Supplementary Information for

Formation of wafer-scale monolayer close packed polystyrene spheres template by thermally assisted self-assembly

SEM images of the monodisperse polystyrene sphere and the size distribution

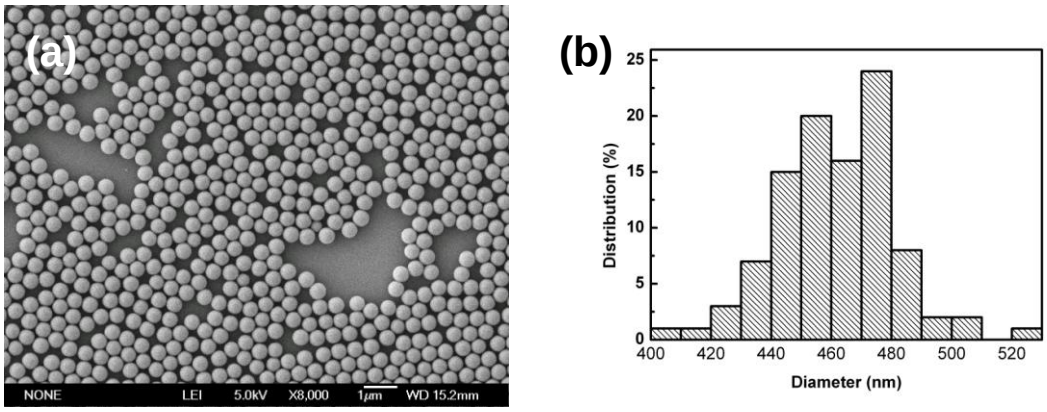
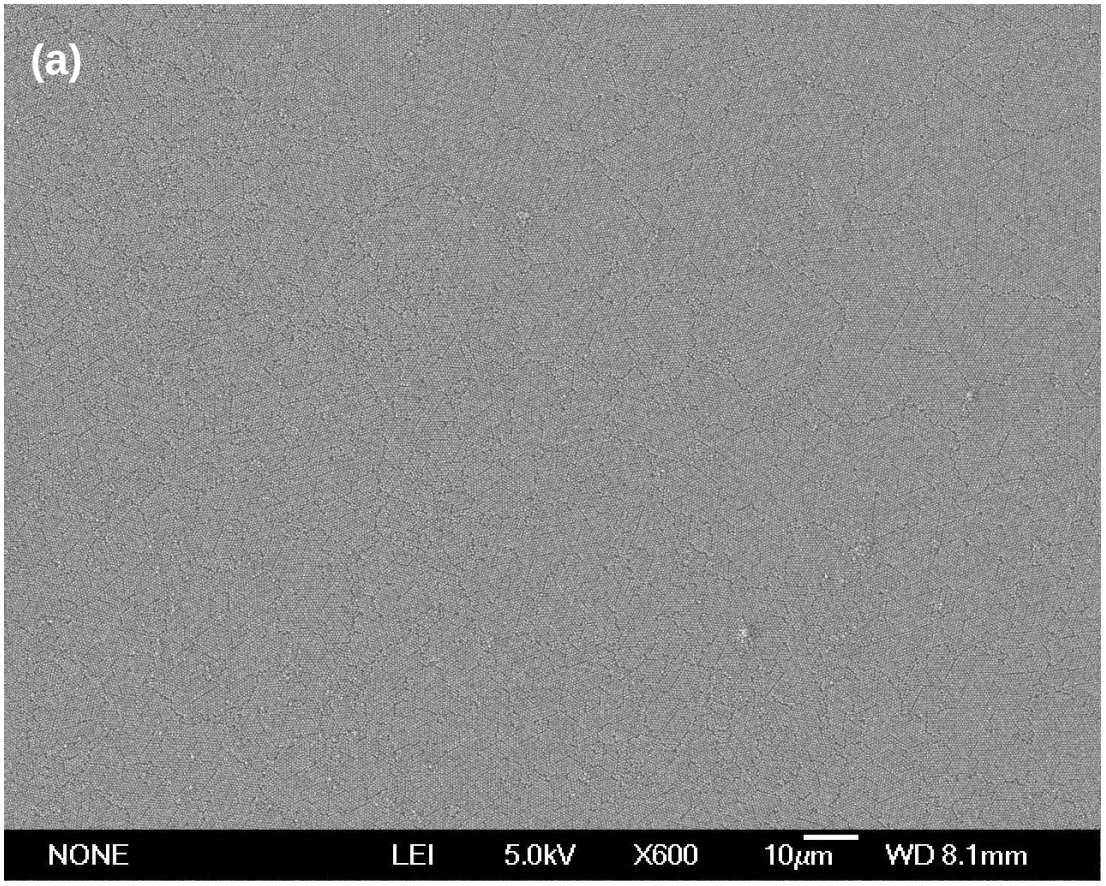
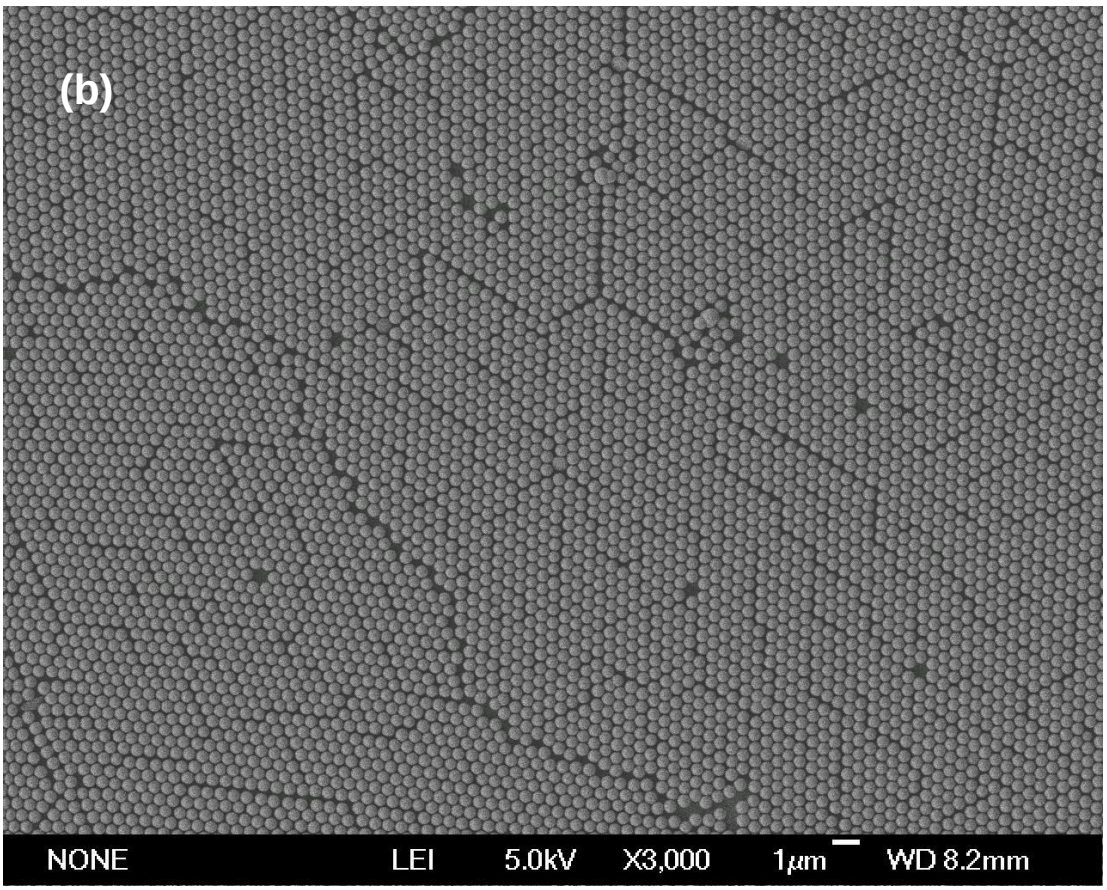


