Electronic Supplementary Information

Soft PDMS-mediated formation of bovine serum albumin 3D coffee stain structures for reversible hydrophilic patterning

Samuel Kok Suen Cheng[a], Kimberly Lopez[a], Maryam Jalali-Mousavi[a], and Jian Sheng[a,*]

[a]College of Engineering, Texas A&M University-Corpus Christi, Corpus Christi, TX 78412, USA

*Corresponding author: Jian Sheng, Department of Engineering, Texas A&M University – Corpus Christi, 6300 Ocean Drive, Corpus Christi, TX 78412, Tel: (361)825-3731. Email: jian.sheng@tamucc.edu

S.1 Methods and methodology

Materials. Heat-shock treated bovine serum albumin (BSA, Fraction V, Cat# BP1600-1) is purchased from Fisher Scientific, and CD®488A conjugated BSA (Cat# 20289) is obtained from Biotum. BSA is reconstituted using DI water produced by Milli-Q, Sigma-Aldrich (Cat# CPDI000L1). PDMS Sylgard™ 184 silicone elastomer kit (Cat# 04019862) is purchased from Dow Silicones Corporation. Octadecyltrichlorosilane (OTS, Cat# 147401000), toluene (Cat# T290-4), hydrogen peroxide (Cat# H325-500), acetone (Cat# A18-20), methanol (Cat# A412- 20), and isopropanol (Cat# A416-20) are purchased from Fisher Scientific. Sulfuric acid (ACS, Cat# 9681-03) is supplied by J. T. Baker.

OTS surface functionalization. The glass slide used for OTS functionalization is first piranha etched by using a mixture of sulfuric acid and hydrogen peroxide (3:1 ratio) at 120°C for 3 hours. The piranha etched glass is then washed with DI water, acetone, methanol, isopropanol, and DI water, followed by drying with N_2 and placed at a 200°C hot plate for at least 2 hours. The etched glass is then plasma etched using an oxygen plasma cleaner (Tergeo Plasma Cleaner, PIE Scientific) for 1 min 20 s and immediately soaked in a mixture of OTS and toluene (0.2% v/v OTS) for 20 mins. After that, the glass is soaked in toluene for 3 mins, dried with N_2 gas, and baked in an oven at 95°C for 30 mins. Next, the glass slide is again soaked in toluene for 3 mins before washing with DI water, acetone, methanol, isopropanol, and DI water. The OTS functionalized glass is dried with N_2 gas and baked on a hot plate at 120°C for 2 hours.

Drop and protein film characterization. The model hyperbolic paraboloid is generated using MATLAB with the following equation,

$$Z = X^2 - Y^2 \tag{1}$$

where both X and Y are between [-1,1]. The two principal curvatures κ_1 and κ_2 of the buckling protein film are measured using ImageJ by fitting a circle to the film at two orthogonal planes and then taking the inverse of the radius. The mean curvature H and Gaussian curvature K are calculated as

$$H = \frac{(\kappa_1 + \kappa_2)}{2} \tag{2}$$

$$K = \kappa_1 \kappa_2 \tag{3}$$

respectively. The contact angle of the drops is measured using the ImageJ plugin 'DropSnake'.[1] The height and diameter of the drops are measured using ImageJ as well.

AFM measurement. The elasticity of PDMS substrates is measured by nanoindentation using an AFM (TT-2 AFM, AFM Workshop). The two cantilevers used have pyramidal tips and calibrated spring constants of 3.499 and 5.723 N/m respectively. The conversion of the TB signal to cantilever deflection is first calibrated by performing nanoindentation on a piranha-etched glass. The nanoindentation experiments are performed on PDMS samples at 8 randomly selected locations per sample. The obtained force-indentation curves are fitted with the standard linear solid (SLS) model with Ting's integral to obtain the 3 parameters in the model: instantaneous elastic modulus E_0, long-term elastic modulus E_∞, and relaxation time τ at each location.[2] The SLS model is as follows:

$$\boldsymbol{E(t) = E_\infty + (E_0 - E_\infty) e^{-\frac{t}{\tau}}} \tag{4}$$

where t denotes the time. The Ting's integral for indentation of a viscoelastic sample reads as follows:

$$\boldsymbol{F\left(t,\delta(t)\right)=\begin{cases}\dfrac{2C_n}{(1-\upsilon^2)}\displaystyle\int_0^t E(t-\xi)\frac{\partial\delta^{\frac{n+1}{n}}}{\partial\xi}d\xi, 0\le t\le t_m\\ \dfrac{2C_n}{(1-\upsilon^2)}\displaystyle\int_0^{t_1(t)} E(t-\xi)\frac{\partial\delta^{\frac{n+1}{n}}}{\partial\xi}d\xi, t_m\le t\le t_{ind}\end{cases}} \quad (5)$$

$$\int_{t_1(t)}^{t} E(t-\xi)\frac{\partial\delta}{\partial\xi}d\xi=0 \quad (6)$$

where F is the force acting on the cantilever, δ is the indentation depth, t_m is the duration of the approach phase, t_{ind} is the time duration of the whole indentation cycle, t_1 denotes the auxiliary function obtained from Eq. (3), ξ is a dummy variable necessary for the integration, E is the Young's relaxation modulus, υ is the Poisson's ratio, n and C_n are indenter shape-dependent constants. Hence, the relaxation modulus in Eq. (4) is used in Eq. (5) and (6) and solved using an in-house developed least square optimization MATLAB code. The final parameter values are estimated by averaging the values obtained for all 8 locations.

Hydrophilic surface patterning. For the hydrophilic patterning via evaporation of BSA drops, 10 µL 5% w/v BSA drops are deposited on a 10:1 PDMS substrate and the drops are left to evaporate at room temperature. Once the buckling protein films are formed, the films are removed from the PDMS using a tweezer without touching the surface. The PDMS substrate is then dipped into dyed DI water and immediately pulled out. Any water adhered to the back of the glass slide is removed using a paper towel while no alteration is done on the PDMS surface.

