

Millimeter-Size Pickering Emulsions Stabilized with Janus Microparticles

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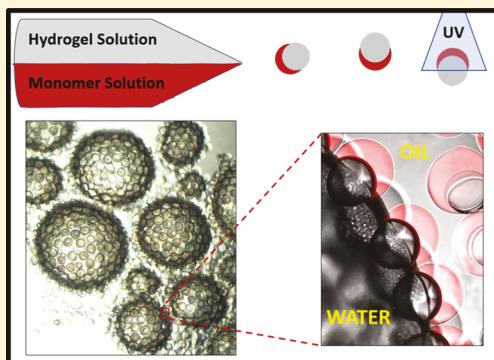
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ABSTRACT: The ability to make stable water-in-oil and oil-in-water millimeter-size Pickering emulsions is demonstrated using Janus particles—particles with distinct surface chemistries. The use of a highly cross-linked hydrophobic polymer network and the excellent water-wetting nature of a hydrogel as the hydrophobic and hydrophilic sides, respectively, permit distinct wettability on the Janus particle. Glass capillary microfluidics allows the synthesis of Janus particles with controlled sizes between 128 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 nonspherical 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 pharmacy,^{1–3} 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 microreactors. 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.

Although 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 emulsions,^{8,9} especially for large droplet sizes.

The bicompartimental surface functionalization of amphiphilic colloidal silica nanoparticles has been reported,¹⁰ 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

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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, permits 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 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 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 a partial particle surface coverage. The stability of these droplets is then studied via centrifugation to promote coalescence.

EXPERIMENTAL PROCEDURES

Materials. Poly(ethylene glycol) diacrylate (PEGDA—45 wt %, Sigma-Aldrich), 5 wt % ethoxylated trimethylolpropane triacrylate (ETPTA—Sigma-Aldrich), 1 wt % 2-hydroxy-2-methyl-propiophenone (Sigma-Aldrich), and 49 wt % water are mixed together to form the hydrophilic portion of the inner phase, which we refer to as “water”. Trimethylolpropane triacrylate (TMPTA—99 wt %, Sigma-Aldrich) and 1 wt % 2-hydroxy-2-methyl-propiophenone 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. Silicone oil (95 wt %) 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 “ θ ” 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 θ 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 θ capillary as inlets for oil and water. Oil and water flow through the θ capillary to form the inner phase, whereas the silicone oil flows through the larger outer capillary in the same direction, resulting in a coflow geometry. Figure 1a,b shows a diagram of the device and flow directions.

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

Emulsion Formation. We first cleaned 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 the addition of varying amounts of water (0.1, 0.6, or 1 mL) and vortexing for 2 min. Figure 1d shows a schematic of a formed emulsion droplet.

Stability Test. We observed the stability of Pickering emulsions using an Allegro X-30R Centrifuge. We spun the samples at different

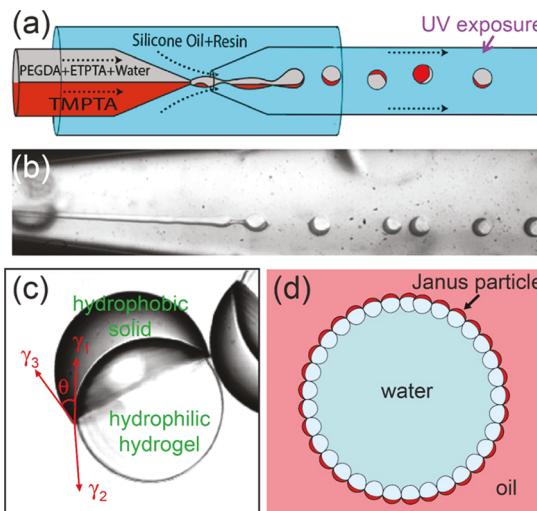


Figure 1. Fabrication of Janus particles with the hydrophilic domain being a hydrogel and the hydrophobic domain being a crescent-moon shape. (a) Coflow of the TMPTA oil and the PEGDA hydrogel solution through the θ capillary forms Janus drops, where UV exposure induces cross-linkage. (b) Real-time image of the particle formation in the glass capillary device. (c) Optical image of the Janus particles with the hydrophilic domain being a hydrogel and the hydrophobic domain being a crescent-moon shape. The shape of the hydrophobic domain depends on the balance of surface tensions, γ_1 , γ_2 , and γ_3 . (d) Stabilization of a water drop in the oil phase by the Janus colloidal surfactant. The hydrogel prefers to submerge in water, whereas the crescent-moon shape of the particle sits at the curvature of the water/oil interface.

relative centrifugal forces (RCFs) 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 θ capillary, where tunable interfacial tension between the continuous and inner phases 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 types 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 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/h 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/h in a single glass device. Using a coflow microfluidic geometry, we form droplets where break-off occurs at the end of a jetting stream. Figure 2a

