Self-Assembly of Coated Colloidal Particles for Optical Applications

Introduction

Nearly two decades ago, theoretical predictions indicated the possibility of creating omnidirectional photonic-band-gap materials that would prevent the propagation of certain wavelengths of light in all directions, while allowing transmission of other light wavelengths.[1,2] Since that time, there has been a growing interest in creating these materials experimentally due to the wide variety of potential applications afforded by the control of light propagation, including use in optical computing and telecommunications.[3] Researchers have taken two approaches to construction of photonic-band-gap materials: (1) lithographic technologies similar to that used in microelectronics manufacture and (2) colloidal self-assembly of spherical particles. The self-assembly approach is promising due to its simplicity and low cost.

Under appropriate conditions, spherical colloidal particles will self-assemble to form a hexagonal close-packed structure called a "colloidal crystal." There are regularly spaced air voids in the interstitial regions between colloidal particles making up the crystal. Since air has a much lower refractive index than the particles, the refractive index of the crystal varies periodically on a length related to the diameter of the particles making up the crystal. The periodic variation of refractive index within the colloidal crystal leads to preferential reflection of certain wavelengths of light. The maximum reflectance occurs at a wavelength equal to roughly twice the diameter of the particles making up the crystal. Therefore, the position of the band gap and thus the color of the crystal may be adjusted by adjusting the size of the particles making up the crystal. Colloidal crystals are often referred to as "photonic crystals" due to the photonic-band-gap properties. They are also referred to as "artificial opals" due to the similarity with gemstone opal. Naturally occurring opal is a colloidal crystal of spherical silica particles. The "opalescence" observed in gemstone opal is caused by preferential reflection of light within the photonic band gap.

Colloidal crystals exhibit a "pseudo" photonic band gap; that is, only a portion of the light in the photonic band gap is reflected while some fraction propagates into the crystal. The rejected fraction of light can be enhanced by increasing the refractive index contrast between the particles and air voids in the structure. The photonic band gap is also very sensitive to the quality of the crystal. A few faults or dislocations in the crystal structure will greatly diminish the intensity of the reflected light. It is desirable to have a complete photonic band gap with 100% of the light in the band gap reflected. Theoretical predictions have indicated, however, that even with a perfect colloidal crystal, a full band gap may not be attained, no matter how high the refractive index contrast.[4] Since a simple colloidal crystal is unable to form a complete band gap, researchers have focused on creating more complex structures to attempt to create a complete photonic band gap. One approach is to form binary colloidal crystals made up of two different-sized particles.[5] Another approach is to use the colloidal crystal as a template for creating an "inverse opal" structure in which the air voids within a colloidal crystal are filled and then the colloidal particles are removed, leaving spherical hexagonally close packed holes in a solid matrix.[6] The inverse opal structure has been shown to yield a complete photonic band gap.[3] Yet another approach is to form colloidal crystals from core-shell structured particles.[7] Theoretical predictions indicate that colloidal crystals of some types of core-shell particles should exhibit a full photonic band gap.[8]

In the present study, core-shell structured particles were formed using electrostatic layer-by-layer self-assembly as depicted in Fig. 97.32. In the layer-by-layer technique, coatings of polyelectrolytes with alternating charges are deposited onto colloidal particles through electrostatic attraction.[9] In addition to polyelectrolytes, other charged species may be deposited during the coating process, including proteins and luminescent nanoparticles.[10] The thickness of the polyelectrolyte shell surrounding the particle may be adjusted by the number of layers deposited. Each layer deposited is typically of the order of 1 nm thick. Layer-by-layer self-assembly is a simple, versatile technique for controlling size and composition of colloidal particles with nanometer-scale precision. Typically, only a small fraction of the ionic groups in the

polyelectrolytes are neutralized during deposition. After coating, therefore, ionic species such as organic dyes or fluorophores may be immobilized in the shell via ion exchange with the polyelectrolyte counterions. By introducing luminescent or high-refractive-index species in the shell surrounding the particles, the technique offers potential as a simple route for creating optically modified particles that may be used to create photonic crystals with enhanced properties.

