Electronic Supplementary Infomaton

Pickering emulsion engineering: Fabrication of materials with multiple cavities

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Materials

Unless otherwise stated, all materials were guaranteed reagent grade. Ammonium persulfate (> 95.0%: APS), sodium alginate (alginate Na: molecular weight, 110,000; viscosity, 500-600 mPs·s at 10 g/L and 20°C), methyl myristate (> 95.0%), strontium chloride (> 95.0%), barium chloride (> 95.0%), aluminium chloride (> 98.0%), iron(II) chloride tetrahydrate (99.0-102.0 %), iron(III) chloride hexahydrate (99.0 %) were obtained from Wako Chemicals. Styrene, aluminium oxide (activated, basic, Brockmann 1, standard grade, ~150 mesh, 58 Å), calcium chloride (> 96.0%), acetone (> 99.5%), poly(vinyl alcohol) (PVA: polymerization degree, 500; saponification degree, 88.0±1.5 mol%), potassium hydroxide (85 %), ammonia aqueous solution (28 wt%) were obtained from Sigma-Aldrich. Styrene was purified by passing through a column of the activated basic alumina prior to storage at –15 °C before use. Deionized water (< 0.06 μS cm^{-1}) was prepared using a deionized water producing apparatus (Advantec MFS RFD240NA: GA25A-0715) and used for synthesis and purification of the PS latex particles and fabrication of Pickering emulsions and their assemblies.

Preparation of PS Latex via Emulsion Polymerization

Emulsion polymerization of styrene was performed in the presence of alginate Na stabilizer in batch mode at 70°C using APS initiator. Alginate Na (0.500 g; 10 w/w % based on styrene) and APS (0.05 g; 1 w/w% based on styrene) were added to water (50 mL) in a one-necked, round-bottomed 100 mL flask containing a magnetic stir bar. This reaction mixture was vigorously stirred at 0°C until the alginate Na and APS had dissolved completely. The reaction mixture was then degassed using five alternating cycles of evacuation and pressurization with nitrogen (starting with evacuation). Styrene (5.00 g) was then added to the reaction mixture, and the flask was heated to 70°C. Initiator radicals generated by thermal decomposition of APS can abstract hydrogen atoms from the alginic acid backbone, and polymerization initiated by the polymer radicals produces graft polymers, which act as a colloidal stabilizer. The reaction was allowed to proceed for 24 h with continuous stirring at 250 rpm under a nitrogen atmosphere. This latex was purified by repeated centrifugation-redispersion cycles (typically 15,000 rpm for 60 min) using deionized water.

Characterization of PS latex

Particle size analysis

The sizes and size distribution of the latex particles were determined using a particle size analyzer (Malvern Mastersizer 2000) equipped with a small volume sample dispersion unit (Hydro 2000SM; *ca.* 150 mL including flow cell and tubing), a HeNe laser (633 nm), and a solid-state blue laser (466 nm). The stirring rate was adjusted to 2000 rpm. The raw data was analyzed using Malvern software. The mean particle diameter was taken to be the volume mean diameter (D_v), which is mathematically expressed as $D_v = \Sigma D_i^4 N_i / \Sigma D_i^3 N_i$, where D_i is the diameter of individual particles and N_i is the number of particles corresponding to the specific diameter.

Scanning electron microscopy study

Scanning electron microscopy (SEM; Keyence VE-8800, 12 kV) was conducted with Au sputter-coated (Elionix SC-701 Quick Coater) dried samples.

Chemical composition

The alginic acid loading of the alginic acid-stabilized PS particles was determined by comparing the oxigen contents determined by CHN elemental microanalysis (Yanaco CHN-Corder MT-5) with that of the alginate Na. Oxgen contents were determined using the following equation: 100% - C% - H% - N%, assuming that the polymers consist of C, H, N and O. The CHN microanalysis of the alginic acid-adsorbed PS particles after extensive centrifugal washing to remove free unadsorbed alginic acid indicated that an adsorbed amount of alginic acid on the PS seed particles was 1.29 wt% based on the PS particles.

