

Millimeter-Size Pickering Emulsions Stabilized with Janus Micro-Particles

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3 **Millimeter-Size Pickering Emulsions Stabilized with Janus Micro-Particles**
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ABSTRACT

The ability to make stable water-in-oil and oil-in-water millimeter-size Pickering emulsions is demonstrated using Janus particles – particles with distinct surface chemistries. The use of a highly cross-linked hydrophobic polymer network and the excellent water wetting nature of a hydrogel as the hydrophobic and hydrophilic sides, respectively, permits distinct wettability on the Janus particle. Glass capillary microfluidics allows the synthesis of Janus particles with controlled size between 128 μm and 440 μm and control over the hydrophilic to hydrophobic domain volume ratio of the particle from 0.36 to 12.77 for a given size. It is shown that the Janus particle size controls the size of the emulsion drops thus providing the ability to tune the structure and stability of the resulting emulsions. Stability investigations using centrifugation reveal that particles with the smallest size and a balanced hydrophilic-to-hydrophobic volume ratio (Janus ratio), form emulsions with the greatest stability against coalescence. Particles eventually jam at the interface to form non-spherical droplets. This effect is more pronounced as the hydrogel volume is increased. The large Janus particles permit facile visualization of particle-stabilized emulsions, which result in a better understanding of particle stabilization mechanisms of formed emulsions.

INTRODUCTION

Pickering emulsions, or particle stabilized emulsions, have a wide range of applications in major industries such as, but not limited to, food, cosmetics, and pharmacy¹⁻³, where the traditional surfactant-stabilized emulsions can have adverse effects.⁴ The particles' enhanced and often irreversible adsorption to the liquid-liquid interface is ideal for creating stable drug carrying systems and micro reactors. For example, Pickering emulsion systems have proven to be useful as templates for microcapsules for drug delivery with biocompatible colloidal particles serving as the outer shell of oil-in-water emulsions.⁵ They have also been used to form microspheres of various polymers through controlled polymerization within the enclosed Pickering emulsion boundaries.⁶ The stability and applications of Pickering emulsion drops depend on the emulsifier's secure attachment to the oil/water interface, and a better understanding of how to maximize the particle's adsorption is needed.

While it is possible to use particles of homogeneous surface functionality to stabilize emulsions, using particles with modified surfaces of both hydrophilic and hydrophobic parts affords better stabilization. In some cases, these types of emulsifier particles were formed by simply adding oleic acid to aqueous solutions of hydrophilic silica nanoparticles.⁷ Although this procedure was simple and reproducible, it afforded limited control of the hydrophobicity of the particles and therefore Pickering emulsions were subject to phase separation and Oswald ripening. Effective control of the emulsifying particle's wetting features is beneficial to achieve enhanced emulsion stability. Janus particles, or particles whose surface has two distinctly different physical properties, are promising candidates for emulsion stabilization. Janus particles offer the ability to tune the particle contact angle at the oil/water interface by changing the hydrophilic/hydrophobic domain size ratios, which is not feasible using particles with just a single functionality. Thus, understanding the influence of the particle architecture on the emulsion stability is necessary to achieve stable Pickering emulsions⁸⁻⁹, especially for large droplet sizes.

The bi-compartmental surface functionalization of amphiphilic colloidal silica nanoparticles has been reported¹⁰ where the improved stability (~ 15 days) of the particle-stabilized emulsions (~ 30 μm) was the result of opposing hydrophilic and hydrophobic sides on the silica particles achieved through a tedious synthesis procedure. Although these Janus silica particles were useful, this surface functionalization method allowed no control of the size of the functionalized areas- an important feature in studying Pickering emulsion stabilization mechanisms and for the control of the particle-liquid contact angle. Another attempt at controlling the size and shape of Janus particle emulsifiers includes the polymerization of Janus droplets formed from two aqueous solutions of two immiscible monomers.¹¹ However, due to the nature of the synthesis, the synthesized particles were polydispersed with some particles as small as 20 μm and some as large as 100 μm . Flow synthesis in microfluidic devices, however, permit the control of monodispersed Janus droplets as particle templates.

Herein, we report stable millimeter-size Pickering emulsions formed using amphiphilic Janus particles. We achieve good control over the overall size of the emulsion droplets by precisely varying the size of the particles. We fabricate the Janus particles in a continuous and facile flow synthesis, which enables the tunability of the particle size from ~ 100 μm to 500 μm with controlled

degrees of hydrophobic/hydrophilic portions on each particle. We synthesize the hydrophilic side of the particle as a hydrogel to increase the interaction between the aqueous phase and the Janus particle for enhanced adsorption of the emulsifying particle at the oil-water interface. The formed Pickering emulsions are shown to be stable over months at partial particle surface coverage. The stability of these droplets is then studied via centrifugation to promote coalescence.

EXPERIMENTAL PROCEDURES

Materials. 45 wt% polyethylene glycol diacrylate (PEGDA – Sigma Aldrich), 5 wt% ethoxilated trimethylpropane triacrylate (ETPTA – Sigma Aldrich), 1 wt% 2-hydroxy-2-methyl-propiofenone (Sigma Aldrich), and 49 wt% water are mixed together to form the hydrophilic portion of the inner-phase, which we refer to as “water”. 99 wt% trimethylpropane triacrylate (TMPTA - Sigma) and 1 wt% 2-hydroxy-2-methyl-propiofenone are added together to form the hydrophobic portion of the inner-phase, which we refer to as “oil”. The oil was colored red using Nile red dye. 95 wt% silicone oil and 5 wt% Dow Corning Resin 749 (surfactant) are added together to form the continuous phase. Janus particles are formed using the flow of these solutions in a glass capillary microfluidic device and characterized using confocal microscopy.

Methods

Device Fabrication and Janus Particle Synthesis: A circular glass capillary with an outer diameter of 1.5 mm is heated and pulled using a pipette puller to create a tapered fine orifice of 300 μm for the outlet capillary. A 1.5 mm “theta” capillary, with a glass wall splitting it into two separate channels, is also heated and pulled until the opening orifice diameter is 80 μm . The two capillaries are inserted inside another wider diameter circular glass capillary to form a coaxial alignment. The “theta” capillary ensures that the water and oil come in contact only at the orifice opening to form Janus droplets. Two tapered 1 mm glass capillaries are inserted into the two compartments of the “theta” capillary as inlets for oil and water. Oil and water flow through the “theta” capillary to form the inner-phase while the silicone oil flows through the larger outer capillary in the same direction, resulting in a co-flow geometry. Figures 1a and 1b show a diagram of the device and flow directions.

At a continuous phase flow-rate of 20 mL/hr and an inner-phase flow-rate (combined oil and water flow-rates) of 0.2 mL/hr, external pressure from the high continuous phase flow-rate extends the inner-phase to jet that breaks into drops due to instability caused by the surface tension.¹² The droplets are immediately photo polymerized with a UV light intensity of 25 W/cm² for 2 seconds at a 1 cm distance using an Omnicure Series 1000.

Emulsion Formation: We first clean the Janus particles of the silicone oil and surfactant by rinsing in acetone three times. To form the water in oil emulsion drops, 11 mL toluene is first added to the acetone-dried particle vial followed by addition of varying amounts of water (0.1, 0.6, or 1 mL) and vortexing for 2 minutes. Figure 1d shows a schematic of a formed emulsion droplet.

Stability Test: We observed stability of Pickering emulsions using an Allegra X-30R Centrifuge. We spun the samples at different relative centrifugal forces (RCF) and imaged the size of the emulsion droplets after each run. The procedure continued until coalescence occurred.

RESULTS AND DISCUSSION

In this work, we use a simple glass microfluidic device with a two-sided “theta” capillary where tunable interfacial tension between the continuous and inner-phase permits the controlled formation of Janus particles. At a fixed surfactant concentration, variations of the flow rate ratio of water-to-oil lead to the formation of amphiphilic Janus particles of different hydrophilic to hydrophobic domain ratios. We add the particles to a surfactant free oil and water mixture to form millimeter-size Pickering emulsions, which are stable for up to a year to date. In addition, through the control of particle size and degree of hydrophobicity, stable Pickering emulsions of varying droplet sizes and type are formed with the latter demonstrated via catastrophic phase inversion. Due to the ease of visualization of these particles and the formed emulsion drops, this experimental system will give a better understanding of how surface coverage of particles and orientation at the water/oil interface influence emulsion stability.

Formation of Particles – Tuning Particle Size for Emulsification

We show that by increasing the total inner phase flow rate at a constant continuous phase flow rate results in larger particle sizes. The ratio of the oil and hydrogel flow rates in the inner phase is constant at 1:1 to study the effect of only varying the overall flow rates. Thus, the particles discussed in this section exhibit a constant ratio between the hydrophobic and hydrophilic domains while the overall particle size increases.

We keep the continuous phase flow-rate constant at 20 mL/hr while changing the overall flow rate of the inner-phase (oil and hydrogel) to 0.2, 0.4, 0.6, 0.8, and 1 mL/hr in a single glass device. Using a co-flow microfluidic geometry, we form droplets where break-off occurs at the end of a jetting stream. Figure 2a shows the resulting cross-linked particles with particle sizes (d_p) of 128.1, 166.7, 216.8, 270.1, and 311.3 μm . The coefficient of variation (CV – standard deviation/ mean size) for the different particle sizes are 0.164, 0.226, 0.1908, 0.114, and 0.081 respectively. Figure 2b shows a linear relationship between the flow rate of the inner-phase and the Janus droplet size where the decreasing viscous drag permits larger droplet formations and subsequently larger particle size.

