

Synthesis of Colloidal Particles with the Symmetry of Water Molecules

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We describe a method for synthesizing “colloidal water”: monodisperse micrometer-sized polymer particles with the symmetry of water molecules. Our approach is based on multistep seeded polymerization with variation of cross-linker concentration in each step. This enables precise control of swelling selectivity and phase-separation, which control the particle morphology.

Introduction

Suspensions of colloidal particles have been widely employed as model systems to study melting, freezing, and glass transitions. Their phase behavior is similar to that of atoms or molecules, yet they are readily imaged and manipulated with optical tools.^{1–4} Colloidal interactions can be readily tuned by modifying the composition of the particles and solvent or applying external fields.^{5,6}

Even though most condensed phases are made of nonspherical molecules, most research with colloidal models has used spherical particles.^{7–10} Some simple shapes such as rods and ellipsoids have been exploited as model systems to understand colloidal arrays and packings.^{11,12} The use of nonspherical particles in studying the physics of condensed matter is challenging. The primary reason for this is difficulty in controlling particle shape and uniformity. Most synthetic methods have been based on the modification of spherical particles.^{13–17}

In this letter, we describe the synthesis of nonspherical micrometer-sized particles that capture the essential symmetries of water molecules. These particles are members of the C_{2v} point group and represent a concrete step toward the direct visualization

of the structure and dynamics of model condensed phases of water.^{18–20} We synthesize these particles using multistep seeded polymerization. In a typical synthesis, we first swell micrometer-sized spherical polymer colloids with a monomer solution. Heating drives phase separation and polymerization of the monomer to create a new lobe on the spherical seed particle. The morphology of the new lobe is controlled by the cross-linking density of two interpenetrating polymer networks (IPN).^{21–23} Previous work has exploited this strategy to generate symmetric dimers, trimers, and planar tetramers.²⁴ We expand the technique by varying the cross-linking density in subsequent lobes. This enables selective swelling and sequential phase separation of lobes and, thereby, control of the overall particle morphology, ultimately producing uniform H₂O-shaped particles (Figure 1).

Materials and Methods

Synthesis of Spherical Polystyrene Seed Particles. We synthesize spherical polystyrene (PS) particles, which are 2.2 μm in diameter, via dispersion polymerization. Polyvinylpyrrolidone (PVP k-30, 0.36 g, Aldrich) and 0.08 g of dioctyl-sulfosuccinate (sodium salt, Aldrich) are measured into a 40 mL glass vial, followed by the addition of 22.5 mL of ethanol. After mixing, the solution turns into a transparent liquid. We then add 2.2 mL of styrene (Aldrich) and 33 mg of initiator (azobisisobutyronitrile, Aldrich) to the solution. After mixing all the ingredients completely, we polymerize the solution by heating the vials to 70 $^{\circ}\text{C}$ for 24 h with tumbling. After polymerization, we wash all the particles several times with methanol to remove the stabilizer and unreacted monomer.

Synthesis of H₂O-Shaped Particles. We synthesize the particles through a four step seeded polymerization method. In each step, we swell the templating particles with a monomer mixture that is composed of styrene, divinylbenzene (DVB, 55% isomer, Aldrich), and initiator (0.5 wt %, benzoyl peroxide, Wako).

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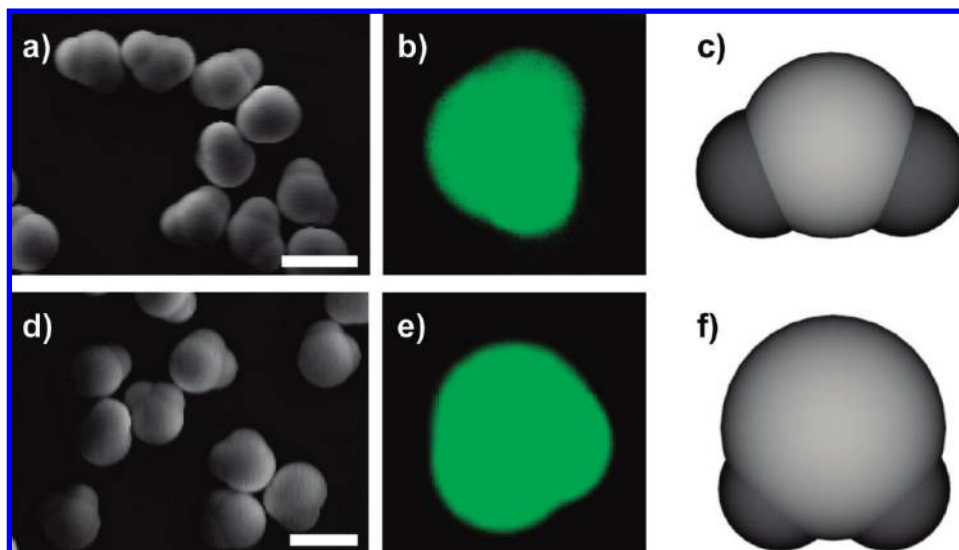