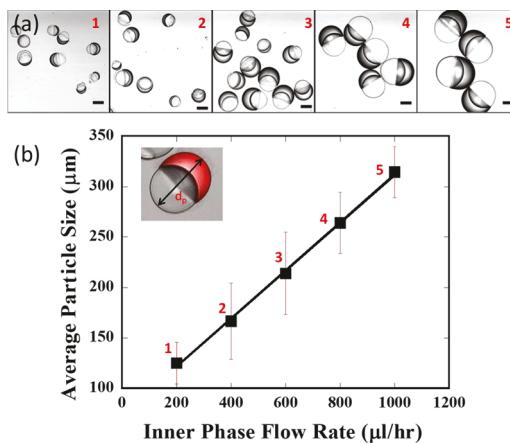


Figure 2. Janus particles of different sizes fabricated by adjusting the inner-phase flow rate. (a) Confocal images of Janus particles of different sizes fabricated at different inner-phase flow rates. The average sizes of the particles from left to right are 128.1, 166.7, 216.8, 270.1, and 311.3 μm . The coefficients 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. (b) Linear dependence of the average particle size as a function of the total inner-phase flow rate. The ratio of the hydrogel to TMPTA oil is constant at 1:1. The error bars represent standard deviations in particle size. The inset shows the longitudinal length of the particle as the measured average size. Experimental points are solid squares, whereas the line is a linear fit to the experimental data. The numbers in part (b) correspond to the numbers in part (a). The scale bars are 100 μm .

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 coefficients 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 sizes.

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 Rayleigh–Plateau instability result in a small perturbation in the cylindrical flow that eventually pinches the jet into droplets. The increase in the 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 that pinch-off occurs at the same time for different flow rates one would expect that 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 experimental parameters on jet widening and droplet pinch-off to predict the final particle sizes.

Upon the formation of the droplet, the TMPTA oil phase immediately spreads on the surface of the PEGDA hydrogel droplet to reduce the interfacial area with high surface tension between water and silicone oil (continuous phase). This spreading is mitigated by the addition of Dow Corning resin 749 into the silicone oil, where it acts as a surface-acting agent to decrease tension between the continuous phase and water. The relative surface energy of the three fluids determines the amount of spreading and results in an embedded particle for our system, as seen from Figure 1c. The spreading is quantified by the spreading coefficient (S),¹⁴ where a negative S value results in particle shapes with one sphere embedded in the other. For S greater than zero, core–shell particles form. Thus, we achieve negative spreading coefficients in our particle system by keeping the resin concentration constant, which gives rise to the observed particle shapes.

We therefore achieve complete control of the Janus particle size through glass capillary microfluidics. There has been extensive research on the factors that govern droplet break-off and subsequent particle size as a function of the flow rates. However, these data are limited to systems where the inner-phase fluid is composed of just a single phase.^{13,15–17} Although it follows a trend similar to the single-phase fluid flow, current work deals with a system in which the inner phase is composed of two fluids with different viscosities and surface tensions and both of these phases are exposed to the continuous phase. The physics of such a system (jet widening, droplet pinch-off) is not yet clear, and more insight into such systems is therefore needed.

Controlling Particle Domain Sizes. The glass capillary device permits control of the hydrophilic and hydrophobic domains of the Janus particle. We vary the volumes of the hydrophilic and hydrophobic sides of the Janus particle, also called Janus ratio, by changing the ratio of the flow rates of water to oil while keeping their total flow rate constant. We analyze volumes of the respective domains geometrically by treating the Janus particle as a sphere embedded in a spherical cap. By dividing the particle into two sections, we obtain three distinct sphere cap volumes that form the hydrophilic and hydrophobic portions of the particle. The flow rate of the continuous phase is 20 mL/h, whereas the flow rate of the inner phase is 0.2 mL/h to achieve a particle size of $\sim 128 \mu\text{m}$. We change the ratio of the flow rates of water to oil to produce particles with varying Janus ratios.

At a 1:1 ratio, the coflow of water and oil forms a jetting stream, and droplet break-off occurs in the manner as described above. At a 7:1 ratio, the coflow of water and oil forms a jetting stream, and the final Janus particles have a large hydrophilic part. Figure 3a shows the resulting Janus particles produced in a single glass device at flow rate ratios of 0.28, 0.5, 1, 3, and 7. At the smallest flow rate ratio of water to oil, we can see that individual cross-linked particles have a large volume of oil (red) as the hydrophobic side and a much smaller volume of water (colorless) as the hydrophilic side. At the other extreme with a 7:1 ratio, individual cross-linked particles formed large hydrophilic and small hydrophobic domains. This illustrates the ability of a single glass microfluidic device to produce particles of varying Janus ratios.

