Fabrication of Centimeter-Sized Single-Domain Two-Dimensional Colloidal Crystals in a Wedge-Shaped Cell under Capillary Forces

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Self-assembly of colloidal spheres confined within cells of different shapes formed with two slides under capillary forces are studied. It is found that by controlling the shape of the cells the curvature of the drying front can result in a significant effect on the self-organization process. A curved drying front formed within parallel slides is always associated with growth of colloidal crystal structures with a high density of disorder. We demonstrate that single-domain two-dimensional colloidal crystals with centimeter size can be grown under capillary forces under a straight drying front formed in a wedge-shaped cell. These findings are demonstrated by laser diffraction, microscopy imaging, and off-normal optical transmission measurements. The present growth method should be of importance in expanding colloidal crystal applications in angle-resolved nanosphere lithography, as well as in preparation of high-quality quasi-three-dimensional plasmonic crystals.

Introduction

Monolayer colloidal crystals exhibit a two-dimensional (2D) periodicity, making it extremely attractive as a low-cost promising alternative approach to microfabrication technique.1,2 For example, 2D colloidal crystals have found important applications in many areas, including nanosphere lithography,3–5 as templates for epitaxial growth of binary colloidal crystals,6–11 and optical devices like optical filters, lasers, waveguides, and sensors.12–15

Recently, there is renewed interest in using 2D colloidal crystals as templates to prepare novel plasmonic crystals, as it provides an efficient way to pattern a metal film into a quasi-three-dimensional structure with a nanohole array.16,17 For these applications, it is quite desirable to develop economical and efficient methods to grow high-quality 2D colloidal crystals with a large-area single domain. For example, in an angle-resolved nanosphere lithography, it is impossible to pattern an entire substrate with nanoparticles of an identical shape if the domain orientation of colloidal crystal masks cannot be controlled.5,7

Also, in the assembly and stretch technique which is used to create none-close-packed sphere arrays, anisotropic particle arrays or surface patterns with different bravais lattice, colloidal crystal films with a controlled orientation are crucial to determine the stretching direction.18 When it comes to optical applications, disorder and grain boundaries in colloidal crystals may result in degradation of their optical properties.

Up to now, 2D colloidal crystals have been grown by self-assembly under capillary forces,9 electrophoresis deposition,10–22 spin coating,23,24 Langmuir–Blodgett deposition,25 and other sophisticated micromanufacturing assisted self-assembly processes.26,27 Due to its robustness and simplicity, convective assembly,28–30 which was first proposed by A. S. Dimitrov et al., has been one of the most frequently used methods.28 This technique usually involves an evaporating liquid film which forms a three-phase contact line at the meniscus of the suspension film; when the solvent thickness becomes comparable to the colloidal volume fraction, the solvent vapor pressure exceeds the capillary pressure and the film stretches.28

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particle size, a laterally capillary force will be induced between adjacent particles, bringing them into contact. Driven by both the evaporation and convective flow, more and more free particles move toward the settled colloids and thus assemble to an entropy-favorable close-packed triangular lattice.

To fabricate uniform 2D colloidal crystals, convective assembly confined between two planar substrates has been demonstrated. However, the presence of polycrystalline structure produced using this method is still a big obstacle for these colloidal crystals to find wide application. For this reason, patterned substrates which were introduced for nucleation guide of colloidal crystals were employed with an effort to overcome these drawbacks. Although such techniques provide an effective way to control the domain orientation of the colloidal crystal, it is difficult to transfer the prepared colloidal crystal onto flat substrates, which may be necessary for subsequent material preparations.

So far, although numerous studies on convective assembly of colloidal microspheres was devoted to, there has been very little study on improving uniformity and single domain of colloidal crystal with centimeter-sized area via controlling macroscopically the shape of the drying front of the suspension. In this communication, we demonstrate a simple and robust self-assembly method to grow centimeter-sized single-domain 2D hexagonal-close-packing (HCP) colloidal crystals without exploiting any auxiliary patterned substrates. Our method relies on a controlled convective assembly process by which the orientation of colloidal crystal growth can be fixed via the formation of a straight drying front line in a wedge-shaped cell. We found that polycrystalline formation of colloidal crystals can be suppressed to an utmost degree when the assembly process was confined in a wedge-shaped cell. However, curving the contact line of the drying front by modifying the cell shape will result in structures with a high density of multidomains. Laser diffraction and microscopy were adopted to characterize the structural and optical properties of the prepared colloidal crystals. Measured near-infrared transmission spectra are found to agree well with theoretical calculations, which also confirm the high ordering of the prepared colloidal crystals. In addition, using the high-quality 2D colloidal crystals as substrates, we show experimental measurements on optical dispersion properties of quasi-three-dimensional plasmonic crystals.