Figure 1. Examples of monodisperse H₂O-shaped particles synthesized with multistep seeded polymerization: (a,d) scanning electron micrographs, (b,e) maximum projection of a three-dimensional confocal microscopy image of dye-labeled particles. (c,f) schematic diagrams of particle morphology. Nominal swelling ratio of monomer to templating trimer particle is 2/1 (vol/wt) for panels a, b, and c, and 4/1 for panels d, e, and f. The scale bars are 10.0 μm .

In all steps, we prepare template particle dispersions and monomer emulsions using a 1.0% w/v polyvinyl alcohol (PVA; 87–89% hydrolyzed, $2.1 \times 10^4 \text{ g mol}^{-1}$, Aldrich) aqueous solution. We allow the particle to swell with monomer by mixing the two solutions for 12 h. After swelling, we polymerize the mixture by heating the bottle to 72.5 $^{\circ}\text{C}$ for 8 h with tumbling. After polymerization, we wash all the particles several times with water and methanol to remove the stabilizer and unreacted monomer. In Step I, we synthesize cross-linked PS spheres using linear PS particles as seeds. PS particles (0.25 g; 2.2 μm prepared via dispersion polymerization as described above) are dispersed in 2.25 mL of a PVA aqueous solution. Separately, 1.0 mL of monomer mixture is emulsified with a PVA aqueous solution by homogenizing at $6 \times 10^3 \text{ rpm}$ (IKA Homomixer) to give a 10.0 vol % monomer emulsion. The concentration of DVB in Step I, $[\text{DVB}]_1$, is fixed at 2.0 vol % to the total monomer content. In Step II, we synthesize dimers by using the cross-linked PS spheres as templating particles. The particles (0.25 g) are dispersed in 2.25 mL of PVA aqueous solution. A 10 mL portion of 10 vol % monomer emulsion is also prepared and mixed with the particle dispersion. The $[\text{DVB}]_2$ is fixed at 1.0 vol % to the total monomer content. In Step III, we synthesize trimers by swelling the dimers. Dimers obtained from Step II (1.0 g) are dispersed in 2.25 mL of a 1.0% w/v PVA aqueous solution. A 10.0 mL portion of 10 vol % monomer emulsion is also prepared and mixed with the cross-linked particle dispersion. The $[\text{DVB}]_3$ is fixed at 2.0 vol % to the total monomer content. Finally in Step IV, we use trimers as templating particles to synthesize H₂O-shaped particles. Trimers obtained from Step III (0.5 g) are dispersed in 4.5 mL of a 1.0% w/v PVA aqueous solution. A 5.0 mL portion of monomer emulsion is also prepared and mixed with the cross-linked particle dispersion. The $[\text{DVB}]_4$ is fixed at 1.0 vol % to the total monomer content.

Microscopy. We observe the morphology of the nonspherical particles with a scanning electron microscope (SEM) and confocal microscopy. For SEM, we fix the particles on an aluminum stub using two-sided carbon tape and sputter-coat them with gold under vacuum in an argon atmosphere at a sputter current of 40 mA (model 108auto, Cressington, UK). We use a Philips XL-30 ESEM with an accelerating voltage of 10 kV to image all of

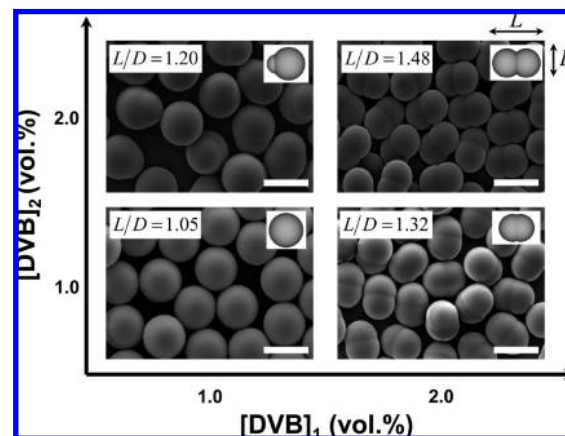


Figure 2. Effect of cross-linker concentration on the particle geometry in a two-step seeded polymerization. The scale bars in the scanning electron micrographs are 5.0 μm .

