

Synthesis of Highly Charged, Monodisperse Polystyrene Colloidal Particles for the Fabrication of Photonic Crystals

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We have developed a series of emulsion polymerization recipes for the synthesis of highly charged, monodisperse polystyrene colloids of diameters between 100–400 nm. These spherical colloidal particles were crosslinked with divinyl benzene and functionalized with 1-allyloxy-2-hydroxypropane sulfonate. These highly charged, monodisperse colloidal particles readily self-assemble into robust three-dimensionally ordered crystalline colloidal arrays (CCAs). These CCAs operate as photonic crystals that Bragg diffract light in the ultraviolet, visible, and infrared regions of the spectrum.

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INTRODUCTION

Latex polymer colloids are important in many areas of technology, such as in paint and coatings, ceramics processing, and biotechnology (1). These particles are often prepared by emulsion polymerization, which can produce highly monodisperse spherical particles from polymers such as polystyrene, polymethylmethacrylate, etc.

A group from Dow Chemical Corp. in 1947 was the first to demonstrate the synthesis of monodisperse polystyrene latex colloids (2). The remarkable size uniformity of these colloids was demonstrated in the early electron microscopy studies of Backus and Williams (3). This work was followed by demonstrations of different synthetic approaches that produce monodisperse colloidal particles. These approaches include emulsion polymerization, seeded emulsion polymerization, emulsifier-free copolymerization, precipitation polymerization, and dispersion polymerization (4–19). At high particle concentrations these monodisperse particles readily form highly ordered, close-packed structures which Bragg diffract light. These close-packed structures often show a random stacked hexagonal ordering.

In contrast, Krieger *et al.* (2, 20) in 1968 showed that highly charged, monodisperse colloidal particles, which have covalently attached ionizing groups, will self-assemble in solution into highly ordered, non-close-packed three-dimensional arrays, known as crystalline colloidal arrays (CCAs), in which the lattice spacings are much greater than the particle diameters. These charged particles electrostatically repel one another and the system minimizes its free energy (2, 20–23) by self-assembling into either a body-centered cubic (BCC) or face-centered cubic (FCC) lattice (24–26).

These monodisperse colloidal particle dispersions undergo phase transitions between macroscopic, long-range ordered BCC and FCC crystalline phases. In addition, decreases in the particle repulsive interactions (induced, for example, by increasing the solution ionic strength) will cause these CCAs to undergo a phase transition to a liquid-like ordered phase that shows only short-range ordering. At higher ionic strengths the CCAs undergo phase transitions to an unordered gas-like phase in which the particle positions are uncorrelated (27–29). Since these phase transitions depend mainly upon the electrostatic interactions between the colloidal particles (30, 31), they depend upon the particle charge, screening by other ionic species (32), the particle size polydispersity (33), the charge polydispersity, and the particle volume fraction (32). It is easy to induce phase transitions merely by addition of micromolar amounts of salt, thus screening the repulsive interactions. The most robust crystalline phases occur when electrostatic interactions are maximized, i.e., at the highest particle charge densities and at the lowest solution ionic strengths.

Alfrey, Bradford, and Vanderhoff were the first to study the light-scattering properties of CCAs (34) and showed that these BCC or FCC crystal lattices efficiently Bragg diffract light (22, 35). This CCA Bragg diffraction results in unique optical phenomena that give these materials applications in optics and spectroscopic instrumentation. We were the first to demonstrate that CCAs act as photonic crystals which function as narrow-band radiation filters (36). These CCAs have also been immobilized within hydrogel matrices (polymerized CCAs, or PCCAs), and this composite material has been used to make photonic crystals that are nanosecond optical switching and limiting

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devices (22e,f, 37). These PCCAs can be functionalized with molecular recognition agents to create chemical sensing materials that sense specific analytes by undergoing hydrogel volume phase transitions. These volume changes cause diffraction wavelength shifts proportional to the analyte concentrations (38).

