

Supporting Information for

**Fabrication of wafer-size monolayer close-packed colloidal crystals via slope
self-assembly and thermal treatment**

*Yizhi Wu, Cheng Zhang, Ye Yuan[†], Ziwen Wang, Weijia Shao, Huijie Wang and Xiaoliang Xu**

Department of Physics, University of Science and Technology of China, Hefei City Anhui
Province, China

* Address correspondence to xlxu@ustc.edu.cn

Typical assessment process of the colloidal monolayer

Two-dimensional Discrete Fourier Transform (DFT)¹, is a well-established method to evaluate the lattice ordering of the colloidal crystal.

$$F(u, v) = \sum_{x=0}^{M-1} \sum_{y=0}^{N-1} f(x, y) \exp(-i2\pi ux / M) \exp(-i2\pi vy / N)$$

where $f(x, y)$ represents the spatial domain function and $F(u, v)$ is the corresponding FT.

The SEM images were captured with the same magnification, brightness, and contrast along the film normal. We have carried out a statistical analysis on them. Each sample was examined base on a series of SEM images taken from 14 equidistant positions at 1mm separation across the sample. Figure S1 illustrates the process of the quantitative assessment of the ordering of the wafer-scale monolayer colloidal crystal.

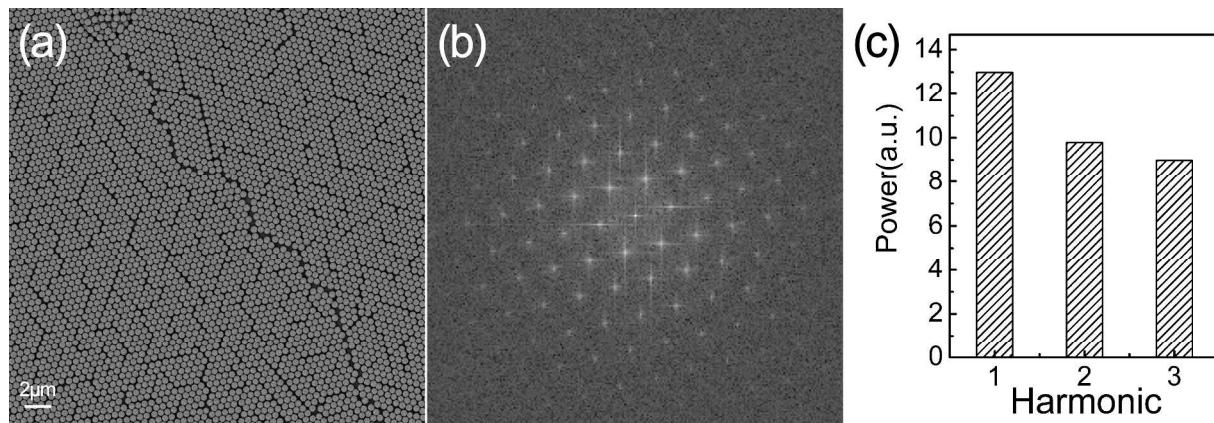
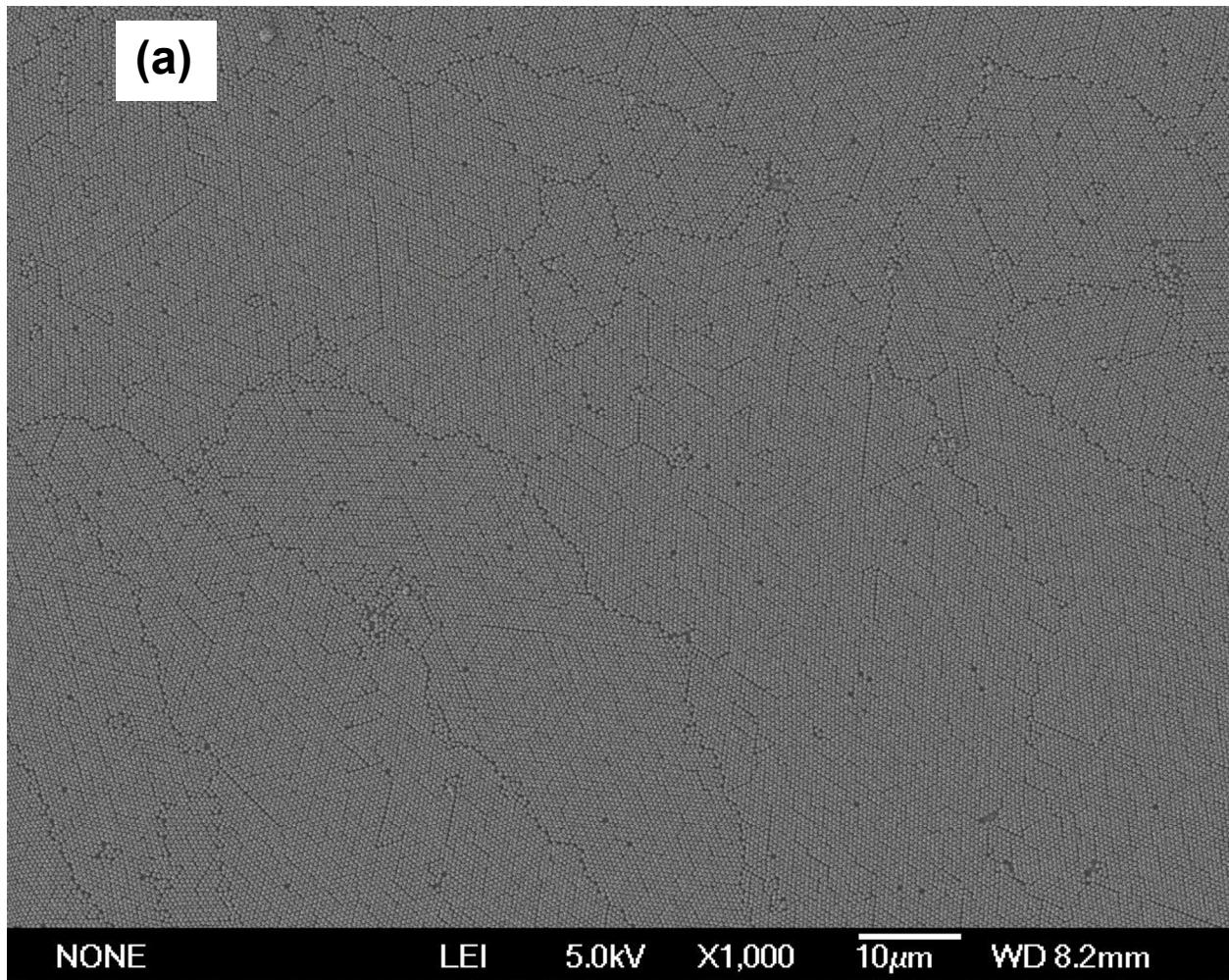