S.2 Supplemental figures and tables

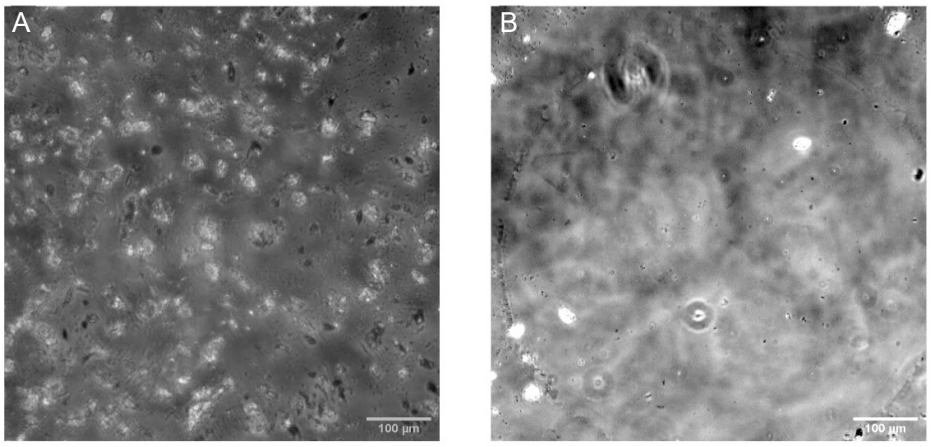

Fig. S1. Differential interference contrast (DIC) images of (A) a pristine PDMS surface and (B) the same surface after the formation of a 3D saddle coffee stain structure (CSS). The surface after removing 3D saddle CSS has much less debris. Scales: 100 µm.

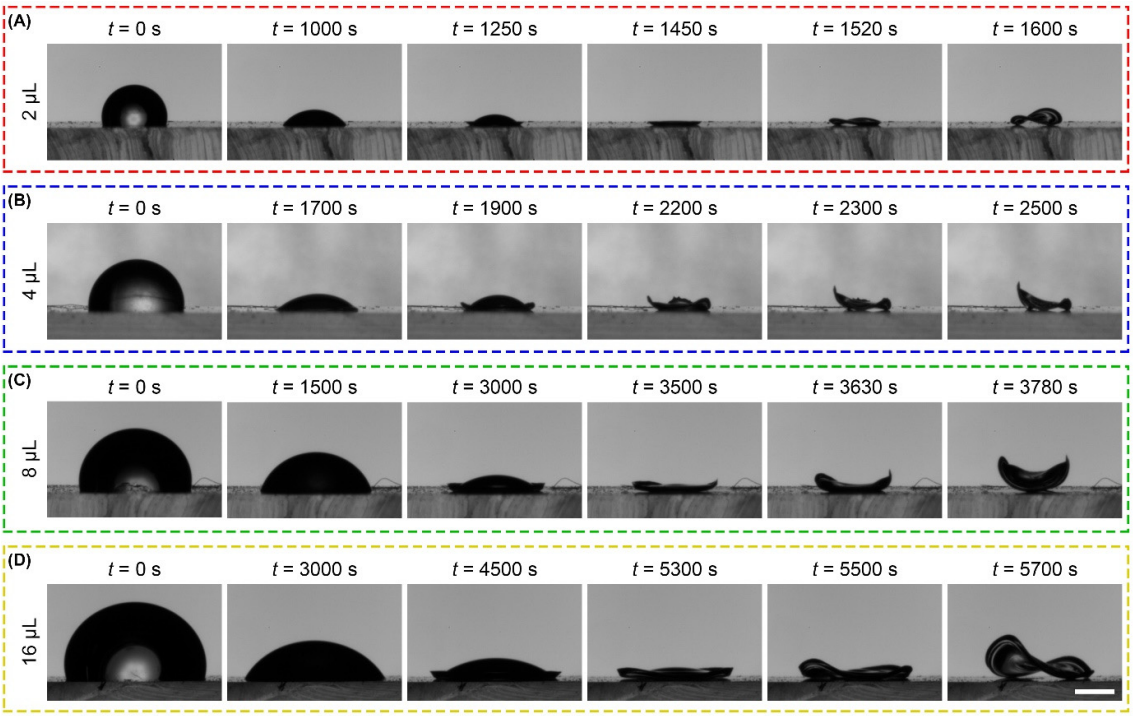

Fig. S2. Evaporation of a (A) 2 µL, (B) 4 µL, (C) 8 µL, and (D) 16 µL 5% w/v BSA sessile drop on a PDMS surface (monomer-to-curing agent ratio = 10:1). Scale: 1 mm.

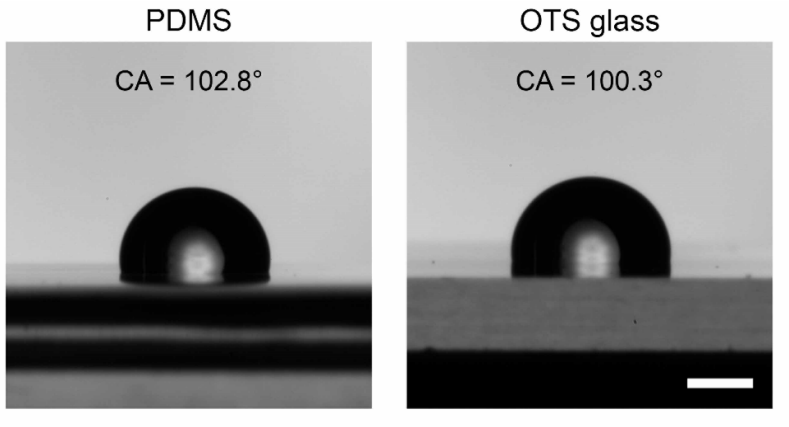

Fig. S3. Contact angle measurement of 5% w/v BSA drop on PDMS and OTS functionalized glass. Scale bar: 1 mm.

