

Communication

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Programmed Co-assembly of One-dimensional Binary Superstructures by Liquid Soft Confinement

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Supporting Information

ABSTRACT: Precisely ~~controlling~~ control of particles co-assembly has attracted great attention for fabricating intricate structures and functional materials. However, achieving precise co-assembly of one-dimensional (1D) binary superstructures remains challenging due to the constrained thermodynamic stability and ~~the~~ lack of general strategies to control ~~the~~ 1D ordered arrangement of mixed particles. Here, we propose a facile strategy to achieve programmed co-assembly of 1D binary superstructures by liquid soft confinement without particles modification or external field. It reveals that binary particles undergo stepwise confinement and programmed co-assembly in the gradually shrinking and spatially tunable liquid soft confinement. Through tuning the liquid confined space and particles composition, diverse 1D binary superstructures with precisely controlled periodicity, orientation and symmetry are achieved, which shows generality for various particles of different sizes and materials. This work provides a promising route to refined patterning and manufacturing complex materials.

Programming particles co-assembly is of scientific significance for exploring new assembly mechanisms,^{1,2} and is of particular interest to bottom-up manufacturing a wide range of intricate structures and complex materials.^{3,4} ~~In the past~~ Over the past two decades, a large variety of particle-based superstructures with ~~high~~ long-range order (such as crystalline materials or superlattices)^{5,6} have been achieved by programmed two- or three-dimensional co-assembly, driven by entropy-dictated ordering,^{7,8} grafted molecule interactions (such as DNA hybridization),^{9,10} ~~interparticle~~ magnetic forces¹¹, ~~or~~ electrostatic interaction,¹² and so on.¹³ ~~So far~~ Currently, programmed 1D co-assembly has been reported by linkers mediated¹⁴, solvent guided^{15,16} and magnetic field induced^{17,18} assembly approaches based on specific interaction mechanisms. However, these methods require specific particle modification or external field to control the selective and directed interparticle interaction, and the long-range orientation of the 1D co-assembled superstructures is intrinsically difficult to control.^{19,20} Here, we propose a general and facile strategy to pro-

gram the particles co-assembly by liquid soft confinement, and achieve a series of precisely controlled 1D binary superstructures, needless of particle modification or external field.

The strategy presented in this work is based on confined co-assembly of two sized particles. Here, we build ~~the~~ gradually shrinking and spatially tunable liquid soft confinement to endow the particles assembly with 'time_selectivity' and 'space_selectivity'. As shown in Figure 1a-c, ~~the~~ evaporation mediated rupture of binary particles suspension is controlled by ~~a~~ microfabricated pillars array,²¹ and the ~~yielded~~ resulting capillary bridge provides ~~the~~ gradually ~~reduced~~ shrunk confined space for particles that are transported by outward capillary flow.²² ~~As~~ Because the pillar interval of the template influences the formed liquid pattern; ~~resulting~~ from ~~through~~ competition of ~~the~~ Laplace pressure,²³ ~~here~~ the vertical interval of the pillars array is designed ~~to be~~ double the horizontal interval (i.e., the distance between two nearest neighboring pillars). Utilizing anionically stabilized polystyrene particles labeled with different fluorescent dyes and a superhydrophilic substrate, direct real-time microscopy analysis reveals the stepwise confinement of binary particles. In the liquid soft confinement, large particles are ~~firstly~~ first confined; ~~first~~ and serve as ~~the~~ a secondary template for the ~~following~~ subsequent co-assembly ~~with~~ of small particles (Video S1). ~~Besides~~ Furthermore, the number ratio of small to large particles (N_S/N_L) influences the time selectivity of ~~the~~ binary particles assembly. When N_S/N_L is ~~about~~ approximately 6–8 (Figure 1d and Video S2), small particles are confined to co-assemble with the already assembled large particles. Then, a 'grafting' 1D binary superstructure is formed, in which closely arranged large particles are surrounded by small particles. Given that ~~the~~ particles assembly in the liquid soft confinement proceeds from ~~a~~ unfixed via semifixed to fixed state, when N_S/N_L is increased to ~~about~~ approximately 12–16 (Figure 1e), small particles are confined to co-assemble with large particles that are still in semifixed state, followed by an error-and-repair process²⁴ (Video S3). Finally, ~~a~~ 'segmented' 1D binary superstructure is formed, in which large particles are evenly spaced by a cluster of small particles. For an intermediate case with N_S/N_L ~~about~~ approximately 8–10, a graft-

ing superstructure is obtained, in which a single particle locates is located at the saddle site²⁵ between each two large particles (Figure S1). Therefore, the formation of the secondary template, constituted by large particles, overcomes the chaos²⁶ in the co-assembly process. For a given size ratio of small to large particles (D_S/D_L), N_S/N_L can be tuned to program the binary particles assembly process to achieve different 1D co-assembled superstructures.

