Fabrication and Light-Transmission Properties of Monolayer Square Symmetric Colloidal Crystals via Controlled Convective Self-assembly on 1D Grooves**

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Two-dimensional (2D) colloidal crystals have intriguing properties, which make them quite useful in a wide range of applications. For example, 2D colloidal crystals have been widely used as physical masks in, for example, nanosphere lithography,[1] for preparation of metal nanoparticle arrays with a variety of particle morphologies,[2] as templates for growth of binary colloidal crystals,[3] and recently even as templating substrates for preparation of novel plasmonic crystals.[4] Up to now, several methods have been developed to grow 2D colloidal crystals, including self-assembly by capillary force,[1] spin-coating,[2a,6] electrophoretic deposition,[7] and Langmuir–Blodgett deposition.[8] Among them, convective self-assembly induced by solvent evaporation has been shown to be an effective approach for self-organizing colloidal beads into 2D crystals with hexagonal close-packing geometry.[5] In a typical process,[5a] immersion capillary force at the suspension drying front tends to bring particles into contact when the liquid suspension thickness becomes comparable with the colloidal sphere diameter. Evaporation-induced flow brings more particles towards the suspension front and the crystal grows larger.

A patterned substrate provides an effective way to control the packing symmetry and orientation of colloidal crystallizations,[9,10] which is quite important for further extending colloidal crystal applications. Several research groups have reported using a 2D-patterned substrate to drive the growth of colloidal crystals.[9,10a] Self-assembly in the presence of one-dimensional (1D) patterned substrates has also been studied in combination with thermal equilibrium assembly,[10a] convective assembly,[10b] electrostatic assembly,[10c] and electrophoretic deposition process.[10d] Although 2D centered-rectangular lattice colloidal crystals have been fabricated on a 1D-patterned substrate, high defect densities and short-range ordering were often observed in those previously reported results.[10a,10b,10d] To the best of our knowledge, an efficient method to prepare high-quality monolayer square-lattice colloidal crystals has not been reported yet.

In this Communication, we report our study of self-assembly of colloidal polystyrene (PS) spheres on a 1D-patterned substrate. Previous studies showed that colloidal structures formed on a 1D-patterned substrate are highly sensitive to the ratio between sphere diameter ($d$) and groove period ($p$).[10a] Here, we explore other factors that could have a key influence on the formation of 2D square symmetric colloidal crystals using a 1D-patterned substrate. By introducing an experimental cell that allows simultaneous actions and strong competition of forces on colloids exerted by the suspension drying front and the patterned substrate, we have identified distinct effects of convective assembly on the growth of colloidal crystal by controlling the angle orientation ($α$) between the colloidal suspension drying front and 1D template grooves. We find that those experimental configurations with $α$ having a large deviation from $α = 45°$ will introduce a large amount of defects during the self-assembly process. We demonstrate that, by controlling the angle $α$ in the vicinity of $45°$, convective assembly in a cell with a 1D groove template as the substrate can induce a highly ordered 2D square-lattice colloidal crystal with a minimum density of defects. The long-range ordering of the prepared 2D square symmetric colloidal crystals is characterized by electron and optical microscopy, laser diffraction, and light transmission. Transmission spectra of the prepared square symmetric colloidal crystal are measured at normal and off-normal incidence under different polarizations and are shown to be in good agreement with theoretical calculations.

