Assembly and Dynamic Analysis of Square Colloidal Crystals via Templated Capillary Assembly

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Supporting Information

ABSTRACT: Capillary assembly has the ability to engineer centimeter-sized regions of discrete colloidal superstructures and microarrays. However, its use as a tool for directing crystallization of colloids into surface-bound nonclose-packed arrays is limited. Furthermore, the use of quantitative particle tracking tools to investigate evaporative assembly dynamics is rarely employed. In this contribution, we use templated capillary assembly to fabricate square-packed lattices of spherical, organosilica colloids using designed patterned boundaries. Particle tracking algorithms reveal that the assembly of square-packed regions is controlled by the interplay between confinement-driven nuclei formation and osmotic pressure-driven restructuring. We find that the incorporation of a square template increases the yield of particles bearing four nearest neighbors (\(Z_n = 4\)) from 4 to 39%, obtained using a heavier and more viscous solvent. Maximal square-packed domains occur at specific initial particle concentrations (1.75−2.25 wt % or \(φ = 0.013−0.017\)), indicating that rearrangements are a function of osmotic force. We use particle tracking methods to dynamically monitor conversions between square and hexagonal packing, revealing a cyclical transition between 4 and 6 coordinated particles throughout meniscus recession. Our method is highly scalable and inexpensive and can be adapted for use with different particle sizes and compositions, as well as for targeted open-packed geometries. Our findings will inform the large area, defect-free assembly of nonclose-packed lattices of unexplored varieties that are necessary for the continued expansion of colloid-based materials with vast applications in optical electronics.

INTRODUCTION

The self-organization of nano- and microscale building blocks imparts remarkable properties to the ensuing material that result from its periodic dimensions and the building block composition. For example, colloidal particles with dimensions akin to the wavelength of visible light can assemble into dielectric lattices that diffract electromagnetic waves, emit structural color, and can be used for optical circuitry. Additionally, periodic nanopatterns capable of transmitting mechanical waves, electrons, and analytes are promising candidates for the fabrication of sensors, nanoelectrodes, and heterogeneous catalytic frameworks.

Engineering colloidal crystals for technological applications necessitates refining fabrication schemes for generating precise spatial organization of particles over large areas. Nearly all functional colloid-based materials that have been applied to actual optical or technological devices are close-packed crystals fabricated from isotropic spheres. Engineering nonclose-packed colloidal crystals such as the Kagome14 and diamond lattices5,16 is required for three-dimensional (3D) photonic applications. However, implementing complex lattices into devices and materials has currently not been reported. Programmable assemblies of colloidal molecules with functional patches17−20 or anisotropic shapes14,21−25 have so far only produced small (i.e., low yielding) open-packed crystalline domains in liquid suspensions. Ionic lattices with geometries mimicking those of molecular crystals26,27 and structures assembled under the influence of electric or magnetic fields28−30 have been fabricated at larger length scales but are rarely surface-bound. For device fabrication on a chip, nonclose-packed colloidal lattices are required. Such materials, however, are not well studied, with only a few examples engineered from micromachined templates to direct epitaxial colloidal crystal growth,31,32 assembly at air/water interfaces33−38 and packing confinement between rigid surfaces.39,40 The reason behind this lack of advances is that the spontaneous self-assembly of isotropic colloids is limited to a few structurally simplistic unit cells, namely, the thermodynamically favored face-centered cubic (FCC) or hexagonally close-packed lattices.41,42 Compelling particles to deviate from their equilibrium geometry is not trivial, particularly when considering transferring the colloidal crystals onto a substrate. Constructing a surface-bound crystal requires drying a particle suspension and therefore introducing strong, long-range drag forces that might disrupt weaker interactions (e.g., electrostatic, hydrogen bonding) and reorganize any preformed lattice structures.43

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In this contribution, we fabricate on-chip open-packed lattices using geometric constraints to harness long-range drag forces and introduce directionality to an inherently nondirectional process. We use this method of capillary assembly to spatially arrange particles into square lattices and use particle tracking algorithms to quantitatively investigate their nucleation and growth mechanisms.

