

Synthesis and Utilization of Monodisperse Hollow Polymeric Particles in Photonic Crystals

Xiangling Xu and Sanford A. Asher*

Contribution from the Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania 15260

Received January 30, 2004; E-mail: asher@pitt.edu

Abstract: We developed a process to fabricate 150–700 nm monodisperse polymer particles with 100–500 nm hollow cores. These hollow particles were fabricated via dispersion polymerization to synthesize a polymer shell around monodisperse SiO₂ particles. The SiO₂ cores were then removed by HF etching to produce monodisperse hollow polymeric particle shells. The hollow core size and the polymer shell thickness, can be easily varied over significant size ranges. These hollow polymeric particles are sufficiently monodisperse that upon centrifugation from ethanol they form well-ordered close-packed colloidal crystals that diffract light. After the surfaces are functionalized with sulfonates, these particles self-assemble into crystalline colloidal arrays in deionized water. This synthetic method can also be used to create monodisperse particles with complex and unusual morphologies. For example, we synthesized hollow particles containing two concentric-independent, spherical polymer shells, and hollow silica particles which contain a central spherical silica core. In addition, these hollow spheres can be used as template microreactors. For example, we were able to fabricate monodisperse polymer spheres containing high concentrations of magnetic nanospheres formed by direct precipitation within the hollow cores.

Significant progress has been made in the design and fabrication of hollow polymeric and ceramic colloidal particles.^{1–18} The resulting monodisperse hollow nano- and meso-spherical particles are of great technological importance because of their potential utility for use as confined nano- and meso-reaction vessels, as drug carriers, and as protective shells. One of the earliest processes for making hollow latex particles was developed by Kowalski and colleagues at Rohm and Hass.^{19,20}

Their approach involved making a core particle from a carboxylated polymer and covering it with one or more outer shells. Addition of base ionized the carboxylated core, which swelled the core to produce hollow particles containing water and polyelectrolyte. Hollow polymer spheres were also produced by McDonald et al.⁸ by encapsulating hydrocarbon solvents within polymer particles during an emulsion polymerization. The hollow spheres were produced by removal of the hydrocarbon in a vacuum.

Wong et al.¹¹ used a lysine–cysteine diblock copolypeptide polymer as the framework for producing robust hollow spheres. Gold nanoparticles were used to bind to the cysteine hydrophobic blocks to form submicron aggregates. The aggregates stabilized by the positively charged lysine block polymer have gold nanoparticle aggregate interior shells organized around a core filled with solvent. When negatively charged silica particles were attached to lysine blocks, they formed a dense exterior silica layer. In another approach, Liu et al.⁴ recently described the synthesis of stable polymeric hollow particles (nanoballoons) through a cross-linking polymerization of supermolecular assemblies of polymerizable liposomes. Additionally, Jiang et al.¹⁸ reported a lost-wax approach for colloid particle synthesis within an inverse opal. They were able to synthesize both solid and hollow colloid particles through a sol–gel process by adjusting the adhesion between the filling phase and the polymer wall.

Obviously, the simplest method to fabricate hollow particles is to coat a sacrificial core particle with a shell, and then to decompose or dissolve away the core. We previously used this approach to incorporate CdS spheres within monodisperse silica spheres during a microemulsion condensation of silica. We then

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used acid to dissolve away the CdS spheres, leaving monodisperse hollow silica spheres.^{21,22}

Hollow silica spheres have also been synthesized through the seeded polymerization of tetraethoxysilane (TEOS) shells on the surface of polystyrene particles^{16,23} or ZnS particles.²⁴ The cores were then removed to produce hollow silica spheres. Yin et al.¹³ grew silica shells on polystyrene spheres containing surface-bound magnetic particles. The magnetic particles were then dissolved, and the polystyrene particles were calcined to yield hollow spheres with templated interior walls.

Recently, a layer-by-layer self-assembly technique was utilized by Caruso et al.^{1–3,17} to coat submicron polymer particles with nanoparticles. For example, nanoparticle shells were deposited on negatively charged polymer particles. Positively (negatively) charged polyelectrolytes were attached to these shells. This was followed by deposition of the oppositely charged nanoparticles. This layer-by-layer growth cycle was repeated until the desired shell thickness was obtained. The polymer core was then removed by calcination or dissolution to create the desired hollow particles.