Our interest in fabricating mesoscopically periodic smart materials through the use of CCA self-assembly has motivated us to develop syntheses that easily and reliably prepare monodisperse, highly charged colloidal particles of different diameters. This work has benefited from the numerous previous studies on the synthesis of monodisperse latex particles with surface charge groups (39–55). We describe here recipes for the synthesis of highly charged, monodisperse polystyrene colloids with diameters between 100–400 nm that form robust CCAs.

EXPERIMENTAL

Synthesis

Monodisperse, highly charged polystyrene spheres were synthesized by emulsion polymerization using a jacketed cylindrical reaction vessel (Kontes #612100, 613200), which contained a reflux condenser, and a Teflon stirrer (Ace Glass #8093-22, #5030-40) powered by a high-torque mechanical stirrer (Ace Glass #3584-10). The vessel also contained a temperature sensor (Ace Glass #12103-18) and a nitrogen/reagent inlet. The temperature was maintained through the jacket with the use of a circulating temperature bath (Fisher #13-265-5).

Styrene (Aldrich) and divinyl benzene (DVB; Aldrich) were used after inhibitor was removed by passing the monomers through a column of aluminum oxide (Aldrich). Sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS-1) ionic comonomer (Rhone-Poulenc) and Aerosol MA-80-1 surfactant (Cytec), a solution of sodium di-1,3-dimethylbutyl sulfosuccinate in isopropanol and water, were generously donated by their manufacturers and were used as received. Sodium bicarbonate (Fisher) and ammonium persulfate (Sigma) were also used as received.

The reaction vessel was charged with 138 ml of ultrapure water (Barnstead Nanopure water purification system) containing 0.171 g of sodium bicarbonate. A nitrogen blanket and a stirring rate of 350 rpm were maintained throughout the reaction. The water solution was deoxygenated by bubbling with nitrogen for 40 min. After thorough deoxygenation, the Aerosol MA-80-1, dissolved in 10 ml of water, was added and the temperature was increased to 50°C. Previously deinhibited and deoxygenated styrene and DVB were injected at a rate of 4 ml/min. The COPS-1 was dissolved in 10 ml of water and was injected 5 min after the addition of styrene and DVB was completed. The temperature was increased to 70°C ($\pm 1^\circ\text{C}$), at which point the solution of ammonium persulfate in 5 ml of water was injected. The reaction was left to reflux for 3–4 h.

Upon completion of the reaction, the product appeared milky white. After it was allowed to cool, the colloid was filtered through previously boiled glass wool and was dialyzed (Pierce Snakeskin™ Pleated dialysis tubing 10,000 MWCO, Spectra/Por Biotech Cellulose Ester Dialysis Membranes 1,000,000 MWCO, or Spectra/Por Dialysis Membranes, Polyvinylidene Fluoride 2,000,000 MWCO) against water, which was replaced at least daily for 14–21 days. Ion-exchange resin (Bio Rad mixed bed; AG501-X8 used as received) was added to the solutions for storage.

Characterization

Particle sizes were measured using quasi-elastic light scattering (QELS; Malvern Zetasizer 4 and Brookhaven 90Plus) and transmission electron microscopy (TEM; Zeiss EM 902A). Optical diffraction measurements were performed by using either a UV/vis/NIR spectrometer (Perkin Elmer Lambda 9) or a CCD array UV-Vis spectrophotometer (Spectral Instruments 400 Series). The particle charge densities were measured by conductometric titration (56, 57).

RESULTS AND DISCUSSION

Monodisperse, highly charged polystyrene colloidal particles with diameters between 100–400 nm were synthesized using the recipes listed in Table 1. Obviously, the particles charge and diameter depend upon the reaction stoichiometry. All of these colloids readily formed CCAs, which exhibited sharp diffraction peaks in the UV/vis/NIR region, depending upon colloid concentration.

Figure 1 shows TEM micrographs of the synthesized highly charged, monodisperse polystyrene spheres. The particles are very spherical and monodisperse up to around 250 nm, but larger particles are more polydisperse and less uniform. At the lowest particle diameter the QELS measurements are somewhat greater than that from the TEM, but this difference becomes negligible at the higher diameters (Fig. 2). Only a small fraction of this difference is likely to result from the larger hydrodynamic radius that is monitored by QELS.

