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Particle-stabilized Janus emulsions that exhibit pH-tunable stability

Janus emulsions stabilized by nanoparticles exhibit unprecedented stability. These droplets can be created by direct mixing, and can be controlled in size, geometry and also stability.
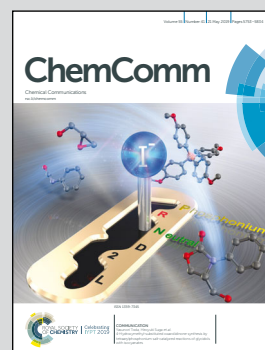
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Particle-stabilized Janus emulsions that exhibit pH-tunable stability†

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By developing a deeper understanding of the formation mechanism and the origin of the stability, we report a simple and large-scale fabrication approach to create Janus emulsions that can be controlled in size, geometry and stability.

Janus emulsions, *i.e.*, droplets consisting of two immiscible phases, have attracted significant attention and become one of the most exciting soft materials. In addition to serving as a model for the research of emulsion coalescence,[1] these complex droplets can also be employed as structural templates in the fabrication of micro-carriers and anisotropic colloids.[2] Recently, it was recognized that Janus-like structures can be helpful to elucidate the intracellular phase behaviors.[3] As a result, systematic studies have already been carried out to explore the relevant mechanisms.[4] Nevertheless, a series of fundamental mechanisms about Janus emulsions are still unclear. Previous studies have indicated the important role played by interfacial tensions in determining the droplet geometry. However, a rapid, simple and large-scale fabrication approach to prepare Janus droplets with tunable size and geometry has not been achieved. Moreover, to date, little has been done to investigate/improve the stability of Janus emulsions. The reported systems were mostly stabilized by non-ionic surfactants (*e.g.*, Tween 80),[5] which cannot preserve the droplets long term.[5d,6] These challenges would seriously restrict their applications in science and industry.

Herein, we develop a deeper understanding of the formation mechanism and the origin of the stability for Janus emulsions. By harnessing the interfacial tensions between water and another two immiscible oils, spherical Janus droplets can be created by direct mixing. In the absence of any added stabilizers, these droplets can only be transiently stabilized by the negative charge on the oil–water interface. To improve their stability, colloidal nanoparticles are successfully applied in these systems. At neutral pH, the particles form a viscoelastic network in the continuous phase to prevent coalescence and drainage. Lowering the pH causes them to be trapped at the oil–water interface, granting the droplets unprecedented stability (~ six months). The novelty of this work lies not only in the simple and versatile approach for preparing Janus emulsions, but also in the fact that the created Janus emulsions are controllable in size and geometry, and exhibit pH-tunable stability.

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

$$G_i = (\sigma_{ij} + \sigma_{ik}) - \sigma_{jk} \qquad (1)$$

where *i*, *j*, and *k* are each an immiscible liquid, and σ is the interfacial tension between them.[7] When G_i is negative, *i.e.* $\sigma_{jk} > (\sigma_{ij} + \sigma_{ik})$, phase *j* and *k* will be separated to form separated droplets or multiple emulsions (Fig. S1a and b, ESI†), since this costs less energy per unit area than having them in contact.[8] Janus configuration can be achieved when G_i, G_j and G_k are all positive, *i.e.*, no phase will preferentially wet another.

When mixing water, silicone oil and a pure triglyceride (*e.g.*, glycerol trioctanoate or triolein) to create a Janus system (see the Experimental section in ESI†), the high interfacial tension between water and silicone oil (~37.0 mN m^{-1}) can easily make $G_{\text{glycerol trioctanoate}}$ or G_{triolein} negative (eqn (1)). In this case, separate droplets or multiple emulsions with a core–shell geometry would be greatly favoured compared to Janus configuration. Confocal images confirm this prediction. As can be seen in Fig. 1a, when mixing 1.2 g of water, 1.45 g of silicone oil and 1.45 g of triolein at a shear rate of 13 700 s^{-1}, small water droplets (green) and large silicone oil droplets (black) are separated and dispersed in triolein (red). Mixing water, silicone oil and glycerol trioctanoate can create droplets with a core–shell geometry at equilibrium (marked yellow in Fig. 1b). Here, surprisingly, some droplets exhibit Janus topology. This can be related to the similar volume fraction of silicone oil and glycerol trioctanoate (35.5% and 35.2%, respectively), which makes the

