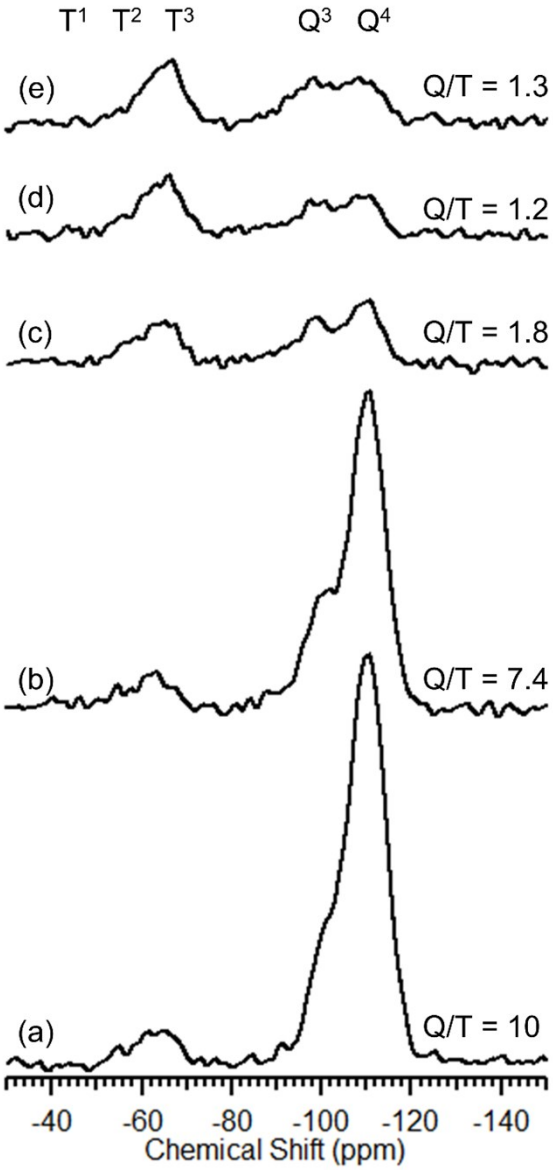

Figure S4 Solid-state ^{29}Si MAS NMR spectra of the samples after the treatment with 1 M NaOH aq. at 80 °C for (a) 1 h, (b) 8 h, (c) 24 h, (d) 96 h, and (e) 167 h.

