Electronic Supplementary Information (ESI) for

Fabrication of High-Quality Non-Close-Packed 2D Colloid Crystals by Template-Guided Langmuir-Blodgett Particle Deposition

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E1. Discussions of the Structural and Mechanical Properties of the Langmuir Monolayer of the 1.5-µm Silica Particles

For in situ imaging of the silica colloid monolayer at the air-water interface under various compression conditions, the miniaturized Langmuir trough equipment (Kibron Microtrough X-LB) was staged on a Leica DMIRB inverted microscope. All in situ imaging was performed in a vibration-controlled environment within a plexiglass chamber which prevents any disturbance of the silica monolayer at the air-water interface by air flow in the room and contamination of the interface due to dust accumulation. The representative images shown in Figure E1 were taken at an objective lens magnification of $40 \times$.

At low compression, the mean particle separation distance is sufficiently large (i.e., in the gas limit) (Figures E1(A) and E1(B)), and the dependence of π on A is almost unnoticeable in the linear presentation of the π vs. A plot. With further compression (i.e., when the interparticle distance is significantly decreased), the increase of π becomes slightly pronounced even though the system is still in the fluid phase (Figure E1(C)). At $A \approx 2.4 \ \mu\text{m}^2$ per particle, further compression of the monolayer causes an abrupt increase of π , indicating the onset of formation of dense hexagonal close-packed structures (Figures E1(D) through E1(F)) due to the hard-core repulsive interaction among the silica particles. From the π -A isotherm data, the monolayer collapse pressure is estimated to be about 10 mN/m for the hydroxy silica particles used in this study; this value is considerably lower than those reported in the literature for hydrophobically surfacemodified silica particles (> 15 mN/m),¹⁻⁵ indicating a weaker interaction between adjacent particles in the solid phase in the hydroxyl functionalized case. The limiting area A_{0} (the x-intercept of the extrapolated linear regression of the steepest section of the solid portion of the isotherm curve) is estimated to be approximately 1.97 μm^2 per particle. This limiting area can be interpreted as the theoretical onset of the hard-spherelike repulsion, and the estimated value is consistent with the theoretical surface area that would be occupied by a particle when the particles are packed into an HCP lattice (= $2\sqrt{3}r^2$ where r is the particle radius), i.e., 1.95 μ m² per particle for the 1.5- μ m silica, indicating that the actual range of the hard core exclusion is quite comparable to their physical diameter.

We performed optical microscopy imaging under the identical sequence of compression conditions or in real time simultaneously to the measurements of the π -A isotherms, and identified the exact structures of the Langmuir monolayer which characterize the various states in the π -A isotherm that occur during the lateral compression of the particle monolayer; the results are shown in Figure E1. From the images taken from the fluid regime (Figures E1(A) through E1(C)), it was estimated that approximately 7% of the particles were lost from the water surface due to sedimentation into the subphase during the initial spreading process; however, it was confirmed that at least in the fluid regime and in the early stage in the development of the solid phase during the compression. It should be mentioned that in constructing the π -A isotherm shown in Figure 2 of the main text, we used the surface area per particle values corrected for the amount of the sedimented particles. As shown in Figures E1(A) though E1(D), we found that the transitions from the gaseous state (A and B) to the condensed liquid state (C) to the solid state (D) are rather smooth and continuous; we observed no evidence for a

