Electronic Supplementary Information

Shape design of aqueous bubble stabilized with millimeter-sized polymer plates

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Materials

Unless otherwise stated, all materials were guaranteed reagent grade. The following chemicals were used without further purification: 2-propanol (≥99.5%, Sigma-Aldrich), trichloro(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)silane (≥97%, FUJIFILM Wako Chemicals), *n*-hexane (≥95.0%, Sigma-Aldrich), glycerol (≥99.5%, Sigma-Aldrich), diiodomethane (99%, Sigma-Aldrich), ethylene glycol (≥99%, Sigma-Aldrich), 1,1,2,2-tetrabromoethane (98%, Sigma-Aldrich), 1-undecanol (99%, Sigma-Aldrich), *n*-dodecane (≥99%, Sigma-Aldrich), heptane (≥99.0%, TCI) and ethyl-2-cyanoacrylate (NO04612, >95%, Toa Gosei Co. Ltd.). Poly(ethylene terephthalate) (PET) plates were obtained from Nakajima Metal Leaf, Powder Co. Ltd. PET board (PET-6010) was purchased from C.I. Takiron Co. Ltd. PET film (Lumirror #38-S10) was obtained from Panac Co. Ltd. Water purification was performed using an Advantec MFS RFD240NA (GA25A-0715), and the deionized water (non degassed) was used for all experiments.

Preparation of square and triangle poly(ethylene terephthalate) (PET) plates

Transparent and square- and triangle-shaped PET plates with one side length of 2, 3, 4, 5 mm and thicknesses of 38 μm were prepared from the PET sheets using a cutting machine (SDX1200, CNZ0531, Brother Industries, Ltd., Nagoya, Japan) fitted with thin fabric auto blade (Brother Industries, Ltd., Nagoya, Japan) and replacement blade for automatic adjustment (CADXBLDQ1, Brother Industries., Ltd., Nagoya, Japan). The transparent PET film was adhered onto low tack adhesive mat (Brother ScanNCut SDX Low tack adhesive mat CADXMATLOW12, Brother Industries, Ltd., Nagoya, Japan) in order for the plates not to scatter away, and was cut into the square- and triangle-shaped plates using a commercial software (Brother CanvasWorkspace). The low tack adhesive mat with PET plates was placed in a glass bottle (5-128-25, As One Co., Osaka, Japan) containing 300 mL toluene, and the PET plates were then peeled off from the low tack adhesive mat by sonicating in an ultrasonic bath (Branson Co., St. Louis, US) for 30 min.

Hydrophobization of polymer plates

Hydrophobization was conducted using hydrophobic silane coupling agent, as reported previously[1-2]. The pristine PET plates (70 g) were sonicated in 2-propanol (300-400 mL) for 10 min and the supernatant was discarded. This cycle was repeated 3 times. The washed PET plates were firstly dried in ambient atmosphere for a week and then left under vacuum overnight. The dried PET plates (10 g) were dispersed in n-hexane (40 mL), followed by addition of trichloro(1H,1H,2H,2H-heptadecafluorodecyl)silane (40 μL). During the reaction time of 30 min, the dispersion was shaken every 5 min for approximately 30 s to ensure homogeneous surface modification of the PET plates. Subsequently, the modified PET plates were rinsed three times with n-hexane. The hydrophobized PET plates were firstly dried in atmosphere for 24 h and then left under vacuum overnight. PET board and PET films (2 cm × 2 cm) were hydrophobized in the same manner as the PET plates.

Contact angle measurement

The static contact angles of water droplets (5 μL) in air were measured 30 s after they were deposited onto the PET film at 20 °C using a contact angle measuring instrument

(SImage 02 V, Excimer Inc.). The static contact angles of air bubbles (5 μL) in water were measured 30 s after they were deposited onto the PET film at 20 °C using a contact angle measuring instrument (DMs-401, Kyowa Kaimen Kagaku Co. Ltd.).

Observation of bubbles using optical digital camera and stereo microscopy

Bubbles were observed using an optical digital camera (STYLUSTG-6, Olympus Co., Ltd.) and a stereo microscope (STZ-161-TLED-1080M, Shimadzu Rika Co.) with an attached multioutput digital camera (Moticam1080BMH, Shimadzu Rika Co.). The scale bars were obtained by using a micrometer scale ruler (14028, Shinwa Rules Co. Ltd.).

