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Supporting Information

Facile Microcapsule Fabrication by Spray Deposition of a Supramolecular Hydrogel

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1. Materials

Water, after distillation with an Autostill WG33 (Yamato Scientific Co., Ltd.) and successive deionization with a Milli-Q Lab (Millipore) was used for the hydrogel formation. For confocal laser scanning microscopic (CLMS) observation, sodium 8-anilino-1-naphthalenesulfonate (ANS) purchased from Tokyo Kasei Chemical Co. was used as received. Deuterated water (D_2O) and dimethyl sulfoxide (DMSO-d_6) purchased from MERCK & Co. Inc. and Cambridge Isotope Laboratories, Inc., respectively, were used for the Fourier transform infrared (FT-IR) spectroscopy.

N-palmitoyl-Gly-His trifluoroacetate (PalGH) was synthesized according to the previously-reported method (ref. 5 in the main text).
^{1}H-NMR (400 MHz, DMSO-d_6) δ: 8.11-8.07 (2H, m), 7.53 (1H, s), 6.80 (1H, s), 4.34 (1H, q, J = 6.0 Hz), 3.66 (2H, m), 2.88 (2H, m), 2.12 (2H, t, J = 7.6 Hz), 1.48 (2H, t, J = 6.3 Hz), 1.23 (24H, m), 0.85 (3H, t, J = 6.7 Hz)

2. Confocal laser scanning microscopy

A methanol solution of ANS with a concentration of 10^{-3} M was prepared. An aliquot of 3 μL dye solution was added to a vial and methanol was evaporated by a nitrogen flow. Then, an aqueous dispersion of PalGH with a concentration of 0.5 wt% was added into the vial containing the dye. The dispersion was heated for 2 min at 363 K. The resultant hot solution was then placed in a glass bottom dish (MATSUNAMI GLASS Inc. Ltd.) and sealed with a cover glass and vacuum grease. The sample was left undisturbed for 24 hours to equilibrate at room temperature prior to the observation by confocal laser scanning microscopy (CLSM). Three-dimensional image of the hydrogel was obtained using a CLSM equipped with a semiconductor laser and a DAPI filter block (LSM700, Carl Zeiss Microscopy Co., Ltd.).

The gel containing the ANS dye (60 μM) was prepared in a spray vial (Maruemu Co., Japan). The gel was sprayed on a glass slide (MATSUNAMI GLASS Inc. Ltd.) in a perpendicular direction to the surface. The distance between the spray nozzle and the glass slide was kept to be 30 mm. The sprayed deposition was dried under an ambient atmosphere for 6 hours and then was further dried under a vacuum for 24 hours. The fluorescence image at the confocal plane was obtained by the CLSM.

3. Fourier-transform infrared spectroscopy

For the Fourier-transform infrared (FT-IR) measurements, 10 mg of PalGH was well-dispersed in 2 mL of D_2O by sonication and then this dispersion was then kept for 2 min at 363 K, to prepare the gel. The gel was sprayed on a CaF_2 substrate at a

perpendicular direction to the substrate surface. D_2O on the substrate was removed by pre-drying under an ambient atmosphere for 6 hours and then further dried off under a vacuum for 24 hours, to obtain a film. The gel and the film were used as samples. Also, a DMSO-d_6 solution of PalGH having the same concentration was prepared to serve as a reference sample. Each of the samples was sandwiched between CaF_2 substrates with a 0.5 mm gap. The FT-IR spectra were recorded with a FT/IR-620 spectrometer (JASCO Co.) equipped with a triglycine sulfate (TGS) detector. All spectra were obtained with a resolution of 2 cm^{-1} and 64 scans at 298 K.

4. Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) experiments were carried out at the BL40B2 beamline of SPring8 in Japan. The wavelength of the incident X-rays and the sample-to-detector distance were 0.10 nm and 2171 mm, respectively. Each of the samples was placed in an aluminum pan and the pan was installed on a sample stage. The scattered X-rays were recorded using a Rigaku R-AXIS IV+++ system (300 x 300 mm imaging plate) for 300 s. By circular averaging of the two-dimensional pattern on the image plate, a one-dimensional scattering profile of the sample was obtained.

5. Scanning electron microscopy

Prior to the scanning electron microscopic (SEM) observation, the film obtained by the spray deposition was coated with a 5 nm-thick layer of platinum by a JFC-1600 Auto Sputter Coater (JEOL Ltd.) The film morphology was observed by a Superscan SS-550 (Shimadzu Co.). Accelerating voltage was set at 10 kV.

Imaging software, Image J ver. 1.48 (National Institutes of Health, USA), was employed for the analysis of the diameter of the microcapsules. The diameter averaged over 100 different microcapsules was 55 μm.

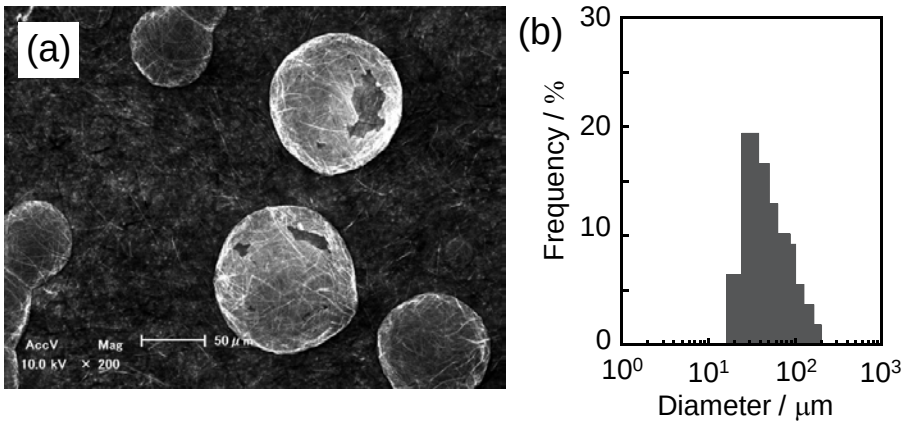

Fig. S1 (a) SEM image of the film obtained by the spray deposition and (b) the size distribution of the microcapsules observed for the film.

6. High-speed camera observation

The spraying behavior was observed by a PHANTOM Miro M310 camera (Nobby Tech. Ltd.) equipped with a magnifying lens. The images were acquired at a frame rate of 20 MHz. PCC ver. 2.14 software (Nobby Tech. Ltd.) was employed for the analysis of the size and the velocity of the droplets.