discontinuous change in the surface area of the system (such as a plateau in the π -A isotherm) throughout these transitions, suggesting that these transitions are unlikely to be first-order phase transitions. It is also of note that unlike what has been hypothesized in the literature (based on imaging studies of LB-deposited films of colloid monolayers),^{2,5} the fluid-solid transition occurs at the high-surface area end of the upturn region in the π -A isotherm. From the imaging results, the critical area fraction for the onset of the confinement-induced 2D crystallization is estimated to be $\phi_{c_{2D}} = 0.65 \pm 0.02$ (in this work we did not attempt to resolve the precise boundaries for the 2D hexatic phase), and this result deviates from the predicted value of $\phi_{c,2D} \approx 0.735$ for the crystallization of hard-sphere colloids in 2D based on simulations;⁶ note the measured crystallization threshold is lower than even the predicted fluid-hexatic transition boundary of $\phi_{h_{2D}} \approx$ 0.70.⁶ In the solid regime, further compression after crystallization causes the formation of buckled structures (see Figures E1(E) and E1(F)), and in the linear up-slope region, the buckled domains ("mesas") were found to be significantly larger than the single particle dimension (Figure E1(F)). We also note that in our system, we have not observed formation of particle clusters in the fluid regime. This observation is attributed to the following factors: (i) successful purification of the particles and maintenance of a contaminant-free environment within the Langmuir apparatus (incorporation of any surface active impurity can induce uncontrolled agglomeration of colloids at the air-water interface);^{7,8} (ii) the strong hydrophilicity of the particle surface;^{1,9} (iii) the uniform distribution of the hydroxyl groups on the surface of the silica sphere (long-range anisotropic dipolar interactions between colloids on the water surface (due to a nonuniform distribution of the charge on the colloid surface) can give rise to formation of such morphologies as strings, rings or foam-like agglomerates of particles).^{7,8,10}

Figure E1. Representative optical micrographs of the Langmuir monolayer of the silica particles at seven different monolayer areas of A = (A) 6.0, (B) 4.1, (C) 2.6, (D) 2.4, (E) 2.2, (F) 1.9, and (G) 1.3 μ m² per particle. Compression of the particle monolayer in 2D typically causes transitions in the structural state of the monolayer film from the gaseous (A and B) to the liquid (C) to the crystalline (D through F) and finally to the irreversibly deformed (G) states.



(G)



E2. Demonstration of the Template-Guided LB Deposition of Silica Microspheres onto a Square-Patterned Substrate

We tested the pattern-guided LB colloid deposition method for a square substrate pattern at a pattern density comparable to that of the hexagonal pattern; the pattern densities are 26% and 28% for the hexagonal and square substrates, respectively. On this square-patterned substrate, LB particle monolayers were constructed at the six different values of *A* used in the previous set of experiments with the hexagonal substrate (Figure 3 of the main text), and scanning electron microscopy (SEM) images of the resulting samples are presented in Figures E2(A) through E2(F). As shown in these figures, despite the difference in symmetry, the overall trend observed with the square substrate is almost identical to that observed in the hexagonal case (Figure 3). Notably, a nearly defect-free 2D NCP square crystal was obtained at the same value for the surface area of the precursor monolayer at the air-water interface as in the hexagonal case (i.e., $A = 2.4 \,\mu\text{m}^2$ per particle).

Figure E2. Representative SEM images of the LB colloid monolayers transferred onto the square patterned substrates at six different initial monolayer areas of A = (A) 6.0, (B) 4.1, (C) 2.6, (D) 2.4, (E) 2.2 and (F) 1.9 μ m² per particle and at a fixed substrate lifting speed of U = 1.0 mm/min.



Figure E3. Low-magnification optical microscopy images of the LB-deposited particles on the hexagonally patterned substrate demonstrating the oscillations of the deposited particle densities inside the micro-patterned region of the substrate (along the direction of the substrate movement during the deposition). These samples were prepared at four different values of the surface area of the precursor monolayer at the air-water interface: i.e., A = (A) 2.4, (B) 2.6, (C) 4.1 and (D) 6.0 μ m² per particle and at a fixed substrate lifting speed of U = 1.0 mm/min. Plots of the particle density (ϕ) as a function of the distance from the pattern edge (*L*) calculated from higher-magnification images of the samples are presented in Figure 4 of the main text.



