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Pickering emulsion engineering: Fabrication of materials with multiple cavities

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Materials with millimeter to centimeter dimensions containing multiple cavities were fabricated based on Pickering emulsion engineering: The Pickering emulsion was solidified by continuous phase gelling. The shape and cavity size can be controlled by the choice of solidification method and the droplet size of the emulsion.

Liquid emulsions consist of mixtures of immiscible liquids in which one liquid is finely dispersed within another continuous phase. These emulsions are widely used in food, cosmetics, pharmaceuticals, and other industries, and are useful templates for complex materials synthesis [1]. Typical conventional emulsions are stabilized using molecular-level surfactants, including small molecule surfactants, block copolymers, and branch polymers, and generally are not thermodynamically stable because the dispersion has a tendency to separate over time. To investigate the potential application of these emulsions, Weaver *et al.* [2] proposed a concept called "emulsion engineering," which involves emulsion droplets that are kinetically trapped to assemble in specific geometries *via* hydrogen-bonding interactions among droplets stabilized with amphiphilic branched copolymer surfactants based on methacrylic acid and poly(ethyleneglycol) methacrylate with hydrophobic dodecane chain ends.

The emulsifying properties of fine solid particles have been recognized for more than a century [3]. Particles attached to the oil-water interface can stabilize emulsions, producing Pickering emulsions. Particulate emulsifiers could offer more robust and reproducible formulations compared to conventional molecular-level surfactants [4]. Furthermore, Pickering emulsion stabilized solely with solid particles could show lower toxicity, because the molecular surfactants which are suspected of causing allergy-like reactions and carcinogenicity are not used [5].

Pickering emulsions have found use in a variety of functional materials such as capsules [6], Janus particles [7], composite particles [8], and emulsion assemblies [9-11]. Ngai and coworkers showed that oil droplets stabilized with poly(*N*-isopropylacrylamide) (PNIPAM) microgels carrying carboxyl groups could be trapped in a hydrogel-like continuous aqueous phase to form an emulsion droplet assembly [9]. Destribats *et al.*
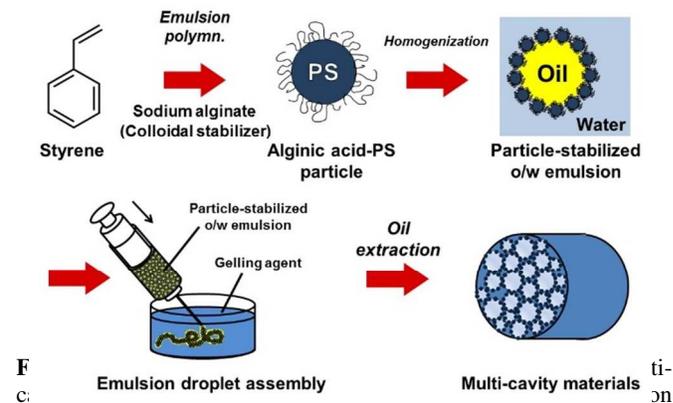
Figure 1. ...ti-cavity...on engineering)

reported that adhesion among oil droplets stabilized with PNIPAM microgel through bridging led to emulsion assembly [10]. Bon *et al.* succeeded in fabricating an emulsion assembly from PNIPAM nanogel-stabilized emulsion *via* non-covalent crosslinking through 2-ureido-4[1*H*] pyrimidinone quadruple hydrogen bonding [11]. These Pickering emulsion-based assemblies require tailor-made water-swollen soft microgel-based particulate emulsifiers, which can involve expensive chemicals and multi-step syntheses.
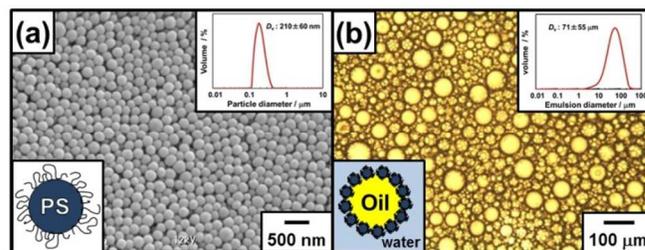

Figure 2. (a) SEM images of alginic acid-PS particles and (b) optical microscope image of alginic acid-PS particle-stabilized methyl myristate-in-water emulsion. Insets show laser diffraction particle/droplet size distribution measurement results.