Silica particles are often used as core particles because HF can easily dissolve them. For example, gold nanoclusters were attached to functionalized silica particles, and reductive growth and coalescence resulted in the formation of a gold layer around the silica particle.²⁵ Polymer shell–SiO₂ core particles can be fabricated through the colloidal self-assembly of small polymer spheres onto the larger silica core particle surfaces through electrostatic interactions or by specific chemical or biochemical interactions.^{1–3,17,26} These polymer shell–SiO₂ core particles can also be fabricated by polymerizing the shell around the core particle during an emulsion or dispersion polymerization reaction.^{27–29}

Recently, a surface-confined living polymerization of vinyl monomers on silica surfaces was used to synthesize well-defined polymer shell–SiO₂-core particles.^{5,30–33} Removal of the SiO₂ cores produced hollow polymer particles. This process enables the synthesis of uniform polymer shells with predictable thicknesses. By first coating gold particles with silica shells, Kamata et al.¹⁵ used a similar technique to fabricate monodisperse hollow polymeric particles containing a free gold nanoparticle within the hollow core.

In the work here, we describe a process to fabricate 150–700 nm highly monodisperse polymer hollow particles with monodisperse hollow cores in the 100–500 nm size range. These monodisperse polymer-shell–SiO₂ core particles were produced by a dispersion polymerization reaction. The SiO₂ core shells were removed by HF etching to produce monodisperse

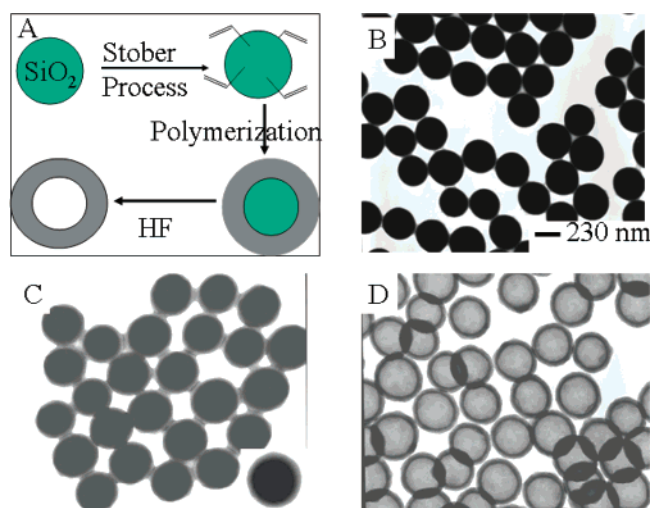


Figure 1. (A) Synthesis scheme for monodisperse hollow polymeric particles. (B) ~ 300 nm silica particles with a polydispersity of 4%. (C) Silica particles were coated with 48 nm polystyrene shells with a polydispersity of 4%. (D) Hollow polymeric particles were produced by etching out the silica cores with HF.

hollow polymeric particles. These hollow polymeric particles are sufficiently monodisperse that they readily form colloidal crystals, upon centrifugation from ethanol, which show strong Bragg diffraction.

Results and Discussion

Monodisperse Hollow Polymeric Particles and Close-Packed Photonic Crystals. We chose SiO₂ as the sacrificial core material because monodisperse SiO₂ spheres can be easily synthesized with the Stober process. The size of silica and the monodispersity can be controlled by use of specific concentrations of water and ammonia.^{34–36} In addition, the SiO₂ colloidal particle surfaces can be readily modified via commercially available silating agents. A typical Stober recipe utilizes a mixture of 25 mL of deionized water and 2 mL of ammonium hydroxide (14 mol/L), which was poured into a mixture of 70 mL of ethanol and 6 mL of TEOS (tetraethyl orthosilicate, Aldrich) under stirring. After 2 h, ~ 300 nm monodisperse silica particles are formed, with relative standard deviations of 4%.

