Supporting Information for

Multicomponent Colloidal Crystals that are Tunable over Large Areas

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1 Experimental Section

Materials

All the colloidal particles used in this study were purchased from Polyscience Inc (USA), Bang Lab (Germany) and Kisker Gmbh (Germany). These particles were stored at 4 °C. Prior to use the particles were brought to room temperature and sonicated for 30 min to disperse them before being used for assembly formation. Sodium chloride (NaCl), hydrofluoric acid (HF) and toluene (≥99.5%) were purchased from Sigma Aldrich.

Preparation of BCC and MCC crystals

The substrates (glass or silicon wafer) were cleaned by 15 minute sonication each in solutions of ethanol, toluene and ethanol followed by drying with N_2 gas. Substrates were then UV-ozone treated to make the surface more hydrophilic and remove unwanted organic contamination. MilliQ water was used as a solvent during colloidal assembly. Rubber rings of size 1 cm were used for confinement experiments. The approximate concentration of the particles (V_P in μl) confined in the ring of particular diameter (D_R in cm) can be calculated by the following derived formula:

$$V_P = \frac{10 \times \pi \times \rho \times D_P \times D_R^2}{12 \times w} \tag{1}$$

Where ρ is the density of particles (g/cm^3), D_P is the diameter of the particle (μm), and w is the % solid content of the particle suspension. The calculated amount of the particles is enough to make a monolayer from large particles, and the number of colloidal layers can be built up by increasing the centration of particles. For example, to fabricate a BCC from 200 nm A-PS and 2 μm C-PS particles using a 1 cm rubber ring, 0.6 μl of 200 nm and 1.5 μl of 2 μm particles were mixed in 200 μl of MilliQ water. This amount is enough to make a monolayer of the larger particle. Multilayers were formed simply by increasing the concentration of particles employed to the amount required for the desirable number of layers. After mixing the colloidal particles at the appropriate concentration, they were left for one hour to allow for them to be well dispersed in the solvent. After mixing the colloidal particles to the appropriate concentration, the mixture was left for one hour to allow for them to be well dispersed in the solvent. The ring was cleaned thoroughly by sonication in ethanol for 15 minute. After fixing the ring to the substrate, the colloidal particle suspension was drop-cast inside the ring and was then kept in a vacuum desiccator at room temperature. The evaporation typically took 2-3 hours, depending upon the surrounding temperature and humidity. Similarly, we have grown TCCs and QCCs. For an ionic strength experiment, a 1 M NaCl stock solution was prepared from which different concentrations NaCl were made (1 mM, 2 mM, 5 mM, 10 mM, 20 mM, 40 mM, 80 mM and 150 mM) by dilution with water. A 2 µm C-PS/200 nm and A-PS combination was used to make BCCs at different salt concentrations under the same conditions of the confinement experiment.

Characterization Techniques

Field emission scanning electron microscopy (FEI Nova 600 NanoSEM) was employed for imaging samples. Prior to imaging, colloidal assemblies were sputtered with gold for 1 minute to avoid charging effects. Zeta potentials were measured using a Zetasizer Nano series instrument (Malvern instrument, UK), in which a few microliters of each particle suspension was dispersed in 1 mL of MilliQ water.

2 SI Text: Interaction energies between the colloidal particles:

According to DLVO theory, the total interaction energy is taken as a sum of the repulsive and van der Waal interactions:

$$E_{DLVO} = \frac{64\pi R_f \rho k_B T}{\kappa^2} e^{(-\kappa d)} - \frac{A R_f}{6d} \tag{2}$$

Where R_f is the average of the interacting particles radii ($R_f = \frac{R_L R_S}{R_L + R_S}$), ρ is the concentration of ions, κ^{-1} is the Debye length, k_B is the Boltzmann constant, T is absolute temperature, A is Hamaker constant, and d is the interparticle separation. For van der Waal attractive interaction of the DLVO plots, Hamaker constant value for polystyrene-water-polystyrene system was taken from J. Israelachvili, *Intermoleculer and Surface Forces*, 2nd edition, Academic Press, London, 1992.