Scanning electron microscopy

Scanning electron microscopy (SEM) images were taken with a VE-8800 instrument (Keyence, Japan) at gun voltages of 12 kV. To avoid charging, the samples were sputter-coated with gold using an Au coater (SC-701 Quick Coater, Elionix, Japan).

Position of PET plate at air-water interface

The position of the PET plate at air-water interface was studied based on superglue method[3]. Ethyl-2-cyanoacryate can react with water and initiate its polymerization. This polymerization proceeds rapidly upon exposure to water surface. By exposure of the PET plates, which was brought to air-water interface from bulk water phase, to the ethyl-2-cyanoacrylate vapor generated at approximately 50 °C in an enclosed box for 30 min, bare air-water surface, where no plate was adsorbed, was covered with poly(ethyl-2-cyanoacrylate) film and the PET plates were trapped at air-water interface. The trapped PET plates were observed by SEM.

Adsorption energy of the plate at air-water interface

The adsorption energy (ΔG) is the free energy for a plate to adsorb from the bulk water phase to the air-water interface and is defined as the difference in free energy between a system $E_{\text{interface}}$, where one large face of a plate is in contact with water, the other large face is in contact with air, and the side faces of the plate are in contact with air half and water half (Here, it was assumed that the PET plate adsorbed to the air-water interface

with equal volumes to both the aqueous and vapor phase sides.), as compared to a system E_{water}, where the plate is entirely in contact with water plus a free air-water interface ($E_{\text{interface}} - E_{\text{water}}$). The energies $E_{\text{interface}}$ and E_{water} for hexagonal plates are given by Equations S1 and S2, respectively.

$$E_{\text{interface}} = \left(\frac{3\sqrt{3}}{2}S^2 + 3ST\right)(\gamma_{AS} + \gamma_{WS})$$

(Equation S1)

$$E_{\text{water}} = \left(3\sqrt{3}S^2 + 6ST\right)\gamma_{WS} + \frac{3\sqrt{3}}{2}S^2\gamma_{AW}$$

(Equation S2)

where S is the side length of the hexagonal plate; T is the thickness of the plate; and γ_{AS}, γ_{WS}, and γ_{AW} are the air-plate, water-plate, and air-water interfacial energies, respectively. Using Equations S1 and S2, ΔG is given by Equation S3.

$$\Delta G = \frac{3\sqrt{3}}{2}S^2(\gamma_{AS} - \gamma_{WS} - \gamma_{AW}) + 3ST(\gamma_{AS} - \gamma_{WS})$$

(Equation S3)

In the similar manner, the ΔG value was calculated for the plate with adsorption position that one large face of a plate is in contact with air, and the other faces of the plate are in contact with water, using the Equation S4.

$$\Delta G = \frac{3\sqrt{3}}{2}S^2(\gamma_{AS} - \gamma_{WS} - \gamma_{AW})$$

(Equation S4)

The ΔG value was calculated for the plate with adsorption position that one large face of a plate is in contact with water and the other faces of the plate are in contact with air, using the Equation S5.

$$\Delta G = \frac{3\sqrt{3}}{2} S^2 (\gamma_{AS} - \gamma_{WS} - \gamma_{AW}) + 6ST(\gamma_{AS} - \gamma_{WS})$$

