# Shape-Changing and Amphiphilicity-Reversing Janus Particles with pH-Responsive Surfactant Properties

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Ⓢ *Supporting Information*

ABSTRACT: Janus particles are biphasic colloids that have two sides with distinct chemistry and wettability. Because of their amphiphilicity, Janus particles present a unique opportunity for stabilizing multiphasic fluid mixtures such as emulsions. Our work is motivated by one class of molecular amphiphiles that change their surfactant properties in response to environmental stimuli. Depending on the environmental conditions, these stimuli-responsive molecular amphiphiles are able to assemble into different structures, generate emulsions with different morphologies, and also induce phase inversion emulsification. We present a new synthesis method utilizing a combination of polymerization-induced phase separation and seeded emulsion polymerization, which allows for the bulk synthesis of highly uniform pH-responsive Janus particles that are able to completely reverse their surfactant properties in response to solution pH. One side of these

Janus particles is rich in a hydrophobic monomer, styrene, whereas the other side is rich in a pH-sensitive hydrophilic repeating unit, acrylic acid. These Janus particles change their aggregation/dispersion behavior and also transform into different shapes in response to pH changes. Furthermore, we demonstrate that these Janus particles can stabilize different types of emulsions (oil-in-water and water-in-oil) and, more importantly, induce phase inversion of emulsions in response to changes in solution pH. The pH-responsive aggregation/dispersion behavior of these Janus particles also allows us to tune the interactions between oil-in-water emulsion droplets without inducing destabilization; that is, emulsion drops with attractive or repulsive interactions can be generated by changing the pH of the aqueous phase. Our study presents a new class of colloidal materials that will further widen the functionality and properties of Janus particles as dynamically tunable solid surfactants.
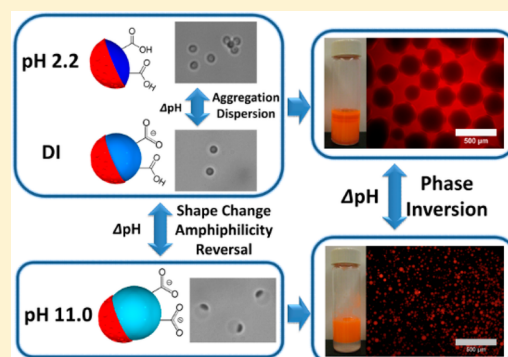
■ INTRODUCTION

Janus particles are biphasic colloids that have two sides with contrasting properties.[1−4] One of the most promising and practical applications of these Janus particles is in the stabilization of multiphasic mixtures such as emulsions.[5−12] Theoretical and experimental studies have shown that Janus particles offer advantages over their homogeneous counterparts as solid surfactants. The adsorption energy of a spherical Janus particle to an oil−water interface, for example, can be as large as 3 times that of its homogeneous counterpart.[13] Such a result indicates that Janus particles have a very strong tendency to segregate to and remain at fluid interfaces. More recently, theoretical studies based on free energy calculations have shown that thermodynamically stable emulsions can be generated using Janus particles as solid surfactants.[14,15] In contrast, most Pickering emulsions generated with homogeneous particles, with a few notable exceptions,[16] are only kinetically stable. The thermodynamic stability of particle-stabilized emulsions can be understood by determining the free energy change during emulsification. While the free energy change is positive for emulsions stabilized with homogeneous particles,[17] it can become negative for emulsions stabilized with Janus particles due to the large energy needed for their detachment from the fluid interface.[14,15] Experimentally, it has

been reported that a Janus particle-laden interface has a significantly smaller interfacial tension than a liquid−liquid interface with homogeneous particles, which indicates that Janus particles have much higher surface activity.[18−21] In addition, some emulsions that cannot be easily stabilized by homogeneous particles exhibit excellent stability when Janus particles are used as emulsifiers.[22] Taking advantage of such excellent surfactant properties of Janus particles, recent studies have shown that Janus particle-stabilized emulsions can be used as microreactors for biofuel upgrade reactions and the subsequent separation of the reaction products.[23,24]

An emerging idea in this area is that the shape of Janus particles, in addition to their amphiphilicity, has a significant influence on their behavior and functionality as surface-active agents.[25] Such a concept is inspired by the fundamental parameters that govern the behavior and properties of molecular amphiphiles: shape, characterized by the so-called packing parameter, and amphiphilicity, quantified in terms of hydrophile−lipophile balance (HLB).[26] The type of emulsions that can be stabilized by a particular molecular amphiphile, for example, can be accurately predicted by analyzing its packing

parameter and HLB number.[26] Recent reports provide ample evidence that the behavior and properties of Janus particles as solid surfactants indeed depend on the shape as well as the chemistry of Janus particles. Both theoretical and experimental studies, for example, have shown that shape anisotropy is a critical factor that determines the configuration of Janus particles as well as interparticle interactions at fluid interfaces.[27−30] The adsorption kinetics and packing behavior of nonspherical Janus particles also have been found to depend strongly on the particle shape.[31]

