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Large-scale synthesis of colloidal bowl-shaped particles

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Large-scale synthesis of colloidal bowl-shaped particles[†]Kazem V. Edmond,^{*a‡} Tess W. P. Jacobson,^{a§} Joon Suk Oh,^a Gi-Ra Yi,^b Andrew D. Hollingsworth,^a Stefano Sacanna,^c and David J. Pine^{a,d}Received Date
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We describe a general procedure for the large-scale fabrication of bowl-shaped colloidal particles using an emulsion templating technique. Following this method, single polymeric seed particles become located on individual oil drop surfaces. The polymer phase is subsequently plasticized using an appropriate solvent. In this critical step, the compliant seed is deformed by surface tension, with the droplet serving as a templating surface. Solvent evaporation freezes the desired particle shape and the oil is subsequently removed by alcohol dissolution. The resulting uniformly-shaped colloids were studied using scanning electron and optical microscopy. By adjusting the droplet size and the seed particle diameter, we demonstrate that the final particle shape can be controlled precisely, from shallow lenses to deep bowls. We also show that the colloid's uniformity and abundant quantity allowed the depletion-mediated assembly of flexible colloidal chains and clusters.

1 Introduction

Colloidal particles with unique non-spherical shapes are useful models of existing complex molecular materials and also serve as building blocks for the self-assembly of new meta-materials^{1–5}. Lens-shaped colloidal particles, for example, have recently gathered interest as building blocks of novel, self-assembling structures.^{6–9} Packings of these particles exhibit a rich variety of unique structural configurations and phase behaviors, recently observed in both simulations and experiments, and serve as models of ferroelectric fluids, exotic liquid crystals, and more^{3,10–13}. Alternatively, a bowl-shaped particle's concavity provides a “lock and key” engagement with an appropriately-sized sphere, mimicking the binding regions of an antibody and antigen, for example. This particular shape also enables the self-assembly of colloidal building blocks for meta-materials^{1,14–17}.

The practical application of such materials requires the fabrica-

tion of relatively large quantities of the constituent particles while maintaining precise control over their morphology. These requirements are generally at odds with one another. There are a number of ways to produce bowl-shaped particles: typically by emulsion templating^{7,15,18,19} or by performing chemical vapor deposition on solid particles^{9,20}. However, a means of scaling up production while retaining precise control over particle morphology is lacking.

In this communication we describe a means for the bulk fabrication of charge-stabilized, bowl-shaped colloidal particles. Our method is based on a general emulsion templating strategy recently described by Sacanna, et al.¹⁶. We demonstrate our method's scalability, through the production of several grams of monodisperse, micron-sized colloidal particles in liter-sized batches, and its flexibility, by fabricating particles with a range of curvatures and sizes. Despite the challenges of producing relatively large quantities of particles, we are able to precisely vary particle size and shape with ease. Our technique is also versatile in that it works with a variety of different materials. Additionally, we demonstrate the utility of these particles by assembling, via depletion interactions, colloidal chains and also reconfigurable colloidal clusters.

2 Synthesis overview

The synthesis of bowl-shaped colloidal particles involves four steps, described schematically in Fig. 1(a–d). First, aqueous dispersions of biphasic particles are prepared by heterogeneous nucleation of oil droplets in the presence of the solid polystyrene (PS) microspheres, or ‘seed’ particles. The uniformly-sized seed particles each collect an approximately equal volume of oil droplets wetting their surface. Upon droplet coalescence,

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† Electronic Supplementary Information (ESI) available: a time-series video of colloidal chains formed via depletion; a time-series video of cap-shaped particles diffusing across a droplet's surface; photographs of the reaction vessel. See DOI: 10.1039/cXsm00000x/