the samples. For confocal microscopy, we use a Nikon inverted microscope equipped with a spinning disk confocal head (Andor Revolution). Fluorescent images are obtained with a 100 \times objective at room temperature. To label the particles, we use rhodamine B as a fluorophore. Dimethylenechloride (DCM) containing 1 mM rhodamine B is emulsified and mixed with the particle dispersion. Particles are allowed to swell with the DCM/rhodamine B mixture in a sealed glass vial with magnetic stirring for 3 h. Then the DCM is removed by evaporation at room temperature. The labeled particles are washed with water and recovered by centrifugation. After drying, we mix these labeled particles with a liquid which has an n_D of 1.5894 ± 0.0002 (from Cargille Laboratories) to reduce light scattering. We take 140 images for individual particles with a step size of 0.1 μm in the z -axis.

Results and Discussion

Cross-linking density is a sensitive parameter for controlling particle morphology in multistep syntheses.^{21,23} The essential features are highlighted by a series of two-step dimer syntheses, where we vary the concentration of cross-linking agent, DVB, in

each swelling step. First, we synthesize spherical cross-linked PS particles from linear PS spheres by swelling them with styrene monomer containing DVB. In this step, the concentration of DVB, $[DVB]_1$, is varied from 1.0 to 2.0 vol % relative to the total monomer. Upon heating, the swollen particles polymerize. Later, we swell these cross-linked PS spheres at room temperature with another monomer mixture. The volume ratio of monomer mixture to cross-linked PS is fixed at 3:1. In this step, the cross-linker concentration, $[DVB]_2$, is varied from 1.0 to 2.0 vol %. Upon heating and polymerization, the resulting particles display various shapes, as shown in Figure 2. We quantify the morphology of the resulting dumbbell particles using the ratio of length to diameter, L/D . When the cross-linker concentration is low (1.0 vol %) in both steps, the final particles are nearly spherical. At higher cross-linker concentrations, heating and polymerization drive

significant phase separation, creating a second spherical lobe, with tunable L/D from 1.05 to 1.48, as shown in Figure 2. This control of particle morphology with cross-linking density during subsequent swelling and polymerization plays a central role in our synthesis of H_2O -shaped particles.

We synthesize H_2O -shaped particles in a four step process, where we control the swelling and degree of phase separation in each step, illustrated in Figure 3a). The first two steps are identical to the synthesis of $L/D = 1.32$ dimers described above. Next, we swell these symmetric dimers with a monomer mixture (2.0% DVB). Most of the monomer is absorbed into lobe 2, the lobe with low cross-linking density. Upon heating, phase separation drives the formation of a third lobe, colinear with the first two. This colinear arrangement of the lobes is likely due to long-range elastic forces. This linear trimer consists of two end lobes with relatively high cross-linking density and a center lobe with lower cross-linking density. In the final step, we swell the linear trimer with monomer solution. The concentration of $[DVB]_4$ is fixed at 1.0 vol.% to the swelling monomer content. Once again, the monomer mostly resides in lobe 2, which has the lowest cross-linking density. After swelling, the suspension is heated up and polymerized. Since the cross-linker density of lobe 2 and the swelling monomer are both 1.0 vol %, no phase separation occurs. Thus, the central lobe is expanded while maintaining its spherical shape.

In the final step, preferential swelling of the central lobe displaces its center from the line connecting the centers of the end lobes. The magnitude of this displacement can be controlled by varying the swelling ratio in the final step, as shown in Figure 1. For relatively small swelling ratios, the three lobes are nearly colinear, and the final particle has a relatively high aspect ratio. For larger swelling ratios, the internal angle between lobes 1 and 3 is reduced, and the final particle has a lower aspect ratio.