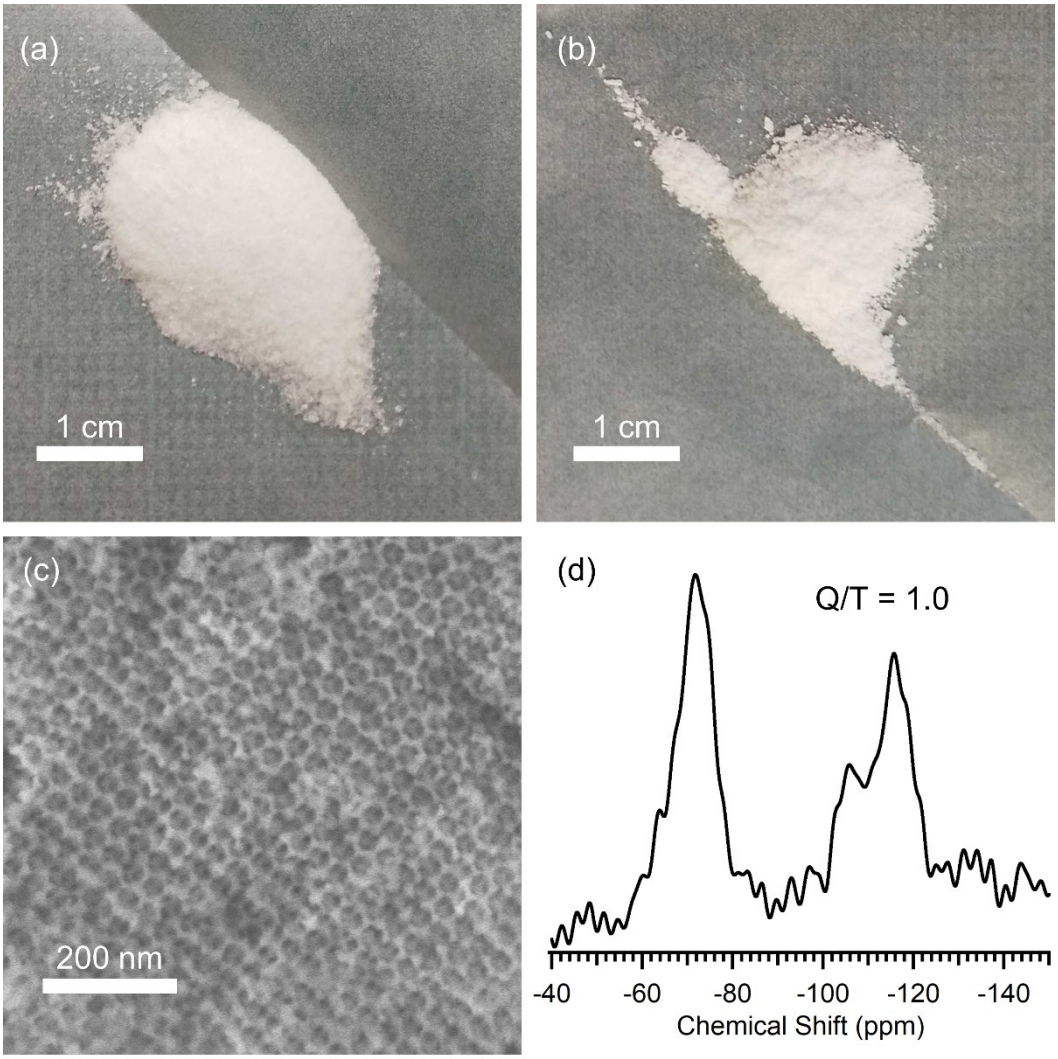

Figure S5 Appearances of (a) SCC43 pulverized in an agate mortar and (b) PMO43_BTEE1 using pulverized SCC43 as a template, (c) SEM image of PMO43_BTEE1 using pulverized SCC43 as a template and (d) solid-state ^{29}Si MAS NMR spectra of PMO43_BTEE1 using pulverized SCC43 as a template.

