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COMMUNICATION

Polyelectrolyte hydrogel capsules as stabilizers for reconfigurable complex emulsions†

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Responsive complex emulsions are increasingly of interest for use in diagnostics, optics, and chemical sensing due to their tunable chemical and physical properties. A significant limitation of such fluid droplets for long-term applications is their eventual breakdown over time by pathways such as coalescence and Ostwald ripening that lead to variations in droplet size and composition. Elucidating approaches by which to enhance droplet stability while simultaneously maintaining their reconfigurability and responsive character is therefore important. This report explores the behavior of reconfigurable hydrocarbon and fluorocarbon droplets in water that are encapsulated in a polyelectrolyte hydrogel shell. Surfactant-free gelation pathways are investigated to form oil-core calcium alginate capsules, and the effects of the hydrogel capsule structure on droplet stability and reconfigurability in the presence of surfactants are characterized.

Emulsions, which are mixtures of immiscible fluids stabilized by surfactants, have far-reaching impact and use in fields as diverse as medicine,[1,2] cosmetics,[3,4] food,[5] and coatings.[6,7] Reconfigurable complex emulsions, which often consist of biphasic hydrocarbon and fluorocarbon oil droplets in water that can transition between double emulsion and Janus morphologies, have recently been of particular interest due to their tunable physical and chemical properties.[8] Such droplets can be sensitized to a wide range of stimuli including light,[8–10] pH,[8] bacteria,[11] or enzymes,[12] enabling potential use in applications ranging from sensors and displays to tunable lenses.[9,10,12,13] However, despite the promising opportunities for complex droplets, a disadvantage of fluid emulsions more broadly is that they are not thermodynamically stable and will eventually succumb to breakdown by pathways such as Ostwald ripening and coalescence, leading to changes in droplet size and composition.[14,15] This inherent instability limits the use of responsive complex emulsions in situations that may require long shelf life, monodisperse size, and precise compositional control.

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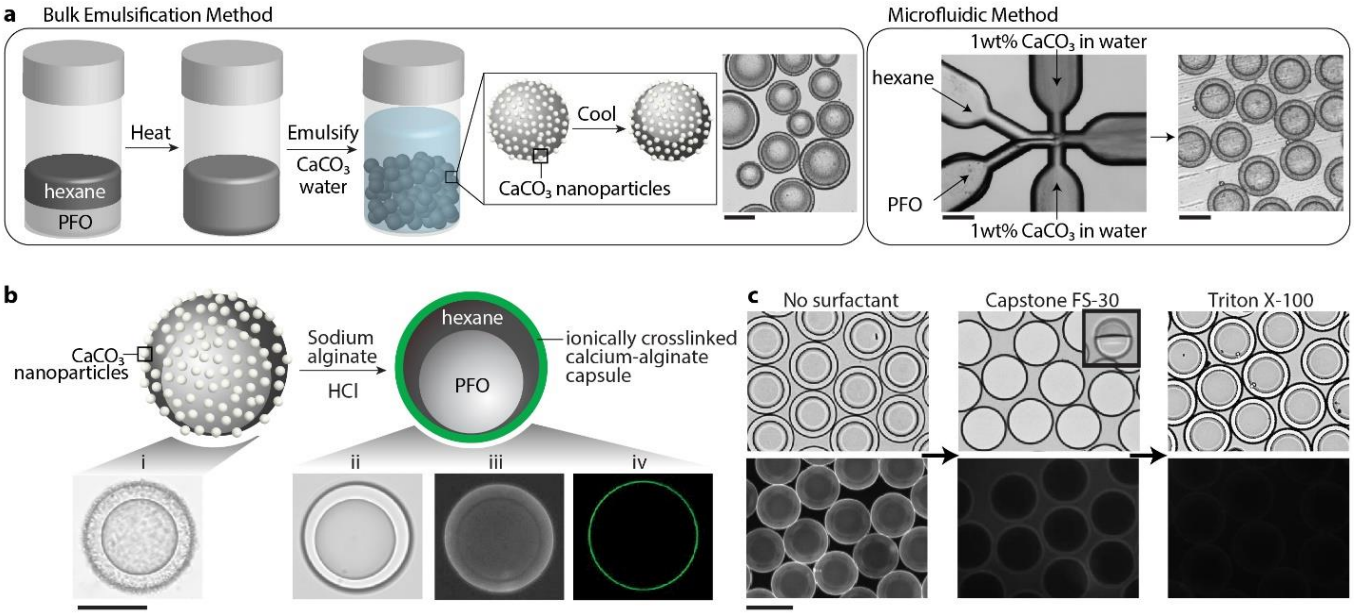