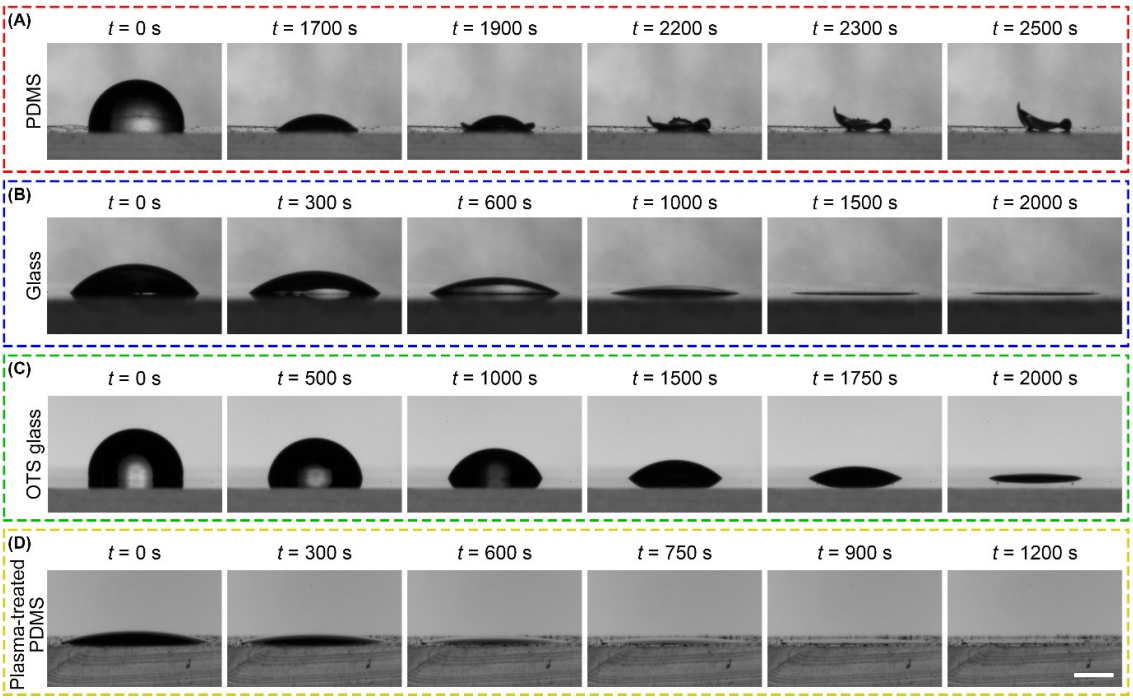

Fig. S4. Evaporation of a 4 µL 5% w/v BSA sessile drop on (A) PDMS (monomer-to-curing agent ratio = 10:1), (B) glass, (C) octyltrichlorosilane (OTS) functionalized glass, and (D) plasma-treated PDMS. Scale bar: 1 mm.

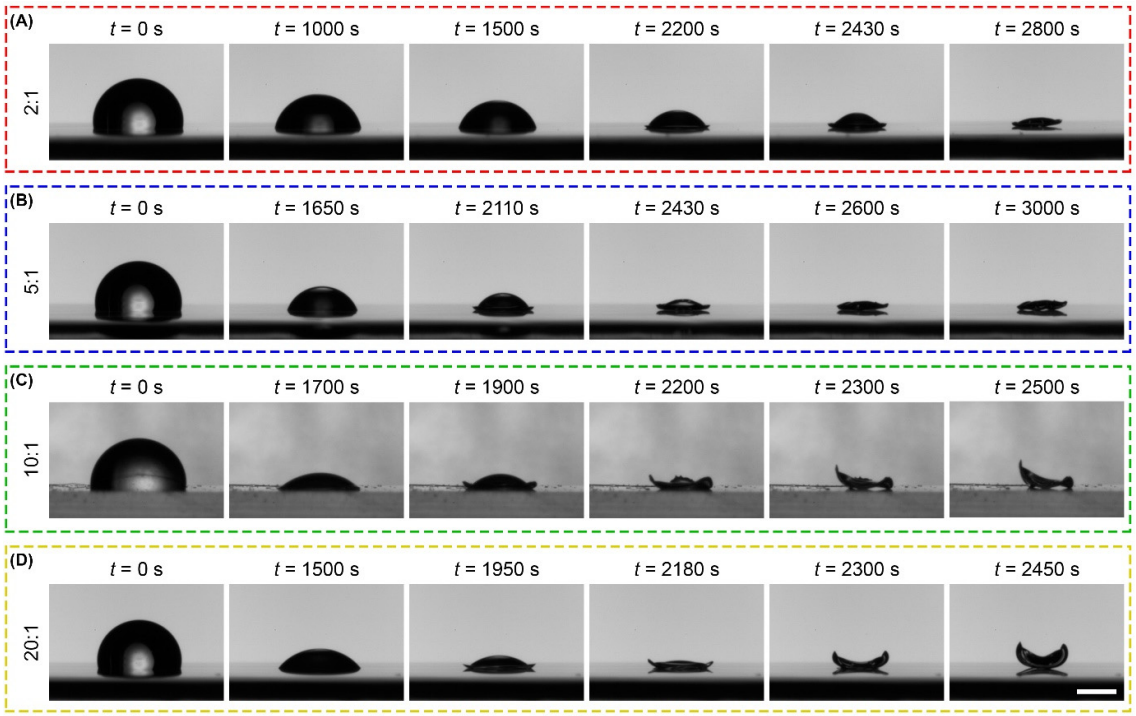

Fig. S5. Evaporation of a 4 µL 5% w/v BSA sessile drop on a PDMS surface with a monomer-to-curing agent ratio of (A) 2:1, (B) 5:1, (C) 10:1, and (D) 20:1. Scale bar: 1 mm.

