Reversible Morphology Switching of Colloidal Particles

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ABSTRACT: A facile method has been discovered that enables switching of non-crosslinked poly(styrene) (Nx-PS) colloidal particle morphologies, including spherical and anisotropic convex-convex, plano-convex, and concave-convex. The anisotropic morphologies can be achieved readily from spherical Nx-PS particles through control of annealing time at elevated temperatures or surfactant concentration. These anisotropic morphologies can be reversed to spherical at lower temperatures, and reversible morphology switching between any pair of anisotropic morphologies also can be attained. This approach to particle morphology switching establishes a straightforward method for the synthesis of designer anisotropic particles using commercially available spherical particles as starting materials.

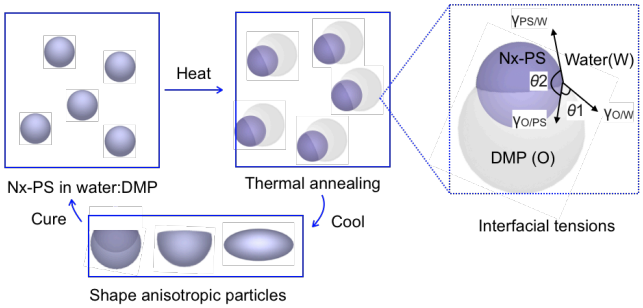
The shape of colloidal particles plays a critical role in biomedicine (shape influence on cellular internalization and vascular dynamics for drug delivery),[1] catalysis (facet-dependent electrocatalytic activity and durability),[2] emulsion stabilization (*e.g.* Pickering–Ramsden emulsions)[3] and, importantly, in the assembly of colloidal structures for new functional materials.[4-9] Particles with anisotropic shapes[10-18] have been used to create complex colloidal structures, including lock-and-key assemblies,[19-20] staggered linear chains[21] and cubic crystals,[22] which are either difficult or impossible to access using spherical colloids.

Controlled transformations of colloid particle morphologies represent a pathway to creating ordered structures and reconfigurable materials on demand.[15, 23-27] The use of pH or light has been reported to trigger a change in particle shape.[25,28] Solvent,[29] temperature[30] and chemical additives[24, 30-31] also have been used to transform colloid particle shapes. Most of these approaches, however, are limited with respect to particle shapes and they are not reversible.

Herein we report a method for reversible morphology switching of micron-sized non-crosslinked poly(styrene) (Nx-PS) particles between spherical and three anisotropic morphologies – convex-convex, plano-convex, concave-convex – using a thermo-responsive water:2,6-dimethylpyridine (DMP) mixture. This approach relies on the swelling capability of the Nx-PS particles in DMP and temperature-dependent solubility of DMP in water. Particle morphology can be regulated by controlling temperature and surfactant concentration, and the morphology transformations are fully reversible.

Deformation of particles at the fluid-fluid interface has been used as a strategy to fabricate non-spherical particles.[12-13, 17-18] These methods, however, suffer from either long reaction times,[12] the need for a sacrificial polymer phase,[13] or low yields.[17] The protocol for controlling and transforming particle morphology described herein relies on the thermo-responsive mixture of water and DMP (Scheme 1). Spherical Nx-PS particles dispersed in a 10:1 water:DMP mixture are heated to 70 °C (above the water-DMP phase separation temperature of 44 °C[32]). This results in adsorption of DMP on the particles, inducing a change in the particle morphology driven by an imbalance of interfacial tensions between the Nx-PS particle and water ($\gamma_{PS/W}$), DMP and water ($\gamma_{O/W}$), and DMP and Nx-PS particle ($\gamma_{O/PS}$). These parameters can be controlled by temperature and surfactant concentration.[13] Rapid cooling of the suspension to room temperature preserved the metastable anisotropic morphologies, which are indefinitely stable at room temperature. In contrast, the anisotropic particles can be reversed to their original spherical morphologies if allowed to stand near the phase separation temperature.

Scheme 1. Protocol for colloidal morphology transitions.



A 0.1 wt/wt % suspension of spherical Nx-PS particles with diameters of 2.4 μm (Figure S1) were prepared by dispersion in a 10:1 water:DMP mixture. The suspension then was heated to 44°C, causing phase separation[32] and adsorption of DMP on the particle surfaces to form liquid lobes (Video S1a). The suspension was heated at 70°C for several minutes (annealing time), during which the size of DMP lobes on the particle surface grew and caused further deformation of the particles (Figure 1). The particle suspension then was cooled to room temperature

and the anisotropic particles harvested. Different annealing times resulted in different particle morphologies. As stated above, this morphology deformation can be attributed to the imbalance of interfacial tensions. In the absence of added surfactant, convex-convex shaped particles were obtained. The introduction of Pluronic F127 surfactant, however, tuned the interfacial tensions to enable the formation of plano-convex and concave-convex shaped particles. The three particle morphologies can be characterized by the diameter D_{CC} of the convex-convex particles, the edge-to-edge distance D_{PC} of the planar surface of the plano-convex particles, and the diameter D_C of the concave feature of the concave-convex particles (Figures 1,2).