Figure 1. Ionically crosslinked calcium alginate hydrogel encapsulation of reconfigurable complex emulsion droplets. a) Schematic detailing the two methods used in emulsion formation. Bulk emulsification produces polydisperse droplets rapidly; hexane and PFO are heated until miscible, emulsified with calcium carbonate nanoparticles, then cooled. Scale, 100 µm. Microfluidics utilizing a flow focusing device (scale, 200 µm) forms monodisperse droplets stabilized by calcium carbonate (scale, 100 µm). b) Schematic illustrations and optical micrographs showing the encapsulation of F/H/W droplets, starting from calcium carbonate coated droplets as produced in (a). Top: sodium alginate is added to the emulsion and acidified with HCl, releasing Ca^{2+} that crosslinks the alginate into a capsule. Bottom, optical micrographs of exemplary droplets (scale, 50 µm). (i) Optical micrograph of a calcium carbonate-coated droplet before capsule formation. (ii-iv) Optical micrographs of droplets after capsule formation. The hydrogel is not easily seen in (ii) brightfield transmission, but (iii) fluorescence and (iv) confocal laser scanning microscopy images allow visualization of a fluorescein-trigged capsule. c) Brightfield transmission optical micrographs (top) with corresponding fluorescence micrographs (bottom) of encapsulated droplets after addition of 1 wt% Capstone FS-30 (triggering a F/H/W to Janus transition) and 0.5 wt% Triton X-100 (triggering a Janus to F/H/W double emulsion transition). Inset shows a side-view image of the Janus droplets to visualize the hexane-PFO interface. While the droplets do reconfigure between Janus and double emulsion morphologies, the addition of surfactant in the continuous aqueous phase causes destabilization of ionically crosslinked calcium alginate hydrogel as seen by the decrease in fluorescence intensity of the capsule and an increase of fluorescence intensity in the water. Scale, 100 µm.

One approach to enhanced stabilization of droplets is by encapsulation, where a solid shell, often a polymer, encases the liquid droplet in order to prevent coalescence and limit exchange of droplet contents with the continuous phase.[16] A common approach to droplet encapsulation is interfacial polymerization, where monomers dissolved in immiscible phases react at interfaces to form capsules via either polycondensation to produce polymers such as polyurethanes or polyamides,[17–20] or where an initiator (e.g. for radical polymerization) is localized at the interface to trigger polymerization.[21] Interfacial complexation of polyelectrolytes is another approach to generate capsules where two oppositely charged species interact across an oil-water interface.[22–27] However, it has recently been shown that even a partial, hemispherical shell produced by interfacial polymerization on a Janus droplet hampers changes in the droplet morphology,[28] suggesting that the high interfacial activity of capsules produced by interfacial polymerization or complexation is perhaps not well suited for stabilization of reconfigurable droplets. On the other hand, polyelectrolyte hydrogels,[29,30] which are composed of crosslinked, charged polymers swollen in water, may have lower interfacial activity at the oil-water interface;[31] recent work examining the wetting behaviour of various hydrophobic liquids on polyelectrolyte brushes has shown the tendency for hydrocarbon oils to bead away from a charged polymer's surface when submerged in water.[31] A strategy for encapsulation of oil droplets in an alginate polyelectrolyte capsule has been recently developed by ionic crosslinking through a Pickering emulsion intermediate exclusively in the aqueous phase.[32] Furthermore, such hydrogel capsules are highly permeable to molecules in the aqueous phase[16,33–35] and would permit the diffusion of surfactants or other analytes to the droplet surface to trigger a response in droplet configuration. Thus, a polyelectrolyte hydrogel capsule may provide opportunities for improved stabilization and lifetime of reconfigurable droplets while still preserving their dynamic nature and sensitivity to desired stimuli.

