Electronic supplementary information (ESI)

# Particle-Stabilized Janus Emulsions that Exhibit pH-Tunable Stability

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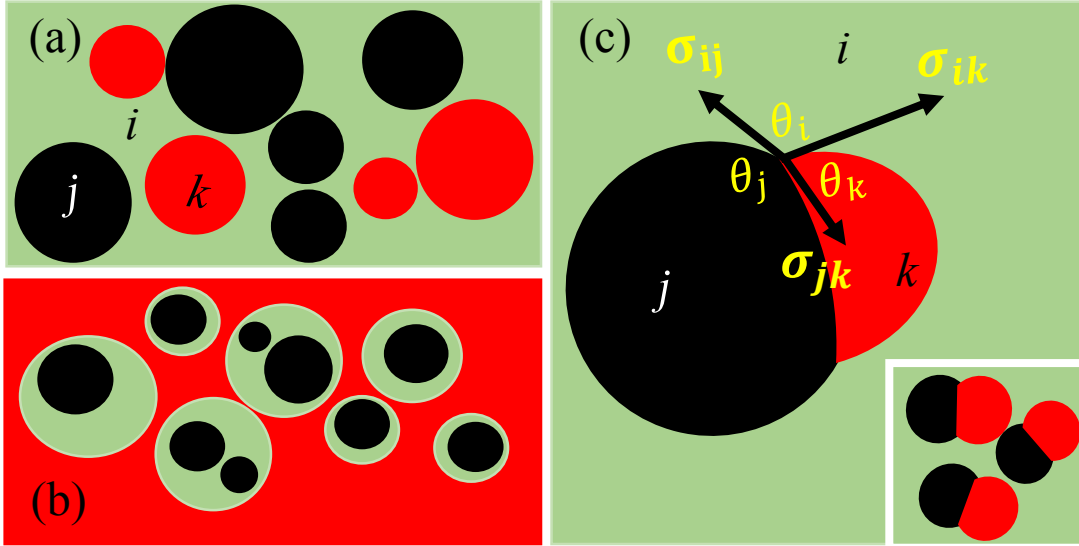Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China.

**Fig. S1** (a) Separate droplets formed when $G_i$ is negative and liquid $i$ is the continuous phase. (b) Multiple droplets formed when $G_i$ is negative and liquid $k$ is the continuous phase. (c) A Janus droplet with geometry typified by three contact angles ($\theta_i$, $\theta_j$ and $\theta_k$). (Inset) Dumbbell droplets when $\sigma_{ij} \approx \sigma_{ik} \approx \sigma_{jk}$ ($\theta_i = \theta_j = \theta_k = 120°$).

In a three immiscible liquid system, the change in the Gibbs free energy per unit interfacial area can be written as:

$$G_i = \left(\sigma_{ij} + \sigma_{ik}\right) - \sigma_{jk} \tag{1}$$

The curvature is normally characterized by the contact angle $\theta$ between these three liquids (Fig. S1c), which can be expressed by:[1]

$$\cos\theta_i = \frac{\sigma_{jk}^2 - \sigma_{ij}^2 - \sigma_{ik}^2}{2\sigma_{ij}\sigma_{ik}} \tag{2}$$

where $i$, $j$, and $k$ are each an immiscible liquid, and $\sigma$ is the interfacial tension between them (see also Fig. 1c, d).[2] When $G_i$ is negative, *i.e.* $\sigma_{jk} > \left(\sigma_{ij} + \sigma_{ik}\right)$, phase $j$ and $k$ will be separated as this costs less energy per unit area than having them in contact.[1a] In this case, if liquid $i$ is the continuous phase, the system will form separate droplets (Fig. S1a); if liquid $i$ is one of the dispersed phases, it will completely engulf liquid $j$ (assuming liquid $k$ is continuous), leading to multiple emulsions (Fig. S1b). Janus configuration can be achieved when $G_i$, $G_j$ and $G_k$ are all positive, which also means that no phase will preferentially wet another. When all interfacial tension values are equal ($\sigma_{ij} \approx \sigma_{ik} \approx \sigma_{jk}$), the three contact angles are all 120º.