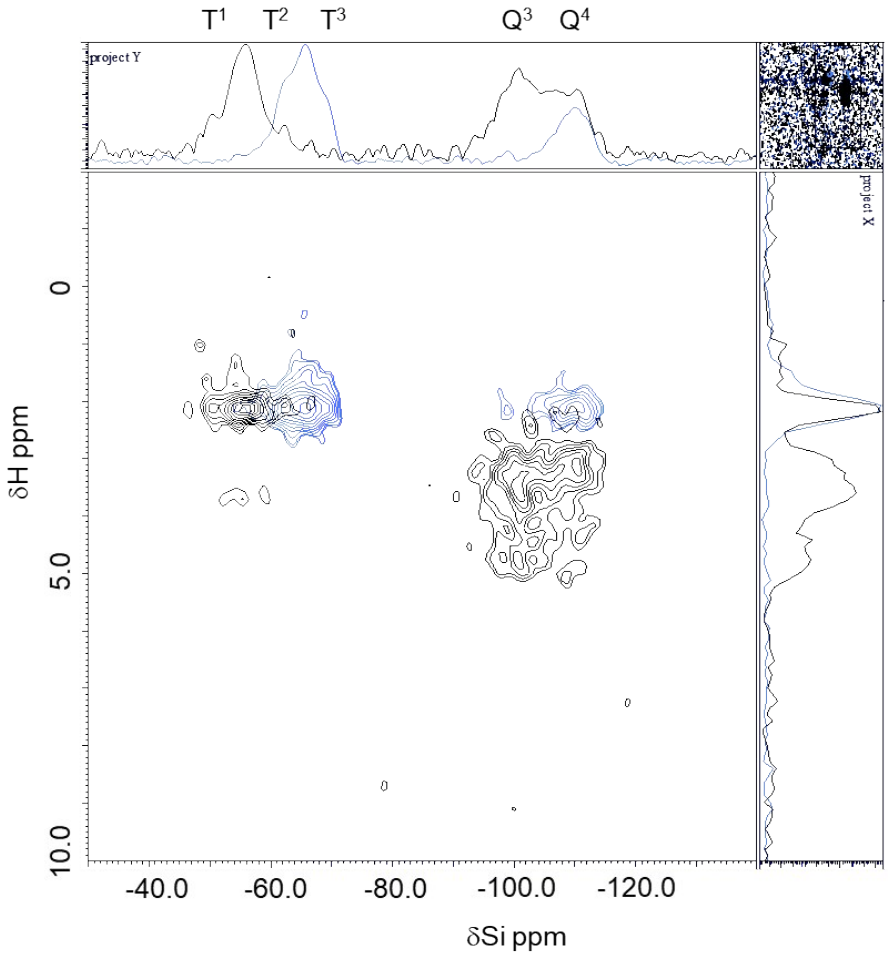

Figure S6 Solid-state two-dimensional ^{1}H–^{29}Si heteronuclear correlation (HETCOR) NMR spectra of (black) SCC43–organosiloxane composite prepared using BTEE1 and (blue) PMO43_BTEE1.

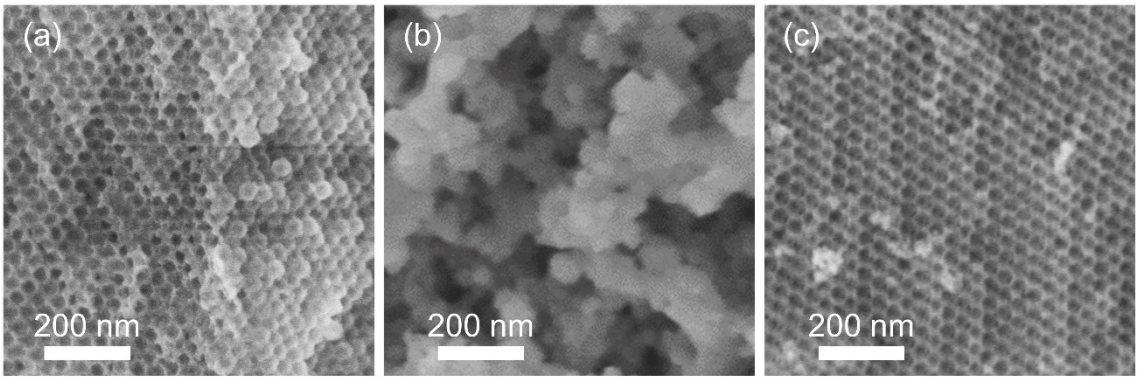

Figure S7 SEM images of the samples prepared by impregnation of SCC43 with ((a) and (b)) unhydrolyzed BTEE1 and (c) BTEE1 hydrolyzed for 4 and 5 h followed by the treatment with NaOH aq.

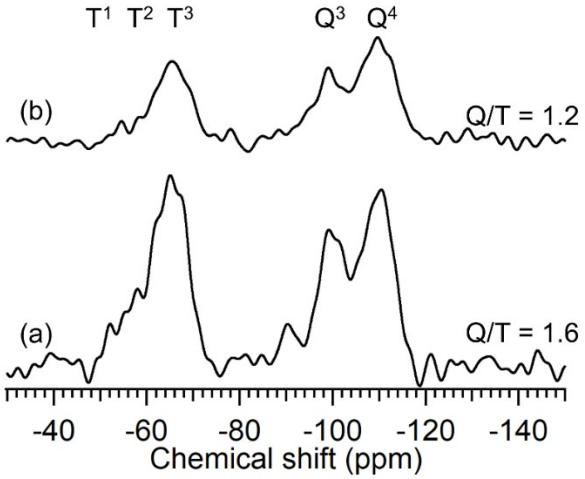

Figure S8 ^{29}Si MAS NMR spectra of the samples prepared by the impregnation of SCC43 with (a) unhydrolyzed BTEE1 and (b) BTEE1 hydrolyzed for 4 and 5 h followed by the treatment with NaOH aq.

Table S1 Integral ratio, and residual ratios of organosiloxane and silica.