As expected, we observe that holding the flow rate of the continuous phase constant while increasing that of the inner phase serves to generate larger droplets in the microfluidic device. While keeping the flow rate of the continuous phase constant, an increase in the flow rate of the inner-phase into the jetting regime leads to large shear at the interface caused by velocity differences. This results in the deceleration and widening of the jetting stream under our experimental conditions.¹³ Undulations in this jetting stream due to Raleigh-Plateau instability result in a small perturbation in the cylindrical flow that eventually pinches the jet into droplets. The increase in droplet size is a result of the combination of an increased flow rate and widening of the jetting stream coupled with the pinch-off occurring later. If we assume pinch-off occurs at the same time for different flow rates, one would expect the particle size, as measured as the length shown in the inset of Figure 2b, scales as $d_p \sim Q_i^{1/3}$. However, analysis of the experimental data in Figure 2b suggests that increasing the flow rate of the inner-phase does not proportionally increase the size. This suggests that for this experimental system one needs to understand the effects of the

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3 experimental parameters on jet widening and droplet pinch off in order to predict final particle
4 sizes.
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6 Upon formation of the droplet, the TMPTA oil phase immediately spreads on the surface of the
7 PEGDA hydrogel droplet to reduce the interfacial area with high surface tension between water
8 and silicone oil (continuous phase). This spreading is mitigated by the addition of Dow Corning
9 resin 749 into the silicone oil, where it acts as a surface acting agent to decrease tension between
10 the continuous phase and water. The relative surface energy of the three fluids determines the
11 amount of spreading and results in an embedded particle for our system as seen from Figure 1c.
12 The spreading is quantified by the spreading coefficient (S)¹⁴ where a negative S value results in
13 particle shapes with one sphere embedded in the other. For S greater than zero, core-shell particles
14 form. Thus, we achieve negative spreading coefficients in our particle system by keeping the resin
15 concentration constant, which gives rise to the observed particle shapes.
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19 We therefore achieve complete control of the Janus particle size through glass capillary
20 microfluidics. There has been extensive research on the factors that govern droplet break off and
21 subsequent particle size as a function of the flow rates. However, these data are limited to systems
22 where the inner phase fluid is composed of just a single phase.^{13, 15-17} Although it follows a trend
23 similar to the single phase fluid flow, current work deals with a system in which the inner phase is
24 composed of two fluids with different viscosities and surface tensions and both of these phases are
25 exposed to the continuous phase. The physics of such a system (jet widening, droplet pinch off) is
26 not yet clear and more insight into such systems is therefore in need.
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30 **Controlling Particle Domain Sizes**

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32 The glass capillary device permits control of the hydrophilic and hydrophobic domains of the Janus
33 particle. We vary the volumes of the hydrophilic and hydrophobic sides of the Janus particle, also
34 called Janus ratio, by changing the ratio of the flow rates of water to oil while keeping their total
35 flow-rate constant. We analyze volumes of the respective domains geometrically by treating the
36 Janus particle as a sphere embedded in a spherical cap. By dividing the particle into two sections,
37 we obtain three distinct sphere cap volumes that form the hydrophilic and hydrophobic portions
38 of the particle. The flow rate of the continuous phase is 20 mL/hr while the flow rate of the inner-
39 phase is 0.2 mL/hr to achieve a particle size of ~128 μm . We change the ratio of the flow rates of
40 water to oil to produce particles with varying Janus ratios.
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44 At a 1:1 ratio, the co-flow of water and oil forms a jetting stream and droplet break-off occurs in
45 the manner as described above. At a 7:1 ratio, the co-flow of water and oil forms a jetting stream
46 and the final Janus particles have a large hydrophilic part. Figure 3a shows the resulting Janus
47 particles produced in a single glass device at flowrate ratios of 0.28, 0.5, 1, 3, and 7, respectively.
48 At the smallest flow rate ratio of water to oil, we can see that individual cross-linked particles have
49 a large volume of oil (red) as the hydrophobic side and a much smaller volume of water (colorless)
50 as the hydrophilic side. At the other extreme with a 7:1 ratio, individual cross-linked particles
51 formed large hydrophilic and small hydrophobic domains. This illustrates the ability of a single
52 glass microfluidic device to produce particles of varying Janus ratio. Particles of lower (0.36) and
53 higher (12.77) Janus ratios were also created using a separate device for further experiments.
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Figure 3b shows the relationship between the volume domain ratio of Janus particles and the flow rate ratio of water to oil. While the relationship between the volume domain ratio and the flow rate ratio seems close to linear as seen from the graph, we see slight deviations in our experimental results. The deviation might be due to the evaporation of water, evident in the slight hydrogel deformation in figure 3a. This effect is more pronounced for the smaller size Janus particles (128 microns) the data of which is presented in Figure 3. This is also in accordance with previous work¹⁸⁻¹⁹ in literature where a 1:1 flow rate ratio of the inner phase did not produce a 1:1 domain volume ratio.

Pickering Emulsion Formation and Stability

We use Janus particles synthesized in the previous sections to make Pickering emulsions in water and oil mixtures. The large size of our particles allows us to observe emulsion drop shapes and sizes without a microscope. These large particles should also afford easier visualization at the water/oil interface when studying the effects of particle orientation on stability. Figure 4a shows millimeter-size water in oil (toluene) Pickering emulsions droplets using Janus particles of approximately 440 μm in size. Upon mixing the vial contents (0.55g water, 9.54g toluene, 0.19g particles), polydispersed emulsions form, some of which have only partial coverage of the droplet surface by the Janus particles as observed by a microscope. The formed emulsions were stable over long periods (\sim year so far) without any coalescence or instability.

We count an emulsion drop as a droplet of the dispersed phase with any number of particles on the surface greater than or equal to 800 μm in diameter. Because the focus of this work is on mm-scale droplets, we use 0.8mm as the threshold. Upon emulsification of our water-oil-particle system, we observed a dense packing of particles on the sides of the droplets. This is also seen in figure 4a where the 440 μm particles emulsify the water but leave free surface on the top of the droplet. While this is an expected effect for large particles, stable emulsions are still formed. The average surface coverage of our emulsion droplets across various size particles can be estimated by relating the particle size to the droplet diameter. Because the size of Pickering emulsion drops is dependent on the size of the stabilizers, it is possible to predict the droplet size based on our synthesized Janus particles. Assuming complete surface coverage at a hexagonal close packing fraction and a circular particle cross section at the oil-water interface²⁰, we can express the emulsion drop diameter (D_e) as

$$D_e = 0.9 \frac{24\rho_p}{\rho_{water}} \beta \left(\frac{V_p}{\pi d_A^2} \right) \quad (1)$$

Where, ρ_p is the particle density (1.1 g/mL), ρ_{water} is the water density, V_p is the average volume of a single particle, d_A (particle width) is the diameter of the widest domain of the particle that sits above or below the oil/water interface, and β is the mass ratio of emulsified water to Janus particles. A similar equation has been used for spherical silica nanoparticles where it was found that a mass ratio of emulsified fluid to stabilizer as low as 3 yielded smaller emulsions than could be predicted.²¹ Aiming for smaller emulsions drops, we keep our ratio at 3 for droplet size predictions. When using equation 1 for 90% surface coverage, we predict drop diameters of 2.74,

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3 4.85, and 6.22 mm for particles of 172, 333, and 441 μm respectively. These sizes were higher
4 than diameters experimentally observed. Figure 4b shows how emulsion droplet size changes with
5 increasing particle size using a constant β value. At 42% surface coverage, the equation gives an
6 almost perfect prediction of droplet size suggesting that our water droplets are, on average, half
7 covered by the particles upon initial emulsification. We expect emulsion droplet diameter to
8 increase with particle size since large and small particles pack at the oil-water interface in the same
9 way as depicted in Figure 4c. As particle size increases, particle amount decreases, depleting the
10 total amount of surface area that can be created. This leads to larger droplets.
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14 As others have reported²¹⁻²³, our particle-stabilized emulsions of partial coverage can remain stable
15 under normal gravity conditions. We further studied emulsion stability using a centrifuge to
16 increase the gravitational load on the water droplets. After cleaning and loading cross-linked
17 particles into a centrifuge tube of about 11mL of toluene, we conducted studies on (1) three
18 different size particles at a fixed Janus ratio and (2) three different Janus ratio particles at a fixed
19 size. To compare the emulsion stabilities of the different particle types, β in all tests is kept at
20 about 3.0, where the particle's size is the only changing variable. Once the appropriate amount of
21 water is added, commensurate to the weight of particles, the tube contents are vortexed for 2
22 minutes and imaged to size the emulsion droplets. Centrifugation was done on a vortexed sample
23 at increasing RCF's (measured relative to the acceleration to gravity – g force) to observe how the
24 initial emulsion droplet size increases with RCF. As droplets became irregularly shaped, the full
25 area was calculated with an image from a top view while droplet depth/height was calculated with
26 an image of the side. For the large droplets in Figures 5 and 7, the height imaged from the side was
27 almost the same except at the edges where it curves. The diameter of a sphere with this same
28 volume was then used as the effective diameter of the emulsion droplet. Experiments were repeated
29 a minimum of three times and the average diameter with standard deviation reported in the figures.
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34 Figure 5a shows how the average emulsion droplet diameter changes with RCF where the initial
35 droplet sizes, before centrifugation, increased with particle size. We also observe that the 172 μm
36 particle stabilized emulsions are almost unaffected by the increase in RCF. We observed a much
37 smaller size distribution of Pickering emulsions formed from small particles. Although our form
38 of emulsification is known to produce polydispersed emulsions¹¹, smaller particles permit smaller
39 emulsion droplets with lower polydispersity. Upon initial emulsification, before centrifugation,
40 polydispersity, represented by coefficient of variation (standard deviation/average), for the 172
41 μm particles is about 0.02 compared to 0.06 for the 441 μm particles. It is not yet clear to us
42 however, why the smaller particles would create the more monodispersed system. A systematic
43 study on the particle size, homogenization technique, and interfacial surface area is needed to make
44 a sound conclusion. Figure 5b shows particle size effects on emulsion droplet sizes, before and
45 after centrifugation.
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50 For Janus particles with a fixed hydrophilic to hydrophobic ratio, we observe that Pickering
51 emulsions with initial average sizes below 2 mm exhibit the strongest resistance to coalescence.
52 Emulsion droplets that are initially larger than this size is likely to destabilize, or they are so large
53 that not much more coalescence can occur. Emulsions formed with 441 μm particles form > 2 mm
54 droplets and experience a large degree of coalescence when centrifuged. These initial droplets are
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3 large and partially covered with Janus particles. Initial fraction of total particles adsorbed to an
4 interface was roughly estimated (assuming constant droplet size) to be 0.63 for droplets formed
5 with 441 μm particles. As RCF increases, past 45xg, the size remains relatively constant as most
6 of the water is already coalesced in one phase. Although these Janus particles are effective at
7 stabilizing millimeter size droplets, their large size leave more uncovered surface before
8 centrifugation and may be more susceptible to coalescence. Because the rate of size change is
9 faster for larger particle stabilized droplets, observed from figure 5a, stability must be affected by
10 more than just the initial droplet size. In our experiments performed in current work, the mass (or
11 volume) of particles and water is kept fixed across the different size particles. Hence the stability
12 of the emulsion for a given size particle can be dependent on other factors - such as surface
13 coverage during centrifugation, and the fraction of particles adsorbed and desorbed on and from
14 the droplet interfaces. While we conclude that particle size influences the initial droplet size, these
15 additional factors will need to be analyzed in tandem to gain a complete understanding of the
16 particle and emulsion stability.
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21 We also conducted phase inversion experiments on formed emulsions. Figure 6a-c are pictures of
22 formed water-in-oil emulsions stabilized by 128 μm particles in equal amounts of the two liquids.
23 As can be seen from the figure, the emulsion droplets are clear (water phase) while the surrounding
24 oil which has been dyed, is red. After doubling the amount of added water and vortexing the vial,
25 the type of emulsions flips to form oil-in-water emulsions, with the red oil dispersed in a clear
26 water continuous phase. Figure 6f shows this phase inversion where we see red spherical emulsion
27 droplets suspended in clear water. Some of the oil-in-water drops have air bubbles that pull them
28 to the top of the water. The largest droplet in the microscope image for Figure 6c and 6f are 1.5
29 mm. Phase inversion is an important qualitative measurement of Pickering emulsion stability, as
30 most applications require the emulsion drop to retain its type. Because Janus particles can have
31 different ratios of hydrophilic to hydrophobic domains, one can thus tune the wettability of the
32 particle and hence influence phase inversion. Utilizing these Janus particles, we will study how
33 factors such as Janus ratio affect emulsion stability.
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38 **Janus Ratio Effects on Emulsion Stability**