Capillary assembly has rapidly increased in scope throughout the last decade. There has been significant progress in creating colloidal assemblies by manipulating the attractive immersion capillary force that a particle experiences at the three-phase contact line when a suspension is dried on a substrate.\textsuperscript{44} If the substrate is flat, the method is referred to as convective assembly and can be used to create large crystalline domains from both isotropic and anisotropic particles.\textsuperscript{34,45–49} When combined with surfaces containing topographical features, capillary assembly has proven to be a robust method for the targeted delivery of nano- and microparticles into desired patterns.\textsuperscript{44} Capillary assembly produces a diverse collection of well-resolved arrays including gradients of different particles,\textsuperscript{50,51} anisotropic metallic particles,\textsuperscript{52–54} and colloidal clusters with defined structures and sizes.\textsuperscript{55–57} Additionally, multiple particles of different composition can be deposited by successively refilling partially filled wells;\textsuperscript{55,58,59} the result is a library of physically anisotropic colloidal molecules that can be bound by sintering, removed from the template, and resuspended. Despite the programmable use of geometrically constrained capillary assembly for creating on-chip discrete particle arrays, its use to structure colloidal crystal packing remains enigmatic. The use of convective assembly (i.e., no surface pattern) to fabricate close-packed crystals has been reported,\textsuperscript{60} as well as the fabrication of crystals using convective assembly from isotropic and anisotropic particles. However, these studies seldom include data-driven image processing methods to quantify the yield and coordination environment of deposited particles, thereby subverting rigorous analysis of their assembly mechanism. Although particle tracking methods exist,\textsuperscript{60} this contribution applies these algorithms for the first time to capillary assembly analyses, in particular, for tracking particle coordination environments as a function of time.

We use templated guidelines, rather than periodically spaced holes, to restructure thermodynamically favored hexagonal (HX) lattices into square-packed domains using capillary assembly. A successfully close-packed to open-packed transition depends strongly on the geometry of the template and on the overall osmotic force exerted by the meniscus on the growing crystal. The key features of our geometric templates are the boundaries separating individual wells that are much thinner and shallower than the diameter of the particle, in contrast to the larger spacing (s\textsubscript{p}) and depths (d) observed when creating discrete particle assemblies (Figure 1). This shallowness permits geometrically constrained square nuclei to affect a solid-state rearrangement across the patterned boundaries. The osmotic force is tuned by adjusting the particle volume fraction, and we identify a critical range in which the close- to nonclose-packed phase change is maximized. We find that the lattice parameters are sensitive to both the osmotic pressure and the template design, or confining geometry. Quantifying packing by tracking the change in particle coordination number throughout crystal growth elucidates vital microscopic considerations that underpin the square mechanism.

![Figure 1. Template design for a square crystal featuring 25 particle square boxes. The inner length of each bounded region is equal to the number of desired particles (n = 5) multiplied by the particle diameter minus the spacing between boxes, or l = w = 2rn − sp. The depth of each boundary is set so that flanking particles can interact with each other to form a uniform crystal. The particles used in experiments have r = 1.05(0.09) μm; therefore, l = 9.7(0.3) μm and sp = 597(10) nm.](image)

The insights procured from this work will impact scalable, defect-free colloidal crystal fabrication, as open-packed lattices can themselves be used as templates for epitaxial growth and colloidal lithography to create 3D architectures. We envision that templates with more complex shapes can produce yet undiscovered surface-bound frameworks and extend the development of colloidal-based photonic materials to include those fabricated from open-packed structures.

### RESULTS AND DISCUSSION

**Experimental Design.** Evaporative colloidal assembly processes consist of two components that can be adjusted independently to achieve the desired structures: the substrate and the colloidal suspension.\textsuperscript{34} Our substrates are glass wafers coated with a layer of metal (to facilitate photoresist adhesion) and patterned with an array of squares using photolithography. To achieve square lattices from minimal templates, the dimensions of the pattern must follow several requirements: the length and width of each box must equal an exact multiple (n) of the radii of the particles minus the template spacing (s\textsubscript{p}) such that particles flanking a boundary still can make contact to form a continuous crystal (i.e., l = w = 2rn − sp; Figures 1 and S3B). Particles deposited into wells with additional space (l > 2rn − sp) arrange into a hexagonal structure. When fabricating discrete particle superstructures using capillary assembly, the template depth is consistently reported to be greater than or equal to the particle radius (d ≥ r) resulting in partially or completely filled wells, respectively.\textsuperscript{34}

