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Surfactant-Free Switchable Emulsions Using CO_2-Responsive Particles

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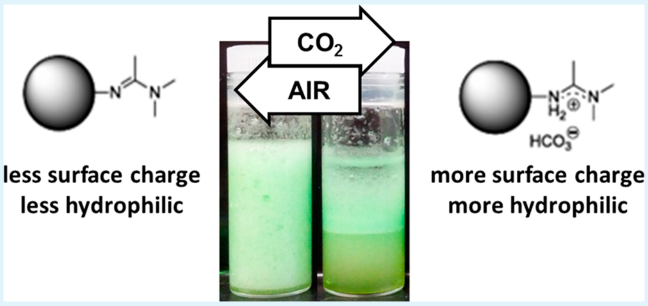

ABSTRACT: Surfactant-free emulsions are prepared using bi-wetting particles which occupy the oil−water interface to effectively reduce the oil−water interfacial area. The equilibrium position of the particle at the interface is determined by its wettability. CO_2-reponsive chemical functional groups are grafted onto the surface of silica particles. Particles with only CO_2-switchable functional groups are capable of stabilizing oil-in-water emulsions. Particles prepared with both CO_2-responsive and hydrophobic chemical functional groups on its surface are capable of stabilizing water-in-oil emulsions. Emulsion stability is disturbed when the wettability of the stabilizing particle is altered by introducing CO_2 gas to the biphasic mixture, leading to phase separation of emulsions prepared using the functionalized particles. The emulsion stability can be re-established by the removal of CO_2 through air sparging. The presence of CO_2 imposes positive surface charge to the responsive particles, increasing wettability and, consequently, the ability of the particles to destabilize emulsions.

KEYWORDS: *switchable emulsions, CO_2-responsive wettability, surface modification*

■ INTRODUCTION

Emulsions are commonly encountered in chemical processes where both organic and aqueous phases coexist. In some cases, stable emulsions are desirable as the high specific interfacial surface area benefits mass transfer in extraction processes; also, the lower viscosity of oil-in-water emulsions facilitates transport of very viscous material. In other cases, however, stable emulsions are undesirable, as most unit operations do not tolerate multiphase mixtures. Stable emulsions must therefore be broken if generated during an intermediate process step. Unfortunately, well-stabilized emulsions may persist for months, even years. Breaking these stable emulsions by physical methods requires capital and energy intensive equipment such as centrifuges. The use of chemical methods requires continuous addition of demulsifiers and other additives.

Surfactants stabilize emulsions by their accumulation at the oil−water interface, effectively reducing the interfacial tension. Droplet coalescence in surfactant-stabilized emulsions is retarded by either electrostatic repulsion for ionic surfactants or by steric hindrance for polymeric surfactants adsorbed/accumulated at the oil−water interface. Emulsions with controllable and switchable stability are prepared using responsive surfactants. Various types of responsive surfactants are available including compounds sensitive to pH,[1−5] temperature,[3,6−9] electrical potential,[10−12] irradiation,[13−17] carbon dioxide (CO_2),[18,19] and other stimuli.[20−25] CO_2 is unique and forms a chemical equilibrium with carbonic acid in aqueous solutions. Unlike most acids, dissolved CO_2 can be removed by sparging the solution with nitrogen or air which contains very little CO_2 (400 ppm). The addition or removal of CO_2 is therefore reversible without requiring very specialized equipment. CO_2 has other attractive attributes such as low cost, wide availability, and is generally benign to human and environment.

In addition to surfactants, particles are also capable of stabilizing emulsions by irreversibly occupying the oil−water interface, effectively decreasing the oil−water interfacial area.[26−28] Wettability is a critical physical property for emulsions stabilized by solid particles, as the equilibrium immersion depth of a particle is controlled by the wettability of stabilizer particles, see Figure 1.[29−36] The energy required to displace a small spherical particle from the oil−water interface into the bulk liquid is given by the equation as the insert of Figure 1, which reaches a maximum when the contact angle is 90°.[30] Hydrophobic particles with a contact angle greater than 90° will be mostly immersed in the oil phase and preferentially stabilize water-in-oil (W/O) emulsions. Hydrophilic particles with a contact angle lesser than 90° will be mostly immersed in the aqueous phase and preferentially stabilize oil-in-water (O/

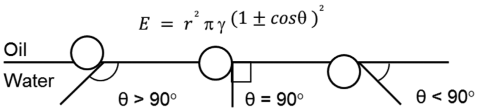

Figure 1. Illustration of spherical particles with different wettability at an oil−water interface.

