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Biocompatible Amphiphilic Hydrogel−Solid Dimer Particles as Colloidal Surfactants

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S *Supporting Information*

ABSTRACT: Emulsions of two immiscible liquids can slowly coalesce over time when stabilized by surfactant molecules. Pickering emulsions stabilized by colloidal particles can be much more stable. Here, we fabricate biocompatible amphiphilic dimer particles using a hydrogel, a strongly hydrophilic material, and achieve large contrast in the wetting properties of the two bulbs, resulting in enhanced stabilization of emulsions. We generate mono-disperse single emulsions of alginate and shellac solution in oil using a flow-focusing microfluidics device. Shellac precipitates from water and forms a solid bulb at the

periphery of the droplet when the emulsion is exposed to acid. Molecular interactions result in amphiphilic dimer particles that consist of two joined bulbs: one hydrogel bulb of alginate in water and the other hydrophobic bulb of shellac. Alginate in the hydrogel compartment can be cross-linked using calcium cations to obtain stable particles. Analogous to surfactant molecules at the interface, the resultant amphiphilic particles stand at the water/oil interface with the hydrogel bulb submerged in water and the hydrophobic bulb in oil and are thus able to stabilize both water-in-oil and oil-in-water emulsions, making these amphiphilic hydrogel−solid particles ideal colloidal surfactants for various applications.

KEYWORDS: *microfluidics, Janus particle, amphiphilic particle, colloidal surfactant, Pickering emulsion, hydrogel*
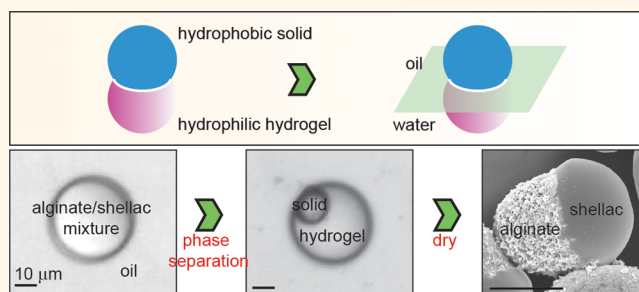
Emulsions of two immiscible liquids, for example, water in oil or oil in water, are attractive for various applications, such as in food and cosmetics. They are generally formed by input of external energy such as by shaking, stirring, or homogenizing,[1] and surfactant molecules, which are amphiphiles containing both hydrophobic and hydrophilic groups, are generally used to kinetically stabilize the emulsions through adsorption at the interface.[2] However, these emulsions are sometimes unstable due to coalescence[3,4] or Ostwald ripening.[5] Therefore, the wide range of applications of emulsions often demand means of stabilization other than molecular surfactants. One widely used alternative is solid particles, forming Pickering emulsions;[6,7] unlike surfactants, the reduction of energy per particle when anchored at the water/oil interface is generally much larger than thermal energy. When the particles are mostly wetted by one liquid, they are susceptible to desorption from the interface into the

preferentially wetting fluid, resulting in decreased stability.[8,9] To achieve the optimum stability, amphiphilic particles (also called Janus particles) with one hemisphere hydrophilic and another hydrophobic are desirable, and they show three times larger energy barrier to desorb from the interface than that of isotropic spherical particles, due to the attraction of each hemisphere to its wetting liquid.[10−13] Therefore, to ensure their partial wettability and strong anchoring at the water/oil interface, the surfaces of precursor isotropic particles are modified to obtain well-defined surface hydrophobicity,[14−18] or amphiphilic particles are directly made from different compositions.[19−25] To further enhance the emulsion stability,

nonspherical amphiphilic particles are prepared to better fit at the curved interface.[26−32] Among them, amphiphilic dimer particles, which consist of two different bulbs fused together, are of particular interest;[33−35] by tuning the ratio of the hydrophilic and hydrophobic bulbs, these particles provide flexible control over the preferred dispersed phase,[36−39] and, in analogy to the behavior of surfactant molecules, may be used to adjust the intrinsic curvature of the interface.[40] However, when the difference in hydrophobicity between the two bulbs is not large enough to overcome the large surface energy of the water/oil interface, amphiphilic dimer particles still tend to lie flat or have a tilted orientation at the interface to minimize the total energy (Figure 1a);[41] particles with highly anisotropic
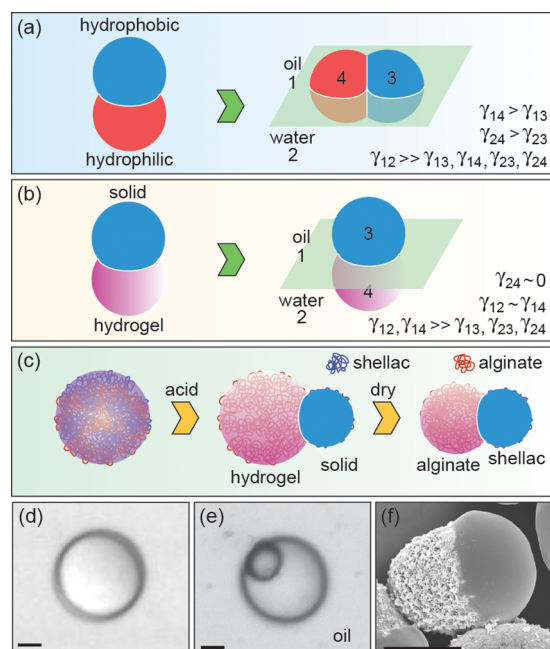