The concentration of the surfactant, Aerosol MA-80-1, is the primary determinant of the particle diameter (Fig. 3) (1, 9). The diameter decreases as the surfactant concentration increases. Lower surfactant concentrations allow for formation of fewer micelles resulting in larger particles (58). Unfortunately, we also observed that low surfactant concentrations often result in particle agglomeration. Some coagulation occurred in the synthesis of particles larger than 200 nm. Recipes for 300-nm-diameter particles typically resulted in a large amount of coagulum due to a decreased stability of the colloid.

Highly charged particles can be synthesized by the addition of COPS-1, a sulfonated comonomer. Figure 4a shows that the number of charges per particle increases with

TABLE 1
Recipes, Diameters, and Particle Number Densities

Sample ID	Water (ml)	MA-80-1 (g)	DVB (g)	COPS-1 (g)	Diameter ^a (nm)	Surfactant concentration ^b	Particle density ((no./ml) × 10 ⁻¹³)	Charges/particle	Charges/nm ²	Charge density (μC/cm ²)
JKS001	162.5	1.997	2.331	2.873	118.0	1.229	19.20	9.46 × 10 ³	0.216	3.46
31299	162.5	1.997	2.331	2.873	119.6	1.229	9.80	7.60 × 10 ³	0.169	2.71
92999	162.5	2.000	2.339	2.880	129.9	1.231	12.70	6.67 × 10 ³	0.126	2.01
20400	162.5	2.043	2.337	2.880	140.3	1.257	7.20	9.90 × 10 ³	0.160	2.57
SPS001A	260.0	2.756	4.642	5.756	179.1	1.060	9.46	3.66 × 10 ⁴	0.359	5.76
10499	162.5	1.342	2.334	2.876	191.3	0.826	3.77	1.99 × 10 ⁴	0.173	2.77
SPS002A1	162.5	1.280	2.334	2.892	233.1	0.788	4.14	4.03 × 10 ⁴	0.216	3.46
SPS002B	162.5	1.280	2.335	2.892	246.4	0.787	2.45	5.62 × 10 ⁴	0.246	3.94
SPS002A	187.5	1.280	2.334	2.892	259.8	0.682	2.22	5.48 × 10 ⁴	0.250	4.01
72399	162.5	1.279	2.340	2.893	267.2	0.787	2.01	7.84 × 10 ⁴	0.350	5.61
PSS003A	162.5	0.945	2.324	2.880	303.8	0.582	1.03	1.04 × 10 ⁵	0.329	5.27
11899	162.5	1.000	2.332	2.878	321.9	0.615	0.75	9.46 × 10 ⁵	0.291	4.66
CG033-7	162.5	0.691	2.326	2.880	365.6	0.425	4.17	1.69 × 10 ⁵	0.342	5.47

Note. All systems contained 60 ml of styrene, 0.17 g of NaHCO₃, and 0.75 g of ammonium persulfate. SPS001A used double these amounts.

^a Diameters reported are QELS values.

^b Weight percent of MA-80-1 used with respect to water.