A variety of techniques may be employed to crystallize electrostatically charged colloidal particles. The simplest technique is simple evaporation of a few drops of an aqueous colloid on a clean, flat surface. If the surface has the same electrostatic charge as the suspended particles, opalescent colloidal crystals will form as the water evaporates. At room temperature, complete drying occurs in a few hours. Crystals are generally deposited on the outer fringes of where the droplets were placed on the surface, similar to "coffee ring" formation. While simple evaporation provides a relatively rapid route to crystallization, crystal quality is usually poor with small domain sizes. Also, it is not possible to control crystal area and thickness to obtain a uniform crystalline film over a large area of the surface.

If the liquid interface is moved across the surface at a constant velocity while evaporating, a colloidal crystal can be deposited as a uniform thin film. Colvin *et al.*[11] demonstrated that a uniform crystalline film can be deposited as a liquid interface moves down a solid surface, referred to as "vertical deposition." The technique involves placing a clean glass slide oriented perpendicular to the liquid surface of the colloidal suspension so that the glass is partially submerged. As the solvent evaporates, a crystalline deposit forms where the meniscus meets the slide surface. A thin crystal film forms over a large area of the slide surface as the meniscus slowly moves downward due to solvent evaporation. Vertical deposition was first reported for colloidal silica suspended in ethanol and is effective because of the relatively rapid rate of evaporation of ethanol. For aqueous colloids, vertical deposition is also effective, but the lower rate of evaporation makes the time required prohibitively long. Fujishima *et al.*[12] recently modified the vertical deposition technique by slowly lifting the glass slide from the colloidal suspension, as shown in Fig. 97.33. By lifting, aqueous colloids can be crystallized more rapidly than in the case where the meniscus moves
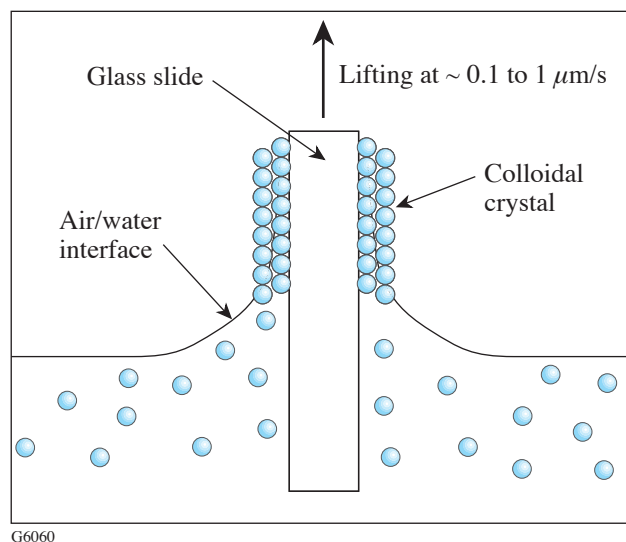

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Figure 97.33
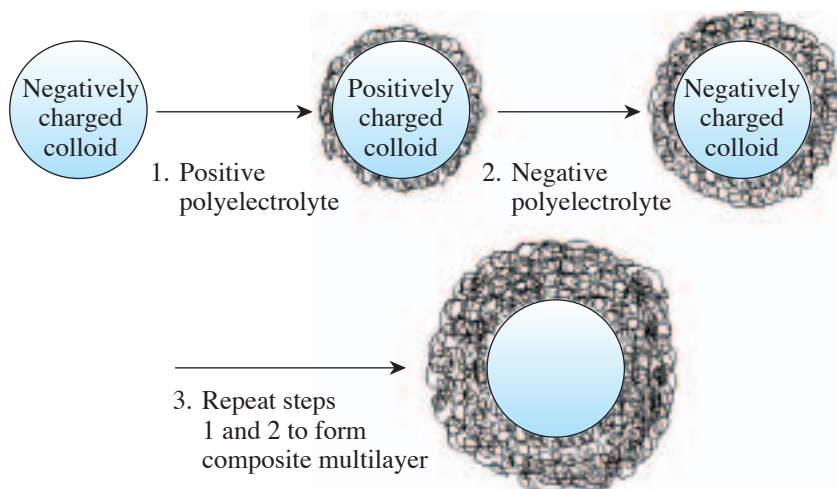Vertical deposition technique for colloidal crystallization.