One intriguing class of molecular surfactants that exhibit behaviors that have both fundamental and practical significance is the stimuli-responsive amphiphiles. These molecules change their shape and amphiphilicity in response to external stimuli such as temperature, pH, and light, which in turn change their properties and functionality as surfactants.[32,33] A diblock copolymer composed of a hydrophobic block and a pH-sensitive hydrophilic block, for example, assembles into a variety of different aggregate structures depending on the pH of the solution.[34−36] Another study has shown that the type of emulsions [i.e., oil-in-water (O/W) vs water-in-oil (W/O)] generated with a hydrophobically modified pH-sensitive polymer as the stabilizer depends on the pH of the aqueous phase.[37] A recent study has even shown that the generation and phase inversion of multiple emulsions is possible using single pH-sensitive amphiphilic copolymer surfactant.[38] The changes in the shape and HLB of these amphiphilic molecules in response to changes in the solution pH are responsible for these observed phenomena. Despite many interesting and important examples of stimuli-responsive molecular surfactants, only a few examples have been reported on the application of stimuli-responsive Janus particles as solid surfactants. These Janus particles have been shown to stabilize and destabilize emulsions in response to environmental stimuli.[39−41] However, Janus particles that can induce phase inversion of emulsions or stabilize different types of emulsions, as have been demonstrated with stimuli-responsive molecular surfactants, have not been reported.

In this study, we present the synthesis of pH-responsive Janus particles that can completely *switch* their amphiphilicity due to drastic changes in their shape and chemistry. The surfactant properties of these Janus particles can be drastically altered to enable stabilization of different types of emulsions and induce phase inversion of emulsions. Our synthesis method utilizes seeded emulsion polymerization, thus enabling the generation of a large amount of highly uniform particles.[42−50] The pH-responsiveness of these Janus particles can be tailored by changing the composition of the particles generated via seeded emulsion polymerization. We demonstrate that the type of emulsions stabilized by these amphiphilicity-reversing and shape-changing Janus particles depends on the solution pH and that these emulsions undergo phase inversion in response to changes in the pH of the aqueous phase. We also demonstrate that the interaction between emulsion droplets stabilized by these particles can be controlled by changing the pH of the continuous phase. Our results present a new class of colloidal materials that will further widen the functionality and properties of Janus particles as dynamically tunable solid surfactants.

■ EXPERIMENTAL SECTION

Synthesis of Amphiphilic Janus Particles. Amphiphilic Janus particles are synthesized by seeded emulsion polymerization followed by acid hydrolysis. The monodisperse seed particles composed of linear polystyrene (LPS) are synthesized by dispersion polymerization. First, 0.03 g of poly(vinyl pyrrolidone) ($M_w \approx 55\,000$) is dissolved in 75 mL of isopropyl alcohol (99.9%) in a 100 mL flask. Then 9 mL of deionized (DI) water containing 0.02 g of ammonium persulfate (98%) as initiator is added to the flask followed by adding 6.6 mL of styrene (≥99%). After the flask is sealed with a rubber stopper and Teflon tape, the mixture is well mixed by shaking the flask for 60 s. Subsequently the mixture is purged with nitrogen for 5 min. The flask is mounted onto a tumbler (IKA RW 16 basic) and immersed in an oil bath at 70 °C. The flask is tumbled at 100 rpm for 24 h for polymerization. After polymerization, the particles are washed four times with DI water using centrifugation. A 20 wt% LPS dispersion is prepared by dispersing LPS particles in 1 wt% poly(vinyl alcohol) (PVA, M_w = 13 000−23 000, 87−89% hydrolyzed) aqueous solution. A 20 wt% monomer emulsion is prepared by vortexing a mixture consisting of styrene, *tert*-butyl acrylate (*t*BA, 98%), 1 vol% divinylbenzene (DVB, 55%), and 0.5 wt% initiator 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65B, Wako) with 1 wt% PVA aqueous solution. LPS particles are swollen with the monomer mixture by mixing the LPS dispersion and the monomer emulsion. The volume ratio of the LPS and the monomer mixture is 20:80. The particle−monomer mixture is mounted on a rotator (Glas-Col) and rotated for 8 h at 60 rpm. Seeded emulsion polymerization is performed by tumbling the particle−monomer mixture in an oil bath at 70 °C at 100 rpm for 10 h. After seeded emulsion polymerization, the particles are washed with DI water at least six times by centrifugation to remove PVA and unreacted monomer. The particles from seeded emulsion polymerization are then stirred in an acid mixture consisting of 80 vol% trifluoroacetic acid (TFAA, 99%) and 20 vol% formic acid (FA, ≥95%) at 1200 rpm for 24 h for hydrolysis of *t*BA. The volume ratio of particles and acid mixture is 1:40. The hydrolyzed particles are washed with DI water 10 times by centrifugation.