E3. Analyses of the Spatial Variations of the Densities of the LB-Deposited Silica Particles on the Square-Patterned Substrate

The same set of analyses as discussed in Section III.2 of the main text were performed on the LB monolaver samples prepared on the square-patterned substrate at the four different initial surface area values (Figures E4(A) through E4(D)). Interestingly, in these square-substrate cases, the spatial variations of the deposited particle densities were observed to be significantly irregular, which is in contrast to the far more regular behavior observed in the hexagonal cases under the identical LB deposition conditions (Figure 4). We speculate that this non-regular variation of the particle density in the square cases resulted from the fact that because of the larger spacing between lattice lines along the substrate lifting direction, a particle that is initially adsorbed in an interstitial position on the square-patterned substrate will have to travel a longer distance until it finds and enters an empty pattern site (that is, the particles become pinned to the lattice sites at distances farther from the contact line) than in the hexagonally-patterned cases, and therefore in the square cases, the final distributions of the deposited particle positions will be influenced not only by the contact line stick-slip motion at the initial stage of the particle deposition but also by further displacement of the particles within the LB film due to the gravity as well as the drying of the film in the later stage of the LB monolayer transfer. Nonetheless, in these LB films prepared on the square-patterned surfaces, despite the spatial variations of the deposited particle densities, the average particle density was found to be a systematic (i.e., monotonically decreasing) function of the initial compression area with a dependence similar to that observed in the hexagonal case (Figure 7(A)).

Figure E4. Low-magnification optical microscopy images of the LB-deposited particles on the square patterned substrate, and the respective particle density profiles inside the patterned region ($\phi(L)$). The particle monolayers (initially constructed at the air-water interface) were transferred onto the patterned substrates at four different initial compression areas of A = (A) 2.4, (B) 2.6, (C) 4.1 and (D) 6.0 μ m² per particle and at a fixed substrate lifting speed of U = 1.0 mm/min.



500 µm









500 µm

Figure E5. Representative low(left) and high(right)-magnification microscopy images of the LB colloid monolayers on the hexagonally-patterned surfaces, produced at four different substrate lifting speeds (i.e., U = (A) 1.0, (B) 2.0, (C) 4.0 and (D) 8.0 mm/min) and at a fixed initial monolayer area of $A = 2.4 \ \mu\text{m}^2$ per particle.



10 µm

500 µm











500 µm



500 µm

E4. Derivation and Use of the Theoretical Model in the Interpretation of the Results from the LB Particle Deposition Experiments

We consider a force balance on a differential volume element located at the threephase contact line to model the time-dependent motion of the contact line (L(t)). The contact line motion along the y-direction will be determined by a balance among the ycomponents of the following three driving forces acting on the control volume: (a) the force due to the surface tension $(\gamma|_{y=y_c+dy/2})$ acting upward on the deposited film side of the control volume, (b) the surface tension $(\gamma|_{y=y_c-dy/2})$ in the opposite direction on the original Langmuir film side, (c) the shear stress due to the water velocity gradient at the bottom surface of the particle monolayer, $\frac{\partial v_y}{\partial x}\Big|_{x=\delta}$ (this force is normally in the downward

direction because of the gravitational drainage of water in the subphase gap), and (1) the gravitational body force exerted on the control volume. Hence, the force balance on the control volume can be written as

$$\left(Wdy^{2}\right)\rho\frac{d^{2}L}{dt^{2}} = \left(W\right)\left(\gamma\Big|_{y=y_{c}+dy/2} - \gamma\Big|_{y=y_{c}-dy/2}\right)\cos\theta - \left(Wdy\right)\eta\frac{\partial v_{y}}{\partial x}\Big|_{x=\delta} - \left(Wdy^{2}\right)\rho g \quad (E1)$$

where W, dy, ρ , θ , η and g denote the width of the Langmuir film, the thickness of the control volume, the density of the control volume (\approx density of water), the contact angle, the viscosity of water and the gravitational acceleration, respectively. Approximating the surface tension difference as $\gamma|_{y=y_c+dy/2} - \gamma|_{y=y_c-dy/2} = d\gamma|_{y=y_c} \approx c(\gamma - \gamma_o)$ (where *c* is a proportionality factor, and γ and γ_o respectively denote the surface tensions of the LB-deposited monolayer right above the contact line and of the pristine monolayer in the bulk limit (i.e., far away from the contact line)), and setting the size of the control volume equal to the particle diameter (i.e., $d\gamma \approx D$), the balance equation can be re-written as

$$\rho \frac{d^2 L}{dt^2} = \left(\frac{1}{D^2}\right) c \left(\gamma - \gamma_o\right) \cos \theta - \left(\frac{1}{D}\right) \eta \frac{\partial v_y}{\partial x}\Big|_{x=\delta} - \rho g.$$
(E2)