Figure S1. (a) Scanning electron micrographs of the monodisperse polystyrene spheres; (b) the size distribution of the monodisperse polystyrene spheres.

Figure S1 shows SEMs of monodisperse polystyrene spheres. The mean diameter of the spheres is 462 nm and the standard deviation of the diameter is 20 nm.

SEM images of the colloidal crystal prepared under optimum condition


(a)
NONE
LEI
5.0kV
X600
10μm
WD 8.1mm


(b)
NONE
LEI
5.0kV
X3,000
1μm
WD 8.2mm

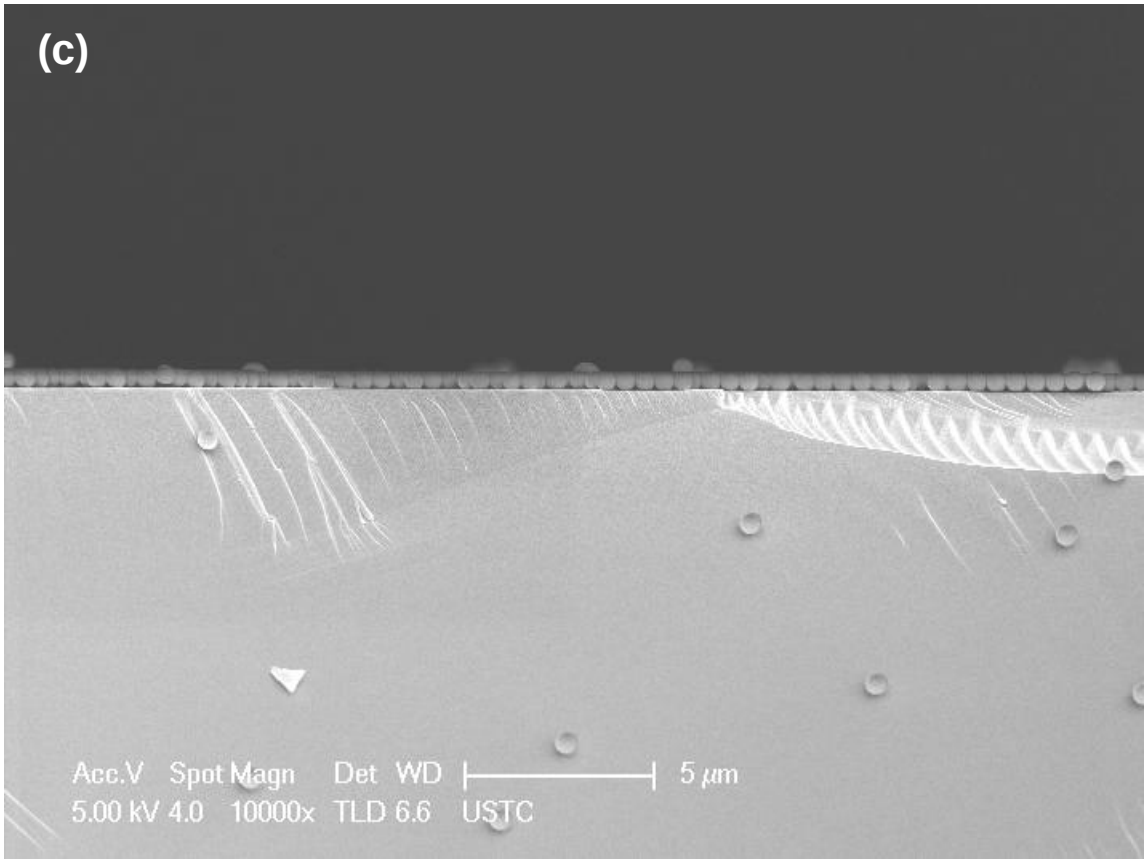


Figure S2. SEM images of the wafer-scale monolayer close-packed PS spheres prepared in condition of 40% volume fraction and 45 ℃ self-assembly temperature. (a) low magnification, top-view; (b) high magnification, top-view; (c) high magnification, side-view.

Force analysis

1. Polystyrene spheres parameters

Polystyrene spheres density: 1.04~1.06 g/cm^3, set to $\rho = 1.05 g/cm^3$

Diameter: $d = 2r = 460nm$

Volume: $V = \frac{4}{3}\pi r^3 = 5.0965\times10^{-14} cm^3$

Mass: $m = \rho V = 5.3513\times10^{-14} g$

Gravity: $G = 5.2243\times10^{-16} N$

2. Parameters of dispersion systems:

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

Ethanol density: $\rho_1 = 0.78945g / cm^3$

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

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

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

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

At room temperature, the density of the mixture of ethanol ethylene and glycol equal-proportion [1]: $\rho_c = 0.95424g / cm^3$

At room temperature, the viscosity of the mixture of ethanol ethylene and glycol (equal-proportion mix) [1]: $\mu_c = 4.471 \times 10^{-3} Pa \cdot s$

(1) Gravity $\boldsymbol{G}$

$\boldsymbol{G} = mg$

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

(2) Buoyancy $\boldsymbol{F_b}$

$$\boldsymbol{F_b} = \rho_c \times \frac{4}{3} \pi r^3 \times g$$

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

(3) Supportiveness ($\boldsymbol{T}$)

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

$\boldsymbol{T} = (|\boldsymbol{G}| - |\boldsymbol{F_b}|)$

(4) Capillary force ($\boldsymbol{F}_x$)