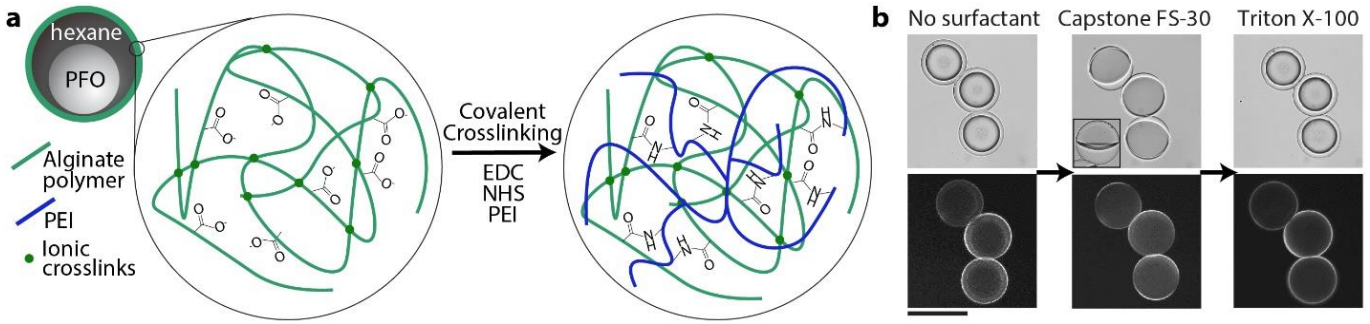

Figure 2. Covalent crosslinking enhances alginate capsule stability while preserving droplet reconfigurability. a) Schematic detailing the covalent modification of calcium alginate capsules, wherein EDC-NHS crosslinking chemistry is used to couple PEI to carboxylic acid groups on the alginate. b) Hexane-PFO complex droplets stabilized with the covalently crosslinked alginate capsules reconfigure from F/H/W to Janus upon addition of 0.5 wt% Triton X-100 (inset: side view of an exemplary droplet) and back to F/H/W with the addition of 1 wt% Capstone FS-30 as seen in brightfield transmission optical micrographs (top). Corresponding fluorescence micrographs (bottom) of the FITC-tagged covalently crosslinked capsules demonstrate that the capsules retain their fluorescence and remain intact even in the presence of the surfactants. Scale, 100 µm.

In this report we explore methods for the encapsulation of hydrocarbon and fluorocarbon oil droplets in water in a calcium alginate polyelectrolyte hydrogel capsule and investigate the effects of the capsule on droplet stability and reconfigurability. By using calcium carbonate stabilized droplets as the precursors to calcium alginate hydrogel capsules, we can prepare encapsulated droplets in a surfactant-free environment, thereby reducing coalescence and Ostwald ripening and allowing storage of the droplets in water for months. We further show that covalent crosslinking of the calcium alginate capsule significantly enhances stability of emulsions in the presence of aqueous surfactant and prevents wetting of the oil droplets on hydrophobic surfaces. The addition of surfactants to either the aqueous or oil phases allows tuning of the responsive droplet morphology, even while the capsule remains intact. We expect that the ability to encapsulate reconfigurable droplets while preserving their responsiveness will facilitate use of these emulsions in situations requiring long shelf life or conditions that would otherwise trigger droplet destabilization, as well as provide opportunities for functionalization of the droplets via the capsule for droplet patterning and tagging.

In order to test whether a hydrogel capsule would enhance droplet stability but still allow droplet reconfiguration, we first developed a fabrication strategy by which to encapsulate biphasic hydrocarbon-fluorocarbon oil droplets within polyelectrolyte hydrogel shell. A commonly used polyelectrolyte encapsulant is ionically crosslinked calcium-alginate hydrogel, but the ionic crosslinking is typically conducted by interfacial complexation of calcium ions and sodium alginate polymer at water-water interfaces; encapsulation of oil-in-water droplets required a slightly different strategy,[32] as outlined in **Figure 1**. In short, biphasic droplets of perfluorooctane (PFO)-in-hexane-in-water (F/H/W) double emulsions were first fabricated either by a bulk scale heating and phase-separation method (for polydisperse drops) or by microfluidics (for monodispersed drops) in an aqueous solution of dispersed calcium carbonate ($CaCO_3$) nanoparticles (1 wt%, 50 nm).[8] Once the nanoparticle-stabilized emulsion was formed, we washed away the excess calcium carbonate from the aqueous continuous phase, leaving behind only the particles adhered to the oil-water droplet interface (**Figure 1a**). We then added low viscosity (4-12 cP) sodium alginate to the continuous aqueous phase (2.5 wt%) and reduced the pH to 4.5 by adding concentrated hydrochloric acid (HCl). At this low pH, the calcium carbonate dissolved and released Ca^{2+} ions into the water, ionically crosslinking the alginate polymers in the vicinity of the droplet surface and forming a capsule. Although the thin, calcium alginate capsule is not visually apparent in brightfield transmission optical microscopy (**Figure 1b(ii)**), the droplets were stable in the absence of any surfactant, suggesting that the capsule was present. By