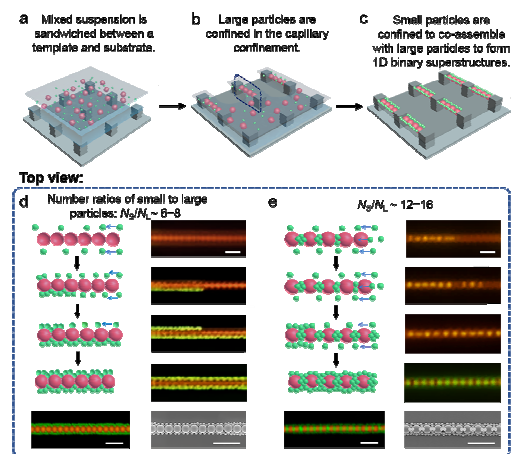


Figure 1. Programmed co-assembly processes of 1D binary superstructures by liquid soft confinement. (a-c) The liquid soft confinement is resulted results from the evaporation induced rupture of binary particles suspension controlled by a designed pillar-template. The arrows indicate the time sequence, indicating that large particles are firstly confined, followed by confined co-assembly with small particles. (d, e) By-Using a square-pillar-template with the pillar height (H) of $3.0\ \mu\text{m}$, two types of co-assembly processes from binary particles with diameters of $1.00\ \mu\text{m}$ (red-ones) and $0.34\ \mu\text{m}$ (green-ones) are shown by the schematic images (left panels) and snapshots from videos (right panels). Blue arrows indicate the transporting direction of particles dragged by capillary flow. When N_S/N_L is about approximately 6–8, small particles arrange progressively along two contours of the closely arranged large particles, forming the ‘grafting’ 1D binary superstructure. When N_S/N_L is about approximately 12–16, small particles first occupy and accumulate at the 2-fold saddle sites, and then arrange along contours of and in the space between large particles, thus generating the ‘segmented’ 1D binary superstructure. Scale bars, $3\ \mu\text{m}$.

Besides, the space selectivity of binary particles assembly is critical to precise co-assembly of 1D binary superstructures, and can be programmed by tuning the liquid confined space. Formed between a superhydrophilic template and substrate, the liquid confined space has the shape of a quadrangular column with the a waisted cross section. Driven by lowering the decreasing surface energy, large particles are prior-first confined in the capacious middle region, followed by confined assembly of small particles in the residual space. Firstly, to control the large particles assembly, the width of liquid confinement (W), which is defined as the distance between the two three-phase contact line (TCL) of the liquid confinement, is investigated. When $W \gg D_L$, large particles would assemble into multi-particle chains^{21,23}; when $W < D_L$, large particles would be prevented from migrating into the

liquid confined space, thus failing the to achieve 1D assembly. By Using a square-pillar-template with H of $5.0\ \mu\text{m}$, programmed co-assembly from binary particles with diameters of $3.00\ \mu\text{m}$ and $0.34\ \mu\text{m}$ is achieved (Figure 2a and 2b, Figure S2 and Video S4). By measuring W by-for the templates with different pillar heights of $1.7\ \mu\text{m}$, $3.0\ \mu\text{m}$, $5.0\ \mu\text{m}$ and $7.0\ \mu\text{m}$, it is found that W increases with H , which is adjustable for the assembly of particles with different sizes (Figure 2c). For another case when W is slightly larger than D_L (Figure S3), typical grafting or segmented 1D binary superstructures are not formed, but another segmented superstructure is obtained. The large particles in the limited confined space tend to be fixed,²⁷ and the spacing between large particles is mainly-primarily influenced by the local number of large particles, nearly independent of the small particles. Subsequently, small particles are confined to co-assemble with the fixed large particles to form another segmented superstructure. Generally, the space selectivity of large particle assembly can be programmed by controlling W through tailoring H . Then Moreover, to program the space selectivity of the small particles assembly, the residual space excluding large particles in the liquid confinement can be controlled by tuning the receding angle of the substrate (θ_R). Critical width of liquid confinement when large particles is confined decreases with θ_R ,²⁸ leading to reduced space to accommodate small particles, thus the 1D binary superstructures is-are formed with decreased (Figure 2d and 2e) or none loading of small particles (Figure S4). With the a hydrophobic substrate, the programmed co-assembly is frustrated due to the instability of the liquid confinement. It should be noted that the vacancy near the TCL (dotted framed region in Figure 2d) is also influenced by D_L under-below a certain pillar height, thus the range of D_S/D_L is limited for programmed co-assembly. A series of experiments with different D_S/D_L values are-were conducted, and it is found that-determined that D_S/D_L should be smaller than 0.5 to achieve well-controlled-well-controlled co-assembly (Figure S5). When D_S/D_L is larger than 0.5, the vacancy near the TCL is not large enough to match the size of the small particles, and the programmed co-assembly fails (Figure S6). Besides microscale particles, nanoparticles co-assembly can also be programmed to achieve a variety of well-defined 1D binary superstructures (Figure S7) by synthetically tuning the pillar height, receding angle of the substrate and particles composition. To sum up, programmed co-assembly of various 1D binary superstructures can be achieved by tuning the liquid confined space and particles composition.