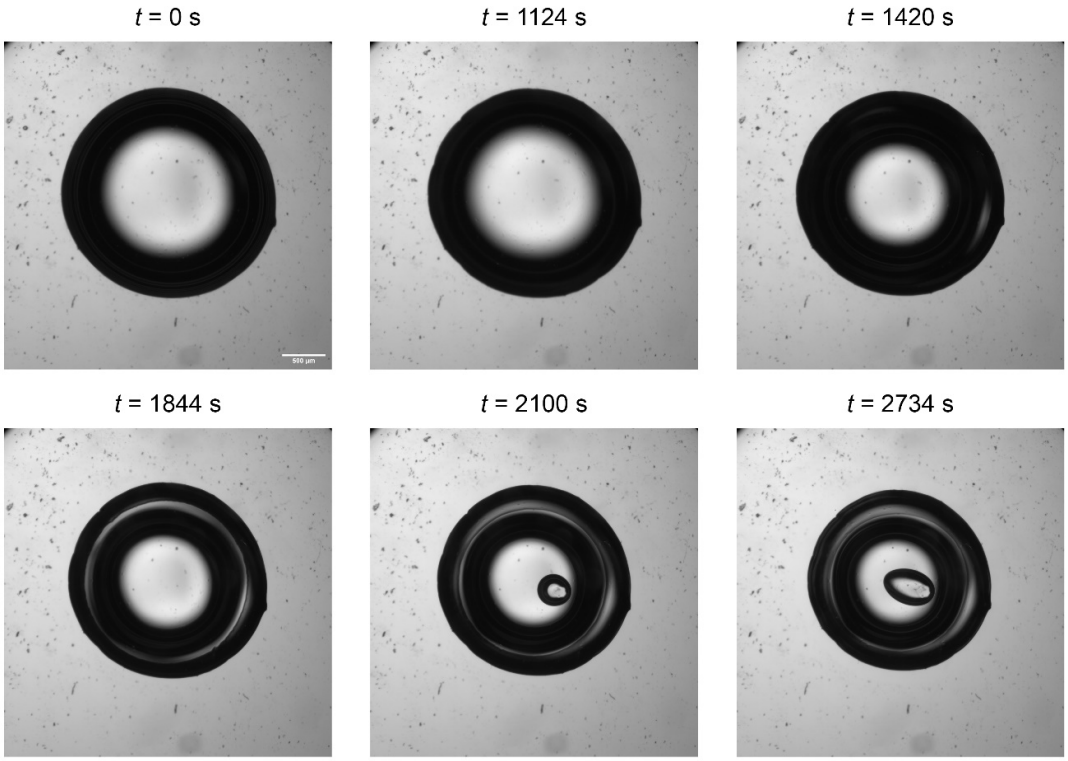

Fig. S6. Top view timelapse images of an evaporating 25% w/v BSA sessile drop on PDMS. Scale: 500 μm.

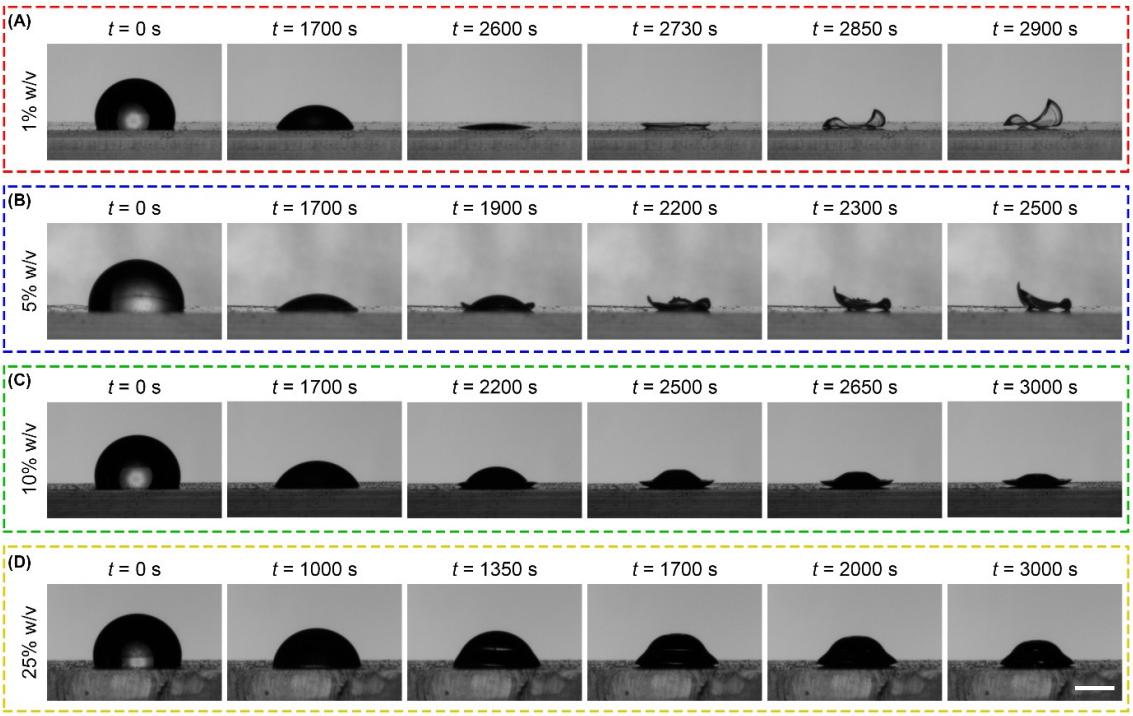

Fig. S7. Evaporation of a 4 µL BSA sessile drop with a concentration of (A) 1%, (B) 5%, (C) 10%, and (D) 25% w/v on a PDMS surface (monomer-to-curing agent ratio = 10:1). Scale: 1 mm.