Here, the surface tension of the monolayer is a function of the particle area fraction in the monolayer (ϕ , in dimensionless units), and in our system, the exact dependence of γ on ϕ can be estimated from the measured π -A isotherm (Figure 2). Over the particle densities corresponding to the fluid regime of the isotherm, the relationship between γ and ϕ can be reasonably approximated by a linear equation (because of the ideal gas-like behavior of the system in this regime)

$$\gamma = \gamma_o + \frac{\partial \gamma}{\partial \phi} \Big|_{\phi = \phi_o} \left(\phi - \phi_o \right).$$
(E3)

In our case, the value of $\frac{\partial \gamma}{\partial \phi}\Big|_{\phi=\phi_o}$ was estimated to be -3.2×10^{-4} mN·m from the fitting of

the fluid portion of the π -A isotherm to a linear equation. The force balance, therefore, can now be expressed in terms of ϕ and ϕ_o

$$\rho \frac{d^2 L}{dt^2} = \left(\frac{1}{D^2}\right) c \cos \theta \frac{\partial \gamma}{\partial \phi}\Big|_{\phi = \phi_o} \left(\phi - \phi_o\right) - \left(\frac{1}{D}\right) \eta \frac{\partial v_y}{\partial x}\Big|_{x = \delta} - \rho g .$$
(1)

To be able to calculate the viscous drag force on the control volume, the velocity profile for water flowing through the gap between the substrate and the contact line (i.e., $v_y(x)$ from x = 0 to $x = \delta$) needs to be known. To a simplest (but reasonable) approximation, we assume a quadratic form for this velocity (i.e., $v_y(x) = Ax^2 + Bx + C$), because this is the simplest possible form of the equation that allows us to capture the anticipated flow separation behavior in the subphase gap due to the downward drainage of water. Due to the no-slip boundary condition at the substrate surface (i.e., $v_y(x = 0, t) = U$) and the particle mass balance in the monolayer film above the contact line (i.e., $v_y(x = \delta, t) = -L'(t)$), we obtain

$$v_{v}(x,t) = A(t)x(x-\delta) - (U+L'(t))(x/\delta) + U.$$
(2)

Here, A(t) can be determined from the mass balance for water. In setting up the water balance, we assume that using the ΔL concept introduced earlier in this section, only the water evaporation from the surface of the monolayer in the region between the contact line $(y = y_c)$ and a position ΔL above the contact line $(y = y_c + \Delta L)$ will be compensated by the inflow of water from the subphase into the air-water meniscus of the monolayer film, and will therefore influence the subphase water velocity profile; beyond this region $(y > y_c + \Delta L)$, because of the absence of the subphase gap, further evaporation of water will only result in a gradual depletion of water in the deposited monolayer film, which is initially wet, eventually leading to a dried monolayer film of the particles on the substrate. Within this picture, the molar water evaporation rate over the ΔL region should be balanced by the molar rate of water inflow through the cross section of the film at $y = y_c$:

$$J_{e}(t)\left\{W\Delta L - \int_{L(t)}^{L(t)+\Delta L} \phi(L)WdL\right\} = J_{c}(t)W\delta$$
(3)

where $J_e(t)$ and $J_c(t)$ denote the molar water evaporation flux and the average molar flux of water through the $y = y_c$ cross section of the subphase layer; $J_c(t)$ is related to $v_v(x,t)$ by

$$m_w J_c(t) = \frac{1}{\delta} \int_0^{\delta} \rho v_y(x, t) dx$$
(4)

where m_w is the molar mass of water. Eqs (1) though (4) now provide a closed set of equations for all the relevant variables. Further, these equations provide useful insights on why the water evaporation causes the undulation of the contact line; (i) as can be seen from eq (3), water evaporation in the ΔL region increases $J_c(t)$ and reduces the downward flow velocity of the subphase water (eq (4)), and as a result, the shear stress in eq (1) becomes less negative; (ii) the reduction in the shear stress accelerates the upward motion of the contact line, and causes a ϕ increase (eq (1)); (iii) the increase in ϕ reduces $J_c(t)$ (eq (3)); (iv) the decrease in $J_c(t)$ now reverses the trends described in the above sequence of events; (v) finally, these processes repeat over time, giving rise to a stable periodic oscillation of the properties.