X-ray photoelectron spectroscopy study

XPS measurements were carried out using an XPS spectrometer (Shimadzu/KRATOS, Axis Ultra) with a Mg Kα X-ray gun. Dried alginate Na-stabilized PS powder sample was placed under reduced pressure by continuous operation of a diffusion pump just before the XPS measurement. The dried powder sample was spread at the surface of an indium plate with a spatula and mounted onto sample stubs using conductive tape. The base pressure was $<1.0\times10^{-8}$ Torr. Pass energies of 80 eV and 20 eV were employed for the survey spectra and elemental core-line spectra, respectively. Quantification of the atomic percentage composition was obtained from high resolution spectra according to the manufacturer sensitivity factors. Spectra were aligned to the hydrocarbon component of the C 1s peak set at 285 eV.

Characterization of Pickering emulsion and emulsion assemblies

Optical microscopy

A drop of the diluted latex was placed on a microscope slide and observed using an optical microscope (Shimadzu Motic BA200) fitted with a digital system (Shimadzu Moticam 2000).

Particle size analysis

The sizes and size distributions of the Pickering emulsion were determined using the particle size analyzer (Malvern Mastersizer 2000) equipped with a small volume sample dispersion unit (Hydro 2000SM; *ca.* 150 mL including flow cell and tubing), a HeNe laser (633 nm), and a solid-state blue laser (466 nm).

Calculation of % alginic acid-PS particles attached to oil-water interface

The number of alginic acid-PS particles attached to the oil-water interface is expressed using the following equation.

$$\frac{\text{Total surface area of emulsion droplets}}{\text{The area of one PS particle occupied at the emulsion droplet surface}}$$

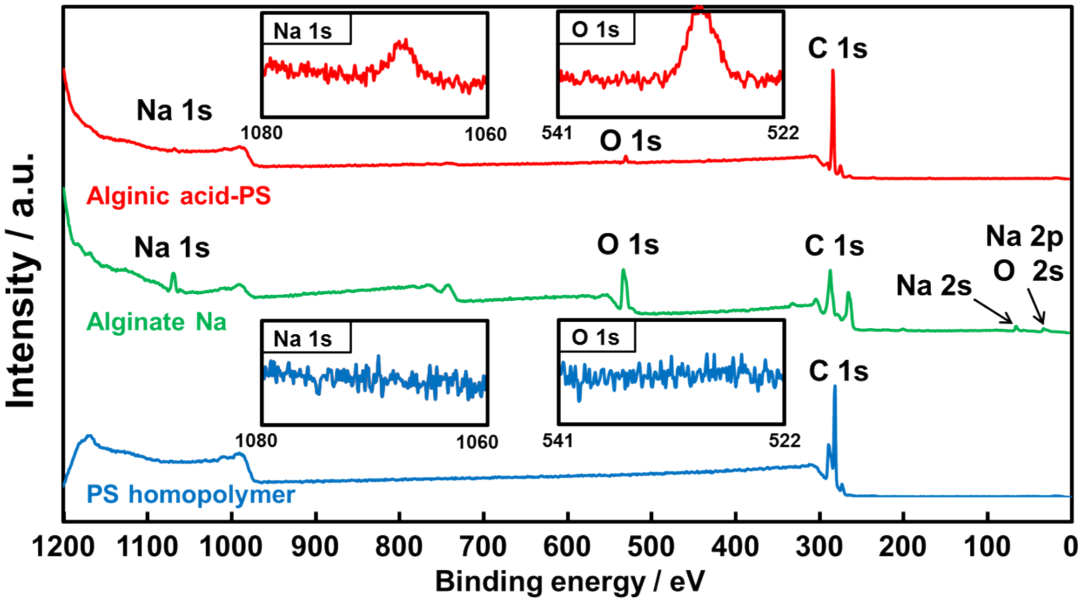
$$= \frac{4\pi R_{oil}^{2}\, N_{oil}}{(2R_{part})^{2}} = \frac{\pi R_{oil}^{2}\, N_{oil}}{R_{part}^{2}} \quad (Eq.\, S1)$$