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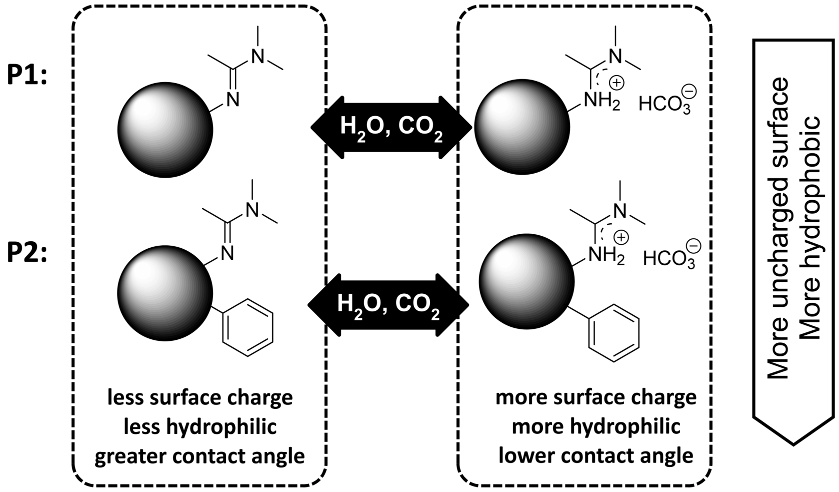


Figure 2. Illustration of switchable particles (**P1** and **P2**), functionalized with CO$_2$-responsive surface groups, becoming more ionic in the presence of CO$_2$, leading to a decreased hydrophobicity and lower contact angle.

W) emulsions. Bi-wetting particles with a contact angle close to 90° are the most effective emulsion stabilizers. In contrast, particles with both very hydrophilic (much lesser than 90°) or very hydrophobic (much greater than 90°) surfaces are poor emulsion stabilizers.

■ CONCEPT OF SWITCHABLE PARTICLE

Here we propose CO$_2$-responsive particles of variable initial wettability that are capable of controlling the stability of surfactant-free emulsions by applying an appropriate trigger to induce changes in emulsion properties. As shown in Figure 2, for CO$_2$-responsive particles with original contact angle around 90°, the addition of CO$_2$ gas or its removal from the system by sparging the system with air may be sufficient to induce substantial changes in emulsion stability.

To this end, the surface properties of particles functionalized with CO$_2$-responsive surface groups (**P1** and **P2**) are modified in the presence of CO$_2$, which causes functionalized particles to become more hydrophilic by increasing the density of ionic moieties. Particles with different initial wettability, capable of stabilizing O/W and W/O emulsions, are prepared by surface functionalization with a combination of responsive hydrophilic groups and non-responsive hydrophobic surface groups. **P1** particles are less hydrophobic as compared to **P2** particles which contain additional non-responsive hydrophobic aromatic moieties. We put forward a control mechanism for emulsion stability by an *in situ* change in the surface properties of stabilizer particles. Particles with tunable wettability are capable of stabilizing emulsions in one specific state and destabilizing the emulsion in another, thus providing a viable mechanism for triggering phase separation.