First, a 1 mm thick cell was built by sandwiching two far-separated straight parallel enamel wires (1 mm in diameter) between a glass slide and a 1D patterned substrate (Fig. 1a). As examples, polystyrene microspheres with a diameter of 1020 nm were used in all the experiments. Correspondingly, a 1D patterned polycarbonate (PC) substrate having a groove period of 730 nm was used. The ratio of colloidal sphere diameter to the template period was 1.40, a value smaller only by 1 % than the perfect-match value $\sqrt{2}$ that is required for a commensurate square lattice of the 1D template substra-
In this case, particles located in adjacent grooves could contact each other during self-assembly process. After injecting a certain amount of colloidal suspension into the cell, a straight drying front of the colloidal suspension parallel to the wire could be formed, which receded in a direction towards the wire as the evaporation of water continued. When protruding from a meniscus at the drying front, latex particles experience an immersion capillary attraction. The attraction forces bring the spheres in physical contact along the drying front. This process, however, is strongly influenced by the substrates, because self-assembling spheres in the presence of topological patterned substrates have a tendency to stay in the groove center. This can be understood by considering the fact that the presence of a sphere deviating from the groove center will cause an asymmetric deformation of the contact line of the residual suspension drop on the groove surface and, thus, induce a horizontal capillary force perpendicular to the template grooves towards the groove center. Nevertheless, the structure morphologies differ significantly when the angle between the wire and the template grooves is changed between 0° and 90°.

Figure 2a–c (left panel) shows schematic graphs of the experimental configuration in which the 1D pattern (solid lines) and the suspension drying front (dashed lines) for a set at a) 0°, b) 90°, and c) 45°; and scanning electron microscopy images (right panel) of the samples obtained at the corresponding configuration. The arrows in the left panel denote the suspension receding direction. The insets in the right panel show the corresponding 2D coordinate autocorrelation graph. Scale bar is 10 μm.
not be uniform or flat as some of the particles would become highly elevated during self-organization process due to an increasing mismatch of a planar hexagonal close-packing with the 1D template. When protruding too much, those particles will be pulled into the neighboring groove by the capillary force to minimize surface free energy. As a consequence, high density gaps are created between sphere chains (Fig. 2d). Such a feature of surface morphology is also exhibited in the 2D-CACF of the sample image (Fig. 2d, inset), in which white spots along the horizontal axis in the central area of the figure represent a relatively strong correlation between particles within the chains. But the intensity of these peaks decreases rapidly away from the origin along y-axis and becomes eventually invisible after four rows from the center, which reflects the short-range order of the sample along the receding direction of the drying front.

Figure 2e shows a SEM image of the sample obtained at $\alpha = 90^\circ$. It is evident that in this case the spheres cannot be lined well even when protruding from the drying front, in contrast to the case in Figure 2a, because the sphere diameter is much larger than the groove period. Although this configuration could allow nucleates of square symmetric assemblies at the drying front (Fig. 2b), vacancies formed at the front due to a large mismatch between the sphere diameter and the groove period destroy any correlation of neighboring micro-domains. Thus high density line-shaped vacancies parallel to the receding direction are produced. The corresponding 2D-CACF depicted in the inset of Figure 2e clearly shows that at $\alpha = 90^\circ$, the positional correlations of spheres located at different grooves are much weaker than those within the grooves oriented along the receding direction of the drying front.

Figure 2f shows a SEM image of the sample prepared at $\alpha = 45^\circ$. In this case, the prepared colloidal crystal shows a perfect 2D square symmetric structure. From the schematic, it is seen that all the spheres at the drying front can be located within the groove centers and line up to form a sphere chain that fits the 1D groove template well. Although the attractive forces induced by the already deposited rows have a tendency to attract the incoming spheres towards the niches between neighboring spheres at the drying front, the horizontal capillary forces on elevated spheres point towards the groove center with a component parallel to the drying front and drives the spheres away from the niches into a more stable location. Such a self-assembly process leads to a continued growth of a nearly perfect square symmetric colloidal crystal. Here in Figure 2f, no anisotropy corresponding to the 1D grooves is observed in the 2D crystal plane. In the 2D-CACF shown in the inset of Figure 2f, all peak positions are in excellent correspondence with an ideal 2D square lattice. The average widths of the peaks in the directions parallel and perpendicular to the drying front are found to be equal within the errors.