Experimental Section

Colloidal Particles and Glass Substrates. Monodisperse polystyrene microspheres with a diameter of 1.587 μm (size dispersion ~1.6%) were purchased from Duke Company as an aqueous suspension of 1 wt%. Prior to use, the suspension was further diluted to 0.5 wt% with an equal volume of deionized water. The glass slides serving as substrates were cut into 2.5 cm × 4 cm pieces in the experiment. To create a hydrophilic surface, the glass slides were immersed in a hydrogen peroxide solution at 80 °C for 30 min and then rinsed with deionized water.

Assembly of Colloidal Crystals. The assembly processes of colloidal crystals in three different types of cells were compared. The rectangular cell used in this experiment was built by sandwiching a U-shaped (Cell A) or strip-shaped (Cell B) spacer into two parallel glass slides. Here, the spacers (1 mm thick) were made of an enamel wire and a plastic plate, respectively. The wedge-shaped cell (Cell C) is composed of two contact glass slides holding at an angle of ~2°. All these cells were held horizontally and kept at room temperature (20–30 °C) with a relative humidity of ~40% after a small volume (50–100 μL) of colloidal suspension was injected into them. At first, owing to capillary forces, the suspension was immediately sucked into the space regions. Then, the 2D sphere arrays were crystallized via convective assemblies by evaporation from a colloidal solution. Finally, 2D colloidal crystal films would be grown onto the lower substrate.

Fabrication of Plasmonic Crystals. The prepared large-area single-domain 2D colloidal crystals acted as a topographic pattern and gold was then sputtered on the top of the microspheres in a vacuum of 5 × 10⁻⁶ Torr at a rate of 1.2 A/s to the desired thickness by an Ion-Beam Coater (IBC model 682, Gatan Corp.). Since the polystyrene microspheres were densely packed, the gold half-shells on adjacent polystyrene microspheres were interconnected after a certain amount of deposition, thus forming large-area single-domain plasmonic crystals on the colloidal crystal templates.

Sample Characterization. To show the large-area single-domain quality of the 2D colloidal crystal, sample structures were characterized by optical microscopy (Olympus BX51) and digital camera. A helium–neon laser was used to carry out the laser diffraction experiment for as-prepared 2D colloidal crystals to probe their long-range-order qualities. The spot size of the laser beam (λ = 633 nm) is about 1 mm. The optical responses of prepared large-area single-domain colloidal crystals and plasmonic crystals were measured by zero-order Fourier-transform infrared (FTIR) spectroscopy ( Nicolet 5700, Thermo Electron Corp.). In all transmission measurements, the size of optical spot impinging on the samples was about 0.8 mm, and all transmission spectra were normalized to the transmittance of a pure glass substrate. The angle-resolved optical transmission of these high-quality colloidal crystals and plasmonic crystals were performed for components of the incident wavevector projected along both major axes of the first Brillouin zone (Γ-K and Γ-M directions) under p and s polarizations.

Results and Discussion

Assembly of Colloidal Crystals. The upper panel of Figure 1 schematically shows three types of the capillary cells employed in our study. A rectangle-shaped cell with only one opening (Cell A, Figure 1a) is formed by sandwiching a U-shaped spacer into two parallel glass substrates. Cell B (Figure 1b) also has a rectangular shape, but with three sides left open. Cell C (Figure 1c) has a different shape from the cells A and B, in which the two glass substrates form a small angle (~2° in our experiment) so that the cell has a wedge shape with three sides open. After injecting a certain amount of polystyrene colloidal suspension, a contact line would be formed at the liquid–air interface with each cell held horizontally (Figure 1d–f). As an example here, the diameter of the polystyrene colloidal beads is 1.587 μm and the concentration of the diluted suspension is 0.5 wt %. Driven by minimum of surface energies, the suspension drying front adopts different morphology depending on the cell shape and specific opening. After complete evaporation of the suspension, a monolayer colloidal crystal with a dramatic variation in ordering degree corresponding to different capillary cell could be formed via a self-assembly process on the lower substrate.
For Cell A, colloidal suspension penetrates into the interstices between the substrates and the U-shape spacer under the action of capillary forces. In this case, a concave contact line is formed of which the curvature increases as the liquid evaporates (Figure 1d). As a consequence, the receding direction varies from point to point along the drying front within Cell A, which is demonstrated schematically in Figure 1g. For Cell B with three open sides, the colloidal suspension also sticks to the spacer but a convex contact line is formed in this case (Figure 1e). The receding direction also keeps changing along the drying front when the liquid amount decreases during evaporation, as shown in Figure 1h.