■ EXPERIMENTAL SECTION

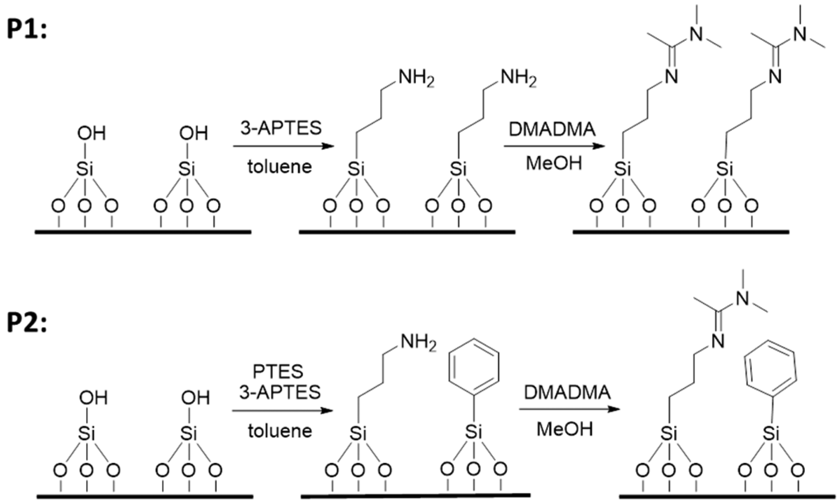
Unless otherwise indicated, all chemicals were used as received without further purification. CO$_2$ gas (Praxair, medical grade) and N$_2$ gas (Praxair, 99.998%) were used as received. Air was supplied by in-house compressors. CO$_2$ and air were injected into emulsions through an 18-gauge blunt-tip syringe at a flow rate of approximately 0.5 L/min. Deionized water was used throughout and supplied from a Thermo Fischer Barnstead Nanopure ultrapure water purification system.

For particle functionalization, 3.1 g of fumed silica particles (Sigma-Aldrich) was charged into a round-bottom flask equipped with magnetic stirrer and well-dispersed in approximately 100 mL of toluene (ACS grade, Fischer). Ten milliliters of ethanol (99%, Commercial Alcohols) along with 3.0 mL (13.5 mmol) of 3-aminopropyltriethoxysilane (99%, Sigma-Aldrich) and/or 3.0 mL (12.5 mmol) of triethoxy(phenyl)silane (95%, Sigma-Aldrich) were added to the mixture. After the mixture was stirred at ambient temperature for 24 h, functionalized particles were recovered using a Hettich Rotanta 460R high-speed centrifuge and washed with excess toluene and ethanol. Recovered particles were charged into a round-bottom flask equipped with magnetic stirrer, dispersed in approximately 70 mL of methanol (ACS grade, Fisher), and treated with 2.0 mL of *N,N*-dimethylacetamide dimethylacetal (DMA-DMA) (90%, Sigma-Aldrich). After the mixture was stirred at ambient temperature for 10 h, particles were recovered, washed with ethanol, and dried in an oven at 70 °C under reduced pressure. In the form of a white solid, 3.0 g of **P1** and 2.9 g of **P2** were recovered, crushed into a free-flowing powder, and stored inside a desiccator. Functionalized particles dispersed in potassium bromide (KBr) were characterized using a BioRad 2000 Fourier transform infrared spectroscopy instrument by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) method. **P1** (KBr): 797 cm^{-1} (s), 1093 cm^{-1} (s), 1652 cm^{-1} (s), 2863 cm^{-1} (w), 2922 cm^{-1} (w), 3621 cm^{-1} (w). **P2** (KBr): 696 cm^{-1} (w), 795 cm^{-1} (s), 1089 cm^{-1} (s), 1430 cm^{-1} (w), 1644 cm^{-1} (s), 2858 cm^{-1} (w), 2920 cm^{-1} (w), 3052 cm^{-1} (w), 3054 cm^{-1} (w), 3613 cm^{-1} (w). The degree of particle functionalization was determined using a TA Instruments Q500 thermogravimetric analyzer (TGA) by tracking the mass loss during heating to 900 °C.

The zeta-potential of particles was measured using a Malvern Nano-Zetasizer instrument. Particle samples (50 mg) were well-dispersed into a small amount of methanol and diluted into 30 mL of deionized water. Dispersions were treated with either compressed air or CO$_2$ gas from a gas cylinder for 30 s. Particle partitioning was determined gravimetrically. Equal amounts of particles were, separately, well-dispersed into water and organic solvent using an ultrasonic bath. The two immiscible phases were combined, and the mixture was homogenized using a vortex mixer for 30 s. Emulsion was broken using a low-speed centrifuge. After phase separation, the amount of particles in the aqueous phase, toluene phase, and interfacial region was subsequently determined, after solvent was removed by evaporation under reduced pressure, from aliquots taken from each phase.