% Alginic acid-PS particles attached to oil-water interface is calculated from the following equation.

$$\frac{The\ number\ of\ PS\ particles\ attached\ to\ oil-water\ \mathrm{int}erface}{The\ number\ of\ PS\ particles\ added\ in\ the\ emulsion\ system}\times 100\ \%$$

$$=\frac{\dfrac{\pi R_{oil}{}^{2}\ N_{oil}}{R_{part}{}^{2}}}{N_{part}}\times 100\ \% = \pi\ \frac{R_{oil}{}^{2}\ N_{oil}}{N_{part}\ R_{part}{}^{2}}\times 100\ \%\ (Eq.\ S2)$$

Figure S1. XPS survey spectra obtained for alginic acid-PS particles, alginate Na, and PS homopolymer.



Atomic conc. %	C	O	Na
PS homopolymer	100	~ 0	~ 0
Alginate Na	48.08	43.04	8.88
Alginic acid-PS	97.53	1.78	0.69

Alginic acid on the PS particles should play an important role to modify wettability of PS particles against oil-water interface in order to obtain oil-in-water emulsion. Simple charge-stabilized PS particles were known to stabilize water-in-oil emulsions [see B. P. Binks and S. O. Lumsdon, *Langmuir* **2001**, *17*, 4540.], which are not suitable for our Pickering emulsion engineering. Alginic acid on the PS particles should also help oil droplet stabilized with the PS particles well dispersed in the aqueous media where alginate Na was dissolved.

Figure S2. Effect of height and $CaCl_2$ concentration on Pickering emulsion assembly shape (alginate Na aq.: 0.5 wt%).

