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Synthesis and Assembly of Colloidal Particles with Sticky Dimples

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S *Supporting Information*

ABSTRACT: The preparation of anisotropic colloidal particles by a simple yet versatile temperature-controlled swelling process is described. The resulting polymeric particles feature a surface dimple, the size and shape of which were determined by the amount of oil captured in particles and the interfacial tension between the three phases: polystyrene (PS), decane, and the suspending medium. Following the removal of free or physically adsorbed surfactant from the swollen particles, hydrophobic dimples were produced upon evaporation of the oil phase. We demonstrate the spontaneous assembly of these 'dimpled particles' into dumbbell shapes or trimers through a site-selective hydrophobic interaction.

Colloidal particles have been widely used as building blocks for photonic architectures.[1] In most cases, isotropic spherical particles with a narrow size distribution were prepared by various methods and assembled into face-centered cubic lattices by increasing their number density in a controlled manner, or by repulsive interparticle forces.[2] Recently, spherical particles have been dispersed in UV-curable resins and then crystallized over a large area or volume by a spin-coating technique, emulsion droplet formation, or using a high-output optofluidic device.[3] These composite, controlled-shape photonic structures are of great importance in several immediate practical applications.[4] However, anisotropic particles are expected to yield better optical properties when assembled into new types of photonic structures such as diamond or pyrochlore lattices.[5] To date, only a few types of anisotropic particles have been prepared, some of which were assembled into periodic structures.[6] For example, cubic hematite particles were synthesized from condensed ferric hydroxide gel, followed by a silica deposition process. The particle cores were then dissolved, and the resulting colloidal silica cubes self-assembled using microgel particles as a depletant.[7] Colloidal clusters were prepared by an emulsion drying procedure and fractionated into dimers, trimers, tetramers, and higher-order clusters.[8] Dumbbell particles were prepared by seeded emulsion polymerization, which were recently assembled into crystalline structures using an external electric field.[9] Alternatively, spherical particles with patches or distinctive surfaces have been prepared by selective melting[10] or the deposition of metal[11] on substrates. Then, through their surface modifications, a colloidal Kagome lattice and other new colloidal structures were demonstrated.[11] More recently, dimpled particles have been prepared by polymerization-induced buckling instability, and their lock-and-key assembly was demonstrated by using depletion attraction.[12]

Here, we report that various dimpled particles can be prepared by temperature-controlled swelling of spherical polymeric particles with a hydrocarbon oil. Moreover, the resultant dimpled particles can spontaneously assemble into dumbbells or trimers by a site-selective attraction. By varying the swelling ratio during preparation, the phase-separated morphologies can be precisely controlled. After evaporation of the oil, various nonspherical particles are produced. The resulting shapes include dimpled particles with a flat surface, hemispheres, and asymmetric disks.

The process we describe below takes advantage of the fact that polymer particles can be swollen with an oil that is slightly soluble in a water/alcohol medium. The swelling is driven by the osmotic pressure difference between the continuous and dispersed phases.[13] Since the swelling process is relatively slow, all polymer particles imbibe an equal amount of oil to maintain equal chemical potential in all the particles. Similarly, particles can be grown via polymerization by swelling them with monomer.[6] In emulsion polymerization, however, the molecular weight of polymer comprising the particles is generally high and narrowly distributed, and the monomer swelling capacity is relatively low. Therefore, swelling agents such as 1-chlorodecane are used, with results in accord with Flory—Huggins theory. In the case of polymer particles prepared by dispersion polymerization, the molecular weight distribution is relatively broad. Consequently, a low molecular weight polymer, e.g., oligomers inside particles, can actually enhance the swelling capacity, serving as a swelling agent. In this work, we have prepared three different polystyrene particles by dispersion polymerization, which have relatively high polydispersity in molecular weight (PDI > 3.0) as shown in Figures S1 and S2 in the Supporting Information.