The dependence of particle morphology on surfactant concentrations and annealing times was explored *in situ*, as revealed in Videos S1A, B, and C. Particle suspensions (0.1 wt %) were heated at 70°C for various times (ranging from 2-8 minutes). Longer annealing times produced more substantial shape deformation (Figure 2). The morphology transformation of spherical to convex-convex over time is provided in Figure S2. Adjustment of the Pluronic F127 concentration up to 1.0 wt% caused a surface curvature change from convex-convex (< 0.5 wt %)

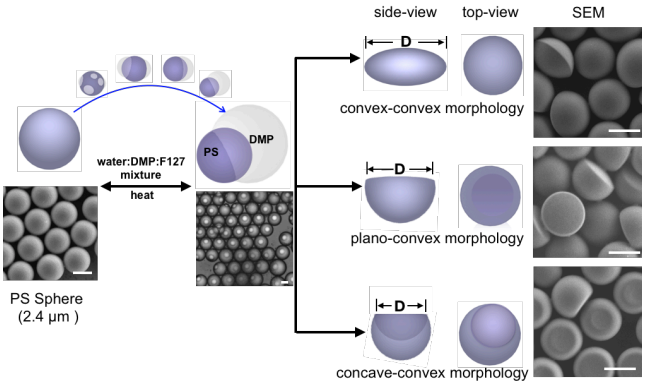


Figure 1. Schematic illustration of the strategy to engineer particles with anisotropic morphologies from spherical particles in 10:1 water:DMP mixtures. Particles with convex-convex, plano-convex or concave-convex morphologies can be formed. Diameter (D_{CC}) of convex-convex morphology, edge to edge distance (D_{PC}) of plano-convex morphology and diameter (D_C) of the open space of concave-convex morphology, respectively is used. Scale bars, 2 μm.

