Supporting Information

Binary Colloidal Crystals Fabricated with a Horizontal Deposition Method

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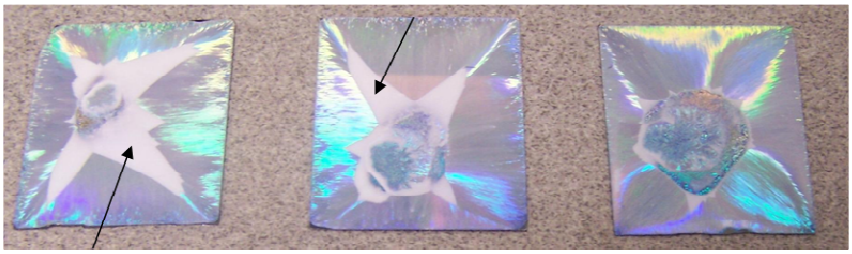
S1. The influence of colloidal concentration on the quality of binary colloidal crystals (bCCs).

We have carried out a set of experiments on silicon wafers of 3×3.5 cm, which have been treated with Piranha solution to oxidize their surfaces to make them hydrophilic. The intention of changing the substrate material (silicon vs. glass) and the substrate geometry (3 x 3.5cm vs. 2.2 x 2.2 cm) is to illustrate the versatility of the horizontal deposition method. The spheres used are 789 nm and 175 nm. These two types of colloids were washed and mixed together and five different concentrations were prepared as listed in the following table, where the number ratio of the small spheres to large spheres was controlled to 2:1 and the total amount of the beads dropped were kept the same in all the samples of different concentrations.

Table 1. The experimental parameters of the samples

Samples	*Concentration of 789 nm spheres*	*Concentration of 175 nm spheres*	*The volume dropped on the substrate*	*The number ratio of small to large*
1	11.84%	0.26%	40 μL	2:1
2	8.59%	0.188%	55 μL	2:1
3	5%	0.110%	95 μL	2:1
4	3%	0.066%	160 μL	2:1
5	1.50%	0.033%	320 μL	2:1



1 2 3

4 5

Figure S1-1. The photo images of the binary colloidal crystal films formed on the silicon substrates with varied concentrations. Arrows point to the white-colored areas of the films.

From the observation of the images shown in Figure S1, we found that on the 3× 3.5 cm silicon substrate, the concentration of large 789nm spheres should be preferably controlled between 5-8.59%. If the concentration is larger than 8.59%, the area of the colloidal crystals (the iridescent area) becomes smaller with the increase of the concentration; while the white-colored area (the non-crystal area) in the central part as pointed by the arrows in the images enlarges as the concentration increases. On the other hand, when the colloidal concentration is smaller than 5%, the colloidal crystal area becomes smaller due to the insufficient supply of the colloidal particles; the void area in the middle becomes larger as the concentration decreases, affecting the quality of the crystal film.