Figure 1. Fabrication of biocompatible amphiphilic hydrogel−solid dimer particles as colloidal surfactants. (a) Amphiphilic dimer particle with one bulb hydrophilic, and the other hydrophobic tends to lie down with both bulbs at the water/oil interface to minimize the total water/oil interfacial area when the energy cost of the water/oil interface is much larger than that of water/particle and oil/particle interfaces. (b) Amphiphilic hydrogel−solid particle tends to stand at the water/oil interface with the hydrogel bulb in water and the hydrophobic bulb in oil, mimicking surfactant molecule at the interface. (c) Schematic illustration of the method to make biocompatible hydrogel−solid particles *via* phase separation. (d) Single drop of alginate and shellac solution in fluorocarbon oil. (e) When the emulsion is exposed to acid, shellac phase separates from the solution, forming a solid bulb at the periphery of the drop. (f) Scanning electron microscopy image shows an amphiphilic dimer particle that consists of one porous bulb of alginate and one solid bulb of shellac when the particle is dry. The scale bar is 10 μm in (d−f).

hydrophobicity are preferred to extend into both phases like a surfactant molecule (Figure 1b).[34] Therefore, the full potential of amphiphilic dimer particles has yet to be realized, and a simple preparation of biocompatible colloidal surfactants that mimic the behavior of surfactant molecules at the water/oil interface remains an important challenge.

In this paper, we report a facile approach to make biocompatible hydrogel−solid particles that mimic the structure of surfactant molecules. These particles are highly

anisotropic in their hydrophobicity, consisting of two joined bulbs: one hydrogel bulb of alginate in water and one hydrophobic bulb of shellac. These particles are energetically favored to stand at the water/oil interface with the hydrogel bulb submerged in water and the hydrophobic bulb in oil, thereby mimicking the behavior of surfactant molecules at the interface. These amphiphilic particles are able to stabilize the water/oil interface against coalescence, thereby resulting in very stable Pickering emulsions. Since both alginate and shellac are biocompatible and the hybrid particles combine the merits of both hydrogel and solid, the potential applications of the amphiphilic hydrogel−solid particles are numerous, for example, in foods and cosmetics.

RESULTS AND DISCUSSION

To prepare the biocompatible amphiphilic hydrogel−solid dimer particles, we use alginate as the hydrogel bulb and shellac (Figure S1) as the hydrophobic bulb, both of which are FDA-approved, and follow the strategy illustrated schematically in Figure 1c−f and Figure S2. We dissolve alginate and shellac together in the alkaline aqueous solution, which is emulsified into monodisperse droplets in the outer fluorocarbon oil phase with a triblock nonionic surfactant using a flow-focusing polydimethylsiloxane (PDMS) microfluidic device, as shown in Figure 2a,b. Droplet formation of the alginate/shellac mixture in the microfluidic device results from the competition between the interfacial tension between the inner aqueous and outer oil phases that holds the drop to the tip and the viscous drag of the outer oil phase that pulls the drop downstream,[42] and monodisperse water-in-oil single emulsions are, therefore, generated in the dripping regime. The emulsions are subsequently collected in a reservoir of fluorocarbon oil containing 1% acetic acid. Because shellac is only soluble in alkaline water when most of its carboxylic groups are ionized, shellac precipitates from the alginate water solution when acetic acid diffuses into the droplets and forms a distinct bulb at the periphery, which anneals into regular hemispherical shape, as shown by the small dark portions in Figure 2c. Then, the water droplets containing alginate form the hydrogel bulbs. As water in the hydrogel bulbs evaporates from the air/fluorocarbon oil interface, the hydrogel bulbs slowly shrink, as shown in Figure 2d. After the evaporation of both the fluorocarbon oil and water in air, scanning electron microscopy (SEM) images of the dried particles show that they are dimers consisting of two distinct but perfectly joined bulbs, where the dried alginate bulb is rough and porous and the shellac bulb is solid and smooth, as shown in Figure 2e and magnified in Figure 2f. The dimer particles are quite monodisperse with an average size of ∼25 μm long and ∼20 μm wide, and the ratio of the alginate bulb to the shellac bulb is ∼1.5. To obtain stable particles, we cross-link the alginate hydrogel using Ca^{2+} cations; each cation binds to two carboxylic groups of the alginate chains, thereby forming a stable cross-linked 3D network, as shown in Figure S3a. The cross-linking of alginate can be achieved by *in situ* pH-triggered release of Ca^{2+} from $CaCO_3$ nanoparticles or Ca-EDTA complex that was previously added to the alginate/shellac mixture, as shown in Figures S3b and S4a,b, respectively. After the particle preparation, the triblock nonionic surfactants are removed and the continuous fluorocarbon oil phase is replaced with fresh oil without any surfactants to minimize the effect of molecular surfactants in the following tests.