<div align="right">(Equation S5)</div>

For the calculations, $S = 1$ mm, $T = 38$ μm, $\gamma_{AS} = 7.6$ mN/m, $\gamma_{WS} = 41.8$ mN/m, and $\gamma_{AW} = 72.8$ mN/m were used. Here, γ_{AS} was determined based on Zisman plot[4-5] using the liquids shown in the Material section of te Supplementary Information.
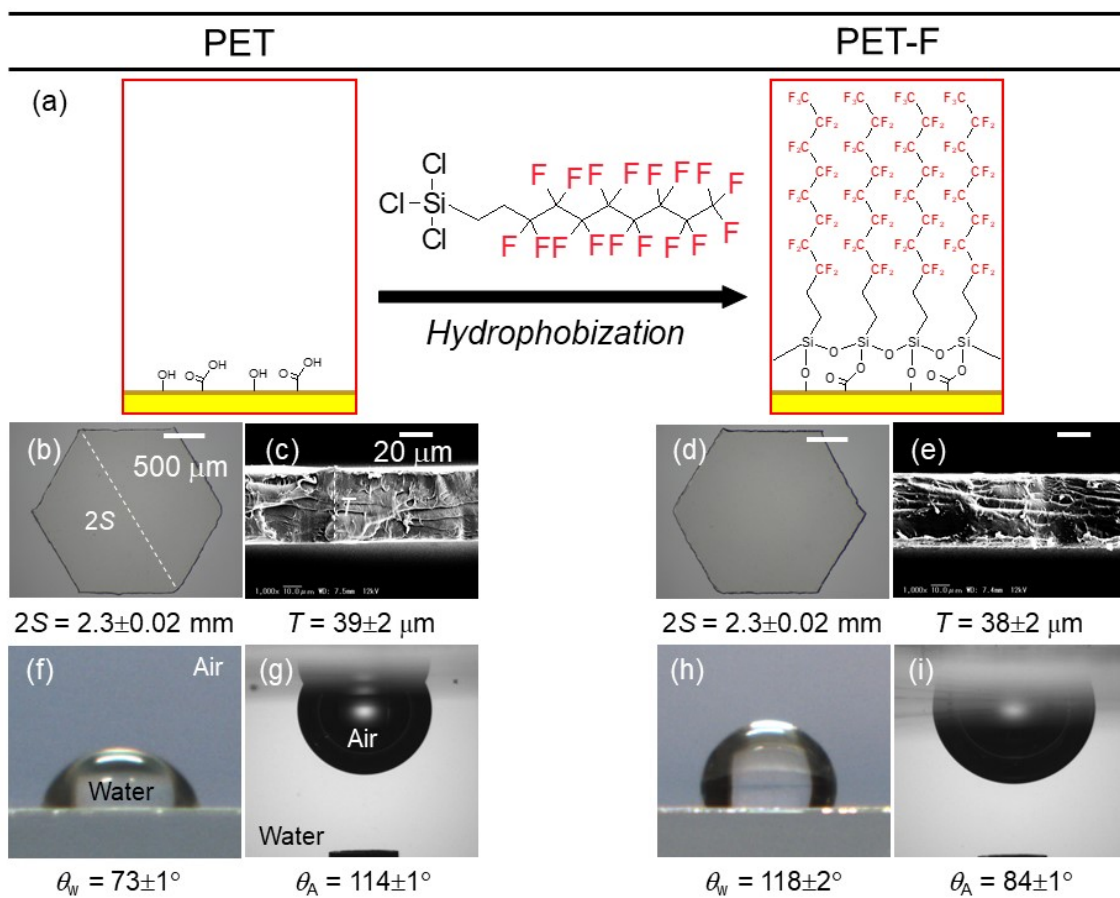
Figure S1   (a) Schematic representation, (b,d) stereo microscopy and (c,e) SEM images of PET plates/films (b,c) before and (d,e) after hydrophobization. Contact angles of (f,h) water droplet (5 μL) in air and (g,i) air bubble (5 μL) in water placed on PET films (f,g) before and (h,i) after hydrophobization.