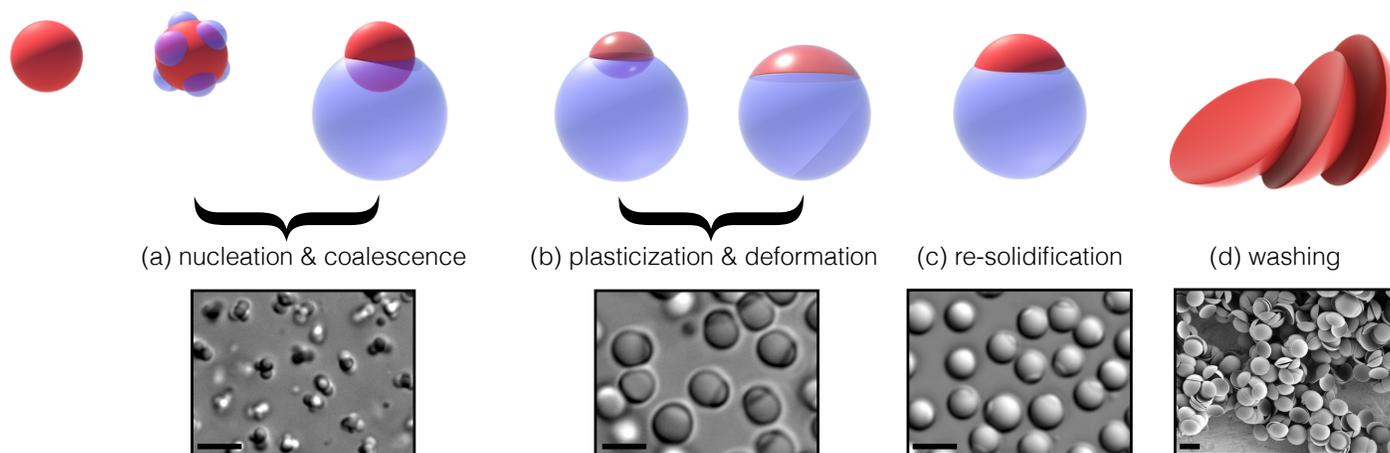


Fig. 1 Basic outline of particle fabrication, with cartoon schematics and corresponding micrographs of the changing particle morphology. Oil droplets (blue) are (a) nucleated and grown on polystyrene particles (red) to serve as a template, (b) an organic solvent is dispersed to plasticize and deform the particles across the droplet surface, (c) the solution is heated to evaporate the solvent, re-solidifying the particles, and then (d) the entire solution is transferred to an alcohol solution to dissolve and remove the TPM oil phase. Scale bars are $2\ \mu\text{m}$.

each seed will be attached to a single oil drop, as shown in Fig. 1(b). The oil phase consists of 3-(trimethoxysilyl)propyl methacrylate (TPM) oligomers that are generated *in situ* via a base-catalysed condensation reactions between hydrolyzed TPM molecules (hTPM). Next, the seed particles are reshaped with a solvent. The plasticized PS does not mix with the oil phase but is instead deformed by surface tension, conforming to the oil drop's shape, using it as a template. In the third step, we re-solidify the polymer particles by removing the solvent via evaporation. Finally, we remove the oil phase by transferring the colloid into alcohol, which dissolves the organosilicon droplets, leaving behind the solid, bowl-shaped PS particles. Using centrifugation, decantation and redispersion, we repeatedly clean the colloid in alcohol to completely remove residual TPM oil before transferring the particles to pure water. At this stage, we use depletants to assemble supracolloidal structures, for example, flexible chains or stacks of colloidal bowls. Alternatively, in the presence of appropriately-sized spherical particles or droplets, the bowls arrange themselves onto the particle surfaces forming reconfigurable colloidal clusters.

Herein, we describe the procedure in detail, building on the aforementioned work of Sacanna, et al.¹⁶ by exploring the routes necessary for scaling up particle production and for tailoring the particle size and shape as desired. We have used our technique to successfully produce monodisperse particles with batches as small as 1 mL in volume to as large as 1 L, using seed particle diameters ranging from 500 nm to 1,000 nm, with curvatures ranging from virtually flat to spherical shells.

3 Experimental

All materials were used as received. For the PS seed particles, we use either commercially available particles (Thermo Scientific) or synthesize them in-house using an established surfactant-free emulsion polymerization procedure²¹. Before use, we thoroughly clean the seed particles using deionized water to remove any surfactant: this important step prevents generation of secondary nu-

clei in the continuous phase, instead enabling heterogeneous nucleation of TPM droplets on the surfaces of the seed particle. The cleaning procedure involves either dialysis, or repeated sedimentation, decanting, and redispersion. The TPM oil (Sigma-Aldrich $\geq 98\%$) is aliquoted into amber glass septum vials upon receipt and stored under an inert gas to suppress hydrolysis reactions and prevent the premature formation of oligomeric species.

