Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information for

Crystal capillary origami capsule with self-assembled nanostructures

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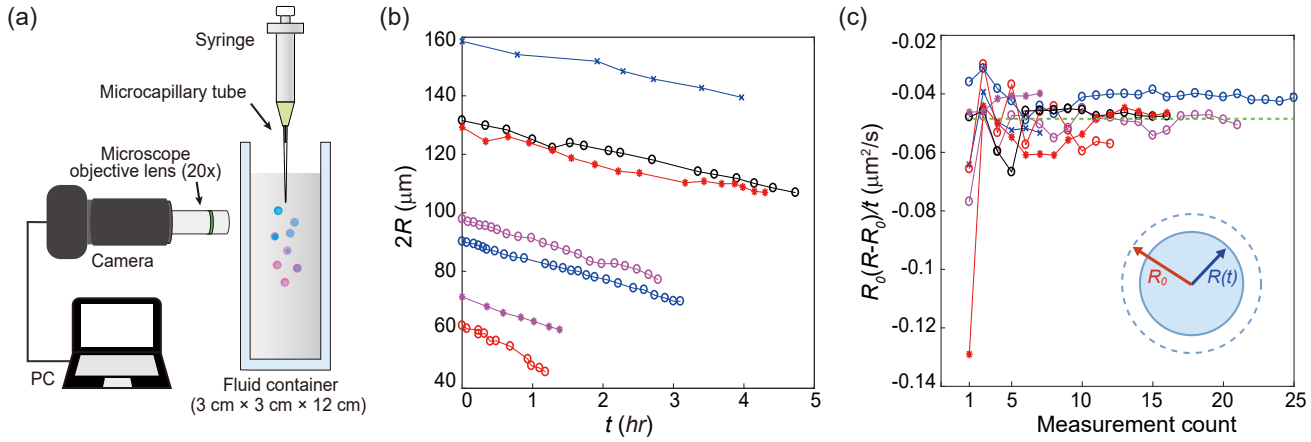

Fig. S1. Observation of the size change of water-in-oil emulsions containing saturated calcium propionate. (a) Schematics of the optical measurement. (b) Measured emulsion diameter $2R$ with time t. The crystallization was observed using the optical measurement setup in which the saturated aqueous solution of calcium propionate was emulsified in silicone oil. In the container, the blue and pink droplets indicate emulsions and crystallized shells, respectively. (c) The value of $R_0(R-R_0)/t$ for each measurement. The green dashed line indicates the average value -0.049 $\mu m^2/s$ except for the first measurement in each case. The viscosity of the silicone oil was 10,000 cSt for the experiment.