Figure S1. Typical assessment process of the colloidal monolayer: (a) scanning electron micrographs of wafer-scale monolayer colloidal crystal; (b) FT patterns of the SEM image in panel (a). The panel (c) shows the magnitude of the first three harmonics in the FT patterns shown in panel (b).

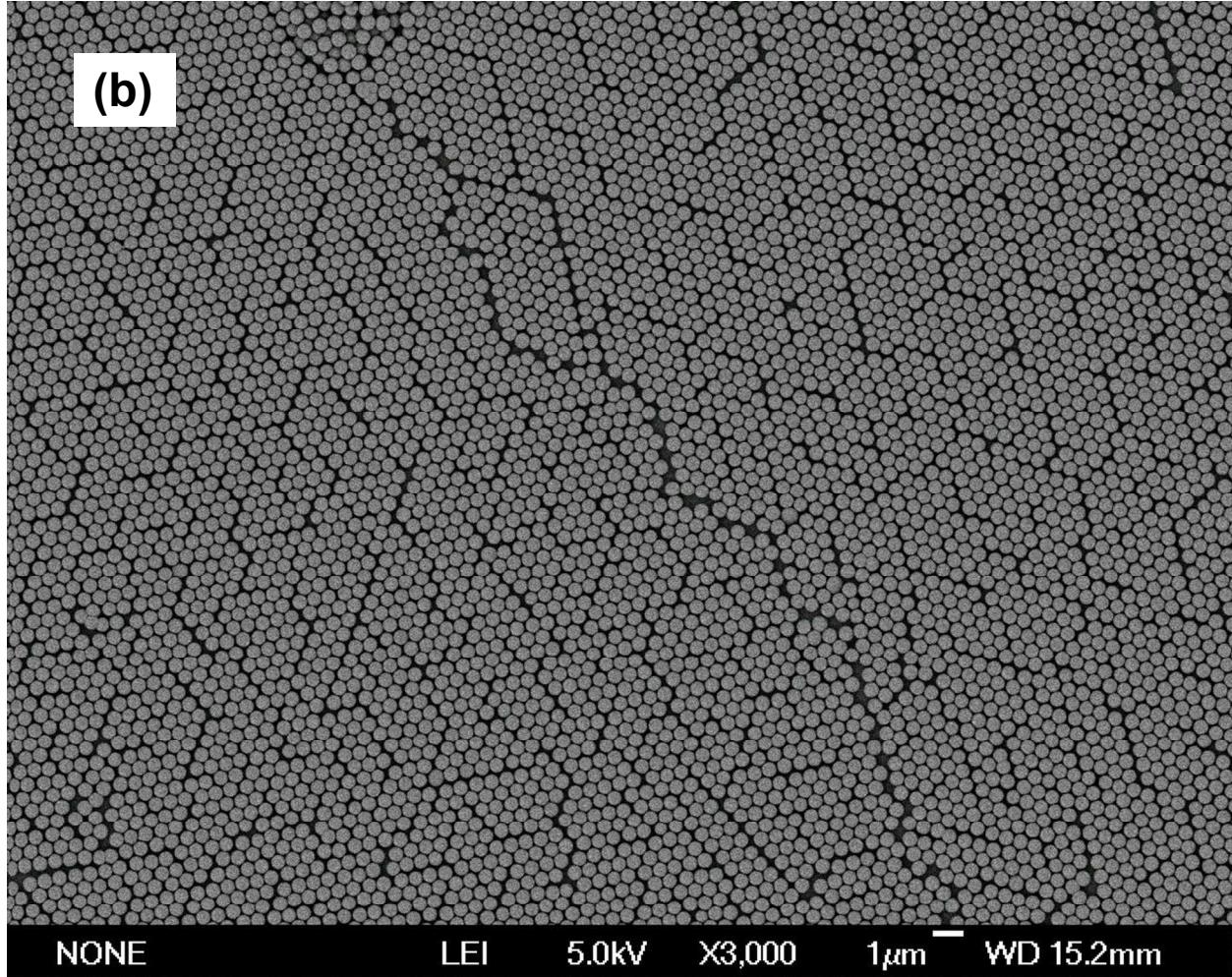
The colloidal crystal shown in Figure S1 (a) was obtained under the condition of the latex concentration of $\phi = 32\%$, 45°C self-assembly environment, 50° slant angle and using the mixture of ethanol and glycol as the dispersion system. Figure S1 (b) shows the corresponding FT pattern and the bright spots is sharp and regular, which results from the close-packed and monolayer spheres in the spheres array. The magnitudes of the first three harmonics (M_1 , M_2 , M_3) in the FT pattern were shown in Fig. 7 (c) and they are 12.99, 9.78 and 8.98, respectively.

Wafer-scale monolayer colloidal crystal obtained under optimized conditions

(a)



(b)