Silica wafers (NanoFab; University of Alberta) were cut into small pieces and pre-conditioned by immersing in Piranha solution comprising one part aqueous hydrogen peroxide and one part concentrated sulfuric acid. (***Caution:*** Piranha solution is aggressive and explosive. Never mix piranha waste with solvents. Check the safety precautions before using it.) Clean wafers were subsequently rinsed

Scheme 1. CO$_2$-Responsive Particles Prepared by Functionalizing Silica Particles Using 3-APTES Alone (P1) or in Combination with PTES (P2) in Toluene at Room Temperature, and Subsequent Treatment with Dilute DMA-DMA in Methanol



with water and dried using N$_2$ gas. In one instance, silica wafers were functionalized by chemical vapor deposition of 3-APTES under ambient conditions for 3 h. Silica wafers were also functionalized, in a similar manner as **P1** and **P2** particles, using solutions of 3-APTES and/or PTES in toluene. Amino-functionalized silica wafers were washed with ethanol, dried with N$_2$ gas, and treated with a solution of 3 vol % DMA-DMA in methanol. Contact angle was measured by Sessile drop method using Krüss DSA10. A small drop of water was placed in contact with a surface in either air or toluene using a syringe. To investigate the effect of surface switching on surface wettability, the functionalized silica wafers were placed in a beaker with water while a stream of CO$_2$ or N$_2$ gas was bubbled directly into the beaker for 60 s.

Emulsions were prepared by first dispersing the stabilizer particles in either the aqueous or organic phase using an ultrasonic bath. To facilitate visualization, a water-soluble green dye was added to the aqueous phase. Biphasic mixtures were emulsified using a Fischer Scientific PowerGen high-speed homogenizer. The continuous phase of the emulsion was determined by placing small droplets of the emulsion into Petri dishes containing either water or organic solvent. Emulsion micrographs were taken using a Zeiss Axioskop 40 optical microscope after emulsification. Functionalized **P1** (top) or **P2** (bottom) silica particles were added to biphasic mixtures (4 mL) of toluene and water (1:1), emulsified for 20 s using high-speed homogenizer, and left under ambient conditions for 30 min.

■ RESULTS AND DISCUSSION

Two types of silica-based switchable particles were prepared by grafting CO$_2$-responsive functionalities onto particle surfaces using appropriate reagents, see Scheme 1. Particle size and morphology of silica particles was measured by transmission electron microscopy (TEM). The TEM micrograph shown in Figure 3 indicates primary silica particles of irregular shapes and average diameter ranging from 30 to 40 nm. Silica particles were functionalized by hydrolysis of 3-aminopropyltriethoxysilane (3-APTES) and/or triethyoxy(phenyl)silane (PTES).[37,38] Using dilute *N,N*-dimethylacetamide dimethylacetal, primary amino functionality was converted to *N,N*-dimethylacetamidine in methanol.[39,40] Particles functionalized solely with 3-APTES were referred to as **P1**. In contrast, more hydrophobic **P2** particles, functionalized with both 3-APTES and PTES, contain additional aromatic surface functional groups. Functionalized particles were characterized using Fourier transform infrared spectroscopy. Spectra in Figure 4a obtained for both **P1** and **P2** particles show broad peaks at 3621, 1093, and 797 cm^{-1} assigned to Si−O−Si vibrations. The functionalization of **P1** particles leads to the bands at 2863 and 2922 cm^{-1} due to aliphatic C—H stretching, and a band at 1652 cm^{-1} due to C=N stretching. As anticipated and shown in Figure 4a, **P2** particles showed additional aromatic bands at 3054, 3052, 1430, and 696 cm^{-1}, attributed to arene C—H vibrations.

