

# Alignment-free construction of double emulsion droplet generation devices incorporating surface wettability contrast

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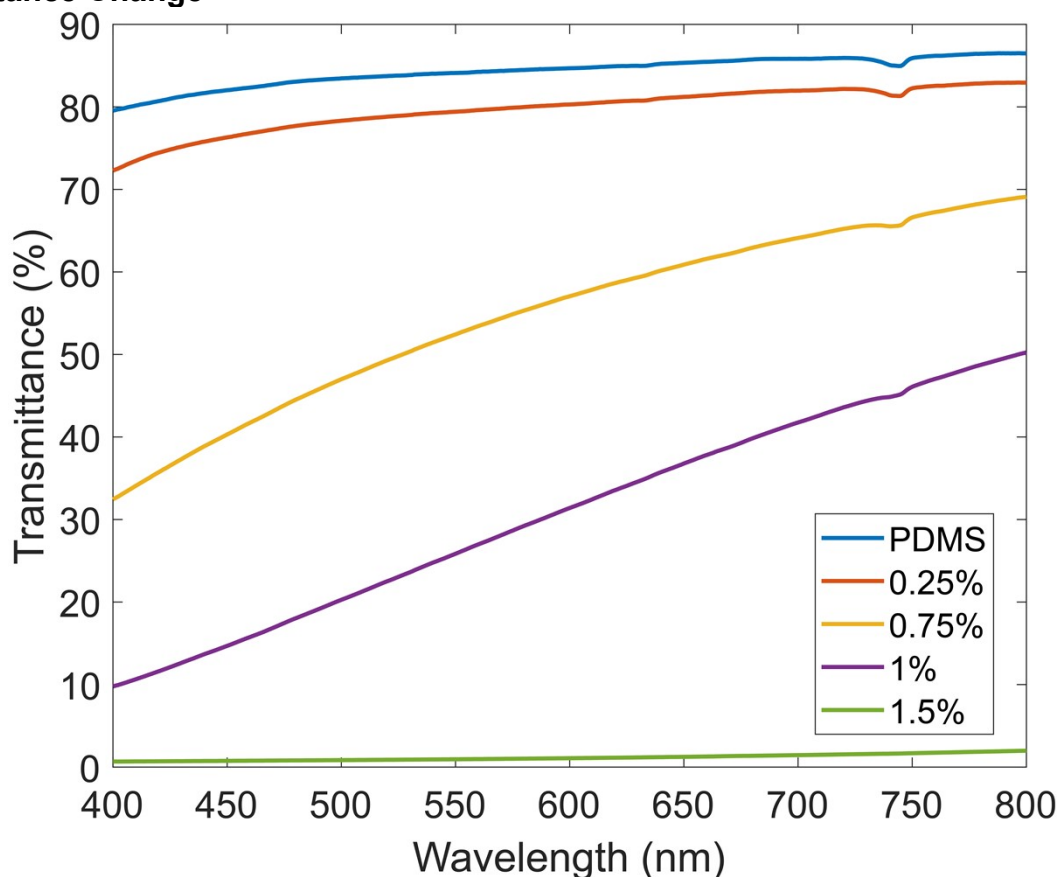
## Supplementary Information

### Videos

ESI Video 1: One-by-one droplet encapsulation.

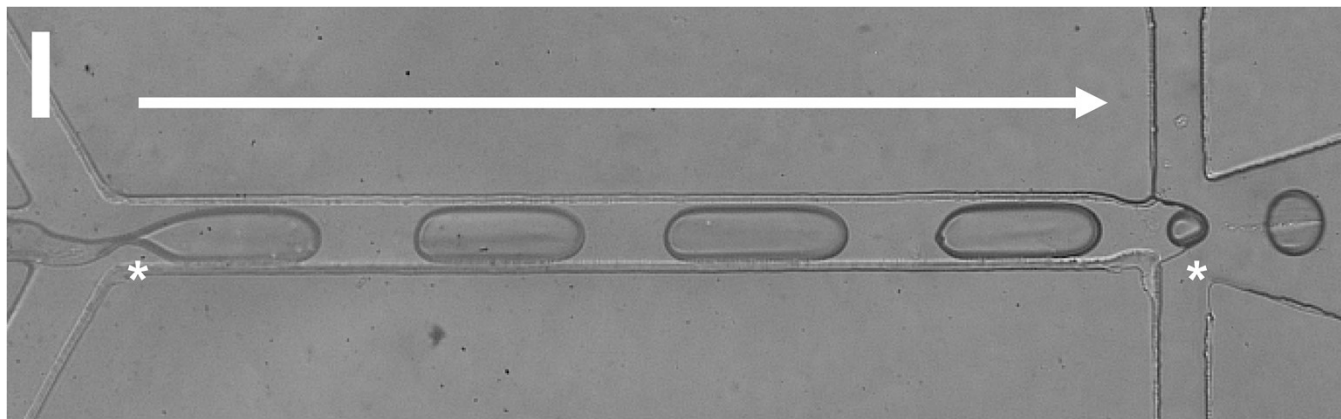
ESI Video 2: Split droplet encapsulation.