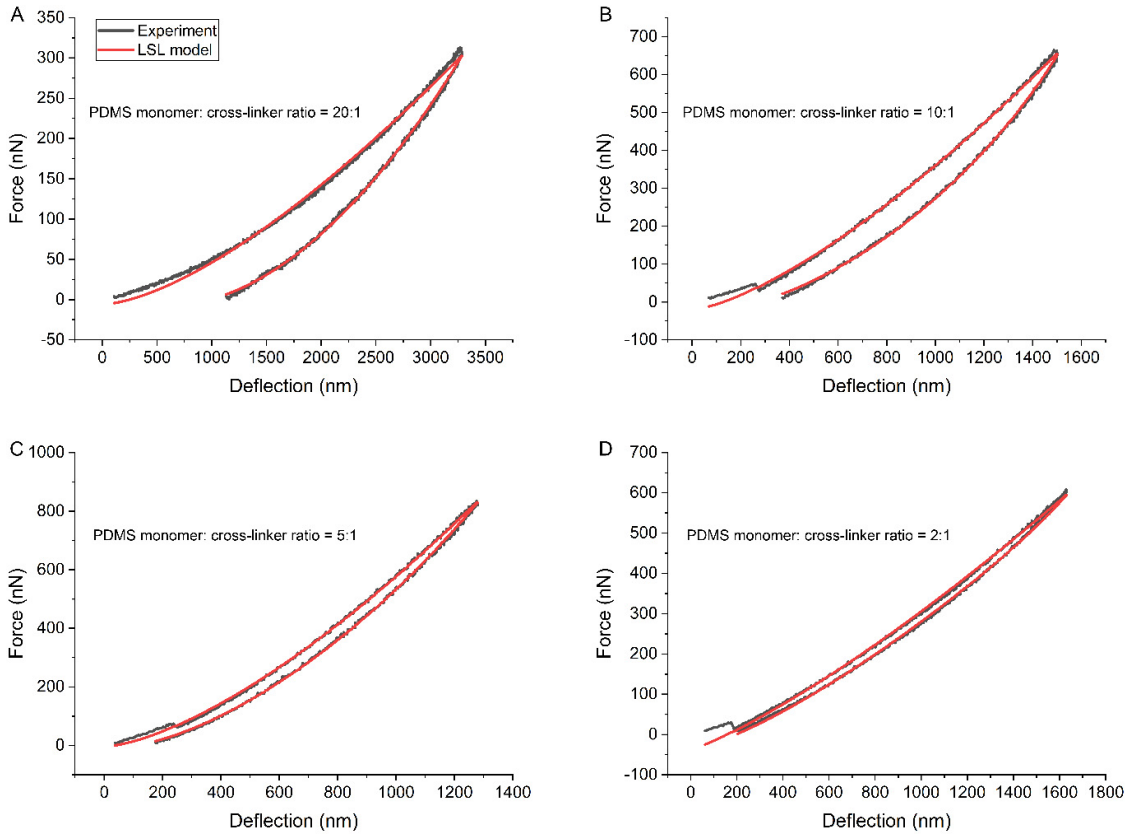

Fig. S8. Experimental force-deflection curves obtained from AFM measurements and the fitted SLS model with Ting's integral model for (A) 20:1, (B) 10:1, (C) 5:1, and (D) 2:1 monomer-to-curing agent ratio PDMS surfaces.