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40 We studied the emulsion stability using particles with different volume ratios of hydrophilic to
41 hydrophobic domains. To understand the results, it is important to consider how the Janus ratio
42 affects particle orientation at the oil/water interface. Figure 7 shows the average emulsion droplet
43 diameter as a function of applied RCF along with the bright field images of the Pickering emulsions
44 at two instances in time – (1) before any centrifugation and (2) after the application of an RCF of
45 156xg. We use particles with Janus ratios of 0.51, 1.46, and 12.77 in this study. However, when
46 these particles sit at the oil/water interface, the measured particle volume domain ratio does not
47 fully represent the amount of particle sitting in the water and amount in the toluene. Instead a
48 particle surface area ratio is more accurate to indicate the amount of particle area covered by water
49 and the area covered by oil. These surface area ratios of particle submerged in water to oil are 0.27,
50 1.12, and 13.8 for particles with Janus ratios of 0.51, 1.46, and 12.77 respectively. Binks et al¹
51 reported that the smallest and most stable particle stabilized emulsions occur at the point where
52 particles sit at the interface with a contact angle close to 90 degree. This is also consistent with the
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3 results seen in Figure 7a where emulsion droplets using particles with a Janus ratio closest to 1.46
4 show the least response to increases in RCF when compared to Janus ratios of the other two
5 extremes. These 1.46 Janus ratio particle stabilized droplets still, however, experience a size
6 increase upon centrifugation. Figure 7b shows that the droplets stabilized by the 1.46 ratio particles
7 almost increase in size by 50% as RCF is increased. Nevertheless, this size change is much smaller
8 than those when using particles of Janus ratio 0.51 and 12.77 and this observation is good evidence
9 that the 90 degree particle contact angle at the oil water interface indeed enhances the energy
10 required for detachment²⁴. The almost 1:1 Janus ratio on the particles permits strong absorption to
11 the oil/water interface²⁵.
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15 From Figure 7a and c, we can see that particles with Janus ratio of 0.51 initially form the largest
16 emulsion drops before centrifugation compared to those with higher Janus ratios. This may be due
17 to the large hydrophobic part of the particle, which prefers the toluene phase to the water phase.
18 This might lead to the particles staying in the toluene phase rather than at the interface leading to
19 less particles available for emulsification and hence large emulsions droplets²¹. These initially very
20 large droplets resist further coalescence. The second row in Figure 7c shows the largest emulsion
21 drop before and after centrifugation to highlight the small change in size.
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24 We see that particles with a Janus ratio of 12.77 gives the largest change under external forces as
25 can be seen in Figure 7(a,c). As seen in Figure 7a, emulsions formed with high Janus ratio particles
26 immediately formed droplets of non-spherical shape before any centrifugation. Upon application
27 of force, droplets continue to change shape while increasing in average size. Eventually the
28 droplets form a single structure that encompasses the full water volume where continued
29 centrifugation can only change its shape. This could be for a number of reasons. The shape and
30 hydrophilicity of the particle may contribute to its instability. Similar to the Bancroft rule for
31 surfactant molecules, emulsion stabilizers that are more hydrophilic, tend to form preferred oil-in-
32 water emulsions.²⁶ This means that the particles in the current work with very large hydrophilic
33 sides may be unstable in the formed water-in-oil emulsions. We can visualize this in Figure 8a-c,
34 where we see how the Janus ratio affects the interface position of a particle with a hydrophilic to
35 hydrophobic volume ratio of 0.38, 1.22, and 10.12 respectively. The hydrophobic portion of the
36 Janus particle has a red outline, along with an arrow to show its point of contact with the water/oil
37 interface. In studying the stability of Pickering emulsions using bare silica nanoparticles, Ridet et
38 al¹⁷ showed that at constant pH, hydrophilic silica particles formed stable oil-in-water Pickering
39 emulsions. As they increased the volume percent of the dispersed oil phase past 60%, they obtained
40 emulsion instability with un-emulsified oil. The hydrophilic silica particles were able to stabilize
41 oil-in-water emulsions when the continuous phase was water, but when the oil phase became
42 continuous, instability ensued, as the very hydrophilic particles could not form the preferred oil-
43 in-water emulsions.
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48 The dramatic droplet size changes using particles of 12.77 Janus ratio could also be attributed to
49 the lateral compression of the particles' large hydrogel sides. Interfacial jamming or tight packing
50 of particles, when stabilizers are packed and compressed at the interface, occurs immediately
51 before centrifugation, for particles of high Janus ratio. This may be a result of the cohesive effects
52 of the short dangling polymer chains on the hydrogel surfaces, common for hydrogels at liquid-
53 liquid interfaces²⁷⁻²⁸. This would essentially create several irregular shaped droplets covered with
54 compressed particles that encase small volumes of water. Here, hydrogels inevitably touch surface-
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3 to-surface as depicted in figure 8c. Particles of 0.51 Janus ratio never form non-spherical droplets
4 while those with a Janus ratio of ~ 1.41 start to jam at different RCF according to size. These
5 irregular shaped droplets, indicative of interfacial jamming, starts at RCF of 156, 94, and 48g for
6 particles of size 172, 333, and 441 μm respectively. It may be that the larger the particle size, the
7 more likely for them to concentrate at the bottom of droplet surfaces where it is easier for them to
8 be jammed together.
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10 11 12 **CONCLUSION**

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14 We demonstrated the use of an easily fabricated glass capillary microfluidic device to create
15 amphiphilic particles (Janus particles) that can stabilize emulsions in place of surfactants. The
16 device permits full control of the size and structure of the Janus particle by varying the flowrates
17 of the entering fluids. We obtained particles of different sizes (128- 440 μm) at a constant flow
18 rate of the continuous phase while increasing the total flow rate of the inner-phase. In addition,
19 when the flow rate ratio of water to oil is varied, particles with varying hydrophilic and
20 hydrophobic portions were synthesized in a single device (hydrophilic to hydrophobic domain
21 volume ratios of 0.8 – 8.57). The increase in particle size at a fixed total particle volume diminishes
22 the number of overall particles in the experiment. This subsequently decreases the total amount of
23 surface area that can be created, leading to larger droplets. The amphiphilic nature of the particles
24 allows the formation of water-in-oil or oil-in-water emulsions based on whichever fluid acts as the
25 dispersed phase. We demonstrated that with increasing size of the Janus particles, the millimeter
26 emulsion droplets also increase in size. Emulsion droplets of repeatable size and distribution were
27 possible by simple vortexing and droplet sizes could be predicted at about half the maximum
28 particle surface coverage. Induced coalescence via centrifugation makes particles jam at the
29 interface to form non-spherical droplets where this effect is more pronounced as the hydrogel
30 volume (or Janus ratio) is increased and the hydrogel surfaces come into contact. Using Janus
31 particles (smallest sizes) with a fixed Janus ratio, emulsions with initial average droplet sizes below
32 2 mm exhibit the least coalescence when centrifuged. The closer particles are to a 1:1 Janus ratio,
33 the stronger they are against coalescence. Although different from the particle stabilizers
34 commonly used for Pickering emulsions, use of these larger particles allows un-aided visual
35 observation of formed emulsion, which leads to better interpretations on how factors such as the
36 orientations of amphiphilic particles at the water/oil interface affect Pickering emulsion stability.
37 Moving forward, our utilization of hydrogels introduces an interesting tool for Pickering emulsion
38 applications because of the ease at which we can tune their ability to deform at an oil/water
39 interface, swelling nature, and chemistry all in a microfluidic device. Further studies on how
40 factors such as Janus ratio and particle orientation at the water/oil interface using hydrogel
41 amphiphilic particles will be useful for understanding Pickering emulsion stability.
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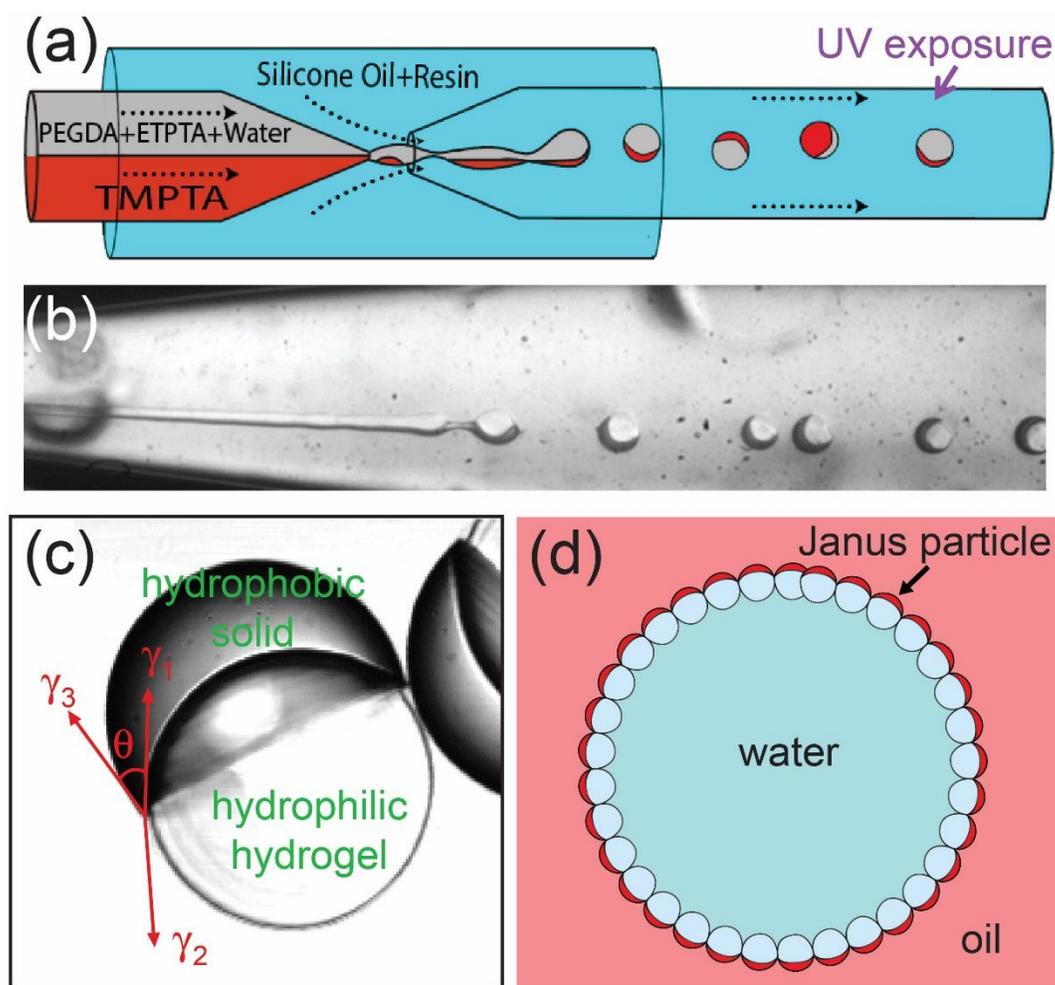


