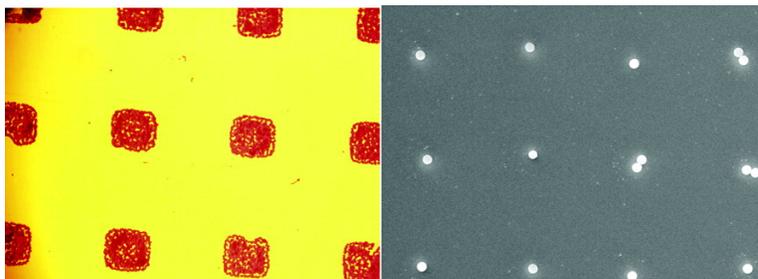Research Article

Assembly of Colloidal Particles by Evaporation on Surfaces with Patterned Hydrophobicity

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Assembly of Colloidal Particles by Evaporation on Surfaces with Patterned Hydrophobicity

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Drops containing suspended particles are placed on surfaces of patterned wettability created using soft lithography; the drop diameter is large compared to the dimensions of the patterns on the substrate. As the three-phase contact line of the drop recedes, spontaneous dewetting of the hydrophobic domains and flow into the hydrophilic domains create discrete fluid elements with peripheries that can mimic the underlying surface topography. Suspended particles are carried with the fluid into the wetted regions and deposit there as the discrete fluid domains evaporate. If particle volume fractions are sufficiently high, the entire wetted domain can be covered with colloidal crystals. At lower volume fractions, flow within the evaporating fluid element can direct the deposition of colloidal particles at the peripheries of the domains. High-resolution arrays of particles were obtained with a variety of features depending upon the relative size of the wetting regions to the particles. When the wetting region is larger than the particles, three-dimensional and two-dimensional arrays of ordered particles mimicking the shape of the wetting pattern form, depending on the particle volume fraction. For lower volume fractions, one-dimensional (1-D) arrays along the wet/non-wet boundaries form. When the particle size is similar to the height of fluid on the wetted domain, zero-dimensional distributions of single particles centered in the wet regions can form for wetted squares or 1-D distributions (stripes) form along the axis of striped domains. Finally, when the wetting region is smaller than the particle size, the particles do not deposit within the features but are drawn backward with the receding drop. These results indicate that evaporation on surfaces of patterned wetting provides a highly parallelizable means of tailoring the geometry of particle distributions to create patterned media.

Introduction

The development of highly parallelizable means of creating ordered assemblies of colloidal particles of micrometer to nanometer length scales is a recent focus of research. Electrostatically guided deposition of particles on patterned substrates is one means of creating ordered structures. In this technique, patterned surfaces containing charged and uncharged regions are created by soft lithography to pattern alkanethiols on gold,[1] by photolithography to pattern siloxane layers on glass,[2,3] by layer-by-layer adsorption of polyelectrolytes,[4] or by creating holes in an insulating substrate formed using a focused ion beam.[5] Colloidal particles bearing charge of the opposite sign of the patterned patches are then exposed to those regions. The particles adsorb to the charged regions via Columbic interactions and pack to form arrays of single particles or multiple particles, depending upon the relative size of the particles to the charged regions. In the case of multiple particles adsorbing on a site, the particles, which in general are well-wet by the suspending

fluids, are pulled into ordered structures in the late stages of fluid evaporation by the contraction of capillary bridges connecting them.

Evaporation also provides a means of collecting particles near three-phase contact lines and so has been exploited as a means of particle self-assembly. Three-phase contact lines with contact angles less than 90° are sites of rapid evaporation. Continuity demands that an outward flow be generated toward contact lines that are pinned. In the absence of surface tension driven instabilities,[6] the flow toward the contact line is dominant. The flow carries suspended particles with it, collecting them near the contact line. Evaporating capillary bridges again drive the particles into ordered assemblies. This effect has been exploited in a variety of geometries. For example, plates have been immersed in suspensions to collect particles at the wetting meniscus. By retracting the plate at rates comparable to the rate of evaporation, large ordered sheets of colloidal crystals have been formed.[7−10] Other geometries in which evaporation has been exploited include the

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formation of "coffee-ring" patterns at three-phase contact lines of drops of partially wetting fluids placed on energetically homogeneous substrates.[11−15] Similar mechanisms have been used to direct the deposition of DNA to form extended structures near three-phase contact lines on microarrays.[16] Recently, this idea has been extended to include evaporation on patterned surfaces, including a channel between two large drops,[17] and surfaces with striped wet and nonwet domains.[18] As the evaporating liquid dewets the hydrophobic regions, particles were drawn with the host fluid to sit atop the hydrophilic domains, where subsequent evaporation allowed colloidal crystals to form.

