Electronic Supplementary Material (ESI) for Soft Matter.

Ordered Non-Close Packed Colloidal Array with Morphology Control

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Electronic Supporting Information

Section S1. Silica Nanoparticles synthesized by Stöber's method.

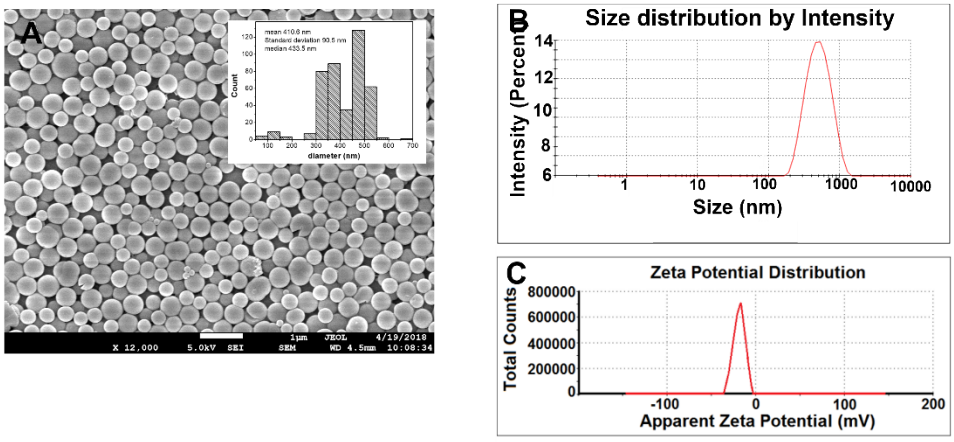

Figure S1: (A) SEM image (size distribution as inset), (B) Size distribution from Dynamic Light Scattering and (C) Zeta potential of silica colloids synthesized by Stöber's method.

Section S2: HCP Array and replicas of 3000 nm colloidal particles.

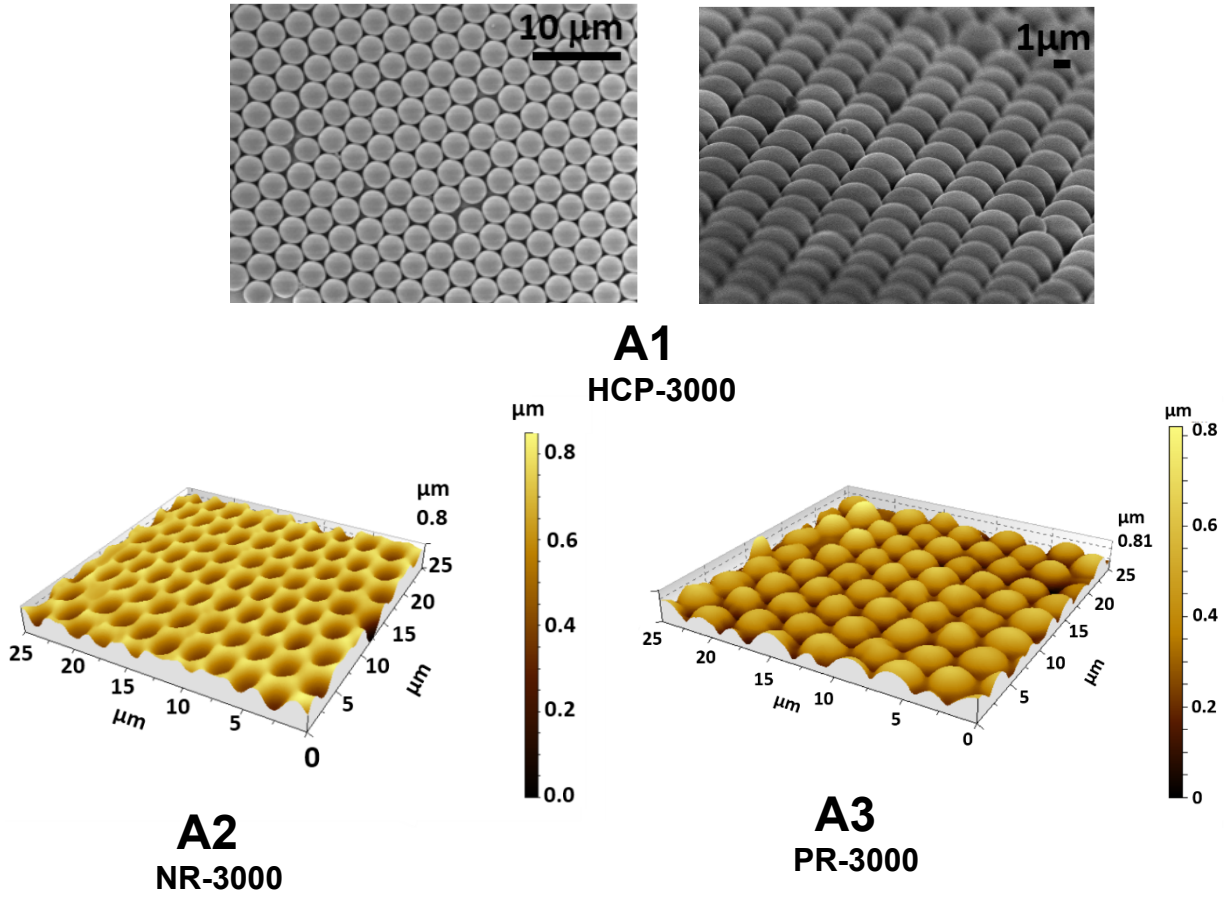

Figure S2: (A1) HCP array of 3000 nm colloidal particles (HCP-3000), (A2) negative replica of HCP-3000 in sylgard (NR-3000) and (A3) positive replica (PR-3000) of HCP-3000 in PMMA.