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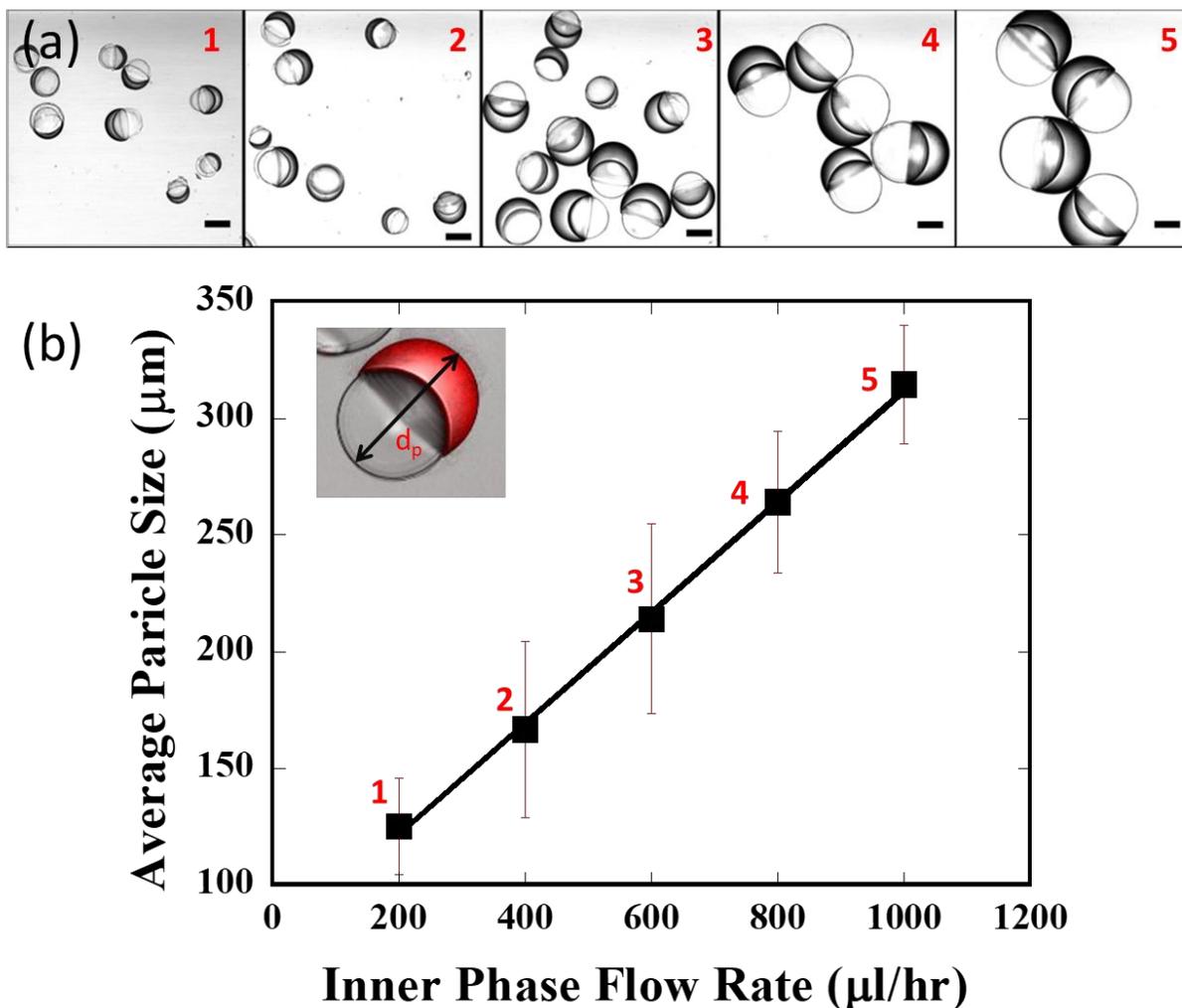


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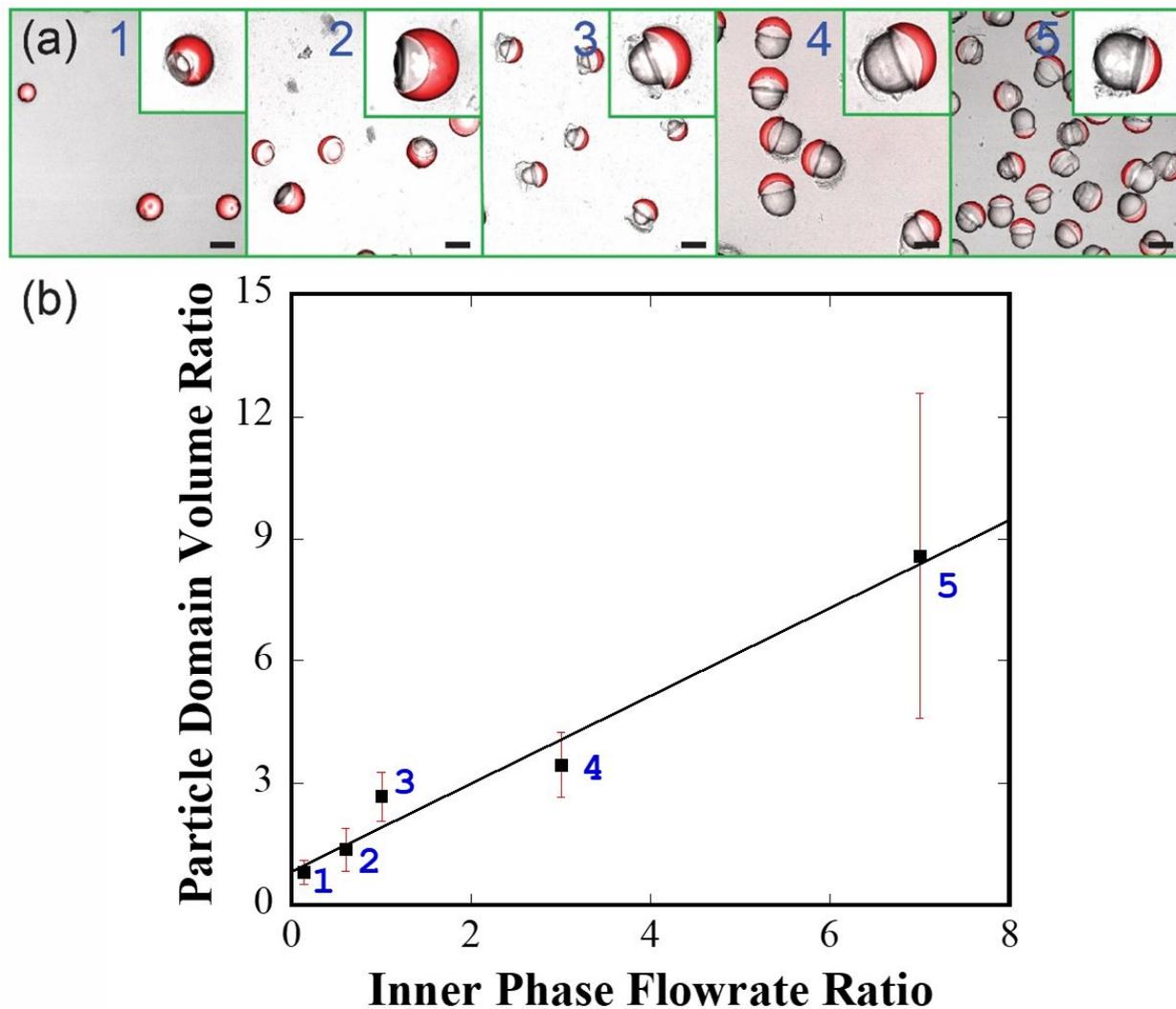