Here we investigate the use of patterned substrates with hydrophilic domains of length scale ranging from 1 to 50 μm to guide the evaporative deposition and ordering of particles with diameters ranging from micrometers to tens of nanometers. Drops of fluid containing suspended particles are deposited on the patterned substrates, with the drop radius being far larger than the underlying pattern. As the drop evaporates, discrete fluid elements are formed, with heights determined by the length scale of the underlying features and the apparent contact angle of the receding drop. The contact lines of the discrete fluid elements are pinned at the wet−nonwet boundaries. Depending on feature size, the diameter of the particles suspended in the fluids, and the volume fraction of the suspension, a variety of patterns form. If the suspended particles are larger than the fluid element height, they are excluded from the fluid element and recede with the parent drop.

Materials and Methods

Substrates were prepared from silicon wafers (Montco Silicon Technologies, Inc.) coated with 1−3 nm of Cr and 100 nm of Au. Patterned self-assembled monolayers (SAMs) were formed using microcontact printing, as described in detail elsewhere,[19] and reviewed only briefly here. Elastomeric poly(dimethylsiloxane) (PDMS) stamps with various microstructures were inked with a 1 mM solution of $HS(CH_2)_{15}COOH$ in ethanol, brought into contact with the gold surface for 1 min, and rinsed with ethanol to produce discrete domains covered with a carboxylic acid terminated SAM on the substrate. The substrates were subsequently immersed in a 1 mM solution of $HS(CH_2)_{17}CH_3$ in ethanol for 1 h to cover the remainder of the surface with a methyl-terminated SAM. Suspensions of particles of various volume fractions were made in water of pH 2 (adjusted by the addition of HCl) in order to prevent disassociation of the carboxylic acid headgroup on the patterned SAM. A homogeneous SAM of $HS(CH_2)_{15}COOH$ has an advancing contact angle of 31° with water at pH 2; a homogeneous SAM of $HS(CH_2)_{17}CH_3$ has an advancing contact angle of 103° with water at pH 2.

Polystyrene spheres (Interfacial Dynamics, Corp.) with a range of diameters from 200 nm to 10 μm were suspended in distilled water of pH 2 over volume fractions ranging from 1% to 10^{−4}%, as reported in the figure captions. Some of the particles were

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Table 1. Properties of Particles Used in Experiments

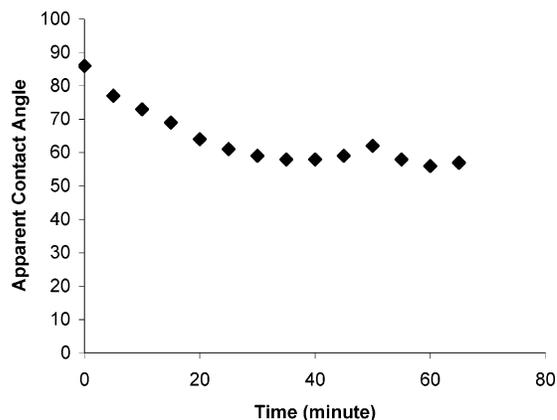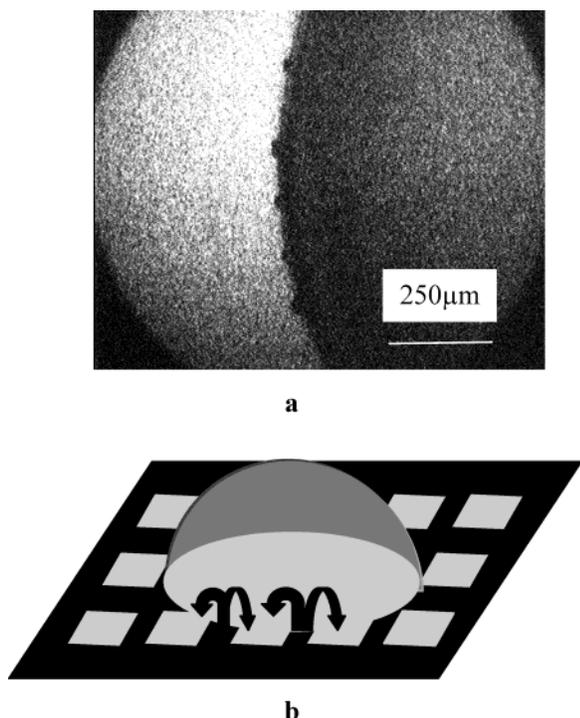| diameter of particle	surface functionalized group	charge	charges/particle[a]
10 μm	sulfate	−	N/A
1.2 μm	amidine	+	3.1×10^6
0.8 μm	amidine	+	2.45×10^6
0.8 μm	sulfate	−	7.8×10^5
200 nm	amidine	+	6.8×10^4
40 nm Au	Au	none	none

[a] As reported by the manufacturer.

