Assembling and positioning latex nanoparticles via controlled evaporative self-assembly†

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By capitalizing on a simple, robust, and fast approach based on controlled evaporative self-assembly in a cylinder-on-flat geometry, two kinds of polystyrene (PS) latex nanoparticles with different diameters (i.e., D = 50 nm and 500 nm, respectively) were deposited on the Si substrate, forming ordered “coffee rings” composed of PS nanoparticles. Within a “coffee ring”, the packing of PS nanoparticles was found to be dependent upon the particle diameter. More intriguingly, when the aqueous solution of mixed two PS nanoparticles was used, “coffee rings” of small particles were positioned at the edge of three-phase contact line (D = 50 nm), followed by the adjacent deposition of large particles (D = 500 nm). These assembled deposits consisting of monolayer- or multilayer-thick latex nanoparticles over large areas may offer potential for applications in electronic devices, photonic bandgap materials, biosensors, particle sorting, and disease diagnosis.

1. Introduction

The ability to assemble and position colloidal particles is of practical interest for developing miniaturized optical, electronic, optoelectronic, information-storage materials and devices, and biosensors.1-2 A variety of methods have been adopted for structuring particles on a flat substrate, including gravitational sedimentation,3-4 electrophoretic deposition,5 and surface modification.6,7 Recently, a template-directed assembly approach has been widely used to guide the deposition of colloidal particles into well-ordered arrays. However, these pre-defined templates are commonly prepared by top-down conventional lithography techniques (e.g., e-beam lithography, soft lithography, and nanoimprint lithography) that are costly, complex and require a multi-step process. In this regard, evaporation-driven convective self-assembly has emerged as an extremely simple, appealing strategy to assemble and position the particles into useful structures.8-14 However, due to the lack of control over the evaporation of volatile solvent, it is difficult to achieve a regular pattern over large areas.

In order to fully capitalize on the evaporation as a simple, lithography and external field-free route to producing intriguing, ordered structures over large areas, it is crucial to control the evaporative flux, solution concentration, interfacial interaction between the solvent, the solute and the substrate, etc. To this end, a few elegant studies have centered on precise manipulation of the evaporation process in confined geometries (e.g., two parallel plates with the top one sliding on the lower stationary substrate,15,16 cylindrical tube,17 or curve-on-flat geometries18-37) from which self-organized mesoscale patterns are readily obtained. Herein, we report a simple yet versatile method to assemble latex nanoparticles into regularly arranged stripe patterns (i.e., coffee ring-like deposits) over large areas by subjecting a drop of polystyrene (PS) latex nanoparticle aqueous solution to evaporate from a liquid capillary bridge formed by confining the solution between a cylindrical lens and a Si substrate (i.e., cylinder-on-flat geometry). A distinct difference in the surface morphology of PS stripes was observed with different nanoparticle diameters; that is, stripes composed of single layer nanoparticles were formed when large PS latex particles were used (D = 500 nm), while stripes composed of multilayer nanoparticles were yielded when small PS latex particles were utilized (D = 50 nm). Quite intriguingly, when the mixed aqueous solution of these two PS nanoparticles was employed within a coffee ring-like stripe, small PS particles were positioned at the capillary edge, followed by positioning large PS particles next to them. The implementation of a cylinder-on-flat geometry suppressed the temperature gradient and associated convective flow, thus providing remarkable control over the solution evaporation during the deposition of nanoparticles. This method is fast and cost-effective, eliminating the need for multistage lithography and externally applied forces.

2. Experimental section

Evaporative self-assembly of the PS latex particle aqueous solution in a cylinder-on-flat geometry

The aqueous solutions containing PS latex particles with diameters of 50 nm and 500 nm labeled with red and blue fluorescent...
A thin film of hexamethyldisilazane (HMDS, 99.9%) was rinsed extensively with deionized (DI) water and blow-dried with a mixture of sulfuric acid and Nochromix, then quartered with a ratio of 50 nm PS : 500 nm PS nanoparticles at the same concentration, solution was also prepared by mixing 50 nm and 500 nm PS nanoparticles without further purification. A mixed nanoparticle aqueous solution was transported from the solution to the capillary edge and pinned the contact line (Fig. 1c), thereby forming a coffee-ring like deposit. During the deposition process, the initial contact angle of the meniscus at the capillary edge gradually decreased to a critical value due to continuous evaporative loss of water, at which the depinning force (i.e., capillary force) became larger than the pinning force. This caused the contact line to jump to a new position, where it was pinned again and a new “coffee ring” was thus yielded (Fig. 1c). Consequently, the repetitive pinning and depinning (i.e., “stick–slip” motion) of the contact line produced a lateral surface pattern consisting of hundreds of highly ordered concentric “coffee rings”. Locally, they appeared as parallel stripes (Fig. 2). This is in stark contrast with the generally irregular surface patterns formed from sessile droplet evaporation as in copious past work.38