Emulsification, Phase Inversion, and Emulsion Characterization. First, 3 mL of toluene (99.8%) containing 0.01 wt% Nile Red (technical grade) and 3 mL of an aqueous suspension containing 0.5 wt% (Sty50/AA50) Janus particles are added in a glass vial and homogenized at 9500 rpm for 60 s using a homogenizer (IKA Ultra-Turrax T25 basic). The pH of the aqueous phases is adjusted using 1.0 M NaOH or 1.0 N HCl solutions. For phase inversion, 20 μL of 1.0 N HCl and 1.0 M NaOH are added in O/W emulsion (6.0 mL) generated with (Sty50/AA50) Janus particles in pH 11.0 and W/O emulsion (6.0 mL) generated with (Sty50/AA50) Janus particles in DI water, respectively. The emulsions are thoroughly mixed using a vortex mixer for 30 s and subsequently homogenized at 9500 rpm for 60 s. To image emulsion droplets using fluorescence microscopy, a drop of emulsions is placed in between two glass slides. To image W/O emulsions, glass slides are silanized using 1 vol% octadecyltrichlorosilane (≥90%) in toluene for 30 s, followed by heat treatment on a hot plate at 150 °C for 30 min. To image (Sty50/AA50) Janus particles on emulsion surfaces, we replace toluene with styrene and add 1 wt% V-65B to enable polymerization of the oil phase. Polymerized emulsion samples are washed thoroughly with DI water before imaging.

To characterize the interactions between emulsion droplets, toluene-in-water emulsions are prepared by first homogenizing a mixture of 1 mL of toluene and 4 mL of 0.5 wt% (Sty50/AA50) Janus particles dispersed in aqueous solution of either pH 2.2 or pH 11.0 at 9500 rpm for 60 s, followed by vortexing for 30 s. The emulsions are transferred into a glass syringe and injected into a glass microchannel with a 1 × 1 mm² square cross-section. The flow pattern of the toluene-in-water emulsions is recorded by a fast camera (Vision Research Phantom v7.1).

■ RESULTS AND DISCUSSIONS

Synthesis of Amphiphilic Janus Particles. The generation of amphiphilic Janus particles is inspired by the synthesis of pH-responsive amphiphilic diblock copolymer, poly(styrene-*block*-acrylic acid) (PS-*b*-PAA). PS-*b*-PAA diblock
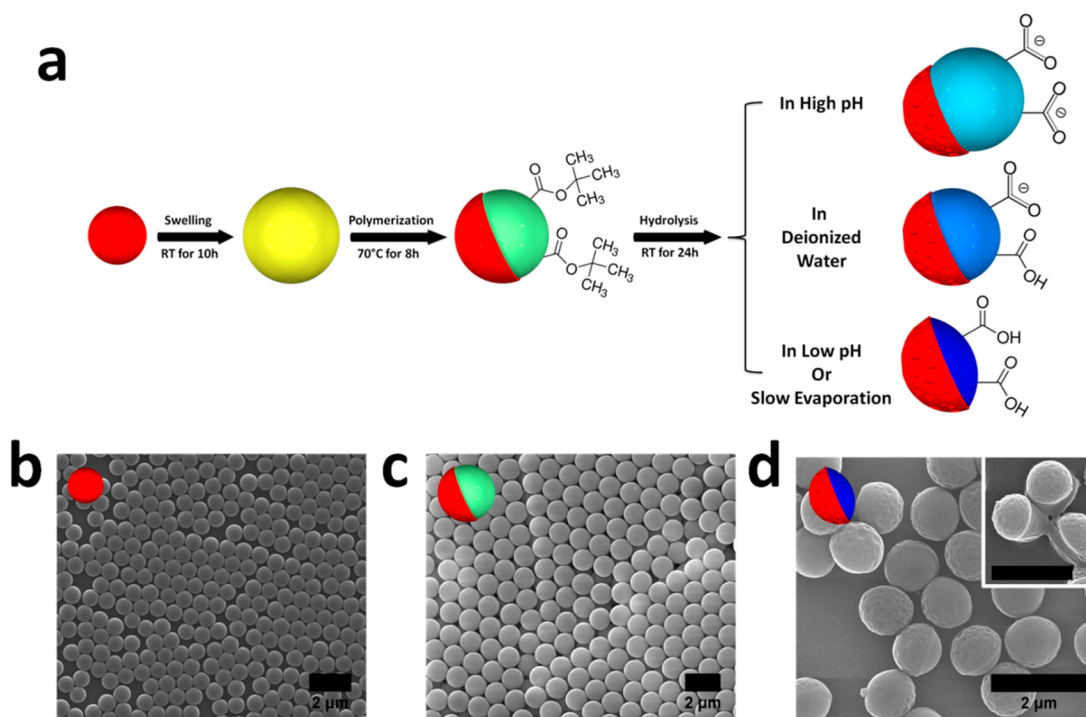
Figure 1. (a) Schematic illustration for the synthesis of amphiphilic Janus particles by seeded emulsion polymerization followed by acid hydrolysis. (b−d) Scanning electron microscopy images of (b) linear polystyrene (LPS) seed particles, (c) P(S-*co*-*t*BA)/LPS composite particles, and (d) (Sty/ AA) Janus particles after hydrolysis. The inset of the image in (d) shows hydrolyzed composite particles prepared by fast evaporation with AA-rich side collapsed. Scale bar = 2 *μ*m.

copolymers are typically synthesized by sequentially polymerizing styrene and *t*BA to make poly(styrene-*block*-*t*BA) and then subsequently hydrolyzing the *t*BA repeating units to form the acrylic acid (AA) block.[51−54] We use an analogous method to synthesize amphiphilic Janus particles using seeded emulsion polymerization as schematically illustrated in Figure 1a.