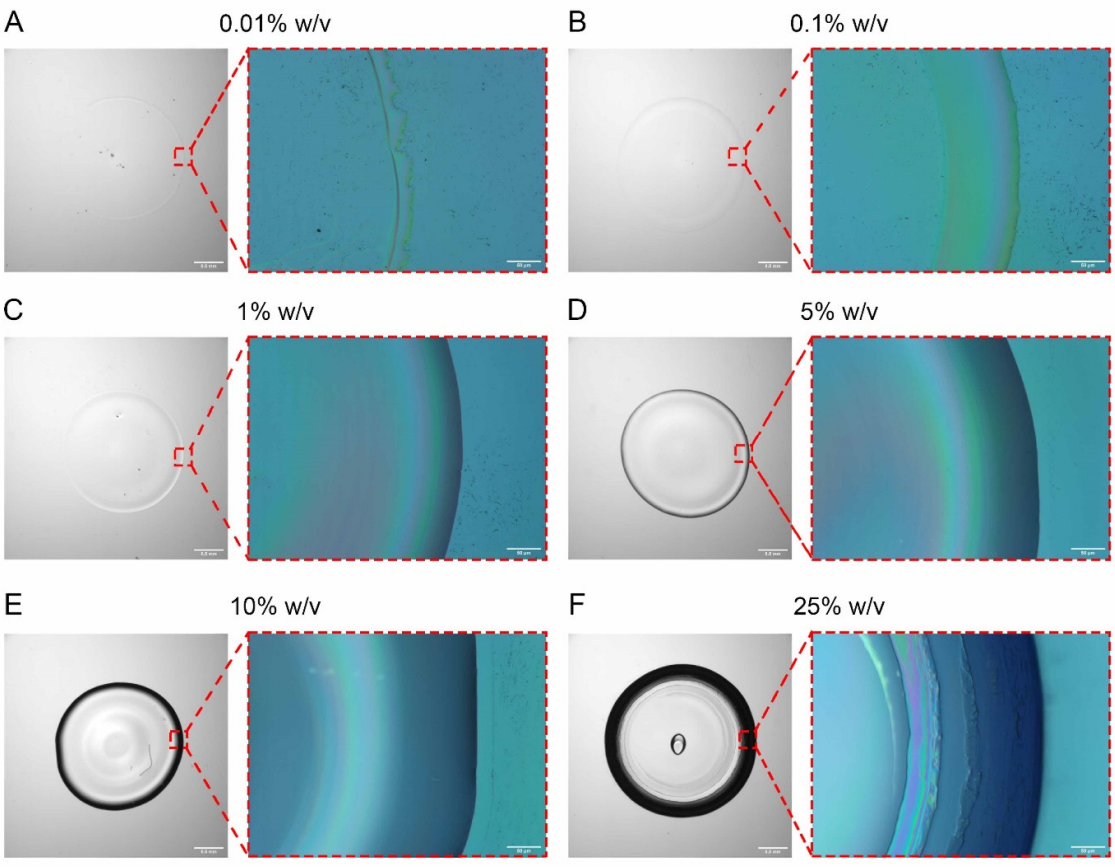

Fig. S9. Final coffee stain structure of (A) 0.01%, (B) 0.1%, (C) 1 %, (D) 5%, (E) 10%, and (F) 25% w/v BSA drops on OTS functionalized glass. Images on the left represent an overall image of the structure imaged using a 4× objective whereas images on the right represent a zoom-in view imaged using a 10× objective. Scale: 0.5 mm (left) and 50 µm (right).

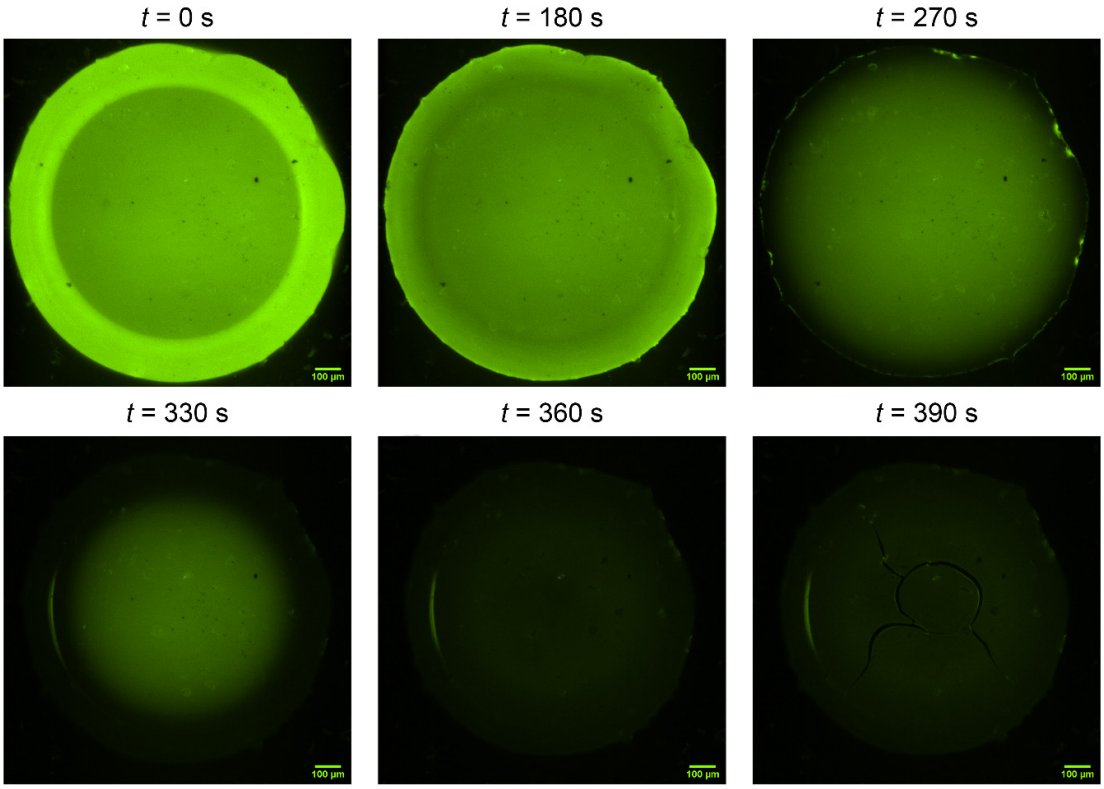

Fig. S10. Time-lapse images of a pure 5% w/v fluorescently-label BSA drop evaporating on a PDMS surface. Scale: 100 µm.

