

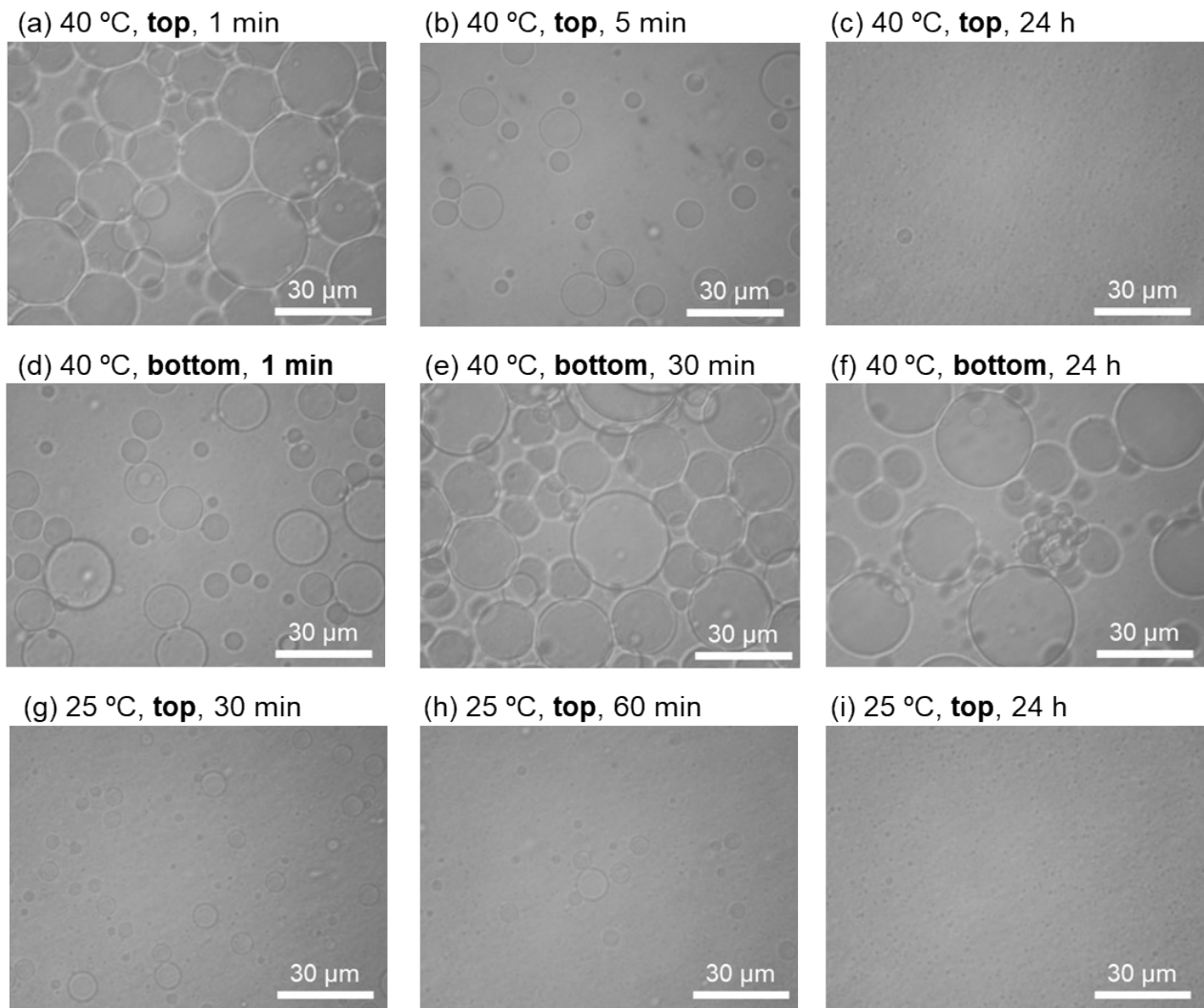
## Supplementary Information

### Synthesis of Porous Aluminate Microbeads from Emulsion Droplets: Interphase Alcohol Extraction-Driven Assembly of Sub-10 nm Nanoparticle