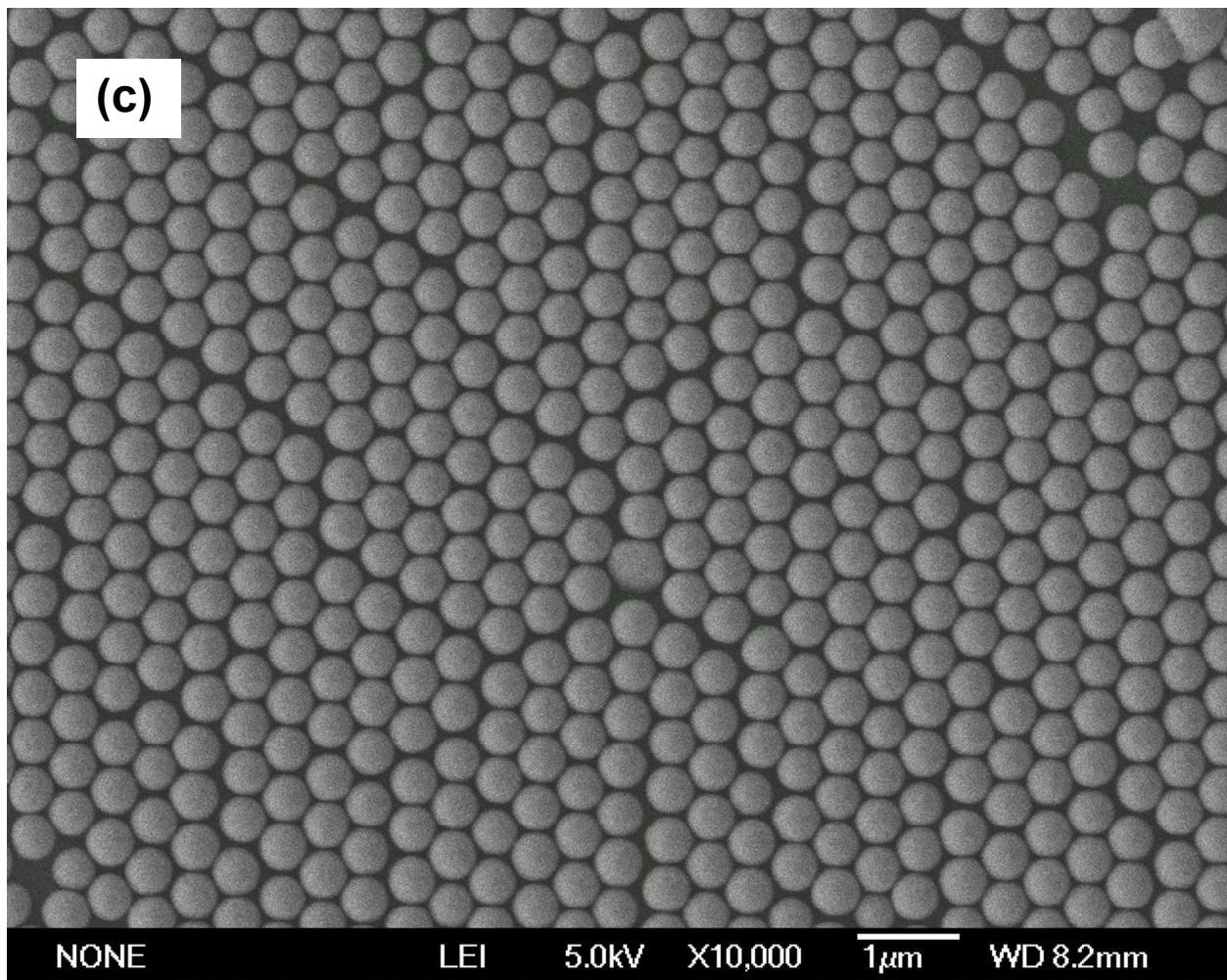


Figure S2. SEM images of wafer-scale monolayer colloidal crystal, which was obtained with the latex concentration of $\phi = 32\%$, $45\text{ }^{\circ}\text{C}$ self-assembly environment, 50° slant angle and using the mixture of ethanol and glycol as the dispersion system.

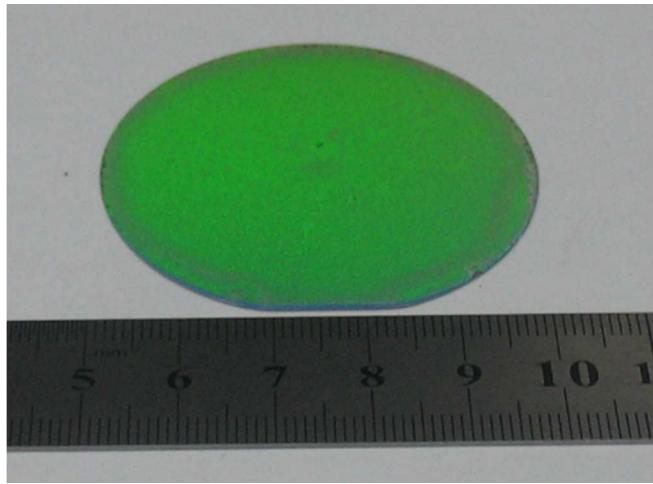


Figure S3. Macrograph of wafer-scale (*2 inch*) monolayer hexagonal close-packed PS spheres array, which was obtained under the conditions of the latex concentration of $\phi = 32\%$, $45\text{ }^{\circ}\text{C}$ self-assembly environment and 50° slant angle and using the mixture of ethanol and glycol as the dispersion system.