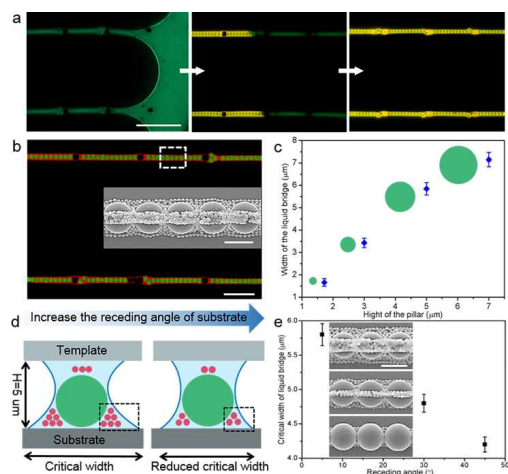


Figure 2. Programmed co-assembly by controlling the liquid confined space. (a) The programmed co-assembly process shows that the aligned large particles serve as the secondary template for following the subsequent co-assembly with of small particles. The arrows indicate the time sequence; s Scale bar, 50 μm . (b) Bottom-view confocal micrograph of the 1D binary superstructures array (Scale bar, 20 μm) and magnified SEM image (Scale bar, 5 μm) of the boxed region. (c) Experimentally measured width of liquid confinement increases with the pillar height, indicating that the pillar height can be adjusted to control the assembly of large particles with different sizes. (d) Schematic for the cross section of binary particles in the liquid confinement, illustrating that the number of small particles accommodated in the vacancy near the TCL (dotted framed region) increases with the critical width when the large particle is confined. (e) Employing the substrates with different receding angles (θ_r) of 5°, 30° and 45°, the measured critical widths and the corresponding SEM images of the resulted resulting 1D binary superstructures, showing show that the critical width decreases with θ_r , leading to different co-assembled superstructures with reduced loading of small particles. Scale bars, 3 μm .

Furthermore, the orientation of the 1D binary co-assembled superstructures can be programmed to achieve different patterns. Induced by a straight stripe- or curve stripe-pillar-template, different liquid patterns can be formed in the gap between the pillars top and the substrate²⁹ (top-view SEM images of the pillar-templates and the scheme for control of the gap are shown in Figure S8). In the liquid soft confinement, the particles moving trajectory is controlled, and the elongation of the assembled region can be directed to form different patterns. Thus, well controlled co-assemblies can be coupled into designed routings, and diverse patterns are achieved, such as straight-line patterns, curve patterns or compound patterns consisting of lines and curves (Figure 3a and 3c, and Video S5). Based on the analysis above, by enlarging the liquid confined space through by increasing the gap (Figure 3b); leads large particles to stack in two layers in the formed resulting 1D binary superstructure, and the number of large particle chains in each layer is exhibits an arithmetic progression (Figure 3d and 3e). Therefore, the orientation and configuration of the 1D binary superstructures can be programmed to achieve different patterns.

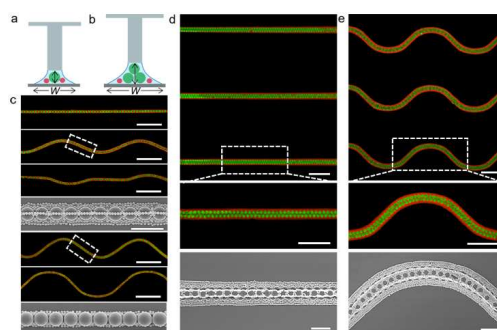


Figure 3. Programmed orientation of the 1D binary superstructures to achieve different patterns. (a, b) Schematic illustrations for the cross-section of the liquid confined system formed in the gap between a hydrophilic substrate and the pillar top of a straight stripe- or curve stripe-pillar-template, showing that the width of liquid confinement, W , is increased when the gap is enlarged, and large particles stack in more than one layer. (c) Corresponding to the schematic sketch in (a), 1D binary superstructures, with well controlled orientation, are achieved. (d, e) Corresponding to the schematic sketch in (b), arrays of straight or curved superstructures with large particles stacking in two layers, are achieved. The number of large particle chains in the upper layer is less than that in the bottom layer. Scale bars are, 20 μm in the confocal micrographs and 5 μm in the SEM images.