This communication describes a facile and versatile fabrication method for emulsion assemblies and multi-cavity materials based on Pickering emulsion engineering (Figure 1). This method allows a wide range of solid particles (including microgels) to be utilized for the fabrication of emulsion assemblies because the gelling reaction (*e.g.*, crosslinking between sodium alginate and a multivalent ion [12] and the gelling reaction of poly(vinyl alcohol) [13]) occur in the continuous aqueous phase of oil-in-water Pickering emulsions. In addition, multi-cavity materials can be fabricated simply by extraction of the liquid phases, and the material geometry can be controlled on a millimeter and centimeter scale. The synthesis of emulsion assemblies and multi-cavity materials on an industrial scale can be based on inexpensive chemicals compared to protocols described previously [9-11].

Colloidally stable alginic acid-stabilized polystyrene (PS) latex particles were obtained after 24 hours of emulsion polymerization using an ammonium persulfate (APS) initiator in the presence of alginate Na at 70°C (Figure 2 and ESI). Optical microscopy and laser diffraction particle size analysis confirmed a colloidally stable aqueous dispersion of latex particles. An APS also can act as a chemical oxidant [14] to abstract hydrogen atoms from the alginic acid backbone, and polymerization initiated by the polymer radicals produces graft polymers, which act as a colloidal stabilizer. Laser diffraction particle size analysis gave a volume-average diameter (D_v) for the PS particles of 210±60 nm. A typical scanning electron microscopy (SEM) image of the PS latex is shown in Figure 2a, which gave a number-average diameter (D_n) of 200±26 nm (D_w/D_n, 1.05). Oxygen, carbon, and sodium were detected both for the alginate Na homopolymer and alginic acid-PS particles in X-ray photoelectron spectroscopy (XPS) spectra. Given that the XPS sampling depth is typically only 2-5 nm, these observations provide good evidence that the grafted alginic acid stabilizer is present at the surface of the alginic acid-PS latex particles, as expected. Moreover, intensity of the O1s signal obtained for the alginic acid-PS particles can be compared to that of the alginate Na homopolymer to provide an estimate of approximately 4.1% surface coverage for alginic acid stabilizer chains on the particle surface. Comparison of the oxygen content of the alginic acid-PS latex to that of the alginate Na homopolymer (O = 43.04%) determined by elemental microanalysis studies indicated an alginic acid stabilizer content of approximately 1.29%. These XPS and elemental analysis results confirmed that the alginic acid stabilizer is located at the surface of the PS latex particles.

These alginic acid-PS particles worked as an effective particulate emulsifier for methyl myristate. After homogenization of aqueous 1% latex dispersion (5.0 mL) and methyl myristate (5.0 mL) at 20,000 rpm for 2 min, emulsions which were stable for longer than 24 h were obtained. Methyl myristate was selected because it is inexpensive, relatively nonvolatile, and soluble in a wide range of solvents, which allows easy extraction from emulsion assembly. Electrical conductivity and droplet test results indicated that an oil-in-water emulsion was obtained. A typical optical microscopic image of the emulsion is shown in Figure 2b. The methyl myristate-in-water emulsion droplets were spherical and fairly polydisperse, with diameters ranging from 16 to 126 μm (D_n, 29±29 μm). The D_v value was estimated to be 53±37 μm by laser diffraction particle size distribution analyzer, which agreed reasonably well with the value obtained by optical microscopy. After still standing for 24 h, creaming occurred a little and change of the D_v value of emulsion droplets was
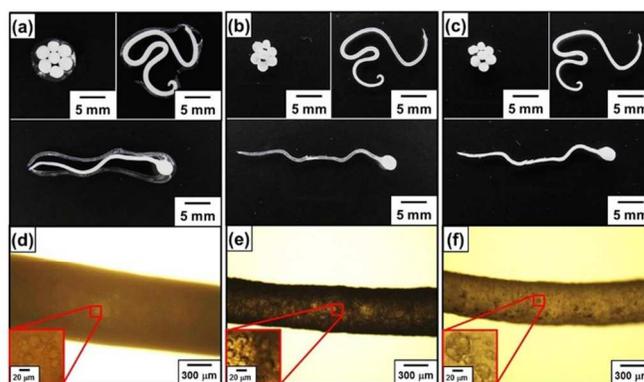
Figure 3. Alginic acid-PS particle-stabilized methyl myristate-in-water emulsion droplet assembly: Digital camera images (a-c) and optical microscope images (d-f) of emulsion droplet assembly (a, d) before and (b, e) after water evaporation, and (c, f) after oil extraction from water evaporated emulsion assembly.