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

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.[2]

Value estimation:

$\sigma \approx 35\times10^{-3} N/m$

$\psi_c = 20°$

$L = 3r = 690nm$

$F_x \approx 2.0\times10^{-9} N$

(5) Convection force: $\boldsymbol{F_c}$

Convection force could be considered that it 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 nine order smaller than r in the order of magnitude, which is reasonable, then the order of magnitude of convection force should be

$\boldsymbol{F_c} \sim \rho_c g r / 10 \sim 10^{-18} N$

(6) Adhesion force of the colloid sphere: $\boldsymbol{F_a}$

$(\boldsymbol{F_a})_{\max} = 6\pi\mu_c \upsilon r \approx 9.6\times10^{-10} N$

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.

A triangular lattice used for the PS spheres self-assembly simulation

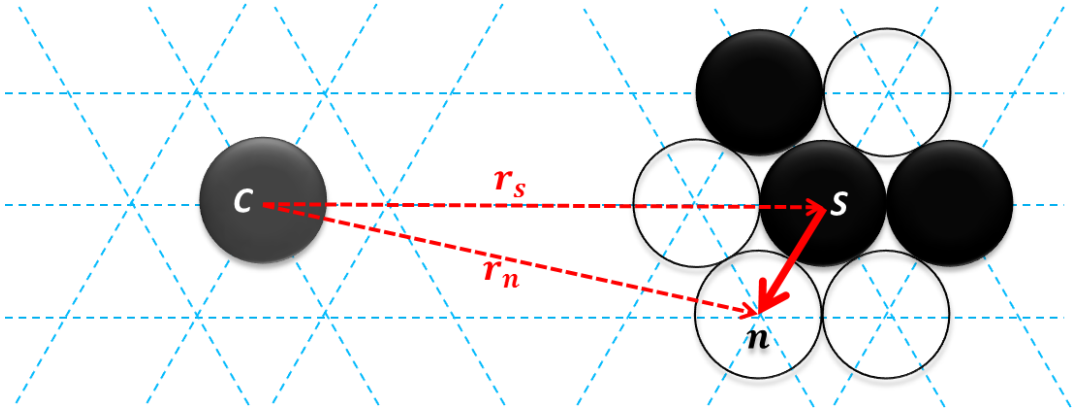


Figure S3. A triangular lattice used for the PS spheres self-assembly simulation. Blue dotted lines denote the triangular lattice, solid black spots denote occupied nodes, hollow black circles denote unoccupied nodes and solid gray spot denotes the nucleating point.

The total energy of the system varying with the evolution steps of the Monte Carlo simulation.

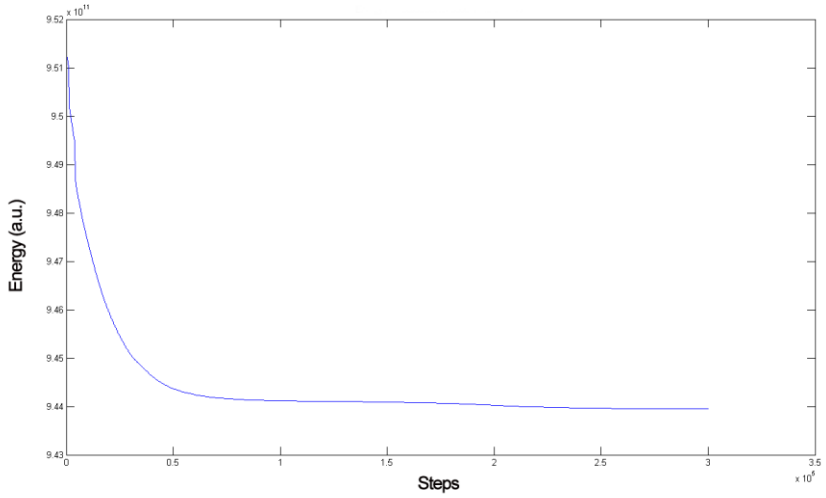


Figure S4. Monte Carlo simulation pattern with the self-assembly condition of: T=30℃, VF=20%.

Monte Carlo simulation patterns and corresponding scanning electron micrographs of colloidal crystal treated under different temperatures.