3.1 Heterogeneous nucleation

During this stage, monodisperse oil droplets are heterogeneously nucleated on the seed particle surfaces via a base-catalyzed hydrolysis and condensation of TPM. The oil droplets coalesce into a spherical shape to serve as a template for PS particle deformation, as indicated in Fig.1(b). The emulsification procedure, adapted from the method of Obey and Vincent²², is described in detail by Sacanna, et al.²³. Specific details of the hydrolysis and condensation reaction itself can be found in Ref.²⁴. Two significant challenges are (1) suppressing droplet polydispersity and (2) minimizing the occurrence of homogeneous nucleation, where so-called secondary droplet nuclei form in the continuous phase. The polydispersity of template drop *size* manifests as polydispersity in particle *curvature*, making nucleation and droplet growth the most important and most sensitive steps of the fabrication procedure.

Disparities in droplet growth rates, and ultimately their size distribution, arise mostly from concentration gradients of hydrolyzed TPM monomer and, to a lesser extent, pH gradients. Uniform and consistent stirring and careful control over the rate at which hydrolyzed TPM is added both improve the sample's quality. As a result, the reaction vessel's shape plays a role in how well the solution is stirred: tall narrow vials should be avoided in favor of broader vials or, ideally, round-bottom flasks. Whenever practical, especially for volumes greater than 100 mL, we prefer an overhead stirrer impeller versus a standard magnetic stir bar, as the shear forces of a stirrer across a vessel's bottom surface can result in droplet coalescence.

For a typical synthesis, in a round-bottom flask, we disperse monodisperse sulfonated PS microspheres in deionized water, producing a particle concentration of less than 0.5% (v/v). The solution's pH is increased to above 9—monitored using standard pH test strips—by adding a sufficient amount of ammonium hydroxide solution (28 wt.% NH_3 , Sigma-Aldrich), typically $4\ \mu\text{L}$ per 1 mL of solution. TPM oil is dispersed into the solution while gently stirring with an impeller at a rate of 100–200 rpm. The TPM monomers hydrolyze and undergo a base-catalysed condensation reaction, nucleating droplets on the surfaces of the seed particles, as described above. The nuclei's initial size is roughly tuned by adjusting the initial concentration of TPM oil and the amount of base^{22–24}. For more precise control, we grow the nuclei by incrementally adding hydrolyzed TPM monomer via pipette until the desired droplet size is achieved²³. Hydrolyzed monomer is typically prepared by hydrolyzing 5 mL of TPM in 100 mL of deionized water under vigorous stirring for 1–2 hours.

The nuclei grow as they coalesce into spherical drops, shown by the sequence in Fig. 1. Alternatively, coalescence can be induced by adding trace amounts of solvent such as toluene or dichloromethane (DCM). This procedure reduces the final droplet volume, thus controlling the template size. The small amount of solvent, absorbed by both the TPM nuclei and PS seed particles, significantly alters the surface tension at the oil-water-particle interface without deforming the seed particles. The choice of optimal solvent is discussed in the next section. The PS seeds sit at the droplets' oil-water interface due to their charge and wetting properties, as described in Ref.¹⁶. Droplet size is periodically monitored by observing a sub-sample in a rectangular glass capillary with an optical microscope.

As mentioned, the occurrence of secondary nucleation can be problematic during this stage. Although the desired primary particles can be separated by sedimentation, as demonstrated by Sacanna, et al.²³, avoiding secondary nucleation simplifies the procedure. In dealing with this matter, we have observed that the formation of secondary nuclei is tied to three interrelated process parameters: (1) seed particle volume fraction ϕ , (2) solution pH, and (3) the concentration of hydrolyzed TPM monomer. For example, a sufficient rate of droplet nucleation on seed particles requires a minimum solution pH of 9. By feeding monomer gradually, with thorough stirring, monomer concentration gradients are reduced, thereby suppressing homogeneous nucleation. Additionally, maintaining a relatively high seed concentration ensures that nuclei form on particle surfaces. The presence of secondary nuclei will, of course, consume TPM monomer, thus affecting template droplet size.

3.2 Scaling up to bulk synthesis

As noted in the prior section, in reactors much larger than 100 mL, concentration gradients of hydrolyzed TPM monomer become significant and increase the likelihood of secondary nucleation and droplet polydispersity. We avoid this potential pitfall by making a number of minor modifications to our standard procedure, accommodating larger reactor volumes to achieve greater particle yields, maintaining a predictable and consistent synthesis.