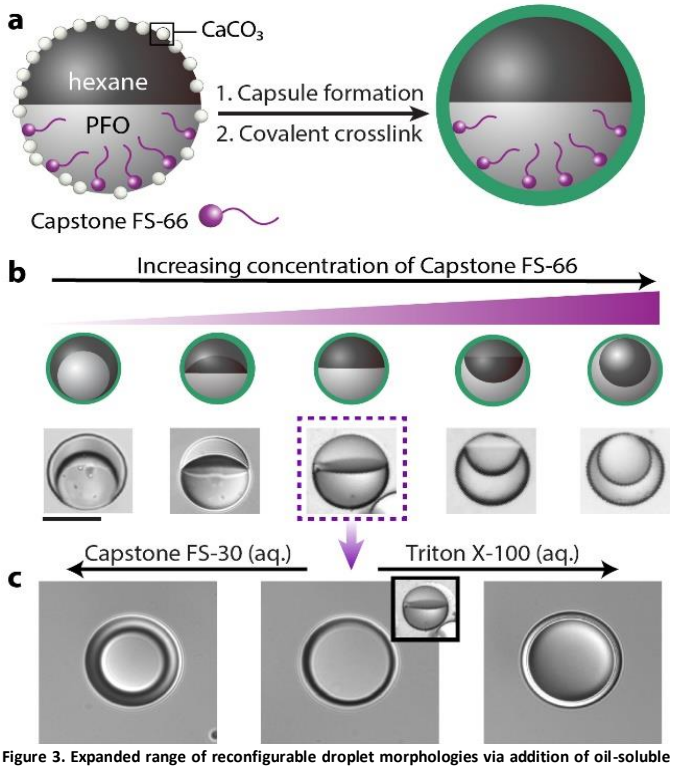

Figure 3. Expanded range of reconfigurable droplet morphologies via addition of oil-soluble surfactant in a covalently crosslinked alginate capsule. a) Schematic representation of the effect of Capstone FS-66, a fluorinated oil-soluble fluorosurfactant, on complex droplet morphology. Without Capstone FS-66, hexane-PFO complex droplets have a F/H/W shape, as shown in Figure 1b; addition of Capstone FS-66 surfactant favors creation of PFO-water interfacial area. b) Diagrams (top row) and side-view brightfield transmission optical micrographs of exemplary droplets (bottom row) detailing the relationship between increasing Capstone FS-66 surfactant concentration and resultant droplet morphology. Concentrations of Capstone FS-66 range from 0 wt% (far left) to 0.008, 0.031, 0.25, and 1 wt% (far right). Scale, 50 µm. c) Top-view brightfield optical micrographs showing how addition of aqueous surfactants to an initial Janus droplet (side-view image inset, Capstone FS-66 concentration of 0.031 wt%) affects morphology. Addition of Triton X-100 favors formation of F/H/W double emulsions and Capstone FS-30 fluorosurfactant favors formation of H/F/W. Scale, 100 µm.

functionalizing the alginate with fluorescein, we were able to use fluorescence microscopy and confocal laser scanning microscopy to verify the capsule existence and we found the capsules to be on the order of about 1 µm in thickness (**Figure 1b(iii-iv)**). These ionically crosslinked, calcium alginate encapsulated double emulsions are stable in reverse osmosis-purified water for at least a month, which is the longest period over which we have observed and which is far more stable than emulsions stabilized by a commonly used surfactant such as sodium dodecyl sulfate (**Supporting Information Figure S1**). The fact that there is little change in dispersity over time demonstrates that the capsule enhances droplet stability against coalescence, and because there is no surfactant in the continuous phase, micellar solubilization does not occur and Ostwald ripening is suppressed.