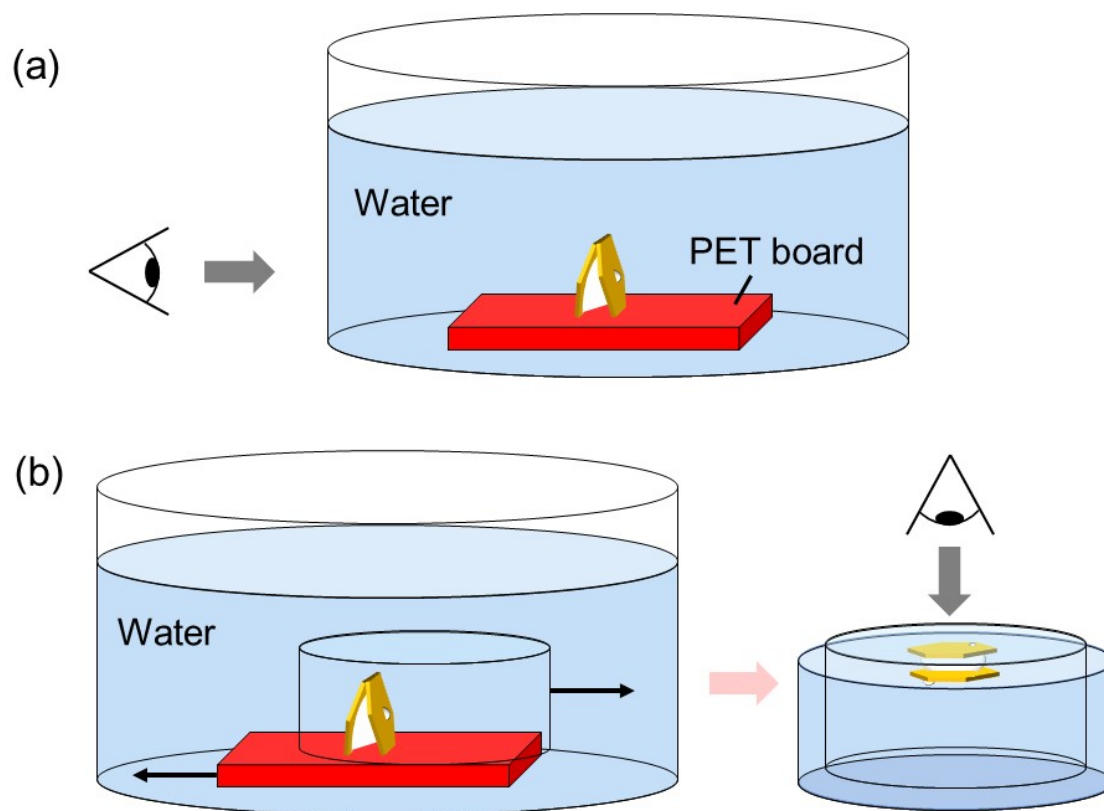
Figure S2 Schematic representation of fabrication/observation of polyhedral bubbles stabilized with hydrophobic PET plates. The bubbles were observed from (a) side and (b) top.
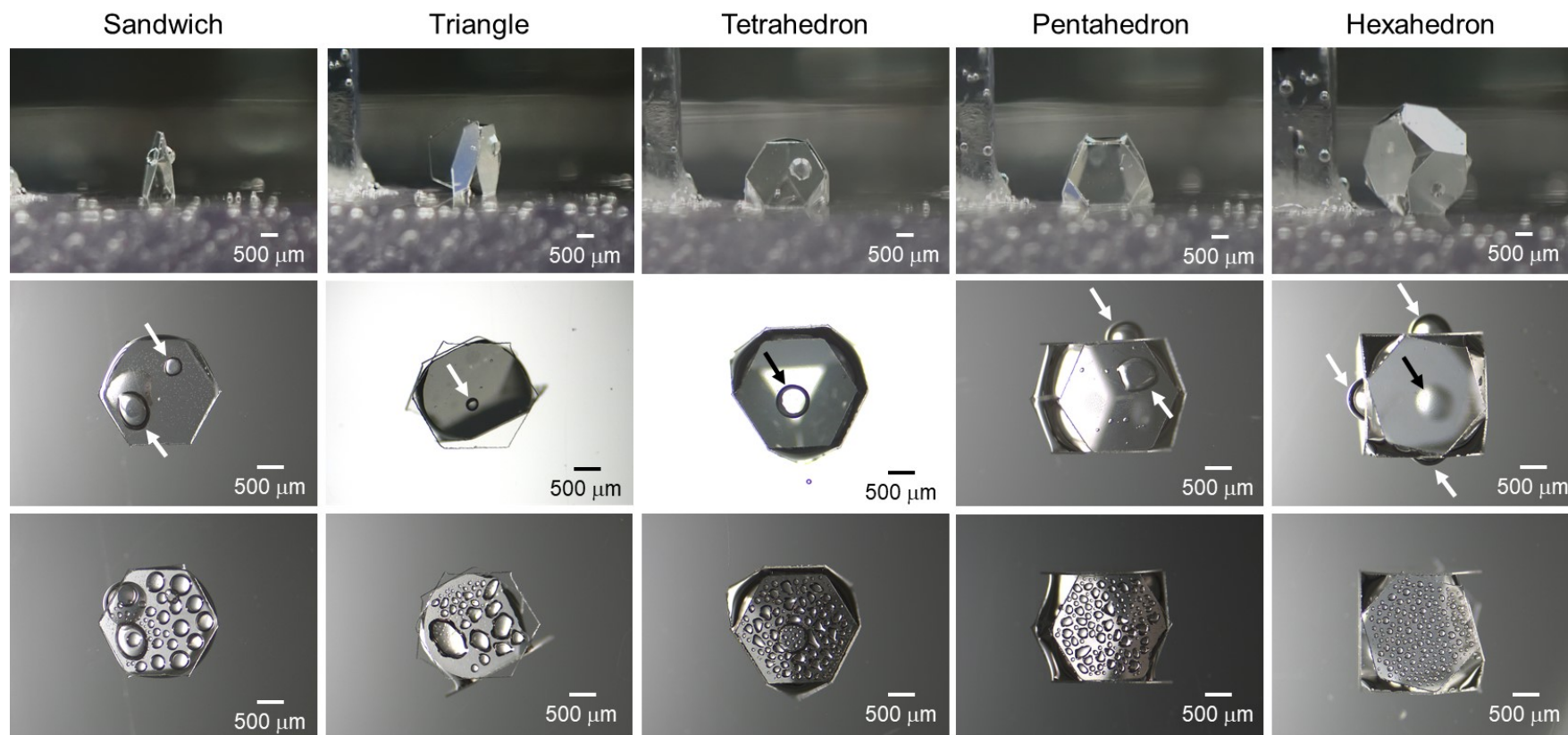
Figure S3 (Top row) Digital photographs and (middle and bottom rows) stereo micrographs of bubbles with sandwich, triangular, tetrahedral, pentahedral and hexahedral shapes in water medium. The images in top row were taken from side and those in middle and bottom rows were taken from