

Supplementary Material

1. Materials and Methods

(a) *Water droplets in decalin coated with PMMA particles:* Poly(methyl methacrylate) (PMMA) colloidal particles were suspended in decahydronaphthalene (decalin). In various samples, particles ranged in size from 0.5 to 1.5 μm diameter and were sterically stabilized with poly(hydroxyl stearic acid). Some particles were dyed with rhodamine (1) for ease of observation, but this had no effect on the final results. Typical particle volume fractions were < 0.01 . An aqueous solution was added to the decalin solution either in a single droplet using a micropipette and micromanipulator or in multiple droplets by adding water and shaking or vortexing. With gentle shaking, spherical aqueous droplets 1-1000 μm in diameter were densely covered in less than approximately one min.

Local crystalline order of the PMMA particles was repeatedly observed in droplets coated with shaking (as in Fig 2 of the main text). A close-packed monolayer was formed, with only occasional, isolated particles in a second layer.

For droplets that were injected with the micromanipulator, coverage was typically much lower, possibly owing to sedimentation of the particles before sufficient time had elapsed for particles to diffuse to the interface. In these sparsely-coated droplets, the particles formed a filamentous two-dimensional gel on the surface, as shown in Fig. S1 (2).

To lock the PMMA beads together and form a rigid shell, we typically first swelled the particles to enhance their overlap by suspending the coated droplets in 65% decalin with 35% chlorobenzene. We then destabilized the steric layer by suspension of the droplets in a solution of 50% toluene and 50% decalin. Droplets were then washed in decalin. Inspection using an optical microscope revealed many non-spherical capsules, evidence of an elastic coating that can withstand surface tension, which would otherwise tend to make the droplets spherical.

To attempt transfer of particle-coated water droplets into a continuous phase of water, 1-5 mL of the above suspension was placed atop a few mL of water in a test tube and centrifuged (up to 9000 g). Intact colloidosomes were not recovered in the water subphase, possibly because the PMMA particles are excessively hydrophobic and tended to collapse at the decalin-water interface rather than passing through. As evidence of the success of locking particle together, we regularly found large elastic fragments of the shells -- two-dimensional arrays of PMMA particles -- in the water (Fig. S2). Fragments were observed in a range of sizes up to of order 100×100 particles.

(b) *Water droplets in various oils coated with polystyrene particles:* Commercial polystyrene (PS) particles, cross-linked with divinyl benzene, were suspended in toluene, silicon oil, vegetable oil, octanol, or mixtures thereof. Aqueous droplets in various oil phases were obtained by addition of water with shaking or vortexing. Close-packed coverage of the droplets was readily obtained. Local crystalline order was observed, as

with the PMMA particles. In most cases, the PS particles diffused laterally on the interface despite the dense packing.

To lock the particles together on the capsule, the polycation, poly-L-lysine, was added to the starting aqueous phase (1 mg/mL, 150-300 kD). With addition of polycation, no lateral motion of adsorbed particles was observed. In vigorously shaken samples, non-spherical droplets were regularly observed, demonstrating the formation of elastic shells. Separate observations with fluorescent-tagged poly-L-lysine indicated that it adsorbs onto the colloidal particles. We infer that the polycation bridges between neighboring colloidal spheres.

In one example of transferring capsules into water, poly-L-lysine/water droplets were formed in 90%toluene/10% octanol containing 1.3- μm -dia PS particles. Capsules were then rinsed by transfer to octanol. Non-ionic surfactant Tween 20 (10 mg/mL) was then added to the octanol to reduce the oil-water surface tension; the coated droplets were not affected by this addition. 1-5 mL of this suspension was placed atop water in a test tube. Centrifugation at up to 9300 g resulted in transferring of order 1000 capsules into the water subphase.

Transferred capsules are semi-permeable: subsequent measurements indicated that these capsules are permeable to solvent and dye molecules and to small colloidal spheres, but not to large colloidal spheres. The size cutoff is consistent with the size of the pores. The permeability to dye was verified in a variety of ways by encapsulating dye and verifying its release. Permeability to small colloidal particles was verified as discussed in the main text.