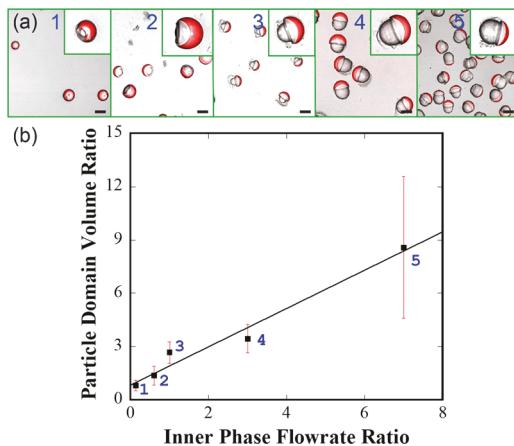


Figure 3. Janus particles with tunable hydrophilic/hydrophobic ratio synthesized in a single device. (a) Confocal images of the Janus particles formed when controlling the hydrophilic-to-hydrophobic domain volume ratios on the cross-linked particle. The red color is the hydrophobic solid domain, whereas the hydrophilic hydrogel domain is colorless. The subsets in each section give a closer look at the particle. The volume ratios of the hydrophilic domain to hydrophobic domain of the Janus particles from left to right are 0.8, 1.36, 2.67, 3.44, and 8.57. The error bars represent standard deviations in the domain volume ratio. All scale bars are 100 μm . (b) Volume ratio of the hydrophilic domain to hydrophobic domain of the Janus particle versus the ratio of the inner-phase flow rates (ratio of hydrogel solution volume flow rate to monomer oil volume flow rate, where these two fluids form the Janus droplet). Solid squares are the experimental points, whereas the line (linear curve fit to the data) is a guide to the eye. The numbers correspond to the different particles shown in part (a).

Particles of lower (0.36) and higher (12.77) Janus ratios were also created using a separate device for further experiments.

Figure 3b shows the relationship between the volume domain ratio of Janus particles and the flow rate ratio of water to oil. Although the relationship between the volume domain ratio and 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 sized Janus particles (128 μm), the data of which is presented in Figure 3. This is also in accordance with the previous work^{18,19} in the 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 emulsion 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 (approximately a 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

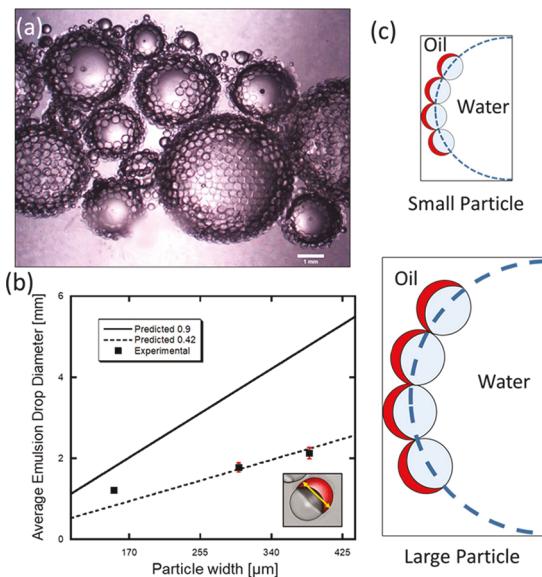


Figure 4. Pickering emulsions using different size particle stabilizers. (a) Water-in-toluene emulsions stabilized by Janus particles via vortex. (b) Average emulsion drop diameter as a function of Janus particle width, d_A . The error bars represent standard deviations in emulsion diameter. The plot inset shows the measuring direction of the particle width used in calculation. (c) Schematic to illustrate the increase in emulsion droplet size when the particle size is increased.

or equal to 800 μm in diameter. Because the focus of this work is on mm-scale droplets, we use 0.8 mm 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 top of the droplet. Although this is an expected effect for large particles, stable emulsions are still formed. The average surface coverage of our emulsion droplets across various sized 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 interface,²⁰ we can express the emulsion drop diameter (D_e) as

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

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 maintain our ratio at 3 for droplet size predictions. When using eq 1 for 90% surface coverage, we predict drop diameters of 2.74, 4.85, and 6.22 mm for particles of 172, 333, and 441 μm , respectively. These sizes were higher than the diameters experimentally observed. Figure 4b shows how the emulsion droplet size changes with the increasing particle size, using a