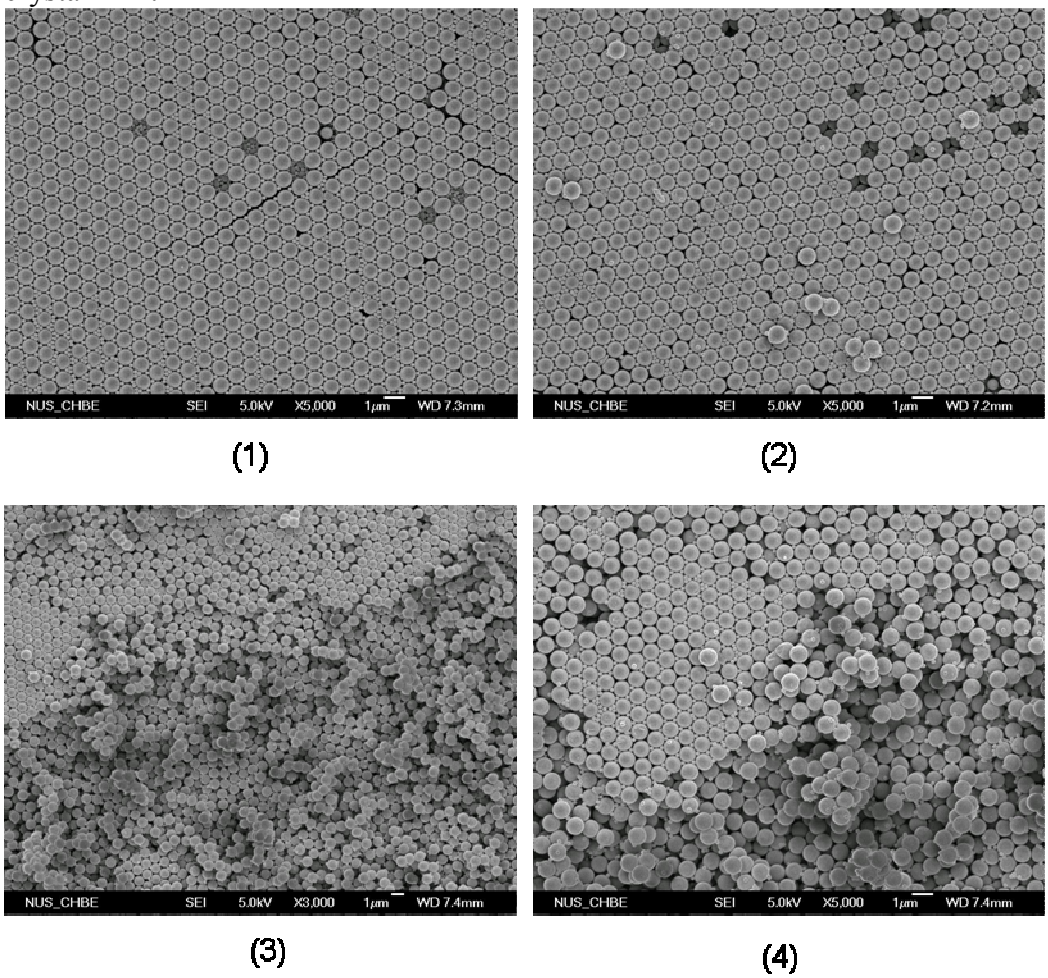
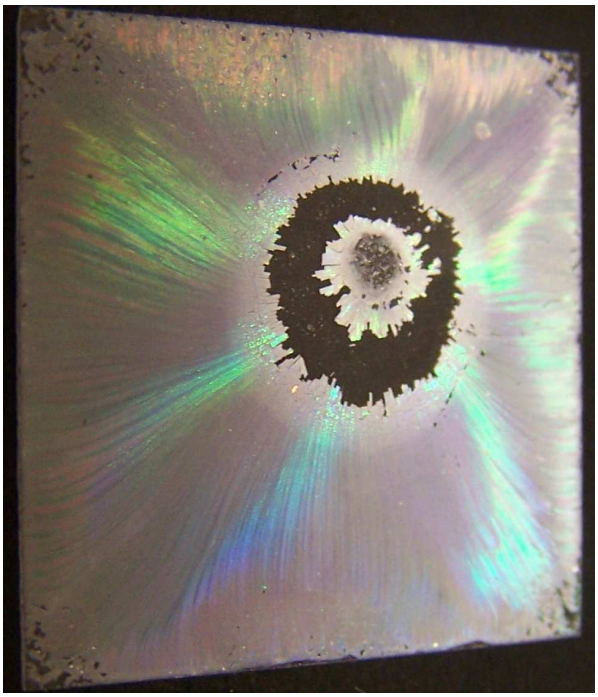


Figure S1-2. SEM images of Sample 3 (1) the top view of the bCC area near the substrate edge, (2) the top view of an area near the center void area; (3) SEM image of the white-colored area on Sample 2; (4) a close-up view of (3).

As demonstrated, the concentration of emulsion plays an important role in the horizontal deposition method. Only a limited range of concentration of colloids (for the 789nm beads, around 8%; for the 1000 nm beads, around 15%) can be used to self-assemble into a quality colloidal crystal film. The larger are the beads, the larger is the volume fraction needed. If the particle concentration is too dilute, the evaporation would be too slow compared to the speed of beads fluxing into the meniscus areas. This would result in that most of the spheres assemble around the edge of the substrate, and only a very limited area of colloidal crystals is formed. The extreme case is the 'coffee ring' phenomenon. On the other hand, if the particle concentration is too high, the evaporation would be too fast to allow the self-assembly to complete, which requires water as the mediator. Hence it would result in non-crystal formation in the central area. Similar concentration influence was observed when our group first reported the horizontal deposition as the 'inward growth method' for monodisperse colloids [1].