To elucidate the underlying mechanism that joins the two distinct bulbs of the amphiphilic dimer particle, we label
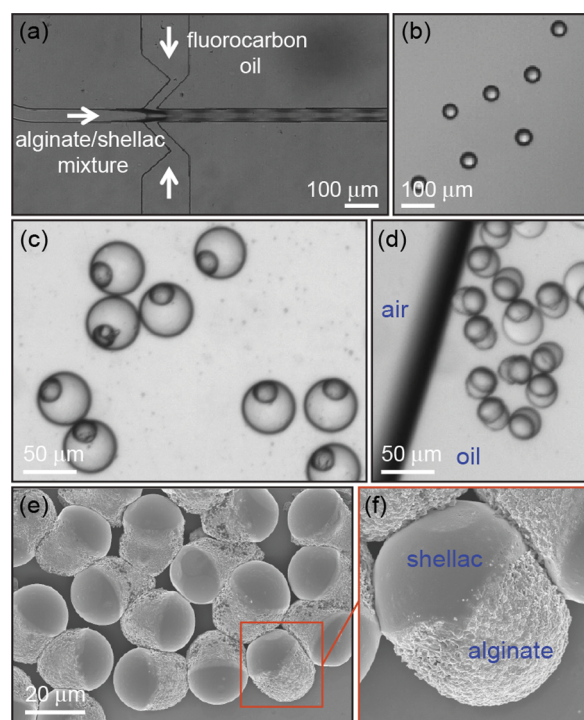
Figure 2. Fabrication of hydrogel–solid particles using single emulsions as templates. (a) Image of a flow-focusing microfluidic device generating single emulsions of the alginate/shellac mixture in the fluorocarbon oil with the triblock nonionic surfactants. (b) Optical image of monodisperse droplets dispersed in the fluorocarbon oil and stabilized by the nonionic surfactants. (c) Shellac precipitates from water under acidic conditions to form a bulb at the periphery of the hydrogel droplet due to its hydrophobic nature. (d) Near the air/fluorocarbon oil interface, water slowly evaporates and the hydrogel bulb slowly shrinks. (e) SEM image and (f) magnified image of dry particles. The shellac bulbs are smooth, whereas the appearance of the alginate bulbs is rough and porous.
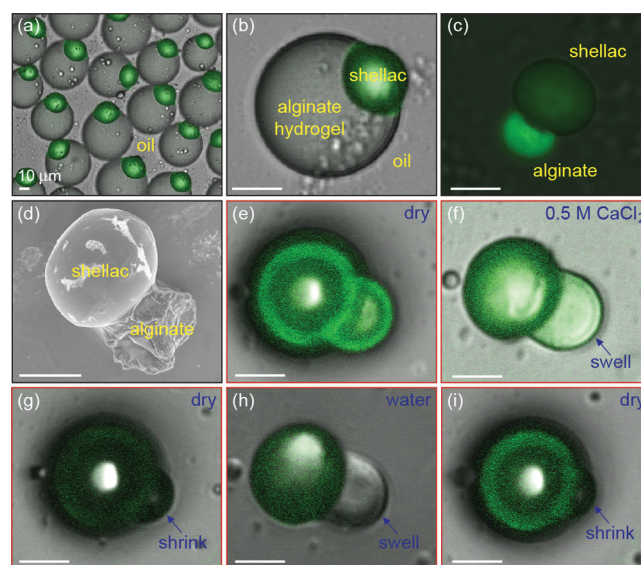