To create a continuous crystal, we set the depth as r/2 such that the boundary is high enough to impel square packing geometry but not so flat as to approach a smooth surface that would give a hexagonal crystal. Substrate wetting and the presence of a surface pattern delineate convective and capillary assembly pathways, which, respectively, give two-dimensional (2D) lattices and discrete colloidal superstructures.\textsuperscript{61} Convective assembly occurs when the substrate is wet by the liquid film with a water contact angle <20°, a condition that produces a vertically narrow meniscus in which the particles at the contact line are only partially immersed.\textsuperscript{61} At higher surface contact angles (>20°), the horizontal force exerted by the meniscus prevents particles from depositing into 2D crystals. When patterns are introduced, the meniscus will pin and unpin as it recedes, generating an elastic restoring capillary force (F\textsubscript{r}) with a vertical component that propels particles downward into...
patterned traps while avoiding unwanted deposition onto the bordering areas. Since the static contact angle of our template was measured to be $45 \pm 0.2^\circ$, the wetting properties dictate that capillary forces dominate the assembly process even though the shallowness of the template approaches conditions more akin to convective assembly, which occurs on flat substrates (Figure S1). The surface wetting was adjusted by tuning the concentration of the nonionic surfactant F108 to 1.0 wt %. Unlike traditional capillary assembly processes, we aspired to create a continuous 2D crystal with well-defined lattice criteria.

We chose spherical organosilica particles synthesized from 3-(trimethoxysilyl)propyl methacrylate (TPM) as described in the literature ($r = 1.05 \mu m \pm 0.09$, Figures 2A and S2). The colloids were injected into a homemade ow cell containing a template substrate described above, two spacers, and a cover slide to enclose the channel (Figure 2B). The substrate and coverslip were cleaned with isopropanol to remove debris and coverslip to enclose the channel (Figure 2B). The substrate and coverslip were cleaned with isopropanol to remove debris but otherwise used without further modification. Adjusting the channel spacing did not significantly affect the assembly yield; the channel spacing (4 mm) and height (400 μm) were kept constant for all experiments.

**Assembly and Particle Reconfiguration.** The evaporation process was monitored and recorded using optical microscopy (Video S1). Solvent evaporation occurs under ambient conditions and concentrates the particles at the edge of the meniscus in the so-called accumulation zone (AZ) due to the hydrodynamic flow of water toward the depleting evaporation front. As the meniscus flattens and recedes, the particles deposit in a 2D layer. In the absence of intervention from templates or external forces, isotropic particles will crystallize hexagonally into the configuration that minimizes their free energy. However, in the presence of square boundaries, there is a trade-off with respect to global energy minimization. Within each confined area, the particles can either maximize template filling (25 particles) or maximize nearest neighbors (23 particles). Thus, particles presented with a square template are more likely to rearrange and pack accordingly to fill their geometric confines. They first populate their preferred hexagonally packing phase as crystal formation occurs horizontally across the template (i.e., parallel to the edges of the channel). If a box containing an HX structure forms below an adjacent square-shaped nuclei, the particles can restructure and propagate the formation of a square lattice (Figure 3A). If square nuclei are unable to bridge the boundary and affect phase restructuring, the colloids remain in an HX or amorphous state, as evidenced by the integration of deeper boundaries ($d = 1.3 \mu m$, Figure S3C).

This geometric restructuring happens because there is the remaining solvent clinging to the surface of the particles after the meniscus has receded, thereby forming liquid bridges that enhance mobility and create an attractive immersion capillary force (Figure 3). Local rearrangement must therefore occur within a time scale that is shorter than that of the residual solvent drying. Each particle experiences roughly three phases throughout crystal growth (Figure 3A(i–iii)). In phase one, particles are immersed or partially immersed in the AZ, where high pressure causes them to pack tightly on the surface. In phase two, the bulk liquid has evaporated baring a small volume of liquid that bridges adjacent particles; particles in this phase are still motile enough to reconfigure into a square. In phase three, the liquid bridges have evaporated and the particles are locked in their final configuration.