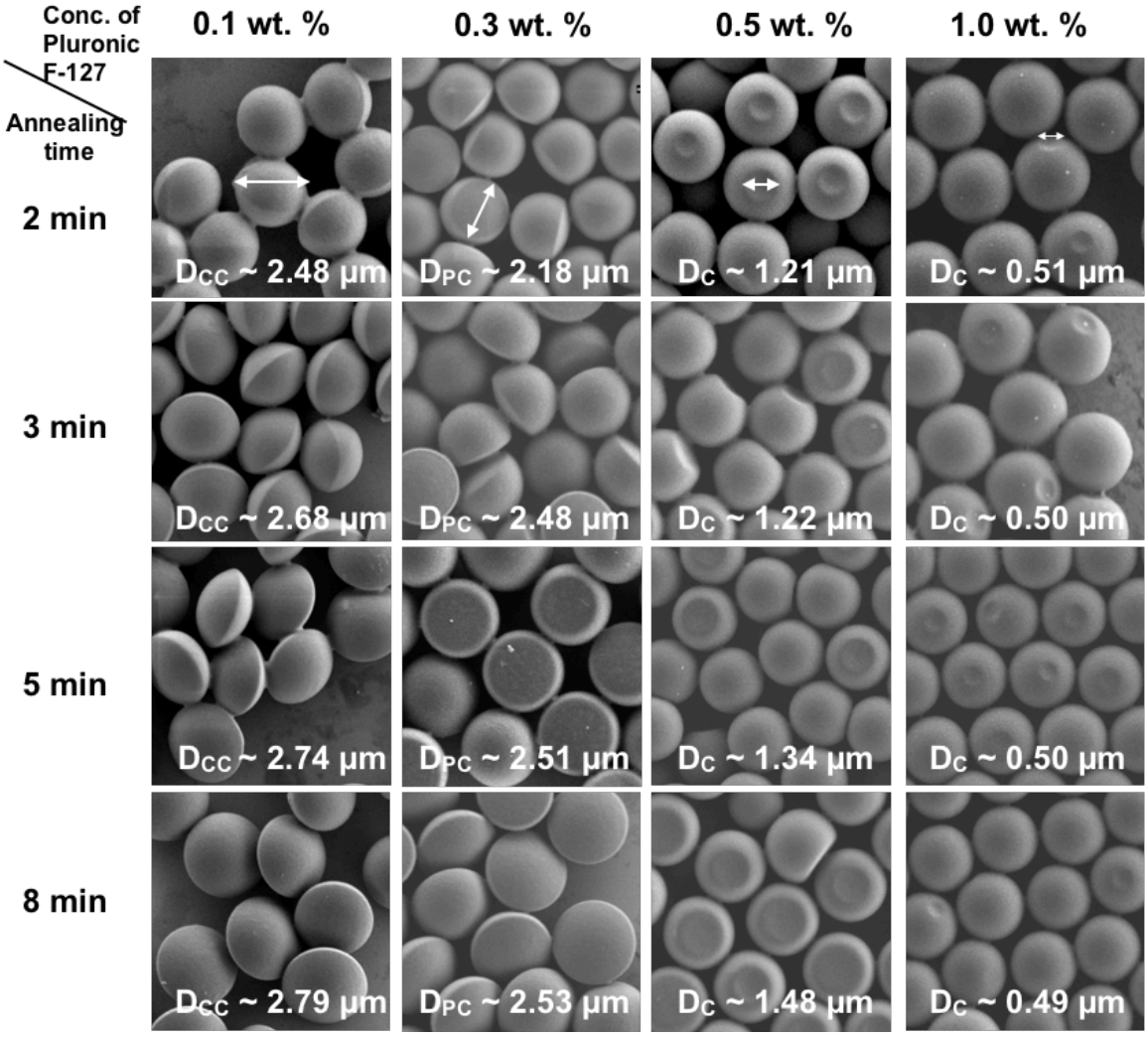


Figure 2. Scanning electron microscope images of anisotropic particles fabricated by varying annealing time (columns) and surfactant concentration of Pluronic F127 (rows). The double arrows in the first row demonstrates the D_{CC}, D_{PC}, D_C value of each morphology.

to plano- convex (~ 0.5 wt %) and concave-convex (> 0.5 wt %) (rows in Figure 2). A concentration of 1.0 wt % or higher afforded minimal deformation (rightmost column of Figure 2). Deformation rates increased with increasing temperatures (Figure S3).

These observations illustrate that particle morphology can be controlled and adjusted readily, allowing large-scale fabrication of anisotropic colloids with designer surface curvatures.

Cooling a suspension of convex-convex particles formed at 70 °C to 44 °C and held at this temperature for three hours resulted in a gradual reversal to the original spherical morphology (Figure 3A, Video S2A). This reversible morphology transformation can be repeated at least five times with temperature cycling (Video S2A). Intermediate states can be captured by quenching the particle suspensions to room temperature at selected times during the transformation cycles. This revealed that the sharp perimeter boundary of the convex-convex particles became smoother with time at 44 °C until the particle returned slowly to the spherical morphology. When a suspension of spherical particles was heated at 70 °C, the sharp perimeter boundary formed initially followed by a comparatively rapid deformation to the convex-convex morphology. Morphology changes from plano-convex or concave-convex to spherical were achieved in the water:DMP mixture following a similar procedure without the addition of surfactant (Videos S2B, S2C).

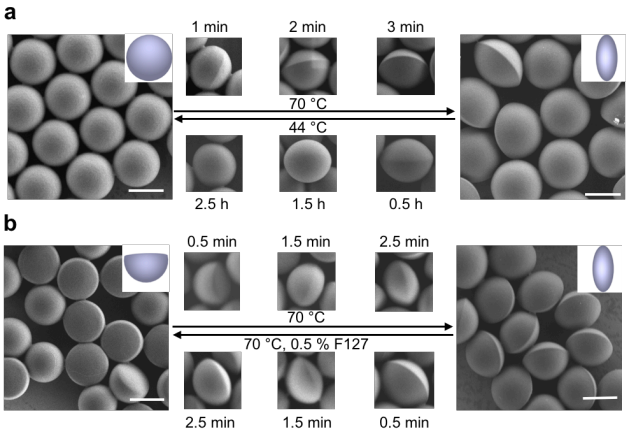


Figure 3. (A) Reversible morphology transformation between spherical and convex-convex shaped particles. Electron micrographs at t = 1, 2, 3 minutes at 70 °C and t = 0.5, 1.5, 2.5 hours at 44 °C in a water:DMP mixture are shown. (B) Reversible shape-shifting between plano-convex and convex-convex shaped particles. Electron micrographs at t = 0.5, 1.5, 2.5 minutes at 70 °C in water:DMP mixture of both directions are shown. Scale bars, 2 μm.

Reversing the morphology of the anisotropic particles to spheres also was achieved by suspending the anisotropic particles in a THF/water solution (illustrated for convex-convex particles in Figure S4 and Video S3). THF has been reported to swell and sphericalize Nx-PS particles to minimize surface energy.[33] The spontaneous transformation to the more stable spherical morphology is instantaneous when the volume fraction of THF exceeds 25%. At lower volume fractions, the D_{CC} values of the convex-convex particles decreased with an increasing volume fraction of THF (Figure S4). Video S3 illustrates the morphology reversal of convex-convex particles *in situ* by allowing diffusion of THF into particle aqueous suspension.