Notably, the use of confined geometry facilitated the creation of highly ordered stripes over large areas. Three representative optical micrographs of parallel stripes obtained by using different particle sizes (D = 50 nm, 500 nm, and their mixture at the weight ratio of 50 nm : 500 nm = 1 : 1). The Si substrate was cleaned with a mixture of sulfuric acid and Nochromix, then rinsed extensively with deionized (DI) water and blow-dried with N₂. A thin film of hexamethyldisilazane (HMDS, 99.9%) was spin-coated (3000 rpm and 60 s) on the Si substrate to change its surface property from hydrophilic to hydrophobic. The cylindrical lens (L = 9.5 mm, H = 4.0 mm, W = 11.0 mm, Fig. 1a and b) was treated with an octadecyltrichlorosilane (OTS) vapor to coat a thin film of OTS on the lens surface and placed on the Si substrate, thus forming a symmetry wetting between the hydrophobic HMDS-coated Si substrate and the hydrophobic OTS-coated cylinder. The resulting cylinder-on-flat geometry was placed in a sealed chamber to minimize possible air convection and maintain constant temperature during the evaporation process. To study controlled evaporative self-assembly of PS latex nanoparticles in the cylinder-on-flat geometry, a drop of nanoparticle aqueous solution (volume, V = 30 µL) was loaded and bridged the cylinder and the Si substrate, yielding a capillary-held solution, where the evaporation rate was highest at the capillary edge (Fig. 1b). After the evaporation was complete, the patterns formed on the HMDS-coated Si were investigated.

Characterization

The stripe patterns formed from controlled evaporative self-assembly were examined by optical microscopy (OM; Olympus BX51 in the reflection mode) and atomic force microscopy (AFM; Dimension 3100 scanning force microscope in the tapping mode (Digital Instruments)). Fluorescent micrographs were obtained with the confocal fluorescent optical microscope (Leica SP5 X). Vista probes (T190) with spring constants 48 N m⁻¹ were used as scanning probes. The patterns were also evaluated by a field-emission scanning electron microscope (FE-SEM; FEI Quanta 250) operating at 10 kV under high vacuum.

3. Results and discussion

Rather than the conventional sessile droplet evaporation, the PS latex nanoparticle aqueous solution was restricted in the cylinder-on-flat geometry. As a result, the evaporation only occurred at the constrained capillary edge. To promote the evaporation of water, the aqueous solution was heated at a fixed temperature of T = 80 °C by placing a heat plate beneath the Si substrate. As water evaporated, PS latex nanoparticles were transported from the solution to the capillary edge and pinned the contact line (Fig. 1c), thereby forming a coffee-ring like deposit. During the deposition process, the initial contact angle of the meniscus at the capillary edge gradually decreased to a critical value due to continuous evaporative loss of water, at which the depinning force (i.e., capillary force) became larger than the pinning force. This caused the contact line to jump to a new position, where it was pinned again and a new “coffee ring” was thus yielded (Fig. 1c). Consequently, the repetitive pinning and depinning (i.e., “stick–slip” motion) of the contact line produced a lateral surface pattern consisting of hundreds of highly ordered concentric “coffee rings”. Locally, they appeared as parallel stripes (Fig. 2). This is in stark contrast with the generally irregular surface patterns formed from sessile droplet evaporation as in copious past work.38