The result of a typical assembly using the conditions described in Table 1 and displayed in Video S1 is shown in Figure 2C. A polymorphic crystal consisting of square regions with HX sections is confirmed by the associated finite Fourier transform (FFT) images. Particle dispersity and template resolution contribute to the presence of some packing nonuniformities and preclude the formation of long-range order. Colloidal crystallization into a close-packed equilibrium structure typically proceeds from the disordered state to an open-packed, amorphous phase before collapsing into an FCC crystal. We observe the opposite trend in our system, in which close-packed crystals transmute into lower coordination number structures by the interplay of confinement-driven nucleation and osmotic force-driven propagation.

**Coordination Mapping and Quantitative Analyses.** The mechanisms of square crystal formation by quantifying the packing environment surrounding each particle using a MATLAB script based on particle tracking methods developed by Crocker and Grier. Briefly, each particle’s center was returned as the peak of a Gaussian distribution based on image contrast intensity. The distance between each particle’s center and its nearest neighbors was calculated and transformed into a coordination matrix. Particles with coordination numbers of 4 and 6 were designated as square and hexagonally packed particles, respectively (Figure S4, Supporting Discussion). When comparing an HX control fabricated using convective assembly to the square templated crystal, the particle fraction...
(Φₚ) of 4-fold (Zₐ = 4) coordinated colloids increased from 0.04 ± 0.01 to 0.32 ± 0.02; conversely, Φₚ for colloids with Zₐ = 6 decreased from 0.77 ± 0.05 to 0.15 ± 0.03. Grain boundaries, edge effects, and vacancies lead to discordances in the measured values such that particles occupying the square or hexagonal phase occasionally display Zₐ values of 3 and 5, respectively. By dispersing in D₂O, a heavier solvent, we were able to increase Φₚ for Zₐ = 4 to 39 ± 0.04 and observed a 50% decrease in Φₚ for Zₐ = 6 (Figure 4). We hypothesized that the inclusion of a heavier solvent would retard the evaporation, however, the meniscus recession rate did not slow down by a measurable value, which is consistent with the reported similarities in evaporation coefficients for H₂O (0.62 ± 0.09) and D₂O (0.57 ± 0.06). We hypothesize that the increase in square packing is caused by the reported differences in the bulk properties between D₂O and H₂O. The increase in density, viscosity, and intermolecular forces of D₂O compared to that of H₂O might slow the evaporation of the residual capillary bridge that binds to the particles after the meniscus unpins. This results in both increased square nuclei formation and a longer time scale for nuclei-bridge-induced restructing.

Further evidence of solvent effects was obtained by tracking the particle coordination profile throughout evaporative crystallization. Videos, sequestered via optical microscopy at 10 fps, were split into their individual frames, and the coordination matrix was extracted from each, as described in the supporting methods. Figure 5A depicts an enlarged time lapse withdrawn from Video S1, in which the evaporation front recedes from top to bottom. Phase-shifting from hexagonal to square occurs in approximately 40 s and propagates downward from the preformed square nucleus. Video S2 shows a clip of the color-coded coordination matrix output, which substantiates that individual particles continuously undergo conversions between disordered, close-packed, and open-packed states. Interestingly, we observed that particles with Zₐ = 3 and 4 follow nearly equivalent and opposing trends to those with Zₐ = 5 and 6; therefore, the corresponding particle coordination fraction values (Φₚ) were plotted as an average with respect to meniscus recession time (Figure 5B,C). The average of these pairs of values produced more precise data profiles due to accommodation of error generated from image edge effects. Packing transitions occurred approximately 25–40 μm above the meniscus; therefore, close-packed regions continuously formed at the meniscus simultaneously as the phase transition to square packing occurred. The outcome is an alternating trend of average coordination fractions emulating a sinusoidal function, in which the curve of the
to two or more different functions for the duration of an 80 s crystallization process, as indicated by the dotted line in Figure 5C. In contrast, the use of D2O generates a more distinguishable profile that can be fit to the sloped dampened sinusoidal function \( \Phi_Z = A \sin(\alpha x) e^{(\alpha x)} + mx + b \) (Figure 5B). This function has a linear slope component that increases for \( Z_n = 3 \) or 4 and decreases for \( Z_n = 5 \) or 6, indicating that the fraction of lower coordinated particles steadily increases as crystallization proceeds.