3 SI Text: Depletion interaction between the colloidal particles:

In the case of binary mixtures of large and small particles, the depletion interaction can be written as

$$U_{dep}(d) = 3k_B T \varphi_{small} \frac{R_L}{R_S} (1 - \frac{d}{R_S})^2 \tag{3}$$

Where $k_B T$ is the thermal energy, φ_{small} is the volume fraction of small particles, and d is the separation between the large particles.

4 SI Text: Capillary interaction between the colloidal particles

The capillary interaction energy is given as

$$\Delta E \propto -2\pi\gamma R_L R_S K_0(qL) \qquad \text{if } L << q^{-1} \tag{4}$$

Where γ is the surface tension, L is the separation between the particles, and $K_0(qL)$ is modified zero order Bessel function. The capillary length q^{-1} is equivalent to Debye screening length in case of electrostatic interaction and the maximum value of q^{-1} when air is in contact with the water surface is ~2.7 mm.

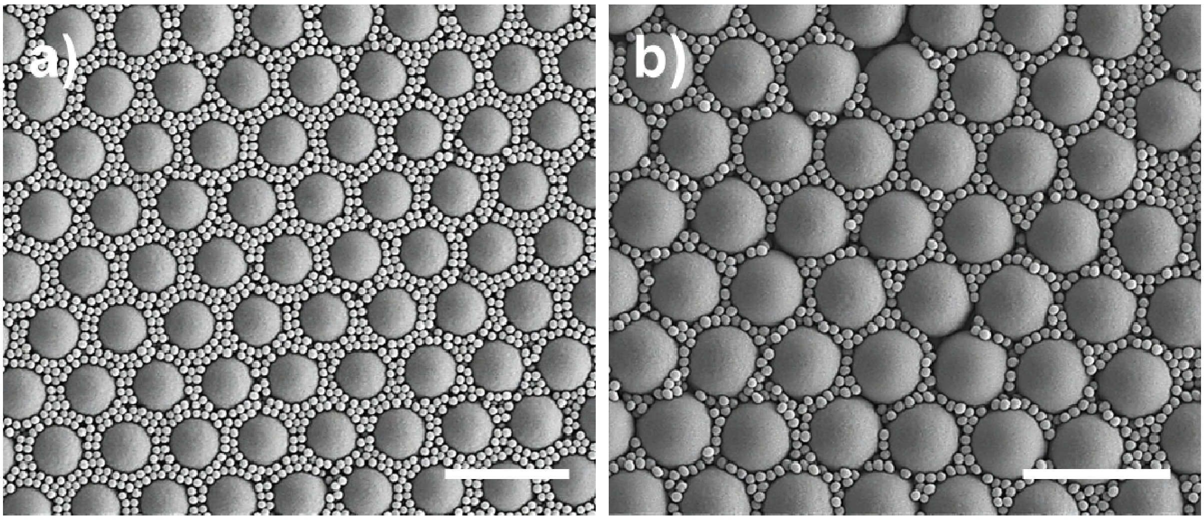

Fig. S1 SEM images show the growth of BCCs (200 nm A-PS/2 μm C-PS) at (a) higher, and (b) lower concentration of 200 nm nanoparticles, scale bar: 3 μm.