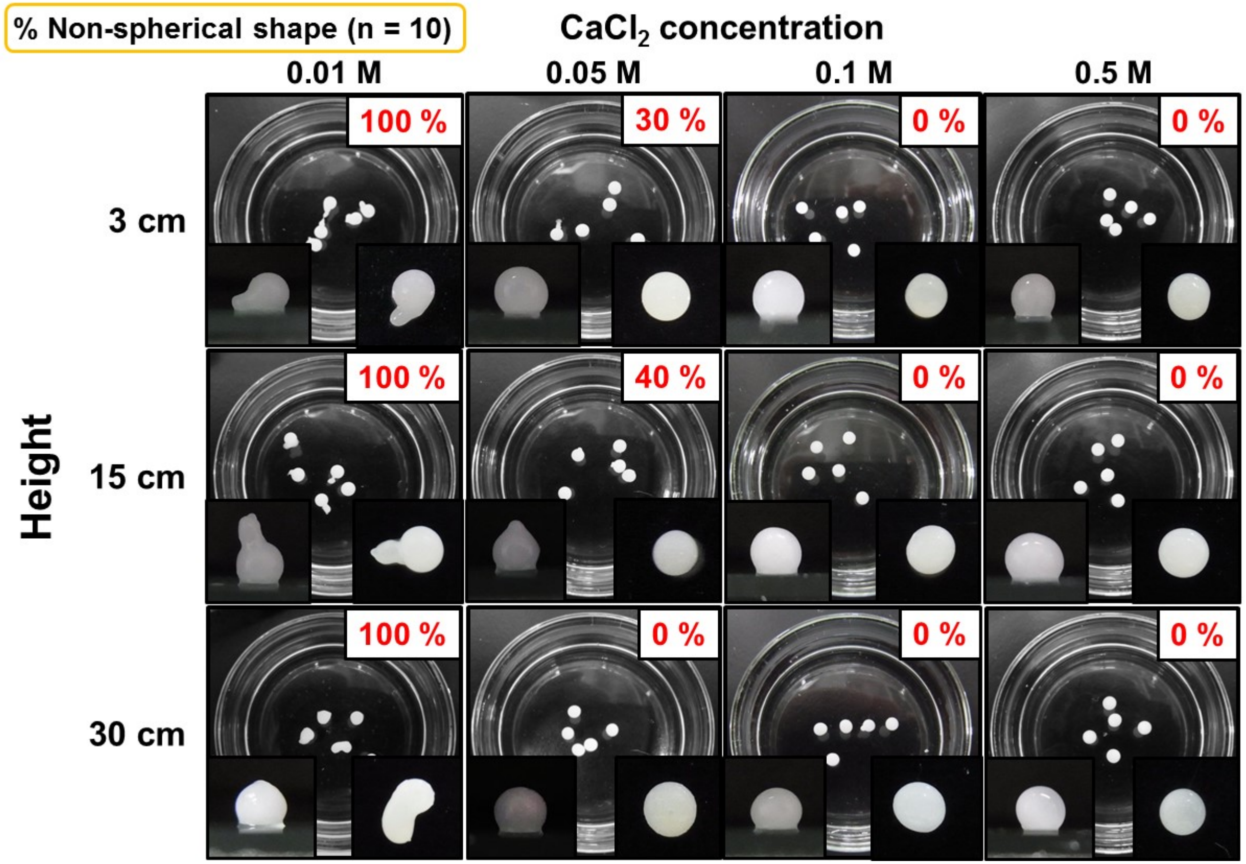


Figure S3. Alginic acid-PS latex particle-stabilized methyl myristate-in-water emulsions prepared at various homogenizing speeds: 10000, 15000 and 20000 rpm.