Monodisperse particles (∼0.75 *μ*m in diameter) composed of LPS are synthesized by dispersion polymerization (Figure 1b).[55] These LPS seed particles are swollen with a monomer emulsion composed of styrene, *t*BA, DVB (1 vol%), V-65B (0.5 wt%; initiator), and 1 wt% PVA aqueous solution for 10 h. The volume ratio of LPS particles and the monomer mixture is 20:80, while the ratio of styrene and *t*BA in the monomer mixture is 50:50. These swollen LPS particles are kept at 70 °C for 8 h for polymerization, which produces ∼1.1 *μ*m composite particles consisting of LPS and a copolymer network of styrene and *t*BA, as shown in Figure 1c. *t*BA repeating units in the copolymer network are subsequently hydrolyzed using a 80:20 mixture of TFAA and FA to form AA. The hydrolysis of the composite particles is confirmed with Fourier transform infrared (FTIR) spectroscopy (see Figure S1 in the Supporting Information).

The hydrolysis of the composite particles leads to a drastic change in the morphology of the particles as seen in Figure 1d. The hydrolyzed particles become acorn-shaped with one smooth side and one rough side. This highly asymmetric shape strongly suggests that some type of phase separation occurred within each composite particle during seeded emulsion polymerization. In fact, a very careful examination of the composite particles before hydrolysis shows evidence of phase separation (see Figure S2 in the Supporting Information).

We believe the copolymerization of the two monomers in the presence of LPS induces phase separation in the composite particles. The reactivity ratios, which characterize the selectivity of an end group of a polymerizing chain to react with either monomer during copolymerization, of styrene and *t*BA are 0.89 and 0.29, respectively, in toluene medium.[56] Because of the reactivity ratios of the two monomers are quite different, composition of the polymer network formed with these two monomers is expected to shift as the polymerization of monomers proceeds; that is, the network strands generated in the early stage of polymerization is rich in styrene (see Figure S3 in the Supporting Information). These strands likely have an appreciable miscibility with LPS of the seed particles. However, as the conversion approaches completion, the network strands synthesized in the late stage become rich in *t*BA. These network strands likely has low miscibility with LPS and also with styrene-rich part of the network because of the high Flory− Huggins interaction parameter between styrene and *t*BA.[57] Thus, the composite particles undergo polymerization-induced phase separation resulting in the formation of styrene-rich and *t*BA-rich regions. Interestingly, no signs of phase separation are observed if particles composed of styrene and *t*BA are synthesized in the absence of LPS, emphasizing the importance of LPS in inducing the phase separation (see Figure S4 in the Supporting Information). Phase separation in seeded emulsion polymerization has been observed in poly(methyl methacrylate)-seeded emulsion polymerization of styrene, in which different particle morphologies were found by changing polymerizing conditions.[58]

Although the evidence for phase separation is quite clear, it is not straightforward to distinguish which side of the hydrolyzed composite particles is rich in AA. To identify the chemical natures of the two sides, we subject these particles to rapid
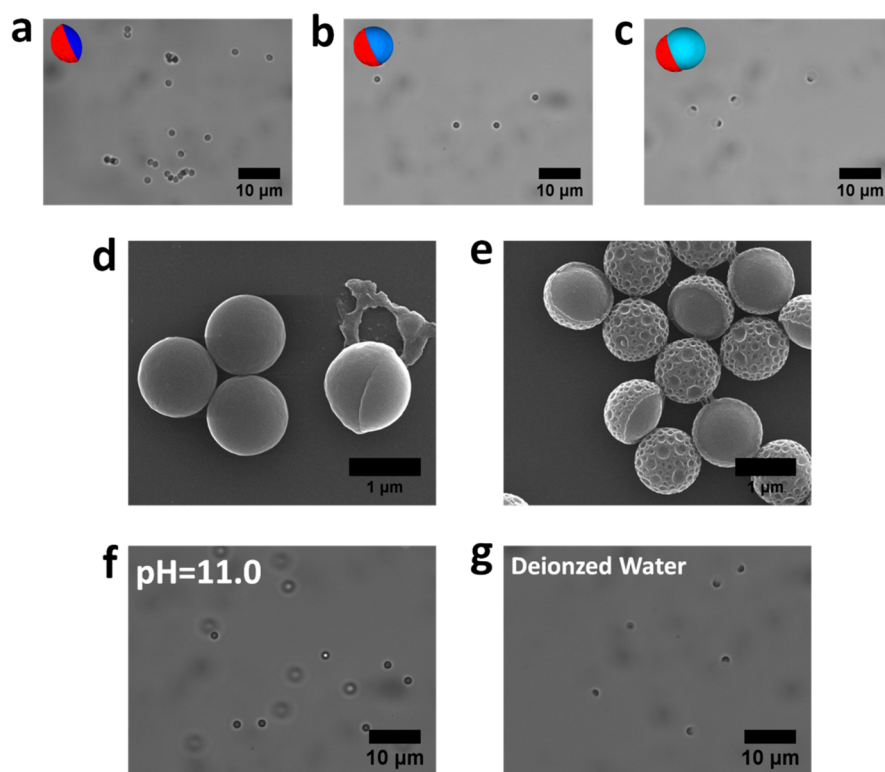
Figure 2. Microscope images of (Sty/AA) Janus particles made with 50 vol% of both styrene and *t*BA in the monomer mixture (Sty50/AA50) in (a) pH 2.2, (b) DI, and (c) pH 11.0 water. (Sty/AA) Janus particles swollen by monomer mixtures with styrene:*t*BA ratios of (d) 75:25 and (e) 25:75. (Sty75/AA25) Janus particles in (f) pH 11.0 water and (g) DI water (pH 5.5−6). Scale bar = 10 *μ*m in a,b,c,f,g; 1 *μ*m in d,e).