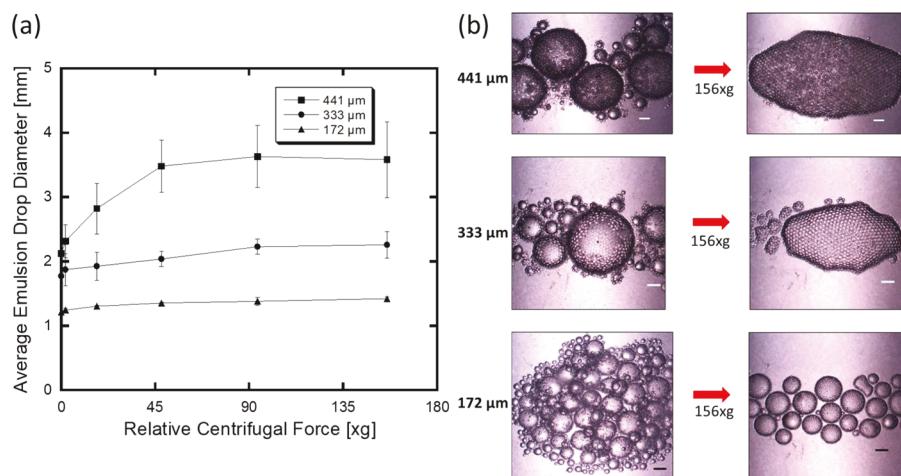


Figure 5. Stability tests using centrifuge. (a) Average Pickering emulsion drop diameter as a function of relative centrifugal force (RCF), using particles of sizes 172, 333, and 441 μm . The Janus ratio for all particle sizes is about 1.41. (b) Microscopic images of the Pickering emulsions formed by the three different Janus particle sizes before centrifuge (left) and after all RCFs up to 156g (right). The oval shape of the larger emulsions is a result of the centrifuge tube turned on its side to take the image. The error bars represent standard deviations in emulsion diameter. All scale bars are 1 mm.

constant β value. At 42% surface coverage, the equation gives an almost perfect prediction of droplet size, suggesting that our water droplets are, on average, half covered by the particles upon initial emulsification. We expect emulsion droplet diameter to increase with particle size since large and small particles pack at the oil–water interface in the same way, as depicted in Figure 4c. As particle size increases, the particle amount decreases, depleting the total amount of the surface area that can be created. This leads to larger droplets.

As others have reported,^{21–23} our particle-stabilized emulsions of partial coverage can remain stable under normal gravity conditions. We further studied emulsion stability using a centrifuge to increase the gravitational load on the water droplets. After cleaning and loading cross-linked particles into a centrifuge tube of about 11 mL of toluene, we conducted studies on (1) three different sized particles at a fixed Janus ratio and (2) three different Janus ratio particles at a fixed size. To compare the emulsion stabilities of the different particle types, β in all tests is kept at about 3.0, where the particle's size is the only changing variable. Once the appropriate amount of water is added, commensurate to the weight of particles, the tube contents are vortexed for 2 min and imaged to size the emulsion droplets. Centrifugation was done on a vortexed sample at increasing RCFs (measured relative to the acceleration to gravity—g force) to observe how the initial emulsion droplet size increases with RCF. As droplets became irregularly shaped, the full area was calculated with an image from a top view, whereas droplet depth/height was calculated with an image of the side. For the large droplets in Figures 5 and 7, the height imaged from the side was almost the same except at the edges where it curves. The diameter of a sphere with this same volume was then used as the effective diameter of the emulsion droplet. Experiments were repeated for a minimum of three times, and the average diameter with standard deviation was reported in the figures.

Figure 5a shows how the average emulsion droplet diameter changes with RCF, where the initial droplet sizes, before centrifugation, increased with particle size. We also observe that the 172 μm particle-stabilized emulsions are almost unaffected by the increase in RCF. We observed a much

smaller sized distribution of Pickering emulsions formed from small particles. Although our form of emulsification is known to produce polydispersed emulsions,¹¹ smaller particles permit smaller emulsion droplets with a lower polydispersity. Upon initial emulsification, before centrifugation, polydispersity, represented by coefficient of variation (standard deviation/average), for the 172 μm particles is about 0.02 compared to 0.06 for the 441 μm particles. It is not yet clear to us, however, why the smaller particles would create the more monodispersed system. A systematic study on the particle size, homogenization technique, and interfacial surface area is needed to make a sound conclusion. Figure 5b shows particle size effects on emulsion droplet sizes, before and after centrifugation.

For Janus particles with a fixed hydrophilic-to-hydrophobic ratio, we observe that Pickering emulsions with initial average sizes below 2 mm exhibit the strongest resistance to coalescence. Emulsion droplets that are initially larger than this size are likely to destabilize, or they are so large that not much more coalescence can occur. Emulsions formed with 441 μm particles form > 2 mm droplets and experience a large degree of coalescence when centrifuged. These initial droplets are large and partially covered with Janus particles. Initial fraction of total particles adsorbed to an interface was roughly estimated (assuming constant droplet size) to be 0.63 for droplets formed with 441 μm particles. As RCF increases, past 45g, the size remains relatively constant as most of the water has already coalesced in one phase. Although these Janus particles are effective at stabilizing millimeter-size droplets, their large size leaves more uncovered surface before centrifugation and may be more susceptible to coalescence. Because the rate of size change is faster for larger particle-stabilized droplets, observed from Figure 5a, stability must be affected by more than just the initial droplet size. In our experiments performed in the current work, the mass (or volume) of particles and water are kept fixed across the different sized particles. Hence, the stability of the emulsion for a given sized particle can be dependent on other factors, such as surface coverage during centrifugation and the fraction of particles adsorbed and desorbed on and from the droplet