Figure 3. Hydration and dehydration of the alginate bulb showing typical hydrogel features. (a,b) Overlays of confocal fluorescent (green) and optical (gray) images of hydrogel–solid particles made with FITC-labeled alginate. The fluorescence observed in the shellac bulb indicates that some alginate is dragged into the shellac when it precipitates. The hydrogel bulb shows only a very weak fluorescent intensity due to the low concentration of alginate in water. (c) When the particle is dried, the alginate bulb shows a fluorescence much stronger than that of shellac, and the whole particle attains a mushroom-like shape. (d) SEM image of an amphiphilic particle made with FITC-labeled alginate. (e–i) Cross-linking of alginate hydrogel bulbs using Ca^{2+} cations forms a stable amphiphilic hydrogel–solid particle. The alginate bulb shows typical features of a hydrogel in that it swells when it is submerged in water and shrinks when it is dry. During the hydration and dehydration processes, the configuration of the particle has changed and the alginate bulb is no longer in the focal plane, thus showing a low fluorescent intensity even when it is dehydrated. (e–i) Images of the same particle. The scale bar is 10 μm in all images.

alginate with fluorescein based on the carbodiimide/*N*-hydroxysuccinimide (EDC-NHS) reaction (see details in Supporting Information Scheme S1) and fabricate dimer particles with FITC-labeled alginate to directly visualize the distribution of alginate in the particles. In these particles, we observe a weak fluorescence signal in the alginate hydrogel bulb due to the low concentration of FITC-labeled alginate in water. We also observe a moderate fluorescence in the hydrophobic shellac bulb, which suggests that FITC-labeled alginate is also present in the shellac bulb, as shown in Figure 3a and the close-up in Figure 3b. When water evaporates from the hydrogel, the alginate bulbs show a much stronger level of fluorescence (Figure 3c). Although alginate is functionalized with fluorescein and the morphology of the alginate bulb is slightly different from that made with unmodified alginate, the distinct alginate bulb again is well joined to the shellac bulb, forming one amphiphilic dimer particle, as shown by the SEM image of Figure 3d. We propose that when shellac precipitates from the aqueous solution, shellac molecules drag some alginate molecules with them to the hydrophobic bulb due to molecular interactions, such as molecular entanglement and hydrogen bonding between the alginate and shellac molecules (Figure S5), which bind the two distinct bulbs of the amphiphilic dimer particles.

To confirm the alginate bulb is a hydrogel, we perform a series of hydration and dehydration steps. After cross-linking, the alginate bulb can repeatedly swell and shrink when it is hydrated and dehydrated, respectively, as shown in Figure 3e–i and Figure S6a–e. In the swollen hydrated state, the alginate bulb is optically transparent because its refractive index mismatch with water is small, whereas in the dehydrated state, the alginate bulb is opaque. In both cases, the shellac bulb remains opaque. Moreover when the cross-linking step is omitted, the dehydrated alginate bulb swells instantly and slowly dissolves in water, which completely disappears when the sample is dried, as shown in Figure S7a–c.

Because the hydrophilic bulb of our dimer particles is a hydrogel, which is the most hydrophilic possible, these dimer particles have a very large contrast in the wetting properties between the hydrophilic and hydrophobic bulbs. When anchored at the water/oil interface, the dimer particles lower the free energy by decreasing the water/oil interface while the water/particle and oil/particle interfaces cost energy; the calculation of the total free energy suggests that the hydrogel–solid dimer particles are energetically favored to stand at the interface with the hydrogel bulb submerged in water and the hydrophobic bulb in oil, as explained in detail in Supporting Information Discussion S1. This configuration