To produce dimpled particles, we first add decane oil to a water—ethanol mixture in which the PS particles are suspended. Next, the temperature is increased to 60 °C, at which point the decane becomes partially soluble in the alcoholic medium and slowly diffuses into the PS phase.[14] This process allows the oil to distribute itself uniformly within the particles until the chemical potential between the microspheres and medium

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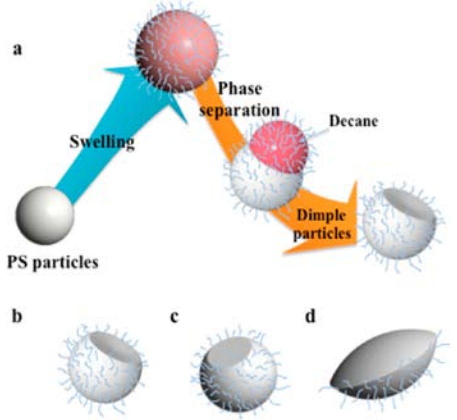
equilibrates.[15] When the temperature is decreased below a critical temperature, the decane becomes immiscible in the medium and trapped oil and polymers phase separates (Scheme 1a). To avoid coalescence between decane lobes or swollen PS particles, we add a polymeric stabilizer (triblock copolymers of polyethylene oxide and polypropylene oxide, Pluronic F108, BASF Corp.) into the suspension with decane.

Scheme 1. Schematic Illustrations of (a) Dimple Particle Formation by Swelling Microspheres with Decane and Internal Phase-Separation and Particles with (b) Crater-like, (c) Flat Dimple, and (d) Asymmetric Disk-like Particles



At 60 °C, the amount of decane relative to polymer inside the spheres is small. Removing the decane oil by centrifugation at 4500 rpm, 10 °C for 3 min produces dimpled particles, as shown in Figure 1a–b. Polymer particles swollen at 80 °C absorb more oil so that biphasic spheres of oil and PS are clearly visible (Figure 1c). Asymmetric flats or hemispheres are formed depending on the degree of swelling (Figure 1b,d)

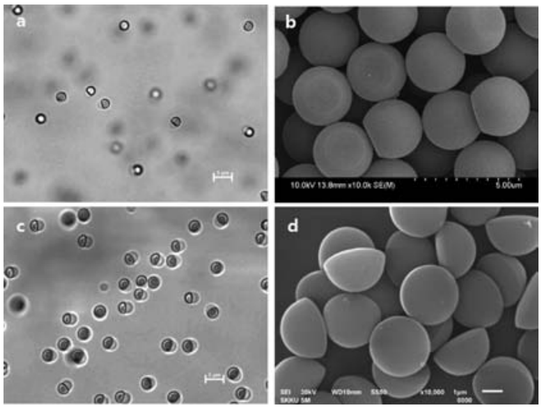


Figure 1. Morphological evolution of polystyrene particles (3 μm) with dimples depending on swelling temperature of (a–b) 60 °C and (c–d) 80 °C in the water–ethanol mixture. Scale bars are 5 μm in (a) and (c).

We illustrate our ability to control particle morphology by temperature-controlled swelling/deswelling using 3-μm PS particles in a water–ethanol mixture (40/60). The particle suspensions (0.49 wt %) are heated to 60 °C in the presence of 0.1 g of decane and held at 60 °C for 6 h. The samples are then cooled down to three different temperatures (10, 30, 40 °C) at a rate of 0.55 °C/min, which corresponds to path A, B, or C in Figure 2, respectively. As shown in the SEM images (Figure 3a–c), the dimple size decreases systematically from 2.4 to 1.6 μm with increasing holding temperature suggesting that kinetics dominate, with decane diffusing more readily from the particles at the higher temperatures and thus producing smaller dimples. The morphologies are maintained when the system is restored to room temperature, which is far below T_g for polystyrene.[14] During the cooling and aging process, the decane oil gradually phase separates from the PS, first forming small lobes and then merging into a single large one. As shown in Figure S3, when samples are quickly cooled to room temperature during the aging process, multiple lobes form and then merge. In the case of the methanol mixture, all lobes merge into a single lobe.