drying from an aqueous suspension. Rapid dehydration under high vacuum does not allow the AA-rich side, which likely becomes swollen in water, to relax back to form a smooth hemisphere, thus leading to disfigurement of the AA-rich side, as shown in the inset of Figure 1d. Because of its hydrophobicity and the lack of swelling in water, the styrene-rich side is not expected to show any significant difference in its morphology even after rapid drying. These results strongly suggest that the rough side of the composite particles is the styrene-rich (Sty-rich) side. We believe the small dimples that are present on the surface of the Sty-rich side are small domains of AA. Despite the presence of these small domains of carboxylic acid groups, we expect Sty-rich domain to remain hydrophobic. Studies have shown that PS particles functionalized with surface carboxylic acid groups have relatively hydrophobic surfaces at the interface between oil and water (three-phase contact angle >130).[59] In the rest of this paper, we refer to these hydrolyzed composite particles as (Sty/AA) Janus particles.

Shape-Changing Property of (Sty/AA) Janus Particles. Polymer networks containing high mole fractions of AA units are known to have pH-responsiveness; that is, they swell and deswell in high and low pH conditions, respectively. Such a stimuli-responsive property of AA-rich network makes our Janus particles change their shape and behavior quite drastically in response to changes in solution pH. As shown in Figure 2a, at pH 2.2, (Sty50/AA50) Janus particles[60] remain oblate-like and form clusters in the suspension. The formation of these clusters indicates that these particles interact attractively, which is reminiscent of the aggregation of amphiphilic molecules in water (e.g., micelle formation). The aggregation of the particles is likely due to the protonation of AA groups and the loss of

surface charge, leading to the reduction of electrostatic repulsive interactions between particles.[61−65] When these (Sty50/AA50) Janus particles are dispersed in DI water (pH 5.5−6.0), however, these particles become individually dispersed and, at the same time, become more or less spherical in shape, as shown in Figure 2b. Such a shape change likely stems from slight hydration of the AA-rich side and partial ionization of carboxylic acid groups, which keep the particles apart via electrostatic repulsion. When the basicity of the suspension is further increased to pH 11.0, these Janus particles transform their shape from spheres to dumbbells (also known as snowmen, dimers, and dicolloids), as shown in Figure 2c. The AA-rich lobes of these Janus dumbbells become almost transparent due to significant swelling in the high pH environment.

The pH-sensitivity of these Janus particles can be tuned by controlling the composition of the monomer mixture that is used for seeded emulsion polymerization. To demonstrate such tunability, we synthesize two additional composite particles with the styrene:*t*BA ratios of 75:25 and 25:75. As shown in Figure 2, the pH-sensitivity of these two amphiphilic Janus particles in different pH solutions are quite different. (Sty75/AA25) Janus particles (Figure 2d) remain spherical at pH 11.0 (Figure 2f), whereas (Sty25/AA75) Janus particles (Figure 2e) transform to dumbbell shapes in DI water (pH 5.5−6) (Figure 2g). The changes in the responsiveness (i.e., swellability) of the AA-rich sides likely stems from the changes in their composition. In short, our results demonstrate that the aggregation/dispersion behavior and shape of (Sty/AA) Janus particles are highly sensitive to the solution pH and that their pH sensitivity can be tailored by tuning the ratio of styrene and *t*BA used for the synthesis of these particles.

One way to characterize the shape changes that are observed in these particles as a function of the solution pH is to use the concept of packing parameter, which is typically used to characterize the shape of molecular surfactants and the size ratio of hydrophilic and hydrophobic segments within a molecular surfactant.[26] For example, while the (Sty50/AA50) Janus particles have a packing parameter that is larger than 1.0 in acidic solutions, the packing parameter of the same particle decreases below 1.0 in basic solutions.[26] Such a drastic shape change, we believe, leads to reversal in the amphiphilicity of these particles; that is, in the language of HLB, (Sty/AA) Janus particles have lipophile-dominant property in acidic solutions, whereas they completely switch to become hydrophile-dominant solid amphiphile in basic solutions. The implications of such an amphiphilicity-reversing property of (Sty/AA) Janus particles are described below.

Controlling the Type of Pickering Emulsion Stabilized by (Sty/AA) Janus Particles. One of the most promising and practical applications of Janus particles is in the stabilization of multiphasic mixtures such as emulsions. As summarized in the Introduction, recent studies have shown that thermodynamically stable emulsions can be generated using amphiphilic Janus particles.[14,15] Because our (Sty/AA) Janus particles comprise two sides with significantly different preferences toward oil and water (i.e., not just the wettability but also swellability in different media), we believe our particles would make excellent solid surfactants. Moreover, the shape-changing and thus amphiphilicity-reversing properties of these (Sty/AA) Janus particles could significantly change their surfactant properties; that is, analogous to how the shape of molecular surfactants determine the type of emulsions they can stabilize, the type of emulsions that can be stabilized by these solid amphiphiles may depend on the particle shape and amphiphilicity.