top. The images in bottom row were taken 48 h after preparation of bubbles. Volumes of air bubble: *ca.* 1.5 µL, 2.5 µL, 5.5 µL, 7.0 µL and 10.0 µL. Arrows indicate bare satellite bubbles.
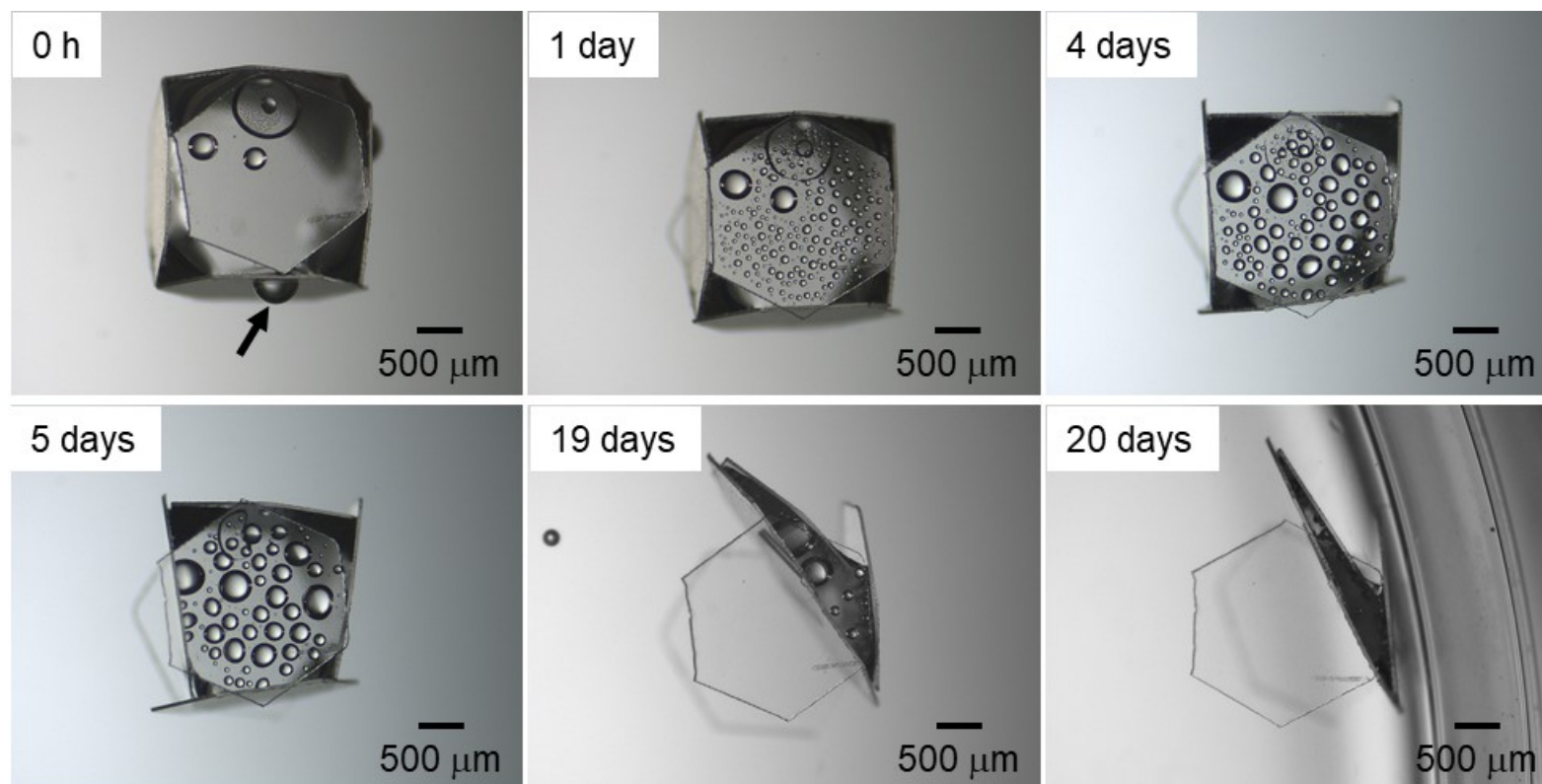
Figure S4   Stereo micrographs illustrating morphological change of a bubble with hexahedral shape after being in water medium (Immediately after preparation, and after 1, 4, 5, 19 and 20 days). The images were taken from top. Arrow indicates a bare satellite bubble.
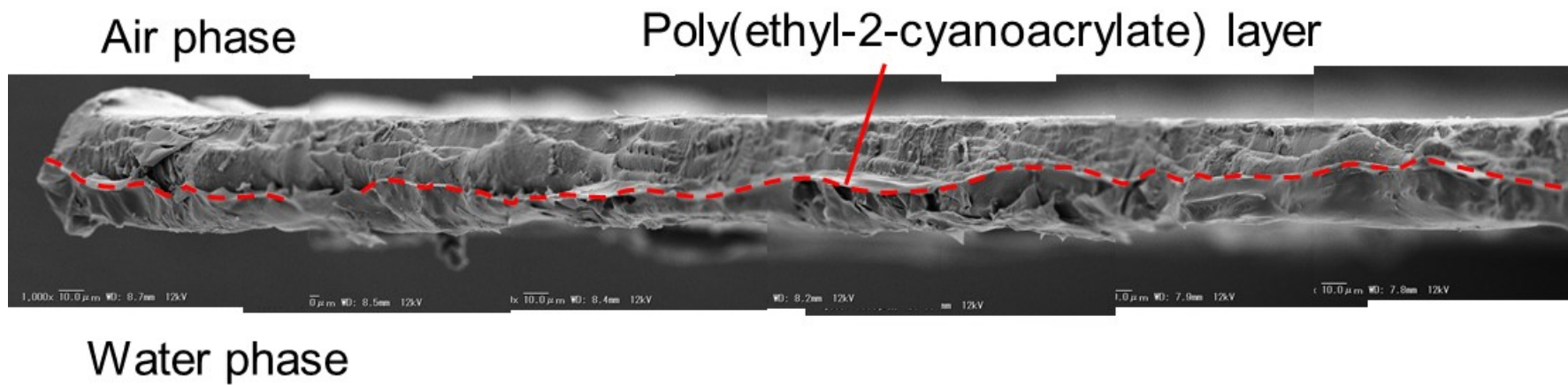
Figure S5   SEM image of PET plate after interfacial anionic polymerization of ethyl-2-cyanoacrylate.