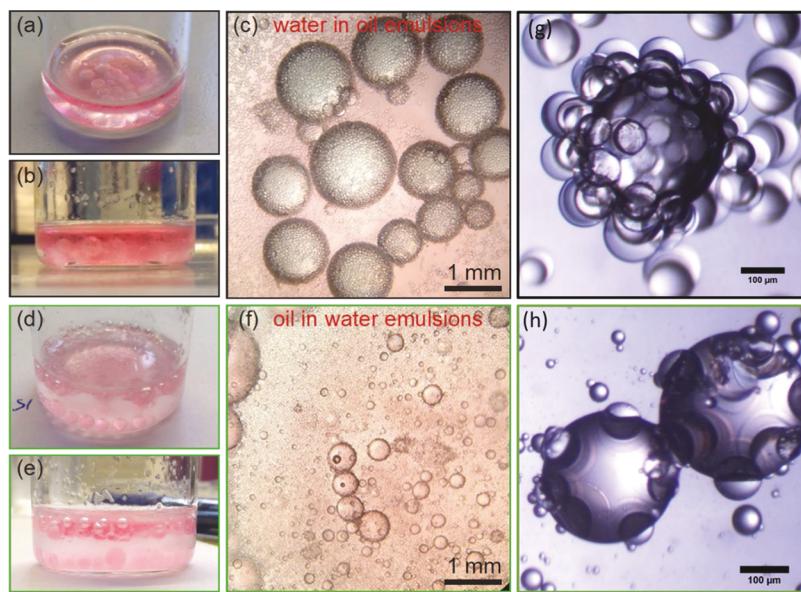


Figure 6. Inversion of water-in-oil Pickering emulsions to oil-in-water emulsions. (a–c) Water-in-oil emulsions with equal amounts of oil and water and stabilized by the Janus particles. The oil phase has a red dye. (d–f) Oil-in-water emulsions after doubling the amount of water in the vial. (g) Water-in-oil droplet covered with particles oriented with the hydrogel into the water and hydrophobic side pointing outward. (h) Phase-inverted oil-in-water droplet covered with particles oriented with the hydrogel pointing outward and the hydrophobic side in the oil. The Janus particles used have an average size of $128\text{ }\mu\text{m}$.

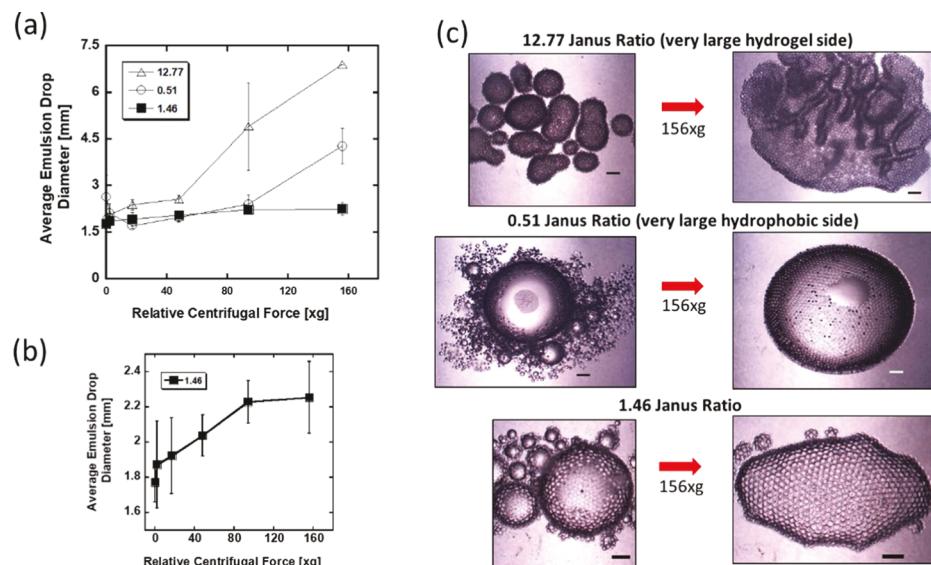


Figure 7. Stability tests using centrifuge. (a) Average Pickering emulsion drop diameter as a function of relative centrifugal force (RCF), using Janus particles with hydrophilic-to-hydrophobic ratios of 0.51, 1.46, and 12.77. The overall size of the particles is about $323\text{ }\mu\text{m}$. (b) Magnified version of the graph given in (a) for the particle with a Janus ratio of 1.46 (the diameter increases by almost 50%). (c) Microscopic images of the Pickering emulsions formed by the particles of three different Janus ratios before centrifuge (left) and after all RCFs up to 156g (right). The 12.77 ratio particles stabilizing the emulsion experience interfacial jamming. The error bars represent standard deviations in emulsion diameter. All scale bars are 1 mm.

interfaces. Although we conclude that particle size influences the initial droplet size, these additional factors will need to be analyzed in tandem to gain a complete understanding of the particle and emulsion stability.