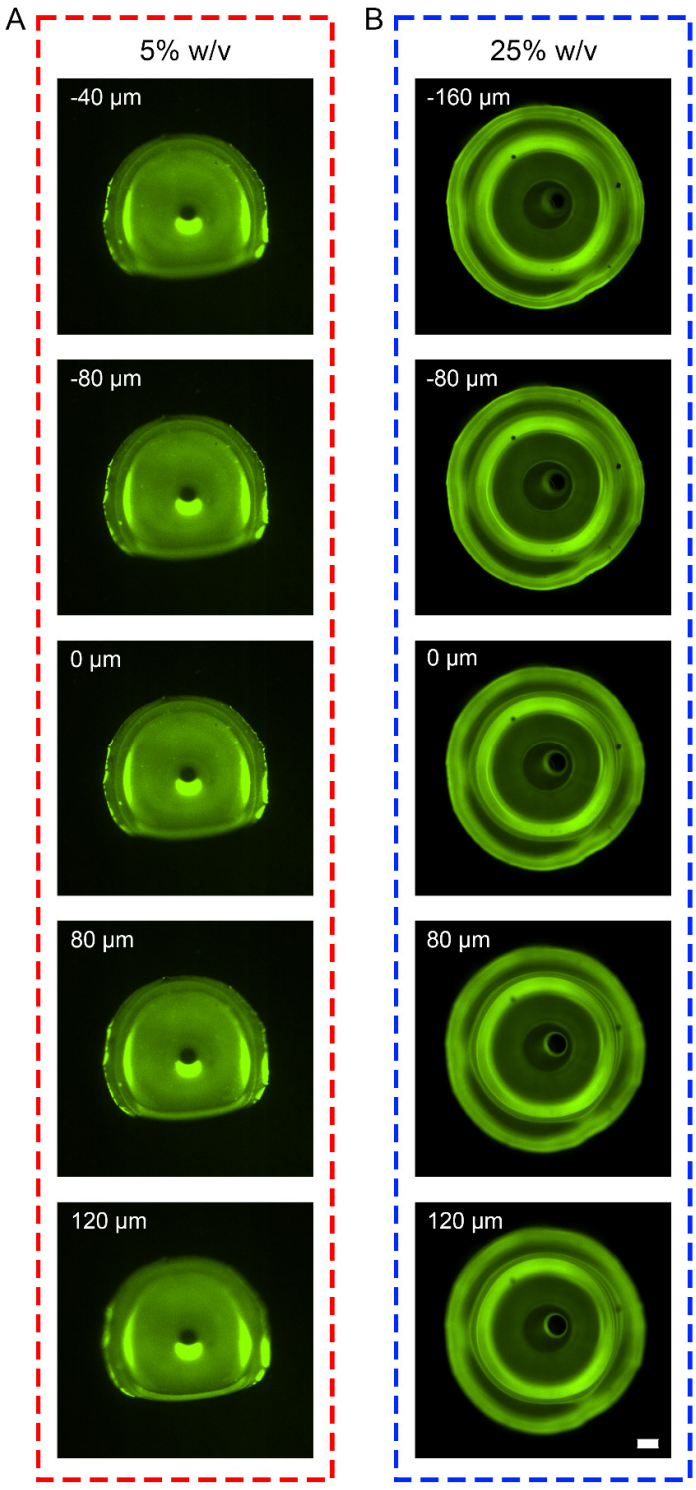

Fig. S11. Z scan images of the 3D coffee stain structure produced by evaporating (A) 5% and (B) 25% w/v mixed fluorescent BSA drops on a PDMS surface. Scale: 200 µm.

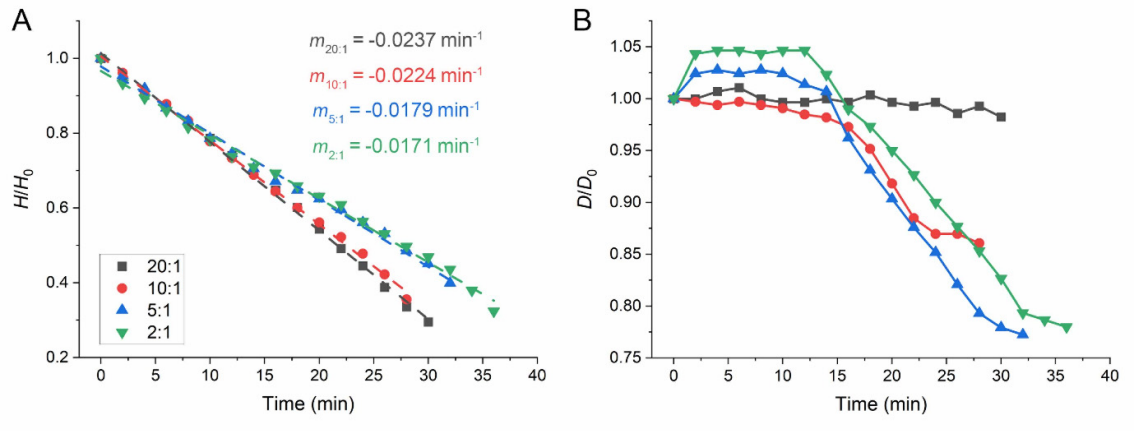

Fig. S12. Variation of the (A) normalized height and (B) normalized diameter of an evaporating 5% w/v BSA drops on PDMS surfaces with varying monomer-to-curing agent ratios.

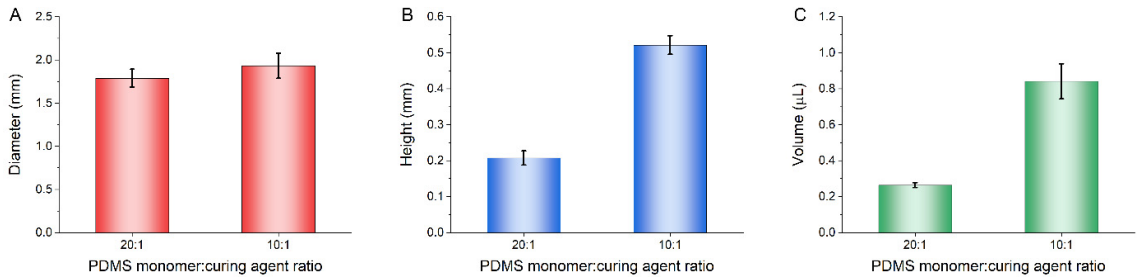

Fig. S13. Characterization of the adhered DI water drop after hydrophilic patterning in terms of the (A) diameter, (B) height, and (C) volume. Error bars represent the standard deviation (n = 3).