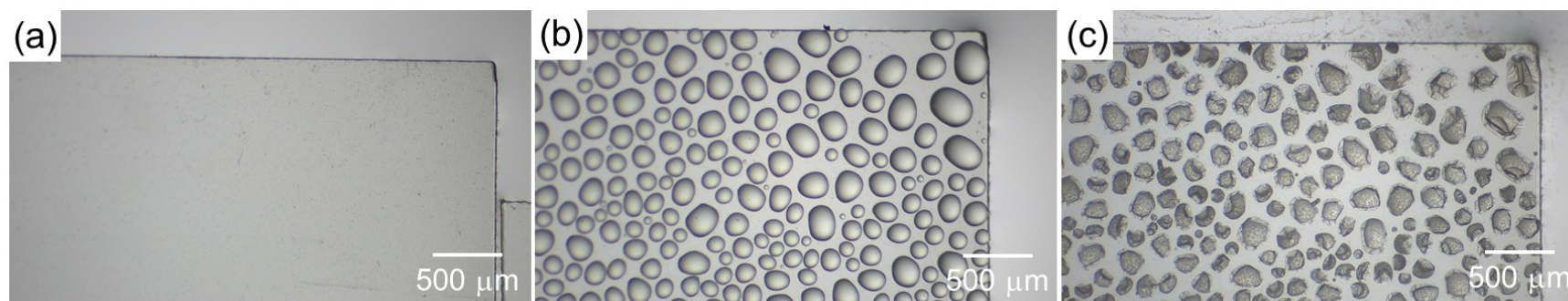
Figure S6 Stereo micrographs of PET film placed on the air-water interface in closed system: (a) Before and (b) after placement on the air-water interface for 24 h. (c) After anionic polymerization of ethyl-2-cyanoacrylate at the surfaces of the water droplets on the PET film, followed by drying.
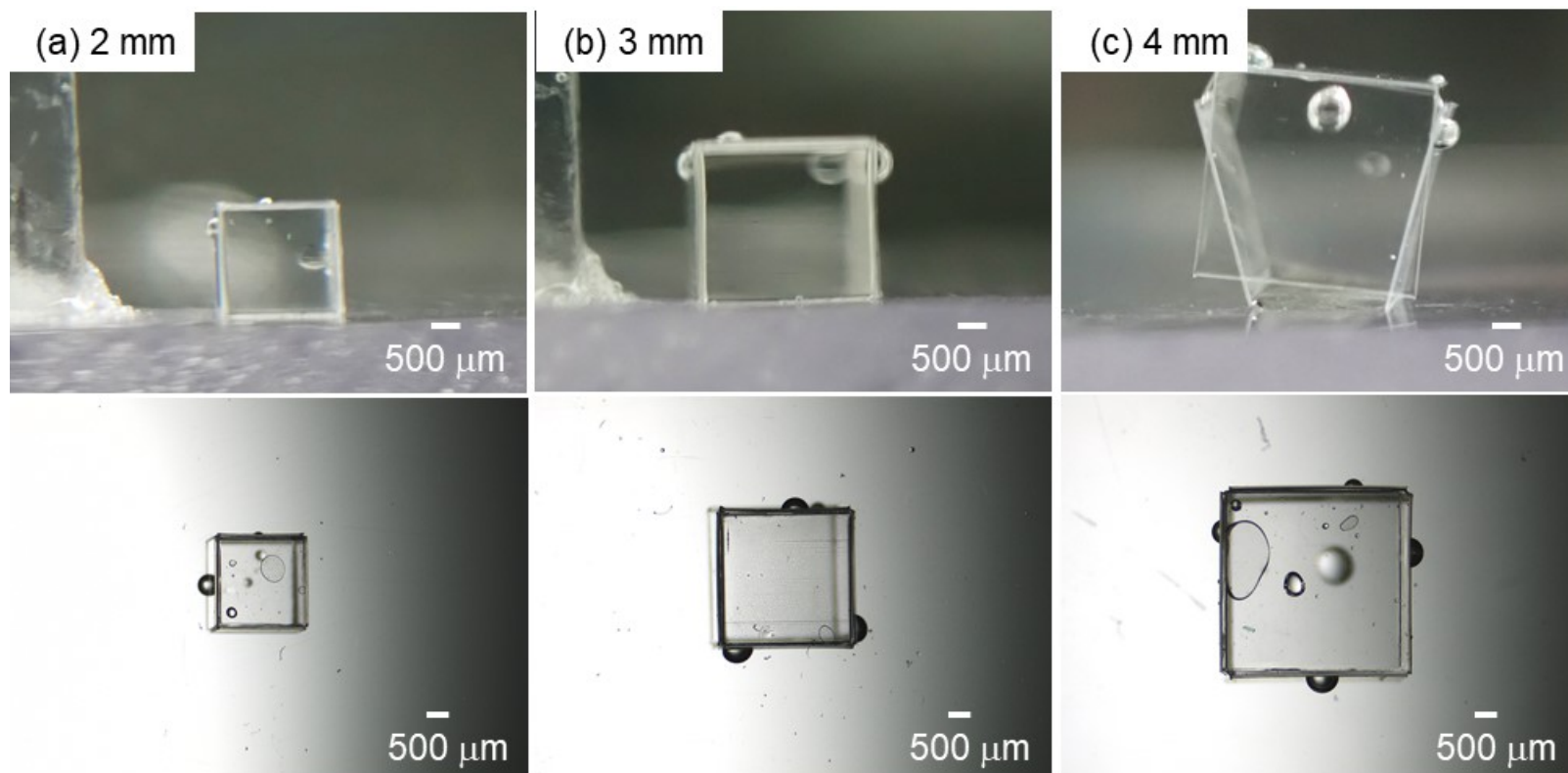
Figure S7 (Top row) Digital photographs and (bottom row) stereo micrographs of bubbles with hexahedral shape stabilized with 6 square plates in water medium. The images in top row were