As outlined in Figure 1A, the resulting monodisperse SiO₂ spheres were then reacted with MPS (3-(trimethoxysilyl)propyl methacrylate, Aldrich) to attach polymerizable vinyl groups onto the silica surfaces. A polymer shell was attached to these modified SiO₂ particles through the copolymerization of St (styrene, Aldrich) and DVB (divinyl benzene, Aldrich) during a dispersion polymerization reaction. In one example, the surface-functionalized silica particles, dispersed in ethanol (250 mL, containing 5 g of silica particles), were mixed with 0.6 g of PVP (poly(vinylpyrrolidone), MW 360K, Aldrich), 0.2 g of AIBN (2,2'-azobisisobutyronitrile, Aldrich), 2.0 g of St, and 2.0 g of DVB, and then heated to 60 °C for 4 h under stirring. The composite particles were collected by centrifugation and cleaned by repeated centrifugation and ultrasonic dispersion in ethanol. The Figure 1C TEM image shows the successful formation of a uniform polymer shell on the SiO₂ core. The composite core–

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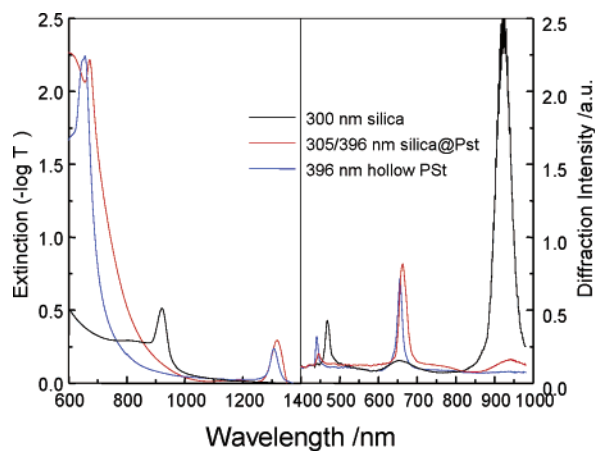


Figure 2. Backscattering diffraction intensities and extinction spectra of near-close-packed colloidal crystals assembled after centrifugation of an ethanol dispersion of silica particles, polystyrene shell–SiO₂ core composite particles, and the resulting hollow polystyrene shell particles.

shell particles are monodisperse ($\sim 4\%$ polydispersity) with an average diameter of 396 nm (Figure 1C). The ratio of the resulting core–shell particle diameter, $D_{\text{composite}}$, to that of the silica core, D_{silica} , follows stoichiometric expectations:

$$\frac{D_{\text{composite}}}{D_{\text{silica}}} = \left(\frac{(W_m/\rho_p) + (W_s/\rho_s)}{W_s/\rho_s} \right)^{1/3} \quad (1)$$

where W_m is the weight fraction of styrene and divinylbenzene monomer, W_s is the weight fraction of silica used in the dispersion polymerization, and ρ_p (1.05 g/cm³) and ρ_s (1.9 g/cm³)³⁷ are the polymer and silica densities.

The monodisperse hollow polymeric particles were produced by etching out the silica core with a 10% HF ethanol solution over 30 min. After cleaning the particles by repeated centrifugation and ultrasonic dispersion in ethanol, we produced hollow particles containing the ethanol solvent. The Figure 1D TEM image clearly shows that the hollow polymer particles are monodisperse in both outer and inner diameter after the ethanol in the core evaporates.

Although our method of using a sacrificial core is similar to strategies reported in refs 5 and 15, our approach has the advantage that it can be utilized to coat silica particles during a dispersion polymerization. This dispersion polymerization can utilize monomers, such as styrene, methyl methacrylate, and vinyl acetate. In addition, our modification of the silica surface with MPS is much easier and simpler than attaching an initiator onto the silica surface to achieve a controlled living polymerization.