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† Electronic supplementary information (ESI) available: The Experimental section, the measured zeta potential for nanoparticles, *etc.* See DOI: 10.1039/c8cc09842e

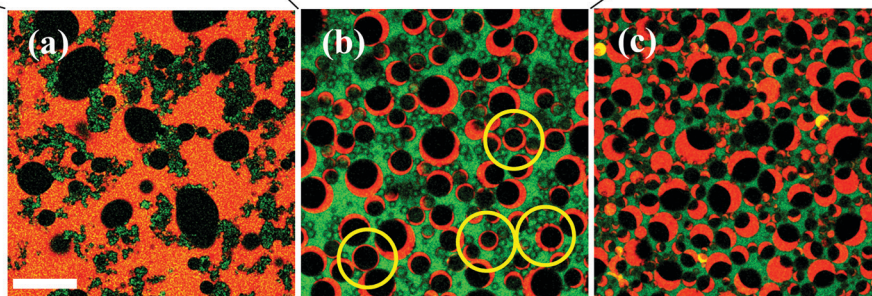| Liquid & liquid	Interfacial tension （mN/m）	Liquid & liquid	Interfacial tension （mN/m）	Liquid & liquid	Interfacial tension （mN/m）
Water & silicone oil	37.0	Water & silicone oil	37.0	Water & silicone oil	37.0
Water & triolein	6.9	Water & glycerol trioctanoate	22.9	Water & sunflower oil	22.5
Silicone oil & triolein	2.6	Silicone oil & glycerol trioctanoate	0.2	Silicone oil & sunflower oil	2.1

Fig. 1 Data in the table are the measured interfacial tensions between the liquids without any added surfactant. (a) Separate droplets created by mixing water, silicone oil and triolein. (b) Droplets created by mixing water, silicone oil and glycerol trioctanoate. Core−shell droplets are marked yellow. (c) Janus droplets created by mixing water, silicone oil and sunflower oil. The water pH is ∼6; the scale bar is 250 μm; the shear rate is ∼13 700 s^{-1}.

core–shell geometry difficult to maintain, and the system rearranges to a Janus geometry with a very narrow crescent.

To create controllable Janus droplets, various surfactants have been previously used to modify the interfacial tensions between the liquids.[5a] In this study, instead of using surfactants directly, we choose sunflower oil as the third phase for the creation of Janus emulsions. It is well known that sunflower oil is a complex mixture of fatty acids and trace molecules; lecithin originating from sunflower oil can be used as an emulsifier.[9] Under high-speed shearing, these surfactant-like molecules from sunflower oil could absorb onto the oil–water interface and significantly reduce its interfacial tension.[5a,10] We have measured the interfacial tension between water and silicone oil after adding 0.01% lecithin into the silicone oil phase. The value dropped from ∼37.0 mN m^{-1} to ∼24.2 mN m^{-1}, which can give rise to the conditions for the Janus configuration as required by eqn (1). Fig. 1c demonstrates the formed droplets by mixing 1.2 g of water, 1.45 g of silicone oil and 1.45 g of sunflower oil. It is clear that the two immiscible oils coexist in the aqueous continuous phase, forming nearly perfectly spherical droplets. Within these Janus droplets, sunflower oil (the red compartment) always exhibits a crescent shape, while the rest of the "moon" is occupied by silicone oil (black).

The measured zeta potential is around −62 mV for the Janus droplets in Fig. 1c, and −7 mV for the droplets in Fig. 1b, confirming that they are stabilized by negative ions.[11] This is similar to the previous reports on emulsion systems in the absence of any added stabilizers.[12] Negative ions cannot stabilize droplets

long term. In the system of Fig. 1c, complete phase separation occurs within two weeks.