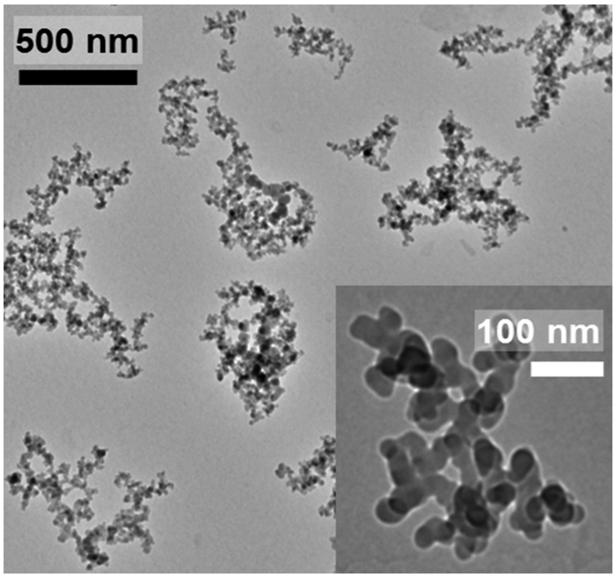


Figure 3. TEM micrograph of silica particles before functionalization showing irregular shapes and average primary particle diameter ranging from 20 to 30 nm. Similar TEM micrographs were obtained for functionalized **P1** and **P2** particles, which are not shown here.

To quantify the degree of functionalization of **P1** and **P2** particles, thermogravimetric analysis was applied. The results in Figure 4b show a 10 wt % loss of **P1** particles after decomposition at 900 °C, indicating the presence of 10 wt % of switchable organic compounds functionalized on silica particles. In contrast, a 16 wt % weight loss was observed for **P2** particles, indicating an additional 6 wt % weight loss organic materials loaded on **P2** particles, most likely as triethoxy-

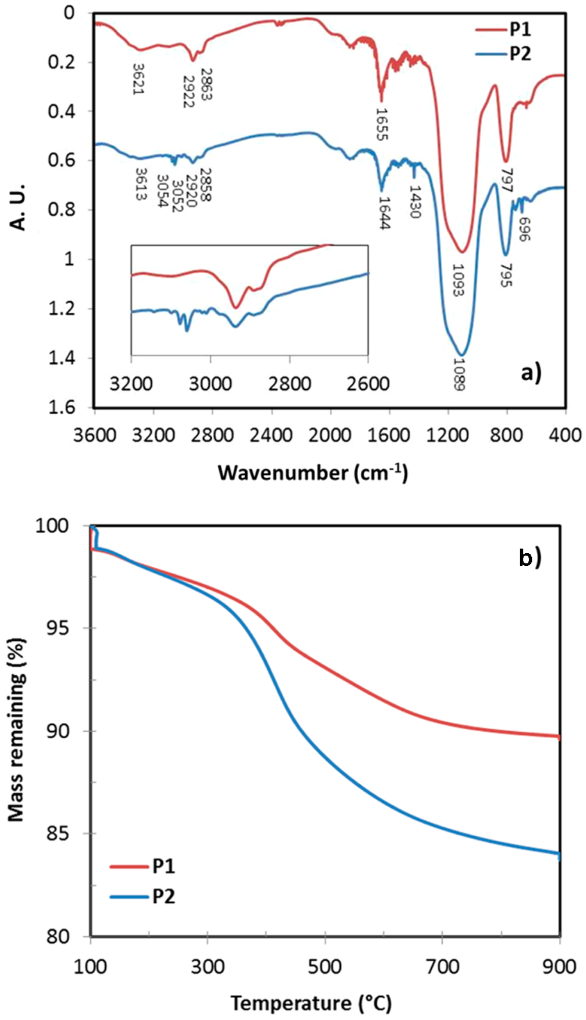


Figure 4. (a) Fourier-transform infrared spectra of functionalized silica particles in KBr; and (b) Thermogravimetric analysis.

(phenyl) silane, which contributed to an increased contact angle of particles to around 90°. The molar ratio of triethoxy(phenyl) silane to acetamidined *N,N*-dimethylacetamide dimethylacetal on **P2** particles was estimated to be 1:1.3.

