Slow Vertical Deposition of Colloidal Crystals: A Langmuir–Blodgett Process?

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Received January 28, 2006. In Final Form: May 8, 2006

For an evaporating colloidal suspension in which the evaporation velocity exceeds the sedimentation velocity, particles will accumulate at the solvent–air interface. If neither diffusion nor convection can disperse this accumulation, it is expected to grow into a colloidal multilayer several microns thick. We observe that the thickness of colloidal crystals vertically deposited from 1 μm diameter polystyrene latex suspensions of 0.002 ≤ φ ≤ 0.008 increases linearly with distance in the growth direction and that these thickness profiles are consistent with their growth from a horizontal colloidal layer accumulated beneath the solvent–air interface. We describe a means for performing vertical deposition at growth rates slower than the evaporation rate by adding solvent to the bottom of the colloidal suspension and observe that halving the growth rate of vertical deposition increases both the thickness and the reflectivity of the resulting colloidal crystals, effects indistinguishable from those of doubling the concentration of the colloidal suspension, data also consistent with the colloidal crystals’ growth from a horizontal layer of particles beneath the interface. If sufficiently little reorganization is involved as particles move from this horizontal layer to the vertically deposited colloidal crystal, slow vertical deposition of polymer microspheres might be thought of as the Langmuir—Blodgett transfer of a horizontal colloidal crystal onto a vertical substrate. Colloidal crystals deposited using both high concentration and slowed growth can have peak IR reflectance in excess of 80%, exceeding most published values. These observations provide a conceptual framework for engineering vertically deposited colloidal crystals that combine thickness with good optical performance.

Introduction

Of the various methods found in the literature for preparing colloidal crystals,1–16 the vertical deposition method introduced by Colvin and co-workers1 has gained considerable attention. It requires no special equipment or training, is not laborious, and reproducibly yields dry crystalline colloidal multilayers with few defects beyond cracks formed upon drying. In some cases, even this cracking can be prevented.11

Many researchers have undertaken to identify the conditions that lead to optimal quality in vertically deposited colloidal crystals. Higher crystalline quality has been reported for low solvent surface tension and low ionic strength,12 high substrate wettability,13 chemical or thermal modification of the particles,11,14 and oscillatory motion in the meniscus,15 and deposition on a tilted substrate.16 For deposition from water, multiple researchers have reported an optimal temperature in the range 55−65 °C17–19 and an optimal concentration of the colloidal suspension,13,17,19 unfortunately, for two quantitative independent variables readily controlled by the experimenter, particle concentration and relative humidity, the literature contains conflicting reports. In one report, the best colloidal crystals were prepared at low (0.1−0.2%) particle volume fraction and high (80−90%) relative humidity.18 These results can be rationalized in terms of the conventional wisdom that crystal quality suffers when a high deposition rate gives self-assembly insufficient time to work.13,17,18 Other researchers, using domain size as their quality metric, produced their best crystals at low (10−20%) relative humidity19 and higher (>1%) particle volume fractions,20 and researchers who have accelerated evaporation using a dry external airstream5,21 have reported no deleterious effect on quality. If, as suggested by Norris and co-workers,22 opaline self-assembly at an air−liquid interface is a hydrodynamic phenomenon, then a greater flow of solvent through the forming crystal may be expected to improve crystal quality.