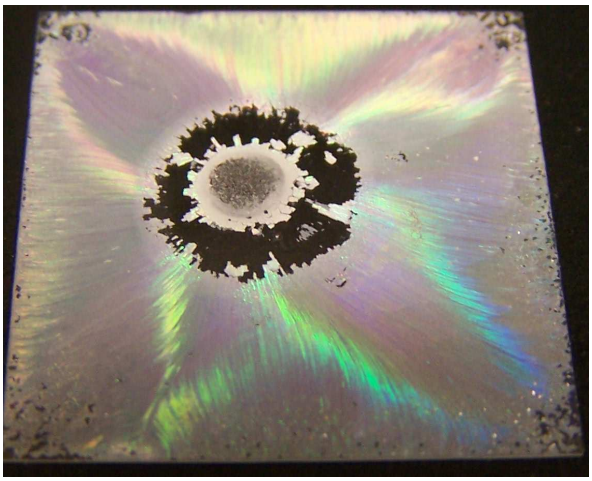
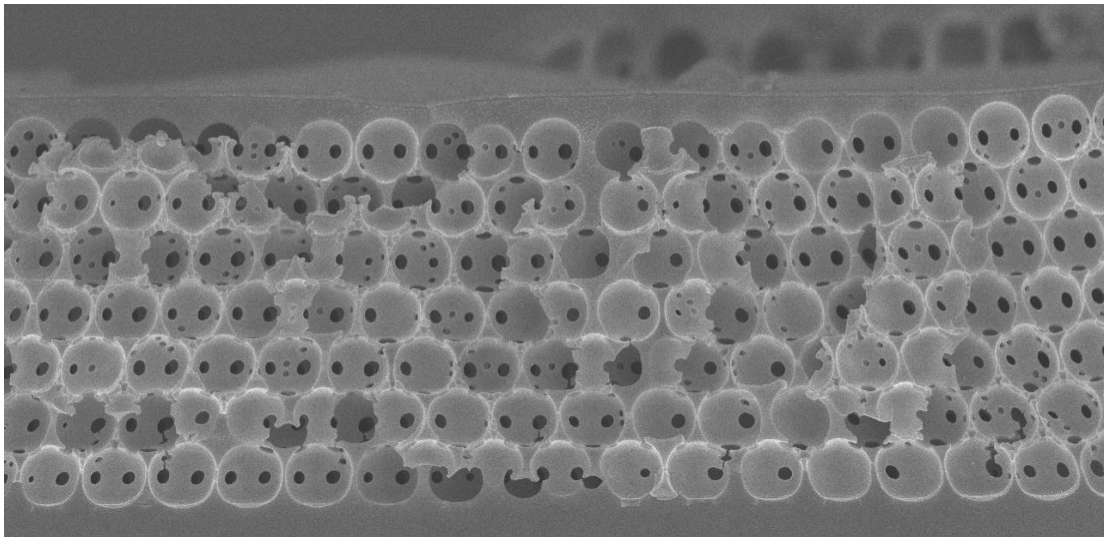
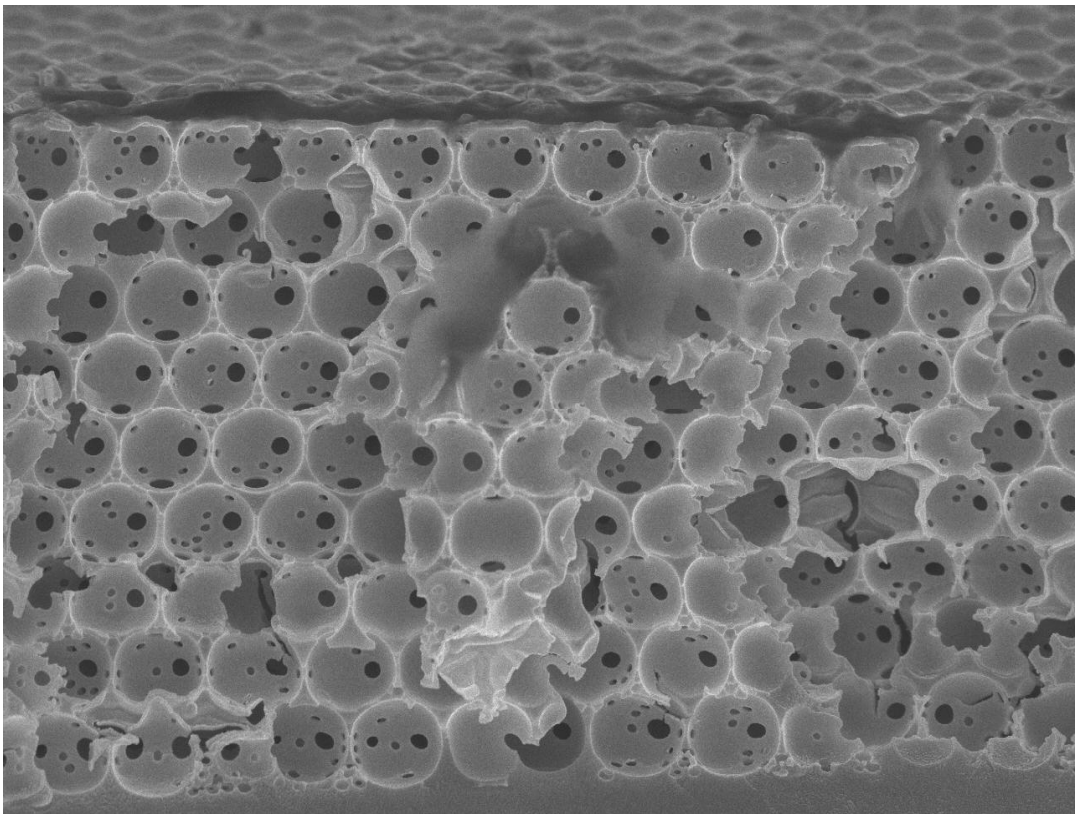