negligible. In principle, the fraction of latex particles adsorbed at the oil/water interface can be readily estimated assuming formation of a monolayer of adsorbed latex. The percentage of alginic acid-PS particles effectively attached on the oil-water interface based on the total amount of alginic acid-PS particles added was calculated using a following simple equation [15] (see also ESI).

$$\% \ PS \ particles = \pi \ \frac{R_{oil}{}^2 \ N_{oil}}{N_{part} \ R_{part}{}^2} \times 100 \ \%$$

where

$$N_{oil} = \frac{3 \ V_{oil}}{4 \ \pi \ R_{oil}{}^3}$$

However, such calculations require some assumptions to be made regarding interfacial packing efficiency, and the relatively polydisperse nature of the droplets can introduce errors. We assume 2D square lateral packing, uniform alginic acid-PS particles and droplet sizes and alginic acid-PS particle dimensions negligible as compared with those of oil droplets. We also assume that there are no alginic acid-PS particles present in the oil phase, because the energy barrier for the alginic acid-PS to enter methyl myristate oil phase is too high. R_{part} and R_{oil} are the radii of the PS particles and oil droplets (R_{oil} values used here were the volume mean radius determined by the laser diffraction method); N_{part} and N_{oil} are the numbers of PS particles and oil droplets, V_{oil} is the volume of oil. Within these constraints, the latex adsorption efficiencies were estimated to be 44%.

Emulsion assembly can be fabricated utilizing a gelling reaction between alginate Na and Ca^{2+} ion (Figure 3). The methyl myristate-in-water Pickering emulsion stabilized with alginic acid-PS particles (2 mL) was mixed with an aqueous solution of alginate Na (1 wt%, 2 mL). The emulsion containing additional free alginate Na was successively dripped into an aqueous $CaCl_2$ solution above the planar air-water interface using a micropipette. Near-spherical emulsion assemblies with narrow size distributions were readily obtained (Figure 3) when the height was ≤ 30 cm and $CaCl_2$ concentration was ≥ 100 mM. Spheres were produced as the liquid emulsion minimized its surface area and the rapid gelling reaction rate ensured that the structures were trapped in these confinement geometries [16]. Sphere diameters were controlled by the volume of emulsion dripped into the $CaCl_2$ solution. Snowman-shaped
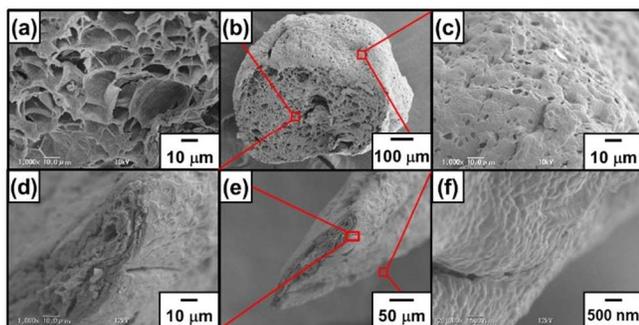
Figure 4. SEM images of (a-c) multi-cavity material fabricated from alginic acid-PS particle-stabilized methyl myristate-in-water emulsion droplet assembly and (d-f) dense material fabricated from sodium alginate-stabilized methyl oleate-in-water emulsion droplet assembly. Figs. 4a, c and Figs. 4d, f are magnified images of Fig. 4b and Fig. 4e, respectively.

emulsion assemblies were obtained using $CaCl_2$ solutions with concentrations < 50 mM, due to a slow gelling reaction rate and formation of a deformable soft gel skin on the surface of the emulsion assemblies (see ESI). Fibrous emulsion assemblies also can be produced by extruding the emulsion from a needle below the surface of the $CaCl_2$ solution (Figure 3). Fiber diameter could be controlled by varying needle diameter, and fiber length was limited only by the volume of emulsion that could be dispensed in a continuous fashion and on the concentration of Ca^{2+}; fiber length could be increased (in principle without limit) using continuous injection methods and continuous addition of $CaCl_2$. By combining the two methods mentioned above, tadpole-shaped emulsion assemblies were fabricated (Figure 3). Investigations also clarified that Al^{3+}, Ba^{2+}, and Sr^{2+} ions can be used to form gels. Emulsion droplets with a diameter comparable to the original droplets were observed within the assemblies using optical microscopy, which indicates that droplets were trapped without demulsification. In the absence of additional free alginate Na in the continuous aqueous phase of the emulsion, oil droplets simply dispersed into the aqueous $CaCl_2$ solution. Steric and charge stabilization effects of alginic acid-PS particles adsorbed on a droplet surface prevent the close proximity of oil droplets that allowed inter-crosslinking with Ca^{2+} ions.