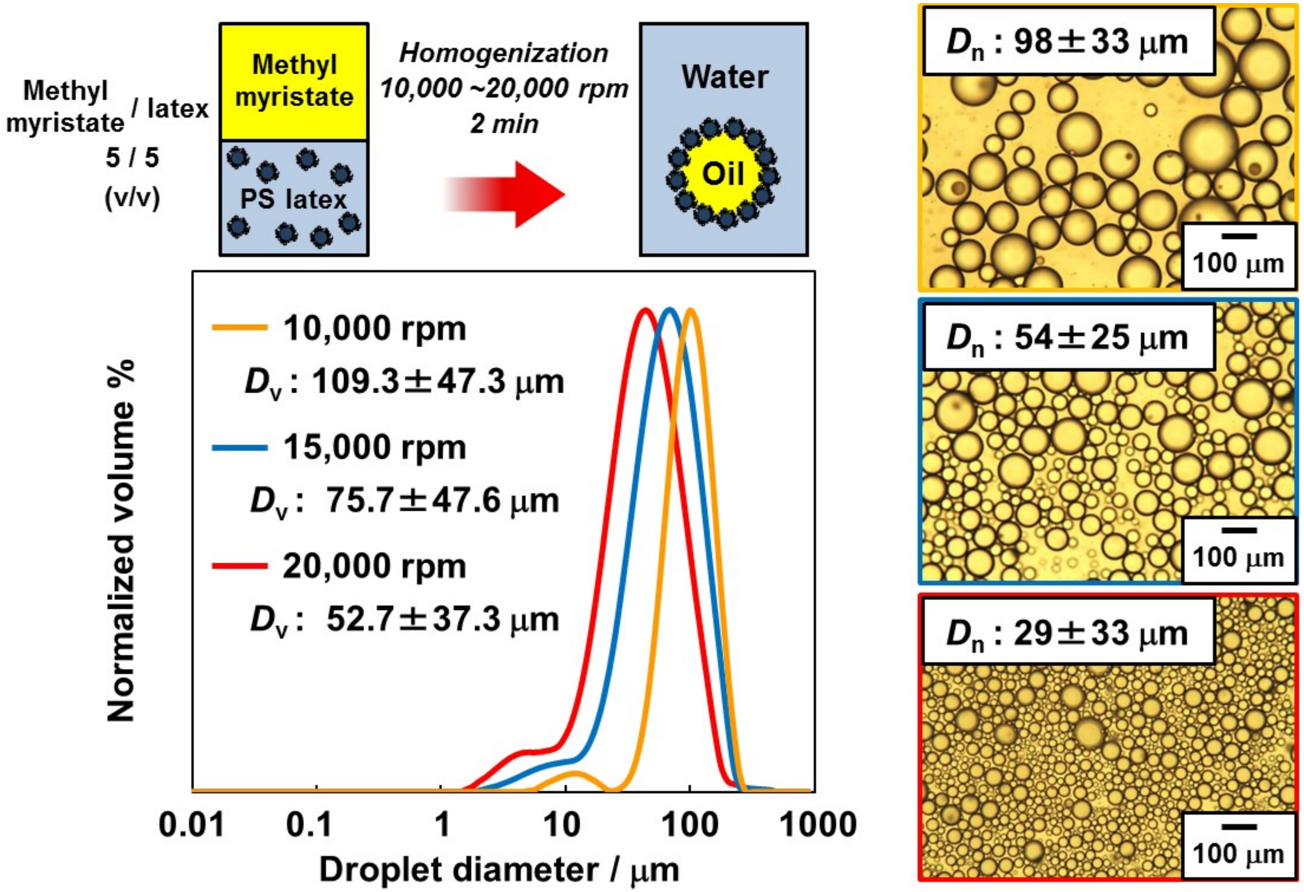


Figure S4. SEM images of multi-cavity materials fabricated using alginic acid-PS particle-stabilized methyl myristate-in-water emulsions with various droplet sizes.