Figure S2. Photographs of the binary inverse opal of B3 (left) and B4 (right). The glass substrates are of a size 22 mm x 22 mm.



(a)



(b)

Figure S3. (a) SEM cross-section view of inv- B1; (b) SEM cross-section view of inv-B2.

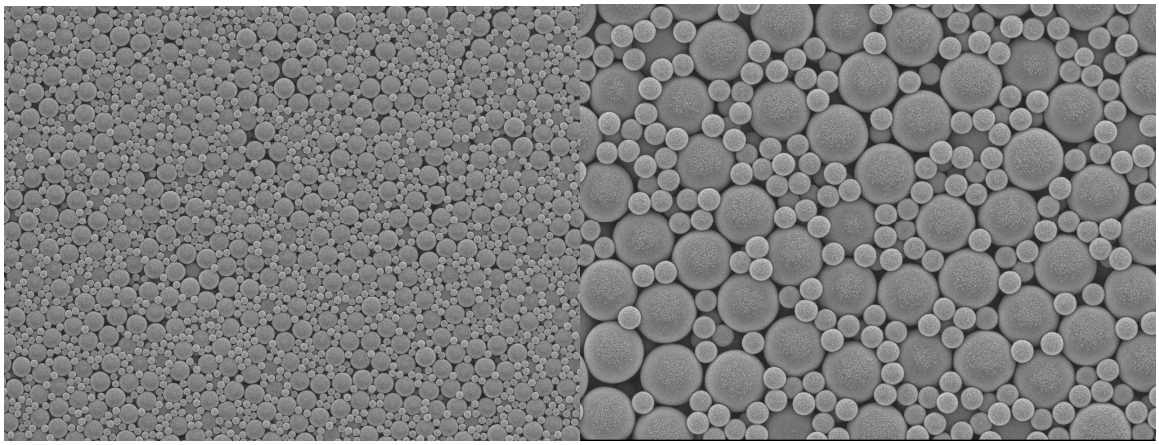


Figure S4. When large spheres of 1000 nm, VF 11.54% and small spheres of 395nm, VF 1.18% were mixed, no ordered structures were obtained.