mimics surfactant molecules that maximize the reduction of energy per particle when anchored at the water/oil interface and is thus better than conventional colloidal surfactants at stabilizing emulsions. To illustrate their superior wetting properties, we pour water on top of a suspension of our amphiphilic particles in the fluorocarbon oil and gently shake the solution. The addition of water creates a water/oil interface. Our particles do not exhibit the general wetting problem that prevents conventional colloidal particles previously suspended in one liquid from being wetted by another liquid and thus prevents them from going to the interface. We observe the particles absorb onto the water/oil interface and move with the interface when the vial is tilted, suggesting a strong adsorption at the interface, as shown in Figure 4a−c and modeled in Figure
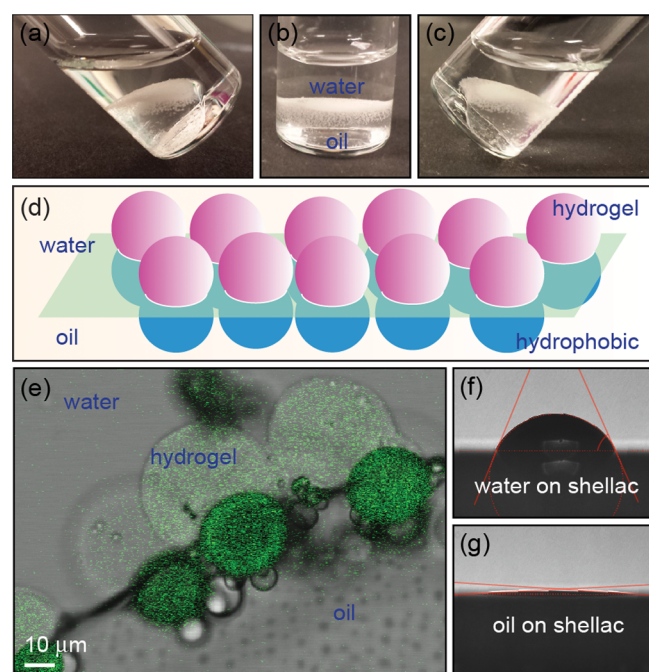

Figure 4. Amphiphilicity of hydrogel−solid particles at the water/oil interface. After the particle preparation, the triblock nonionic surfactants are removed and the continuous fluorocarbon oil phase is replaced with fresh oil without any surfactants. (a−c) Amphiphilic hydrogel−solid particles preferentially adhere at the water/fluorocarbon oil interface even when the interface moves. (d) Model of the amphiphilic hydrogel−solid particles that stand at the interface. (e) Direct visualization of the particles at the interface. Analogous to surfactant molecules, the hydrogel bulbs of the particles are submerged in water, and the hydrophobic bulbs are expelled to the fluorocarbon oil phase. (f) Contact angle of deionized water on the shellac surface is ∼67°, which is larger than 60° and can be regarded as hydrophobic. (g) Contact angle of fish oil on the shellac surface is only ∼3°.

4d. To directly visualize the configuration of the amphiphilic particles at the interface, we pipet a solution containing both water and oil and sandwich them between two glass slides. As expected, the amphiphilic dimer particles stand at the water/fluorocarbon oil interface with the hydrogel bulb submerged in water and the hydrophobic bulb expelled in the fluorocarbon oil phase, as shown in Figure 4e. The hydrophobicity of shellac is confirmed by the large contact angle of a water drop on the shellac surface, as shown in Figure 4f, and its wetting by the oil phase is suggested by the small contact angle of a fish oil drop on the shellac surface, as shown in Figure 4g. We conclude,

therefore, that hydrogel−solid particles are ideal colloidal surfactants because their behavior at the water/oil interface mimics that of surfactant molecules.

To make water-in-oil emulsions using the amphiphilic particles and test their stability, we add a small volume of water to the particle suspensions and vigorously shake the mixture, for example, ∼200 μL of water in ∼5 mL of fluorocarbon oil suspended with 20 μL particles, as shown in Figure S8a. The water breaks into small droplets, which coalesce until the surface of each droplet is uniformly covered by the particles to a sufficient density that prevents direct contact of the inner water between neighboring drops. Such limited coalescence in solid-stabilized emulsions has previously been studied in detail, and it has been shown that limited coalescence is a robust process, capable of achieving narrow droplet size distributions, and the final average droplet diameter is inversely proportional to the total amount of solid particles, with a slope that depends on the mixing intensity.[43] To visualize the particle coverage on the water-in-oil emulsions, we use a confocal microscope and image a stabilized water drop in dodecane, showing that the particles adsorb at the interface and align themselves so that the hydrogel bulbs are submerged in water inside the drop and only solid shellac bulbs are observed at the outer surface, as shown in Figure 5a and Figure S9 and magnified in Figure S10a. Generally, water emulsions of millimeter size are unstable; for example, large water droplets in silicone oil, stabilized by surfactant molecules, readily coalesce after 3 weeks, even when quiescent, as shown in Figure S11. By contrast, the emulsions stabilized by hydrogel−solid particles remain unchanged after 6 months; the particles anchored at the interface of each drop prevent direct contact of the inner water of neighboring drops, even when squeezed together due to the large density mismatch ($\rho_{water} \sim 1$ g/cm^3 and $\rho_{oil} \sim 1.6$ g/cm^3), as shown in Figure 5b. Moreover, the absence of individual particle suspended in the fluorocarbon oil indicates the strong propensity of the hydrogel−solid particles to adsorb and then remain at the interface. If we add ∼200 μL of fluorocarbon oil suspended with 20 μL particles in ∼5 mL of water, due to the catastrophic inversion,[44] we obtain oil-in-water emulsions, as demonstrated in Figure S8b. In an oil-in-water emulsion, the orientation of hydrogel−solid particles is reversed, with the shellac bulbs submerged inside the drop toward the center. A layer of hydrogel is, therefore, observed at the periphery of the drop; fluorescein dissolved in water easily diffuses into the transparent hydrogel layer and shows fluorescence, as shown in Figure 5c and magnified in Figure S10b.