To test whether this proposed model can indeed predict the oscillatory particle density profiles at reasonable values for the unknown parameters in the model (i.e., $c\cos\theta$, δ , $J_e(t)$ and ΔL), the above equations were numerically analyzed. For this purpose, eqs (1) through (4) were further transformed and combined to obtain the following set of ordinary differential equations:

$$(\alpha L''(t) + \beta L'(t))L'''(t) + \chi (L''(t))^{2} + (\gamma L'(t) + \varepsilon)L''(t) = 0$$
(E4)

where
$$\alpha = -J_e(t) \frac{\rho D^2}{c \cos \theta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} \left(\frac{\Delta L}{U} \right)^2$$
, $\beta = J_e(t) \frac{\rho D^2}{c \cos \theta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} \frac{\Delta L}{U}$,
 $\chi = J_e(t) \frac{\rho D^2}{c \cos \theta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} \left(\frac{\Delta L}{U} + \frac{\eta}{\rho D \delta} \left(\frac{\Delta L}{U} \right)^2 \right)$, $\gamma = -2J_e \frac{D\eta}{c \cos \theta \delta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} \frac{\Delta L}{U}$, and
 $\varepsilon = J_e(t) \left[\frac{D^2 \rho g}{C \cos \theta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} + \phi_0 \frac{\Delta L}{U} + \frac{5\eta U D}{c \cos \theta \delta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} \right] \frac{\Delta L}{U} + \frac{\rho \delta}{2m_w};$
 $\phi(t) = \phi_0 + \frac{D^2}{c \cos \theta} \left(\frac{\partial \gamma}{\partial \phi} \Big|_{\phi=\phi_o} \right)^{-1} \left(\rho L''(t) - \frac{\eta}{D \delta} (L'(t) - 5U) + \rho g \right).$ (E5)

In solving eq (E4), the following parameter values and initial conditions were assumed: $c\cos\theta \approx 7.80$ (this estimate was obtained as explained in the later part of this section), $\delta \approx D$, $J_e(t) \approx 3.3 \times 10^{-7}$ mol/cm²·s (taken from the literature),¹¹ L(t=0) = 2 mm, and L'(t=0) = -U. The two remaining unknowns (i.e., ΔL and L''(t=0)) were used as adjustable parameters. As demonstrated in Figures E6(A) and E6(B), it was confirmed that at $\Delta L = 25 \,\mu\text{m}$ and $L''(t=0) = 0.1 \,\mu\text{m/s}^2$, for instance, the model predicts the stick-slip behavior of the contact line at the four different values of ϕ_o with fixed U (used for the experiments described in Section III.2), and also at the four different values of U with fixed ϕ_o (used for the experiments described in Section III.3). Once L(t) is calculated for each of the given conditions, the corresponding ϕ profile was obtained by numerically solving eq (E5). See Figure E6 and also Section III.4 of the main text for discussions of the results.