### Transmittance Change



**Fig. S1** The transmittance change of PDMS and PDMS-Brij mix of varying concentrations (0.25, 0.75, 1, and 1.5%) across the visible and near infrared (wavelength: 400–900 nm). Transmittance drops to near zero for 1.5% mix and the transmittance change is minimal for 0.25% PDMS-Brij.

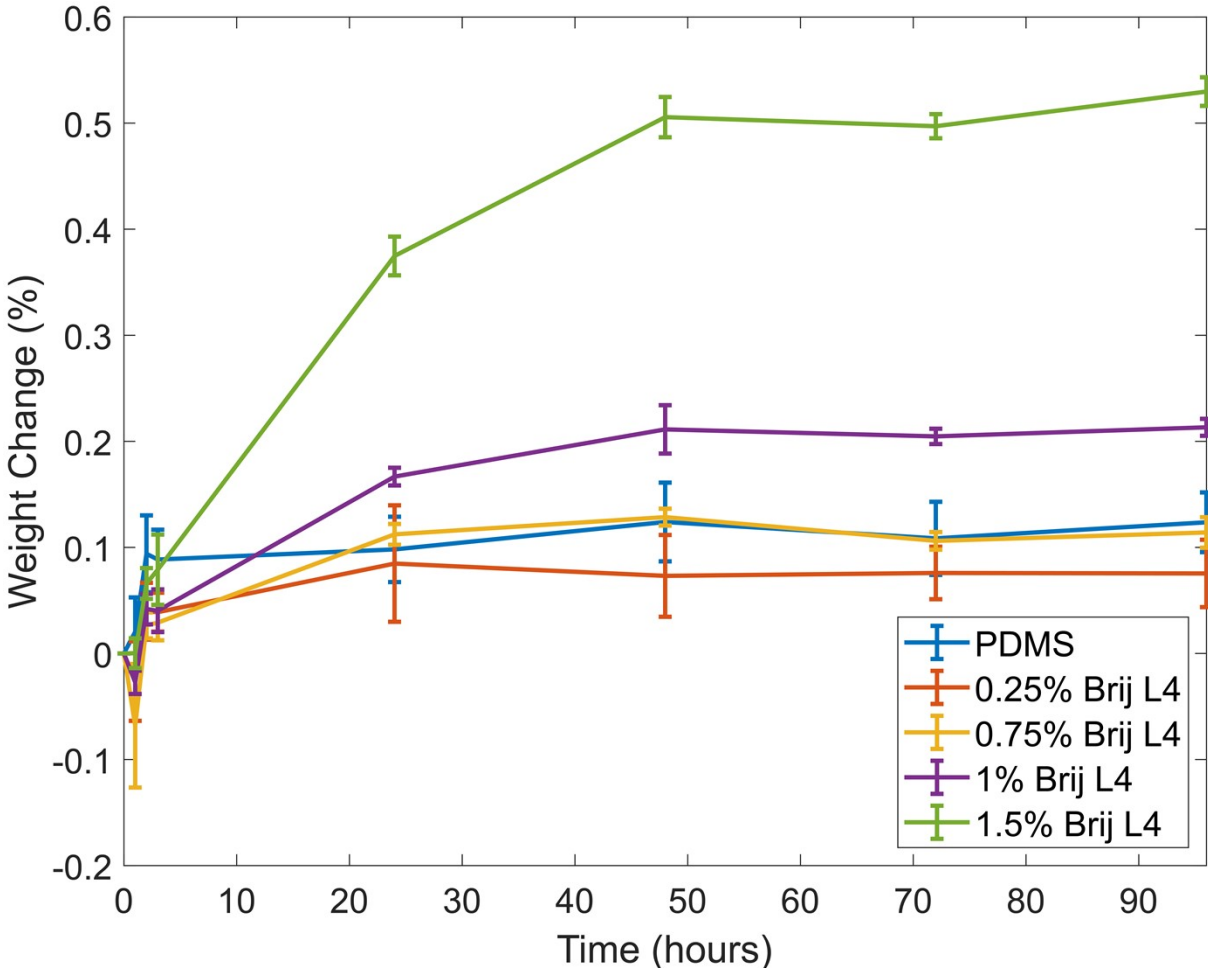
## Double Emulsion Device Design



**Fig. S2** Device design for double emulsion generation including the first and the second junction, white arrow indicates flow direction. The white asterisks show pinching of W/O droplet at the initial junction (left) and W/O/W formation at the second junction (right). Flow rates were  $Q_{in} = 1 \mu\text{l}/\text{min}$ ,  $Q_{mid} = 20 \mu\text{l}/\text{min}$ , and  $Q_{out} = 5 \mu\text{l}/\text{min}$ . Scale bar is  $100 \mu\text{m}$ .

### Swelling Experiment

Four cut pieces, 1 × 1 × 0.5 cm (l × w × h) of pristine PDMS, and PDMS/surfactant mix of concentrations (0.25, 0.5, 1, and 1.5%) were prepared using the fabrication protocol given in manuscript. The weight of the samples was recorded before immersion into a beaker filled with 40 ml of DI water and results were recorded for the first 3 hours (at hourly intervals). Subsequent results were recorded daily until 96 hours. In each measurement, samples were dried with a steam of nitrogen gas after removal from the DI water and weighed on a balance before being immersed again in the beakers. Fig. S3 demonstrates that there is no significant effect of surfactants on the swelling characteristics of the samples. However, prolonged immersion results are unknown. As expected, since increasing hydrophilicity, higher concentrations of the surfactant increase the percentage weight change, although the values are small.