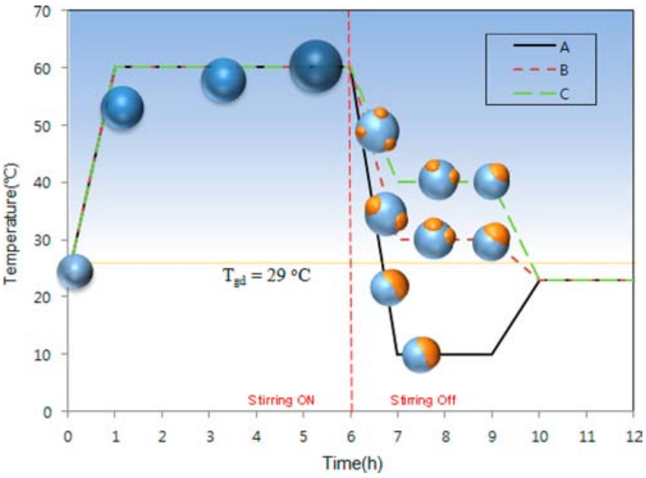


Figure 2. Morphological evolution of polystyrene particles (3 μm) with dimples in temperature-controlled swelling and deswelling process in the water–ethanol mixture. The heating–cooling path can be programmed (A–C) to obtain different particle morphologies.

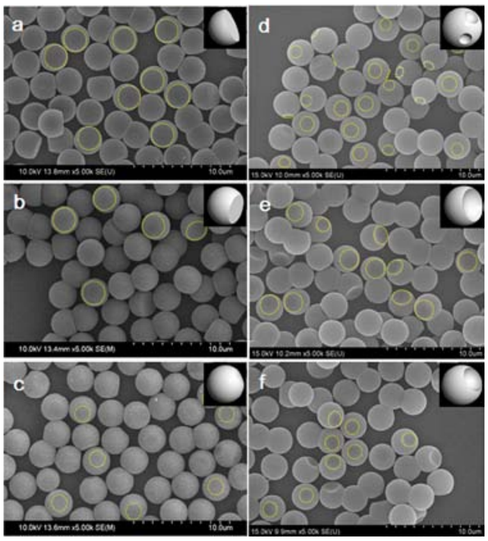


Figure 3. Programmed heating/cooling using different alcohols. SEM images of polystyrene particles (3 μm) with dimples which were swollen at 60 °C and cooled down to (a) 10, (b) 30, and (c) 40 °C in the water–ethanol mixture (40/60) and at 60 °C and cooled down to (d) 10, (e) 30, and (f) 40 °C in the water–methanol mixture (40/60). Cavities are indicated by yellow dotted line.

In another alcohol mixture, water−methanol (40/60), dimpled particles are also produced, as shown in Figure 3d−f. Dimple size is relatively smaller than that in the ethanol mixture because the solubility of decane is smaller at the same temperatures. As for the ethanol mixture, when the temperature is decreased and held at 30 and 40 °C for 2 h (Paths A and B in Figure S4, respectively), uniform dimples 1 μm and 800 nm in size, respectively, are observed. However, when the holding temperature is 10 °C, decane lobes do not merge into a single lobe but are kinetically trapped. In this case, the lobes are relatively small and more time is necessary before the polymer solidifies (Path C in Figure S4). One or two dimples are typically observed, with sizes of about 800 nm or 1.5 μm, as shown in Figure 3a.

The curvature of the dimple is affected significantly by varying the interfacial tension either between polymer and solvent or decane and solvent. When the mixing ratio of methanol is increased or methanol is replaced with ethanol, interfacial tension (γ_{sp} or γ_{sd}) between solvent and polymer or decane decreases but the relative interfacial tension (γ_{pd}) between polymer and decane increases. Curvature can thus be varied so that nearly flat or crater-like surfaces can be created, as shown in Figure 3a−c and 3d−f, respectively. AFM images (Figure S5) have confirmed that the curvature of cavities in dimple particles were different depending on solvent.

