Supporting Information

Fabrication of planar colloidal clusters with template-assisted interfacial assembly

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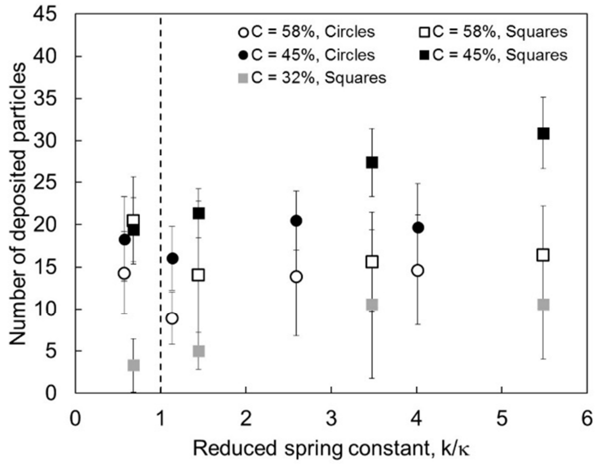
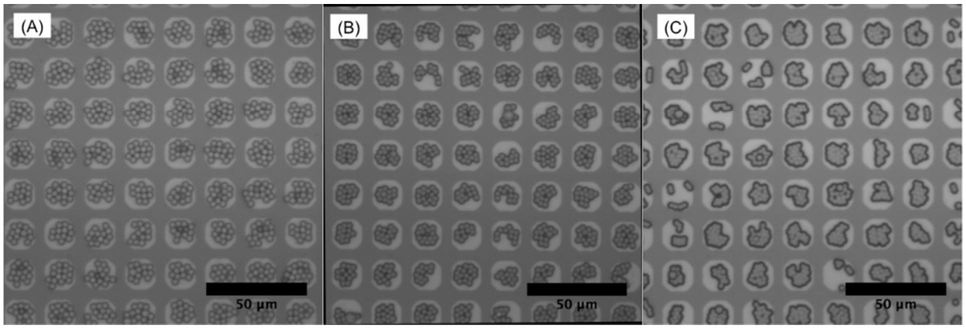
A. Tuning the size of clusters with template geometry



SI Figure 1: Dependence of particle deposition on geometry for *a* = 15 μm patches of varying reduced spring constant k/κ. The number of particles deposited onto circular and square patches with *a* = 15 μm as a function of geometry was tallied for three different initial surface coverages and varying k/κ. The number of particles deposited onto each patch roughly increased with increasing reduced spring constant at k/κ > 1 for *a* = 15 μm squares (square symbols) and circles (circle symbols) at apparent initial surface coverages *C* of 32% (filled grey), 45% (filled black), and 58% (filled white). The non-monotonic increase in particle deposition with initial surface coverage was likely a result of particles being lost to the water sub-phase.