Parameters

1. Polystyrene spheres parameters

Polystyrene spheres density: $1.04\sim 1.06\text{ g/cm}^3$, set to $\rho = 1.05\text{ g/cm}^3$

Diameter: $d = 2r = 460\text{ nm}$

$$\text{Volume: } V = \frac{4}{3}\pi r^3 = 5.0965 \times 10^{-14} \text{ cm}^3$$

$$\text{Mass: } m = \rho V = 5.3513 \times 10^{-14} \text{ g}$$

$$\text{Gravity: } G = 5.2243 \times 10^{-16} \text{ N}$$

2. Parameters of dispersion systems (room temperature):

The density of water: $\rho_w = 1\text{ g/cm}^3$

Ethanol density: $\rho_l = 0.78945\text{ g/cm}^3$

Ethylene glycol density: $\rho_2 = 1.035 \text{ g/cm}^3$

Water's surface tension coefficient: $\sigma_w = 72 \times 10^{-3} \text{ N/m}$

Ethanol surface tension coefficient: $\sigma_1 = 21.97 \times 10^{-3} \text{ N/m}$

Ethylene glycol surface tension coefficient: $\sigma_2 = 47.96 \times 10^{-3} \text{ N/m}$

At room temperature, the density of the mixture of ethanol ethylene and glycol equal-proportion²: $\rho_c = 0.95424 \text{ g/cm}^3$

At room temperature, the viscosity of the mixture of ethanol ethylene and glycol (equal-proportion mix)²: $\mu_c = 4.471 \times 10^{-3} \text{ Pa}\cdot\text{s}$

Force analysis

The establishment of coordinate system: the right-handed rectangular coordinate system. The x axis points downward the slope, the z axis is perpendicular to the slope pointing upward. In the y direction there is no net shear force and the resultant force of other forces in the y direction is zero. So only consider the x - z plane.

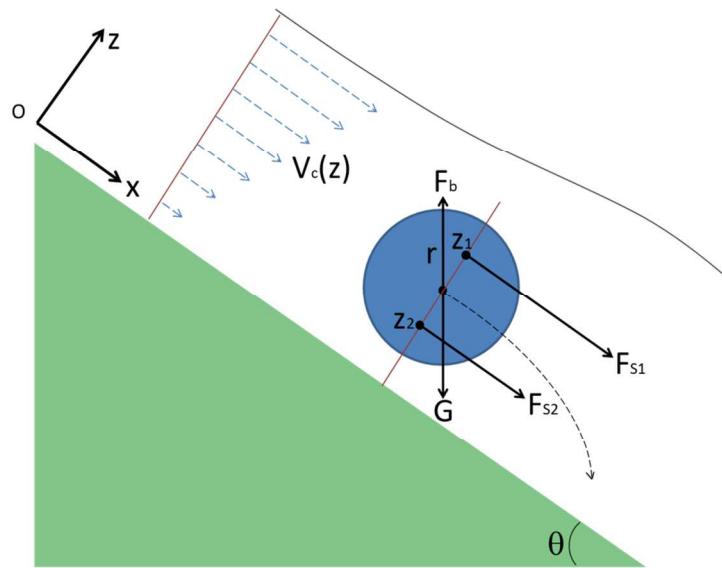


Figure S4. The schematic for force analysis of the PS sphere

(1) Shear Force (F_s)

Shear stress $\tau = \mu_c \frac{dv}{dz}$ (z is perpendicular to the movement direction of colloidal fluid, see figure S4). Suppose the polystyrene sphere's velocity is v , and the colloidal fluid velocity distribution is $v_c(z)$. If the velocity of the polystyrene sphere is not the same as that of the colloidal liquid, there will be a liquid shear force acting on the polystyrene sphere.

Because the upper colloidal fluid velocity was greater than lower colloidal fluid velocity, the liquid flow brought the polystyrene sphere a moment of force. The moment of force caused the rotation of the polystyrene sphere. For simplicity, we only consider the resultant forces of the upper fluid shear forces and lower fluid shear forces respectively (F_{s1} and F_{s2}), with their acting points at z_1 and z_2 (see figure S1), and suppose their directions are parallel to slope downward.

Suppose z_1 is $\frac{r}{2}$ higher than the z coordinate of the center of the sphere, while z_2 is $\frac{r}{2}$ lower than the z coordinate of the center of the sphere.

$$\mathbf{F}_{s1} = \tau \times \pi r^2 \mathbf{e}_x = \mu_c \left. \frac{dv}{dz} \right|_{z_1} \times \pi r^2 \mathbf{e}_x$$

$$\mathbf{F}_{s2} = \tau \times \pi r^2 \mathbf{e}_x = \mu_c \left. \frac{dv}{dz} \right|_{z_2} \times \pi r^2 \mathbf{e}_x$$