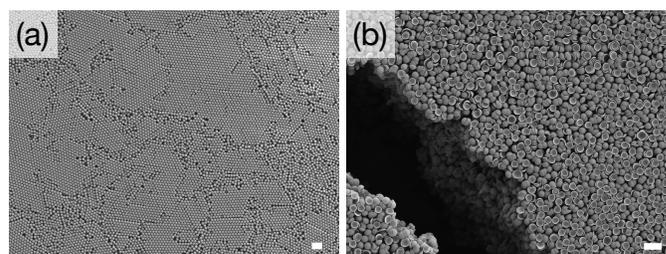


Fig. 2 Scaled up synthesis. Scanning electron micrographs showing 510 nm diameter polystyrene seed particles (a) used to produce 850 nm bowl-shaped particles (b) from a scaled-up synthesis. Horizontal distortions in (b) are due to imaging artifacts. Scale bars are $2\ \mu\text{m}$.

We begin by performing the initial heterogeneous nucleation procedure, until nuclei first begin to form, in a smaller more controlled volume, 50 mL to 100 mL, but at higher particle volume fraction, $\phi \sim 0.05$, before transferring to a larger reactor volume, $\sim 1\ \text{L}$ of deionized water in a 1 L spinner flask (Chemglass), reducing the volume fraction to the desired $\phi \sim 0.005$. Once in the larger vessel, shown in the ESI[†], we follow a scaled-up version of our standard procedure: stirring with an appropriately sized impeller; incrementally adding hydrolyzed TPM monomer via a syringe needle; and rapidly quenching the plasticization process by introducing boiling water to remove solvent if a heating mantle is not available. Following this procedure, we produced 5 g of 850 nm bowl-shaped particles, shown in Fig 2(b), using 510 nm seed particles, shown in Fig. 2(a), in a 1 L flat-bottomed spinner flask (Chemglass).

3.3 Deformation and solidification of the PS phase

The nucleated TPM droplets serve as sacrificial templates for re-shaping the PS particles, ultimately being dissolved and washed away. With droplets of the desired size attached to each particle, we plasticize them by dispersing solvent, under mild stirring, directly into the suspending medium. Once plasticized, the PS particles are stretched across the droplet due to surface tension, thus deforming them into the shape of bowls or “contact lenses”. A time-series of this process is shown in optical micrographs and SEM images in Fig. 1. Once the desired shape has been achieved, as visually confirmed by optical microscopy, the solution is heated in an open container, evaporating the solvent and freezing the particle shape. Our choice of solvent, either toluene or dichloromethane (DCM), depends on the desired rate of deformation and, more critically, the solution's total volume.

Toluene is an ideal solvent for fabricating smaller volumes of particles (less than 30 mL), where gradual particle deformation and re-solidification are desirable, due to its low water solubility (0.6% v/v, 20 °C) and high boiling point (111 °C). Its mass transfer characteristics impart precise control over the particle's form, which is desirable when intermediate particle morphologies are sought¹. Additionally, its high boiling point, coupled with its low solubility, ensures a slow rate of evaporation and therefore gradual re-solidification, resulting in smooth and consistent looking particles.

Alternatively, DCM is an optimal solvent when producing larger

quantities of particles due to its higher water solubility (1.5% v/v, 20 °C) and lower boiling point (39.6 °C). Timing becomes a critically important component of particle fabrication when fabricating larger volumes: significantly more particles must be plasticized, deformed, and re-solidified uniformly throughout an expansive volume. Prolonged stirring, when plasticizing and deforming particles, can induce droplet coalescence, even when using an impeller, while prolonged heating may partially polymerize the sacrificial droplet template. Dichloromethane's solubility is 25 times greater than toluene's, enabling rapid plasticization and deformation. Likewise, its low boiling point enables rapid re-solidification, while ensuring the solvent is thoroughly removed.

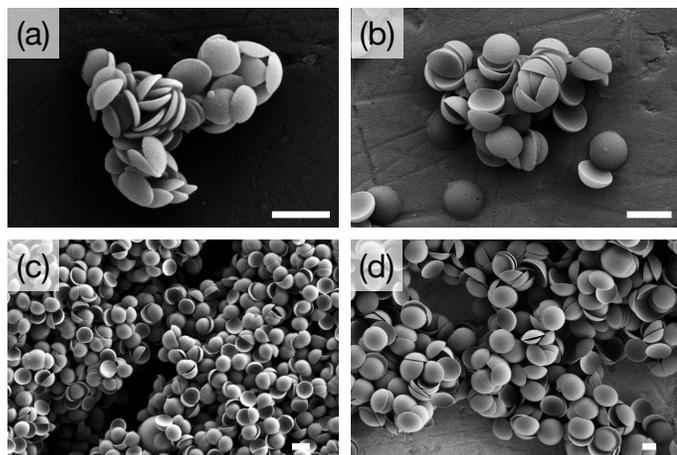


Fig. 3 Range of sizes. Particles made from (a) 320 nm, (b) 510 nm, (c) 630 nm, and (d) 1000 nm diameter PS seed particles. Scale bars are 1 μm .