We also conducted phase inversion experiments on formed emulsions. Figure 6a–c shows pictures of formed water-in-oil emulsions stabilized by $128\text{ }\mu\text{m}$ particles in equal amounts of the two liquids. As can be seen from the figure, the emulsion droplets are clear (water phase), whereas the surrounding oil, which has been dyed, is red. After doubling the amount of

added water and vortexing the vial, the type of emulsions flips to form oil-in-water emulsions, with the red oil dispersed in a clear water continuous phase. Figure 6f shows this phase inversion, where we see red spherical emulsion droplets suspended in clear water. Some of the oil-in-water drops have air bubbles that pull them to the top of the water. The largest droplet in the microscope image for Figure 6c,f is 1.5 mm. Phase inversion is an important qualitative measurement of Pickering emulsion stability, as most applications require the emulsion drop to retain its type. Because Janus particles can

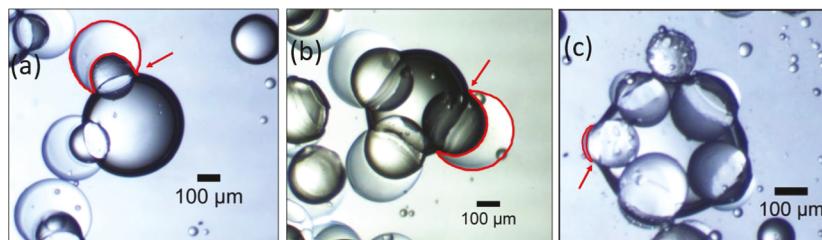


Figure 8. Bright-field images of different Janus particles sitting at the interface of water in a toluene medium, where the different Janus ratios in the images are (a) 0.38, (b) 1.22, and (c) 10.12. The hydrophobic portion of the Janus particle has a red outline, along with an arrow to show its point of contact with the water/oil interface.

have different ratios of hydrophilic-to-hydrophobic domains, one can thus tune the wettability of the particle and hence influence phase inversion. Utilizing these Janus particles, we will study how factors such as Janus ratio affect emulsion stability.

Janus Ratio Effects on Emulsion Stability. We studied the emulsion stability using particles with different volume ratios of hydrophilic-to-hydrophobic domains. To understand the results, it is important to consider how the Janus ratio affects particle orientation at the oil/water interface. Figure 7 shows the average emulsion droplet diameter as a function of applied RCF along with the bright-field images of the Pickering emulsions at two instances in time—(1) before any centrifugation and (2) after the application of an RCF of 156g. We use particles with Janus ratios of 0.51, 1.46, and 12.77 in this study. However, when these particles sit at the oil/water interface, the measured particle volume domain ratio does not fully represent the amount of particle sitting in the water and the amount in the toluene. Instead, a particle surface area ratio is more accurate to indicate the amount of particle area covered by water and the area covered by oil. These surface area ratios of particle submerged in water to oil are 0.27, 1.12, and 13.8 for particles with Janus ratios of 0.51, 1.46, and 12.77, respectively. Binks et al.¹ reported that the smallest and most stable particle-stabilized emulsions occur at the point where particles sit at the interface with a contact angle close to 90 degrees. This is also consistent with the results seen in Figure 7a, where emulsion droplets using particles with a Janus ratio closest to 1.46 show the least response to increases in RCF when compared to Janus ratios of the other two extremes. These 1.46 Janus ratio particle-stabilized droplets still, however, experience a size increase upon centrifugation. Figure 7b shows that the droplets stabilized by the 1.46 ratio particles almost increase in size by 50% as RCF is increased. Nevertheless, this size change is much smaller than those when using particles of Janus ratios 0.51 and 12.77, and this observation is good evidence that the 90 degree particle contact angle at the oil–water interface indeed enhances the energy required for detachment.²⁴ The almost 1:1 Janus ratio on the particles permits strong absorption to the oil/water interface.²⁵

From Figure 7a,c, we can see that particles with a Janus ratio of 0.51 initially form the largest emulsion drops before centrifugation compared to those with higher Janus ratios. This may be due to the large hydrophobic part of the particle, which prefers the toluene phase to the water phase. This might lead to the particles staying in the toluene phase rather than at the interface, leading to less particles available for emulsification and hence large emulsion droplets.²¹ These initially very large droplets resist further coalescence. The second row in Figure

7c shows the largest emulsion drop before and after centrifugation to highlight the small change in size.