The clear differences between the morphologies of the samples grown on 1D grooves set in the three angles relative to the drying front can also be identified through light transmission measurements. The near-infrared transmission spectra of the samples were measured at normal incidence with non-polarized light. The experimental results are summarized in Figure 3a. For all samples, it is seen that the overall transmittance decreases towards shorter wavelength. This phenomenon occurs mainly as a result of increased scattered radiation that is not collected in the zero-order spectroscopic array to a close-packing case. However, for the highly ordered 2D colloidal crystal in Figure 2f, three transmission dips are clearly observed at $\lambda = 1381$, 1045, and 960 nm. These pronounced dips correspond to the photonic eigenmodes of the monolayer dielectric periodic structure, which are excited as resultant of strong coherent coupling of incident light. However, such a coherent coupling is much weaker for the sample with a short-range-order feature obtained at $\alpha = 90^\circ$, where the above three dips are degraded into weak shoulders in the transmittance spectrum. For the sample grown at $\alpha = 0^\circ$, the main dip is sustained but shifted to $\lambda = 1313$ nm and this shift is related to the change in local symmetry from a square-lattice array to a close-packing case. A periodic array of dielectric spheres is a prototypical photonic crystal and has been shown to be valuable for the study of basic physics of photonic crystals. Compared to the extensive experimental studies carried on 3D array of dielectric
spheres\cite{14} much less has been done to reveal optical properties of 2D monolayer of dielectric spheres\cite{12,13}, which should be quite different from the 3D case. To explore the photonic bands of the 2D square-lattice colloidal crystal, we have performed numerical calculations of light transmittance through the periodic dielectric structure using an electromagnetic multiple scattering theory (on-shell method)\cite{16} that is highly efficient for evaluating transmission/reflection spectrum of photonic materials composed of stacking layers of spherical scatters. Our colloidal crystal is modeled as an infinite monolayer of PS spheres with dielectric constant $\varepsilon_{PC} = 2.53$ and a diameter $d = 1.020 \, \mu m$ arranged in a square lattice with a lattice constant $a = 1.032 \, \mu m$, a value determined by assuming an exactly commensurate square symmetric structure with the 1D pattern grooves. In the calculations, excellent numerical convergence is achieved by using $l_{\text{max}} = 7$ in the angular momentum expansions and 37 2D reciprocal lattice vectors in the plane-wave expansions.\cite{17}

Figure 3b shows the calculated transmission spectra for normal incidence of light. The dashed and dotted lines represent the theoretical results for a monolayer of PS spheres with and without a semi-infinite PC substrate (dielectric constant $\varepsilon_{PC} = 2.52$), respectively. It is seen that although the inherent photonic modes of a freestanding 2D square symmetric colloidal crystal manifest themselves as sharp dips in transmittance as a function of wavelength, the presence of a semi-infinite dielectric substrate gives a strong broadening effect such that sharp modes, especially those with closely distributed energies, are much extended to form a broader band dip in the spectrum. The substrate-induced widening phenomenon was first reported by Miyazaki and co-workers and has been explained as due to additional opening of dissipation channels through the substrate which leads to a dramatic decrease in the photon lifetime.\cite{18} With this effect considered in the simulation, three dips are predicted at 1351 nm, 1049 nm, and 949 nm, which fairly fit, respectively, the values at 1381 nm, 1045 nm, and 960 nm observed in our experiment where a thick PC substrate is used. Note that the 1D template pattern protruding into the 2D colloidal crystal was not taken into account in the above calculations.

The high ordering and large area of the fabricated 2D square symmetric photonic crystal, which is demonstrated from an optical image and laser diffraction pattern in Figure 4a, also allows us to obtain a full picture about the photonic bands through transmission spectra under oblique incidence. Our measurement configuration is depicted in Figure 4b. Here, the angle-resolved measurements are made for components of the incident wavevector projected along both major axes of the first Brillouin zone under $p$- and $s$-polarizations. Numerical evaluations of the transmission spectra under oblique incidence are performed for the monolayer PS spheres on a semi-infinite PC substrate with the same structural parameters as in Figure 3b.