One potential drawback of rapid solvent extraction is that the resulting particle surfaces may be left pocked or pitted and the particle edges may have a slightly rough appearance. Examples of this are shown in Fig. 3(b), a micrograph of bowl-shaped particles fabricated using DCM in a 1 L solution. For clarity, a higher resolution version of Fig. 3(b) is included in the ESI[†]. For comparison, see Fig. 4(b) representing particles made using toluene in a more typical ~ 20 mL volume. These surface imperfections have not discernibly influenced our experiments with assembly via the depletion interaction or with phases of densely packed particles. Smoother particles can still be made using DCM by carefully controlling evaporation rates using a rotary evaporator. Examples are shown in Figs. 4(c, d).

3.4 Adjusting size and concavity

The protocol presented here accommodates a range of particle sizes. Figure 3 contains scanning electron micrographs of particles fabricated from seeds of different sizes, (a) 510 nm, (b) 620 nm, and (c) 1000 nm in diameter. Additionally, the particle's concavity can be tuned simply by adjusting the size of the emulsion droplets. By adjusting the size ratio between seed particles and their droplet templates, and duration of the particle deformation, we have produced particles that exhibit a full range of curvatures. Micrographs from a scanning electron microscope (SEM) show examples of these in Fig. 4, from flat platelets to nearly

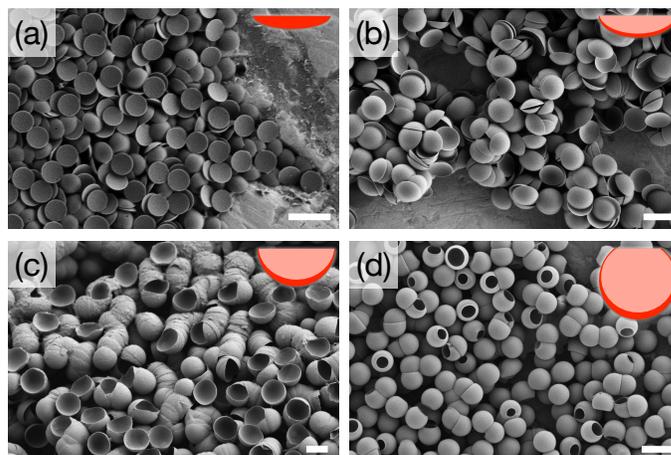


Fig. 4 Tunable concavity. Scanning electron micrographs showing examples of particles with a range of concavities: (a) spherical caps; (b) shallow bowls or contact lenses; (c) hemispherical bowls; (d) spherical urns. Scale bars are 2 μm .

spherical shells.

3.5 Cleaning

The TPM emulsion template is removed by transferring the colloid to ethanol. Sample vials are sedimented, decanted, and refilled with deionized water (half volume) to redisperse the particles. The remaining volume is slowly filled with a solution of ethanol (200 proof) and polyvinylpyrrolidone (PVP, 29,000 MW, 10% w/w) (Sigma-Aldrich), which serves as a good surfactant for PS in alcohol. We homogenize the sample with thorough stirring and gentle sonication, then continue to clean with ethanol at least three times, by repeated sedimentation and decantation. Once the entirety of the TPM has been removed, we transfer the particles to deionized water. Thorough removal of the TPM oil prevents particle flocculation in the aqueous phase.

3.6 Assembly of chains via depletion

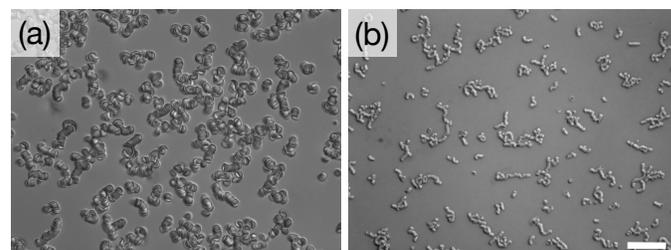


Fig. 5 Chains assembled via depletion. Optical micrographs showing diffusing chains of (a) 2000 nm and (b) 850 nm bowl-shaped particles. Videos of these time-series are provided in the ESI[†]. Scale bar is 10 μm .

