Supplementary Information

TEM images of the silica particles from the solutions with and without polymers.

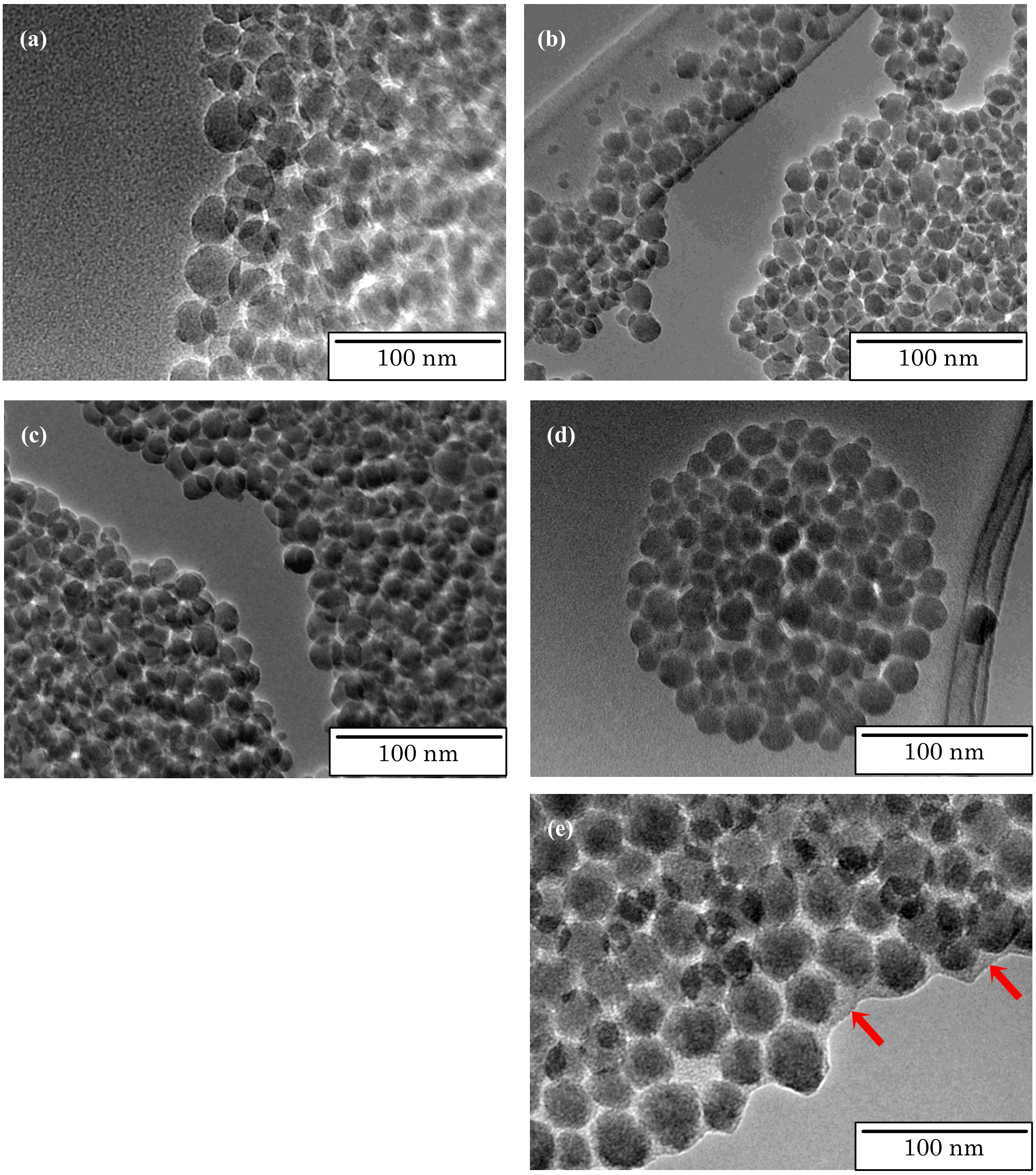

Figure S1. TEM images of silica particles from the colloidal silica solutions; (a) O-40 (b) DX1/O-40 (c) GCD/O-40 (d) PEG/O-40 (e) NSF/O-40. Arrows in (e) indicate the polymer present at interparticles.

Geometrical calculation of the channel size from the wall thickness and the concentration of the starting solution.