Surprisingly, the morphology transformations between anisotropic morphologies also can be triggered readily. For example, convex-convex particles can be converted to a plano-convex morphology by thermal annealing of a dispersion of the convex-convex particles in a water:DMP mixture containing 0.5 wt % Pluronic F127 (Figure 3B, Video S4A). Conversely, plano-convex particles can be transformed to convex-convex particles by dispersion in water:DMP mixture without Pluronic F127 (Figure 3B, Video S4B). Similar transformations between convex-convex and concave-convex morphologies were observed as well (Figure 4, Videos S4C, D). Interestingly, a direct single-step morphology transformation between plano-convex and concave-convex was not observed. Instead, this transformation was realized through a multi-step protocol (Figure 4), with the plano-convex particles first transforming to spherical particles followed by transformation to concave-convex. These morphology transformations provide new ways to fabricate an assortment of anisotropic particles with a minimal number of steps.

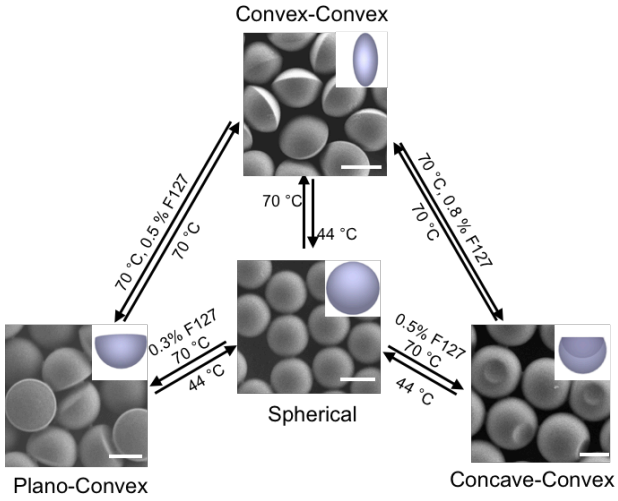


Figure 4. "Transit map" of particle morphologies. Summary of particle morphology switches. Scale bars, 2 μm.

In conclusion, a straightforward and robust methodology to fabricate anisotropic particles, with morphologies of precisely tunable surface curvature starting from isotropic Nx-PS spheres, has been discovered. The methodology relies on the different swelling behaviors of the particles in different solvents and the temperature-dependent phase behavior of water:DMP mixtures. Different morphologies can be reversibly transformed, like modeling clay on the colloidal scale. The simplicity of the protocol suggests potential for large-scale synthesis of unusual shaped colloidal particles. This method also provides a general strategy to engineer the morphology of particles taking advantage of their different swelling ability in different solvents, leading to potential synthesis of anisotropic particles of other sizes and materials. More importantly, the morphology-switching ability of these particles will inform the achievement of *in situ* colloidal phase transition and reconfigurable materials.

ASSOCIATED CONTENT

Supporting Information

Experimental details, particle fabrication conditions, particles morphology transformation conditions and *in situ* videos. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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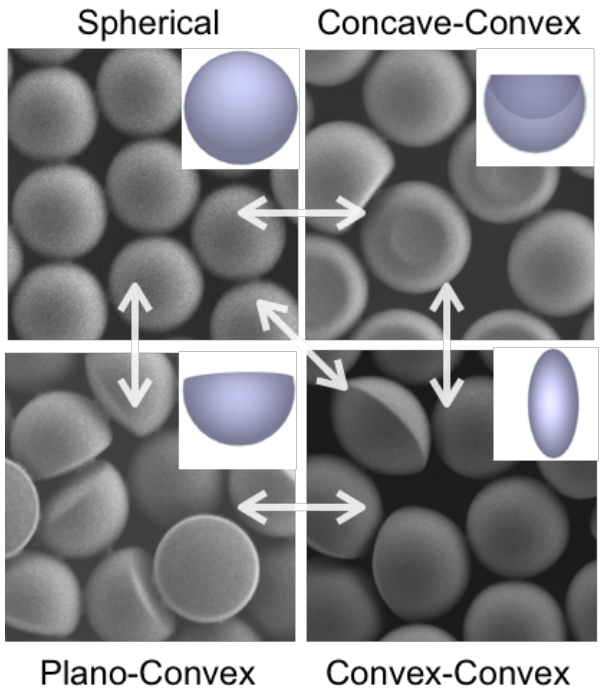
Spherical
Concave-Convex
Plano-Convex
Convex-Convex