**Fig. S3** Weight change of PDMS and PDMS-Brij mix of varying concentrations (0.25, 0.75, 1, and 1.5%) expressed as a percentage change from the initial weight (N = 4) with standard deviation error bars.

## Diffusivity of Surfactants

Water introduced to the surface is promoting molecular diffusion of polar groups to the surface. The Ward-Tordai equation [33-34] gives the time dependent surface excess concentration ( $c_s$ ) of surfactant,

$$c_s(t) = 2c_0 \sqrt{\frac{Dt}{\pi}} - 2 \sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} c_{ss} d(\sqrt{t-\tau})$$

where  $D$  is diffusion coefficient,  $c_0$  is the bulk concentration,  $c_{ss}$  is the subsurface concentration and  $\tau$  is a dummy integration variable. For short time scales, the second term on the right side, representing backwards diffusion can be neglected [34], and Ward-Tordai equation can be simplified to

$$c_s(t) = 2c_0 \sqrt{\frac{Dt}{\pi}}$$

In addition, Gibbs Adsorption Isotherm, which is the basis for a method of measuring the adsorption of molecules at the interface and for ideal systems has the following form

$$d\gamma = -RT\Gamma \frac{dc}{c}$$

where  $R$  and  $T$  are the gas constant and temperature respectively. Combining the two equations and integrating can be used to compare surface tension vs. time [34] as