A model shown in Figure S2 was used for the calculation. The hexagonal ice rods are arrayed parallel to the freezing direction. The model is composed of hexagonal unit structures as is highlighted by the red line in Figure S2. In the model, the following equation is satisfied;

$$x = \frac{S_{\mathrm{w}}\rho_{\mathrm{sa}}}{S_{\mathrm{i}}\rho_{\mathrm{i}}} \qquad \text{(S1)}$$

Here, x, S_{w}, S_{i}, ρ_{sa}, and ρ_{i} mean weight ratio of silica/water in the starting solution (0.67 g-silica g^{-1}-water), area of silica wall in the unit structure, area of an ice rod, apparent density of silica wall, and density of ice (0.92 g cm^{-3}), respectively. ρ_{sa} is defined as follows, by using silica density (ρ_{s} = 2.0 g cm^{-3}) and total pore volume of the silica wall (V_{t} = 0.25 cm^3 g^{-1});

$$\rho_{\mathrm{sa}} = \frac{1}{1/\rho_{\mathrm{s}} + V_{\mathrm{t}}} \qquad \text{(S2)}$$

By using the wall thickness (t_{w}) and the diameter (d_{i}) of ice rod, S_{w} and S_{i} can be described as follows;

$$S_{\mathrm{w}} = \frac{\sqrt{3}}{2}\left\{(d_{\mathrm{i}} + t_{\mathrm{w}})^2 - d_{\mathrm{i}}^2\right\} \qquad \text{(S3)}$$

$$S_{\mathrm{i}} = \frac{\sqrt{3}}{2} d_{\mathrm{i}}^2 \qquad \text{(S4)}$$

From the equations S1, S3, and S4, d_{i} can be described by using t_{w}, as follows;

$$d_{\mathrm{i}} = \alpha\, t_{\mathrm{w}} \qquad \text{(S5)}$$

Here, α is a constant defined as follows;

$$\alpha = \frac{1 + \sqrt{1 + (x\rho_{\mathrm{sa}}/\rho_{\mathrm{i}})}}{x\rho_{\mathrm{sa}}/\rho_{\mathrm{i}}} \qquad \text{(S6)}$$

There is the lower limit for t_{w}, i.e. the size of silica particle (about 25 nm). In the lowest t_{w}, d_{t}

also becomes the lowest, which is calculated as 120 nm from the equation S5, as shown in Figure S3.

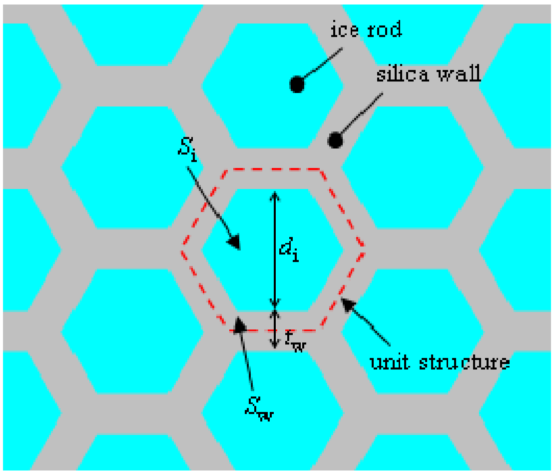

Figure S2. The cross-section of a model of frozen-state. Blue hexagons and gray part correspond to the cross-section of the ice rods and silica wall, respectively. A part surrounded by red line is a unit structure of this model.

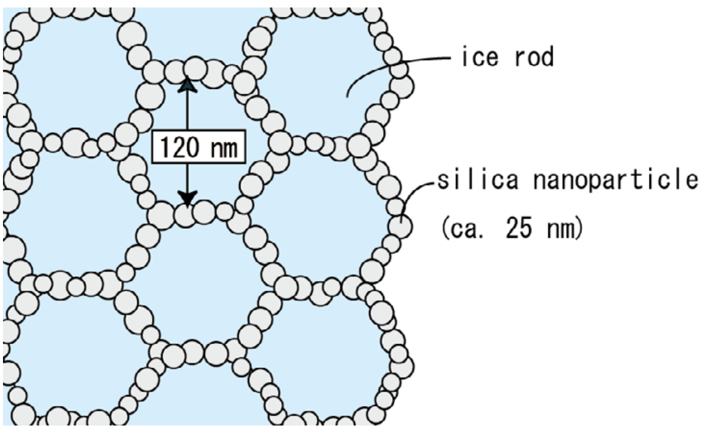

Figure S3. An illustration of an imaginary porous monolith with the smallest channel-wall thickness (25 nm). The pore size can be calculated as 120 nm.