As shown in Scheme 1b, when the excess surfactant is removed by centrifugation and particles are redispersed in pure water, the dimple area is left free of surfactant and thus hydrophobic, causing an attractive interaction between it and other hydrophobic dimples. This hydrophobic attraction drives the spontaneous assembly of dumbbells as shown in Figure 4.

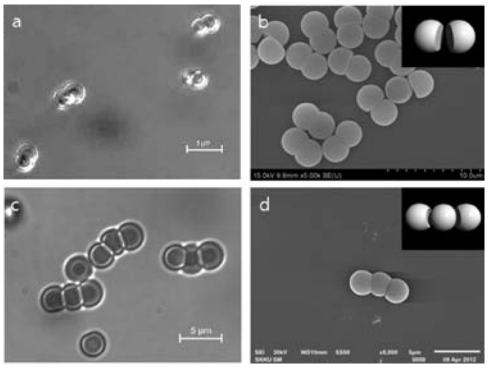


Figure 4. (a) Optical micrograph and (b) SEM image of dumbbells by the assembly of PS dimpled particles. (c) Optical micrograph and (d) SEM image of trimers by the assembly of PS dimpled particles with PS. Scale bars in a and c are 5 μm.

During the swelling process, the hydrophobic part of the surfactant is likely embedded in the surface of swollen particles and is thus bound strongly[16] at the PS surface when particles are cooled, while surfactants at the decane surface remain mobile and thus are removed by repeated centrifugation and redispersion. By removing unbound or weakly bound surfactants, site-selective assembly can be induced between flat dimples of particles. These particles with flat dimples could be also deposited on a polystyrene-coated substrate by a simple dipping and washing process (Figure S6).

Furthermore, such site-selective assembly can be induced between dimpled particles with conventional colloidal spheres. When PS spheres (3 μm) stabilized with PVP in ethanol are added to an aqueous suspension of crater-like dimpled particles as shown in Figure 3e, they assemble into linear trimers as shown in Figure 4c and 4d. PVP layers initially work as a stabilizer in ethanol. However, we speculate that they collapse when they were dispersed in an aqueous suspension of crater-like dimpled particles and then bind with the hydrophobic dimples. Smaller spheres including 2- or 1-μm PS particles were also assembled with crater-like 3-μm dimple particles (Figure S7).

On the other hand, shape-directed assembly of dimpled particles can be also induced by depletion attraction as demonstrated in a previous report.[12] In this case, crater-like dimpled particles are prepared as shown in Figure 3a−c and then combined with spherical particles whose size is comparable to the curvature of the dimples. When a PEG (MW = 600 kg/mol, 10 wt %) solution was added into the mixture of spherical PS particles (10 mL, 1 wt %) and dimpled particles, snowman-like clusters form (Figure S8). By controlling the size ratio of the dimple and sphere diameter, other structures may be produced.

In summary, dimpled colloidal particles can be prepared by the phase separation of decane-swollen particles and subsequent removal of the decane. Dimple size and curvature are determined by the amount of decane absorbed by the particles and by the interfacial tension between three phases: PS, decane, and solvent. By removing the excess amount of surfactant used for stabilizing the swollen particles, the dimple area can be made hydrophobic after the evaporation of decane. Such hydrophobic dimpled particles can spontaneously form dumbbells or other clusters owing to the strong hydrophobic attraction between dimples or plain spheres. Those dumbbells or clusters may be used as a model system for understanding the structure or behavior of molecules which have anisotropic directional interaction while simple spheres can be used as a model system only for limited atoms with isotropic interaction such as metallic or ionic interaction. Furthermore, those dimpled particles can be expanded to hybrid dumbbells by assembling them with different colloidal spheres such as magnetic materials.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, GPC data of polymer beads, size distribution and SEM images of polymer beads, and optical micrographs of lock-and-key assembly. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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