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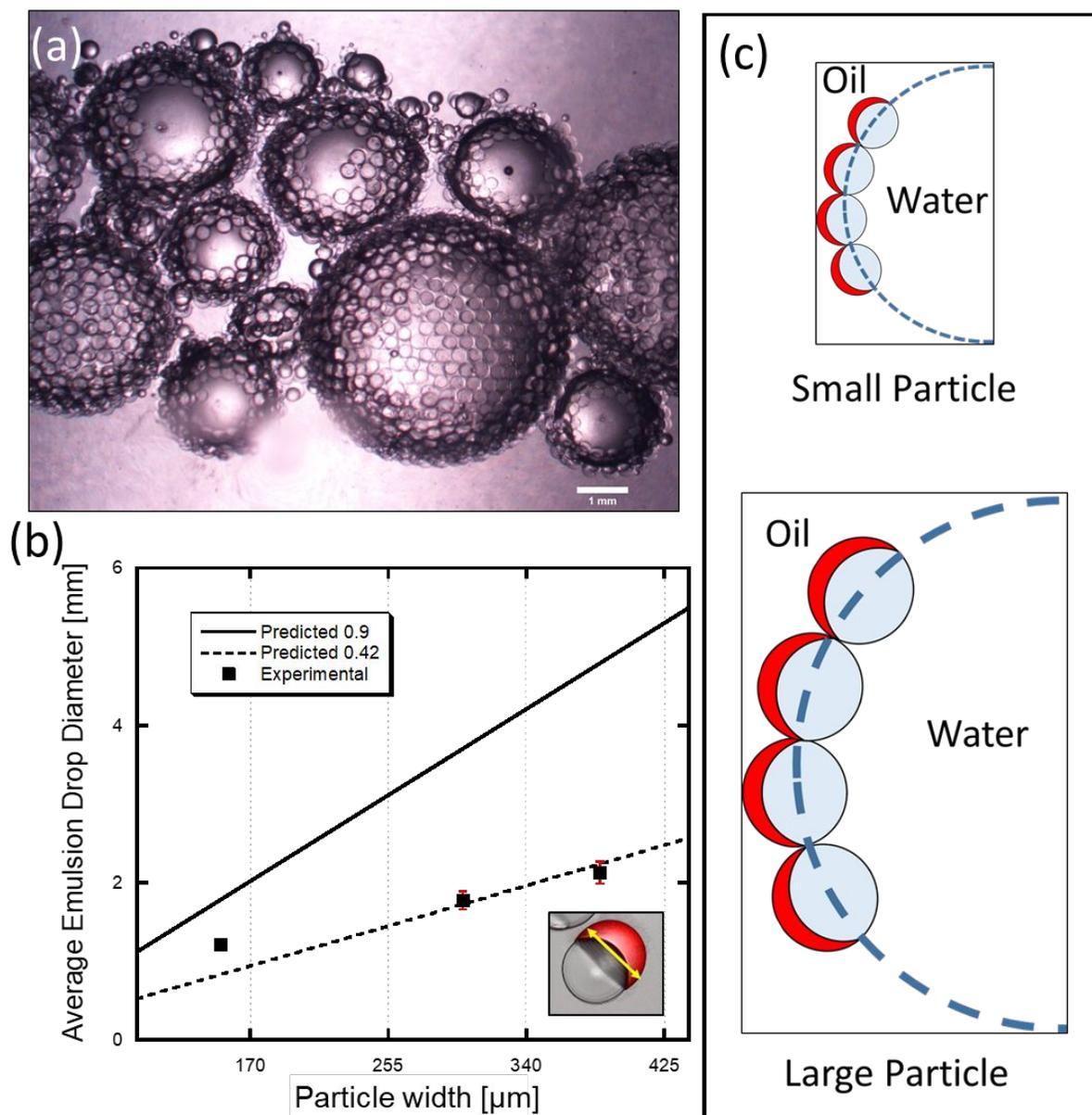


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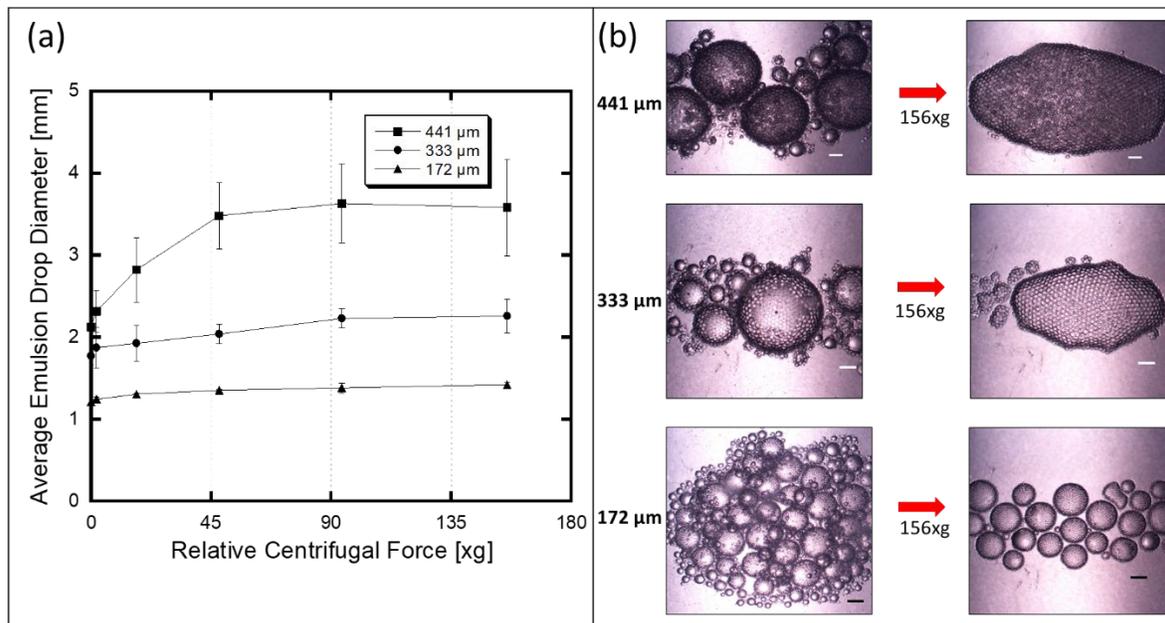


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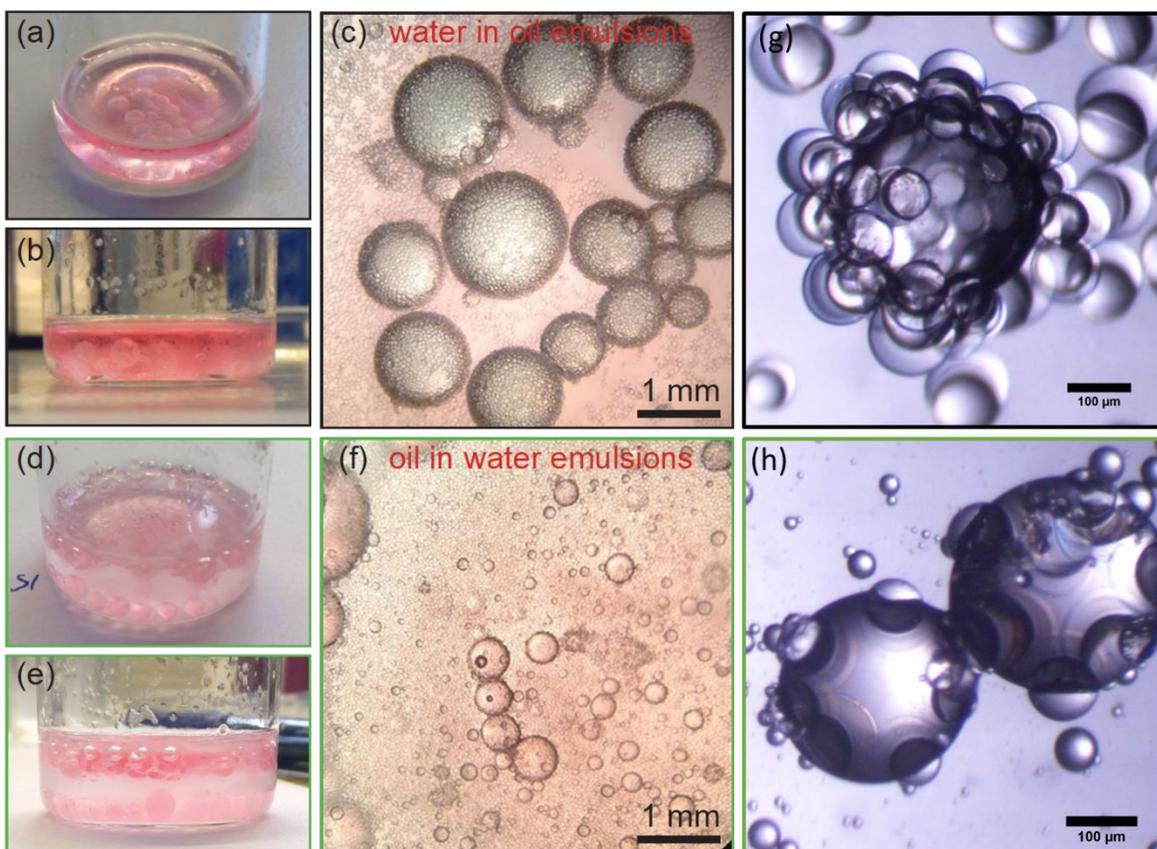