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2 Davis, K. E.; Russel, W. B.; Glansschnig, W. J. Science 1989, 245, 507−510.
To decouple the colloidal crystal growth rate from the evaporation rate, we have developed an apparatus wherein solvent is infused into the bottom of the colloidal suspension while deposition takes place, allowing us to explore conditions where the growth velocity, the rate at which the length of the colloidal crystal grows, is slower than the evaporation velocity, the rate at which the solvent-air interface drops when no additional solvent is infused into the suspension. This approach is complementary to those that accelerate growth by withdrawing the substrate from the suspension or withdrawing the solvent from the substrate. We have found that slowing colloidal crystal growth in this manner increases both the thickness and reflectivity of the colloidal crystal and that the effects of slowing growth by solvent infusion are indistinguishable from those deposited on substrates cleaned in H2O2/H2SO4 (piranha) solution. Our experience is that opals deposited in plastic vials have stronger adsorbed to it by interfacial forces. The change in thickness of the colloidal crystal, where the evaporation rate generally exceeds the sedimentation velocity due to the small density difference between the latex particles and the solvent, the vertically deposited colloidal crystal grows from a horizontal colloidal multilayer that has assembled beneath the solvent, the vertically deposited colloidal crystal grows from a horizontal colloidal multilayer that has assembled beneath the solvent—air interface. Particles may be transferred from this concentrated layer into the growing colloidal crystal with significant rearrangement, or this interfacial layer may be transferred to the substrate largely intact, by a mechanism similar to Langmuir—Blodgett (LB) transfer.

**Experimental Section**

**Preparation of Colloidal Crystals.** Sulfate polystyrene microspheres with a diameter of 1.0 μm (batch no. 2293; CV 4.2%) were purchased from the Interfacial Dynamics Corporation (Eugene, Oregon). These were diluted to the desired concentration with deionized water, and 6 mL of the dilute colloidal suspension was placed in a low-density polyethylene vial, internal diameter 22 mm, total capacity 12 mL (Nalge Nunc International). A glass substrate, 17 mm wide, was cut from a microscope slide (Corning 2947), cleaned by immersion for 5 min in 5% aqueous HF (Caution: HF is highly toxic, and both skin contact and inhalation of its fumes must be strictly prevented.), thoroughly rinsed in deionized water, wicked dry by placing its bottom edge against a Kim-wipe, and then placed vertically in the colloidal suspension, as close to the vial perimeter as its width would permit. We observed no difference between colloidal crystals deposited on HF-cleaned substrates and those deposited on substrates cleaned in H2O2/H2SO4 (piranha) solution. Our experience is that opals deposited in plastic vials have more reproducible thickness and reflectance profiles than do those deposited in glass vials, and we recommend the use of nonwetting templates to prepare free-standing inverse opals. Such colloidal crystals are not single-crystalline but can be formed over large areas and from very large (>100 μm) particles and used as templates to prepare free-standing inverse opals. For an evaporating colloidal suspension in which the evaporation velocity exceeds the sedimentation velocity, as evaporation progresses, the concentration of particles at and near the interface increases.

The first particles to encounter the falling interface become strongly adsorbed to it by interfacial forces. The change in thickness of the colloidal crystal, where the evaporation rate generally exceeds the sedimentation velocity due to the small density difference between the latex particles and the solvent, the vertically deposited colloidal crystal grows from a horizontal colloidal multilayer that has assembled beneath the solvent—air interface. Such colloidal crystals are not single-crystalline but can be formed over large areas and from very large (>100 μm) particles and used as templates to prepare free-standing inverse opals. For an evaporating colloidal suspension in which the evaporation velocity exceeds the sedimentation velocity, as evaporation progresses, the concentration of particles at and near the interface increases.

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interfacial energy for adsorbing a spherical particle from the bulk of a colloidal suspension to the interface is

\[ -\Delta E_{\text{ads}} = \pi R^2 \gamma (1 - \cos \theta)^2 \]  

(1)

where \( R \) is the particle radius, \( \gamma \) the solvent surface tension, and \( \theta \) the contact angle at the solvent–particle interface. The contact angle of water on sulfate polystyrene microspheres such as those used in this work has been measured using gel trapping; the reported angle is \( 73 \pm 4^\circ \).

Thus, our 1 \( \mu m \) polystyrene microspheres adsorb to the water–air interface with an energy of some \( 10^2 k_B T \). As the concentration of particles thus effectively confined to two dimensions increases, lateral capillary immersion forces assemble them into a hexagonally ordered monolayer.