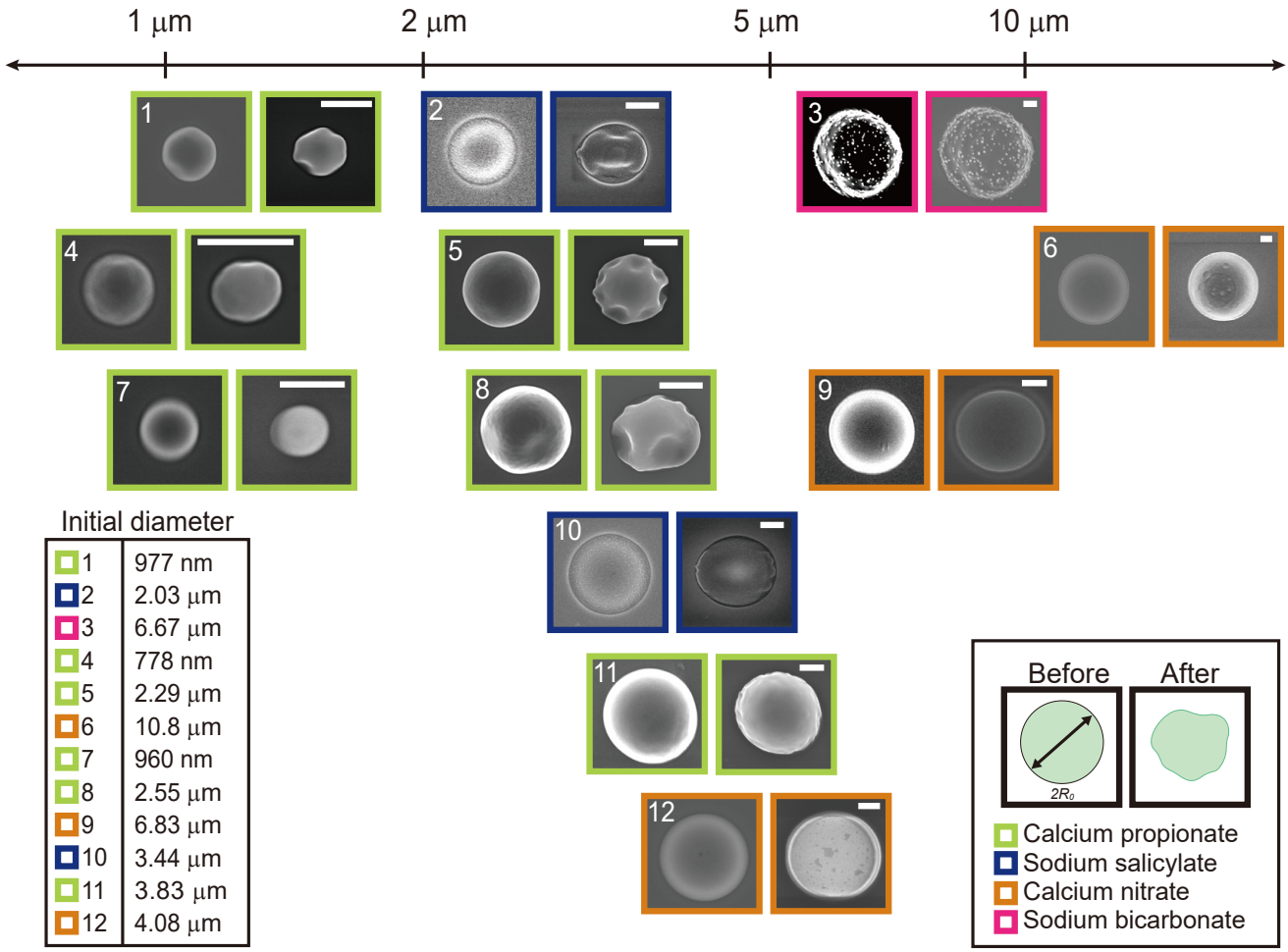

Fig. S2. SEM images about before (left) and after (right) the 10 kV beam exposure for 180 seconds. The images with green, blue, orange and magenta border correspond to those of calcium propionate, sodium salicylate, calcium nitrate and sodium bicarbonate, respectively. The initial diameter of each case is marked at the bottom of each left image. All scale bars: 1 μm.