Hydrolysis time of BTEE1	T:Q (integration ratio)	Residual ratio of organosiloxane / wt%	Residual ratio of silica / wt%
0 min	1.0:1.2	21	3
15 min (normal condition)	1.0:1.1	80	11
4 and 5 h	1.0:1.6	69	14

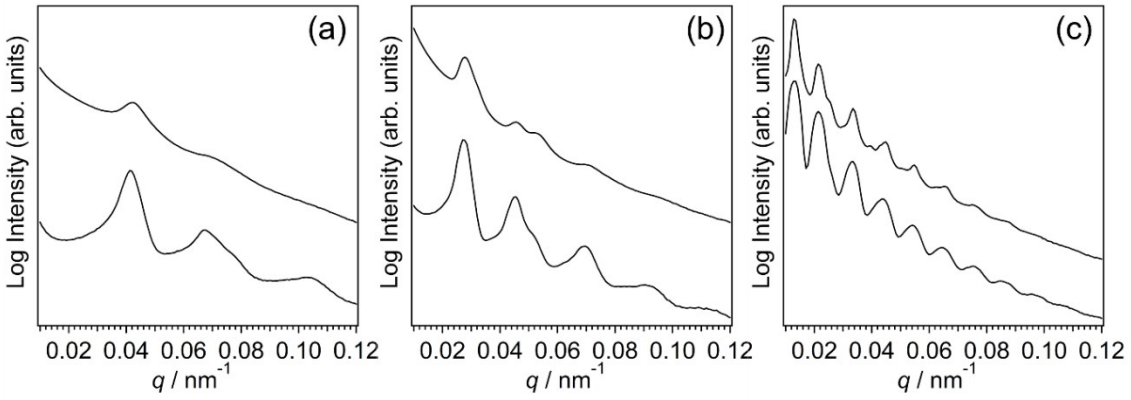

Figure S9 SAXS patterns of (a, top) PMO18_BTEE1, (b, top) PMO28_BTEE1, and (c, top) PMO57_BTEE1(top). For comparison, SAXS patterns of SCCs are also shown: (a, bottom) SCC18, (b, bottom) SCC28, and (c, bottom) SCC57.