Parks has proposed that the monolayer thus assembled dewets, becoming less dense than water as its interstitial space fills with air and that it then rises above the interface due to its buoyancy, leaving room for the same capillary forces to assemble a second layer beneath it, and so on. However, for micron-sized latex particles, the interfacial forces opposing the exposure of additional polystyrene–air interface are several orders of magnitude stronger than the proposed buoyant force that could lift the assembled particles above the water–air interface. On this consideration, in the formation of an ordered colloidal multilayer at the water–air interface, the topmost layer must remain confined at the interface, whereas the lower layers must remain beneath the interface, and a mechanism other than lateral capillary immersion forces must order these lower layers.

The concentration of particles beneath a falling interface is conceptually similar to their sedimentation onto a surface, and the analytical apparatus developed for that problem may be applied to this one. As particles accumulate beneath the interface, their concentration profile is determined by the balance between the gravitational and osmotic forces pushing the particles away from the interface and the viscous force resisting that motion. In a one-dimensional reference frame, with the origin located at the interface, moving toward the bottom of the container with constant velocity \( u_c \) and the \( x \) axis pointing toward the bottom of the container, the dimensionless conservation equation describing this process is

\[ \frac{\partial q}{\partial t} = \frac{\partial q}{\partial x} \left( \frac{u_c}{u_e} \frac{\partial}{\partial x} \left[ qK(q) \right] + \frac{D_0}{h u_e} \frac{\partial}{\partial x} \left[ qZ(q) \frac{\partial q}{\partial x} \right] \right) \]  

(2)

where \( q \) is the particle volume fraction, \( u_c \) and \( u_e \) are respectively the evaporation and sedimentation velocities, \( h \) is the initial height of the colloidal suspension, \( D_0 \) is the Stokes–Einstein diffusion coefficient, \( K(q) \) is the sedimentation coefficient, and \( Z(q) \) is the compressibility factor for the particular colloidal system; \( t \) is dimensionless time, \( t = tu_c/h \), and \( x \) is dimensionless distance, \( \bar{x} = x/h \). The quantity \( hu_e/D_0 \) is an evaporative Peclet number, comparing the power of evaporation to concentrate particles beneath the interface with that of Brownian motion to disperse them. For a 1.5-cm deep suspension of 1 \( \mu m \) polystyrene microspheres in water at 45 \(^\circ\)C, at the measured evaporation velocity of 0.2 \( \mu m/s \), this Peclet number is \( \approx 3850 \), indicating that the microspheres cannot diffuse away from the interface fast enough to prevent their effective concentration.

When the microspheres just beneath the interface become sufficiently concentrated \( (q \geq 0.50 \text{ for hard spheres}) \), it becomes thermodynamically favorable for them to order, while the ordered monolayer at the interface and the flow of solvent through the pores in that monolayer provide a template and driving force for them to assemble into a colloidal crystal with long range order.

Figure 2 shows the evolution of the concentration gradient beneath a falling interface, computed by numerical integration of eq 2, using an initial volume fraction \( q_0 = 0.008 \), \( u_c = 0.2 \mu m/s \), \( u_e = 0.045 \mu m/s \), zero-flux boundary conditions, and values suitable for 1 \( \mu m \) diameter polystyrene microspheres in water at moderate ionic strength: \( D_0 = 7.8 \times 10^{-9} \text{cm}^2/\text{s} \); \( K(q) = (1 - q)^{3.4} \), which is empirically suitable for aqueous polystyrene latex at 1 \( mM \) ionic strength; \( Z(q) = (1 + q + q^2 - 3q)/((1 - q)^4) \) for the fluid phase \( (q \leq 0.494) \); \( Z(q) = 2.22(0.74 - q) \) for the crystalline phase \( (q \geq 0.545) \); and the assumption that in the range \( 0.494 < q < 0.545 \) the ordered and disordered phases coexist.

Under the assumptions of this computation, evaporation of the upper millimeter of the colloidal suspension produces a 4 \( \mu m \) thick, nearly close-packed colloidal crystal at the water–air interface, with a “fan” of decreasing particle volume fraction extending another \( \approx 25 \mu m \) into the suspension. With further evaporation, the thickness of the close-packed crystal increases linearly with time, whereas the shape and thickness of the fan remain unchanged.