To test this idea, we generate emulsions while keeping the volume ratio of oil and aqueous phases constant at 50:50. By keeping the volumes of the two phases equal to each other, it allows the system to generate the type of emulsion that the Janus particles prefer and avoid the influences of dominant fluid phase in determining the final emulsion type.[66,67] An oil-soluble dye, Nile Red, is added to facilitate emulsion characterization, and the Janus particles are dispersed in the aqueous phase. As shown in Figure 3, emulsions made with particles in pH 2.2 water and in DI water sediment to the bottom of the vials with excess oil phase remaining on top of the settled emulsions. In contrast, the emulsion made at pH 11.0 creams with an aqueous phase forming at the bottom. Given that the density of toluene is smaller than that of water, these observations suggest that emulsions made with pH 2.2 and DI water are W/O emulsions, whereas the emulsion made at pH 11.0 is an O/W type. This prediction is further confirmed by the fluorescence microscopy images of the emulsions, as shown in Figure 3. The fluorescence microscopy images indicate that emulsion droplets made at pH 2.2 and DI water are composed of aqueous phase (dark dispersed phase), whereas those made at pH 11.0 are oil droplets (bright dispersed phase). The size of W/O emulsion droplets is significantly larger than that of O/W emulsions likely because of the high charge of (Sty50/AA50) Janus particles at pH 11.0, leading to strong repulsive interparticle interactions. An analogous trend has been observed in emulsions that were stabilized with silica and latex particles.[68] To observe the aggregation structures as well as the orientations of (Sty50/AA50) Janus particles at the interface of emulsion droplets, we replace toluene with a polymerizable
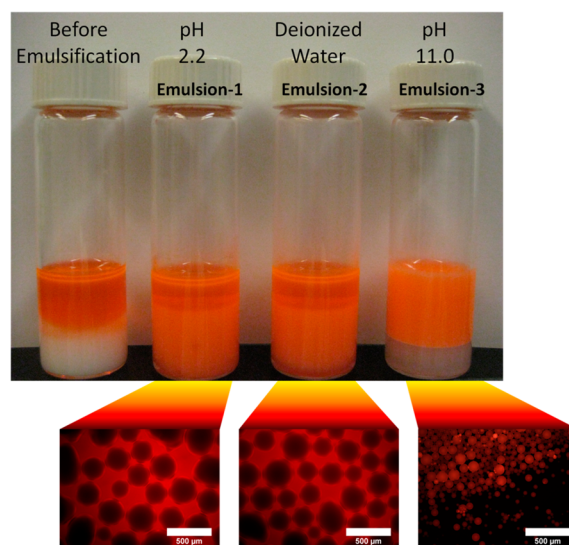

Figure 3. (Top) Macroscopic and (bottom) fluorescence microscopy images of emulsions made with aqueous phases of pH 2.2, deionized water (water-in-oil emulsion), and aqueous phase of pH 11.0 (oil-in-water emulsion). The volume ratio of oil and water phases is kept 50:50 in all cases, and the oil phase contains 0.01 wt% Nile Red. Scale bar = 500 μm.

oil phase, styrene, which has properties and chemical structure similar to those of toluene. (Sty50/AA50) Janus particles attached to the W/O or O/W interfaces of emulsions are observed by polymerizing styrene and performing scanning electron microscopy (SEM).[10,40] Janus particles are seen to attach in the so-called upright orientation in both cases (see Figure S5 in the Supporting Information); that is, each side of these Janus particles fully resides in its preferred fluid phase, and the boundary between the two sides is pinned at the W/O or O/W interface.

Our results clearly demonstrate that (Sty/AA) Janus particles can change their preferred emulsion type in response to pH changes in the aqueous phase and stabilize different types of emulsions. The preferred emulsion type as a function of the solution pH can be attributed to the changes in the shape leading to the reversal of the amphiphilicity of (Sty/AA) Janus particles, which is analogous to the effect of the packing parameter and the HLB of molecular surfactants, respectively, on the type of emulsions that they are able to stabilize. The upright orientation of these Janus particles at the water–oil interface likely plays an important role in maximizing the effect of particle shape change on the emulsion type that can be stabilized with these particles.[15]

The W/O emulsion made with (Sty/AA) Janus particles in DI water presents another unique aspect because it does not conform to the so-called Bancroft or Finkle rules, which state that the continuous phase of an emulsion is the one in which the emulsifier is preferentially solubilized (Bancroft) or dispersed (Finkle).[69] Using the pH-responsiveness and amphiphilicity-reversing properties of the (Sty/AA) Janus particles, it is possible to generate emulsions that both follow (pH 11.0) and violate (DI water) these empirical rules. Interestingly, such behaviors have also been observed in Pickering emulsions stabilized with homogeneous particles with proper choice of aqueous and oil phases.[70,71]