The zeta-potential of functionalized particles, which is indicative of particle surface charge, was measured; and the results are given in Table 1. As anticipated, fumed silica particles, which were negatively-charged initially, became positively-charged after functionalization with 3-APTES. The particles became more positively charged after reaction with DMA-DMA as the product amidine is more basic than analogous amines. The response of **P1** and **P2** particles to CO_2 was investigated after directly bubbling CO_2 gas into particle dispersions prepared in water. Addition of CO_2 increased the surface charge of both **P1** and **P2** particles to 34 ± 2 mV; an increase of 12 ± 4 mV for **P1** particles and 25 ± 2 mV for **P2** particles. The original surface charge was restored after subsequent removal of dissolved CO_2 by sparging dispersion with air, which does not contain a significant concentration of CO_2. The change in surface charge of functionalized silica particles in response to CO_2 exposure was found to be reversible.

Table 1. Zeta-Potential of P1 and P2 Silica Particles Functionalized with CO_2-Responsive Surface Groups

		zeta-potential (mV)	
step	description	**P1**	**P2**
1	unmodified SiO_2	−13 ± 1	
2	treatment with silane agent[a]	+14 ± 2	+9 ± 2
3	further treatment with DMA-DMA	+21 ± 3	+13 ± 4
4	purging with CO_2[b]	+33 ± 1	+34 ± 1
5	subsequent purging with air[b]	+20 ± 3	+9 ± 1
6	subsequent purging with CO_2[b]	+34 ± 1	+34 ± 1
5	subsequent purging with air[b]	+22 ± 3	+8 ± 1

[a] **P1** particles treated solely with 3-APTES; **P2** particles treated with both 3-APTES and PTES. [b] The dispersion was prepared and subjected to a stream of CO_2 or air purging, as indicated.

For a given material with reversible surface charge, the maximum contact angle occurs at the point of zero charge and the presence of surface charge renders the material more hydrophilic.[34] The contact angle is also strongly dependent on the concentration of surface ions and electrolytes.[35,36] CO_2 in aqueous solutions generates carbonic acid and produces bicarbonate ions when a suitable base, such as organic compounds with amidine moieties, is present.[18,19,41−43] Increasing the concentration of charged groups on the particle surface by ionizing surface functional groups renders the surface more hydrated by polar water molecules, as indicated by the lower contact angle upon exposure to CO_2 gas of wafers functionalized using procedures for preparation of **P1** and **P2** particles.

The effect of CO_2 on reversible tuning of particle wettability was verified by preparing a silica wafer with CO_2-responsive surface groups by chemical vapor deposition of 3-APTES, followed by conversion of primary amine groups into CO_2-responsive groups using DMA-DMA. As shown by the results in Table 2, the contact angle, measured using sessile drop method in air, of the functionalized wafer was responsive to CO_2 gas. The wafer, with initial contact angle of water in air of 48 ± 3°, became more hydrophilic after subjecting to CO_2 gas in water, as indicated by a significant depression in contact angle to 38 ± 2°. Upon treating the solution with nitrogen gas (N_2) to remove dissolved CO_2, the depressed contact angle returned to its original value, restoring to the initial wettability. As shown in Table 2, reversible switching between different wettability states was possible using non-toxic gases. Our results are consistent with the results from other studies wherein primary and secondary amines on silicon wafers were transformed into carbamates species in the presence of CO_2, leading to a corresponding decrease in contact angle of approximately 10°.[44]

Table 2. Contact Angle of a Silica Wafer Functionalized with CO_2-Responsive Surface Groups Measured in Air

cycle	treatment[c]	contact angle (deg)[d]
0	none	51 ± 3
1	CO_2	39 ± 2
2	N_2	49 ± 2
3	CO_2	38 ± 1
4	N_2	47 ± 3

[c] Dissolved CO_2 gas was removed from solution by purging the water with N_2 gas. [d] Contact angle of water droplet on functionalized surface measured in air.