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Figure 97.32
Layer-by-layer electrostatic self-assembly technique for coating colloidal particles with polyelectrolytes. The technique may also be employed to coat particles with a variety of electrostatically charged species including nanoparticles and proteins. After shell formation, charged species may be immobilized through ion exchange with the polyelectrolyte counterions.

downward by solvent evaporation. In addition, the thickness of the crystal may be adjusted by varying the lifting velocity, with thinner crystals forming with higher lifting velocity. Fujishima's technique was used in the present study to crystallize core-shell structured particles.

Experimental

Monodisperse-sized polystyrene particles (640 and 270 nm in diameter) were purchased from Microparticles GmbH Berlin, Germany. Poly(sodium 4-styrene sulfonate) (PSS, MW = 70,000 g/mol), poly(allylamine hydrochloride) (PAH, MW = 15,000 g/mol), sodium chloride (NaCl, 99%), hydrogen peroxide (30% aqueous solution), and ammonium hydroxide (28% aqueous solution) were purchased from Sigma-Aldrich and used as received. Glass microscope slides (Fisher Scientific) were cleaned prior to use by heating at 70°C for 15 min in a solution of hydrogen peroxide, ammonium hydroxide, and deionized water in a ratio of 1:1:5, respectively, by volume. After cleaning, microscope slides were stored under deionized water until used. Particles were crystallized through vertical deposition from an ~1-wt% colloidal suspension by lifting a clean glass slide at a velocity of 0.15 μm/s.

Findings

1. Crystallization of Uncoated Colloidal Particles

Vertical deposition of 270-nm-diam polystyrene particles produced the crystals shown in Fig. 97.34. Figure 97.34(a) is a high-magnification image (1-μm bar) showing hexagonal packing and long-range order of the crystal on the surface. The crystal quality is very good, although there are some faults and

dislocations in the structure. In addition, there are periodically cracks in the crystal due to contraction of the crystal upon drying. Figure 97.34(b) is a low-magnification image (10-μm bar) of the same sample showing drying cracks in the crystalline film. It was not possible to eliminate drying cracks in the sample. Overall, however, vertical deposition produces the highest-quality crystals of the techniques investigated. A crystalline film covering a 1-cm^2 area can be formed rapidly (in approximately 12 h), and several crystals can be formed in parallel. In addition, the optical properties of the crystals can be studied using standard reflectance or transmission spectroscopy since the crystals form in a thin film on a microscope slide. Vertical deposition with controlled lifting was used exclusively for crystallization of coated colloidal particles because of the numerous advantages of the technique over the others that were studied.