Resultant force: $\mathbf{F}_s = \mathbf{F}_{s1} + \mathbf{F}_{s2}$

Resultant moment relative to the center of the sphere: $\mathbf{L} = \frac{r}{2} \mathbf{e}_z \times (\mathbf{F}_{s1} - \mathbf{F}_{s2})$

To further simplify, suppose the liquid velocity $v_c(z)$ is a linear function of z , and define v_{c1} and v_{c2} as: $v_{c1} = v_c(z_1)$ $v_{c2} = v_c(z_2)$,

$$|\mathbf{F}_s| = |\mathbf{F}_{s1}| + |\mathbf{F}_{s2}| = (\mu_c \frac{dv}{dz} \Big|_{z_1} + \mu_c \frac{dv}{dz} \Big|_{z_2}) \times \pi r^2 = \mu_c \left(\frac{v_{c1} - v}{r/2} + \frac{v_{c2} - v}{r/2} \right) \times \pi r^2$$

$$|\mathbf{L}| = \frac{r}{2} (|\mathbf{F}_{s1}| - |\mathbf{F}_{s2}|) = \mu_c (v_{c1} - v_{c2}) \times \pi r^2 = \mu_c \left(\frac{dv_c}{dz} \cdot r \right) \times \pi r^2$$

Estimate of order of magnitude (for alcohol and ethylene glycol mixture):

$$r = 230\text{nm}, \mu_c = 4.471 \times 10^{-3} \text{Pa}\cdot\text{s}$$

$$|\mathbf{F}_s| = \left(\frac{v_{c1} - v}{r/2} + \frac{v_{c2} - v}{r/2} \right) \times 7.43 \times 10^{-16} [\text{unit : N}]$$

$$|\mathbf{L}| = \left(\frac{dv_c}{dz} \cdot r \right) \times 7.43 \times 10^{-16} [\text{unit : N}\cdot\text{m}]$$

Through experiments, for alcohol and ethylene glycol mixture, $v_{c(\text{top})} = 1.5\text{cm/s}$, and the thickness of the liquid, $z_{c(\text{top})} = 0.5\text{mm}$. Suppose the velocity of the liquid at the bottom is zero, then $\frac{dv_c}{dz} = \frac{2.5\text{cm/s}}{0.5\text{mm}} = 50\text{s}^{-1}$. If the initial velocity of the polystyrene sphere is zero, then the order of magnitude of the initial shear force should be: $|\mathbf{F}_s| \approx 10^{-10} \text{N}$. The order of magnitude of the moment of force should be: $|\mathbf{L}| \approx 10^{-20} \text{N}\cdot\text{m}$

At the beginning, $\vec{\mathbf{F}}_s$ was the primary force compared to other forces because the velocity of the liquid (v_c) was high. Suppose the velocity of the PS sphere is lower than that of the liquid, then the sphere would accelerate quickly, which was driven by $\vec{\mathbf{F}}_s$ until it reached the flow velocity (v_c). Thereafter, shear force became smaller and the sphere stays in a steady state under the effect of the gravity component and the viscous resistance.

(2) Adhesion force of the colloid sphere: \mathbf{F}_a

$$(\mathbf{F}_a)_{\text{max}} = 6\pi\mu_c vr \approx 9.6 \times 10^{-10} \text{N}$$

where μ_c is the viscosity of the mixture of ethanol ethylene and glycol (equal-proportion mix), v is the velocity of the PS sphere with respect to liquid and r is the diameter of the PS sphere. Adhesion force drives the PS to accelerate until the velocity of PS sphere equaling to the dispersion media's. Consequently, adhesion force also plays an important role to spread latex over the surface of substrate.

(3) Gravity \mathbf{G}

$$\mathbf{G} = mg \sin\theta \mathbf{e}_x - \cos\theta \mathbf{e}_z$$

Value: $|\mathbf{G}| = 5.2243 \times 10^{-16} N$

(4) Buoyancy \mathbf{F}_b

$$\mathbf{F}_b = \rho_c \times \frac{4}{3} \pi r^3 \times g \sin\theta \mathbf{e}_x + \cos\theta \mathbf{e}_z$$

Value: $F_b = 4.677 \times 10^{-16} N$

Through (2) and (3), it is known that gravity was greater than the buoyancy, providing the possibility that gravity plays a role in making polystyrene spheres monolayer.