In contrast to the previous two cases, the contact line in Cell C stays straight, which is parallel to the intersection line of two substrates. Thus, the drying front recedes in a fixed direction during the whole evaporation process (except the very rim of the cell), as shown in Figure 1f. This phenomenon is a resultant of typical capillary effect induced by surface tension as the colloidal suspension prefers to stay in locations where the space between the two glass slides is the smallest, in order to minimize the exposed area to the air due to the intermolecular attraction between liquid and solid substrates.

Figure 1(g–i) illustrates how colloidal particles are self-assembled at the corresponding menisci within each cell as the evaporation of water continues. Dark-gray colored spheres represent those particles deposited in the initial stage, while light-gray ones represent those to be settled. Since colloidal spheres have a tendency to line up along the drying front due to the capillary attractive force between adjacent particles, colloidal particles will be assembled into beaded chains at the initial stage of the assembly process in rectangular cells A and B due to the curved drying fronts (Figure 1g,h). As the solvent evaporates, more particles are brought to the drying front by the convective flow, assembling into small crystalline domains with gradually varying orientations. In contrast, for the wedge-shaped cell, colloidal spheres can be aligned straight along the suspension drying front (Figure 1i), and colloidal crystal grows as new sphere chains are assembled into the already deposited ones, because the contact line recedes along the direction perpendicular to the drying front. On the basis of the analysis, we expect that single-domain colloidal crystals can be obtained with Cell C, whereas multidomain-orientated colloidal crystals are formed with the other two cells.

The left panel of Figure 2 shows the optical images of typical samples fabricated using these different cells. Optical microscopy analysis reveals that all samples are of monolayer or submonolayer structure. It is noted that although the samples prepared

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using rectangular shaped cells show brilliant iridescences (Figure 2a,b), the sample (Figure 2c) fabricated in the wedge-shaped cell exhibits a uniform color across the whole area of the sample.

Laser diffraction has been proven to be an efficient tool to probe the long-range ordering in colloidal crystals. Therefore, diffraction pattern observation was used to further check the domain orientation across the prepared colloidal crystals. In these experiments, a laser beam (wavelength $\lambda = 633$ nm and spot size of 1 mm) was normally illuminated on the samples. The right panel of Figure 2 shows the evolutions of the diffraction patterns when the laser beam scan across the samples along the paths indicated by white dashed lines in Figure 2a–c (the video recordings are also provided in Supporting Information). It is seen that for the 2D colloidal crystal grown in a wedge-shaped cell, six bright and sharp light spots forming a regular hexagon, as well as a central spot caused by the undeflected beam, were recorded under a normal incidence of light, indicating a perfect triangle lattice of the prepared crystal. Upon changing the illuminated region along a path like the white dash line shown in Figure 2c, the single orientation characteristics of the crystal were confirmed by the constantly oriented diffraction pattern, which only exhibits very tiny fluctuations (Figure 2f). Similar results were obtained when repeating the scanning along other parallel paths which indicates that the domain orientation is preserved spatially throughout the 2D colloidal crystal. For the colloidal assemblies obtained in the rectangular cells (Figure 2a, b), however, the sixfold diffracted patterns become seriously blurred and enlarged and even merge into bright rings when the areas illuminated by the laser beam become short-range-ordered with multidomains (Figure 2d,e). The diffraction patterns shown in Figure 2e are more diffuse than those in Figure 2d because of a strong disordering of the sample.