When these monodisperse hollow particles are centrifuged from ethanol, they form near-close-packed arrays. As shown in Figure 2, a 1st order Bragg diffraction peak³⁸ at 1307 nm and a 2nd order Bragg diffraction peak at 655 nm were observed in the transmission spectrum when the sample was normal to the incident light. A 2nd order Bragg diffraction peak at 655 nm and a 3rd order Bragg diffraction peak at 441 nm were observed in the back diffraction spectrum when both incident and diffracted light were at normal incidence. To our knowledge,

these are the first colloidal crystals directly assembled from hollow polymer particles.

The wavelength diffracted by close-packed photonic crystals assembled from the silica spheres, the core–shell composite particles, and the hollow particles can be roughly predicted by Bragg's law, $m\lambda = 2nd \sin \theta$, where m is the order of diffraction, λ is the diffracted wavelength in a vacuum, θ is the glancing angle between the incident light propagation direction and the diffracting planes (the longest wavelength diffracted will occur at $\theta = 90^\circ$ for the fcc 111 planes), and d_{111} is the spacing between the diffracting planes. For a close-packed fcc colloidal array, $d = 0.816 D_p$, where D_p is the particle diameter. Also, n is the refractive index of the system, which we approximate $n \approx \sum \phi_i n_i$, where n_i and ϕ_i are the refractive indices and volume fractions of the individual components.

The expected 1st order diffraction wavelengths are 700 nm for the close-packed 300 nm silica particles in ethanol, 982 nm for the close-packed 300 nm silica particles with 48 nm polystyrene shells, and 965 nm for the 396 nm diameter polystyrene shells containing 300 nm ethanol cores. In contrast, we see much longer wavelength diffraction in all cases (Figure 2). We see a 1st order diffraction at 922 nm for the 300 nm silica spheres, which indicates a 32% increased lattice spacing, a 1st order diffraction at 1317 nm for 396 nm polystyrene shell–silica core (34% expansion), and a 1st order diffraction at 1307 nm for 396 nm hollow polystyrene particles (34% expansion). The increased diffraction wavelengths probably result from repulsions between spheres, which cause the lattice to expand after the centrifugation terminates and the system relaxes.

Control of Core Size and Shell Thickness of Hollow Polymer Particles. Figure 3 shows the TEM images of a series of monodisperse, hollow polymer particles with outside diameters between 200 and 700 nm and with polymer shell thicknesses between 20 and 90 nm, which were synthesized by varying the silica core size, while keeping the monomer/silica weight ratio at 0.9 and maintaining all other conditions constant. The Figure 3 TEM images show an approximately constant value of 0.4 for the ratio of the shell thickness to the interior particle diameter.

These monodisperse hollow polymeric particles show strong Bragg diffraction after centrifugation from ethanol (Figure 4), except for the 144 nm particles, which are the most polydisperse in size. As expected, as the particle size increases, the observed 1st order Bragg diffraction wavelength red-shifts from 800 to 1500 nm. Figure 4 also compares the observed Bragg diffraction wavelength to that expected for a perfect close-packed array for these different hollow core particles. For the largest 683 nm hollow particles, the observed lattice spacing is the same as that expected for a close-packed array, while the smaller diameter spheres show a diffraction wavelength indicating a lattice expansion of 10–40%. The largest spheres may have been so tightly packed by the centrifugation that they remain close packed.

The shell thickness of these hollow polymer particles can also be controlled by altering the monomer/silica weight ratio, while keeping other conditions constant. TEM images indicate that at a high monomer/silica ratio, giving thick shells, the hollow polymeric particles are robust and maintain their spherical shape. However, at low monomer/silica ratios (< 0.5), the resulting polymer shell is thin and flexible, and the hollow