(5) Supportiveness (\mathbf{T})

When the polystyrene sphere drops to the silicon wafer surface or other spheres beneath, it will be affected by supportiveness.

$$\mathbf{T} = (|\mathbf{G}| - |\mathbf{F}_b|) \cdot \cos\theta \mathbf{e}_z$$

(6) Capillary force (\mathbf{F}_x)

$$F_x = 2\pi\sigma r^2 \sin^2\psi_c / L$$

Here σ is the surface tension of the liquid, r is the radius of the three - phase contact line at the particle surface, ψ_c is the mean meniscus slope Angle at the contact line, g is the gravitational acceleration. L stands for the distance between the centers of the two spheres.³

Value estimation:

$$\sigma = 35 \times 10^{-3} N / m$$

$$\psi_c = 20^\circ$$

$$L = 3r = 690 nm$$

$$F_x = 2.0 \times 10^{-9} N$$

(7) Convection force: F_c

Convection force comes from the pressure difference between different levels of the liquid surrounding the sphere. For numerical estimation, suppose the liquid level difference between the two sides of the polystyrene sphere is Δh , then the net pressure should be $p = \rho_c g \Delta h$. Suppose Δh is 1 order smaller than r in the order of magnitude, which is reasonable, then the order of magnitude of convection force should be $F_c \approx \rho_c g r / 10 \approx 10^{-10} N$

Convection force was important in the PS spheres nucleation and assembly process, as it drove the polystyrene spheres to the vicinity of nucleation zone.

The effect of PS size on the optimum slope angle

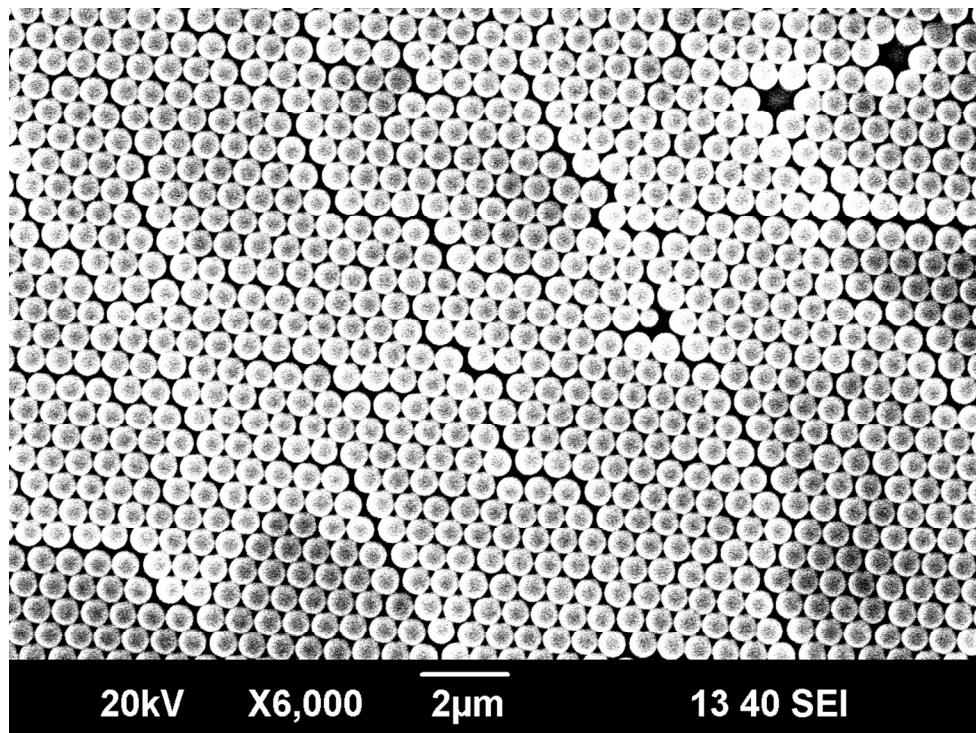


Figure S5. SEM images of monolayer colloidal crystal, which was obtained with the latex concentration of $\phi = 32\%$, 45°C self-assembly environment, 45° slant angle and using the mixture of ethanol and glycol as the dispersion system. The diameter of the PS sphere is approximately 666 nm.

