Dear Sarah,

Recently, we have submitted a manuscript entitled “Formation of wafer-scale monolayer close-packed colloidal crystal of polystyrene spheres via thermally assisted self-assembly” (SM-ART-09-2012-027112). Thank you very much for your timely decision letter and for the reviewers’ comments concerning our manuscript. We write this letter to you to argue some comments of the reviewers.

Referee 2 gives us a good evaluation about our work. We note that referee 1 believes that the Monte Carlo (MC) simulation in our manuscript is not properly implemented, but he have given the detail information about the mistakes we made. However, we have established our theoretical model base on Denkov and Kralchevsky’s work and we obey the rule of MC simulation during the MC implementation. Moreover, our MC simulation results are supported by the experimental results. Referee 3 believes that the rudimentary interaction model for MC simulation is wrong, no self-assembly in the simulation for the reason that the particles are pre-arranged on a triangular and etc. However, The particles are pre-arranged on some special lattice is a common method in simple simulation and it is still a self-assembly process, which could refer to other literature[1]. The rudimentary interaction model because the capillary interaction is limited to the deforming liquid interface.[2] The detail point by point responses to the reviewer’s concerns are given in the file of “Responses to the reviewers' comments”.

Anyway, we respect your decision and we look forward to your reply!

Sincerely yours,

Responses to the reviewers' comments

Referee 2:

The authors have addressed my main concerns, which related to the lack of predictive power of the CA annealing model, by using a monte carlo simulation method and showing that it has moderate predictive utility. The packing of the latex spheres does not have a lot of quality variation over the 25-75 degree temperature range, but such as it is, the monte carlo model predicts it.

Response: Many thanks to your kind comments. Although the packing of the latex spheres does not have a lot of quality variation over the 25-75 degree temperature range in the numerical value results, the defects and multilayer layers are obvious in the SEM images. We believe small numerical value results are caused by background of the graphic and etc (The harmonic magnitudes depending on magnification, brightness and contrast of the graphic).

Referee 1:

1. I am not convinced by the responses of the authors. The MC simulation was not properly implemented.

Response: Thank you for your comments. Physical forces behind the evolution are illustrated in the section of "The mechanism of thermal treatment assisted self-assembly". The initial state and evolution rule are illustrated in the manuscript (page 7, line 58 to page 8, line 17). We obey the rules of MC simulation. We need more detail information where we have not properly implemented the MC simulation to improve our paper.

2. The claimed similarity between simulation and experiment shown in Figure S5 cannot be confirmed.

Response: Thanks for your comments and we are sorry for having not illustrated these clearly. Both the experimental results and simulation results are packed in hexagonal-close-packed way and have vacancy and multiplayers. Figure S5 (a) and S5 (b) have more vacancy and multiplayer at "low temperature". Figure S5 (c) and S5 (d) show that better crystal could be achieved when proper temperature is introduced. Figure S5 (e) and S5 (f) show that multilayers could be decreased at "high temperature" but over high temperature should be avoided. However, we should mention here that each sample was examined base on a series of SEM images taken from equidistant positions at 1mm separation across the sample and the quantitative assessment of the

ordering of the colloidal crystal are over all those SEM images.

3. I don't think the MC simulation implemented by the authors have any predictive power.

Response: The self-assembly temperature could be predicted through our model (page 8-9), which otherwise would consume tedious process to find the optimal temperature. And the predictive power of our model has been checked by referee 2.

4. The authors are advised to read through the paper by Geissler et al. JACS, 2011, 133, 838-848 to have a basic idea of MC method for self-assembly.

Response: Thanks for your comments and kind suggestion. We have read the paper you suggest and find that the system described by Geissler et al, involves the magnetic nanoparticles. They are more complex and complete than our simulation. In their model, the giant balance ensemble and Gaussian distributions are adopted, allowing the particles to move continuously in two-dimensional phase. These simulation setting is required by their self-assembly (involving dipole moments and transient connections). However, it is different from ours where the capillary potential is dominant in the colloidal system consisting of PS spheres, but both us obey the MC simulation rule, such as adopting “Metropolis acceptance criterion” and etc. Consequently, we could simplify the simulation. We believe harvesting an accepted simulation results through simply physic view is a useful attempt (Ising model being a simple but important model).