We see that particles with a Janus ratio of 12.77 give the largest change under external forces, as can be seen in Figure 7a,c. As seen in Figure 7a, emulsions formed with high Janus ratio particles immediately formed droplets of nonspherical shape before any centrifugation. Upon the application of force, droplets continue to change shape while increasing in average size. Eventually, the droplets form a single structure that encompasses the full water volume, where continued centrifugation can only change its shape. This could be for a number of reasons. The shape and hydrophilicity of the particle may contribute to its instability. Similar to the Bancroft rule for surfactant molecules, emulsion stabilizers that are more hydrophilic tend to form preferred oil-in-water emulsions.²⁶ This means that the particles in the current work with very large hydrophilic sides may be unstable in the formed water-in-oil emulsions. We can visualize this in Figure 8a–c, where we see how the Janus ratio affects the interface position of a particle with hydrophilic-to-hydrophobic volume ratios of 0.38, 1.22, and 10.12, respectively. The hydrophobic portion of the Janus particle has a red outline, along with an arrow to show its point of contact with the water/oil interface. In studying the stability of Pickering emulsions using bare silica nanoparticles, Ridel et al.²⁰ showed that at constant pH, hydrophilic silica particles formed stable oil-in-water Pickering emulsions. As they increased the volume percent of the dispersed oil phase past 60%, they obtained emulsion instability with unemulsified oil. The hydrophilic silica particles were able to stabilize oil-in-water emulsions when the continuous phase was water, but when the oil phase became continuous, instability ensued, as the very hydrophilic particles could not form the preferred oil-in-water emulsions.

The dramatic droplet size changes using particles of 12.77 Janus ratio could also be attributed to the lateral compression of the particles' large hydrogel sides. Interfacial jamming or tight packing of particles, when stabilizers are packed and compressed at the interface, occurs immediately before centrifugation for particles of high Janus ratio. This may be a result of the cohesive effects of the short dangling polymer chains on the hydrogel surfaces, common for hydrogels at liquid–liquid interfaces.^{27,28} This would essentially create several irregularly shaped droplets covered with compressed particles that encase small volumes of water. Here, hydrogels inevitably touch surface to surface, as depicted in Figure 8c. Particles of 0.51 Janus ratio never form nonspherical droplets, whereas those with a Janus ratio of ~1.41 start to jam at different RCF according to size. These irregularly shaped droplets, indicative of interfacial jamming, start at RCFs of 156, 94, and 48g for particles of sizes 172, 333, and 441 μ m,

respectively. It may be that the larger the particle size, the more likely for them to concentrate at the bottom of droplet surfaces, where it is easier for them to be jammed together.