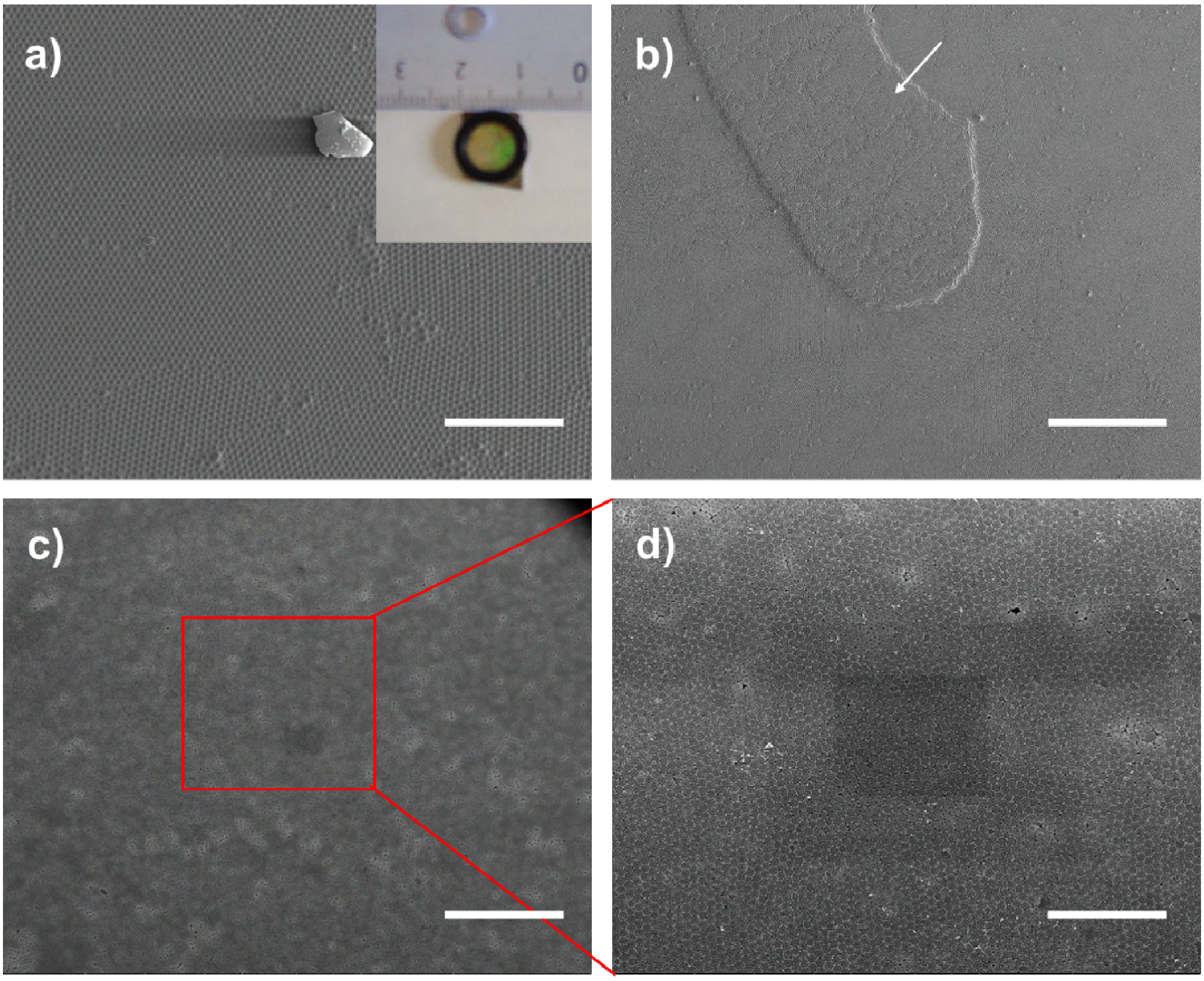

Fig. S2 SEM images show very long range ordering of the BCCs. (a) 350 nm plain-PS/3.1 μm S-PS, scale bar: 50 μm and inset photograph shows wafer scale (cm^2) growth of BCC area inside the ring. (b) 200 nm A-PS/2 μm C-PS, scale bar: 100 μm. The white arrow indicates the formation of second over the first layer of binary crystal. (c) 200 nm A-PS/50 nm C-Si, scale bar: 10 μm. (d) Blown-up region from the image c, scale bar: 5 μm.