Figure 1. Apparent contact angle of water at pH 2 on the surface with 50 μm hydrophilic squares spaced 50 μm apart on a continuous hydrophobic substrate.

functionalized with positively charged amidine groups, others with negatively charged sulfate groups. Surface functionalization renders the polystyrene spheres hydrophilic, allowing them to be dispersed in water. The results described in this work do not depend on electrostatic interactions; identical results for the particles of diameter 0.8 μm were obtained with both amidine and sulfate functionalized microspheres. The particular functionalization for each particle used in any given experiment is reported in Table 1 along with the nominal charge/particle.

Suspensions of 40 nm diameter gold nanoparticles (Ted Pella, Inc.), suspended in water of pH 5−6, were also studied at volumes fractions of 0.01−0.0001%. Because these particles are not charged, the pH was not adjusted to prevent disassociation of the carboxylic acid headgroup.

In each experiment, a 100 μL drop containing suspended particles was deposited on the patterned surfaces. All experiments were performed at 20% relative humidity and at 25 °C unless otherwise noted; for these conditions and for drops of the radii studied, the drop evaporated completely in roughly 6 h. The structures formed by the dried particles were investigated with an optical microscope and scanning electron microscope after the drop had evaporated. Each deposition experiment was repeated three times.

The surface tension of the suspensions was monitored by the pendant drop method for 50 min for each suspending system to confirm that the suspension of particles was surfactant-free.

Results and Discussion

When a drop is placed on substrates patterned with square features, it spreads to attain some initial diameter. The contact line remains fixed for some period of time, after which it begins to recede. If a sessile drop profile is recorded, and the contact angle is inferred from apparent angle of the fluid wedge as determined from a drop silhouette, the contact angle evolution looks much like that of a drop on an energetically homogeneous substrate, as reported in Figure 1 for a surface with 50 μm hydrophilic squares spaced 50 μm apart. The initial contact angle is high (an apparent advancing contact angle). During the time that the contact line remains fixed, the contact angle

Figure 2. (a) Optical micrographs of the contact line of a droplet of water (dark region on the right) at pH 2 on a patterned substrate with 50 μm hydrophilic squares spaced 50 μm apart on a continuous hydrophobic surface. The corrugated edge of the drop is created by the flow into the well-wet patches, out of the hydrophobic domains. (b) A schematic of the formation of discrete fluid elements in the hydrophilic patches. Once a wet feature fills with liquid, the contact line jumps backward to the next feature in the direction of the receding drop.

Table 2. Receding Contact Angle and Particles Excluded from Patterns

patterned surface	apparent receding contact angle (deg)	cap height calculated (μm)	heights of particles excluded (μm)
50 μm square hydrophilic features spaced 50 μm apart	60	14.4	none
5 μm square hydrophilic features spaced 5 μm apart	30–50	1.14	1.2, 1.6, 2

decreases to some value (an apparent receding contact angle), after which the drop recedes with a fixed angle. These apparent angles depend on the underlying pattern and are bounded by the contact angles of the pure carboxylic-terminated or methyl-terminated SAMs. The apparent receding contact angles for two patterns (50 μm squares spaced by 50 μm, and 5 μm squares spaced by 5 μm) are reported in Table 2.

The contact line dynamics are complex, exhibiting two-dimensional (2-D) percolation. When the receding contact line encounters a wetted feature, it becomes pinned at the wet/nonwet edges but pulls back from the nonwet domains. These local dynamics cause liquid to flow out of the hydrophobic regions and into the hydrophilic regions, as shown in Figure 2. In Figure 2a, an optical image of the receding contact line of the droplet is shown on a SAM of 50 μm square hydrophilic features spaced 50 μm apart. The dynamics of this contact line were also recorded by video. The bright regions are relatively free of liquid, the large dark region is the drop, and the corrugated edge is created by the flow out of the hydrophobic regions into the hydrophilic features. As each hydrophilic domain fills with fluid, the contact line depins from that site and jumps backward from the feature, tearing off to form a discrete

fluid element in the hydrophilic patch (see schematic in Figure 2b). Since each element does not fill at the same time, different segments of the contact line jump at different times, so the recession of this line is characterized by a series of depinning events, and the geometry of the corrugated edge varies as it jumps from one pinning feature to another, always in the direction of the receding parent drop. These dynamics are similar to those reported in prior work on contact angle hysteresis on heterogeneous surfaces.[20]