2. Crystallization of Coated Colloidal Particles

Initial coating experiments were conducted using 640-nm-diam polystyrene colloids that had sulfate groups on their surface. These negatively charged particles were coated with alternating PAH/PSS layers using an established procedure from the literature.[7] The coating procedure has been optimized for particles near 640 nm in diameter. Briefly, each polyelectrolyte layer was deposited from an aqueous solution containing 1 mg/mL of polyelectrolyte and 0.25 M of NaCl. The high salt concentration has been shown to produce thicker polyelectrolyte layers by screening electrostatic repulsion in the polyelectrolyte chain to allow a more-coiled polymer conformation. After each coating step, the particles were washed three times
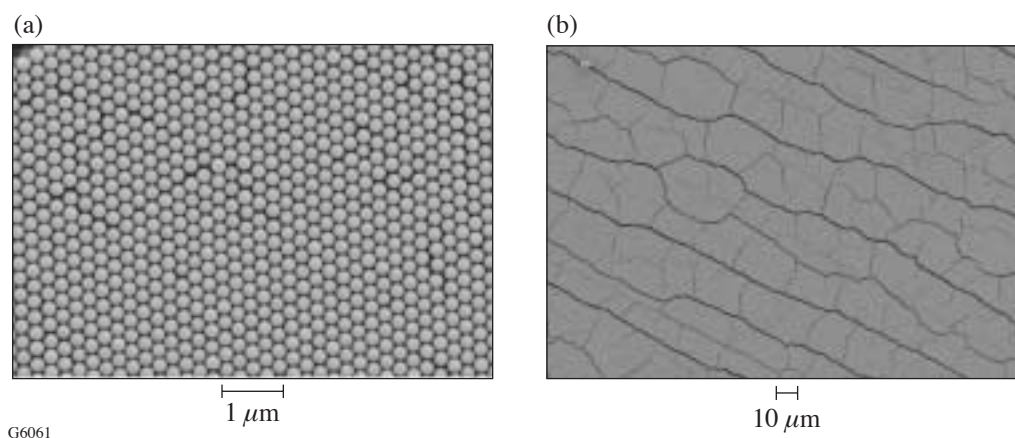

(a)

(b)

1 μm

10 μm

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Figure 97.34
Crystals of uncoated polystyrene colloids (270-nm diam) formed through vertical deposition. (a) A high-magnification image (1-μm bar) shows the hexagonal packing and long-range order of the crystal. (b) A low-magnification view (10-μm bar) of the same sample shows drying cracks in the crystalline film.

with pure deionized water using repeated centrifugation/redispersion steps prior to coating the next layer. Particles coated in this manner had minimal aggregation and could be crystallized rapidly by placing a few drops of an ~1-wt% suspension onto a clean glass slide and allowing it to evaporate as reported by Liang.[7] While crystal formation is rapid, the crystal area is small and difficult to control, as discussed above. We focused on vertical deposition to create high-quality crystals from coated colloids over a large surface area.

The position of the photonic band gap is at a wavelength equal to roughly twice the diameter of the particles making up the crystal, which, for 640-nm-diam particles, places the band gap in the near-infrared region. Our interest is in creating photonic crystals with band gaps in the visible-light wavelength range (~400 to 700 nm). Therefore, we began investigating methods to coat and crystallize smaller 270-nm-diam particles. An initial attempt at coating these smaller particles was made using the same coating procedure that had been effective for 640-nm-diam particles. It was found, however, that gross aggregation of the particles occurred after the first layer was deposited. The particles were very difficult to redisperse after centrifugation. Aggregation could be minimized by placing the particles into an ultrasonic cleaning bath to disperse. Once dispersed, the particles were centrifuged slowly for several minutes to sediment aggregated particles. The aggregated particles were redispersed by the ultrasonic cleaning bath. This sedimentation/redispersion process was repeated several times to minimize aggregation of particles; however, aggregation could not be completely eliminated.

In the first attempts to crystallize the coated 270-nm particles via vertical deposition, nothing was deposited onto the glass surface because of slow flocculation of the particles. It was postulated that some rearrangement of the polyelectrolyte multilayers was occurring and leading to flocculation. If the polyelectrolytes rearrange so that portions of the oppositely charged layer beneath the outermost layer are exposed, this will lead to patches of both positive and negative electrostatic charge on the particle surface. Flocculation will then occur via electrostatic attraction between particles. To maintain electrostatic repulsion, the coated particles were kept in a dilute solution (0.1 mg/mL) of polyelectrolyte with the same charge as the outermost layer on the particle surface. If any oppositely charged patch is exposed, the free polyelectrolyte in solution around the particles can adsorb to cover it more rapidly than a charged particle will attach via flocculation. The stability of the particles was greatly enhanced by the small excess polyelectrolyte. In pure water, the 270-nm-diam polyelectrolyte-coated polystyrene particles flocculated and sedimented in less than one day. In 0.1-mg/mL polelectrolyte solution, there was no visible flocculation of the particles even after two weeks.