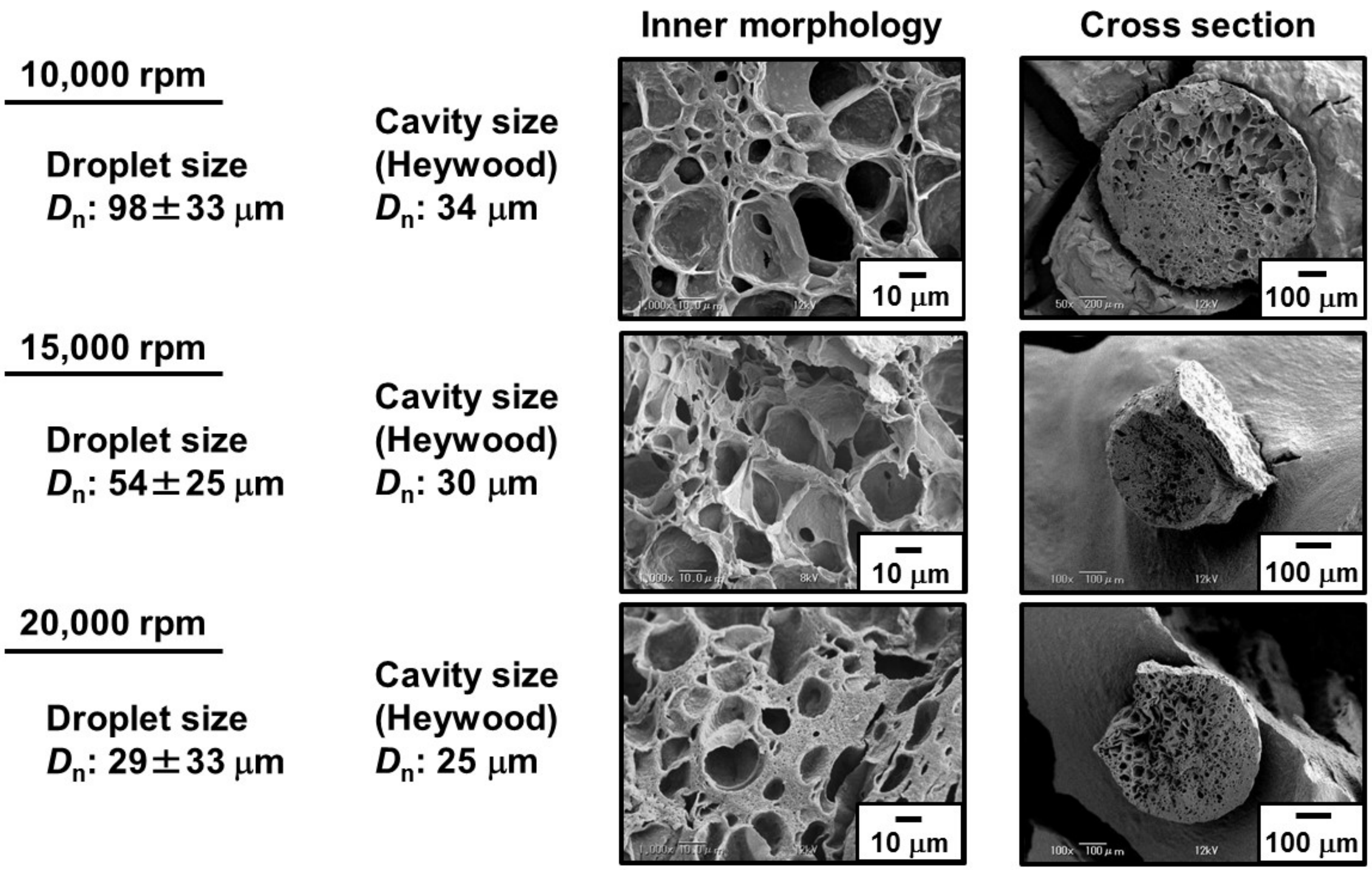