Silica particles, as received, did not stabilize emulsions. However, after introducing CO_2-responsive and/or hydrophobic aromatic groups, functionalized silica particles (**P1** and **P2**) are capable of stabilizing different types of emulsions, as shown in Figure 5. As designed, O/W and W/O emulsions could be stabilized by particles with contrasting wettability. Emulsions were prepared with 10 mg of functionalized particles, 2.0 mL of water, and 2.0 mL of toluene using a high-speed homogenizer. It should be noted that the mechanical force generated by the bubbling of air through the **P1** and **P2** particle-stabilized emulsions showed a negligible effect on the stability of the emulsions. To facilitate visualization of emulsions, a water-soluble green dye was added to the aqueous phase. The continuous phase of the emulsion was determined by adding a few emulsion droplets into water or toluene. In the absence of CO_2, the more hydrophilic switchable particles with contact angle around 66° (**P1**) stabilized a toluene-in-water emulsion. The more hydrophobic switchable particles with contact angle around 89° (**P2**) stabilized a water-in-toluene emulsion. The emulsions prepared using **P2** particles were of smaller droplet sizes and more stable as compared with the emulsions prepared using **P1** particles. The type and stability of an emulsion stabilized by particles can be wholly tuned by adjusting the coverage of different types of surface functional groups. This is an important advantage over switchable emulsifiers,[18,45−47] which typically experience significant changes to inherent physiochemical properties such as solubility when additional functional groups are incorporated into its structure. Without greatly modifying the structure of the emulsifier such as increasing the molecular weight of emulsifier, only limited engineering of switchable emulsion is possible. Particles as emulsion stabilizers are much more versatile, as additional properties such as magnetic susceptibility are readily imparted to the particles independently of its surface wettability.

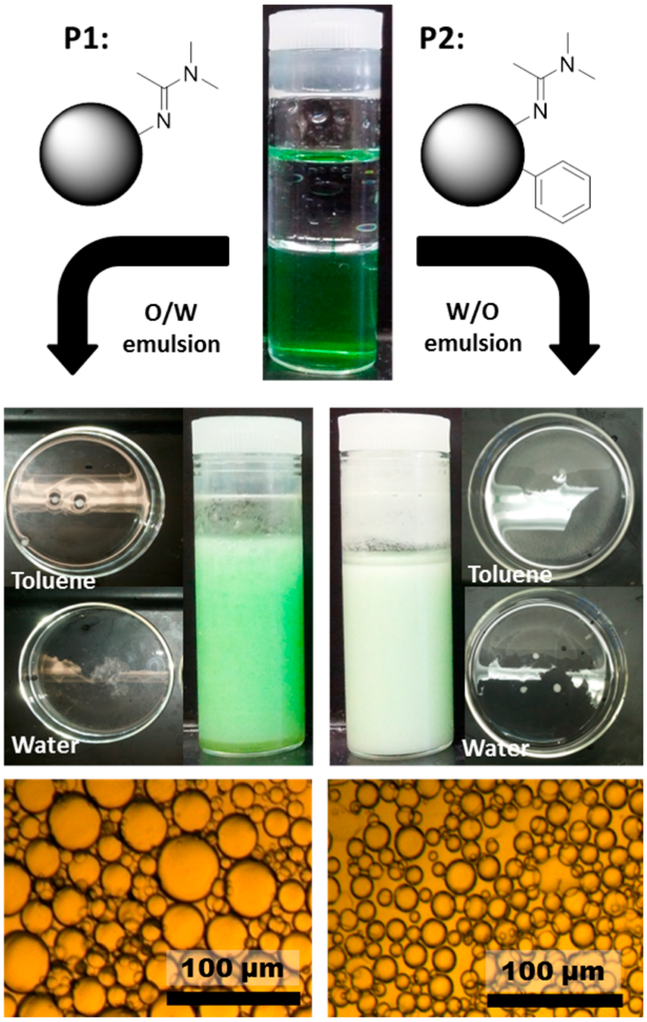


Figure 5. Images of different types of emulsions stabilized by more hydrophilic **P1** particles (left) and more hydrophobic **P2** particles (right).