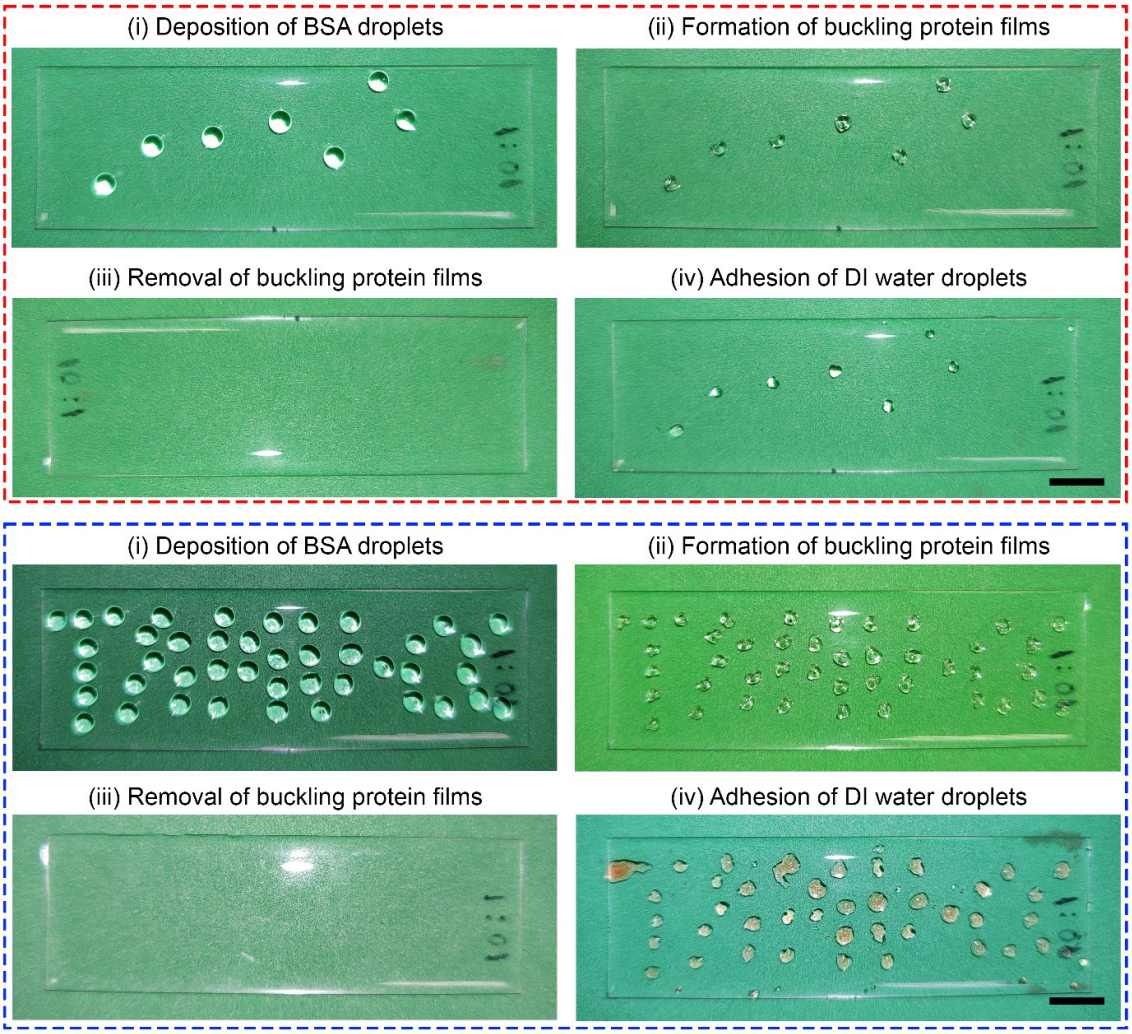

Fig. S14. Hydrophilic patterning of a Big Dipper shape (red dashed box) and 'TAMUCC' shape (blue dashed box) via the evaporation of BSA drops on PDMS surfaces. All the PDMS used have a monomer-to-curing agent ratio of 10:1. Scale: 1.5 cm.

Table S1. Fitted SLS model parameters for PDMS surfaces with different monomer-to-curing agent ratios.

PDMS monomer-to-curing agent ratio	E_0 (MPa)	E_{inf} (MPa)	τ (s)
20:1	0.45 ± 0.26	0.27 ± 0.18	4.57 ± 1.30
10:1	5.61 ± 0.71	4.21 ± 0.51	1.11 ± 0.14
5:1	10.24 ± 1.09	8.75 ± 0.91	1.57 ± 0.33
2:1	59.94 ± 11.27	15.16 ± 9.54	0.78 ± 0.50

Supplementary movie captions

Movie S1: Evaporation of a 4 µL 5% w/v BSA sessile drop on a 10:1 ratio PDMS.

Movie S2: Evaporation of a 4 µL 5% w/v BSA sessile drop on a glass slide.

Movie S3: Top view of the evaporation of a 25% w/v BSA sessile drop on a 10:1 ratio PDMS.

Movie S4: Top view fluorescent imaging of a 0.01% w/v BSA drop on a 10:1 ratio PDMS.

Movie S5: Top view fluorescent imaging of a 5% w/v BSA drop on a 10:1 ratio PDMS.

Movie S6: Top view fluorescent imaging of a 25% w/v BSA drop on a 10:1 ratio PDMS.

Movie S7: Attachment of a DI water drop on the PDMS surface after the evaporation and peeling off the buckling protein film.

Reference

1. A. F. Stalder, T. Melchior, M. Müller, D. Sage, T. Blu and M. Unser, Low-bond axisymmetric drop shape analysis for surface tension and contact angle measurements of sessile drops, *Colloids Surf. Physicochem. Eng. Aspects*, 2010, **364**, 72-81.
2. Y. M. Efremov, W. H. Wang, S. D. Hardy, R. L. Geahlen and A. Raman, Measuring nanoscale viscoelastic parameters of cells directly from AFM force-displacement curves, *Sci. Rep.*, 2017, **7**, 1541.