Colloidal particles are very effective emulsion stabilizers that have yet to be used in Janus emulsions. Here, we successfully introduced silica nanoparticles into our systems. Fig. 2a compares the bulk phase behavior of systems with and without particles. During the observation period, no obvious phase separation can be noticed in the sample containing ∼12 mg of silica nanoparticles (the left sample in Fig. 2a). On the contrary, a clarification takes place at the bottom of the right sample (which microscopically is identical to that in Fig. 1c) one week after preparation. Meanwhile, an oil globule aggregation process starts at the top of the tube (marked black), which persists until complete phase separation is achieved.

Fig. 2b and c illustrate the luminous flux of the systems in Fig. 2a, measured with Turbiscan analysis for 24 hours. Fig. 2b demonstrates the changes in backscattering intensity with time (ΔBS) in the lower part (1/3) of the tubes; Fig. 2c shows the time evolution of transmission intensity (ΔT) at the upper part (1/3). The red data correspond to the system without colloidal particles, which decreases quicker as ΔBS, and increases more remarkably as ΔT. In comparison, the system containing particles exhibits more stable ΔBS and nearly constant ΔT (the black curve). In fact, this system is found to be stable for more than three months.

The obtained Janus emulsions with colloidal particles are found to be more uniform in droplet geometry, i.e., the internal structure of the droplets. Usually, the curvature of a Janus
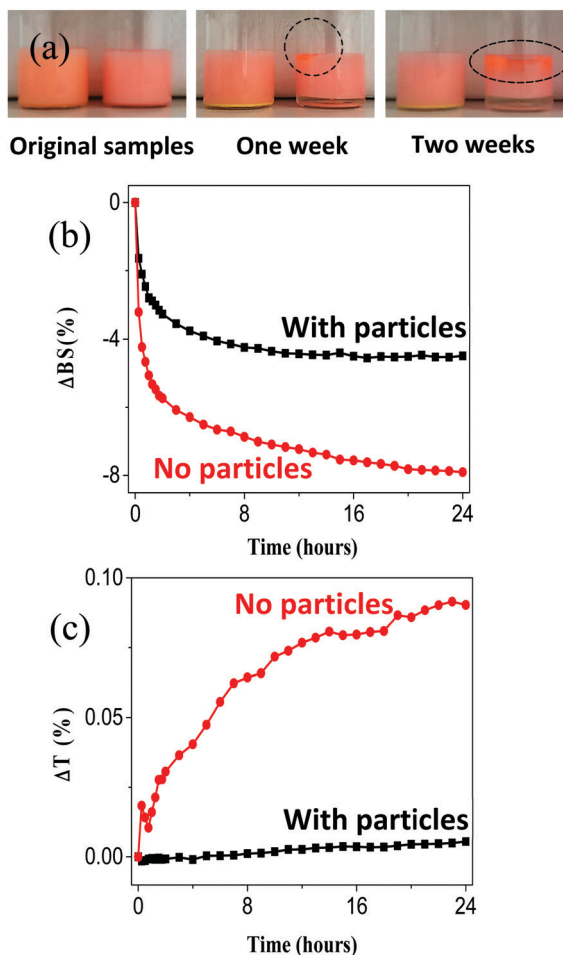
Fig. 2 (a) The bulk phase behavior of the Janus emulsions created by mixing water, silicone oil and sunflower oil. In each panel, the left sample contains ∼12 mg of silica particles; there are no particles in the right sample. Oil globule aggregation process starts at the top of the right sample (marked black). (b) Time evolution of the backscattering intensity with time (ΔBS) at the lower part (1/3) of the samples in (a). (c) Time evolution of the transmission intensity (ΔT) at the upper part (1/3) of the samples in (a).