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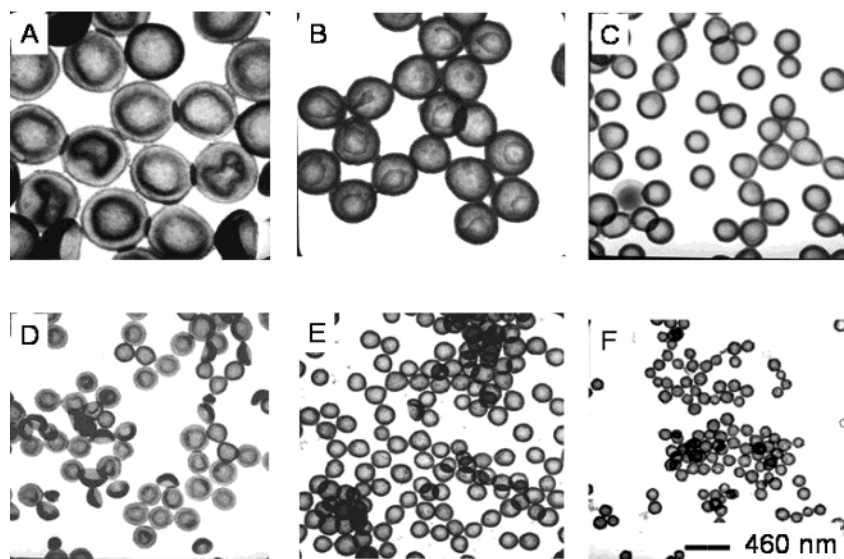


Figure 3. Fabrication of hollow polymeric particles of different core size: (A) 683 nm hollow particles prepared from 499 nm silica cores. (B) 500 nm hollow particles from 381 nm silica cores. (C) 320 nm hollow particles from 236 nm silica cores. (D) 265 nm hollow particles from 203 nm silica cores. (E) 209 nm hollow particles from 153 nm silica cores. (F) 144 nm hollow particles from 105 nm silica cores.

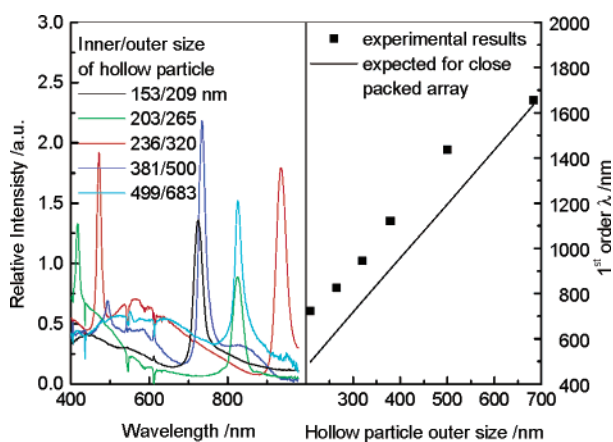


Figure 4. Bragg diffraction of close-packed colloidal crystals centrifuged from ethanol. The right-hand figure compares the observed 1st order diffraction (■) to that expected (—) for a close-packed array.

particles tend to deform, even though the polymer is highly cross-linked (44 mol % cross-linker). For example, the Figure 5A TEM image shows that 740 nm hollow particles with 60 nm thick shells deform into a bowl-like shape.

We examined the origin of the hollow particle deformations by AFM measurements of the particle topography. The Figure 5B AFM image of the particles in water after HF etching shows that the hollow particles are still spherical. In contrast, the Figure 5C AFM image shows that the hollow spheres collapse into bowl-like shapes after being dried by exposure to room-temperature air for 1 h. This deformation is irreversible; AFM images of the dried particles immersed in deionized water for 24 h still show the bowl-like shape.

Sulfonate-Functionalized Hollow Polymeric Particles Self-Assemble into a Crystalline Colloidal Array. If these monodisperse hollow particles are functionalized with sulfonates, they will self-assemble into a crystalline colloidal array (CCA) in deionized water. For example, a 5 mL ethanol dispersion containing 2 g of hollow polymeric particles (~ 340 nm outer and ~ 220 nm inner diameter) was mixed with 45 mL of an aqueous solution containing 0.3 g of APS (ammonium persulfate,