This complexity notwithstanding, we infer that the height of the fluid element formed is determined by the apparent receding contact angle of the drop. If the height of the fluid element is larger than the diameter of the particle to be placed on it, particles can be accommodated in the fluid element and organized by the flow field within the element. If the particles are larger than the fluid element height, they are excluded from the fluid element and are pulled backward with the parent drop. Consider a spherical cap of radius R with a pinned contact line, created by a fluid wedge with contact angle θ. The height of the spherical cap h is determined simply by

$$\tan\frac{\theta}{2} = \frac{h}{R} \qquad (1)$$

Generalizing this argument to a feature of characteristic length scale R, the height of the fluid elements varies with the contact angle, and with the length scale of the feature itself. In Table 2, results from a series of experiments are summarized in which suspensions of particles with differing diameters were evaporated on substrates patterned with 5 μm squares. Particles larger than the feature height as inferred from eq 1 were not deposited on the array, but were convected backward with the parent drop. If the particle diameters were less than the height of the fluid element, they were accommodated in the fluid element and deposited in patterns influenced by the flow within the wetted feature. Because all of the particles used in our deposition experiments were smaller than the inferred height of the fluid element on the 50 μm square features, particles were deposited consistently on the wetted domains of this length scale.

Results for micrometer-sized particles deposited on a surface pattered with 50 μm squares are presented in Figure 3. As the fluid element evaporates, its contact line is pinned as its contact angle evolves from its initial value to the receding contact angle on the wetted patch itself. Depending upon the volume fraction, the flow within the element can organize the suspended particles within it. At high volume fractions, the particles pack to form dense multilayers and are not influenced by convection within the feature. In Figure 3a, 0.1 vol % suspensions of 0.8 μm spheres deposit to form a regular array of colloidal particles on the hydrophilic patches, with the hydrophobic regions being nearly free of particles. In Figure 3b, an scanning electron microscopy (SEM) image reveals particles packed in highly ordered multilayers, with a monolayer on the border. In parts c and d of Figure 3, optical and SEM images show that a more dilute suspension (0.01 vol %) of the same microspheres form an ordered incomplete monolayer. The edges of these patterns are more densely packed monolayers, with a "coffee-ring" of particles formed by convection to the pinned contact line. When the particles are just less than the feature height and lateral dimension, only a few particles are retained in each feature, as shown in Figure 3e, where clusters of 10 μm particles (0.07 vol %) form on each feature.