The discrepancy between the H2O and D2O results is corroborated by our previously stated hypothesis: the slower depletion of residual heavier solvent due to stronger intermolecular forces between D2O molecules generates more time for the particles to reconfigure, thereby creating both a larger ratio of 4-fold coordinated particles and a more uniform oscillatory process of assembly and reconfiguration. There is some variability in the precise contour of coordination fraction curves across one sample; however, crystallization from H2O delivers consistently less uniform data than that from D2O.

**Volume Fraction Controls Particle Rearrangement.** Fabrication of discrete colloidal superstructures using capillary assembly is usually reported at low particle concentrations (0.1–0.5 wt %) so as to discourage undesired deposition of excess particles to the areas surrounding the cavities. We observed template-directed crystallization into square lattices at 2.0 wt %. By varying the concentration from 0.5 to 3.0 wt %, we were able to determine that there is a specific range in which nuclei bridging and proliferation of square packing are maximized (Figure 6A). At low concentrations (0.5–1.0 wt %), the AZ is not sufficiently populated by particles and partially filled boxes ensue. At 1.5 wt %, filled boxes with hexagonal packing dominate due to an osmotic pressure that is insufficient to foster the extension of particles across the boundaries; particles therefore arrange into their minimum energy structure. We begin to observe connectivity between boxes and depression of 6-fold coordination at 1.75 wt %. Four-fold coordination and square nuclei bridging are maximized at 2.0 wt % to form a continuous crystal, while particles with 6-fold coordination approach a minimum. This trend is reversed as the concentration increases to 3.0 wt %, upon which the osmotic pressure is elevated enough to impel an irreversible collapse into segmented HX domains (Figure 6A). In summary, there is a narrow range of input concentrations in which square packing is maximized. This peak in \( Z_n = 4 \) at 2 wt % is inversely proportional to the fraction of particles bearing \( Z_n = 6 \) (Figure 6C).

Previous reports have surmised that particles within the AZ pack closely and occupy nearly all available space, resulting in volume fractions between 0.6 and 0.7 that approach the face-centered cubic packing (0.72). It has been implied that the volume fraction in the AZ is independent of the starting particle concentration due to the overpowering accrual of particles caused by the strong convective flow. Our results do not follow this trend. The pressure in the AZ generates an osmotic force that acts transversely upward across the plane of the assembled crystal to affect reconfiguration. Since the particle volume fraction is directly proportional to the osmotic pressure and, by extension, the osmotic force (see the Supporting Information), and square packing restructuring only occurs at a certain concentration, changes in the initial particle concentration must alter the osmotic pressure specifically within the AZ. Thus, unlike what is reported in

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**Figure 4.** Particle fraction distributions for lattices crystallized from H2O (pink) and D2O (purple) compared to those for a hexagonally close-packed standard (teal). The addition of a square template increases the fraction of 4-fold coordinated particles by a factor of 10 and decreases the fraction of 6-fold coordinated particles by the same factor. The overlaid curves show the particle coordination number distributions for each sample. We observe that for particles assembled from D2O the distribution is skewed furthest left toward \( Z_n = 6 \), whereas the HX control is skewed furthest right toward \( Z_n = 6 \). Symbols indicate statistical significance, in which matching pairs from each data set denote a statistically significant difference (\( p < 0.5 \)). Statistics for \( Z_n = 1, 2, \) and 7 were omitted for clarity. \( p \) values were calculated using Student’s two-tailed \( t \) test, type 3. All solvents contain 2.0 wt % particles and 1.0 wt % F108. Scale bar = 10 \( \mu \)m.