## Experimental Section

**Materials.** Silicone oil (50 cSt) was purchased from Sigma Aldrich and used as received. Sunflower oil (chemical grade, batch number: BCBV5320), glyceryl trioctanoate and triolein were all purchased from Sigma Aldrich and dyed with Nile red. Deionized water (pH ~ 5.87) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA).

Silica particles (~150 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. [3]. After synthesis, these particles were silanized in a solution of ethanol (Sigma Aldrich), ammonia (Aladdin Reagent Co., Ltd) and hexamethyldisilazane (HMDS, Aladdin Reagent Co., Ltd). After this, they were washed with ethanol and water several times, and were dispersed in water at a known mass fraction.

**Emulsification.** An aqueous solution containing 1.2g water and ~12mg of silica particles, or no particles but a low concentration of FITC–Dextran (average $M_w$ 3,000-5,000, Sigma Aldrich), was first prepared. Then 1.45g of silicone oil was added to the aqueous solution, followed by 1.45g of the other oil (sunflower oil, glyceryl trioctanoate or triolein). The entire blend was first stirred by vortex mixing for ~20s, and then sheared using an Ultra-Turrax homogenizer (IKA T18 basic) with a 1 cm diameter head operating at ~13700 s$^{-1}$ (8000 rpm) for 40s.

**Characterization.** A confocal laser scanning microscope (Leica, SP8, Germany) with a 10× objective (N.A. = 1.4) was used to observe the structures of different systems. A small amount of sample was placed on a microscopy slide. 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.

All interfacial tensions were measured using a pendent drop technique with an OCA-20 contact angle system (Dataphysics, Germany). Zeta potential measurements were performed using Malvern Zetasizer Nano ZS (Malvern Instruments, UK) at 25 ºC.

The stabilities of the obtained emulsions were demonstrated by measuring the luminous flux (transmission and backscattering) with a Turbiscan Lab apparatus (Formulaction, France) with a pulsed near-infrared light source ($\lambda = 880$ nm). A microrheometer Rheolaser Lab (Formulaction, France) based on diffusing wave spectroscopy (DWS) was used to investigate the microrheological

behaviour of the emulsions. The instrument measures the Brownian motion of the droplets, reported as mean square displacement (MSD) *versus* decorrelation time.

All pH values were measured using a FiveEasy Plus pH meter (Mettler-Toledo Instruments, Shanghai, China). The size of the droplets were measured using ImageJ.[4]
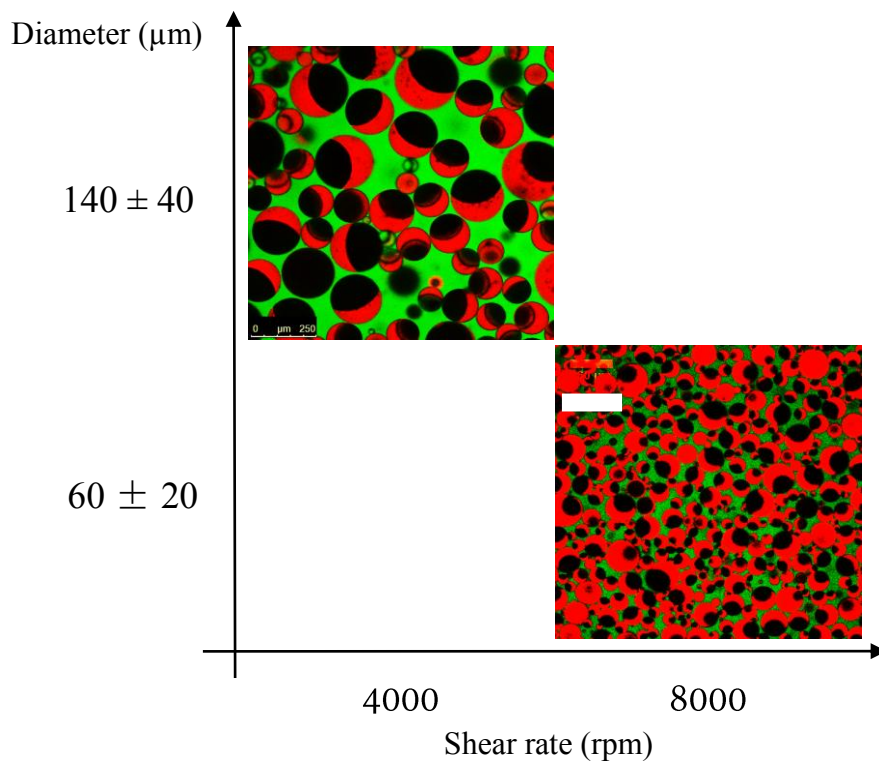