There are various reports on emulsions stabilized by particles.[45−49] The main advantages of our amphiphilic hydrogel−solid dimer particles include the following: (i) Our particles are made of food-grade materials, which could be used in foods and cosmetics. (ii) They are prepared using single emulsions as templates and via one-step phase separation. Different size of the Janus particles can be prepared, and their production can be scaled up. (iii) The Janus particles consist of two distinct bulbs: one hydrogel bulb of alginate in water and one hydrophobic bulb of shellac. Therefore, the Janus particles are highly anisotropic in their hydrophobicity. (iv) The hydrogel bulbs are essentially water. The Janus particles have a natural tendency to go to the water/oil interface with the hydrogel bulbs submerged in water, mimicking the behavior of surfactant molecules at the interface.
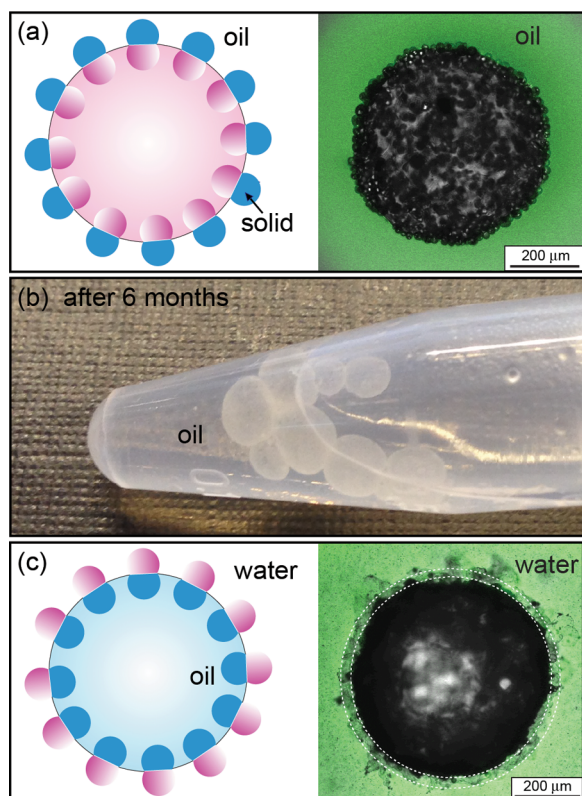
Figure 5. Water-in-oil and oil-in-water emulsions stabilized by amphiphilic hydrogel−solid particles. (a) Model and overlay of confocal fluorescent and optical images of a water drop in dodecane stabilized by the hydrogel−solid particles. In a water-in-oil emulsion, the hydrogel bulbs stay inside the water drop and the hydrophobic shellac bulbs are observed at the periphery, showing a clear boundary contacting the oil phase. Nile red is added in the oil phase. (b) Long-term stability of water emulsions in fluorocarbon oil. Water drops are uniformly covered by the hydrogel−solid particles and are cloudy in appearance because the particles at the interface scatter the light as it passes through the emulsions. Because the hydrogel−solid particles at the water/oil interface prevent direct contact between the water of neighboring drops, these drops are stable and remain unchanged even after 6 months. (c) Overlay of confocal fluorescent and optical images of a fluorocarbon oil drop in water. In an oil-in-water emulsion, a layer of hydrogel surrounding the oil drop is observed. Fluorescein is added in the water phase.