CONCLUSIONS

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

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Binks, B. P.; Fletcher, P. D. I.; Holt, B. L.; Beaussoubre, P.; Wong, K. Phase inversion of particle-stabilised perfume oil-water emulsions: experiment and theory. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11954–11966.
- (2) Li, X.; Li, H. Y.; Xiao, Q.; Wang, L. Y.; Wang, M. L.; Lu, X. L.; York, P.; Shi, S. L.; Zhang, J. W. Two-way effects of surfactants on Pickering emulsions stabilized by the self-assembled microcrystals of alpha-cyclodextrin and oil. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14059–14069.
- (3) Timgren, A.; Rayner, M.; Sjoo, M.; Dejmek, P. Starch particles for food based Pickering emulsions. *Procedia Food Sci.* **2011**, *1*, 95–103.
- (4) Effendy, I.; Maibach, H. I. Surfactants and experimental irritant contact-dermatitis. *Contact Dermatitis* **1995**, *33*, 217–225.
- (5) Wei, Z. J.; Wang, C. Y.; Zou, S. W.; Liu, H.; Tong, Z. Chitosan nanoparticles as particular emulsifier for preparation of novel pH-responsive Pickering emulsions and PLGA microcapsules. *Polymer* **2012**, *53*, 1229–1235.
- (6) Zhou, H. O.; Shi, T. J.; Zhou, X. Preparation of polystyrene/SiO₂ microsphere via Pickering emulsion polymerization: Synergistic effect of SiO₂ concentrations and initiator sorts. *Appl. Surf. Sci.* **2013**, *266*, 33–38.
- (7) Sadeghpour, A.; Pirolt, F.; Glatter, O. Submicrometer-Sized Pickering Emulsions Stabilized by Silica Nanoparticles with Adsorbed Oleic Acid. *Langmuir* **2013**, *29*, 6004–6012.
- (8) Noguchi, T. G.; Iwashita, Y.; Kimura, Y. Dependence of the Internal Structure on Water/Particle Volume Ratio in an Amphiphilic Janus Particle-Water-Oil Ternary System: From Micelle-like Clusters to Emulsions of Spherical Droplets. *Langmuir* **2017**, *33*, 1030–1036.
- (9) Kang, C. J.; Honciuc, A. Influence of Geometries on the Assembly of Snowman-Shaped Janus Nanoparticles. *ACS Nano* **2018**, *12*, 3741–3750.
- (10) Cao, W.; Huang, R. L.; Qi, W.; Su, R. X.; He, Z. M. Self-Assembly of Amphiphilic Janus Particles into Monolayer Capsules for Enhanced Enzyme Catalysis in Organic Media. *ACS Appl. Mater. Interfaces* **2015**, *7*, 465–473.
- (11) Wei, D.; Ge, L. L.; Lu, S. H.; Li, J. J.; Guo, R. Janus Particles Tempted by Janus Emulsions and Application as a Pickering Emulsifier. *Langmuir* **2017**, *33*, 5819–5828.
- (12) Umbanhowar, P. B.; Prasad, V.; Weitz, D. A. Monodisperse emulsion generation via drop break off in a coflowing stream. *Langmuir* **2000**, *16*, 347–351.
- (13) Utada, A. S.; Fernandez-Nieves, A.; Stone, H. A.; Weitz, D. A. Dripping to jetting transitions in coflowing liquid streams. *Phys. Rev. Lett.* **2007**, *99*, No. 094502.
- (14) Kim, S. H.; Abbaspourrad, A.; Weitz, D. A. Amphiphilic Crescent-Moon-Shaped Microparticles Formed by Selective Adsorption of Colloids. *J. Am. Chem. Soc.* **2011**, *133*, 5516–5524.
- (15) Nunes, J. K.; Tsai, S. S. H.; Wan, J.; Stone, H. A. Dripping and jetting in microfluidic multiphase flows applied to particle and fibre synthesis. *J. Phys. D: Appl. Phys.* **2013**, *46*, No. 114002.
- (16) Utada, A. S.; Lorenceau, E.; Link, D. R.; Kaplan, P. D.; Stone, H. A.; Weitz, D. A. Monodisperse double emulsions generated from a microcapillary device. *Science* **2005**, *308*, 537–541.
- (17) Castro-Hernández, E.; Gundabala, V.; Fernandez-Nieves, A.; Gordillo, J. M. Scaling the drop size in coflow experiments. *New J. Phys.* **2009**, *11*, No. 075021.
- (18) Ge, X. H.; Huang, J. P.; Xu, J. H.; Chen, J.; Luo, G. S. Water-oil Janus emulsions: microfluidic synthesis and morphology design. *Soft Matter* **2016**, *12*, 3425–3430.

(19) Xu, K.; Ge, X. H.; Huang, J. P.; Dang, Z. X.; Xu, J. H.; Luo, G. S. A region-selective modified capillary microfluidic device for fabricating water-oil Janus droplets and hydrophilic-hydrophobic anisotropic microparticles. *RSC Adv.* **2015**, *5*, 46981–46988.

(20) Ridel, L.; Bolzinger, M. A.; Gilon-Delepine, N.; Dugas, P. Y.; Chevalier, Y. Pickering emulsions stabilized by charged nanoparticles. *Soft Matter* **2016**, *12*, 7564–7576.

(21) Frelichowska, J.; Bolzinger, M. A.; Chevalier, Y. Effects of solid particle content on properties of o/w Pickering emulsions. *J. Colloid Interface Sci.* **2010**, *351*, 348–356.

(22) Binks, B. P.; Kirkland, M. Interfacial structure of solid-stabilised emulsions studied by scanning electron microscopy. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3727–3733.

(23) Horozov, T. S.; Binks, B. P. Particle-stabilized emulsions: A bilayer or a bridging monolayer? *Angew. Chem., Int. Ed.* **2006**, *45*, 773–776.

(24) Chevalier, Y.; Bolzinger, M. A. Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids Surf., A* **2013**, *439*, 23–34.

(25) Aveyard, R. Can Janus particles give thermodynamically stable Pickering emulsions? *Soft Matter* **2012**, *8*, 5233–5240.

(26) Binks, B. P. Particles as surfactants - similarities and differences. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21–41.

(27) Li, Z. F.; Ngai, T. Microgel particles at the fluid-fluid interfaces. *Nanoscale* **2013**, *5*, 1399–1410.

(28) Destribats, M.; Wolfs, M.; Pinaud, F.; Lapeyre, V.; Sellier, E.; Schmitt, V.; Ravaine, V. Pickering Emulsions Stabilized by Soft Microgels: Influence of the Emulsification Process on Particle Interfacial Organization and Emulsion Properties. *Langmuir* **2013**, *29*, 12367–12374.