Large-scale synthesis of colloidal bowl-shaped particles

Kazem V. Edmond, Tess W. P. Jacobson, Joon Suk Oh, Gi-Ra Yi, Andrew D. Hollingsworth, Stefano Sacanna, David J. Pine

Detailed protocol
Yield: approximately 4 g particles

Materials

- 1L-capacity centrifuge with 50 mL conical vials for cleaning and separation of particles

- 1L spinner flask, shown on right

- Overhead stirrer with shaft and impeller

- Hot plate, either with attached digital thermocouple or separate thermometer

- Syringe pump

- 100 mL syringe

- Stainless steel 18 gauge hypodermic needle

- Plastic tube with HPLC bottle cap (e.g., ChemGlass #CG-1158) with fittings to attach tubing from syringe to needle, as shown on right

Chemicals

- 1.1 L of ~0.4% v/v ~500 nm diameter polystyrene (PS) microspheres suspended in deionized water. Particles were synthesized and prepared in-house.

- 5 mL of ammonium hydroxide solution (~28 wt.% NH3, Sigma-Aldrich #338818). Typically add 4 µL per 1 mL of solution for desired pH.

- 50 mL of TPM oil, 3-(trimethoxysilyl)propyl methacrylate (Sigma-Aldrich #M6514)

- 30 mL of DCM, dichloromethane (Sigma-Aldrich #270997)

- 50 mL of 5 wt% solution of Pluronic® F-108 in deionized water (Sigma-Aldrich #542342)
- 50 mL of 20 wt% polyvinylpyrrolidone, 29k MW (Sigma-Aldrich 234257) in ethanol
- 1 L of >75% v/v ethanol solution
- 1 L of deionized water

Synthesis protocol

In a fume hood, charge the spinner flask with a 1.1 L suspension of PS microspheres. Stir with impeller at ~100 rpm. Add 5 mL of ammonium hydroxide solution, adjusting pH to ~10. Using a syringe, inject TPM oil in 5 mL increments every 10–15 minutes. Next, add 20 mL of DCM with a pipette. This amount of plasticizer will saturate the aqueous phase. Add an additional 10 mL of DCM: 5 mL at one hour, 5 mL at 2 hours. The PS particles will gradually deform into the desired bowl shape during this period. Continue stirring for 1 to 2 hours, until the PS particles have reached an equilibrium shape. Sample the reactor periodically to observe the particles using an optical microscope. Gradually heat the suspension to 50 °C using a hot plate. You will observe boiling as the DCM vaporizes from the aqueous phase. Continue stirring for 2 hours. If necessary, heating may be accelerated by adding 225 mL of boiling water to the reactor. Add 15 mL of 5 wt% F108 stabilizer solution to the reactor, turn off the hot plate and allow the suspension to cool to room temperature.

Particle cleaning protocol

Transfer the colloid to 50 mL conical centrifuge tubes. Spin down the particles at 3,000 rpm for 30 minutes. Decant the supernatant and resuspend particles by first adding 5 mL of 20 wt% PVP in ethanol solution to the particle pellet. Vortex and sonicate samples until particles are fully dispersed. Add 20 mL of ethanol solution and continue vortexing. Fill the remainder of vials with the ethanol solution, homogenize, and then centrifuge at 2,000 rpm for 2 hours. Monitor progress using an optical microscope. Repeat the process four times to remove TPM oil droplets while minimizing particle aggregation. Next, exchange the ethanol solution with deionized water by replacing the supernatant with 50% v/v solution of ethanol and 5 wt% F108 in deionized water. Centrifuge at 3,000 rpm for 2 hours. Replace supernatant with 5 wt% F108 solution in deionized water. Repeat the prior step at least once. Inspect particles using an optical microscope. The resulting particles will be 800–900 nm, depending on size of initial PS microspheres.

Particle polydispersity

Following the protocol described here, we have observed little to no increase in particle polydispersity than when producing smaller batches, as described in earlier work (S. Sacanna et al. *Nat. Comm.,* 2013, **4**, 1688, doi:10.1038/ncomms2694).

Particle fabrication via emulsion-templating may give rise to size and shape polydispersity primarily from 3 sources:

1. Polydispersity of the “seed” microspheres

2. Polydispersity of the “template” oil droplets

3. Coalescence during the deformation/templating stage, when the PS microspheres have been fully liquefied.

For the procedure described here, we produced 560 nm PS microspheres using the technique described in the text (see J. W. Goodwin et al., *Colloid and Polymer Science,* 1974, **252**, 464–471, 10.1007/BF01554752). We measured a polydispersity index (PDI) of 0.060, which is typical for this synthesis procedure, using a dynamic light-scattering device (Zetasizer, Malvern Instruments).

When sedimented in deionized water in a glass media jar, the microspheres were observed to exhibit Bragg scattering, indicative of a colloidal crystal, which requires a polydispersity of less than 6 to 12% (see W.N. Pusey, *J. Phys. France* (1987) **48**, 709–712, doi:10.1051/jphys:01987004805070900).

The TPM droplets, used for templating, are similarly monodisperse, typically with a PDI of ≤0.06 for the sizes used herein (see C. van der Wel et al. *Langmuir*, 2017, **33**, 8174–8180, doi:10.1021/acs.langmuir.7b01398). Note that the size distribution tends to narrow as the droplets grow.

We approximate the polydispersity of the fabricated particles by combining the polydispersity of both the seeds and oil droplets, without coalescence, which would yield a PDI of 0.12 to 0.18. We assume that this is the approximate PDI of all other fabricated particles shown in the text. Measuring polydispersity of the resulting particles’ shape or curvature could be done using image analysis techniques, but this lies beyond the scope of this work.

A scanning electron micrograph of the PS microspheres is shown in Fig. 2(a). The ~850 nm diameter bowl-shaped particles fabricated from these

microspheres is shown in Fig. 2(b).