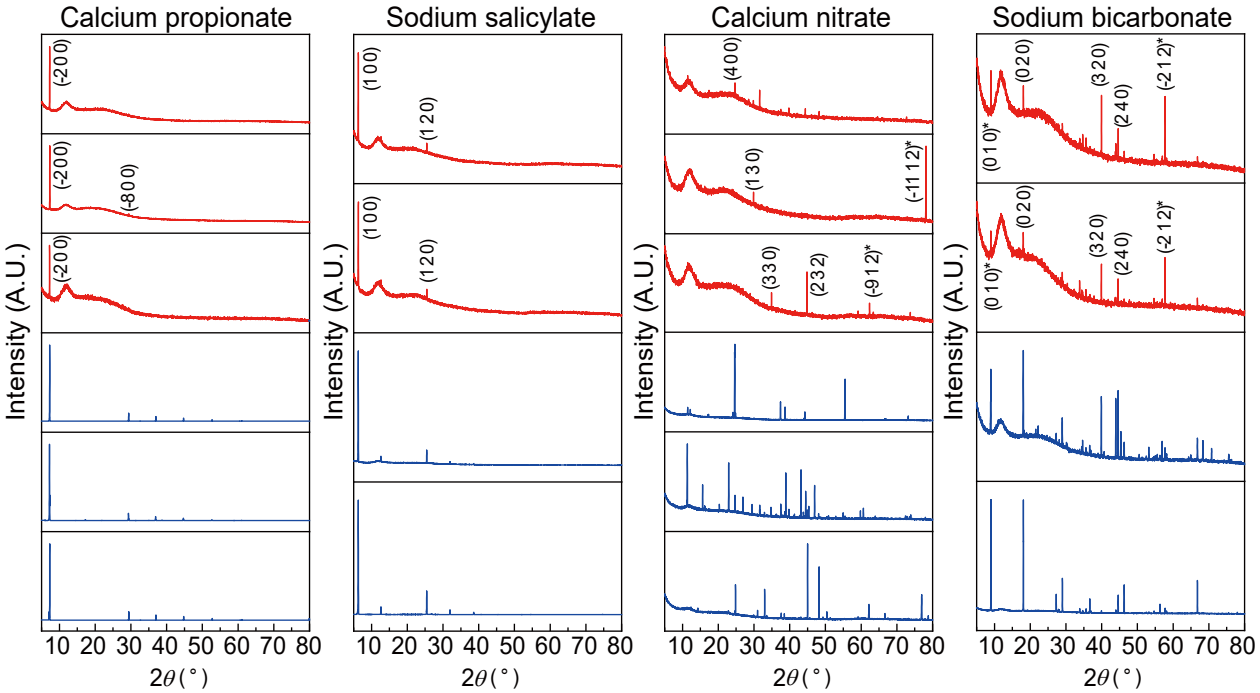

Fig. S3. X-ray diffraction (XRD) results for the different crystal structures of four minerals. For each material, red lines and blue lines are the XRD lines of the spherical crystal shell on the PDMS substrate and the bulk planar crystal structure, respectively. At the XRD results of the spherical crystal shells, Miller indices are marked near the corresponding peaks. Miller indices are mainly determined by corresponding to the standard powder diffraction cards of ICDD. Several indices marked with an asterisk symbol peaks are not found in the cards, and estimated using equation (6) in the manuscript.

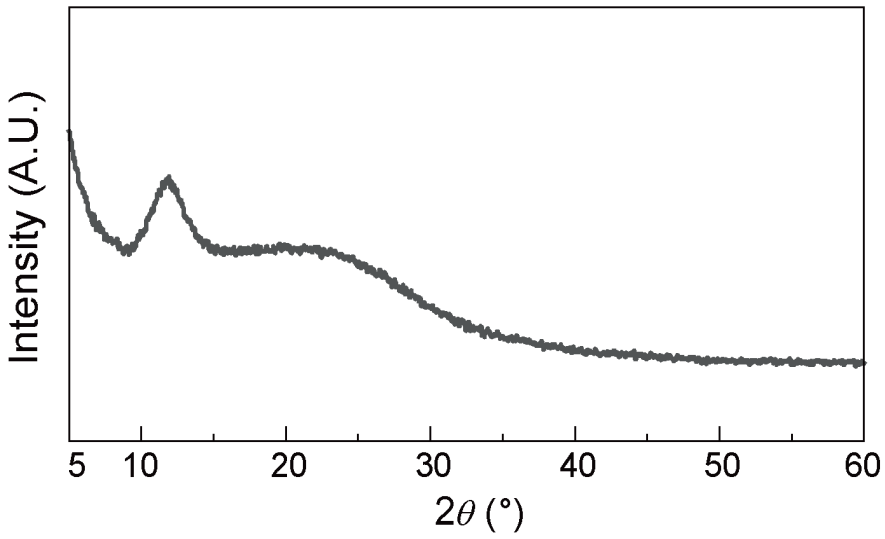

Fig. S4. X-ray diffraction result of the PDMS.

Supplementary Note for Fig. S4. There is no sharp peaks but a hump shape is shown between 10 and 15 degrees, which is observed in Figs. S3, S5, and Fig. 5 of the manuscript.