**Figure 5.** Time lapse of capillary assembly. (A) If \( s_p < r \) and \( d = r/2 \), nuclei bridging promotes force-driven propagation of square packing and a close-packed \( \rightarrow \) square-packed transition occurs. (B, C) Change in particle coordination number fraction \( \Phi_Z \) during crystallization from (B) D2O and (C) H2O. Packing transitions oscillate as close-packed regions in the accumulation zone restructure when adjacent to square nuclei. Particles with \( Z_n = 3 \) and 4 follow the opposite trend to those with \( Z_n = 5 \) and 6. Raw data was fitted to a dampened sinusoidal function: \( \Phi_Z = A \sin(\alpha x) e^{(\alpha x)} + mx + b \) (C) \( \Phi_Z \). Oscillations from H2O are nonuniform and vary in both amplitude and frequency, and there are stark contact line shifts as the meniscus recedes as indicated by the dotted line.
the previous literature, the AZ volume fraction must be a function of inputted volume fraction rather than a tightly packed region generated as a function of drag force. The osmotic pressure $\Pi$ can be estimated based on a model described by Wolf and co-workers derived from the Wigner-Seitz approach, in which $\Pi_{\text{osmotic}}$ is equal to the sum of electrostatic, van der Waals, and entropic interaction components:

$$\Pi_{\text{osmotic}} = \Pi_{\text{en}} + \Pi_{\text{vdw}} + \Pi_{\text{e}}$$

It should be noted that this estimation does not currently consider the effect of different template geometries on the osmotic pressure. Statistically indistinguishable results transpired when highly charged DNA-coated TPM particles were assembled onto patterned surfaces modified with complementary strands: $\Phi_p, Z_n = 6$ is maximized at $0.06 \pm 0.02$ versus $0.32 \pm 0.02$ for nonfunctionalized particles ($p = 0.06$ using Student’s two-tailed $t$ test, type 3). We therefore omitted the electrostatic contributions from the osmotic pressure calculation. A plot of the sum of entropic and van der Waals constituents versus the volume fraction ($\varphi$) for $Z_n = 4$ reveals that $\Pi_{\text{osmotic}}$ is maximal at $\varphi = 0.52$ and minimal at 0.74, which correspond to the packing fractions of a simple cubic and FCC lattice, respectively (Figure S5). Calculated theoretical $\varphi$ values based on particle concentrations and TPM particle density shown in shown in Table S1, however, these values do not reflect those in the AZ. The long-range drag force that draws particles from the bulk into the AZ disrupts the inputted volume fractions.

We hypothesize that $\varphi$ approaches at least 0.52 for particle concentrations of 2.0 wt %, where $\Phi_p$ for $Z_n = 4$ (i.e., square packing) is greatest, where the maximum value of $\varphi$ cannot exceed 0.74. This assumption is consistent with the estimation of high volume fractions ($\varphi = 0.6–0.7$) in the AZ in previous studies and in view of our explanation that $\Pi_{\text{osmotic}}$ is not constant given alterations in particle weight percent.

**Template Geometry Effects.** We have thus far concluded that the ability for particles within a box to interact with those in adjacent boxes enables restructuring into nonclose-packed arrangements. Increasing the boundary depth to 1.3 μm produces disjointed boxes of either amorphously or hexagonally packed colloids (Figure S3). Video S4 qualitatively depicts that there are limited interactions between particles in neighboring boxes and that the square templates fail to induce square packing. This assembly regime is more akin to the targeted deposition of particles into discreet cavities seen in conventional capillary assembly.

We further investigated the effects of minimizing the boundary depth to 400 nm (Figure 6B). Plotting the normal distributions of $Z_n$ with respect to $\Phi_p$ reveals that the range of coordination numbers for samples of different concentrations is much narrower for the shallower template, indicating that the template does not affect particle packing into a preferred structure to the same extent as for the 550 nm fences (Figure 6C,E). A quantitative comparison of $\Phi_p$ for $Z_n = 6$ versus particle concentration is shown in Figure 6C; additional data for $\Phi_p$ for $Z_n = 3–6$ is in Figure S6. From 0.5 to 1.75 wt %, the assembly results for 400 nm boundaries match those of the deeper 550 nm wells. Deviations in $\Phi_p, Z_n=4$ and $\Phi_p, Z_n=6$ for $d = 400$ nm emerge beyond 2.0 wt %: the incidence of square-packed regions increases steadily from 1.5 to 3.0 wt % although the curves are generally more leveled than the normal-type distributions observed for $d = 550$ nm in which square packing peaks at 2.0 wt %.