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produced in the 50 nm particle case (Fig. 3b). The small particles aggregated to form a multilayer stripe (see a cross-sectional view in Fig. S1c† in the ESI). The maximum height of the stripe was about 360 nm, approximately seven times the diameter of single 50 nm PS nanoparticle, suggesting a high degree of aggregation. The formation of these two differently packed patterns can be rationalized as follows. As the solution concentration ($c = 0.01$ wt%) and the solution volume ($V = 30 \mu$L; indicating the same mass of particles) were fixed in the study, the number of 500 nm particles was much less than 50 nm counterparts in the solution (i.e., three orders less assuming the same density of PS particles; $(500/50)^3 = 10^3$). Moreover, because the evaporation rates for the aqueous solution containing different nanoparticles at the capillary edge were the same as a constant heating temperature on the Si substrate was applied, the force dragging nanoparticles from the solution to the contact line can thus be assumed the same for different nanoparticles. However, because of the larger weight of the 500 nm particle, their transportation was much slower during the drying process as compared to the case of lower weight, 50 nm particles. In other words, smaller nanoparticles possessed higher mobility than larger ones. As a result, fewer 500 nm PS particles can easily reach the contact line during the deposition process (i.e., “stick”), thus forming the monolayer by interrupted packing of nanoparticles (Fig. 2a). By contrast, a large amount of 50 nm particles can be readily transported and reach the contact line to form the multilayer by dense packing (Fig. 2b).

We note that the implementation of the cylinder-on-flat geometry greatly suppressed the temperature gradient and convective flow in the experiment. In an evaporating liquid droplet on a heating substrate, the shape of deposits is determined by the competition between two convective flows, i.e., radial flow and Marangoni recirculation, as illustrated in Fig. 4a. The radial outward flow is induced by the solvent evaporation, which is largest at the edge of a droplet. The radial velocity is $V_{rad} \approx j/\rho$, where $j$ is the evaporative mass flux and $\rho$ is the density of drop liquid. In order to compensate for the solution loss due to evaporation, the outward flow carries nonvolatile entrained solutes (e.g., particles) from the inner solution to the droplet edge and pins the contact line, forming the familiar “coffee-ring” patterns. The other relevant convective flow is the Marangoni recirculation. Marangoni flow is caused by temperature-gradient-induced surface tension gradient, which carries particles that are near the free liquid surface of the droplet inward toward the top of the droplet and then plunges them downward, forming bump-like depositions. The loop velocity

Fig. 2 Representative optical micrographs of parallel stripes composed of PS particles formed from (a) the 500 nm nanoparticle solution; (b) the 50 nm nanoparticle solution; and (c) the mixed nanoparticle solution (weight ratio of 50 nm nanoparticles : 500 nm nanoparticles = 1 : 1) by controlled evaporative self-assembly in a cylinder-on-flat geometry. The arrows indicate the receding direction of the solution during the drying process. Scale bars = 200 $\mu$m and 50 $\mu$m in the main image and the inset, respectively.

Fig. 3 Scanning electron microscope (SEM) images of stripe patterns composed of PS nanoparticles of different diameters. (a) 500 nm PS particles with discontinued monolayer particle packing; (b) 50 nm PS particles with highly close packing; and (c) mixed PS nanoparticles packed next to one another; within a stripe closely packed 50 nm particles (upper) were adjacent to 500 nm particles (lower). The arrows indicate the receding direction of the solution during the drying process. Scale bars = 20 $\mu$m and 5 $\mu$m in the main image and the inset, respectively.
of Marangoni flow scales is $V_{Ma} \approx (1/32)(\beta \partial \Delta T/\mu)$ where $\beta$ is the surface tension gradient with respect to temperature, $\partial$ is the wetting angle of the drop, $\mu$ is the dynamic viscosity, and $\Delta T$ is the temperature difference between the edge and the top of droplet.\(^{42}\) The final pattern reflects a balance between the radial flow and Marangoni flow that operate in different directions. However, in our study, due to the use of confined geometry to regulate the evaporation process, Marangoni flow was suppressed due to the application of the upper cylindrical lens (Fig. 4b). As a result, the retained radial flow governed the formation of periodically arranged stripes via the “stick–slip” motion. Additionally, we note that the heating temperature ($T = 80 \, ^\circ C$) was critical in the present study. At a lower temperature ($T = 60 \, ^\circ C$), the evaporation rate was quite low at the water/air/substrate three-phase contact line, thus making the radial flow insufficient to transport particles to the contact line during the evaporation process. Thus, less ordered patterns were formed (Fig. S2a–c in the ESI). On the other hand, the higher temperature ($T = 100 \, ^\circ C$; close to the boiling point of aqueous solution) led to the formation of some bubbles situated on the stripes, breaking the uniformity of stripes (Fig. S2d–f).