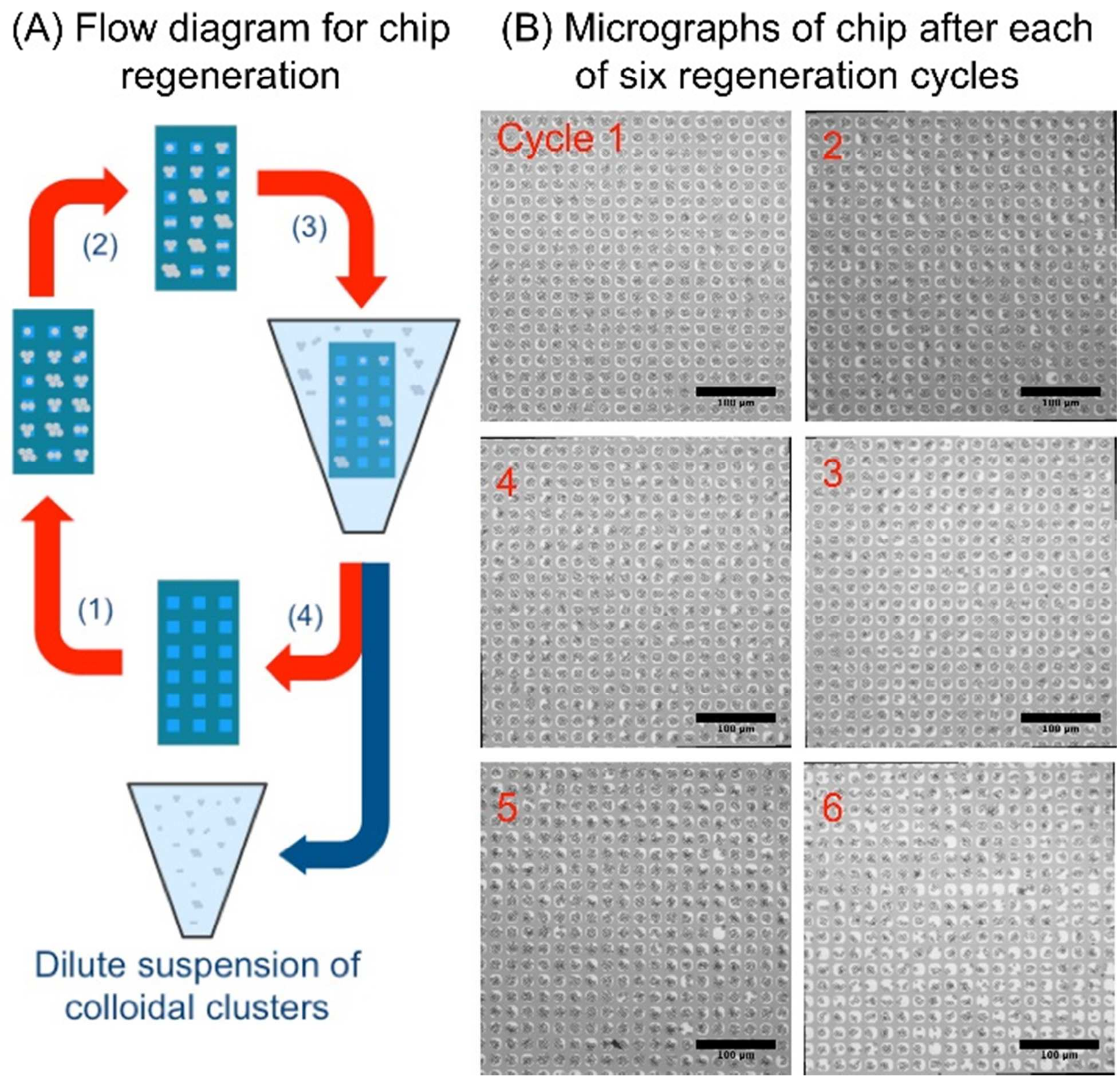
B. Annealing of planar colloidal clusters



SI Figure 2: Colloidal clusters after annealing at 130°C for (A) 0 minutes, (B) 5 minutes, and (C) 7 minutes (different region of interest of same chip). Proximate particles coalesced after annealing above the glass transition temperature of *poly*styrene. The amount of coalescence depended on the length of time heated - this provides an additional lever for controlling the geometry of the colloidal cluster.

C. *Regeneration of chip template*

A chip regeneration scheme was developed and tested that included the following steps (see SI Fig. 3): (1) Deposition of isotropic colloidal particles from a decane - water interface onto a chemically modified substrate, (2) annealing deposited particles to permanently bond neighboring isotropic particles to form anisotropic colloidal clusters, (3) sonication of the substrate with deposited and annealed colloidal clusters, and (4) centrifugation and separation of the colloidal clusters from the chemically modified substrate. The substrate was gently rinsed with ethanol and ultra-pure water following removal of the colloidal clusters. SI Figure 3 shows a schematic of the process and also optical micrographs of the clusters following six regeneration cycles. Particles were deposited from a decane-water interface of an initial surface coverage of 70%. The substrate continued to work well as a template for the assembly of colloidal clusters after five cycles. Clusters synthesized on the sixth cycle were of lower quality (i.e. high size dispersity). Degradation may have been a result of insufficient cleaning after each step, as the chip was only gently rinsed with ethanol and ultra-pure water. The number of regeneration cycles may be increased if a more substantial cleaning step, for example sonication in ethanol/ultra-pure water, was used for the chip following each regeneration cycle.



SI Figure 3: Regeneration of template. A single chip was used multiple times to generate colloidal clusters with only mild washing between each cycle.