With no evaporation of water (i.e., $J_e(t) = 0$), the net flux of water into the film region above the contact line (i.e., $y > y_c$) is zero (i.e., $J_c(t) = 0$) (see eq (3)); otherwise, water will accumulate over time in the LB film, which is unphysical. Using this condition, the value of A(t) in eq (2) is estimated to be $A(t) = 3(U-L'(t))/\delta$, and this gives an equation for the contact line shear stress in eq (1), $\eta \frac{\partial v_y}{\partial x} \bigg|_{x=\delta} = \frac{2\eta}{\delta} (U - 2L'(t))$. Under

this no evaporation condition, the $v_y(x)$ profile and thus the contact line position in the laboratory frame of reference will be stationary (under steady state conditions), and therefore, the contact line becomes displaced from the starting edge of the substrate at a constant rate whose magnitude should be equal to the substrate lifting speed (i.e., L'(t) = -U), which gives L''(t) = 0. Therefore, for this situation, rearranging eq (1) yields

$$\phi = \phi_o + \frac{D^2}{c\cos\theta} \frac{\partial\gamma}{\partial\phi} \bigg|_{\phi=\phi_o} \left(\frac{6\eta U}{D\delta} + \rho g \right)$$
(E6)

which describes the dependences of ϕ on ϕ_o and U; note here that $\langle \phi \rangle = \phi$ in this case, because ϕ is position-independent. Now, the predictions based on eq (E6) can be quantitatively compared with the experimental data shown in Figures 7(A) and 7(B); see Section III.4 for further discussion of this analysis.

Figure E6. The predictions of the model for (A, B and C) the time-dependent variation of the contact line position (L(t)) and (D, E and F) the position-dependent variation of the deposited particle density in the resulting LB monolayer ($\phi(L)$) under various LB monolayer transfer conditions. (A and D) L(t) and $\phi(L)$ calculated at four different particle densities of the precursor air-water monolayer (ϕ_a) (i.e., $\phi_a = 0.67$ (solid curve), 0.63 (dashed curve), 0.56 (dashed-dotted curve) and 0.47 (dotted curve)) and at a fixed substrate lifting speed of U = 1.0 mm/min and a fixed water evaporation rate of $J_e(t) = 3.3$ $\times 10^{-7}$ mol/cm²·s. (B and E) L(t) and $\phi(L)$ calculated at four different substrate lifting speeds (i.e., U = 1.0 (solid curve), 2.0 (dashed curve), 4.0 (dashed-dotted curve) and 8.0 (dotted curve) mm/min) and at a fixed initial particle density of $\phi_o = 0.67$ and a fixed water evaporation rate of $J_e(t) = 3.3 \times 10^{-7}$ mol/cm²·s. (C and F) L(t) and $\phi(L)$ calculated at four different water evaporation rates (i.e., $J_e(t) = 0$ (solid curve), 3.3×10^{-8} (dashed curve), 3.3×10^{-7} (dashed-dotted curve), 3.3×10^{-6} (dotted curve) and 3.3×10^{-5} (dasheddotted curve) mol/cm²·s⁻¹) and at a fixed substrate lifting speed of U = 1.0 mm/min and a fixed initial particle density of $\phi_{a} = 0.67$. In (D) and (E), the horizontal lines represent the deposited particle densities calculated in the limit of no water evaporation (i.e., $J_e(t) = 0$) under the respective deposition conditions.



E5. Surface Charge Characteristics of the 1.5-µm Silica Particles

For characterization of the surface charge of the 1.5-µm silica particles, the asobtained 0.1 g/ml solution of the silica microspheres was diluted with deionized (Milli-Q pure) water to a final particle concentration of 0.01 g/ml. In this suspension, the conductivity (σ) was measured to be 14.38 ± 0.05 μ S/cm, which gives the number concentration of small ions (n_{ion}) of approximately 1.1×10^{-4} M for the system due to the

relation $\sigma = \frac{e^2 n_{ion}}{6\pi \eta a_h}$ where *e*, η and *a_h* respectively denote the elementary charge, the

viscosity of the medium and the hydrodynamic radius of the ions; here we assume for simplicity that all ions are monovalent, and have the same radius equal to the hydrodynamic radius of water (≈ 1.6 Å).¹² Also, the pH value of the suspension was measured to be 7.9. From these pH and salt concentration values, and using the established correlation between the surface charge density of silica and the pH and salt concentration of the medium,¹³ we estimate the charge density of the 1.5-µm silica spheres to be 0.013 e/nm^2 under the given condition. Under the conditions used for the LB particle deposition experiments in the present study, the charge characteristics are expected to be not much deviant from the above result.

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