Fig. 3 (a–c) Janus droplets formed by mixing 1.2 g of water phase with ∼12 mg of silica particles, and 2.9 g of oil phase (consists of silicone oil and sunflower oil). The volume fraction of sunflower oil in the oil phase, $V_{\text{sunflower oil}}/V_{\text{oil}}$ = 36.1% (a), 51.2% (b), and 66% (c). (d) Adding CTAB (∼1 mg) into the system (b) can adjust the interfacial tensions and obtain some dumbbell droplets. (e) Droplet size decreases when more water is added in the system. The water pH is ∼6; the scale bar is 250 μm; the shear rate is ∼6850 s^{-1} (4000 rpm).

droplet is characterized by a contact angle θ between the three liquids (Fig. S1c, ESI†), which is determined by the interfacial tension equilibrium at the contact line. Ignoring any line tension, the contact angle can be expressed by:[5a,b,8]

$$\cos \theta_i = \frac{\sigma_{jk}^2 - \sigma_{ij}^2 - \sigma_{ik}^2}{2\sigma_{ij}\sigma_{ik}} \qquad (2)$$

This indicates that, if only the relative amount of these three liquids is changed, the location of the contact plane inside the Janus droplet can be adjusted, but the curvature of Janus droplet should not be influenced. The systems in Fig. 3a–c contain 1.2 g of water phase with ∼12 mg of silica particles (green), and different amounts of silicone oil and sunflower oil (red). When the volume fraction of sunflower oil in the oil phase is increased from 36.1% to 51.2%, and to 66%, the red crescents inside the Janus droplets increase their volume accordingly. However, as described by eqn (2), all droplets remain spherical, and the curvature of their crescents, i.e., the contact angle between the sunflower oil and the
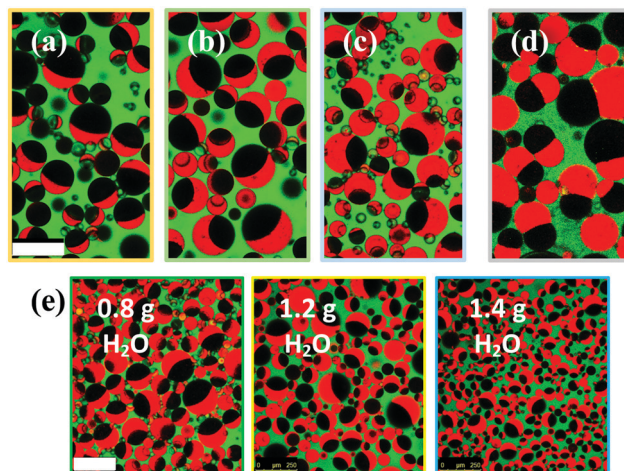
silicone oil, remains approximately constant ($\theta_{\text{sunflower oil \& silicone oil}}$ ∼ 45 ± 6°) as well. Adjusting the interfacial tensions with a surfactant (∼1 mg of cetyltrimethylammonium bromide, CTAB), on the other hand, changes all three contact angles in the system, creating some dumbbell-like Janus droplets (Fig. 3d, all three contact angles ≈120°).

The size of these Janus droplets can also be controlled. Two distinct approaches can achieve this goal. Firstly, the shear rate used for mixing influences the droplet size. Increasing the shear rate from ∼6850 s^{-1} to ∼13 700 s^{-1} can reduce the average diameter of the Janus droplets from 140 ± 40 μm to 60 ± 20 μm (Fig. S2, ESI†). This can be explained by an increased capillary number Ca ($= \frac{\eta_m \dot{\gamma} R_0}{\sigma}$, with η_m the viscosity of the continuous matrix, $\dot{\gamma}$ the shear rate, R_0 the droplet radius, and σ the interfacial tension.), which describes the breakup of droplets in shear flow. Once the value of Ca exceeds a critical value (Ca$_{\text{crit}}$), large droplets would deform and eventually break up into smaller ones under the influence of shear.[13] Interestingly, changing the volume of water can also adjust the size of the Janus droplets. As shown in Fig. 3e, when the water volume is too low, phase separation occurs within 10 minutes after the cessation of shearing. Increasing the water volume reduces the diameter of the droplets. The possible mechanism could be related to the viscoelastic physical network formed in water (see later).