This process of concentration beneath a falling ordered monolayer is similar to sedimentation onto a templated substrate but gives a more compact deposit for a given Peclet number. The enhancement of viscous drag at high particle volume fractions, represented in eq 2 by \( K(q) \), hinders sedimentation, but because solvent continues to evaporate through the concentrated layer, it assists concentration beneath a falling interface. Concentration beneath a falling interface may also be expected to give a more orderly colloidal crystal than sedimentation: as observed by Norris and co-workers, the flow of fluid through an ordered particle array at least a bilayer thick creates a hydrodynamic driving force (in addition to the relatively weak thermodynamic one) for preferring ABC over ABA stacking and may explain the low incidence of stacking faults found in colloidal crystals prepared by vertical deposition compared to those prepared by sedimentation.

**Colloidal Crystal Thickness.** Vertically deposited colloidal crystals grow from polymer latexes increase in thickness with distance in the growth direction. Thickness measurements with high spatial resolution permit the quantification of this thickness profile. Figure 3 shows the thickness profiles of colloidal crystals deposited from 1 \( \mu m \) polystyrene latex suspensions of

\[ \text{(39) Russel, W. B.; Saville, D. A.; Schowalter, W. R. Colloidal Dispersions; Cambridge University Press: New York, 1989.} \]

\[ \text{(41) Carnahan, N. F.; Starling, K. E. J. Chem. Phys. 1969, 51, 635–636.} \]
\[ \text{(42) Cong, H.; Cao, W. Langmuir 2003, 19, 8177–8181.} \]
in a moving fluid to the velocity of that fluid, which approaches

\[ \frac{\beta \mu_e \varphi}{(1 - \epsilon)} \]  

where \( \beta \) is the ratio of the mean velocity of the particles suspended in a moving fluid to the velocity of that fluid, which approaches unity for dilute suspensions of weakly interacting particles, \( L \) an experimentally determined evaporation length, typically a few hundred \( \mu m \), \( \epsilon \) the porosity of the assembled spheres, and \( u_g \) the growth velocity.

The experimental conditions used by many previous researchers prevent the formation of a concentrated layer beneath the interface. Clearly, the use of low concentrations, more rapidly settling silica colloids,\(^1\)\(^4\),\(^4\)\(^4\)\(^4\) accelerating deposition through dip-coating\(^2\)\(^3\)\(^3\),\(^3\) or solvent withdrawal,\(^2\)\(^4\)\(^5\) agitation of the meniscus,\(^1\)\(^5\) and convective mixing in the colloidal suspension\(^3\)\(^3\)\(^3\) all work against the concentration of colloids beneath the falling interface. Under such conditions, previous researchers have applied eq 3 to vertical deposition, using the bulk volume fraction for \( \varphi \), assuming that the particle-to-solvent velocity ratio \( \beta \) is unity, using an experimentally determined constant for the evaporation length \( L \), and generally observing good agreement with experimental data.

However, under conditions where particles have become concentrated beneath the falling interface, these values for the terms of eq 3 seem inappropriate. The volume fraction near the interface is much greater than the bulk volume fraction; and in the concentrated layer beneath the interface, where osmotic and gravitational forces balance viscous forces, \( \beta \) should be less than one. Nor is there any a priori reason to suppose that the evaporation length \( L \) remains constant while conditions within the meniscus change dramatically. At any rate, the use of these values for the terms of eq 3 does not predict the linear colloidal crystal thickness profiles seen in Figure 3, for opals deposited under conditions where a concentrated colloidal layer may be expected to form beneath the solvent-air interface.