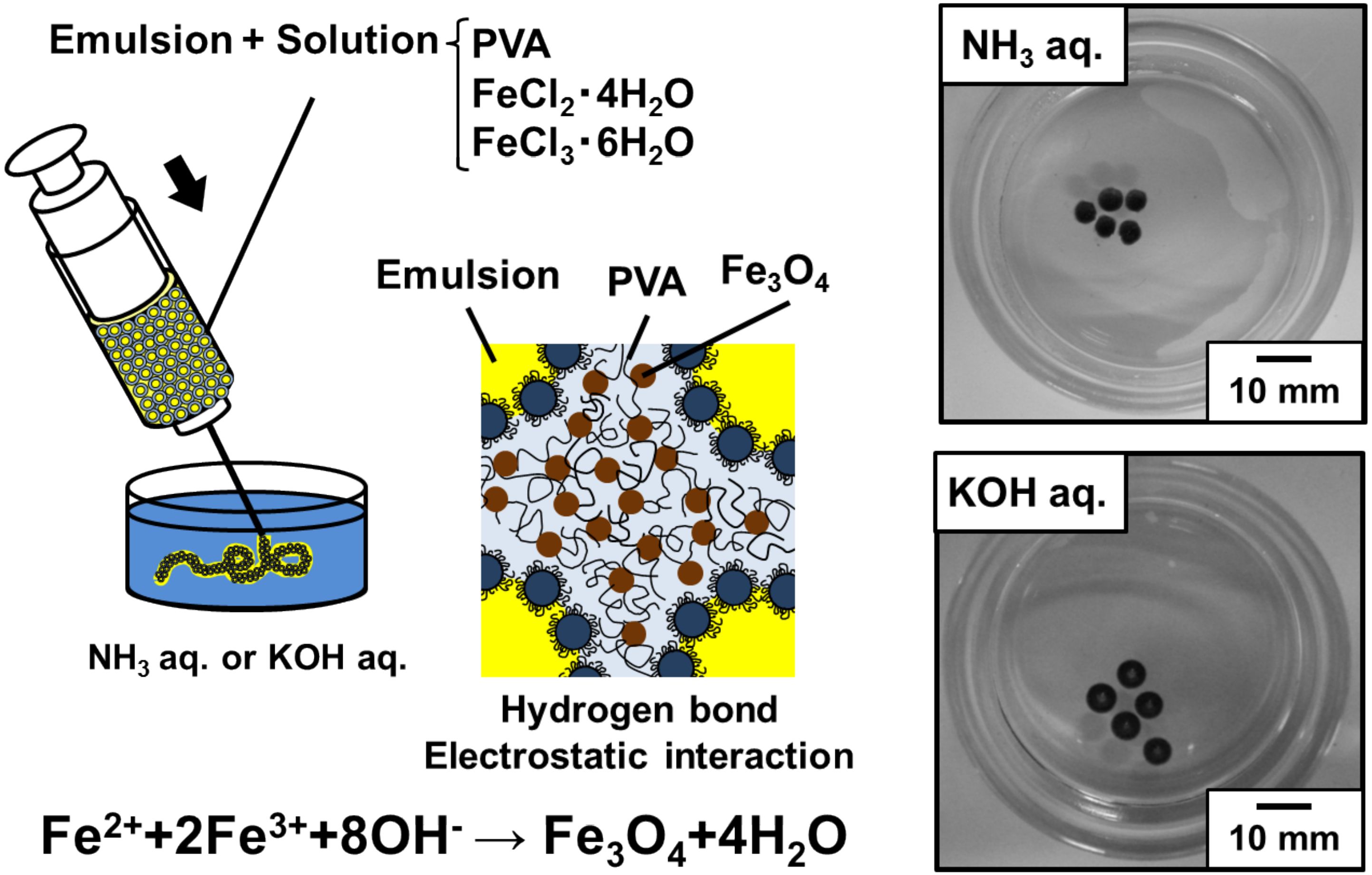