**Optical Response of Large-Area Single-Domain 2D Colloidal Crystal.** Figure 3a shows an optical microscopy image for a typical area of the highly ordered 2D colloidal crystal fabricated in the wedge-shaped cell. Without optical response coming from misaligned domains of polycrystalline array, the large-area single domain makes it possible to figure out a full picture about the photonic bands of the 2D colloidal crystal through measurements of transmission spectrum under oblique incidence. The optical band dispersion properties of the 2D colloidal crystal are evaluated by angle-resolved zero-order transmission measurement at

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**Figure 4.** Comparison between measured (upper panel) and calculated (lower panel) angular resolved transmission spectra of a 2D colloidal crystal supported on a glass substrate. Spectra are displayed separately for the incident-wavevector projection along $\Gamma$-$K$ direction (a): p-polar. and (b): s-polar.] and $\Gamma$-$M$ direction [(c): p-polar. and (d): s-polar.]. The individual measured spectra are offset vertically by 8% for clarity. For calculated results, the offset is 45%.

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the configuration shown in Figure 3b. Measurements are carried out for both transverse magnetic polarization (p-polar) and transverse electric polarization (s-polar). The incidence angle is varied from $\theta = 0^\circ$ to $34^\circ$ with an interval of $2^\circ$.

Numerical evaluations of the transmission spectra under oblique incidence are also performed for this 2D close-packed microsphere array on a glass substrate using an electromagnetic multiple scattering theory,\(^{(35)}\) which has been widely adopted for simulating transmission/reflection spectrum of photonic materials composed of spherical scatterers. In these evaluations, the dielectric constant ($\varepsilon$) for the 1.587 $\mu$m diameter polystyrene microspheres and the glass substrate is set to 2.53 and 2.25, respectively. The measured and calculated spectra are displayed separately in the upper and lower panels of Figure 4 for a direct comparison, each for the incident wave vector projection along $\Gamma$-K and $\Gamma$-M axes with different polarization states (p- and s-polar.).

For the highly ordered 2D colloidal crystal, three transmission dips at $\lambda \approx 1958$ nm, 1601 nm, and 1471 nm can be clearly observed at normal incidence ($\theta = 0^\circ$), which are the result of excitation of photonic eigenmodes of the periodic dielectric structure as a result of its strong coherent coupling with the incident light.\(^{(36)}\) It is noted that the main dip at 1958 nm under normal incidence exhibits different dispersion features for different in-plane (azimuthal) orientation of the dielectric microstructure. For incident light with an in-plane wavevector along $\Gamma$-K axis, the main transmission dip shows a significant red-shift for both p- and s-polarized light when incident angle is increased (Figure 4a,b). When the in-plane wavevector is aligned along the $\Gamma$-M direction, the main mode exhibits the most remarkable red-shift for p-polarization (Figure 4c) but a negligible shift for an s-polarized incident light (Figure 4d). These experimental observations are confirmed in the corresponding calculations. It is noted that, in the measured spectra, the transmittance decreases rapidly as the wavelength is shortened due to an increase in scattered radiation which strongly influences the collection of the zero-order transmitted signal detected by the spectrometer.\(^{(36)}\) Nonetheless, some fine peak structures and their splitting effect can be resolved even in short wavelength region, which also agrees with the calculations.

**Fabrication and Characterization of Plasmonic Crystal.**

In addition to the study of the optical properties, the as-prepared dielectric structures can be directly applied as substrates to fabricate high-quality plasmonic crystals. In previous studies, it has been reported that colloidal crystals covered with a thin layer of metal show extraordinary light transmission,\(^{(16,17)}\) a phenomenon first reported by Ebbesen et al. in hole array metal films.\(^{(37)}\) Although transmission properties have been characterized for such plasmonic structures under off-normal incidence for different polarizations, the prepared samples in previous work were of multidomains,\(^{(16,17)}\) which make the obtained transmitted spectra independent of the in-plane wavevector orientation of the sample.\(^{(17)}\) Disorder or polycrystalline structure in the colloidal crystal template also might broaden the transmission peaks and reduce the peak intensities.