The experimentally acquired transmission spectra are displayed separately for $\Gamma$-$M$ (Fig. 5a and b) and $\Gamma$-$X$ (Fig. 5c and d) directions in the top panel of Figure 5. The angle of incidence is varied from $\theta = 0^\circ$ to $20^\circ$ with an interval of $1^\circ$. Firstly, it is clearly seen that the photonic modes corresponding to the main dip at 1381 nm show remarkable differences in band dispersions along different major axes of the Brillouin zone as $\theta$ is increased from $0^\circ$. Specifically, for $\Gamma$-$M$ axis, the main dip shows a similarity of a red-shift characteristic in the band dispersion for both $p$ and $s$ polarizations (Fig. 5a and b). For $\Gamma$-$X$ axis, the main dip shows a small blue-shift at $s$ polarization (Fig. 5d), but it instead moves steadily towards the longer wavelength at $p$ polarization (Fig. 5c). Such dispersion features of the main dip observed in the experiment is in excellent agreement with the corresponding calculations which are shown in the bottom panel of Figure 5.

The features under off-normal incidence predicted in the short wavelength region in the calculation cannot be easily verified in the experiment, due to a rapid decrease of the overall transmittance in this spectrum region. We have marked those shadow dips in the measured spectra and from the locations of these arrows, it is still possible to identify the splitting effects of the main dip observed in Figure 5a–c as $\theta$ deviates from $0^\circ$. Such dispersion features are also in good agreement with the corresponding theoretical results.

In conclusion, we have studied self-organization of PS colloidal spheres within a channel of which a 1D groove sub-
strate is used as the bottom substrate. Under the coexistence of strong groove-sphere and sphere-sphere interactions mediated by capillary forces, distinct assembly effects have been observed upon the change of the orientation of the suspension drying front in respect to a 1D groove substrate during convective assembly process. 2D colloidal arrays exhibiting long-range order of square symmetry with extremely low density of defects can be induced in a relative orientation of $\alpha = 45^\circ$, that is, where the drying front is parallel to the close packed rows of a commensurate square lattice of the 1D periodic grooves. The measured transmission spectra agree well with the theoretical calculations by taking into account the dielectric substrate broadening effect of the photonic modes. This prepared 2D colloidal crystal could be useful as 2D-patterned substrates in epitaxial assembly. We also expect these colloidal assemblies have potentials for use in optical applications.

**Experimental**

Aqueous suspension of polystyrene microspheres with a diameter of 1020 nm (size polydispersion of 1.1 %) was purchased from Duke Company (1 wt %). The colloidal suspension was further diluted in deionized water in volume dilutions of 1:8. Polycarbonate substrates with a 1D pattern of grooves having a groove period of 730 nm and a modulation of 180 nm were used in the experiment. The PC sheet was pretreated with a sodium dodecyl sulfate solution (2.5 mg mL$^{-1}$) before use. A small volume (about 20 µL) of the latex suspension was injected into the cell formed by sandwiching two far-separated parallel straight enamel wires of 1 mm in diameter between a glass slide and a PC substrate with the 1D pattern contacting the suspension. Owing to capillary forces, the suspension was immediately sucked into the space region between the enamel wires. Then the cell was held horizontally with the PC membrane in bottom side and kept at room temperature (20–30°C) with a relative humidity of 80%.

Scanning electron microscopy (FEI Philips XL-30) was used to characterize the 2D colloidal assemblies. Light transmission spectra of the 2D colloidal crystals were measured using a far-field Fourier-transform infrared (FTIR) spectrometer (Nicolet 7100). The optical spot size of the incident beam on samples under normal incidence had a diameter of about 0.2 mm. The numerical aperture set for the transmission was estimated to be less than 0.01.

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