The PAH/PSS-coated, 270-nm polystyrene particles were crystallized via vertical deposition from an ~1-wt% aqueous suspension (containing 0.1 mg/mL of PSS for maintaining colloidal stability). Figure 97.35 shows scanning-electron-microscopy images of the crystalline deposit. Figure 97.35(a) is the deposit formed by particles coated with two polyelectrolyte layers. By comparison with crystals of uncoated particles (Fig. 97.34), it can be seen that the coated particles produce a much-lower-quality crystal. Hexagonal packing is present, but there are many areas where the crystal structure is disrupted. Figure 97.35(b) shows the deposit formed from particles
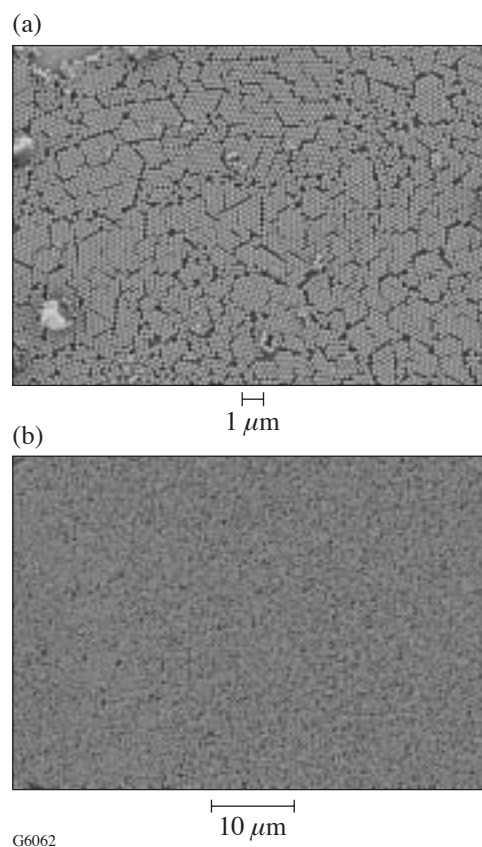
(a)

1 μm

(b)

10 μm

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Figure 97.35
Crystals of 270-nm-diam polystyrene particles coated using the "standard" coating procedure with 0.25-M NaCl concentration. (a) Particles coated with two polyelectrolyte layers (1-μm bar). Some hexagonal packing is observed, but crystal quality is poor. (b) Particles coated with four alternating polyelectrolyte layers (10-μm bar). Crystallization is completely disrupted due to aggregation of the particles during the coating process.

coated with four alternating PAH/PSS layers. After four coating layers, the crystal structure is completely disrupted. The coating process introduces aggregation of the particles, and aggregation increases after each layer is coated. The procedure developed for coating 640-nm particles is clearly not as effective for coating the smaller 270-nm particles.

A greatly improved coating procedure was developed following modifications suggested recently by Gittins.[13] In Gittins' study, gold nanoparticles as small as 11-nm diameter were coated with polyelectrolyte layers without inducing particle aggregation. It was reported that much-lower salt concentration (1 mM) was required to prevent aggregation of the particles. It is well known that salt reduces electrical double-layer repulsion between particles. By lowering the salt concentration, electrostatic repulsion could be maintained while coating the particles. The same approach was applied for coating 270-nm polystyrene colloids. The particles were coated with alternating layers of PAH and PSS using solutions containing 1 mg/mL of polyelectrolyte and 1 mM of NaCl (instead of 0.25 M of NaCl). With the lower salt concentration, the aggregation of particles was greatly reduced. Upon centrifugation of the coated particles, the sediment appeared opalescent, indicating crystal formation. The crystal formation in the sediment also suggested there was very little particle aggregation and strong electrostatic repulsion was being maintained throughout the coating process.