We direct the self-assembly of flexible colloidal chains in an aqueous solution by inducing a depletion interaction between monodisperse bowl-shaped particles. We first disperse the particles in deionized water at a volume fraction of approximately $\phi = 0.005$. To the suspension, we added 10 mmol of sodium chloride (NaCl), 0.01 wt.% of tetramethylammonium hydroxide

(TMAH), and 0.05 wt.% Pluronic[®] F108. The role of each component is as follows: the presence of monovalent salt screens electrostatic repulsion between charged surfaces; the non-ionic surfactant F108 serves as a steric stabilizer for the particles; the quaternary ammonium salt increases the solution pH, increasing the cover-slip's surface charge, preventing the particles from adsorbing to the boundary's walls¹⁴. We use poly(ethylene oxide) (PEO), with a molecular weight of 600k, as a depletant. Using particles with a diameter of approximately $2\ \mu\text{m}$, we add 0.6 g/L of PEO. We observe the formation of chains after only a few minutes. Smaller particles, with a diameter of approximately 850 nm, require a stronger interaction with 0.7 g/L of PEO. Optical micrographs of assembled chains diffusing along the surface of a cover-slip are shown in Fig. 5, for (a) 850 nm and (b) $2\ \mu\text{m}$ particles. Videos are provided in the ESI[†]. Scanning electron micrographs of the particles are shown in Figs. 3(d) and 3(b), respectively.

3.7 Reconfigurable patchy particles

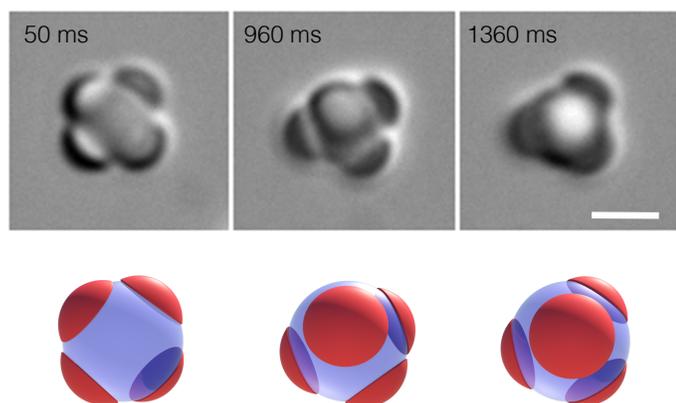


Fig. 6 Reconfigurable patches. First row: optical micrographs from a time-series of a $2\ \mu\text{m}$ droplet (blue) covered with 4 mobile bowl-shaped particles (red), attached via the depletion attraction. Second row: a cartoon schematic of the 3 different particle configurations. A video of the time-series is available in the ESI[†]. Scale bar is $2\ \mu\text{m}$.

To demonstrate the assembly of supracolloidal structures, we decorated spherical particles, solid microspheres or oil droplets, with multiple bowl-shaped particles using a depletion interaction. In a solution of NaCl (10 mmol), TMAH (0.01 wt.%), and F108 (0.05 wt.%), we dispersed both colloidal microspheres and bowl-shaped particles. Here, it is important for the colloidal bowls to have a curvature slightly less than that of the microspheres; an exact match in curvature will require an entropic loss greater than the gain provided by depletion¹⁴. With a sufficiently high number ratio of bowls to spheres, we observed the formation of particles with three or four mobile “patches”, as shown in Fig. 6 and the ESI[†].

4 Conclusions

Building on a general emulsion-templating technique first described by¹, we have described optimal procedures for easily fabricating bulk quantities of bowl-shaped colloidal particles. While

capable of producing grams of material, our procedure allows for precise control over particle curvature and size. We have demonstrated that the colloid's uniform size and curvature allows the formation of flexible colloidal chains and clusters via the depletion interaction. The particles are monodisperse, in both size and curvature, making them well-suited for the self-assembly of unique and interesting micro-structures, such as flexible colloidal chains and clusters, via the depletion interaction. These particles enable experiments focused on a new class of complex colloidal model systems and also studies focused on the self-assembly of novel meta-materials.

Conflicts of interest

There are no conflicts to declare.

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