Having established a fabrication method for encapsulation of the complex droplets by ionically-crosslinked calcium alginate capsules, we next investigated whether the capsule would still allow for reconfiguration of the droplets' morphology. The transition between double emulsion and Janus morphology is most easily triggered by addition of surfactants to the continuous aqueous phase that alter the balance of interfacial tensions at the hydrocarbon-water and fluorocarbon-water interfaces.[8] Because the droplets naturally begin as F/H/W double emulsions when stabilized with the calcium alginate capsule, we added a nonionic fluorosurfactant, Capstone FS-30, in order to preferentially reduce the interfacial tension at the PFO-aqueous interface and induce a droplet morphology transition towards a H/F/W state.[8] Upon addition of as little as 0.003 wt% Capstone FS-30, we observed that the droplets displayed a change in morphology from double emulsion to Janus (**Supporting Information Video S1**), although the droplets never fully inverted to a H/F/W double emulsion even at high (>2 wt%) concentrations as would be expected in the absence of the alginate capsule (**Figure 1c**).[8] Addition of nonionic surfactant Triton X-100 triggered the droplet shape to change from Janus back to a F/H/W double emulsion (**Figure 1c**). Presence of surfactants, however, disrupted the hydrogel ionic crosslinks and the capsule degraded over time as evidenced by the decrease in the fluorescence of the fluorescein-tagged capsule and an increase in the fluorescence of the surrounding aqueous phase (**Figure 1c**). Dilution of the surfactant in the continuous phase resulted in droplet coalescence, indicating that the structural integrity of the capsule is compromised in the presence of surfactants.

Although ionically crosslinked capsules were stable only in the absence of surfactant, we hypothesized that a covalently crosslinked alginate capsule may remain stable under a wider range of conditions.[36] Starting with the ionically crosslinked hydrogel-encapsulated droplets, we used 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) to crosslink the carboxylic acid groups present in the alginate capsule with primary amine groups in branched polyethylenimine added to the aqueous phase (PEI, M_n = 60,000 g/mol) (**Figure 2a, Supporting Information Figure S2**). A small amount of fluorescein isothiocyanate-tagged poly-L-lysine could also be included as a means to visualize the capsule by fluorescence. To examine the effect of capsule crosslinking density on the mechanical stability and responsiveness of the emulsions, we varied the concentration of PEI over the range of 0.1 to 2 wt%. At concentrations of PEI below 0.5 wt%, the capsule still degraded in the presence of 0.5 wt% Capstone FS-30 surfactant. At concentrations of PEI above 0.5 wt%, the capsule remained intact in the presence of surfactant, as indicated by fluorescence microscopy (**Figure 2b**), and even remained stable under addition of a calcium ion chelator, ethylenediaminetetraacetic acid. Covalently crosslinked calcium alginate capsules provided droplet stability with no noticeable change in dispersity for at least three months in reverse osmosis-purified water, which was the longest time period over which we observed (**Supporting Information Figure S1**). Although the covalently crosslinked capsules were more stable than the ionically crosslinked capsules, droplets still only reconfigured between F/H/W and Janus morphologies upon addition of Capstone FS-30 (concentrations up to 2 wt%) for all concentrations of PEI crosslinker tested (0.1 to 2 wt%) (**Figure 2b**).

While covalent crosslinking enhanced the stability of the alginate capsules, the droplets were still somewhat limited in their range of accessible morphologies presumably due to the surface activity of the alginate at the oil-water interface and contributions from the mechanical deformation and surface stress of the capsule at the oil-water interfaces.[37] In order to expand the range of accessible droplet morphologies, and in particular achieve a H/F/W morphology, we hypothesized that we needed to facilitate creation of hydrogel-perfluorooctane interfacial area by reducing the interfacial energy at the PFO-