To test if the new procedure was coating the particles as expected, the zeta potential was measured after each layer was deposited. Figure 97.36 shows the zeta potential results. The zeta potential is related to the surface charge of the particles.
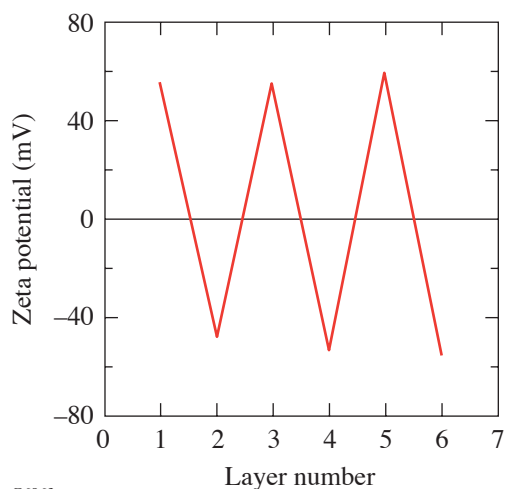
The sign of the zeta potential alternates from positive to negative as expected when the alternating polyelectrolyte layers are deposited. The high magnitude of the zeta potential (>40 mV for every layer) indicates that good colloidal stability is maintained. Unfortunately, we could not measure the growth of the polyelectrolyte layers using single-particle light scattering because the particles are too small for accurate measurement. We can infer, however, that the polyelectrolytes are being deposited from the zeta potential measurements.

The particles coated using the improved procedure were crystallized through vertical deposition from an ~1-wt% aqueous colloidal suspension (containing 0.1 mg/mL of PSS). Figure 97.37 shows the crystalline deposit formed by particles coated with two polyelectrolyte layers. The image shown in Fig. 97.37(a) depicts a broken section of the crystalline film, showing that it is approximately ten particle layers thick. The image shown in Fig. 97.37(b) depicts the hexagonal packing and long-range order of the crystal. There are numerous drying cracks present, but overall crystal quality is very good. The quality of the crystals formed from the two-layer–coated, 270-nm particles is very nearly the same as that for the uncoated particles (shown in Fig. 97.34).

Figures 97.38(a) and 97.38(b) show crystals of particles coated with four and six alternating polyelectrolyte layers, respectively. The particles coated with four polyelectrolyte layers produce very good crystals. There are drying cracks where the crystal has contracted, but the overall packing of the crystal is good. There are some areas where the crystal structure is disrupted. Particles coated with six polyelectrolyte layers produce noticeably poorer-quality crystals [Fig. 97.38(b)].

Figure 97.36
Zeta potential of 270-nm-diam polystyrene particles as a function of layer number during layer-by-layer deposition of PAH/PSS with improved coating procedure. The polyelectrolytes were deposited from a 1-mg/mL solution containing 1 mM of NaCl. Layer 1 is PAH (positive), layer 2 is PSS (negative), and additional layers are deposited with an alternating polyelectrolyte charge. The alternating sign of the zeta potential implies that the polyelectrolytes are adsorbing onto the particles via electrostatic attraction.

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There are regions where the particles are randomly oriented, probably due to aggregation during the coating process. Since the crystal quality degrades as a function of number of layers coated, it can be inferred that some small amount of particle aggregation occurs during the coating process. Each layer applied leads to additional aggregation and further reduction in crystal quality.