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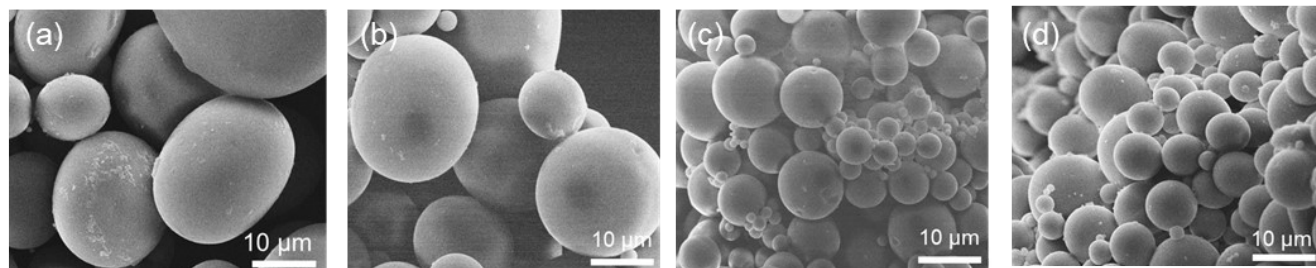
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<b>Figure S1</b>	<b>2</b>
<b>Figure S2</b>	<b>3</b>
<b>Figure S3</b>	<b>4</b>
<b>Figure S4</b>	<b>5</b>



**Fig. S1. Optical micrographs of emulsion droplets after aging at 40 °C at the “top” of a glass container for (a) 1 min, (b) 5 min and (c) 24 h, and at the “bottom” of glass container after aging for (d) 1 min, (e) 30 min and (f) 60 min, and after aging at 25 °C at the “top” of a glass container for (g) 30 min, (h) 60 min and (i) 24 h.**

When the emulsion droplets were aged at 40 °C, the droplets coalesced and grew larger as they moved from the top to the bottom of the glass container. Most droplets, except for small ones, moved to the bottom within 5 min of aging. This is because the density of the oil phase, dodecane (0.75 g/mL), is lower than that of water. Some of the droplets coalesced at the bottom of the glass container, but PLMA-b-PPEGMA prevented the droplets from coalescing, resulting in the formation of assembly of droplets of different sizes. On the other hand, when the emulsion droplets were aged at 25 °C, almost no droplets coalesced, and the droplets did not grow larger. Furthermore, the traveling time of droplets from the top to the bottom of the glass container was extended. As a result, small-sized microbeads were obtained.



**Fig. S2. SEM images of aluminate microbeads prepared with aluminum hydroxide dispersions containing (a) 5 mL, (b)10 mL, (c) 20 mL and (d) 25 mL of ethanol.**

Microbeads were synthesized by varying the amount of ethanol contained in the dispersion. When dispersions containing 5 or 10 mL of ethanol were used, ellipsoidal microbeads were obtained. Compared to the dispersion containing 15 mL of ethanol discussed in the main text, these dispersions had higher viscosity, which likely inhibited spherical micelle formation. On the other hand, when dispersions containing 20 or 25 mL of ethanol were used, spherical microbeads were obtained. In the case of 20 mL, the average diameter was 7.0  $\mu\text{m}$  (standard deviation: 4.0  $\mu\text{m}$ ), and in the case of 25 mL, the average microbead diameter was 6.9  $\mu\text{m}$  (standard deviation: 3.9  $\mu\text{m}$ ). Compared to the compositions discussed in the main text (15 mL ethanol), particle size was slightly smaller with increasing ethanol content. This is due to a decrease in the amount of aluminum hydroxide nanoparticles contained in the emulsion droplets.