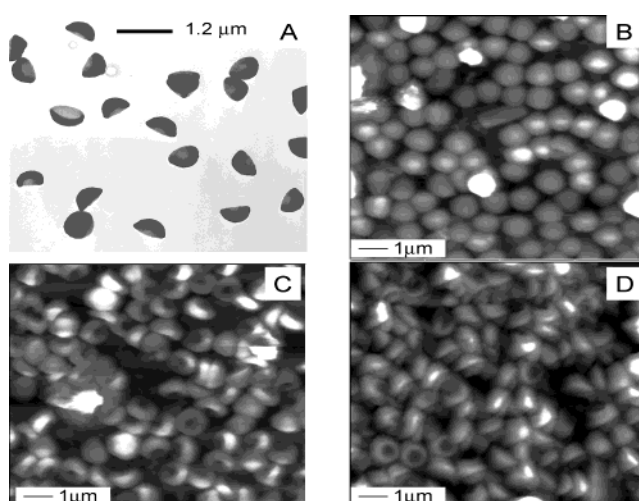


Figure 5. Deformation of 740 nm hollow polymeric particles with a 620 nm inner core. (A) TEM image of hollow particles after the solvent is removed. (B) AFM image measured in water. The AFM image was taken after etching silica with HF, with the inner hollow core filled with water. (C) AFM image measured after the hollow particles were dried in air at room temperature for 1 h. (D) AFM image measured in water after the deformed hollow particles were immersed in deionized water for 24 h.

Aldrich) and 2 g of SSS (sodium styrene sulfonate, Polysciences). The resulting mixture was incubated in a 65 °C water bath for 3 h. The particles were then extensively purified by repeated centrifugation and ultrasonic dispersion in water. The ζ potential of surface-charged hollow particles was measured to be -34 mV by light scattering, in comparison with -7 mV before modification. The total number of sulfonate groups per particle was measured to be 2.5×10^5 /particle by titration. However, this procedure functionalizes both the particle surface and the hollow core.

As expected, these particles self-assemble into a CCA in deionized water, as shown in the Figure 6 reflection and extinction spectra of a 35 μm thick CCA assembled in a quartz cell. The polymer content in the dispersion was measured to be 17 wt %, which corresponds to 23 vol % of hollow polymeric particles. The predicted 1st order diffraction is 1131 nm, while

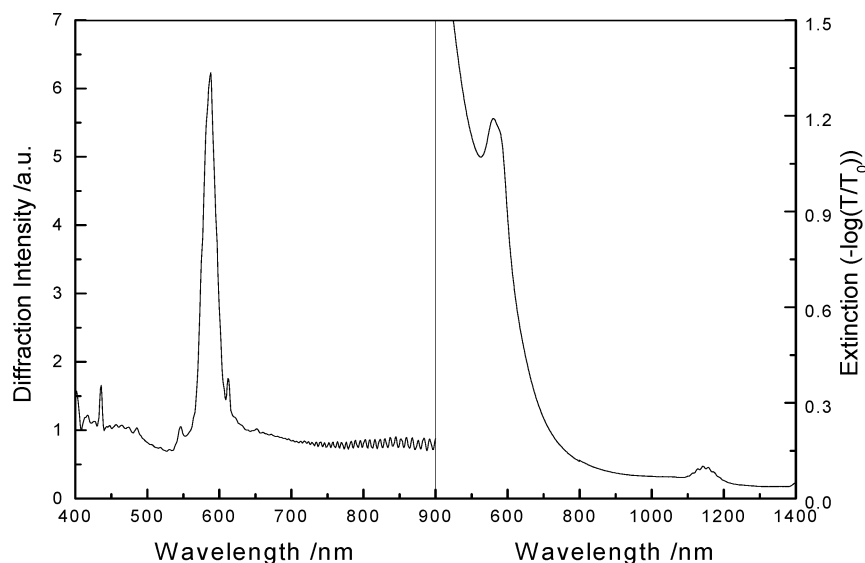


Figure 6. Reflection and extinction spectra of a CCA of sulfonated hollow polymeric particles (340 nm outer and 220 nm inner diameter). The 90° back diffraction shows the 2nd order diffraction peak at 588 nm, while transmission spectroscopy shows the broad 1st order diffraction peak at 1147 nm and the 2nd order diffraction peak at 561 nm.