The photonic band gap of the crystals was probed with reflectance spectroscopy as shown in Fig. 97.39. The peak reflectance located near 575 nm is due to the photonic band gap. The band gap causes the crystals to appear green in color. The most-prominent feature of the reflectance spectra of the samples is the decrease in band-gap intensity with an increasing number of polyelectrolyte layers coating the particles. The
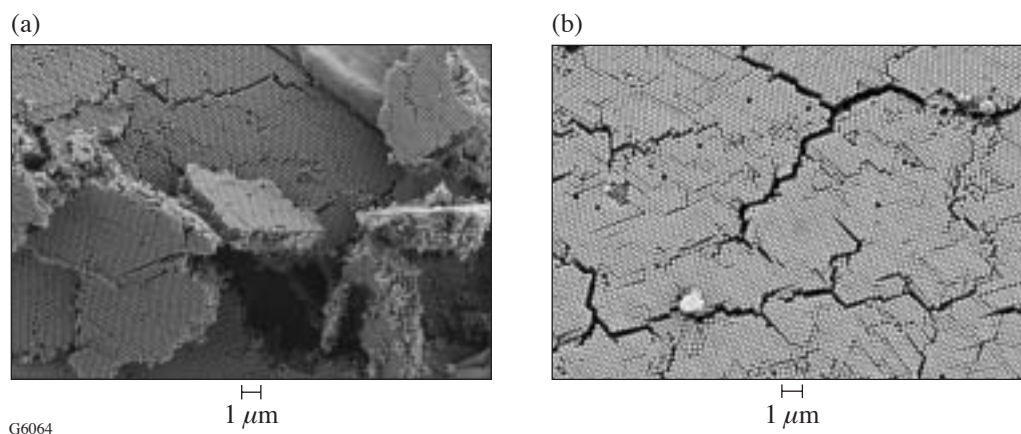
(a)

(b)

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1 μm   1 μm

Figure 97.37
Crystals of 270-nm-diam polystyrene particles coated with two polyelectrolyte layers using the improved coating procedure. (a) Image of a broken section of the film showing the crystal thickness (1-μm bar). (b) Surface of the crystal showing the long-range-hexagonal, close-packed structure with drying cracks visible (1-μm bar).
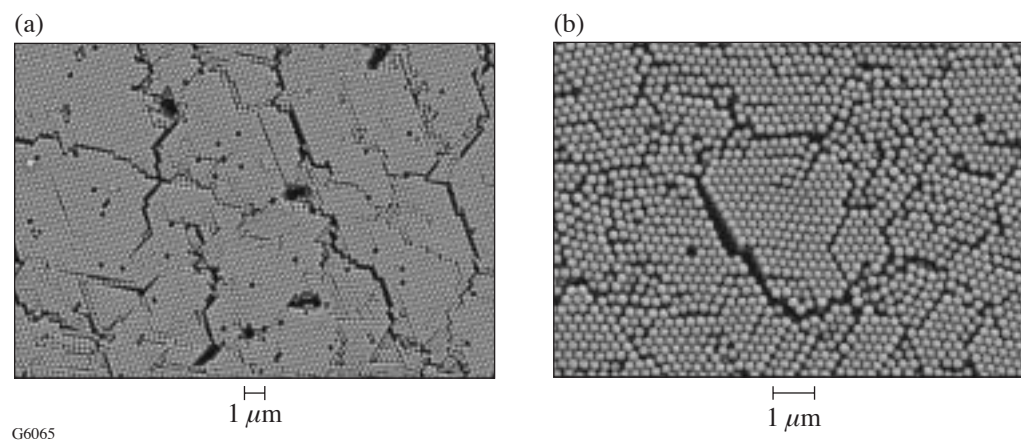
(a)

(b)

G6065

1 μm   1 μm

Figure 97.38
Crystals of 270-nm-diam polystyrene particles coated with (a) four alternating PAH/PSS layers (1-μm bar) and (b) six alternating PAH/PSS layers (1-μm bar). As the number of polyelectrolyte layers increases, the crystal quality decreases. In image (b), regions of randomly aggregated particles are visible.