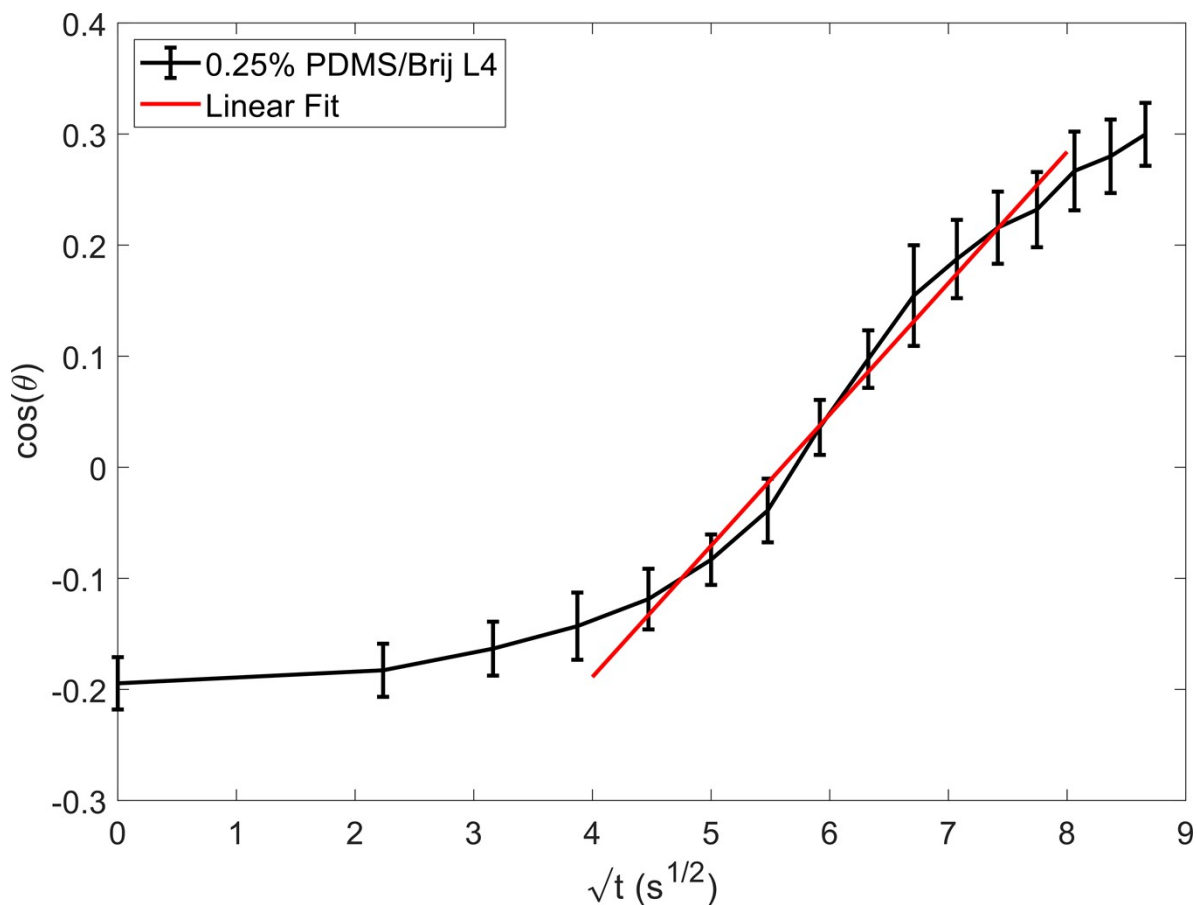
$$\gamma(t) - \gamma_0 = 2c_0RT \sqrt{\frac{Dt}{\pi}}$$

Lastly, adding  $\gamma(t)$  into the Young-Dupre equation [34-35] gives

$$\cos \theta = \frac{2c_0RT}{\gamma_{LV}} \sqrt{\frac{D}{\pi}} \sqrt{t} + \frac{\gamma_{SL} - \gamma_{SV}}{\gamma_{LV}}$$

where  $\gamma_{LV}$ ,  $\gamma_{SV}$  and  $\gamma_{SL}$  are the surface tensions of the water-air, PDMS-air, and PDMS-water interfaces respectively. Thus, surfactant diffusivity  $D$  can be extracted from the slope of  $\cos \theta$  vs.  $\sqrt{t}$ .

Fig. S4 demonstrates the cosine of contact angles and  $\sqrt{t}$  relationship for PDMS/surfactant mix of 0.25% with a linear fit curve to determine the diffusion coefficient. The calculated mean diffusion coefficient is  $D \approx 1.35 \times 10^{-13} \text{ m}^2/\text{s}$  which is in range of reported diffusion coefficients of different surfactants [29]. Furthermore, expression  $l = \sqrt{Dt}$  is commonly used to characterise how far into the domain the species has diffused as a function of time. Thus, monomer diffusion into bare PDMS may reach 100  $\mu\text{m}$  after 20.6 hours of contact with water in solid PDMS networks.



**Fig. S4** Plot shows of  $\cos(\theta)$  vs.  $\sqrt{t}$  relationship for the mean of three measurements with standard deviation error bars. The linear fit is used to extract the surfactant diffusivity. The calculated gradient and y-intercept of the linear fit were 0.12 and -0.66 respectively and  $R^2 = 0.98$ .