Besides-In addition to symmetric 1D binary superstructures, programmed co-assembly of asymmetric 1D binary superstructures is also achieved, and the correlation between the width of the liquid confinement W (marked in Figure 4a) and the pillar height H is quantified experimentally and theoretically. With the pillar top of a stripe-pillar-template closely contacting a superhydrophilic substrate, particles dragged by outward capillary flow are blocked to gather by one side of a pillar (Figure 4a). With the evaporation of solvent, the formed liquid confinement is divided by the stripe-pillar into two parts. In the liquid soft confinement at the particles' gathering side, programmed co-assembly occurs with small particles asymmetrically arranging along one-side of the aligned large particles' contour near the TCL (Video S6). Moreover, we find a linear increase of the measured W dependent on H , with the a slope of about approximately 0.4 (Figure 4b), which is further supported by the theoretical analysis (Supplementary Discussion). The linear dependence of W on H offers the quantitative basis for particles assembly by controlling the liquid confined space through tailoring the pillar height. Accordingly, by utilizing the a template with the pillar height of 18.0 μm , asymmetric 1D binary superstructures, constituted by binary particles with diameters of 3.00 μm and 1.00 μm , are achieved (Figure 4c, d). The co-assembled superstructures can be diversified by intentionally adjusting the N_2/N_1 and θ_r (Figure S9a). By decreasing the pillar height, diverse 1D binary superstructures assembled by particles with the size from micrometer (Figure S10) to nanometer (Figure S9b) can be achieved, and these ordered structures can be well controlled in the long range (Figure S11). SignificantlyPromisingly, this facile strategy shows generality for particles-assembly of various materials, such as inorganic particles, metal particles, or mixed particles with different materials (Figure S12).

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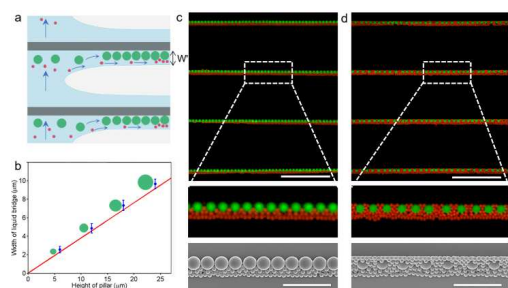


Figure 4. Programmed co-assembly of asymmetric 1D binary superstructures and quantified correlation between width of liquid confinement (W) and pillar height. (a) Particles gather by one side of the straight stripe-pillars (grey), the top of which closely contacts the superhydrophilic substrate. The liquid confinement is divided into two parts, in one of which small particles asymmetrically arrange along one-side of the contour of the aligned large particles' contour near the TCL. Blue arrows indicate the transporting-transport direction of particles. (b) Experimental values (blue dots with error bars) and theoretical values (red line) of W demonstrate a linear increase with the pillar height, which is adjustable to control large particle assembly. (c, d) Bottom-view confocal micrographs with the magnified view of the boxed region and top-view SEM images show the asymmetric 1D binary superstructures, including grafting (c) and segmented (d) superstructures. Scale bars are: 50 μm in the confocal micrographs and 10 μm in the SEM images.

In conclusion, distinct from the specific interparticle interaction mechanisms that enable programmed two- or three-dimensional co-assembly, we present a general and facile strategy by liquid soft confinement to achieve programmed co-assembly of 1D binary superstructures. Through tuning the liquid confined space and particles composition, the binary particles assembly can be programmed with relatively independent control. Accordingly, a wide range of 1D binary superstructures, with precisely controlled periodicity, orientation and symmetry, are achieved. Even free-standing particle chains can be foreseen by a fluidic device. Given that this programmed co-assembly strategy is applicable to different particles combinations, developing multifunctional materials³⁰ organized by multicomponent elements with unique plasmonic, magnetic, or optical properties is anticipated.

ASSOCIATED CONTENT

Supporting Information

Materials and Methods, Supplementary Discussion, Supplementary Figures, Captions for Supplementary Videos, Supplementary Table, References, and Videos S1 to S6.

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Notes

The authors declare no competing financial interests.

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