intensity decreases and the width of the band gap increases due to poorer crystal quality. The optical data in Fig. 97.39 confirm the observation in Figs. 97.37 and 97.38 that crystal quality decreases with an increasing number of polyelectrolyte layers. Even with the improved coating technique, a small amount of particle aggregation occurs during each coating. Particles coated with two polyelectrolyte layers produce crystals nearly as high in quality as the uncoated particles. High-quality crystals are obtainable with up to four polyelectrolyte coatings, but poorer quality is produced with six-layer–coated particles.
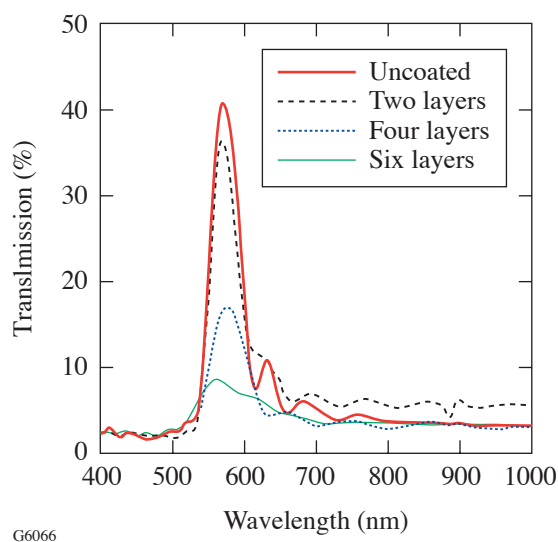

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Figure 97.39
Reflectance spectra of colloidal crystals in Figs. 97.34, 97.37, and 97.38 taken at a 6° angle. The crystals have a pseudophotonic band-gap reflectance peak located at ~575 nm, which visually gives them a green appearance. The peak height and sharpness decrease with an increasing number of polyelectrolyte layers coating the particles because of poorer crystal quality. The decrease in crystal quality is most likely due to a small amount of particle aggregation in each coating step.

It is notable that the band gap does not significantly shift position when coated. Since the position of the band gap is related to the particle diameter, one would expect a shift to longer wavelengths as the particle diameter becomes larger due to deposition of polyelectrolytes. The band gap of the sample coated with two layers is actually slightly shifted to shorter wavelengths. It is unclear at this point why the blue shift occurs. The band gap is slightly shifted to longer wavelengths for the crystals formed with particles coated with four layers. Further coating broadens and weakens the peak so that

the shift is not discernible. It is known that salt increases the thickness of the polyelectrolyte layers during deposition. Since our improved coating process uses less salt, we expect the thickness to be small; unfortunately, we were unable to actually measure the layer thickness. The small layer thickness would cause the band gap to shift only slightly. Coupled with a blue shift, the net effect is that the band gap stays in nearly the same position. Further work is needed to fully understand the optical properties.

Conclusions and Future Directions

We have demonstrated that high-quality crystals of polyelectrolyte-coated particles may be formed by vertical deposition. The colloidal crystals display preferential reflection of light due to the pseudo band gap of the crystal. The crystal quality degrades with the number of polyelectrolyte layers coated on the particles. It is postulated that there is slight particle aggregation during the coating process that disrupts crystallization. The crystal degradation is apparent from the reduction in the maximum intensity of reflected light. Particles coated with two polyelectrolyte layers have a maximum intensity of reflectance nearly the same as the uncoated particles. The reflectance intensity decreases for particles coated with four layers, and there is almost no reflectance for particles coated with six layers. Further work is needed to completely eliminate particle aggregation during the particle-coating process.

The polyelectrolyte-coated particles offer intriguing possibilities for controlling and enhancing the optical properties of the colloidal crystals. The polyelectrolyte shells surrounding the particles have a high number of free ionic groups. A variety of optically active species may be immobilized in the shell through ion exchange. For example, ionic fluorophores may be immobilized in the polyelectrolyte shell by simply dispersing the particles in an aqueous solution of the dye.[14] In addition, optically active species, including fluorescent quantum dots, may be introduced into the shells during the coating process.[15,16] It should be possible to enhance the band gap by choosing a dye that adsorbs near the band-gap maxima. In addition, it should be possible to choose luminescent compounds that emit light at a wavelength near the photonic-band-gap maxima. It has been shown recently that lasing from colloidal crystals is possible when a dye that emits in the band-gap wavelength is incorporated into the structure.[17]

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