Extensive bridging behavior across the boundaries prevails for the shallower template as the depth approaches that of a nonpatterned substrate. Furthermore, there is no collapse into close-packed discrete units at high volume fractions; in fact, the occurrence of square packing is greatest at 3.0 wt %.

Finally, we were further convinced of the delicate nature of template structuring by evaluating the effects of widening the space between boxes and reducing the integrity of the photore sist (Figure 7). Assembly was performed from H2O with 2.0 wt % TPM for square templates with 8 μm × 8 μm dimensions and 6 μm spacing (Figure 7B) and for damaged 10 μm × 10 μm templates. Underexposure for 15 s (Figure 7D) and 10 s (Figure 7E) produces kinks and cracking in the template. We observe that larger spacing produces monolayers
which allows for preformed structures to bridge the boundaries. Square nuclei propagation is the shallowness of the templates. Coordinated particles in our square-packed lattices increase and thereby the overall osmotic pressure of the system. There is a process is highly dependent on the volume fraction and transitions throughout solvent evaporation reveals that square packing is not observed. Quantifying packing phase 4-fold coordinated particles are maximized, outside of which produces a larger fraction of square-packed regions. Finally, we determine that increasing and decreasing the depth of the template, as well as distorting its resolution, produce hexagonal and/or amorphous packing, which confirms the importance of the targeted template design. The emerging use of this simple, scalable technique is promising for creating large domains of functional colloidal materials. The minimization of the underlying template is intentional as ultimately there is a desire to produce nonclose-packed colloidal crystals without the interference of a template, given that templates can be an inherent defect for a photonic crystal. By analyzing the assembly mechanisms within the most diminutive guidelines thus far reported for square packing, we inform the eventual template-free fabrication of square lattices for optical applications. We anticipate that these findings will encourage further use of template-assisted capillary assembly for engineering open-packed 2D lattices, with expectations of extending to anisotropic particle crystallization, 3D structures, binary lattices, and more unique and currently inaccessible geometric architectures.

### EXPERIMENTAL SECTION

**Materials.** Silicon and glass wafers were purchased from University Wafer and chromium photomasks from DigiDat. Gold pellets, chromium pellets, and tungsten baskets used for metal evaporation were acquired from Ted Pella, Inc. SU-8 photoresists and the corresponding developers were purchased from MicroChem. All reagents including 3-(trimethoxysilyl)propyl methacrylate (TPM, 98%) and ammonium hydroxide (35%) were purchased from Sigma-Aldrich and used without modification. Deionized water was obtained from a Millipore Filtration System (Milli-Q gradient A10). Optical microscopy and scanning electron microscopy (SEM) were procured from a Nikon TE300 microscope and a Merlin (Carl Zeiss) field emission SEM microscope, respectively.

**Methods.** Particle Synthesis. The synthesis involves TPM hydrolysis and self-condensation in an aqueous alkaline solution to form a cross-linked oligomeric network that phase-separates into emulsion droplets. The droplets are sequentially swollen with additional monomer and polymerized to achieve the desired particle sizes with low distributions. In detail, TPM (200 \( \mu \)L) was added to deionized water (20 mL) and allowed to soft-condense for 10 min before adding ammonium hydroxide (20 \( \mu \)L, 35% \( \nu/\nu \)) to a final concentration of 9 mM. Ammonium hydroxide catalyzes the hydrolysis and condensation of the methoxy groups, resulting in a siloxyl network of TPM oligomers. As the droplets grow, they phase-separate to form an emulsion, evidenced by the turbidity of the reaction. The emulsion was stirred in a vial, and additional aliquots of 150 \( \mu \)L of TPM were added after 2 and 4 h intervals, for a total condensation time of 6 hours. Emulsion droplets grow as additional monomer diffuses into their core. Once the desired size is attained as verified by optical microscopy, free radical polymerization of the methacrylate groups was induced by the addition of azobisisobutyronitrile (10 mg) and the reaction was stirred 78 °C overnight to yield solid 2 \( \mu \)m spherical particles (Figure 2A). The particles were washed in ethanol five times to remove excess monomer and initiator and then two times in water using centrifugation and resuspension via sonication. The colloids were imaged and analyzed with SEM. All particles were diluted in 1.0 wt % F108 and sonicated to prevent aggregation before assembly experiments.