We now turn our attention to address qualitatively the intriguing observations shown in Fig. 2c and 3c, in which, within a stripe, small PS nanoparticles were first positioned in a densely packed manner and large PS nanoparticles were then positioned in a loosely packed fashion when the mixed nanoparticle aqueous solution was allowed to evaporate in the cylinder-on-flat geometry. The 50 nm and 500 nm particles were labeled with red and blue fluorescent dyes, respectively; thus the resulting surface patterns can be readily visualized by a fluorescence microscope to scrutinize the distribution of PS nanoparticles of different diameters inside stripes. Clearly, individual luminescent stripes were composed of closely packed red nanoparticles ($D = 50 \, nm$) and scattered blue nanoparticles ($D = 500 \, nm$) as evidenced in Fig. 5a and b. Blue nanoparticles were observed using a 405 nm excitation wavelength with an emission filter of 430–500 nm (Fig. 5a). Red nanoparticles were differentiated using a 542 nm excitation wavelength with an emission filter of 605–620 nm (Fig. 5b). The superposition of these two fluorescent micrographs revealed that red-emitting nanoparticles were pinned first to form closely packed deposits, followed by adjacent deposition of blue-emitting nanoparticles to complete the formation of a stripe (Fig. 5c). It is noteworthy that the minimal interstitial space between the 500 nm particles can be calculated by $(\sqrt{6}/2 - 1)R = 0.225R = 112.4 \, nm$, assuming the 500 nm particles were packed into a regular tetrahedron. This minimal space is still larger than the size of small nanoparticles ($D = 50 \, nm$), indicating that small nanoparticles can move freely in the mixed particle solution without the interference from large nanoparticles. Moreover, as discussed above, during the particle transportation process, small nanoparticles could reach the contact line faster than large ones due to their high mobility in the solution, and were thus positioned first at the contact line. The presence of a large amount of small particles ($10^3$ larger than large particles) favored dense packing and yielded a multilayer deposit (Fig. 5d). By contrast, as large nanoparticles reached the contact line later and there were fewer particles in the solution, they formed discontinuous, monolayer-thick deposits adjacent to small nanoparticles within the stripe (Fig. 5d). Notably, the curvature of the meniscus may also promote the separation of nanoparticles of different sizes. Small nanoparticles can be consistently transported to the contact line first due to lower local thickness of the meniscus, at which large nanoparticles cannot be accommodated and had to situate after the positioning of small nanoparticles (Fig. 5d).\(^{43}\) This controlled positioning (i.e., size-dependent separation near the three-phase contact line) technique utilizing controlled evaporative self-assembly in a confined geometry may provide a facile route to size-dependent nanomaterial sorting.

![Fig. 4](image-url) (a) The flow profiles in a sessile droplet. Left: radial flow, Right: Marangoni recirculation. These two flows compete to form deposits on the surface. (b) With the confinement, the Marangoni flow is suppressed while the radial flow is retained, thus forming periodically ordered stripes

![Fig. 5](image-url) Fluorescent micrographs of adjacent packing of PS nanoparticles of different diameters within stripes formed by controlled evaporative self-assembly of the mixed particle aqueous solution under different excitation wavelengths. (a) Under 405 nm excitation wavelength, blue-emitting nanoparticles can be observed ($D = 500 \, nm$); (b) 542 nm excitation makes the red-emitting nanoparticles visible ($D = 50 \, nm$); (c) combined fluorescent micrograph, showing adjacent packing of two nanoparticles of different diameters. (d) Schematic illustration of the formation of adjacent packed particles. Arrows in (a)–(c) mark the moving direction of the solution front during the course of evaporation. Scale bar = 50 µm in (a)–(c).
4. Conclusions

In summary, by subjecting the PS latex nanoparticle aqueous solution to evaporate in a cylinder-on-flat geometry, ordered, monolayer- and multilayer-thick PS nanoparticle stripes were produced via controlled evaporative self-assembly of large and small particle aqueous solutions, respectively. Quite intriguingly, small and large nanoparticles can be positioned adjacently to one another within the stripe when an aqueous solution of mixed PS nanoparticles of different sizes was employed. This controlled evaporative self-assembly technique offers a simple yet robust route to assemble and position particles, mixed particles, and other nanomaterials into spatially regular patterns for use in electronic devices, photonic bandgap materials, biosensors, particle sorting, and disease diagnosis.

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References