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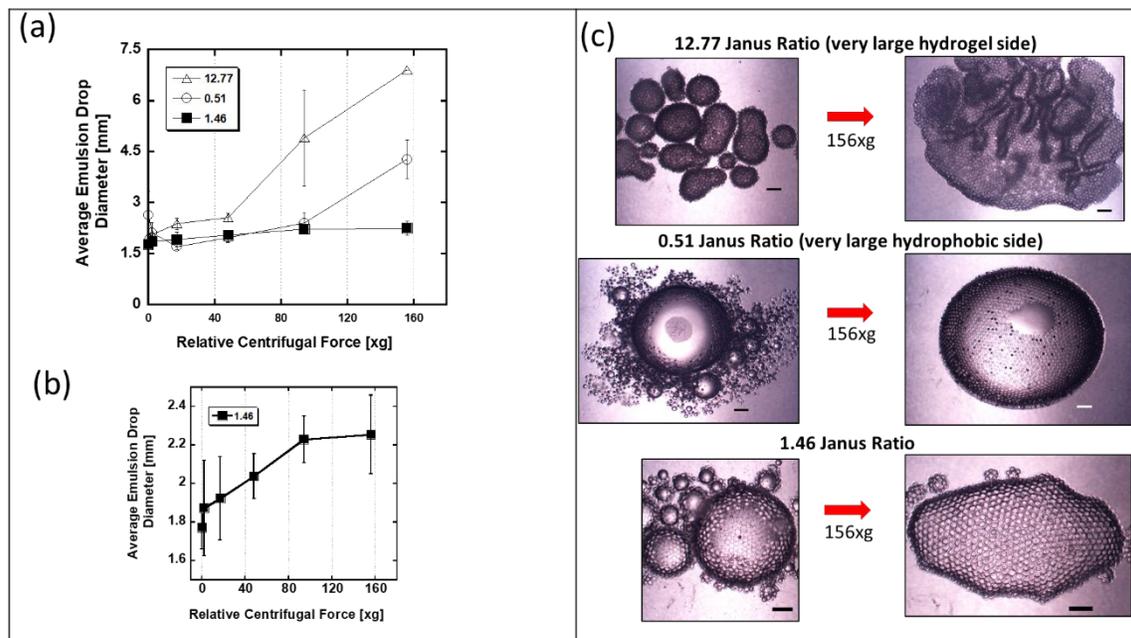


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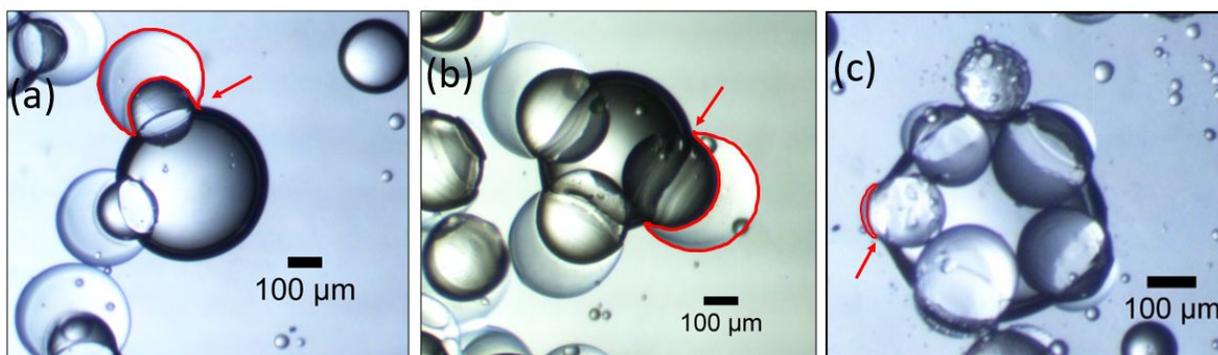
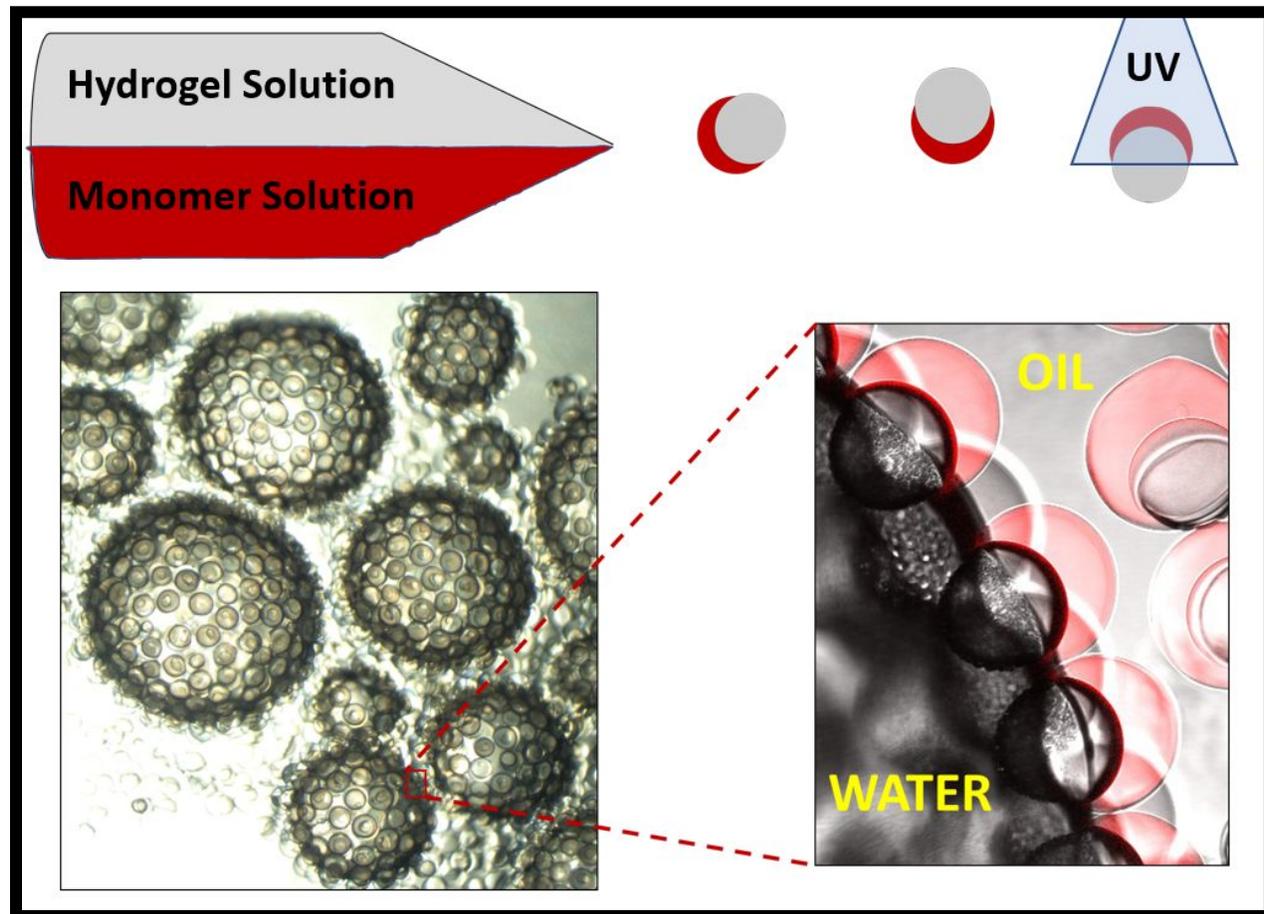


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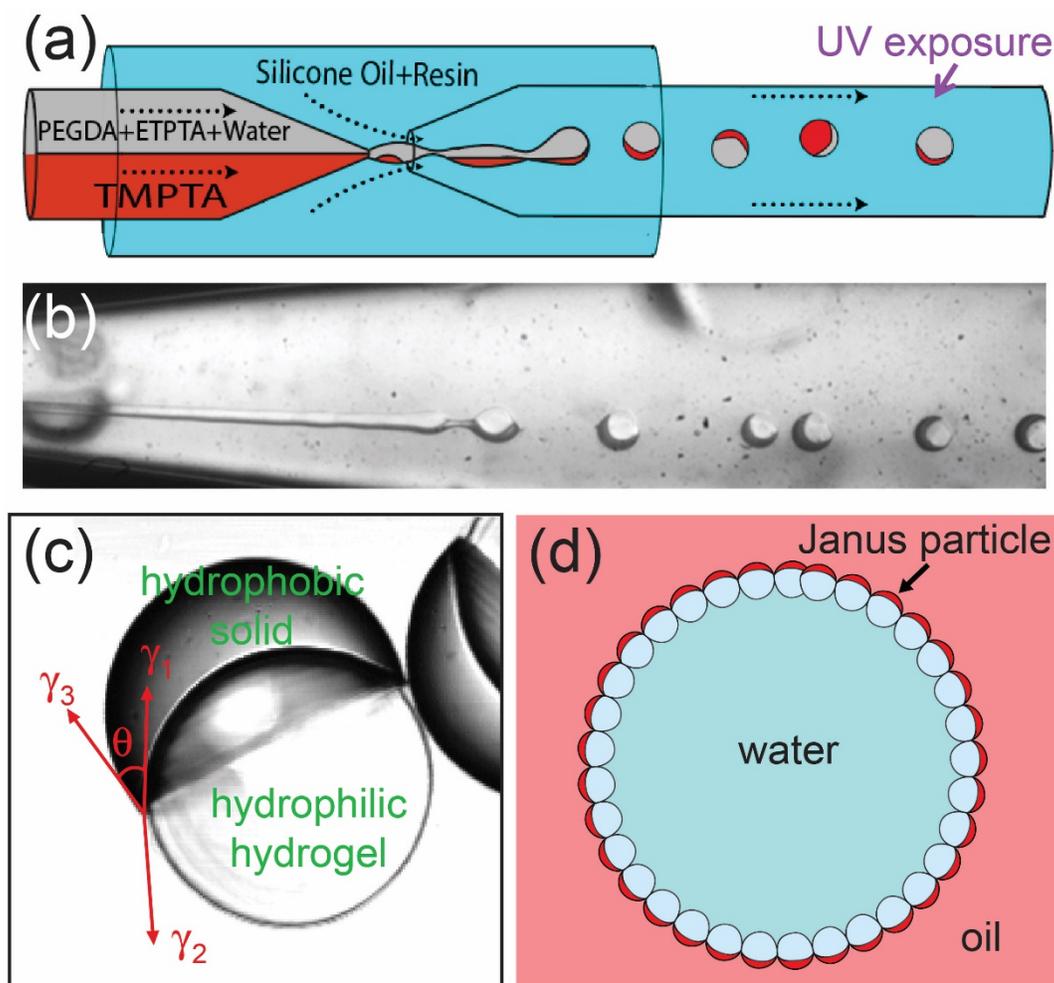