Figure S5. Fabrication of magnet-responsive emulsion assembly.



$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

Figure S6. Alginic acid-PS particle-stabilized magnetic methyl myristate-in-water emulsion droplet assembly: Digital camera images of emulsion droplet assembly (a) before and (b) after water evaporation, and (c) after oil extraction from water evaporated emulsion assembly.

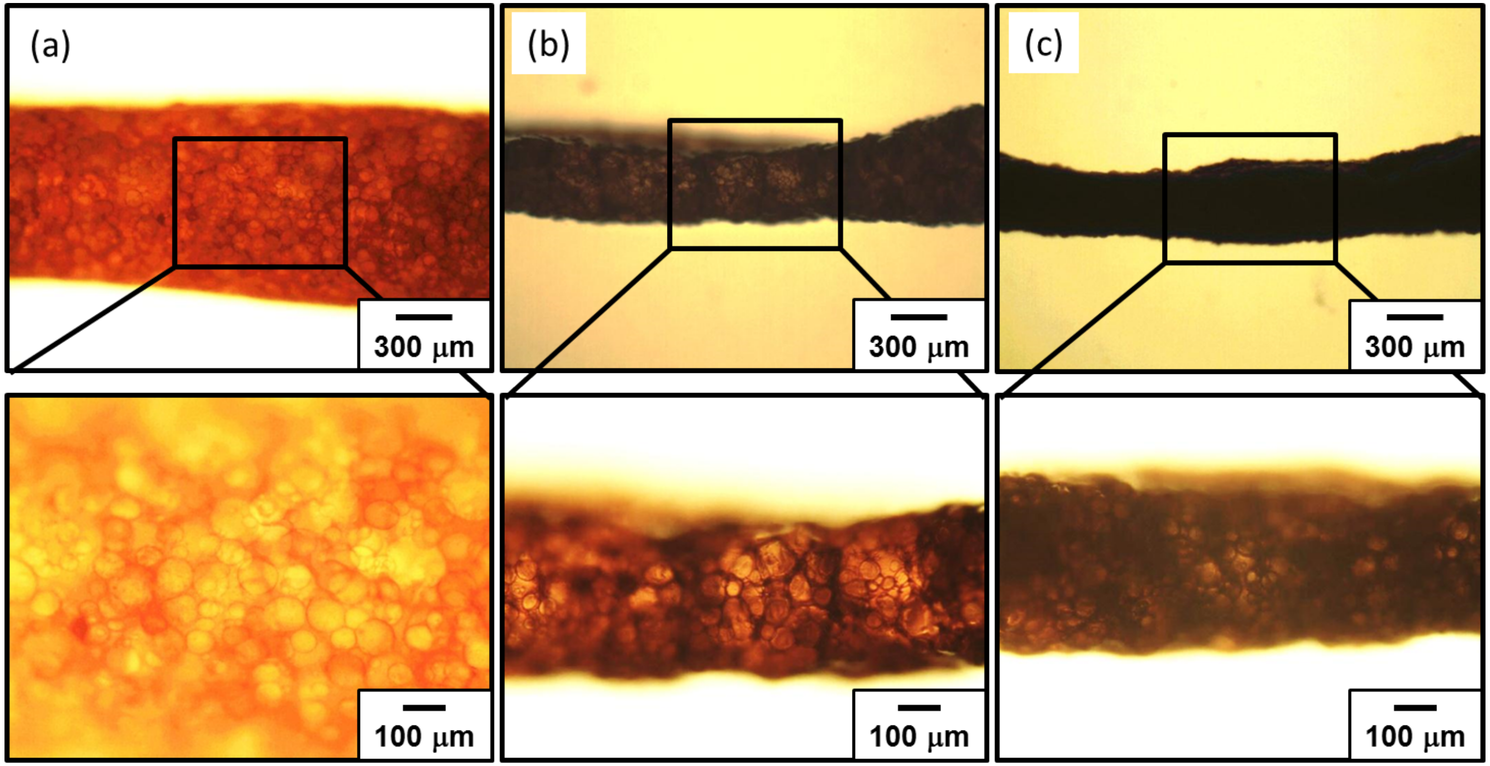
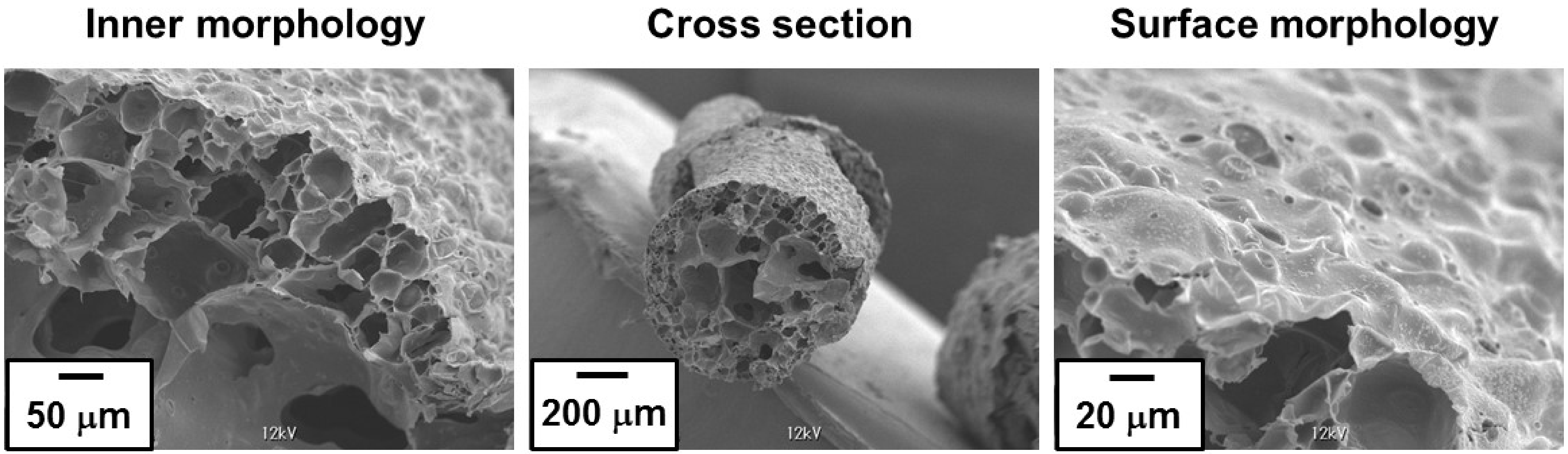


Figure S7. SEM images of magnetic multi-cavity material fabricated from alginate-PS particle-stabilized methyl myristate-in-water emulsion droplet assembly


Inner morphology

Cross section

Surface morphology