taken from side before the sixth plates were adsorbed (the bottom of the bubbles directly attached to the large substrates). The images in bottom row were taken from top after the sixth plates were adsorbed. Length of a side: (a) 2 mm, (b) 3 mm and (c) 4 mm. Volumes of air bubble: ca. 8 μL, 27 μL and 64 μL. The bubble could not be prepared using square plates with side lengths of > 5 mm, because the bubbles were detached from the large substrates.
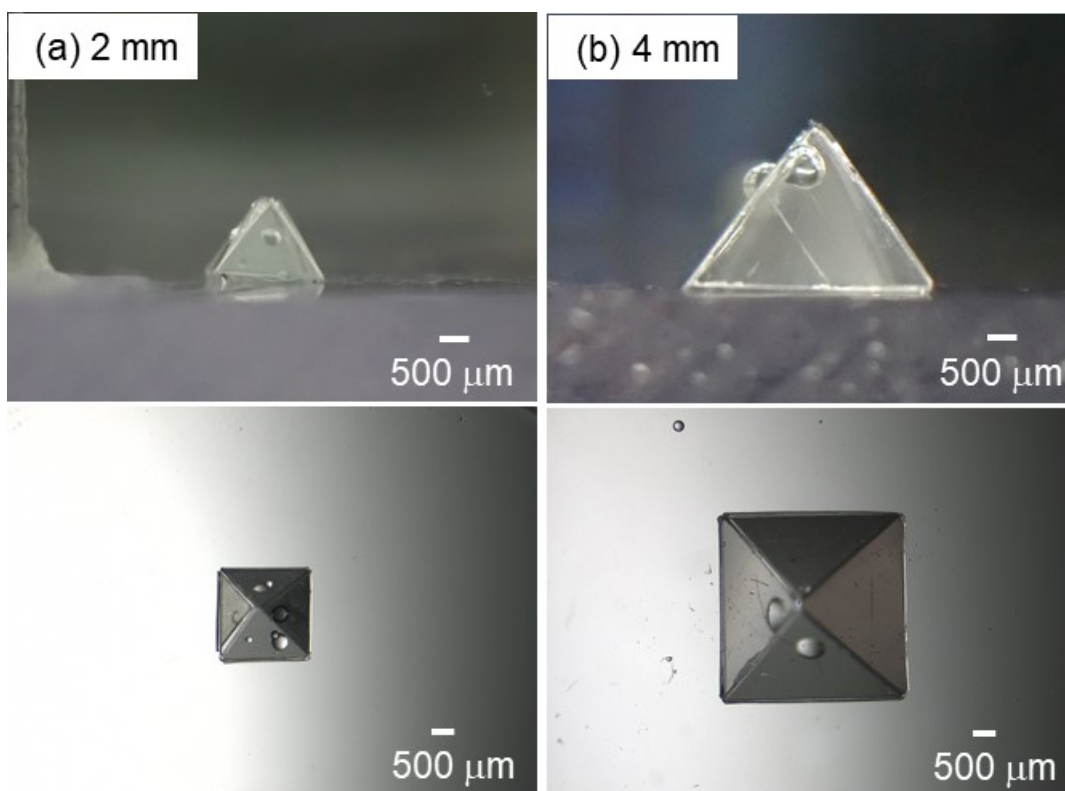
Figure S8 (Top row) Digital photographs and (bottom row) stereo micrographs of bubbles with pyramidal shape stabilized with 1 square plate and 4 triangle plates in water medium. The images in top row were taken from side before the fifth square plates were adsorbed (the bottom of the bubbles directly attached to the large substrates). The images in bottom row were taken from top after the fifth square plates were adsorbed. Length of a side: (a) 2 mm and (b) 4 mm. Volumes of air bubble: 1.8 μL and 17.0 μL.

References

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List of supplementary movie

Supplementary Movie S1   Jointing of two hexahedral bubbles using a metal wire to form a cuboid-shaped bubble.