Referee 3

1. Though I am not an experimentalist, I do not see which is the novelty here besides the synthesis technique. There is a host of self-assembling two-dimensional colloids in the literature and the triangular lattice is the standard one.

Response: There are indeed a lot of self-assembly two-dimensional colloids in the literature and the triangular lattice is the standard one. However, a variety of technologies, such as dip-coating, electric field assisted self-assembly, and floating-transfer method, have been developed to create 2D colloidal crystals. However, these strategies are either favorable to low output or only capable of building polycrystalline colloidal array. Besides, floating-transfer method requires delicate artificial skill while electrophoretic deposition needs specific apparatus. What is more, some of these methods seem infeasible due to tedious fabrication processes and incompatibility to wafer-scale bath micro fabrication which is widely used by the semiconductor industry. Spin-coating method is an alternative strategy to overcome the drawbacks mentioned above.

However, there are few reports using this method to prepare polystyrene spheres monolayer crystal. What is worse, the resultant monolayer spheres arrays have a lot of defects or multiplayer spheres. We introduce thermal treatment and proper dispersion media of the PS spheres to improve the quality of the crystal.

2. There is absolutely no guarantee that this is the right interaction and even less reason to truncate it at the first neighbors. This is left uncommented by the authors but it is not unnoticed. Under this approximation, every connection with the real system is put severely into question.

Response: Many thanks to your comprehensive comments. In the colloidal spheres system, interaction truncated at the first neighbors is allowed because the capillary interaction is limited to the deforming liquid interface.[2] Moreover, the simulation results are also supported by our experimental results.

3. How is it possible that the number of Monte Carlo steps s enters the prefactor Q?

Response: Thanks for your comments. The prefactor Q is introduced for the simplification of simulation. With the Q, we could separate the time parameter (liquid evaporation time) and space parameter (interaction). The operation is accepted in our model because Monte Carlo steps s corresponds to evaporation time of the real system: actually, s denotes the number of accepted steps, not like common MC simulation. In this way, it's acceptable that with s increases, the system would go into equilibrium state, just as the ultimate balance is achieved when time goes by. And similar operation could be seen in other literature.[3]

4. How could possibly the system know how many Monte Carlo steps the authors make and adjust its interaction? This is completely unphysical.

The simulation process would be stopped when the fluctuation of the energy of the system δU_{sum} relative to the total change of energy of the system ΔU is smaller than the predefined final value. During this process, we could monitor the Monte Carlo steps and the interaction ($U_{sum} = \sum_i U_i = \sum_i U_0 \ln(r_i)$) is automatically adjusted when the r_i (the distance between any ith occupied node and its nearst nucleus) varies.

5. 2c. There is no self-assembly in the simulation. The particles are pre-arranged on a triangular lattice which has some voids.

Response: The particles are pre-arranged on some special lattice is a common method in simple

simulation and it is still a self-assembly process, which could refer to other literature[1]. In our model, the particles are uniformly disturbed before simulation, so do the voids. Actually, the particle can move to anywhere in the two-dimensional plane, although is pre-arranged on a triangular lattice (the side length of the lattice being equal to the diameter of the PS sphere). Moreover, the characters of the real crystal, such as point defect, crack and etc, could be seen in our simulation.

6. The modified Monte Carlo technique is simply wrong. The authors bias the steps via Eqs. (8) and (9) but employ the usual Metropolis acceptance criterion, Eq. (10). This violates detailed balance and gives erroneous results.(Their approach does not sample equilibrium)

Response: Metropolis acceptance criterion indeed need meet detailed balance. However, in the real condition, when PS spheres is in the "center" of the packing area, the probability of the PS sphere detaches from the "center" is very low. Consequently, in our simulation, the probe particle would mostly be in the periphery of the packing area and the probability of the particle in the "center" of the packing area is very low, which is also the natural results of locating the minimum potential energy of the system.

References

1. A. T. Skjeltorp and P. Meakin, *Nature*, 1988, 335, 424-426.
2. P. A. Kralchevsky and K. Nagayama, *Advances in Colloid and Interface Science*, 2000, 85, 145-192.
3. A. Li and G. Ahmadi, *Aerosol science and technology*, 1992, 16, 209-226.