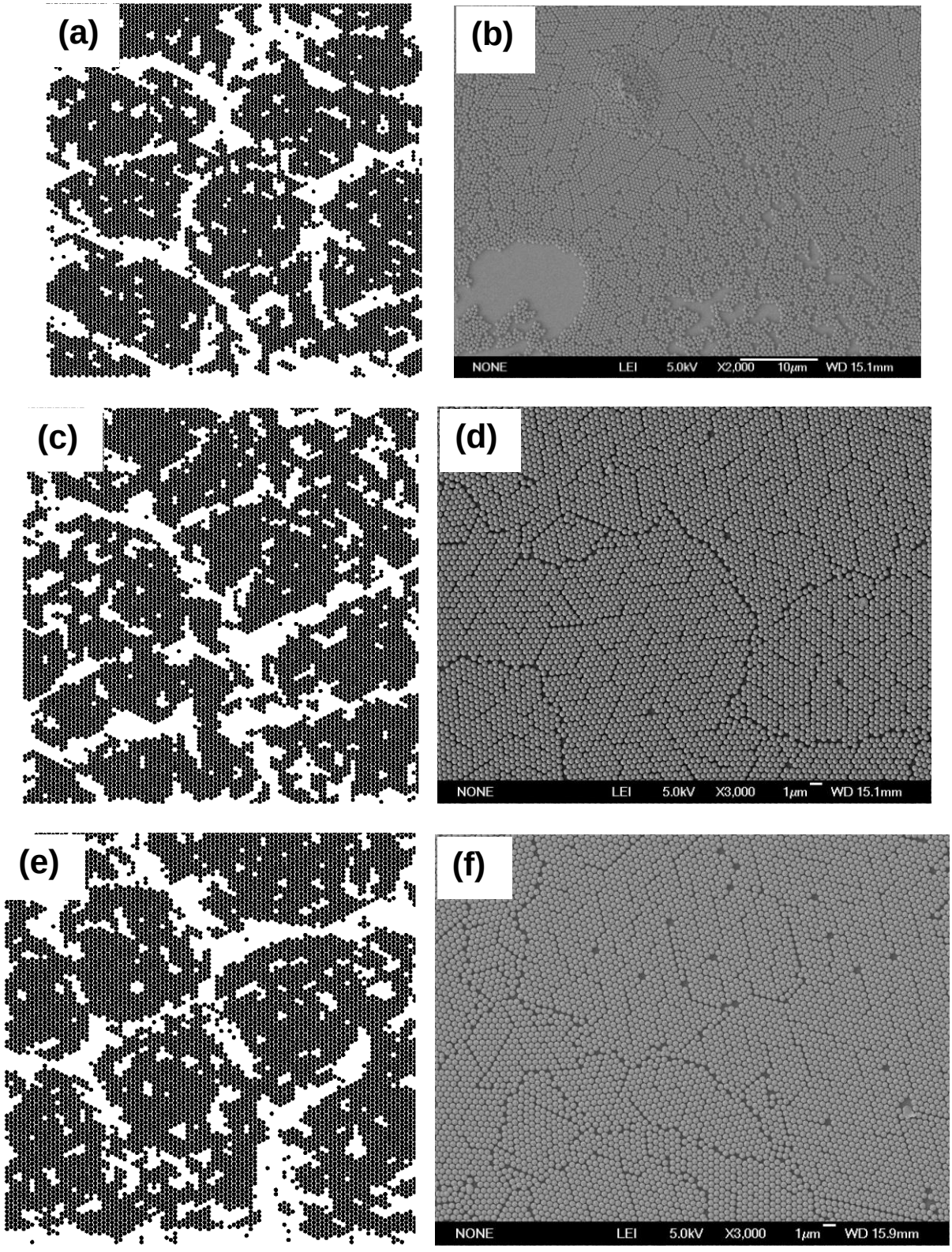


Figure S5. Monte Carlo simulation patterns with the temperature of (a) 35℃; (c) 45℃; (e) 55℃, and the corresponding typical scanning electron micrographs of the colloidal crystal treated under the different self-assembly temperature (b) 35℃; (d) 45℃; (f) 55℃,

Patterns shown in Figure S4 (a), (c) and (e) were re-drawn using the coordinate information of the PS spheres in the colloidal crystal patterns obtained from the simulation results using the new model we proposed. And Figure S4 (b), (d) and (f) were the experiments results of the PS spheres self-assembly under the conditions of the 35℃, 45℃ and 55℃, respectively.

References:

1. E. Quijada-Maldonado, G. W. Meindersma and A. B. de Haan, *Journal of Chemical Thermodynamics*, 2012.
2. N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura and K. Nagayama, *Langmuir*, 1992, **8**, 3183-3190.