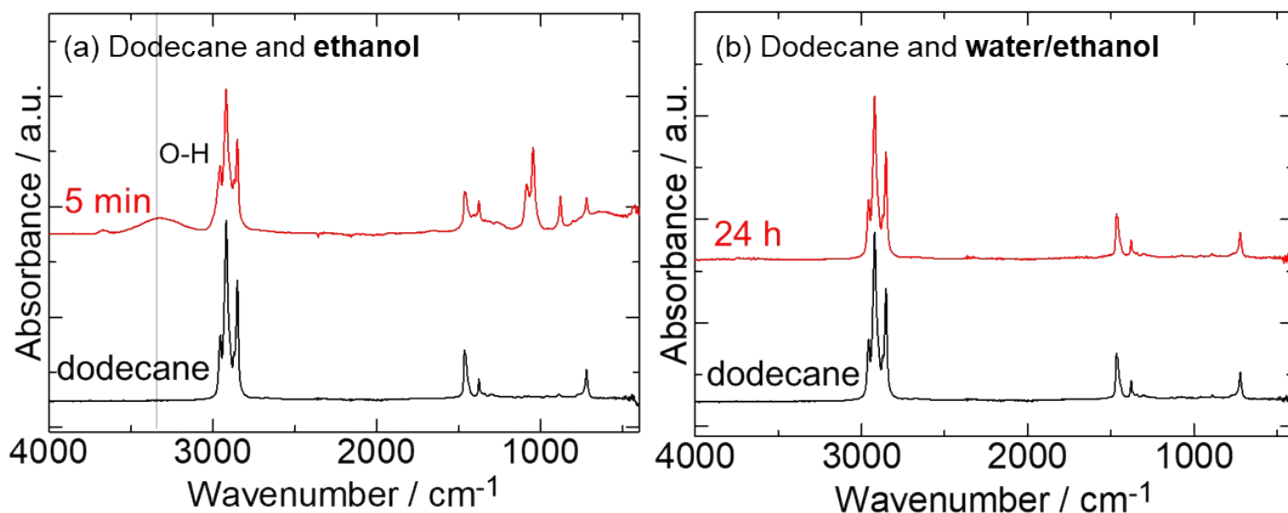


Fig. S4. FT-IR spectra of the oil phases after aging for (a) 5 min with ethanol and (b) 24 h with a mixture of water and ethanol.

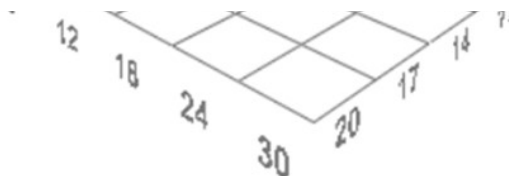
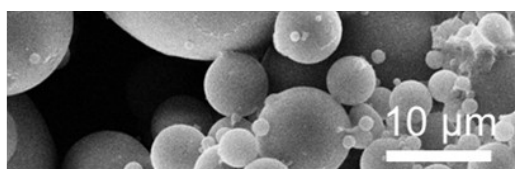


Fig. S3 Appearance of aluminum hydroxide dispersions prepared with 15 mL of (a) methanol, (b) 1-propanol and (c) 1-butanol instead of ethanol. (d) SEM images of aluminate microbeads prepared with the dispersion synthesized with methanol solvent. (e) Three-dimensional Hansen solubility parameter. 1. Dodecane, 2. Ethanol, 3. Methanol. Three axes correspond to contributions influencing on intermolecular interaction;  $dD$ : Dispersion force;  $dP$ : Polar force;  $dH$ : Hydrogen bonding.

Microbeads were synthesized by changing the type of alcohol contained in the dispersion from ethanol to methanol, 1-propanol, and 1-butanol. The solution containing methanol was a transparent dispersion, similar to those containing ethanol. Solutions containing 1-propanol or 1-butanol were turbid suspensions after 24 h since the addition of propylene oxide. Although the particles were dispersed, the dispersion stability was low, making it difficult to maintain emulsion droplets stability. When a dispersion containing methanol was used, microbeads were obtained. The average particle size was 8.7  $\mu\text{m}$  (standard deviation: 7.0  $\mu\text{m}$ ). Compared to microbeads prepared with a dispersion containing ethanol, the particle size distribution was broader and some particles were irregularly shaped.

The oil phase (dodecane) was gently poured on the polar phase (either ethanol or the mixture of water/ethanol) to form macroscopic two-phase separation. Then, the two-phase-separated liquids were aged at room temperature. For the sample using ethanol as the polar phase, the two phases immediately became miscible and formed a one phase, and ethanol-derived peaks appeared at 3380  $\text{cm}^{-1}$ .

On the other hand, for the sample using the mixture of water/ethanol as the polar phase, apparent spectral change was not observed for the oil phase in 24 h. This indicates that water in the polar phase interacts with ethanol and inhibits the extraction of ethanol to oil phase. It is suggested that the successful formation of aluminate porous microbeads in the case of using dodecane is owing to relatively slow and homogenous extraction of ethanol thanks to partition of ethanol between water and dodecane.