(c) *Oil droplets in water coated with polystyrene (PS) spheres:* Silicon oil, vegetable oil, toluene or mixtures thereof were added to an aqueous suspension of commercial PS spheres and vortexed to obtain an emulsion of particle-coated oil droplets. As above, droplets were covered with a close-packed monolayer of colloidal spheres with local crystalline order. Particles were stationary at the interface, probably spontaneously locked together by van der Waals forces. No further chemical steps were taken to lock the beads together.

Sintering (heating) the coated droplets in solution led to controlled coalescence of the particles. As an example, PS particles of diameter 0.9 μm were suspended in 50% vegetable oil/50% toluene. To attain the glass transition temperature, $T_g \approx 100^\circ\text{C}$ of the PS, we formed droplets of a 50% water/50% glycerol solution. Heating the capsule suspension in an oven at 105°C for 0 to 120 min was followed by rinsing in ethanol to remove the interfaces, then drying to remove the solvent and prepare for electron microscopy. The process led to very tough elastic shells with particles connected by necks ranging in size from zero to 150 nm (5 min; see Fig 3 in main text). After longer times, pores of a few nm remain (20 min); at still longer times, pores are closed (120 min). Partially sintered capsules withstood the stresses of drying, whereas unsintered capsules collapsed. Sintering offers a flexible method for sealing the particles; instead of adding glycerol, it should be possible to use a pressurized vessel to attain the required temperature. Alternately, particles with lower T_g could be used to form colloidosomes.

Capsules prepared by sintering were also permeable to solvent, dye molecules and small colloidal spheres, but not permeable to larger colloidal spheres. The size cutoff is consistent with the pore size.

2. Supporting Figures:

CAPTIONS:

Fig. S1: Optical micrograph of a mm-size water droplet in decalin, coated with 1.5- μm -dia PMMA particles. The particles have formed a gel with a highly porous structure at the interface.

Fig. S2: Optical micrograph of an elastic sheet of 0.7- μm -dia PMMA spheres in water. The sheet was formed around a water droplet in decalin and then transferred to water. Scale bar represents 10 μm .

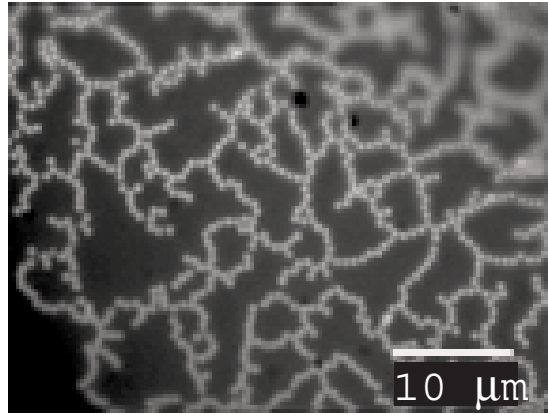


Fig S1, Dinsmore *et al.*

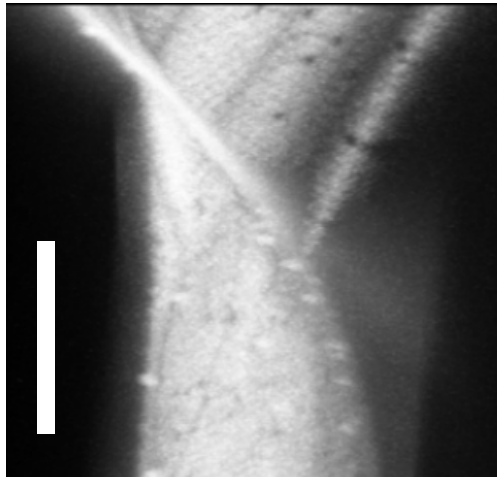


Fig S2, Dinsmore *et al.*

3. References:

1. A. D. Dinsmore, E. R. Weeks, V. Prasad, A. C. Levitt, D. A. Weitz, *Appl. Opt.* **40**, 4152 (2001).
2. M. G. Nikolaidis, Diplomarbeit, Technische Universität München (2001).