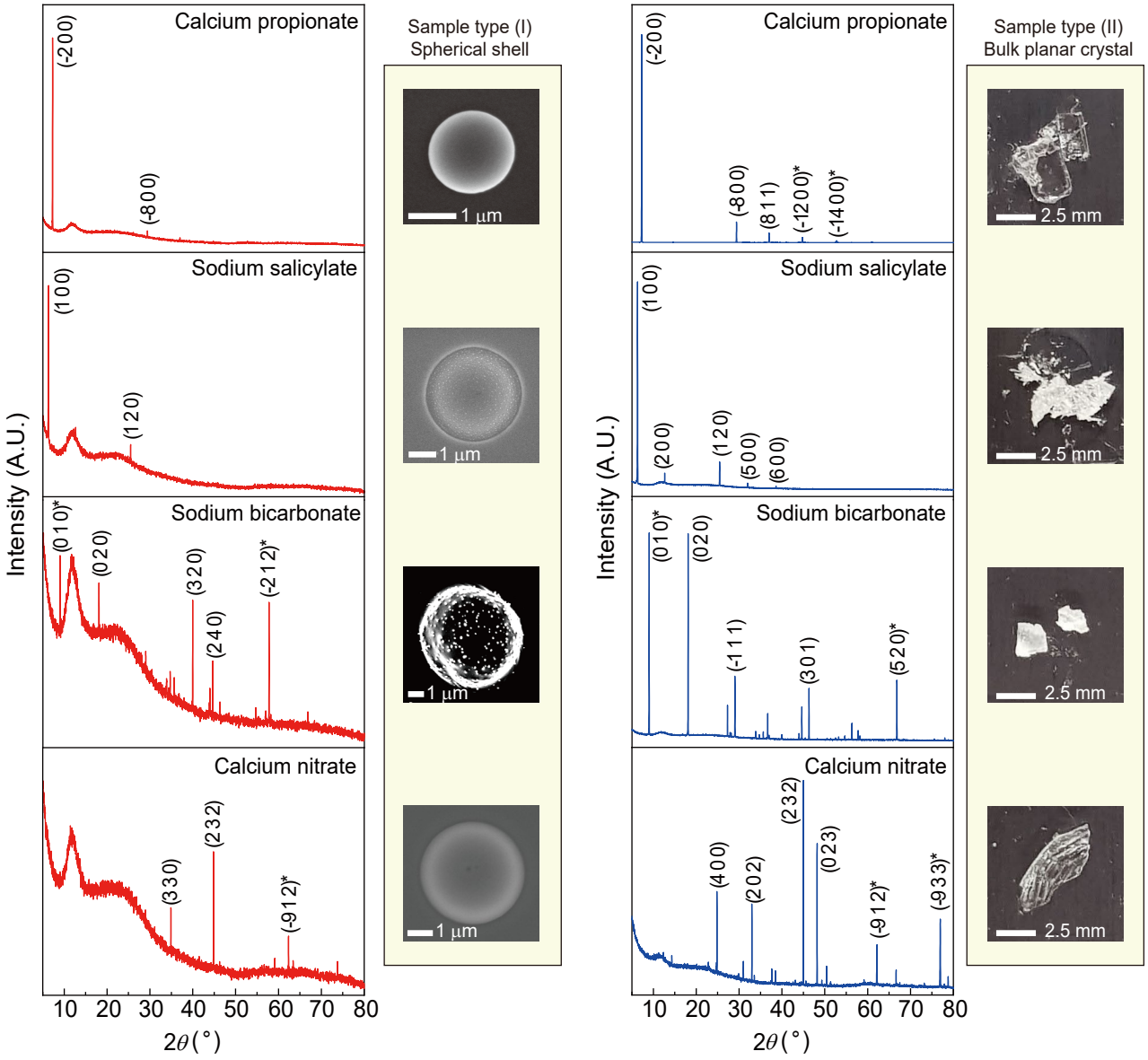

Fig. S5. X-ray diffraction results and images for the two sample types of the four salts. The red and the blue diffraction lines correspond to (I) spherical crystal shells on the PDMS substrate and (II) the bulk planar crystal structures, respectively. Sample type (I) was obtained using the current method as described in Fig. 1a. Sample type (II) was obtained from the dried surface of filter paper that the salt-saturated aqueous solution completely wet, and the crystal structure was created on the paper when the solution dried. Some sets of three digits indicate Miller indices near the dominant peaks in the XRD results. Scale bars: (I) 1 μm and (II) 1 mm.