**Fig. S2** The shear rate effect on droplet diameter. Janus droplets formed by mixing 1.2 g of water (no florescent dye), ~12 mg of silica particles (green), and 1.45 g of silicone oil and 1.45 g of sunflower oil (red). The scale bars are 250 μm.
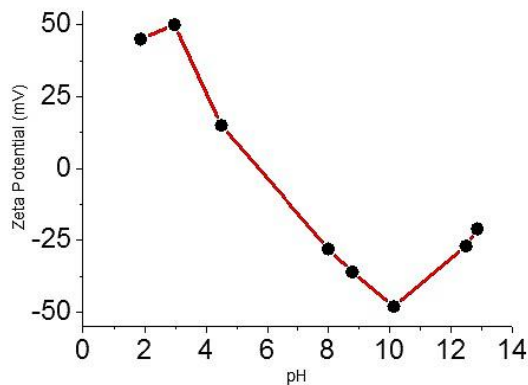


**Fig. S3** Zeta potential measurements of the synthesized silica nanoparticles as a function of pH. These data are consistent with the previous measurements in Ref.[5] (Fig. 3.9).
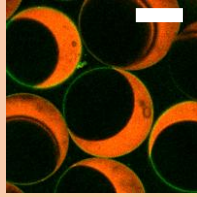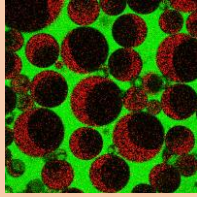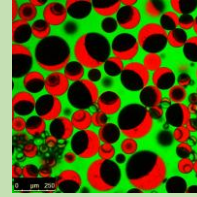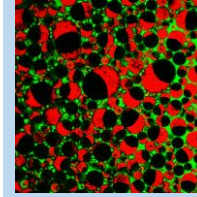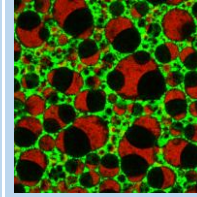
| Water pH | < 4 | 4 ~ 6 | 6 ~ 8 | 8 ~ 10 | > 10 |
|---|---|---|---|---|---|
| Stability | > 6 months | ~ 4-5 months | ~ 3 months | ~ 2-3 weeks | ~ 1-2 days |
| Confocal observations |  |  |  |  |  |

**Fig. S4** The pH-tunable stability of the Janus systems created by mixing 1.2 g of water phase (with different pH values) with ~12 mg of silica particles, and 1.45 g of silicone oil and 1.45 g of sunflower oil. The scale bar is 250 μm for all confocal images.

At pH ~2, the average diameter of the obtained Janus droplets is ~ 300 μm (shearing at ~13700 s$^{-1}$), indicating that coalescence occurs after mixing, and stops once the interface has been coated by the jammed particles. Previous studies indicate that, when all particles are totally and irreversibly adsorbed, the droplet diameter should be inversely proportional to the amount of particles:

$$D = 6V_d/s_f m_p \qquad (3)$$

where $D$ is the droplet diameter, $m_p$ is the mass of particles, $V_d$ is the volume of dispersed phase, $s_f$ is the specific surface area, i.e. the droplet surface covered per unit mass of particle.[6] In our systems, assuming that all particles end up at the oil-water interface, the calculated diameter is ~ 260 μm, close to the observations at pH ~ 2. This indicates that the particles are roughly close packed or jammed at the interface. Increasing particle concentration reduces the size of the droplets, which is consistent with Eq. (3) and the previous studies on oil-water emulsions.[6a,7] It should be noted that in our systems, Eq. (3) cannot be used to predict the droplet size when not all particles are absorbed at the interface. In this case, $m_p$ should be smaller, but $s_f$ would become larger. [6c]
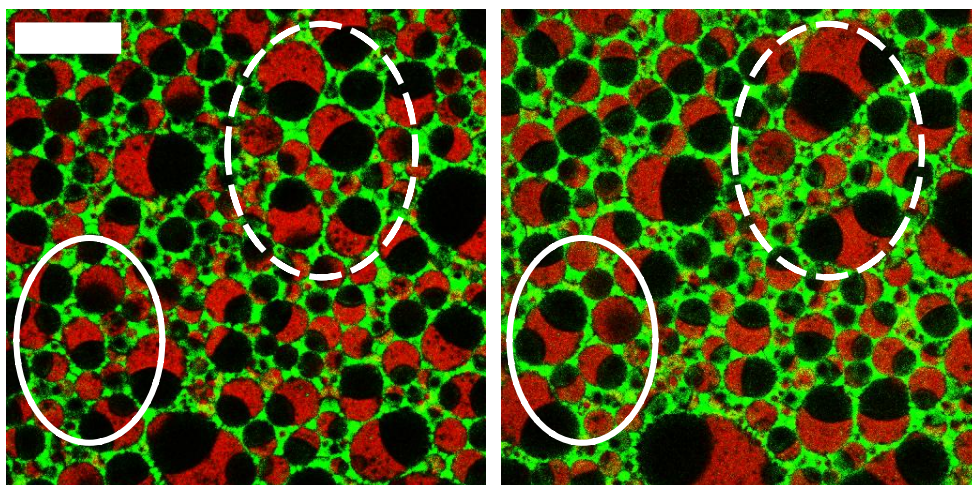
**Fig. S5** The coalescence between the droplets when mixing 1.2 g of water (NaOH, pH ~ 10), ~12 mg of silica particles, 1.45 g of silicone oil and 1.45 g of sunflower oil. The image on the right was taken two hours later than the one on the left. The scale bar is 250 μm.
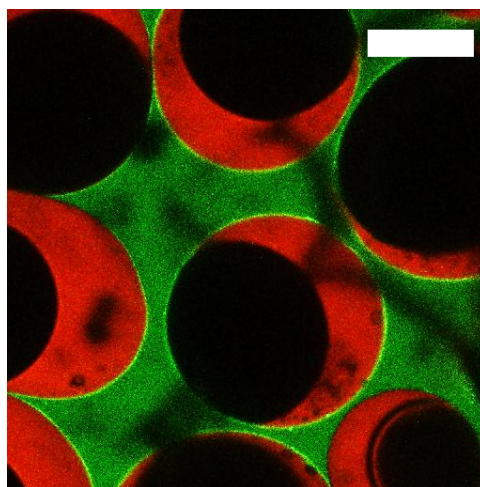


**Fig. S6** The Janus droplets created by mixing 1.2 g of water at pH ~ 7 (with 2.8 mol/g of NaCl), ~12 mg of silica particles, 1.45 g of silicone oil and 1.45 g of sunflower oil. Similar to the observations at pH ~2, particle layers are formed at the surface of the droplets. The scale bar is 250 μm.

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[6]     (a) S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt, F. Leal-Calderon, *Eur. Phys. J. E* **2003**, *11*, 273. (b) S. Arditty, V. Schmitt, F. Lequeux, F. Leal-Calderon, *Eur. Phys. J. B* **2005**, *44*, 381. (c) L. Maurice, R. A. Maquire, A.B. Schofield, M. E. Cates, P. S. Clegg, J. H. J. Thijssen, *Soft Matter* **2013**, *9*, 7757.

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