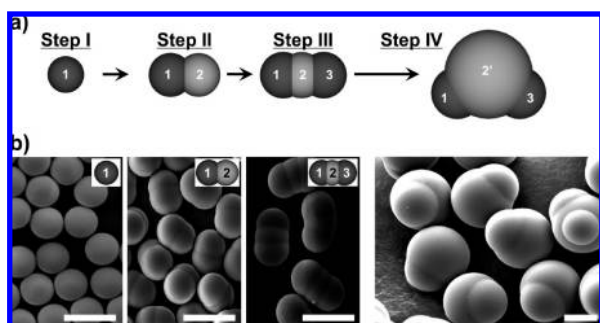


Figure 3. (a) Schematic representation of multistep seeded polymerization for H_2O -shaped particles and (b) stepwise development of particle morphology through the process. We controlled the $[DVB]_n$, the concentration of DVB at the n th swelling step, as follows: $[DVB]_1$, $[DVB]_3 = 2.0$ vol % and $[DVB]_2$, $[DVB]_4 = 1.0$ vol %. The scale bars in the scanning electron micrographs are $5.0 \mu\text{m}$.

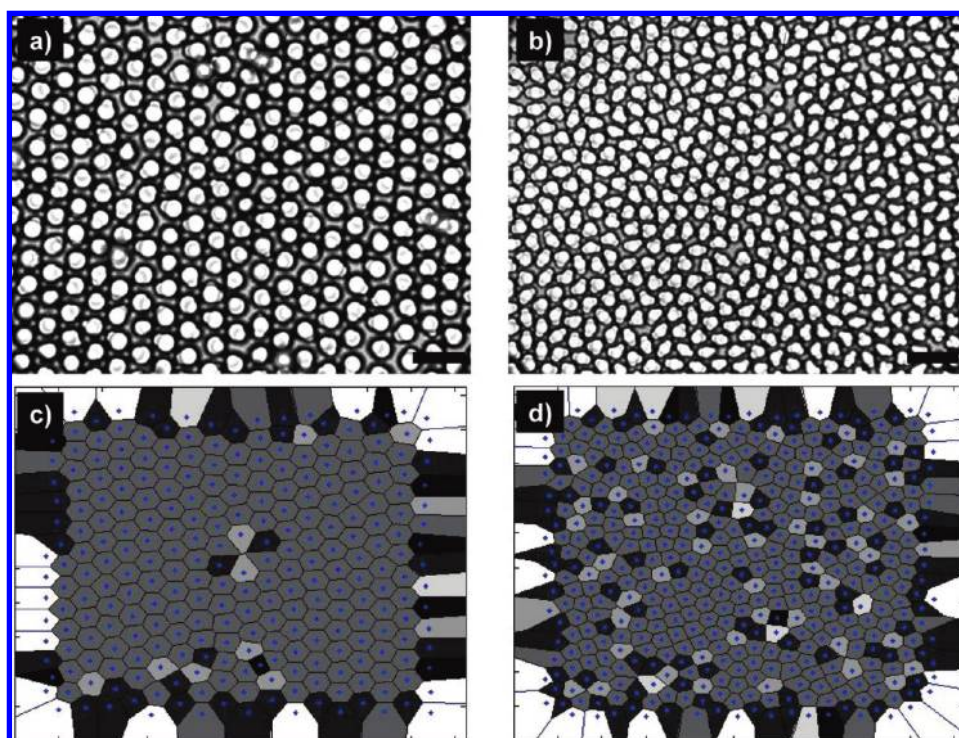


Figure 4. (a,b) optical micrographs of H_2O -shaped particles and (c,d) Voronoi constructions of panels a and b. Gray polygons are 6-fold coordinated; dark gray, 5-fold; gray, 7-fold; dark, 4-fold. Nominal swelling ratio of monomer to templating timer particle is $4/1$ (vol/wt) for panel a and $2/1$ for panel b. The scale bar is $20.0 \mu\text{m}$.

An example of the impact of particle morphology on the structure of condensed phases is highlighted in Figure 4. Here we show monolayers of H₂O-shaped particles self-assembled on a glass surface via sedimentation. Particles with a low aspect ratio readily form 6-fold coordinated crystalline structures in the two-dimensional plane with little interference from lobes 1 and 3 (Figure 4a,c). On the other hand, when the aspect ratio is high, lobes 1 and 3 can frustrate the formation of crystalline domains with the formation of 5- and 7-fold coordinated defects (Figure 4b,d).

In conclusion, the variation of cross-linker density enables precise control of swelling selectivity and phase-separation. We

exploit this to engineer monodisperse H₂O-shaped particles in a multistep seeded polymerization. The morphology of these particles has an impact on their self-assembly. Ultimately, we expect that these particles may be used to study model condensed phases of water. To realize this goal, it will be desirable to make smaller particles and to differentially functionalize the central and end lobes to engineer a permanent dipole moment.

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