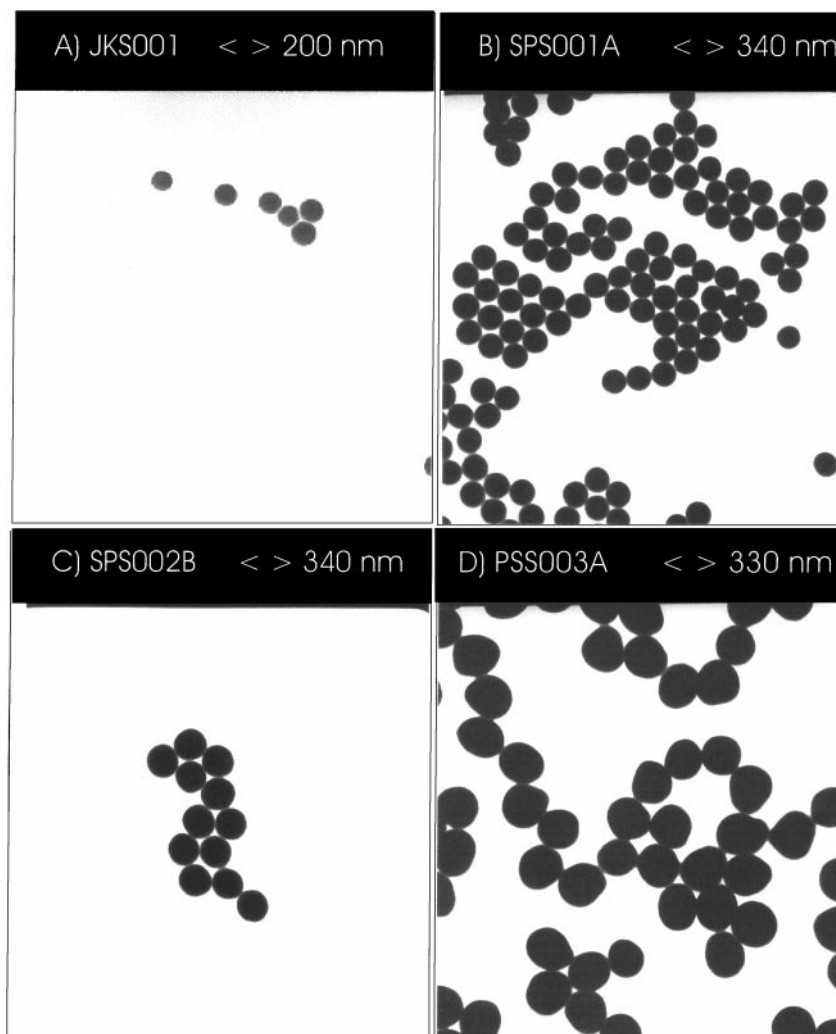


FIG. 1. TEM micrographs of the synthesized polystyrene particles: (A) 118.0 nm colloid, (B) 179.1 nm colloid, (C) 246.4 nm colloid, (D) 303.8 nm colloid. These sizes are the QELS sizes.

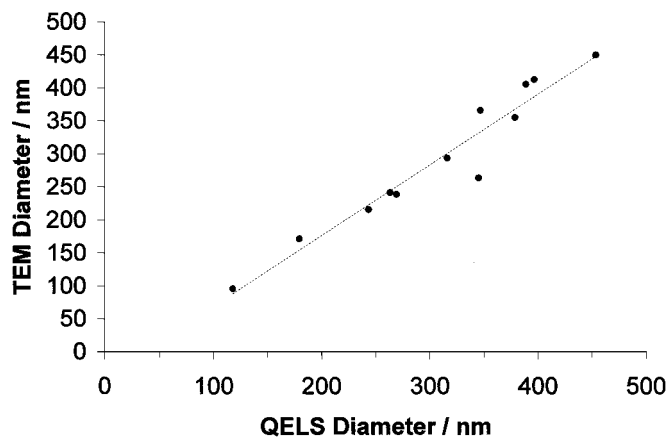


FIG. 2. Comparison of particle diameters measured by TEM and QELS. The QELS diameter is systematically larger than that measured by TEM.

diameter. For example, the recipe for 118.0-nm spheres in Table 1 (JKS001) yields ~ 9000 charges/sphere as measured by titration; the 233.1-nm sphere recipe (SPS002A1) results in $\sim 40,000$ charges/sphere; the 321.9-nm sphere recipe (11899) yields $\sim 95,000$ charges/sphere. If the charge densities were constant, we would expect that the number of charges per particle would increase with the square of the diameter. Figure 4a shows the excellent correlation of the charge, c , to the square of the particle diameter, d ($c = 1.2d^2 - 16,000$). Figure 4b plots the charge density versus particle diameter. The charge densities increase slowly with particle diameter.