Figure 5 shows the angle-resolved zero-order light transmission spectra for the plasmonic crystal obtained by sputtering 33 nm thickness gold layer onto the single domain 2D polystyrene colloidal crystal substrate. This metalodielectric microstructure shows transmission peaks at some specific wavelengths under normal incidence of light and some of the resonances can be understood as the excitation of surface plasmons.\(^{(16,17)}\) Although the transmission spectra are nearly the same under normal incidence of light for either multidomain or single-domain colloidal crystal substrates, the optical properties under off-normal incidence are quite different with a single-domain structure. For example, a flat dispersion feature is observed for the dominant resonance at about 2000 nm for the p-polarized incident light in a randomly oriented microstructure with crystal grains of typically a few micrometers across.\(^{(17)}\) Here, the main resonance in a single-domain plasmonic crystal shows complicated dispersion characteristics especially under off-normal incidence of p-polarized incident light (Figure 5a,c).

When the angle of incidence is small, the transmission responses show similar dispersion behaviors for identical polarization state of light even when the in-plane wavevector is aligned along different major axes of the first Brillouin zone. However, the differences in the resonance dispersion characteristics become noticeable when the incident angle is increased beyond $\theta = 8^\circ$, especially for the transmission spectrum in the short-wavelength region. For example, under p-polarized light with the in-plane wavevector along the $\Gamma$-K axis, the peak at ca. 1420 nm grows in intensity as the incident angle increases and becomes the dominant one at $\theta = 30^\circ$ (Figure 5a). In contrast, when the in-plane wavevector is aligned along $\Gamma$-M direction, the peaks at shorter wavelengths decrease in intensity upon the increase of $\theta$ (Figure 5c). A similar phenomenon, though less obvious, can also be observed under s-polarization.

For the main resonance at ca. 2040 nm observed under normal incidence of light, its dispersion characteristics are found to be insensitive to the relative in-plane wavevector orientations, but depend mainly on the incident light polarization state. For example, under p-polarization this peak initially shows a flat dispersion when $\theta$ is within $8^\circ$, and then, it merges with its neighboring weak resonance (originally at ca. 1870 nm) to form a hybrid mode that red-shifts steadily as $\theta$ is increased from $8^\circ$ for...
both Γ-M and Γ-K in-plane wavevector directions. When light polarization is changed to the s state, this main resonance shifts steadily toward longer wavelength with a decreasing intensity under off-normal incidence as θ increases (see Figure 5c,d), and the weak resonance at ca. 1870 nm gradually turns to a dominant one with a steady red-shift for in-plane wavevector along either Γ-K or Γ-M axis.

It is noted that a new mode in the long wavelength regime is observed only under p-polarization when θ is increased beyond 8° for both sample orientations (Figure 5a,c). This mode could be explained as a result of the excitation of a surface plasmon mode localized on the hemispherical gold shells, under the action of the incident electrical field component perpendicular to the microstructure.38 This mode is absent for the s-polarized light (Figure 5b,d), because in this case, there is no perpendicular electrical component for oblique incidence. As θ is increased, the intensity of this resonance increases, and a red-shift dispersion feature is observed, which is attributed to the reduced symmetry of the gold shell to the incidence.

Conclusions

In conclusion, we have developed an efficient self-assembly method to fabricate centimeter-sized single-domain 2D colloidal crystals under capillary forces within a wedge-shaped cell. It is found that the straight contact line of colloidal suspension formed in a wedge-shaped cell plays a significant role in the growth of single-domain colloidal crystals, as curved contact lines in rectangular cells are shown to result in polycrystalline structures. Long-range order of the prepared samples is characterized by laser diffraction pattern, microscopy, and light transmission spectra that agree well with numerical calculations. We also demonstrate the transmission resonances of plasmonic crystals based on single-domain 2D colloidal crystal templating under different polarizations and in-plane orientations of incident light. The interesting and abundant optical properties could be shown up only from these large-area single-domain samples. We emphasize that the achievement of single-domain colloidal crystals is key to a successful implementation of mask and templating approaches such as angle-resolved nanosphere lithography, which allow fabrication of uniform and large domain microstructures for potential applications in optoelectronics devices, solar cells, and biosensing.

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Supporting Information Available: Three video files showing the dynamic evolutions of diffraction patterns when the laser beams scan across the samples along the paths indicated by white dashed lines in Figure 2(a–c). Here, the spot size of the laser beam is about 1 mm, and the wavelength of laser is 633 nm. The files correspond to the evolutions of diffraction patterns for the samples grown in Cell A, Cell B, and Cell C, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.