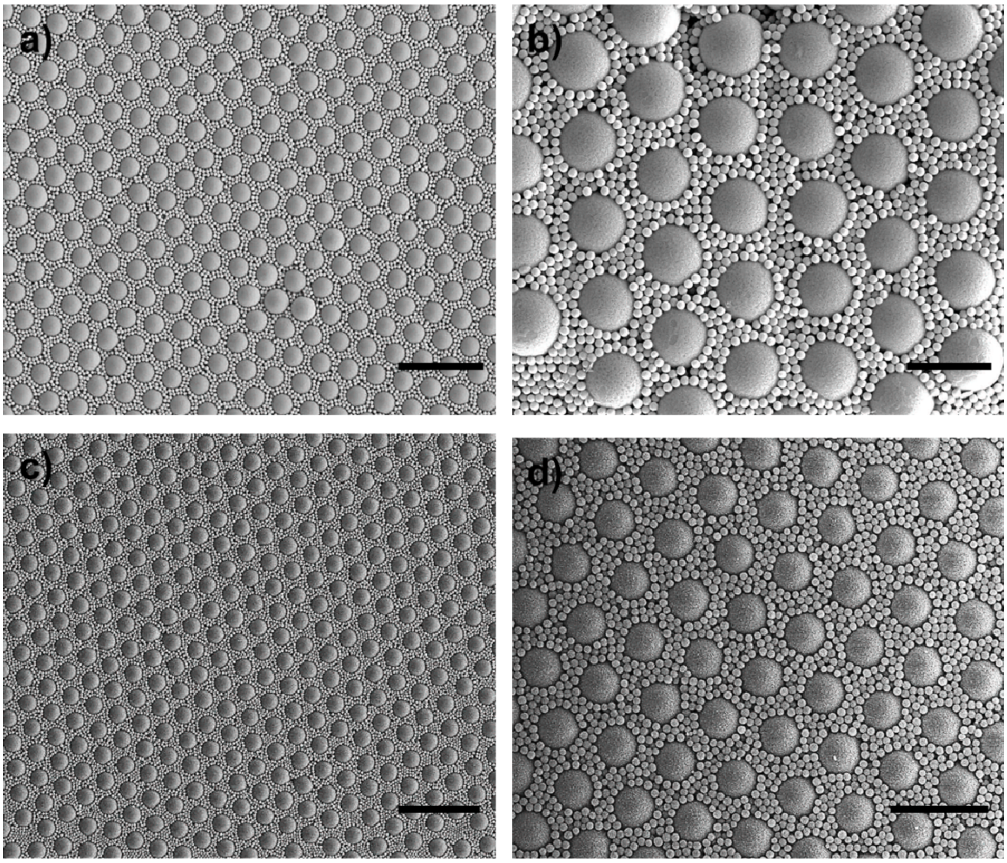

Fig. S3 SEM images demonstrate the BCC fabrication from same charge colloidal particles. (a) 200 nm S-PS/3.1 μm S-PS, scale bar: 5 μm.(b) 200 nm A-PS/2 μm A-PS, scale bar: 2 μm.(c) 350 nm plain-PS /3.1 μm S-PS, scale bar: 10 μm.(d) 250 nm plain-PS/2 μm C-PS, scale bar: 3 μm.´

Particle type	**ζ-potential (mV)**
200 nm S-PS	-48.15
200 nm A-PS	-51.23
250 nm plain-PS	-52.80
350 nm plain-PS	-52.47
2 µm A-PS	-9.93
2 µm C-PS	-43.10
3.1 µm S-PS	-44.78

Table S1. ζ-potential values measurements in MilliQ water (pH=7.4). It should be noted that 200 nm A-PS particles have negative zeta potentials. This may arise from the manufacture process where residual anionic surface functional groups (e.g., amide and carboxyl groups) are present on the particles.