Apart from the size and geometry, the long-term stability of our Janus emulsions given by the nanoparticles is also tunable. At pH ∼ 6, the particles are also negatively charged (Fig. S3, ESI†), and therefore, they prefer to stay in water instead of being adsorbed at the oil–water interface. A microrheological study demonstrates that, without particles, the mean-square displacement (MSD) of the droplets increases linearly with time, as a simple viscous fluid (the red curve in Fig. 4a); the addition of
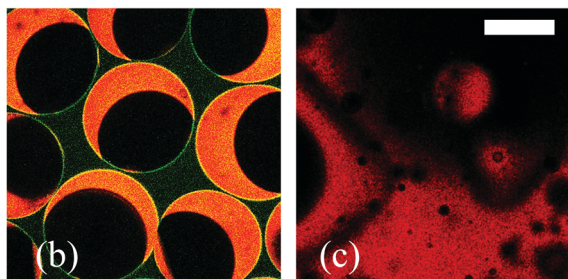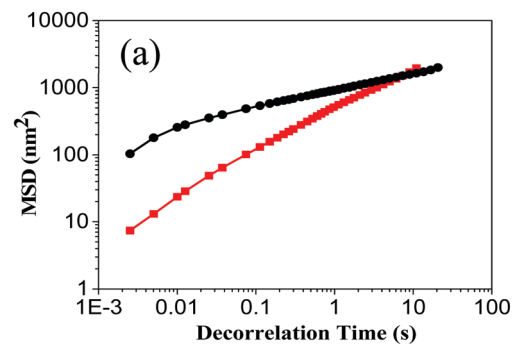
Fig. 4 (a) The mean-square displacement (MSD) of Janus emulsions with (black) and without (red) silica nanoparticles as a function of lag time. (b) Silica particles can be trapped on the oil–water interface at pH ∼ 2. (c) System without particles suffers a quick phase separation at pH ∼ 2. The scale bar is 250 μm.

colloidal particles makes the MSD grow sub-linearly as a visco-elastic system (the black curve, Fig. 4a). The macroscopic viscosity index (MVI), which corresponds to the inversed MSD slope in linear scale, links to the well-known macroscopic viscosity in Pa s. For the particle-containing system, the calculated MVI is 1.2×10^{-2} nm^{-2} s, 4 times higher than that of the system without particles. This indicates that a viscoelastic physical network was formed by the particles, which occupies the entire continuous phase to prevent coalescence and drainage.

Furthermore, the final structure of an emulsion is normally a consequence of both break up during mixing and coalescence after mixing. Increasing the water volume might lower the particle-induced viscosity, but can simultaneously enlarge the inter-droplet distance. This could be helpful for preventing the coalescence at an early stage, and therefore leads to the Janus droplets with smaller diameters. However, too much water may influence the creation of the viscoelastic network, which further affects the formation and the stability of the droplets.

By lowering the water pH with HCl, the role of negative ions at the droplet interface is diminished, and the particles can finally be trapped at the oil–water interface. The resulting particle layers act as solid barriers which can more effectively prevent the coalescence of the droplets.[14] Fig. 4b illustrates the particle-stabilized Janus droplets (at pH ∼ 2), which exhibit unprecedented stability for more than 6 months. Adjusting the water pH between 2 and 12 can obtain Janus emulsions with different stability (ranging from days to weeks, and to months, Fig. S4, ESI†); systems with a large pH value (>10) can dissolve the particles and cause the droplets to coalesce. It should be pointed out that, this tunable stability can also be achieved by using metal cations (e.g., NaCl, Fig. S5, ESI†). Moreover, the adsorption of the particles is influenced by the pH and this then influences the final size of the droplets (eqn (3), ESI†). For the system without particles, complete phase separation occurs within 10 minutes at a low pH (Fig. 4c).

In conclusion, we report a simple and large-scale fabrication approach to prepare Janus emulsions that can be controlled in size, geometry and stability. We first confirm the role played by interfacial tensions in creating the Janus topology, and then use colloidal particles to investigate the origin of the stability for Janus emulsions. The mechanisms uncovered in this work can be easily extended to more general multiple-liquid systems, and can greatly expand their applications in food, personal care products, engineering, and medicine. Specifically, systems exhibiting pH-tunable stability can be applied in drug release and other biological processes.

Conflicts of interest

There are no conflicts to declare.

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