The fact that the type of emulsions generated with (Sty/AA) Janus particles is controlled by the pH of the aqueous phase

strongly suggests that one type of emulsion generated under one condition can be inverted into the other type simply by changing the solution pH. Phase inversion emulsification triggered by an external stimulus (also known as transitional phase inversion emulsification) is an important process by which emulsions with highly viscous dispersed phases can be generated and requires changes in the HLB as well as the shape of stimuli-responsive surfactants or the wettability of homogeneous particles that stabilize the original emulsions.[38,72−75] We demonstrate the transitional phase inversion of emulsions stabilized with (Sty50/AA50) Janus particles by adding a small amount of highly concentrated basic and acidic solution (∼20 μL of 1.0 M NaOH and 1.0 N HCl, respectively) into 6 mL of W/O and O/W emulsions originally generated with DI water and pH 11.0 (Emulsion-2 and Emulsion-3 in Figure 3), respectively. Upon vigorous mixing, Emulsion-2 and Emulsion-3 become O/W and W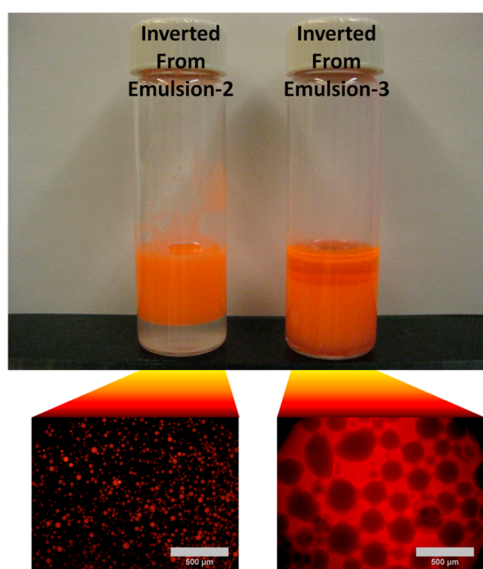/O emulsions, respectively (Figure 4); that is, the types of final emulsions are inverted and opposite of the starting emulsions in both cases. By changing the shape of the AA-rich side and relative size of styrene- and AA-rich sides,

the amphiphilicity of these particles reverses in response to changes in solution pH, which eventually leads to the phase inversion of the emulsions. We believe this is the first demonstration of transitional phase inversion of Pickering emulsions stabilized with Janus particles, which is facilitated by the dynamic tunability of the shape as well as the reversible amphiphilicity of the pH-responsive (Sty/AA) Janus particles.

Controlling the Interactions between Pickering Emulsion Droplets. Interactions between emulsion droplets have an important effect on the rheological properties of emulsions,[76,77] which in turn change the properties of emulsion-based products such as shelf-stability and sensorial properties.[72] Thus, emulsifiers that enable the control over the interactions between emulsion droplets without causing destabilization are highly desirable. The pH-dependent aggregation/dispersion behavior of (Sty50/AA50) Janus particles in the bulk aqueous phase, as seen in Figure 2a, suggests that the interactions of Pickering droplets stabilized with these particles could also depend on the pH of the solution. To test this hypothesis, we generate O/W emulsions at pH 2.2 or pH 11.0 and study the interactions between Pickering emulsion droplets. Unlike the above case when the oil:water ratio was kept 50:50, by decreasing the volume fraction of oil significantly (oil:water = 20:80), O/W emulsions can be generated regardless of the pH of the aqueous phase.

The difference in the interactions between emulsions under acidic and basic conditions can be indirectly observed from the morphology of emulsion droplets. O/W emulsion generated at pH 2.2 shows droplets that are aggregated to form clusters, as shown in Figure 5a. In contrast, when the pH of the emulsion is switched to pH 11.0, the droplets become well-separated, as shown in Figure 5b, indicating repulsive interactions.

The tunable interactions between Pickering emulsions stabilized with (Sty50/AA50) Janus particles can be more clearly demonstrated by observing the flow behavior of these emulsions under different pH conditions. When an emulsion prepared at pH 2.2 flow across a microchannel made of glass (1 × 1 mm² square cross-section), droplets stick to the glass surface and to each other as they flow in the channel, as shown in Figure 6a. Droplets also move in clusters rather than as individual droplets (see Movie 1 in the Supporting Information), strongly indicating that these emulsion droplets interact attractively and are very adhesive. Emulsion droplets prepared at pH 11.0, however, do not stick to the channel wall and flow freely in the channel as single droplets, as shown in
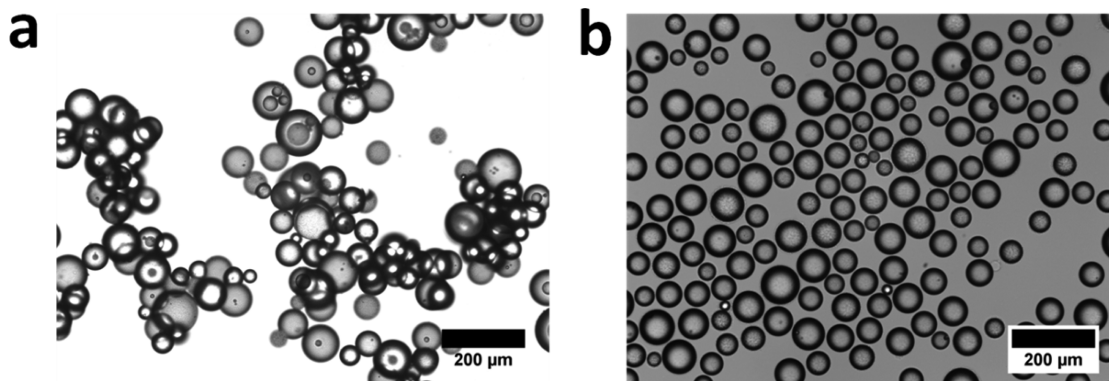