For conditions where a concentrated colloidal layer has formed beneath the solvent-air interface, near the interface, the particle volume fraction \( \varphi = 1 - \epsilon \), assuming a similar volume fraction for the particles concentrated just beneath the solvent-air interface and those deposited on the substrate. Further, if the concentrated particles near the interface resist being entrained by the evaporative flow of solvent, so that they move upward (with respect to the falling interface) no faster than the growth velocity \( u_g \), then under these conditions the particle-to-solvent velocity ratio \( \beta = \epsilon u_e / u_g \). Substitution of these terms into eq 3 leaves only \( h = L \); when a concentrated colloidal layer has formed beneath the interface, the thickness of the opal deposited by vertical deposition is equal to the evaporation length.

The linear colloidal crystal thickness profile seen in Figure 3 may be obtained by supposing that when a concentrated colloidal layer has formed beneath the solvent-air interface, the evaporation length, and so also the thickness of the deposited colloidal crystal, is equal to the thickness of the concentrated layer beneath the interface

\[ h = L = \frac{\varphi_0}{1 - \epsilon} t(u_e - u_g) \]  

where \( \varphi_0 \) is the initial particle volume fraction and \( t \) is the elapsed time. As a test of this supposition, eq 4 predicts that if the growth velocity is halved by infusing fresh solvent into the bottom of the deposition cell at half the evaporation rate, the slope of the linear thickness profile will be doubled, because at any given distance in the growth direction, the suspension will have been

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evaporating twice as long and will have accumulated a concentrated interfacial layer twice as thick. (At this flow rate, the flow of additional solvent into the bottom of the cell is too slow to produce significant convective mixing.)

Colloidal crystals were deposited from 1 μm polystyrene latex suspensions of 0.2%, 0.4%, and 0.8% particle volume fraction, using water infusion to halve the growth velocity. Again, three replicate experiments were performed at each concentration. Figure 4 compares the thickness profiles of colloidal crystals prepared at the same bulk concentration, with and without water infusion. We observe that the slope of the thickness profile does increase 2-fold with water infusion.

The thickness of the colloidal crystals prepared with infusion increases linearly with distance in the growth direction, up to a point, and then plateaus. This is to be expected: evaporation concentrates colloids at the interface until the plug of infused solvent reaches the interface. At this point in time, the suspension would have evaporated to dryness without infusion, and the concentration process is essentially complete. Assuming ideal plug flow for the initial volume and evaporation rate used in these experiments, this is expected to occur after ~22 h of evaporation, when the colloidal crystal’s length has grown to 7.8 mm. Insofar as the experiment falls short of perfectly ideal plug flow, the transition from linearly increasing to plateau is broadened, and in fact, the experimental data begin to level off at distances of ~5 mm. For the colloidal crystals prepared using solvent infusion, the lines in Figure 4 are fit to the initial slopes of the thickness profiles, using the data for distance ≤5 mm.

Table 1 presents the slopes of the least-squares linear fits to the data obtained at each concentration, with and without infusion. The thickness profiles of the opals prepared with infusion have initial slopes 1.8, 1.8, and 2.1 times greater than the slopes of the profiles of the opals prepared without infusion at 0.2%, 0.4%, and 0.8%, respectively.

Empirically, the thickness profiles of all of these colloidal crystals, prepared both with and without solvent infusion, cluster around the sum of the zero-time behavior of eq 3, with constant βL and the long-time behavior of eq 4

$$h = \frac{Q_0 \Delta c}{1 - \epsilon} \left[ \frac{\beta L}{(1 - \eta) \mu_g} + \left( \frac{\eta}{\mu_g} - \frac{\eta_s}{\mu_s} \right) \right]$$

Figure 5 plots the measured thickness of the colloidal crystals prepared with and without water infusion against the predictions of eq 5, using 0.4% and 0.8% particle volume fraction, and 500 μm. The only systematic deviation of the experimental data from the predictions of eq 5 is for the colloidal crystals prepared with water infusion at 0.8%, which plateau at 90 μm thickness, due to the completion of the concentration process, as described above.

At times long enough that a colloidal multilayer can be expected to have formed beneath the water–air interface, the thickness of the colloidal crystal deposited through vertical deposition is approximately the instantaneous thickness of the interfacial layer.