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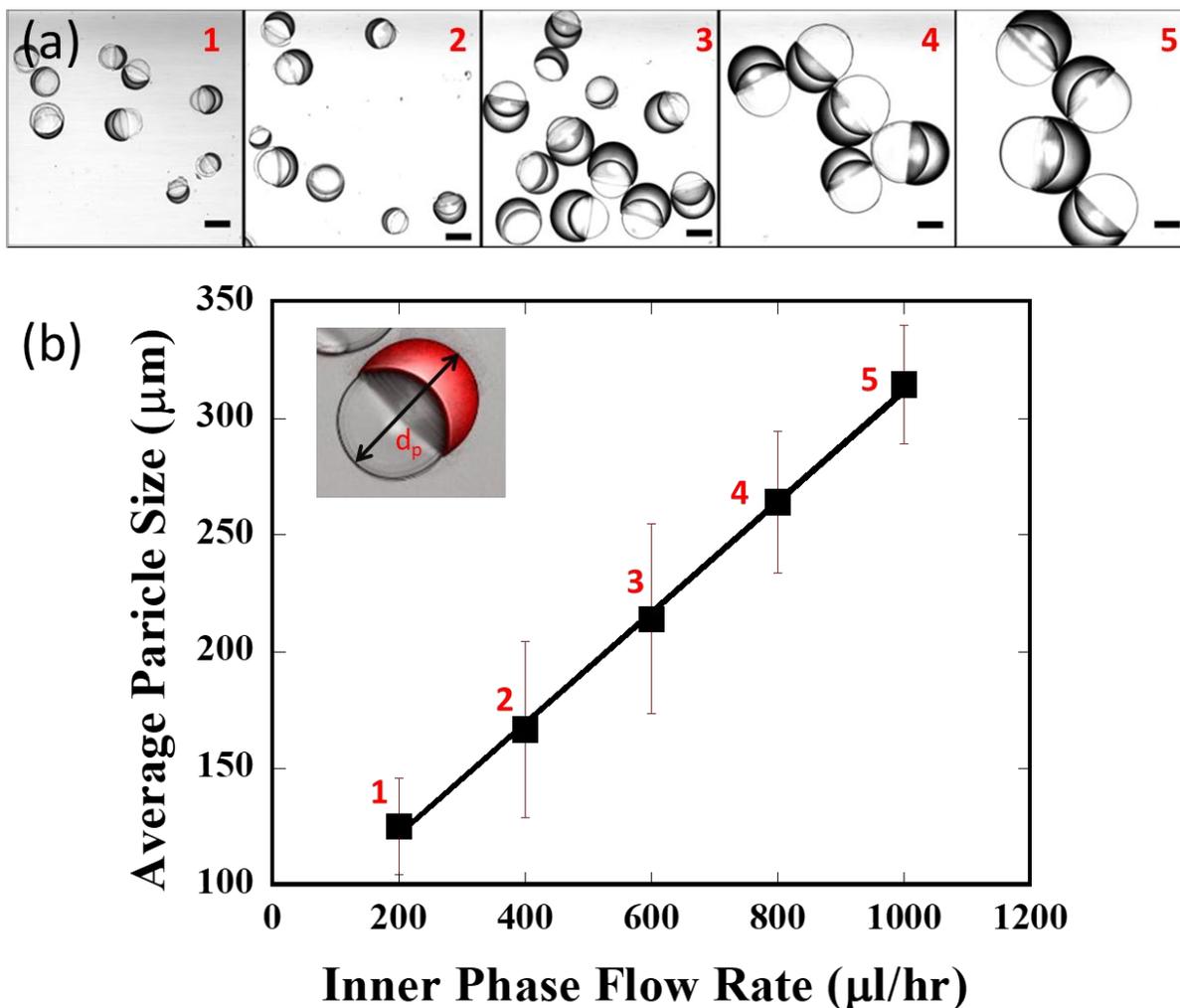


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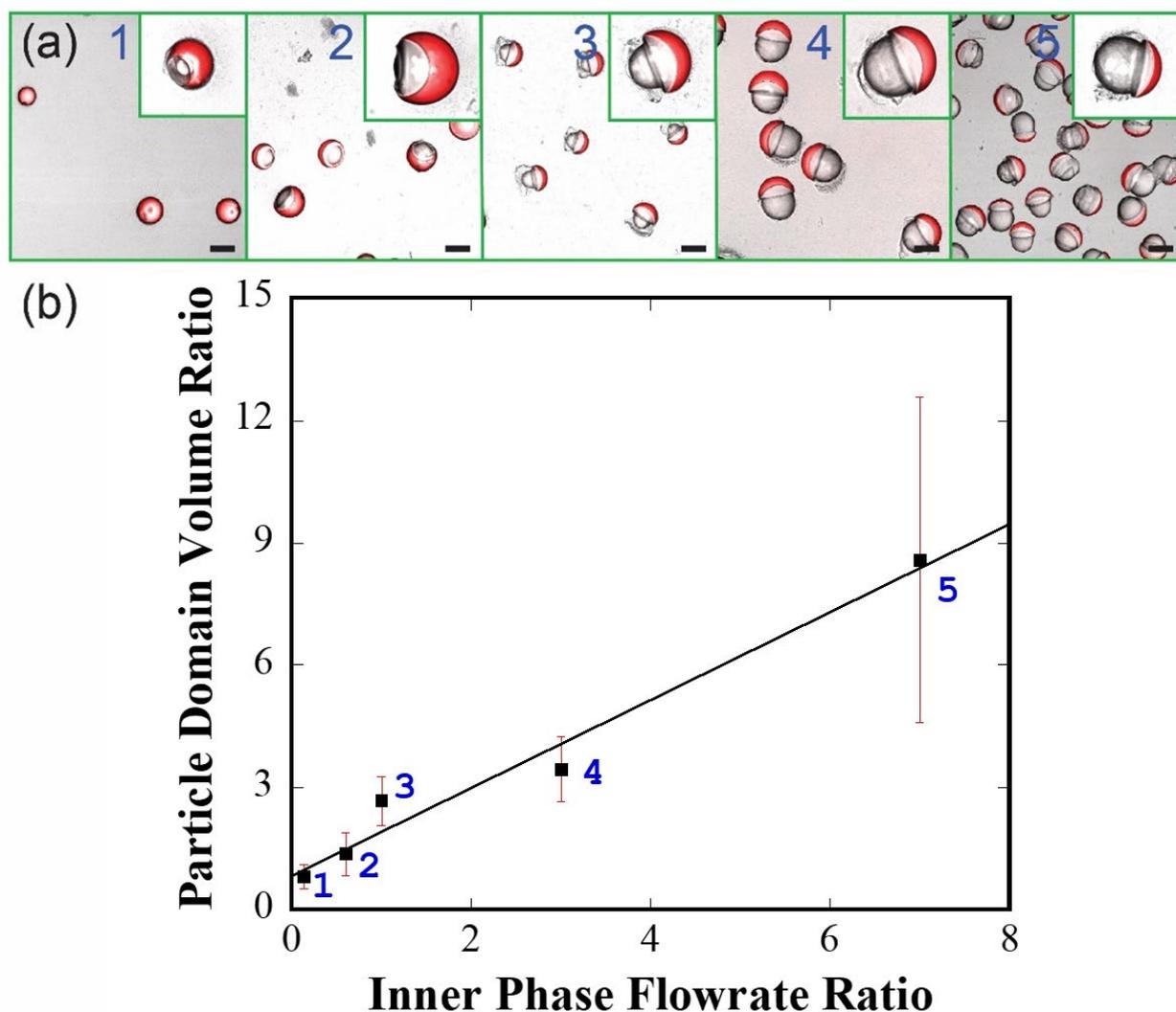


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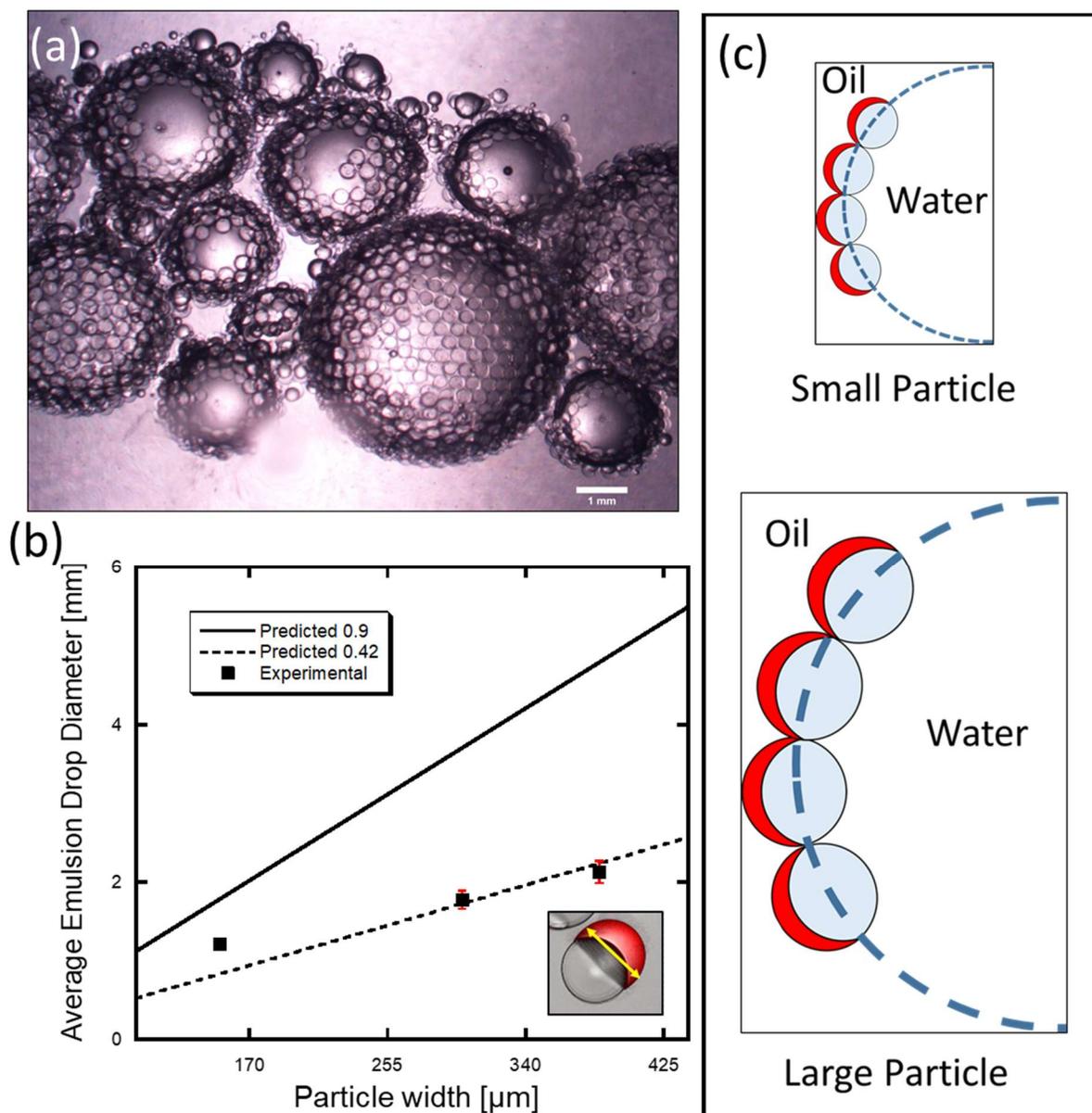