We were unable to synthesize particles larger than 400 nm that form robust CCAs using procedures similar to those discussed above. The use of smaller amounts of surfactant resulted in essentially complete coagulation of the reaction solution. We are continuing our work toward developing syntheses of larger, highly charged monodisperse particles.

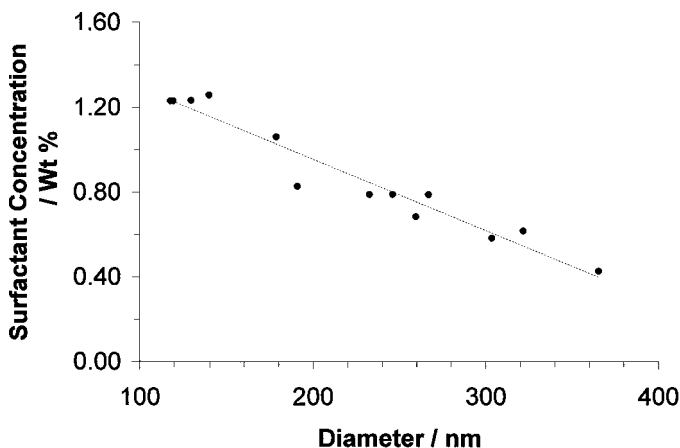


FIG. 3. Dependence of particle diameter on surfactant concentration. (Dashed line is the best-fit line.)

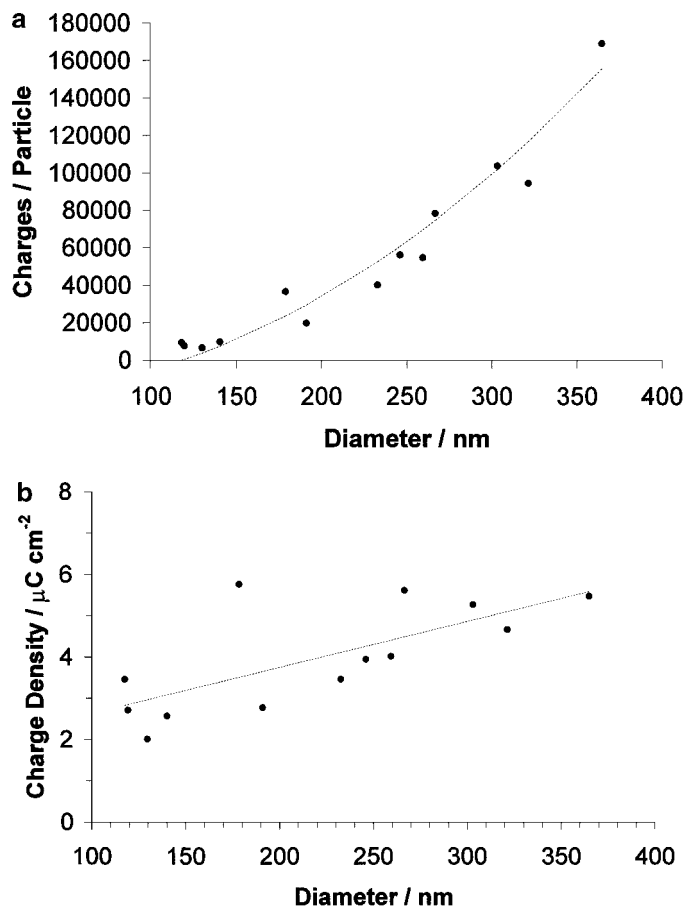


FIG. 4. (a) Correlation between the number of charges per particle and the particle diameter. (The dashed line is the fit to the equation $c = 1.2d^2 - 16,000$, where c is the number of charges per particle and d is the particle diameter.) (b) Correlation between the particle charge density and the particle diameter. (Dashed line is the best-fit line.)

CONCLUSIONS

Recipes to prepare highly charged, monodisperse polystyrene colloids of diameters between 100–400 nm were developed. These particles readily self-assemble into robust three-dimensional crystalline colloidal arrays that diffract light in the UV/vis/NIR region. The number of charges per sphere increases approximately as the square of the particle diameter.

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