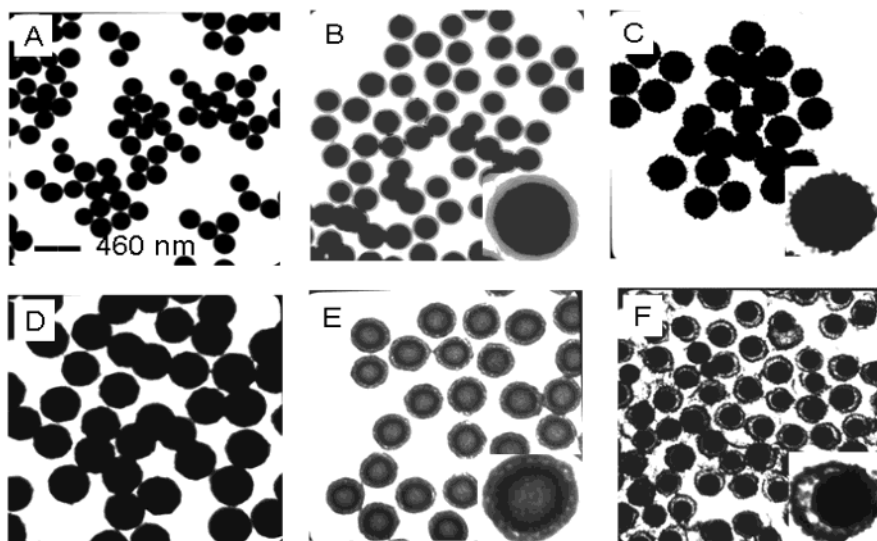


Figure 7. Fabrication of particles with complex morphology. ~ 203 nm MPS-modified silica particles A were first coated with a ~ 43 nm polymer shell to give core-shell particles B (~ 289 nm). Particles B were further coated with an additional ~ 42 nm polymer shell to produce composite particles D (~ 407 nm). Etching of composite particles D with HF yields polymeric particles E with concentric shells. Calcinations of composite particles D yield silica particles F with an extra exterior silica shell.

the observed 1st order diffraction is 1147 nm, which is essentially identical to that observed. We see a surprisingly weak 1st order diffraction and a stronger 2nd order diffraction in the transmission spectrum.^{38,39} Part of the decreased diffraction efficiency from that of typical solid polystyrene colloids ($n = 1.6$) is due to the decreased average refractive index of these particles; the average refractive index of these hollow particles is calculated to be 1.52. The diffraction efficiency is also decreased because of the small sample thickness. A further decrease in efficiency may also result from disorder in the lattice.³⁹

Fabrication of Particles with Well-Defined Structures. The strategies described above are used to produce hollow polymeric particles that can be further processed to fabricate particles with more complex morphologies. For example, we coated a

polystyrene shell-SiO₂ core particle (Figure 7B) with an additional silica shell by following the procedure of Tissot et al.²³ The resulting particles (Figure 7C) were then coated with an additional polystyrene shell by dispersion polymerization to produce the composite particles shown in Figure 7D. Particles with double concentric polystyrene shells (Figure 7E) were produced by etching out the SiO₂ with HF. In contrast, calcination of the Figure 7C or 7D composite particles at 500 °C for 5 h removed the polystyrene shells, resulting in the Figure 7F particles that possess a silica shell surrounding a silica core. We can also fabricate particles with multiple concentric polymer shells possessing different compositions in each shell.

Utilization of Hollow Colloidal Particles as Confined Microreactors. Our monodisperse hollow polymeric particles have uniform hollow cores, which can be used as nanoscale reactors to change the composition within the hollow core. For

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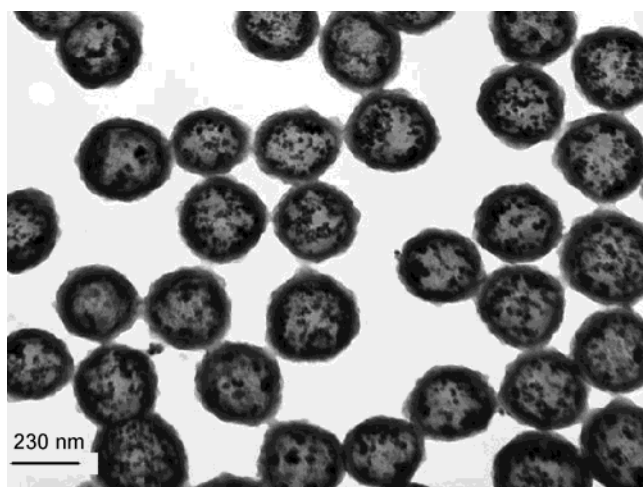