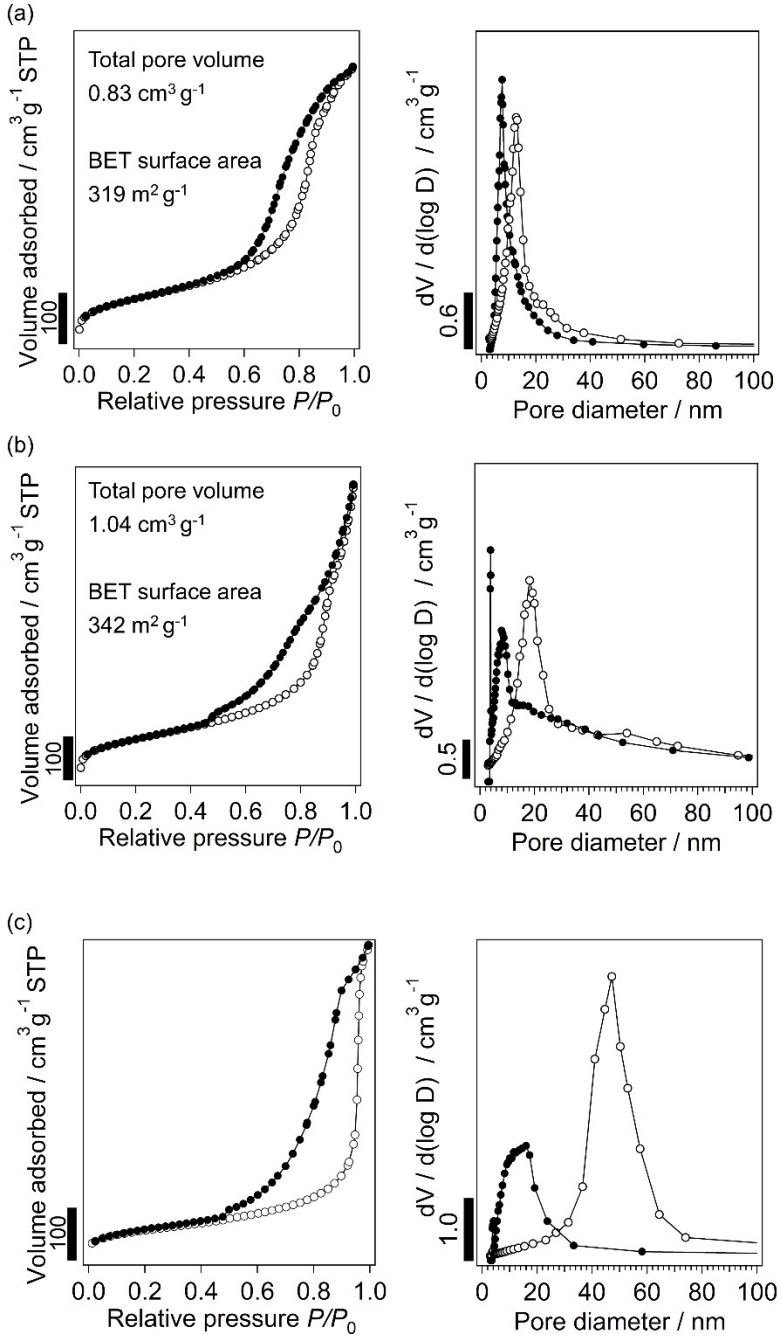

Figure S10 (left) Nitrogen adsorption–desorption isotherms and (right) BJH pore size distributions of (a) PMO18_BTEE1, (b) PMO28_BTEE1, and (c) PMO57_BTEE1. White and black circles denote adsorption and desorption, respectively. (The peak at 4 nm in the pore size distribution of (b) originates from the cavitation.)

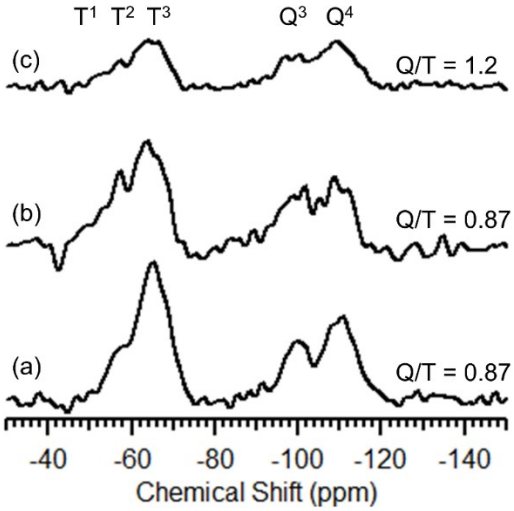

Figure S11 ^{29}Si MAS NMR spectra of (a) PMO18_BTEE1, (b) PMO28_BTEE1, and (c) PMO57_BTEE1.

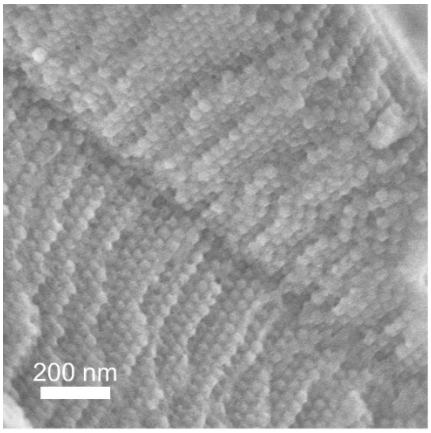

Figure S12 SEM image of PMO43_BTEB.

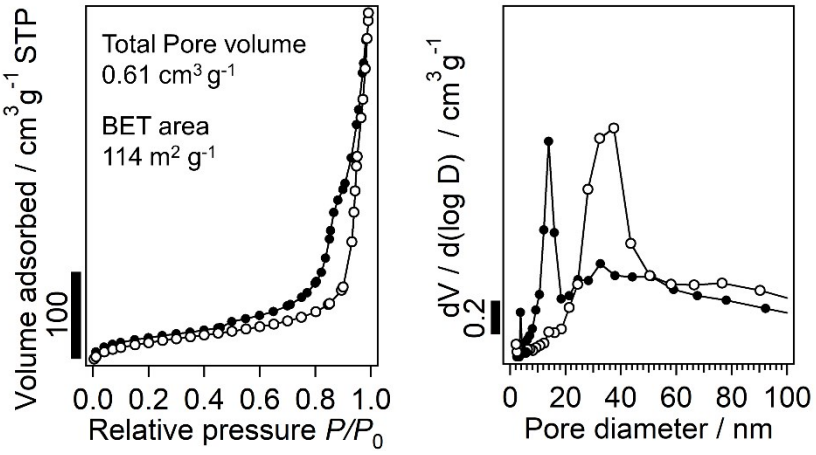

Figure S13 (left) Nitrogen adsorption–desorption isotherms and (right) BJH pore size distributions of PMO43_PTES. White and black circles denote adsorption and desorption, respectively.