Section S3: Table showing feature height obtained during multiple attempts at replica fabrication.

ARRAY	S1	S2	S3	S4	MEAN	STD. DEV.
HCP 800	700	750	580	650	670	72
NRS 800	520	500	520	600	535	44
PR 800	700	600	650	700	662	48
NR 800	350	215	225	220	252	65

Table 1: Feature height (in nm) obtained for the primary HCP array and the subsequent replicas obtained.

The feature height obtained for multiple samples fabricated under identical conditions has been tabulated. The images presented in the manuscript correspond to the best samples.

Section S4: Structures at non-optimum concentrations of smaller colloidal particles in positive replica templates.

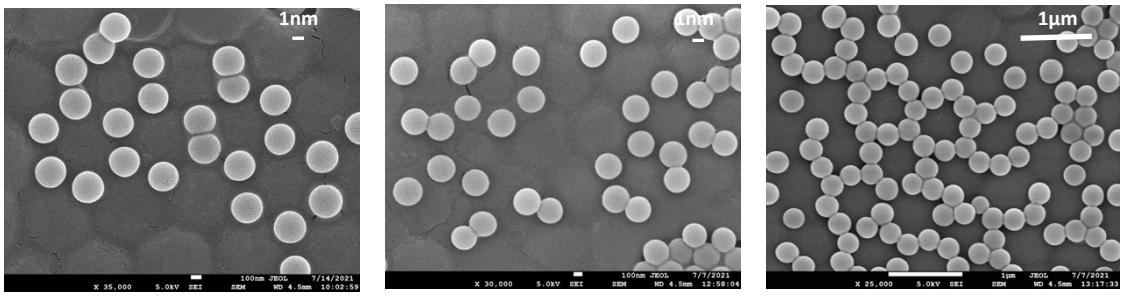

Figure S3: Under filled/ overfilled structures resulting from non-optimum concentration of the smaller colloidal particles.

Section S5: A geometrical analysis showing how different particle size can lead to different NCP structures

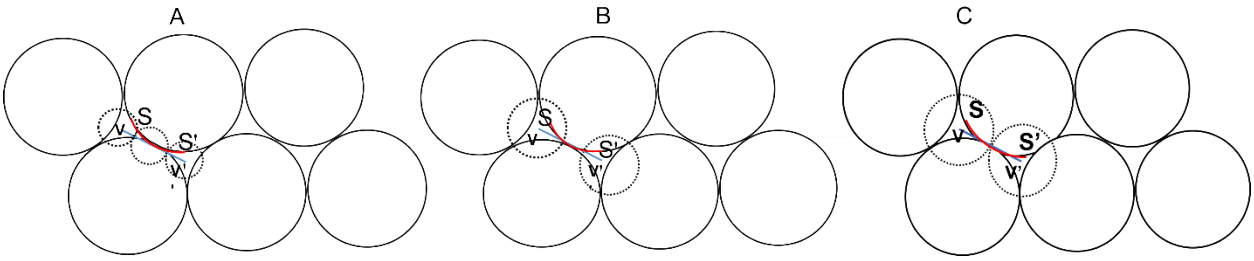

Figure S4 (1) : A simple geometric model is presented to understand how varying the SP to LP size ratio leads to different structures.

Since an LP sphere is surrounded by 6 tetrahedral voids, length of the arc SS' between two voids is obtained as,

$2\pi R=6SS'$

$SS'=1.05R$

where R is the radius of the LP

When 3 SPs can be accommodated between SS' (Figure S5 (1A)), Approximating SS'≈ VV' (the distance between centers of adjacent voids), we have

$$VV'=4r$$

$$\text{or,} \quad 1.05R=4r$$

$$\text{or,} \quad r/R=0.26$$

Where r is the radius of the SP

Thus, if $r \leq 0.26R$, three or more SPs can be accommodated along SS' and ring structures may form. 800 nm SPs form rings in 3000 nm templates. Here $r/R = 0.26$, satisfying the equality. On the other hand, if $r > 0.26R$, two SPs at most may occupy adjacent voids and an H-NCP may form (Figure S5 (1B)). For instance, 300 nm SPs form H-NCPs in 800 nm templates. Here $r/R = 0.375$, satisfying the above condition for an H-NCP.

When the SPs sitting across voids touch (Figure S5 (1C)),

$$1.05R=2r$$

$$\text{or,} \quad r/R=0.53$$

Thus, NCPs may not form in case $r > 0.53$ R. For instance, 600 nm SPs do not form an NCP in a template of a replica of 800 nm LPs ($r/R=0.75$) (Figure S5 (2)).

The relations obtained above assume perfect replication where feature height of the replica is identical to that of the LP array and there are no losses during replication. Moreover, in the manuscript the conditions under which different types of structures are obtained have been laid down on the basis of available particle sizes.

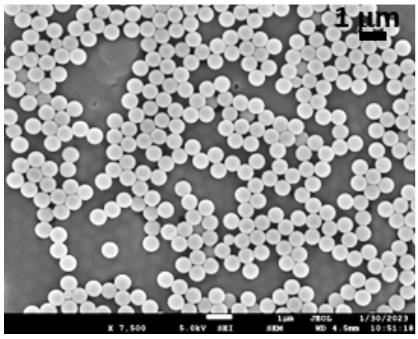

Figure S4 (2): 600 nm SPs in a PR-800 template. NCP arrays do not form for this case where r/R=0.75.