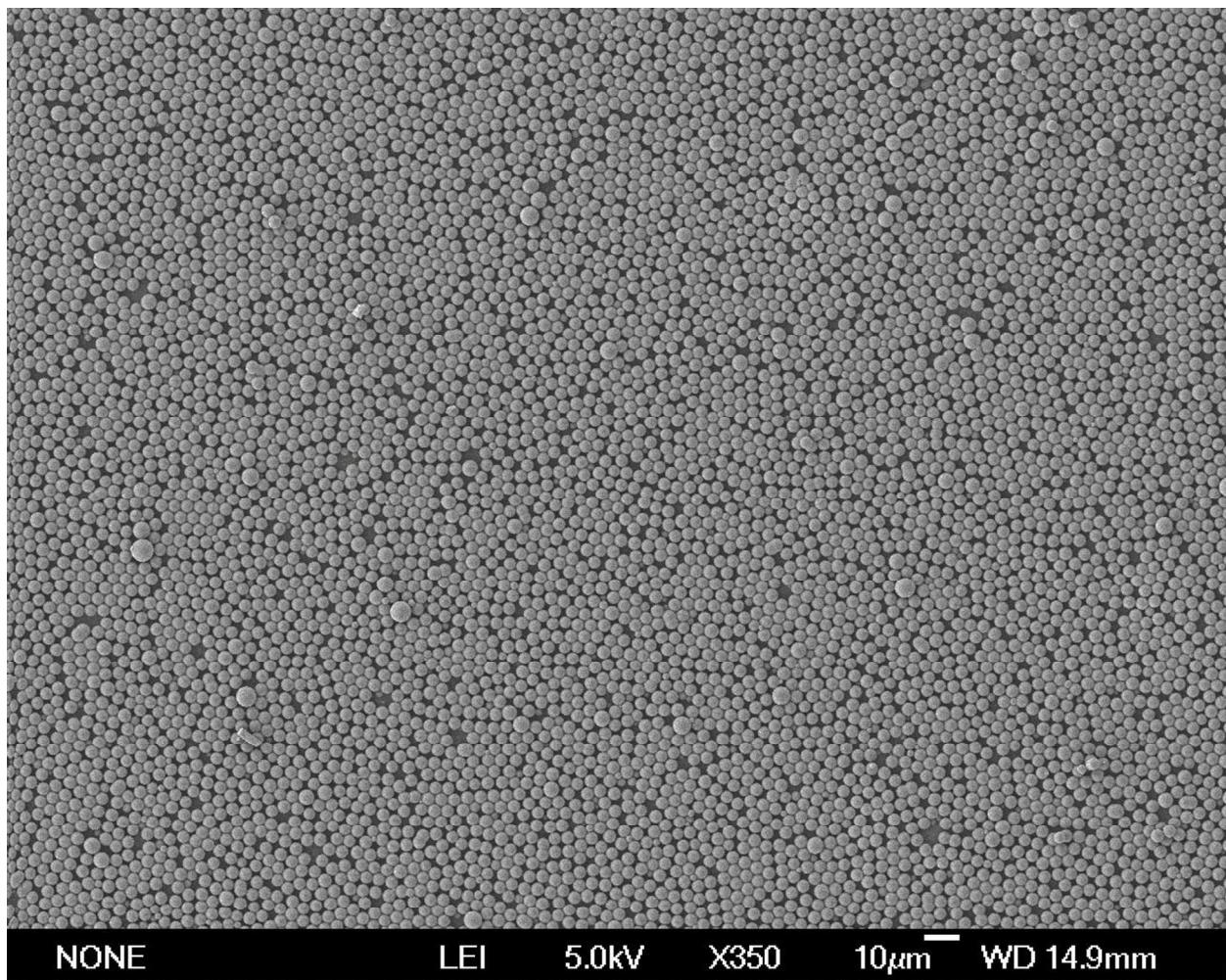


Figure S6. SEM images of monolayer colloidal crystal, which was obtained with the latex concentration of $\phi = 32\%$, $45\text{ }^{\circ}\text{C}$ self-assembly environment, 40° slant angle and using the mixture of ethanol and glycol as the dispersion system. The diameter of the PS sphere is approximately 3500 nm.

References:

1. Khunsin, W.; Kocher, G.; Romanov, S. G.; Torres, C. M. S., Quantitative analysis of lattice ordering in thin film opal-based photonic crystals. *Advanced Functional Materials* **2008**, 18, (17), 2471-2479.

2. Quijada-Maldonado, E.; Meindersma, G. W.; de Haan, A. B., Viscosity and density data for the ternary system water(1)-ethanol(2)-ethylene glycol(3) between 298.15 K and 328.15 K. *Journal of Chemical Thermodynamics* **2012**.
3. Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K., MECHANISM OF FORMATION OF 2-DIMENSIONAL CRYSTALS FROM LATEX-PARTICLES ON SUBSTRATES. *Langmuir* **1992**, 8, (12), 3183-3190.