Figure 8. TEM image of 280 nm polymeric particles with a 200 nm hollow core filled with nanoscale ~ 14 nm Fe_2CoO_4 particles (black dots inside hollow particles).

example, we fabricated magnetic particles via hollow polymeric particles with a 280 nm outside and 200 nm inside diameter. These hollow particles were dispersed in 2.5 M FeCl_3 and 1.25 M CoCl_2 aqueous solution. These particles were separated by centrifugation and redispersed in toluene and then mixed with a solution of 5 M dimethylamine (Aldrich). Dimethylamine diffused into the hollow cores of the particles and reduced the pH, which precipitated out nanoscale magnetic cobalt ferrite particles inside the hollow cores. By repeating this process multiple times, we fabricated composite particles with high magnetic loading. For example, Figure 8 shows the TEM image of these magnetic composite particles after two precipitation cycles. The CoFe_2O_4 weight fraction was measured to be ~ 27 wt %, which is much higher than that (~ 5 – 15 wt %) in the ferromagnetic composite particles we synthesized through emulsion polymerization.^{40–42}

If we functionalize the magnetic particles of Figure 8 with sulfonate groups, the resulting magnetic composite particles are sufficiently monodisperse that they self-assemble into a CCA in deionized water. Figure 9 shows the transmission and reflection diffraction spectrum of a CCA formed between two

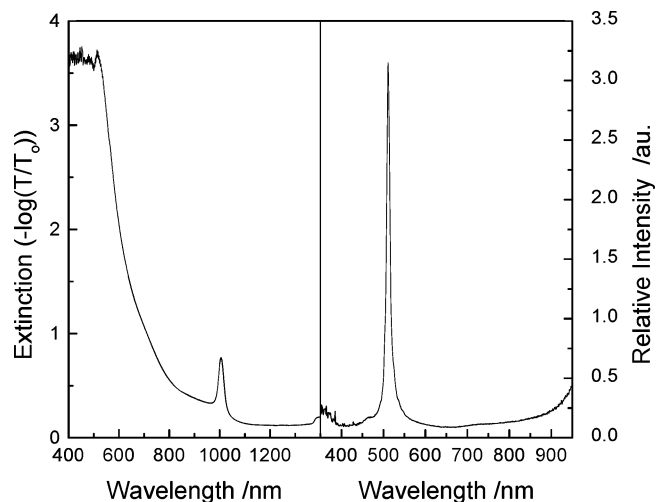


Figure 9. Surface-charged magnetic composite particles (25 wt %) self-assemble into a CCA in deionized water. The transmission spectroscopy of a CCA shows the 1st order diffraction peak at 1007 nm, while the reflection diffraction spectrum shows a 2nd order diffraction peak at 511 nm.

quartz plates separated by a $30 \mu\text{m}$ spacer. The 2nd order diffraction is not evident in the transmission spectra presumably because of the high absorbance of the magnetic nanoparticles.

These hollow magnetic particles form magnetically controlled CCAs similar to those we demonstrated previously using other synthetic methods.^{40–42} However, because these particles have a much larger loading, they have a larger magnetic susceptibility than we could obtain using our previous approach. Thus, they will form a CCA and a polymerized crystalline colloidal array (PCCA), which are much more responsive to magnetic fields.

Conclusions

In summary, a versatile procedure has been developed to synthesize monodisperse hollow polymer colloid particles that can self-assemble into a CCA. We demonstrate that the hollow core size and the polymer shell thickness can be easily tuned over a wide range. These hollow polymeric particles can act as template microreactors to confine the reaction inside the hollow core to fabricate complex, functional composite particles.

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