This suggests that under these conditions vertical deposition is the transfer of particles from the interfacial layer into the deposited colloidal crystal. One possibility is that the interfacial layer is transferred to the substrate largely intact, in a Langmuir–Blodgett like process. Reculusa and co-workers have in fact reported the deposition of successive colloidal monolayers onto a substrate by the LB technique. Alternatively, others have investigated the role of shear forces and drying forces in improving the order of previously formed colloidal crystals, as they are transferred to a substrate. If these re-ordering mechanisms are sufficiently extensive, then any colloidal crystal formed beneath the horizontal solvent–air interface might be essentially melted and reformed on its way onto the substrate. Which of these descriptions better reflects the vertical deposition process is left as an open question at the present time.

Potential applications in photonic devices is the source of much of the current interest in colloidal crystals. Fabricating a three-dimensional waveguide feature within a photonic crystal, for example by multiphoton polymerization, requires a photonic crystal at least as thick as the feature, and lithographic approaches to fabricating photonic materials become less practical with increasing device thickness. If slow vertical deposition is a Langmuir–Blodgett type process, then a thick colloidal crystal with controlled thickness might be fabricated by preparing an interfacial colloidal crystal of that thickness and then transferring it to a substrate.

**Colloidal Crystal Quality.** Researchers have used various means to judge the quality of colloidal crystals. Optical spectroscopy, domain size, and qualitative inspection of scanning electron micrographs (SEM) are all known in the literature. Because it is useful to have a quantitative quality metric and because colloidal crystals’ potential value as templates for fabricating photonic devices is the basis for much of their current interest, the present work uses peak reflectance at normal incidence as its quality metric.

Figure 6a plots peak reflectance versus distance in the growth direction for colloidal crystals deposited with and without water infusion, at 0.2%. (For analogous plots for other concentrations, see the Supporting Information.) For colloidal crystals deposited from suspensions of the same concentration, those formed using water infusion are more reflective than those formed without.

<table>
<thead>
<tr>
<th>particle volume fraction (%)</th>
<th>infusion rate (μL/min)</th>
<th>thickness profile slope (μm/mm)</th>
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<tr>
<td>0.2</td>
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</tr>
<tr>
<td>0.8</td>
<td>2.3</td>
<td>16.38</td>
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**Table 1. Slopes of Linear Fits to Colloidal Crystal Thickness Profiles**

**Figure 5.** Comparison of measured thicknesses to predictions of eq 5 for colloidal crystals deposited with (filled symbols) and without (open symbols) solvent infusion at 0.2% (squares), 0.4% (circles), and 0.8% (triangles). The solid line is the function y = x.
opals more than 30 layers thick have been found to be optically
is the direct result of increased thickness. However, polystyrene
that result are more reflective. Some of this increase in reflectivity
doubling the thickness of the interfacial layer. The thicker crystals
concentration and waiting twice as long have the same result in
indistinguishable reflectance profiles. What these two conditions
have in common is the thickness of the interfacial colloidal
multilayer from which the colloidal crystal was deposited, at a
given distance in the growth direction. Doubling the bulk
concentration and waiting twice as long have the same result in
doubling the thickness of the interfacial layer. The thicker crystals
that result are more reflective. Some of this increase in reflectivity
is the direct result of increased thickness. However, polystyrene
opals more than 30 layers thick have been found to be optically
thick.53 The trend of increasing reflectivity with increasing
thickness observed in these opals at short distances in the growth
direction extends to even thicker opals; this is most apparent in
the opals deposited at \( q = 0.8 \) vol \%. It appears, then, that at
short distances in the growth direction the thicker opals are more
reflective because they are not only thicker, but also more orderly.