The potential applications of the amphiphilic hydrogel−solid particles are numerous. Both alginate and shellac are biocompatible and biodegradable, and the hybrid particle combines the merits of both hydrogel and solid, which have distinct but complementary properties to one another. The property of the particles can be precisely tailored to meet the requirements, and their production could be scaled up. Monodisperse particles ranging in size from several microns to tens of microns are produced using different sizes of single emulsions as templates, as shown in Figure S12a−d, and monodisperse particles with different ratio between hydro-phobic and hydrophilic bulbs are prepared using different concentrations of shellac, as shown in Figure 6, which are expected to provide flexible control over the preferred curvature of the water/oil interface and tunable stability of the particles anchored at the interface. In addition, when shellac bulbs of neighboring particles occasionally merge together during the sample preparation process, we observe bimodal,
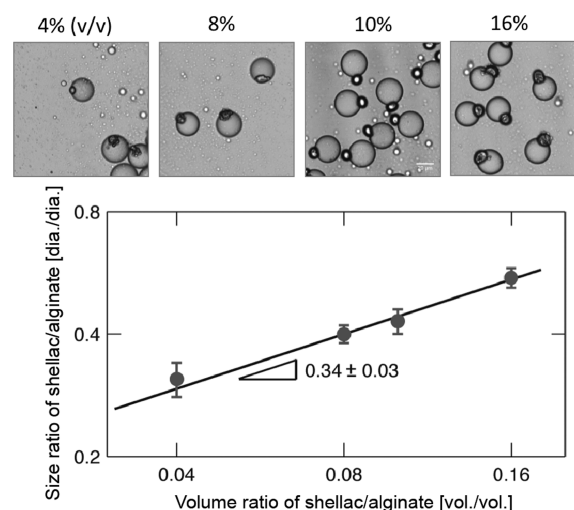

Figure 6. Size ratio of the hydrophobic shellac bulb to the hydrophilic alginate hydrogel bulb increases as the volume ratio of shellac to alginate hydrogel increases.

trimodal and tetramodal particles with multiple hydrogel bulbs (Figure 7a−f), suggesting that more delicate structural complexity, such as patchy particles,[27−29] is also achievable.
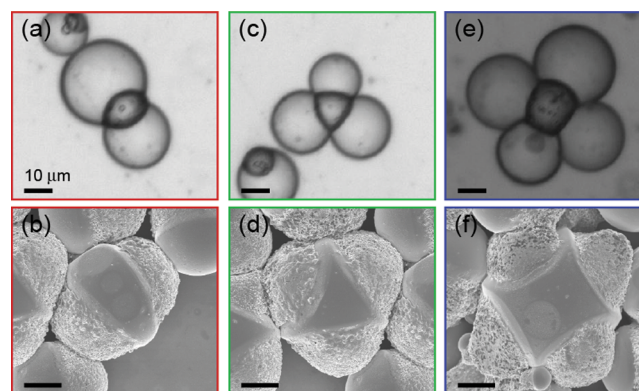

Figure 7. Patchy particles with multibulbs of alginate. When shellac bulbs of neighboring particles occasionally merge together during the sample preparation, they form (a,b) bimodal particles with two alginate bulbs, (c,d) trimodal particles with three alginate bulbs, or (e,f) tetramodal particles with four alginate bulbs. Panels (a), (c), and (e) are optical images of particles in water, and (b), (d), and (f) are SEM images.

CONCLUSIONS

We have developed a versatile method to synthesize biocompatible amphiphilic hydrogel−solid particles using single emulsions as templates. To minimize the total free energy, the amphiphilic particles are energetically favored to stand at the water/oil interface and behave as ideal colloidal surfactants that are able to stabilize both water-in-oil and oil-in-water emulsions. These amphiphilic particles are hybrid hydrogel−solid particles, which combine the advantages of two distinct but complementary materials and provide an amphiphilic structure that can significantly enhance the stability of emulsions. These amphiphilic particles can be custom-tailored to achieve the desired functionality and specific requirements. Their production can easily be scaled up. Therefore, the biocompatible hydrogel−solid particles presented here repre-

sent a basis for further development of various colloidal surfactants that address the demands of different applications such as food and cosmetics.