**Fabrication of Patterned Substrates.** Substrates were patterned using conventional photolithography using a chromium photomask. Rigid templates were used because in contrast to elastic polymer substrates (e.g., poly(dimethylsiloxane)), they do not deform when compressed by the exerted downward capillary force. Glass wafers were cleaned in acid piranha (3:1 H\(_2\)SO\(_4\)/H\(_2\)O) for 1 h at room temperature to remove organic impurities, treated with oxygen plasma for 2 min, and spin-coated with SU-8. The depth of the wells was
tuned using photoresists of different viscosities and/or by adjusting the spin parameters. For 550 nm deep wells, SU-8 2000.5 was spin-coated at 500 rpm and 100 rpm/s for 10 s and then 2000 rpm and 200 rpm/s for 30 s. For 400 nm deep wells, SU-8 2000.5 was spin-coated at 500 rpm and 100 rpm/s for 10 s and then 3000 rpm and 300 rpm/s for 30 s. Both samples were soft-baked at 95 °C for 60 s prior to exposure to a 275 nm UV light for 20 s through a chromium photomask. Templates with reduced integrity were underexposed (15 and 10 s, Figure 7) to examine the effects of poor boundary resolution of crystallization. The patterned wafers were hard-baked for 60 s at 95 °C, developed for 60 s in SU-8 developer, rinsed with isopropyl alcohol (IPA), and dried with nitrogen. For 1.5 μm deep wells, SU-8 2002 was spin-coated at 1000 rpm and 100 rpm/s for 10 s and then 3000 rpm and 300 rpm/s for 30 s. The samples were soft-baked at 95 °C for 90 s before exposure to a 275 nm UV light for 22 s through a chromium photomask. The patterned wafers were hard-baked for 120 s at 95 °C, developed for 60 s in SU-8 developer, rinsed with IPA, and dried with nitrogen. The parameters for lithography and molding were optimized to create feature sizes with suitable resolution and depth (Figure S3).

**Fabrication of Flow Cell and Particle Assembly.** Particle assembly occurs inside of a 4 mm wide channel containing the patterned substrate. The channels were masked with a flat capillary spacer to create a 400 μm gap between the substrate and the top of the channel. The channels were enclosed with a coverslip using a Norland Optical Adhesive 81. A schematic showing a typical flow cell is depicted in Figure 2B. A 10 μL droplet of the particle suspension was deposited at the opening of the channel and allowed towick through. Evaporation typically takes 2–4 h under ambient conditions. The samples were analyzed throughout evaporation using optical microscopy.

**Hexagonally Close-Packed Crystal Fabrication.** Hexagonally close-packed crystals were fabricated using convective assembly. Silicon wafers were cleaned with acid piranha and subjected to air plasma for 2 min to create a hydrophilic surface. A flow cell was constructed to create a small channel, and TPM colloids (2 μm, 0.5 wt %, 1.0 wt % F108) were injected into the cell. The solvent was evaporated at room temperature to give close-packed crystals.

![Image](https://example.com/image.png)

**REFERENCE**

Grafting of DNA onto particles; gold template fabrication with DNA grafting; calculated volume fractions associated with particle concentrations; TPM particle synthesis; fabrication of glass patterned templates using photolithography (PDF).

Representative templated capillary assembly process using conditions described in Table S1 with H2O as the solvent; recorded at 10 frames per s (fps) and is displayed at 5X speed (MP4).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b02124.

Representative templated capillary assembly process using conditions described in Table S1 with H2O as the solvent; recorded at 10 frames per s (fps) and is displayed at 5X speed (MP4).

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C.S. conducted the experimentation and analysis. All authors wrote the manuscript. V.G. fabricated and analyzed the HX controls. V.G. and A.M. contributed to the script for the coordination mapping method. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

TPM, 3-(trimethoxysilyl)propyl methacrylate; HX, hexagonal; FCC, face-centered cubic; AZ, accumulation zone

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