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Controlling the Morphology Evolution of a Particle-Stabilized Binary-Component System

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Experimental section

Materials. Silica particles (~15 nm in diameter) were synthesized in the laboratory and fluorescently labelled with fluorescein isothiocyanate (FITC) dye (isomer I, Sigma Aldrich) according to the methods described in Ref. [1]. Glycerol was purchased from Fisher and dyed with Nile red. Cetyl trimethylammonium bromide (CTAB) was purchased from Fisher and used as received. Ethanol (puriss) and silicone oils of different viscosity (50 cSt, 1000 cSt and 10000 cSt) were purchased from Sigma Aldrich and used as received.

Emulsification. Silica particles were first dispersed in ethanol at a known mass fraction. A certain amount of this ethanol solution (contains ~20 mg of silica particles) was mixed with 1.5 g of glycerol and ~1 mg of CTAB by vortex mixing and sonication. Next 1.5g of silicone oil phase was added to the glycerol solution. The entire mixture was first stirred by vortex for ~20s, and then sheared by using a Polytron homogenizer (PT-MR 3100) with a 1 cm diameter head operating at 3000 rpm (~5100 s^{-1}) for 25-30s. In the experiments which follow, the silicone oil viscosity is controlled by blending pairs of silicone oils with different viscosities. For instance, the silicone oil mixture in Figure 2a (viscosity ratio = 1.65) contains 0.6g silicone oil (~10000 cSt) and 0.9g silicone oil (~50 cSt); for Figure 2b (viscosity ratio = 1.17), its silicone oil phase was made up by 0.55g silicone oil (~10000 cSt) and 0.95g (~50 cSt).

Characterization. The high shear rate viscosity of both phases were characterized by using a Fluidicam (Formulaction, L'Union, France), which is based on optical acquisition of flow in a microfluidic chip.[2] All the measurements were carried out at 25 °C.

Confocal microscopy (Zeiss Observer.Z1) in conjunction with a Zeiss LSM 700 scanning system was used to observe the structures of different systems. A small amount of freshly prepared sample was placed on a microscopy slide. The observation was carried out before the sample starts to dry in the air. Fluorescence excitation was provided by a 488 nm laser (for FITC) and a 555 nm laser (for Nile red); emission filters were used as appropriate.

The sizes of the liquid domains and droplets were measured by hand using ImageJ.[3] Empirical cost function based on the two-dimensional (2D) confocal micrographs were also analysed with ImageJ.[3] For an ideal bijel system, the two continuous phase should have the same area fraction, *i.e.*, $\eta_B = 0.5$. By analyzing confocal microscopy images of the best bijel samples produced in our lab using the software package ImageJ, we find that these structures converge on a domain solidity of 0.7 and a characteristic length scale of 23 µm. The samples were all created with the same concentration of particles and proportions of liquids; if different compositions were chosen the values would as well. Hence in the current manuscript, we recommend the empirical values of $s_B \sim 0.7$ and $\rho_B = 23$ µm.

The effect of CTAB

In this present work, CTAB can modify the surface chemistry of the silica nanoparticles and reduce the interfacial tension between silicone oil and glycerol (from 26.4 ± 0.2 mN/m to 21.2 ± 0.5 mN/m). The former makes the particles wettable by both liquids; while the latter allows more interface to be created during phase demixing. Without CTAB, droplets cannot be stabilized and phase separation occurs very fast.

The effect of shear time

Fig. S1a demonstrates the morphology evolution when continuously shearing the formed bijels at the same rate. The viscosity ratio (λ_o) of the system is ~ 1.05; the shear rate is ~5100 s^{-1}, and the shear time runs from 25s to 1 minute. The formed structures remain bicontinuous during the shearing; only the domain size gets decreased. We believe that further shearing provides the chance for more particles to be trapped at the interface. After the coalescence process, new bijels with smaller domain size can be created. These results support our claim that the final structure of the system is a consequence of both break up during mixing and coalescence after mixing. For spherical droplets, since almost all particles are trapped at the interface already, continuously shearing do not induce obvious changes on the droplets, as shown in Fig. S1b.

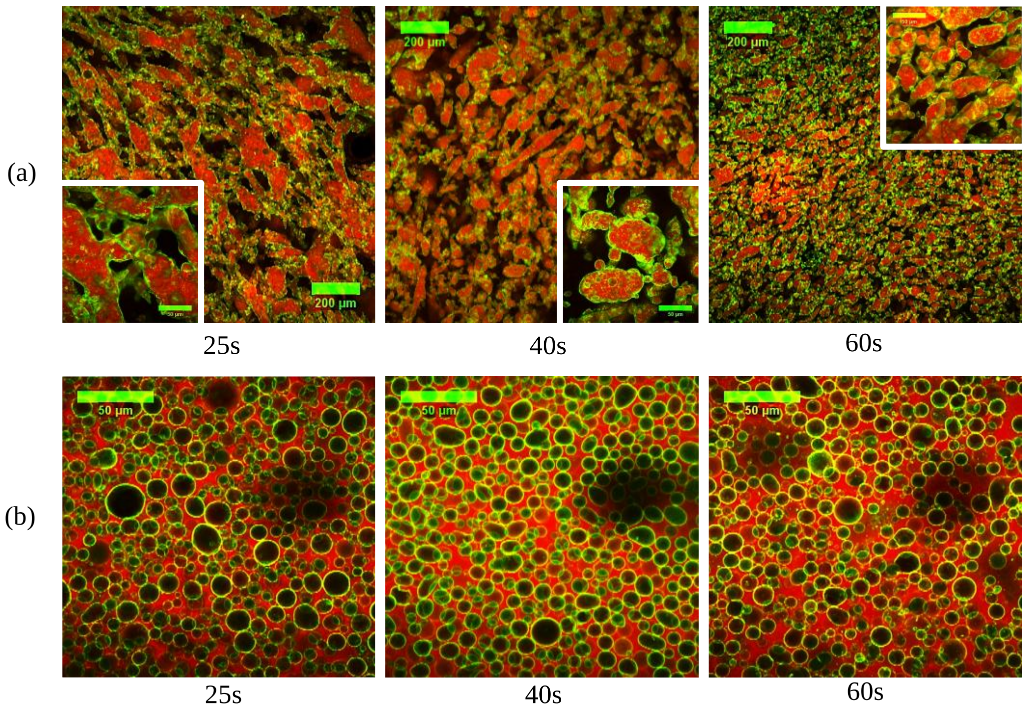

Fig. S1 (a) The morphology evolution when continuously shearing the formed bijels at the same rate. The viscosity ratio (λ_o) of the system is ~ 1.05; the shear rate is ~5100 s^{-1}, and the shear time runs from 25s to 1 minute. (b) The morphology evolution when continuously shearing the formed silicone oil droplets at the same rate. The viscosity ratio (λ_o) of the system is ~ 1.65; the shear rate is ~5100 s^{-1}, and the shear time runs from 25s to 1 minute. Scale bar = 50 µm.

[1] (a) N. Verhaegh, A. van Blaaderen, *Langmuir*, **1994**, *10*, 1427–1438. (b) A. Imhof, M. Megens, J. J. Engelberts, D. T. N. de Lang, R. Sprik, W. L. Vos, *J. Phys. Chem. B*, **1999**, *103*, 1408–1415.

[2] F. J. Galindo-Rosales, Complex Fluid-Flows in Microfluidics. Springer, Cham. **2018**.

[3] W. Rasband, ImageJ 1.50i, http://imagej.nih.gov/ij/.