In the absence of CO_2, functionalized **P1** and **P2** particles stabilized O/W and W/O emulsions, respectively. The bubbling of air to stable emulsion samples stabilized with **P1** or **P2** particles showed a negligible effect on emulsion stability. However, the wettability of both **P1** and **P2** particles is depressed in the presence of CO_2, making them more hydrophilic. The change in wettability of the stabilizer particles, a decrease in contact angle by 10°, has an effect on emulsion stability. As shown in Figure 6, the stability of emulsions prepared using **P1** and **P2** particles was responsive to CO_2 gas. Emulsions stabilized by both **P1** and **P2** particles were destabilized after purging the emulsions directly with CO_2 gas for 30 s, leading to phase separation. Upon removal of CO_2 from the mixture by purging with the air for 60 s, stable emulsions were formed again by re-emulsifying the mixture using the high-speed homogenizer without adding additional stabilizer particles. Successive stabilization−destabilization

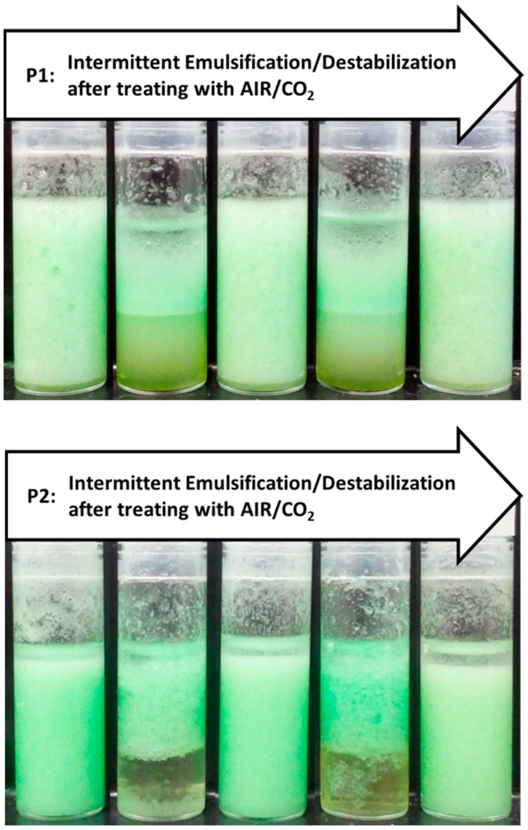


Figure 6. Images of emulsion samples stabilized using more hydrophilic **P1** particles (top) and more hydrophobic **P2** particles (bottom).

cycles were possible by the addition or removal of dissolved CO_2 from the biphasic mixture through alternate sparging of CO_2 gas and air.

Figure 1 shows the basic requirement of forming stable W/O and O/W emulsions by particles of contact angle greater and smaller than, but close to 90°, respectively. For W/O emulsions stabilized by very hydrophobic **P2** particles of contact angle around 90° become inverted to destabilize W/O emulsions when the contact angle of the particles is reduced to 79° by CO_2 purging. In contrast, for the O/W emulsions formed by less hydrophobic **P1** particles, the stability of the emulsion decreased by decreasing the contact angle of the particles from 66° to 56° upon CO_2 purging, as the stability of O/W emulsions would be the highest when stabilized by particles of contact angle close to but less than 90°.

Switchable surface groups grafted onto functionalized particles are ionized when CO_2 is present, as indicated by the corresponding increase in measured zeta-potential. Ionization of surface groups on stabilizer particles lowered wettability of particles and reduced emulsion stability but may additionally contribute to electrostatic repulsion between both dispersed particles and particle-stabilized droplets. This additional electrostatic stabilization upon addition of CO_2 was insufficient to overcome the destabilizing effect of CO_2 on emulsion stability due to reducing wettability of **P1** and **P2** particles. The electrostatic stability imparted by increasing surface ionization is more significant for particles with elevated surface charges. However, electrostatic interactions are less predominant in low polarity, non-aqueous environments such as water-in-oil emulsions.

■ CONCLUSION

CO_2-responsive particles were synthesized to control stability of surfactant-free emulsions. Switching particle-stabilized emulsions was demonstrated by the addition of CO_2 gas and removal of dissolved CO_2 by sparging with air. Triggered phase separation of particle-stabilized emulsions was possible due in part to the reversible change in wettability of stabilizing particles. This hypothesis was verified by monitoring the zeta-potential of stabilizing particles and the contact angle of silica wafer as model surfaces after direct addition of CO_2 gas and the removal of CO_2 by sparging with air or N_2. Our study demonstrates that both O/W and W/O surfactant-free emulsions of tunable responses can be developed by engineering particles with appropriate responsive and non-responsive surface groups.

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Notes

The authors declare no competing financial interest.

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