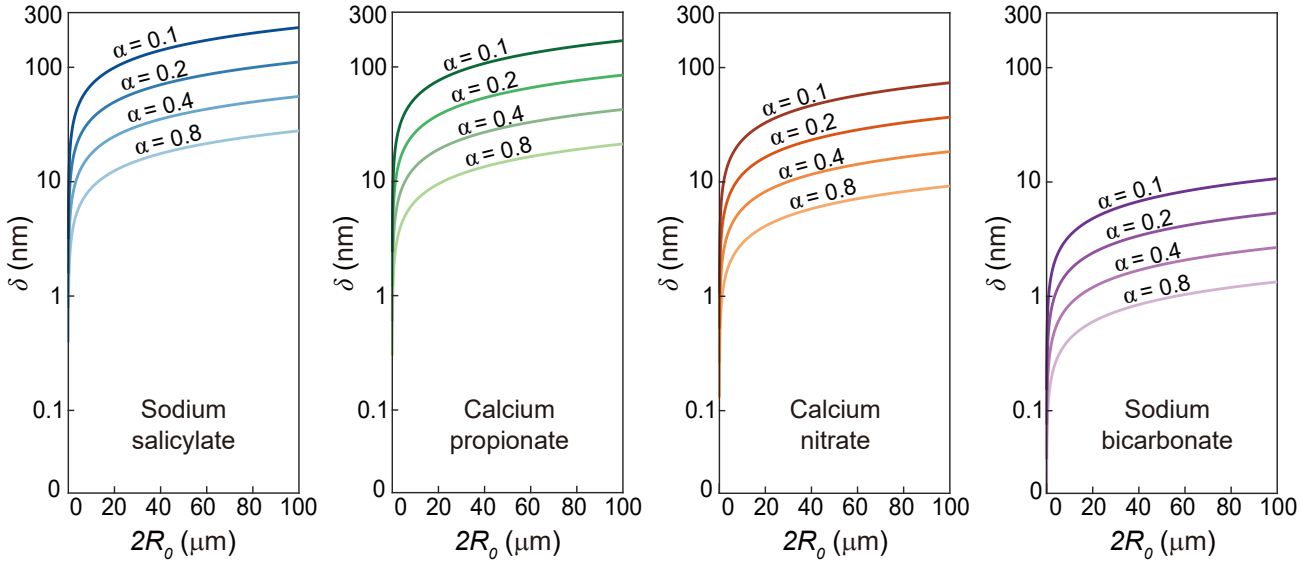

Fig. S6. Estimation of the crystal shell thickness. Prediction of the shell thickness δ for each salt with the initial emulsion size $2R_0$ and the size change ratio α (R_f/R_0) using inequality (4) in the article. Interfacial tension at the W/O emulsion and flexural strength of the salt are set to 40 mN/m and 1 MPa, respectively. All plots are the semi-logarithmic graphs of a lin-log type.

Table S1. Material properties and lattice parameters of the minerals.

	Calcium propionate	Sodium salicylate	Calcium nitrate	Sodium bicarbonate
Molecular weight (g/mol)	186.22	160.11	160.09	84.01
Solution density ρ_w [g/mL]	1.08	1.13	1.40	1.00
Solubility S [g/100 g water]	50	124.6	129	9.6
Young's modulus E [GPa]	$3^{(a)\,1}$	$7.1^{(b)\,2}$	14.04^{3}	$31.2^{(c)\,3}$
Lattice dimension a [Å]	24.3751	14.005	14.477	7.475
Lattice dimension b [Å]	6.8124	7.2197	9.16	9.686
Lattice dimension c [Å]	5.9143	6.7284	6.285	3.481
Skew angle β [°]	95.32	93.50	98.42	93.38

Supplementary Note for Table S1. Young's moduli of calcium propionate, sodium salicylate, and sodium bicarbonate are not exactly known. Instead, in the cases of calcium propionate and sodium salicylate, they are estimated from (a) that of Testosterone propionate and (b) that of acetylsalicylate (aspirin), respectively. In the case of sodium bicarbonate, it is estimated from (c) shear modulus G for sodium carbonate. Young's modulus E is calculated using the relation $E = 2G(1+\nu)$ (Poisson's ratio ν is assumed as 0.3). Lattice parameters of each salt refer to the data of the standard powder diffraction file (PDF) of International Centre for Diffraction Data (ICDD): PDF 55-1317 (calcium propionate), PDF 30-1928 (sodium salicylate), PDF 26-1406 (calcium nitrate tetrahydrate), and PDF 15-0700 (sodium bicarbonate).[4]

References

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[4] S. Gates-Rector and T. Blanton, *Powder Diffr.*, 2019, **34**, 352–360.