The most reflective locations on these colloidal crystals are
found on the thickest crystals, 1–3 mm from their tops. The positive correlation between thickness and quality in the upper
portions of these colloidal crystals may be understood in terms
of the structure of the interfacial colloidal multilayers from which
they are deposited. A thick crystal grows from a thick interfacial
layer. If slow vertical deposition occurs by the LB-like transfer
of the interfacial layer to the substrate, then order in the deposited
crystal may reflect order in the horizontal colloidal crystal from
which it grew. The large osmotic pressure at the top of a thick
interfacial layer certainly provides an impetus toward close
packing.

At greater distances in the growth direction, the reflectance
of all of the colloidal crystals deteriorates, and the thinner crystals
are more reflective than the thicker ones. We speculate that this
optimal distance of 1–3 mm is related to the similar meniscus
height of water on glass and that, once the water is making an
interface not with glass but with a rough, moderately hydrophobic
polymer layer, the increase in contact angle has a deleterious
effect on self-assembly, especially for thicker crystals.13 Consistent with this hypothesis, other researchers have reported
improvement in the quality of vertically deposited polystyrene
colloidal crystals when the polystyrene is rendered more
hydrophilic by a poly-(hydroxyethyl methacrylate) shell54,55 or
by layer-by-layer deposition of polyelectrolytes.14

All three of the colloidal crystals prepared with water infusion
at 0.8% volume fraction had more than 73% reflectance from
their most reflective regions. The best of these had 82% peak
reflectance. Figure 7a shows these reflectance spectra. SEM of
these highly reflective regions (Figure 7b) shows that what defects
exist in these regions are local defects associated with outliers
in the particle size distribution; extended line defects are rare.
While many of the reflectance spectra already published in the
literature have been in arbitrary units, rendering comparison
difficult, in the authors’ experience this optical performance is
exceptionally good for polystyrene opals on glass substrates (on
silicon wafer substrates, the reflectivity of the polished silicon
wafer contributes to the measured reflectance of the colloidal
crystal, and measured reflectances are generally higher than on
glass). At visible wavelengths, these highly IR-reflective regions
are more translucent than the less IR-reflective regions above
and beneath them; in light of theoretical expectations that a
photonic crystal with little disorder gives little random scattering,
this translucency is additional evidence of a high degree of
order.56,57

\[(54)\] Goldenberg, L. M.; Wagner, J.; Stumpe, J.; Paulike, B.-R.; Görnitz, E.

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\[(56)\] Koenderink, A. F.; Megens, M.; Soest, G. v.; Vos, W. L.; Lagendijk, A.


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(53) Galisteo-López, J. F.; Palacios-Lidón, E.; Castillo-Martínez, E.; López,
Conclusion

Colloidal crystals prepared by vertical deposition of polymer latex particles have linear thickness profiles with slopes that can be understood by the hypothesis that these vertically deposited colloidal crystals are grown from a concentrated horizontal layer of colloids that develops just below the water–air interface, perhaps even by the Langmuir–Blodgett like transfer of a preassembled horizontal colloidal crystal to a vertical substrate. Consistent with this hypothesis, doubling the concentration of the colloidal suspension from which a colloidal crystal is deposited, and halving the growth velocity of the colloidal crystal by infusing additional solvent into the bottom of the colloidal suspension during deposition, have indistinguishable effects on colloidal crystal thickness and quality. The peak reflectance of colloidal crystals grown at high concentration and slow growth velocity can exceed 80% near the top of the colloidal crystal. Even greater optical performance, or the extension of this optical performance to a larger area of the colloidal crystal, may be possible using more hydrophilic particles.

Acknowledgment. This work was supported by the Nanoscale Science and Engineering Initiative of the NSF under Award No. DMR-0117792. Research for this publication was carried out in part in the Center for Microanalysis of Materials, University of Illinois at Urbana-Champaign, which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439. R.G.S. acknowledges fellowship support from the Fannie and John Hertz Foundation.

Supporting Information Available: Comparison of thickness profiles of colloidal crystals deposited in glass vs plastic vials. Reflectance profile comparisons for \( \varphi = 0.4\% \) and 0.8%. This material is available free of charge via the Internet at http://pubs.acs.org.

LA060278Q