Figure 4. (Top) Macroscopic and (bottom) fluorescence microscopy images of emulsions inverted from Emulsion-2 and Emulsion-3 in Figure 3 by addition of ∼20 μL of 1 M NaOH and 1 N HCl, respectively. Scale bar = 500 μm.

Figure 5. Microscope images of toluene-in-water emulsions made with (Sty50/AA50) Janus particles dispersed in (a) pH 2.2 and (b) pH 11.0 aqueous solutions. The volume ratio of oil to water is 20:80. Scale bar = 200 μm.
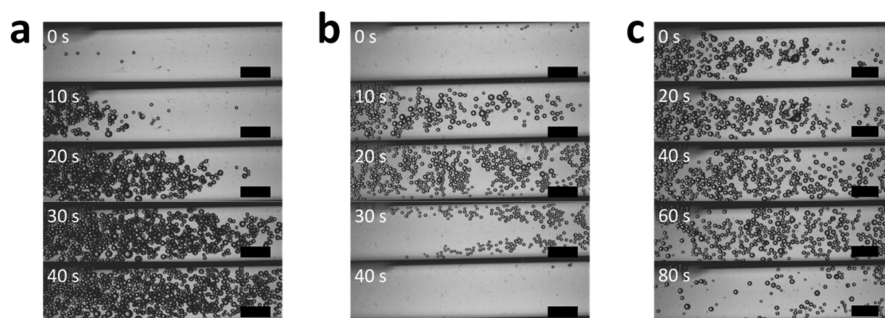
Figure 6. Microscope images of toluene-in-water emulsion stabilized by (Sty50/AA50) Janus particles made at (a) pH 2.2 and (b) pH 11.0 flowing inside a glass capillary microchannel, and (c) attractive toluene-in-water emulsion made at pH 2.2 with particles that are stuck to the microchannel being washed away by a pH 11.0 aqueous solution. See Supporting Information for movies illustrating the flow behaviors of these emulsions. Scale bar = 500 μm.

Figure 6b (see Movie 2 in the Supporting Information), indicating that these emulsion droplets are repulsive. When an emulsion is introduced in the channel at pH 2.2 initially and then the pH of the continuous phase is changed to pH 11.0, the emulsion droplets that are originally stuck to the glass channel surface and to each other suddenly become individually dispersed and flow freely down the channel, as shown in Figure 6c (see Movie 3 in the Supporting Information). Again these results clearly demonstrate that the interactions between emulsion droplets can be readily tuned by changing the solution condition without destabilizing the emulsion.

CONCLUSIONS

In this paper, we have presented a bulk synthesis scheme for generating highly uniform pH-responsive Janus particles. These Janus particles not only drastically change their shape but also completely reverse their amphiphilicity in response to changes in the solution pH. These pH-sensitive changes of shape are analogous to the changes that are observed in pH-responsive amphiphilic molecules; that is, the packing geometry and amphiphilicity of these Janus particles are dynamically tunable using solution pH as environmental stimulus. We demonstrate that the type of emulsions generated using these amphiphilicity-reversing and shape-tunable Janus particles depends strongly on the acidity/basicity of the aqueous phase and that emulsions can be inverted to the opposite types by either lowering or raising the pH of the aqueous phases. The pH-dependent aggregation/dispersion behavior of our Janus particles is utilized to generate both attractive and repulsive emulsions at low and high pH conditions, respectively. Furthermore, attractive and repulsive interactions between emulsion droplets can be controlled on demand by changing the pH of the continuous phase. Our findings offer a new class of dynamically tunable colloidal materials that would widen the functionality and applications of Janus particles as solid surfactants. In particular, the ability to enable phase inversion opens up new possibilities in generating emulsions and particles that are not readily obtainable using traditional emulsion formation processes.[78] Also, dynamically tunable interactions between Janus particle-stabilized emulsions could lead to new applications in pH-responsive complex fluids that can drastically change their rheological properties.

ASSOCIATED CONTENT

Supporting Information

FTIR spectroscopy of Janus particles before and after hydrolysis; images showing evidence of phase separation before hydrolysis; calculation of instantaneous copolymer compositions of styrene and *t*BA; styrene-*t*BA composite particles by emulsion polymerization without seed particles; SEM images showing upright orientation of (Sty50/AA50) Janus particles on emulsion surface; and Movies 1−3 (ja503189r_si_002.avi, ja503189r_si_003.avi, and ja503189r_si_004.avi, respectively) showing toluene-in-water emulsions made at different pH conditions flowing in glass capillary channels. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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