MATERIALS AND METHODS

Shellac wax-free (Ph Eur) is purchased from Sigma-Aldrich and it consists mainly of a mixture of esters (Figure S1). Shellac is only soluble in alkaline water when most of its carboxylic groups are ionized and is dissolved in water using Na_2CO_3.[50] The pH of the shellac solution is around 8. Alginic acid sodium salt from brown algae (purchased from Fluka) is subsequently dissolved in the shellac solution. Typical solutions used in this paper contain 15 mg of alginate and 100 mg of shellac in 1 mL of water, and the alginate/shellac mixture is then used as the inner phase. The outer oil phase is HFE 7500 (purchased from 3M) with 1% Krytox-PEG-Krytox surfactants. HFE 7500 is a fluorinated oil with a liquid density of 1614 kg/m³, a surface tension of 16.2 dyn/cm, and a viscosity of 0.77 cSt. Krytox-PEG-Krytox is a triblock nonionic surfactant, where the brand name Krytox refers to poly(perfluoropropylene glycol) and PEG refers to polyethylene glycol,[51] and is used to stabilize the droplets of the aqueous solution of the alginate/shellac mixture in the outer fluorocarbon oil phase during the emulsification. Emulsions of the alginate/shellac mixture in the fluorocarbon oil are generated using a flow-focusing microfluidic device, which is fabricated using the technique of soft lithography with PDMS. The inner phase of the alginate/shellac mixture is pumped through the inner channel with a typical flow rate of 100 μL/h, and the outer phase of the fluorocarbon oil with the triblock nonionic surfactants is pumped through the outer channel with a typical flow rate of 400 μL/h. All fluids are pumped into the microfluidic device using syringe pumps (Harvard PHD 2000 series; Harvard Apparatus, United States). Water-in-oil single emulsions are formed when the outer oil phase converges at the junction of the microfluidic device and breaks the inner aqueous phase into droplets. The drop size can be varied by changing the flow rates of the inner aqueous phase or the outer oil phase. The resulting emulsions of the alginate/shellac mixture are collected in a fluorocarbon oil reservoir with 1% acetic acid to quickly precipitate shellac from the single emulsions, and shellac bulbs slowly anneal into smooth hemispheres. Alginate bulbs of the amphiphilic dimer particles can be cross-linked using 0.5 M $CaCl_2$ solution to form stable particles. Alternatively, alginate hydrogel bulbs can be cross-linked by *in situ* pH-triggered release of Ca^{2+} cations from $CaCO_3$ nanoparticles or Ca-EDTA complex when exposed to acetic acid;[52] $CaCO_3$ nanoparticles with an average size of ∼80 nm are dispersed in the alginate/shellac solution *via* sonication, or 0.1 M Na-EDTA and 0.1 M $CaCl_2$ is added to the alginate/shellac mixture at pH 9.5. After the particle preparation, the Krytox-PEG-Krytox surfactants are removed from the fluorocarbon oil phase and the surfaces of either the alginate or shellac bulbs using PFO (1H,1H,2H,2H-perfluoro-1-octanol, Sigma-Aldrich); that is, 20 vol % PFO is added to the fluorocarbon oil phase since the surfactants have a higher solubility in PFO.[53] The fluorocarbon oil phase is then replaced by fresh fluorocarbon oil without any surfactants to minimize the effect of the Krytox-PEG-Krytox surfactants in the following tests. Since the residual of surfactants could adsorb at the water/oil interface, which lowers the interfacial tension, and could also adsorb at the particle surface, which changes the wetting property of the particles, thus affecting the emulsion stability,[54−57] it is important to make sure that the surfactants are essentially removed. The interfacial tension between water and fluorocarbon oil after replacement is measured using the pendant drop test, which is essentially the same as that between water and neat fluorocarbon oil, as described in detail in Supporting Information Discussion S2. The fluorocarbon oil phase is also replaced by fresh dodecane without any surfactants to demonstrate the performance of the amphiphilic hydrogel−solid particles.

As described above in the process of the sample preparation, after the emulsification, the emulsions of the alginate/shellac mixture are collected in a fluorocarbon oil reservoir with 1% acetic acid, and shellac precipitates from the water solution and forms a distinct bulb at the periphery when acetic acid diffuses into the droplets. During the precipitation process, shellac bulbs of neighboring particles may occasionally merge together, forming bimodal, trimodal, or tetramodal particles. Currently, these patchy particles are not fabricated in a controlled manner, and the production yield of the patchy particles is low.

To observe the distribution of alginate in the dimer particle, alginate is chemically labeled with fluorescein by conjugating some carboxylic acid groups with 5-amino fluorescein based on the EDC-NHS reaction (Scheme S1). Confocal fluorescence microscopy images are taken using an inverted confocal fluorescence microscope (Leica, USA). The fluorocarbon oil is volatile, and dried particles are obtained by evaporating the fluorocarbon oil in the continuous phase and the water in the hydrogel bulbs in air. The dried particles are then coated with 5 nm Pt/Pd (4:1) and imaged using field emission scanning electron microscopy (Zeiss, model Ultra55).

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b03110.

> Additional experimental details on the fabrication and characterization of hydrogel−solid Janus particles and emulsions stabilized by the particles; synthesis of fluorescein-labeled alginate; fabrication and characterization of hydrophilic−hydrophobic Janus particles; calculation of the free energy of hydrogel−solid Janus particles at the water/oil interface; measurement of the surface tension; preferred emulsion at equal volume of water and oil (PDF)

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Notes

The authors declare no competing financial interest.

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