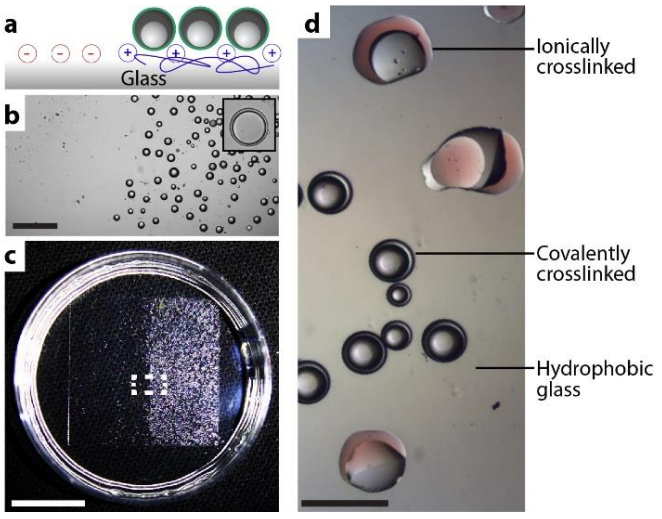

Figure 4. The hydrogel capsule enables patterning and enhanced stability of droplets on chemically treated glass surfaces. a) Illustration depicting the adherence of F/H/W droplets with negatively charged ionically crosslinked capsules to glass coated with positively charged PEI (blue lines). b) Transmission optical micrograph of droplets selectively adhering to patterned PEI-coated glass corresponding to the schematic in (a). Droplets adhere to the substrate on the right where the glass is coated with PEI and droplets do not adhere on the left, where the glass is untreated. Scale, 500 µm. Inset shows a close up of an individual F/H/W double emulsion droplet. c) A macroscopic photograph of the glass coverslip from (b) in a petri dish of water showing the selective droplet patterning. The dotted rectangle corresponds to the region in (b). Scale, 1 cm. d) F/H/W double emulsion droplets with ionically crosslinked capsules (dyed red with Sudan Red) and covalently crosslinked capsules (no dye) on a hydrophobic glass surface modified with n-octyltriethoxysilane. Only the covalently crosslinked capsules provide sufficient stability to prevent wetting of the oil on the hydrophobic substrate. Scale, 200 µm.

hydrogel interface. We added an ionic, fluorocarbon-soluble fluorosurfactant, Capstone FS-66, to the PFO phase and encapsulated the biphasic oil droplets in a covalently-crosslinked alginate capsule (**Figure 3a**). The effect of Capstone FS-66 concentration on biphasic droplet morphology is shown in **Figure 3b**, wherein our range of achievable droplet morphologies is greatly expanded even without the addition of surfactant to the continuous aqueous phase. Subsequent addition of aqueous surfactants, however, still allowed further tuning of the droplet morphology (**Figure 3c**); addition of Triton X-100 to a Janus droplet triggered a transition to F/H/W while addition of Capstone FS-30 generated a H/F/W morphology, thereby facilitating the full H/F/W to F/H/W droplet reconfiguration within the stable, covalently-crosslinked alginate capsule.

Since the capsules provide a polymer-water interface that is separated from the oil-hydrogel interface, we wondered if the polymer shell would thereby offer opportunities for patterning of the droplets on a range of substrates in which surfactant-stabilized droplets alone would not be suitable. In a simple demonstration, we allowed droplets to settle onto a glass substrate that was half-coated with PEI; after waiting 15 minutes we rinsed the substrate and found that droplets adhered well only to the positively charged, PEI-coated regions and were easily washed away from the negatively charged clean glass (**Figure 4a-c**). Upon allowing the encapsulated droplets to settle onto hydrophobic, n-octyltriethoxysilane-modified glass (water contact angle, 60°), we also found that the covalently crosslinked capsules prevented wetting of the oil droplets onto the substrate (**Figure 2c**), whereas droplets stabilized by ionically crosslinked capsules, which are comparatively more weakly bonded, immediately wetted upon settling to the hydrophobic glass surface (**Supporting Information Video S2**). Hydrogel encapsulation may therefore enable these responsive droplets to be applied in conditions that would otherwise trigger droplet destabilization and provide opportunities for selective surface functionalization or patterning of the capsule independently of the droplet composition and sensitivity.

Conclusions

Addressing the challenges posed by inherent emulsion instability is important for facilitating the use of responsive complex droplets in applications ranging from tunable optics to sensors.[9–12] Here, we have demonstrated a simple methodology by which to encapsulate biphasic oil droplets in a calcium alginate hydrogel in order to enhance droplet stability and retain reconfigurability. The ionically crosslinked calcium alginate capsules increase the droplet longevity and preserve monodispersity of droplets stored in water in comparison to traditional molecular surfactants. Further modification of the alginate capsule by covalent crosslinking using PEI prevents degradation of the capsule in the presence of surfactant as well as prevents droplet destabilization on hydrophobic surfaces. Droplets reconfigure between double emulsion and Janus configurations when exposed to aqueous surfactants, and oil-soluble surfactants can be added to the dispersed droplet phase to tune droplet morphology within the capsule. The stabilization of droplets with tailored composition and size is of vital importance to controlling emulsion properties and behavior, and hydrogel capsules provide a route to achieving such enhanced stability while preserving the droplets' dynamic characteristics.

Conflicts of interest

The authors declare no competing financial or commercial conflict of interest.

Acknowledgements

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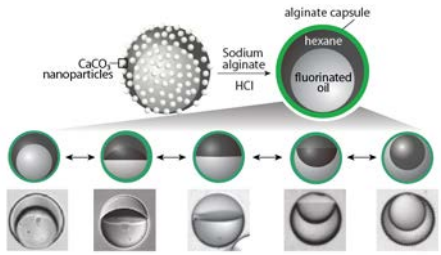

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