Multi-cavity materials were fabricated by evaporation of water followed by extraction of the oil phase from the emulsion assemblies (Figures 3d-f and 4). Extraction of methyl myristate using acetone from the emulsion assembly resulted in shrinkage of the diameter (approximately 50%), while maintaining the shape of the assembly. Optical microscopic studies confirmed the presence of cavities in the materials. Detailed analysis of the inner morphology using SEM confirmed that this material possessed a multi-cavity structure. The number-average cavity size was 25±15 µm, which was slightly smaller than that of the original emulsion droplets (29 µm). Cavity diameter could be controlled by selecting Pickering emulsions with different diameters. A clear trend of increasing droplet size at lower homogenization rate was found: 53±37 µm at 20000 rpm, 76±48 µm at 15000 rpm, and 109±47 µm at 10000 rpm. Multi-cavity materials with a cavity size reflecting the oil droplet size were successfully fabricated (25±15 µm, 30±15 µm, and 34±14 µm). A control experiment using an emulsion assembly fabricated with alginate Na-stabilized oil-in-water emulsion confirmed that the assembly could not maintain its 3-dimensional shape and became flat after evaporation of water, followed by extraction of the oil phase (Figure 4d-f). Oil droplets stabilized with alginate Na seemed to coalesce during evaporation of water within the assembly before extraction of oil phase, which indicates destruction of framework of multi-cavity

structure. These results indicates that utilization of Pickering emulsion rather than surfactant-stabilized emulsion is crucial for retaining the 3-dimensional multi-cavity structure after removal of oil and water.

Finally, emulsion assembly using other gelling reactions was investigated (see ESI). The methyl myristate-in-water Pickering emulsion stabilized with alginic acid-PS particles (2 mL; D_v, 58±19 µm) was mixed with an aqueous solution (2 mL) of $FeCl_3 \cdot 6H_2O$ (232 mg), $FeCl_2 \cdot 4H_2O$ (86 mg), and poly(vinyl alcohol) (PVA) (0.2 g). Addition of the o/w Pickering emulsion into alkaline (*e.g.*, ammonia, NaOH, or KOH) solution (13.8 mol/L), allowed fabrication of an emulsion assembly with superparamagnetic properties based on the simultaneous formation of magnetic iron oxide nanoparticles and three-dimensional crosslinking of PVA chains. The iron oxide nanoparticles can act as cross-linkers to gelate PVA due to the presence of strong hydrogen bonding interactions between the nanoparticles and the hydroxyl groups of the PVA chains. The gelling reaction proceeded rapidly enough to produce emulsion assemblies, and the geometry of the emulsion assembly could be controlled easily by selection of the mixing method, similar to the gelling reaction using alginate Na. The emulsion assemblies could be collected easily using a 533-mT bar magnet and could be released by removing the magnet. Multi-cavity materials with a cavity size reflecting oil droplet size also could be fabricated successfully: a number-averaged cavity size of 41±20 µm.

Conclusions

In this study, the development of a facile and versatile synthetic route for millimeter- to centimeter-sized emulsion assemblies and multi-cavity materials is demonstrated. This method can be applied to wide range of solid particles, such as silica and metals, which cannot be attained using methods previously reported [9-11]. This synthetic route has the advantages of allowing the gelling reaction to occur in aqueous media and requiring no special apparatus. Therefore, scaling up production to an industrial level should be more easily accommodated than that provided by a multi-pot synthetic route. Furthermore, the method developed in this study has higher degree of freedom for design of multi-cavity material shapes comparing to other existing methods, such as Pickering high internal phase emulsion method [17] and Pickering emulsion solvent evaporation method [18]. Potential applications for these multi-cavity materials include use as sensors, microreactors and drug delivery carriers [19].

Notes and references
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assembly and magnet-responsive emulsion assembly]. See DOI: 10.1039/c000000x/

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