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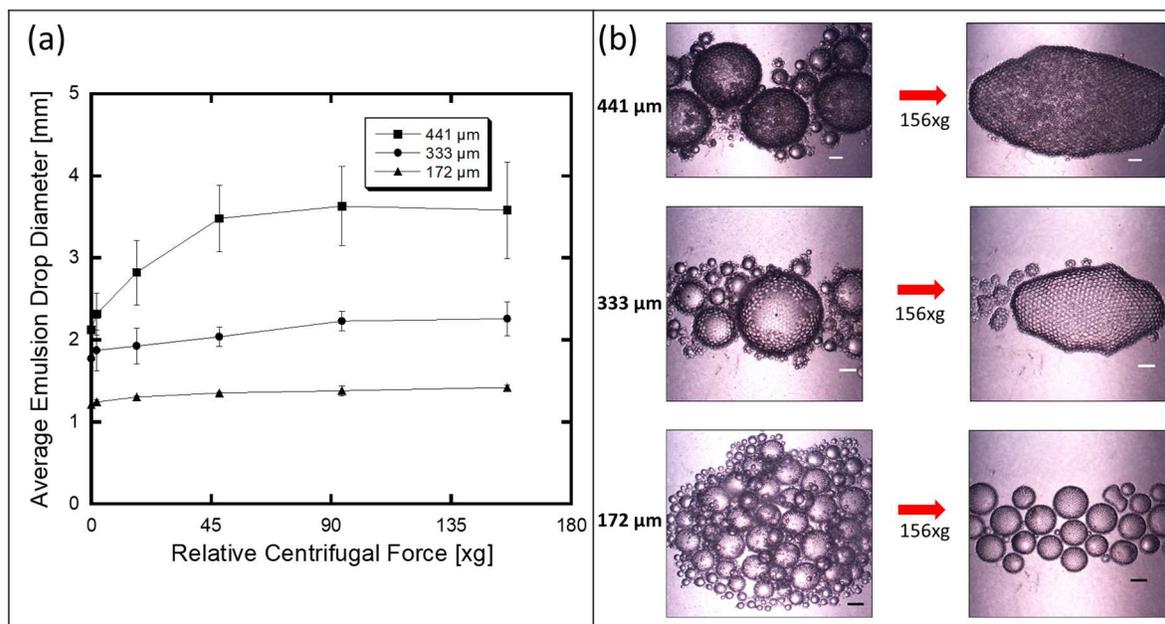


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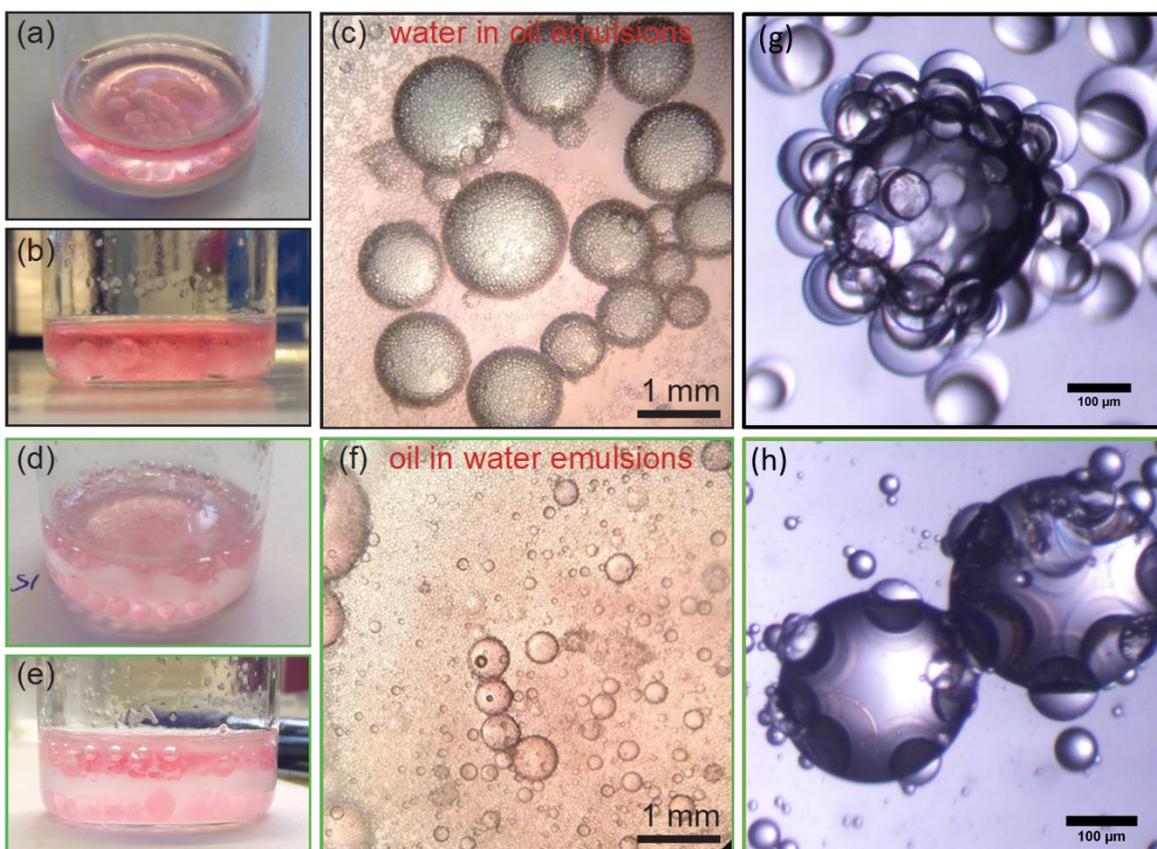


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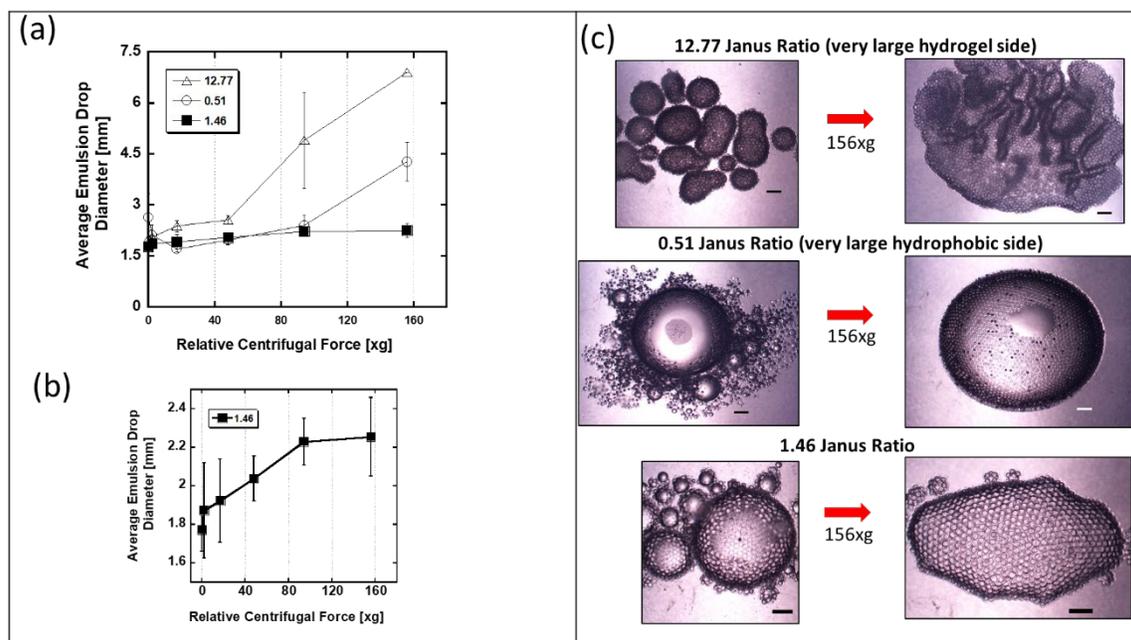


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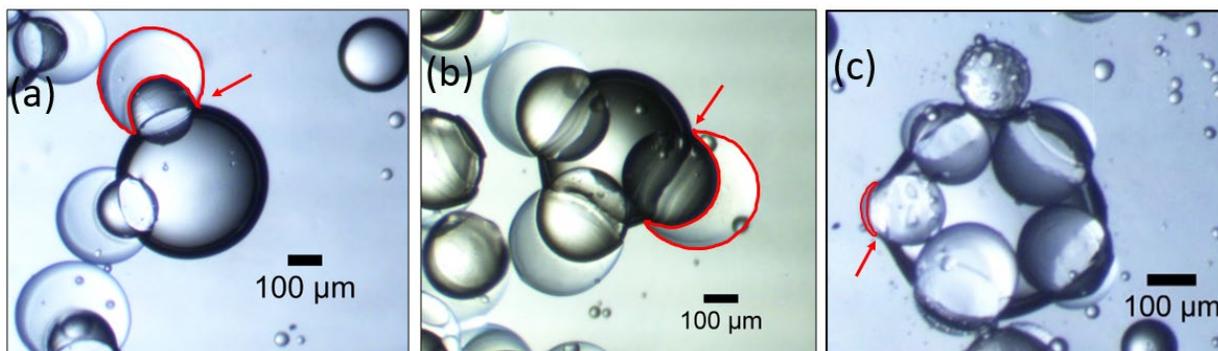


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