(20) Schwarz, L.; Garoff, S. *Langmuir* **1985**, *1*, 219.
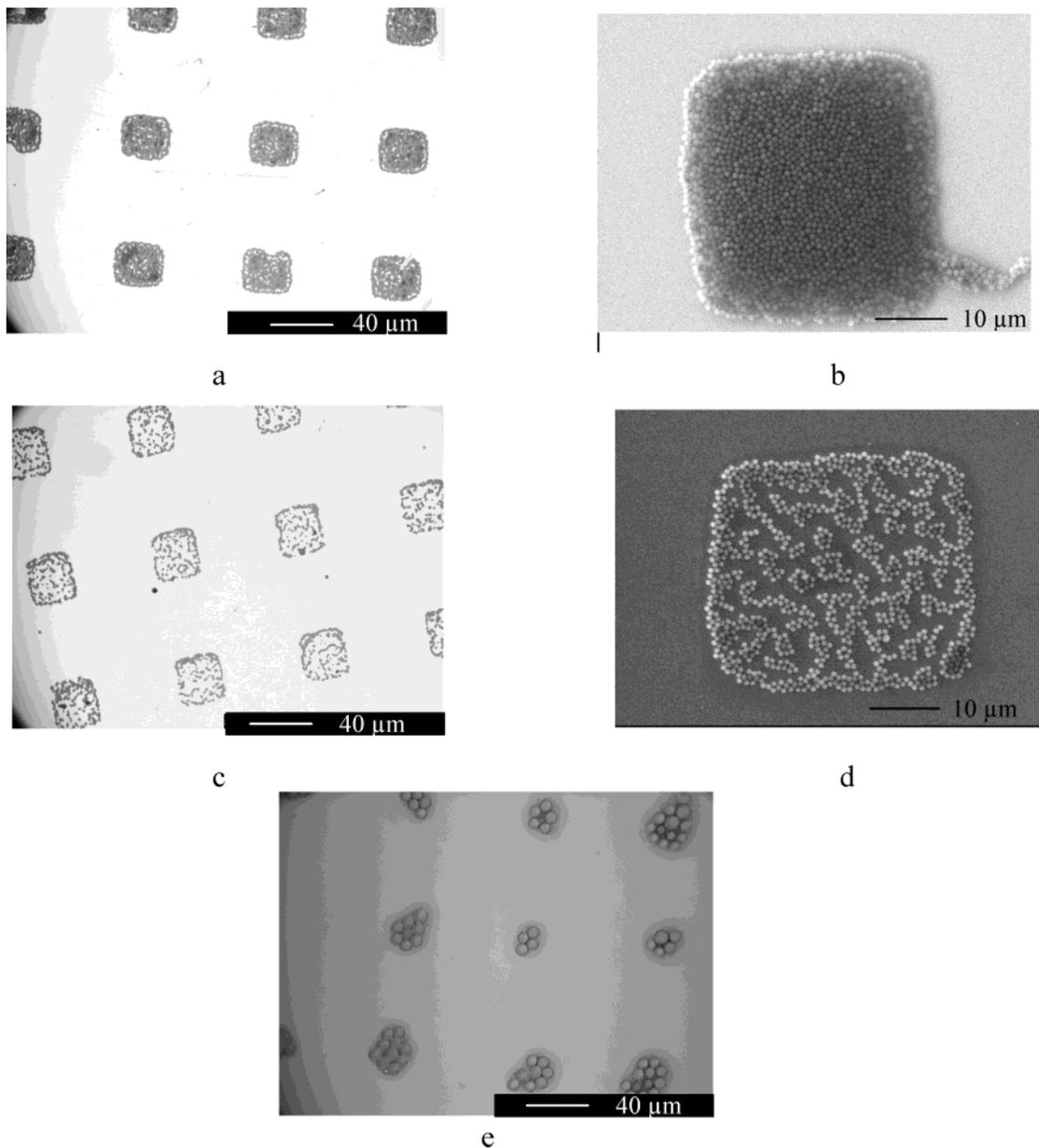
a

b

c

d

e

Figure 3. Colloidal particles assembled on 50 μm carboxylic acid terminated square patterned surfaces on a continuous methyl-terminated surface at pH 2, 24.5 °C, 21% humidity. (a) An optical micrograph of 0.8 μm amidine functionalized microspheres deposited at 0.1% volume fraction. (b) SEM image. (c) An optical micrograph of 0.8 μm microspheres deposited at 0.01% volume fraction. (d) Corresponding SEM image. (e) An optical micrograph of 10 μm sulfate-functionalized microspheres deposited at 0.07% volume fraction.
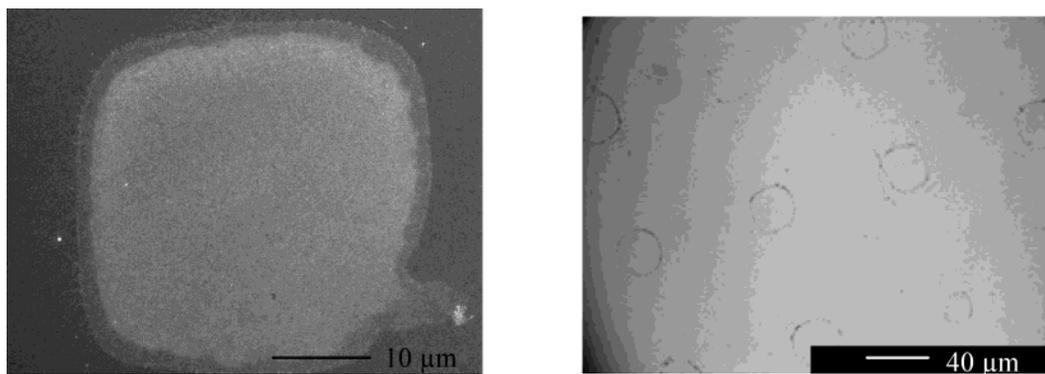

Figure 4. Nanoparticles (40 nm Au particles) assembled on 50 μm carboxylic acid terminated square patterned surfaces on a continuous methyl-terminated surface at pH 5.8, 24.5 °C, 21% humidity at (a) 0.01% volume fraction. An SEM image of a multilayered ordered structure (b) 0.0001% volume fraction suspension. An optical image of particles accumulated at the edge of the feature.

These surfaces can also be used to deposit particles with diameters on the nanometer length scale. For example, when 200 nm particles are deposited on 50 μm squares, similar arrangements of particles form (images not shown).
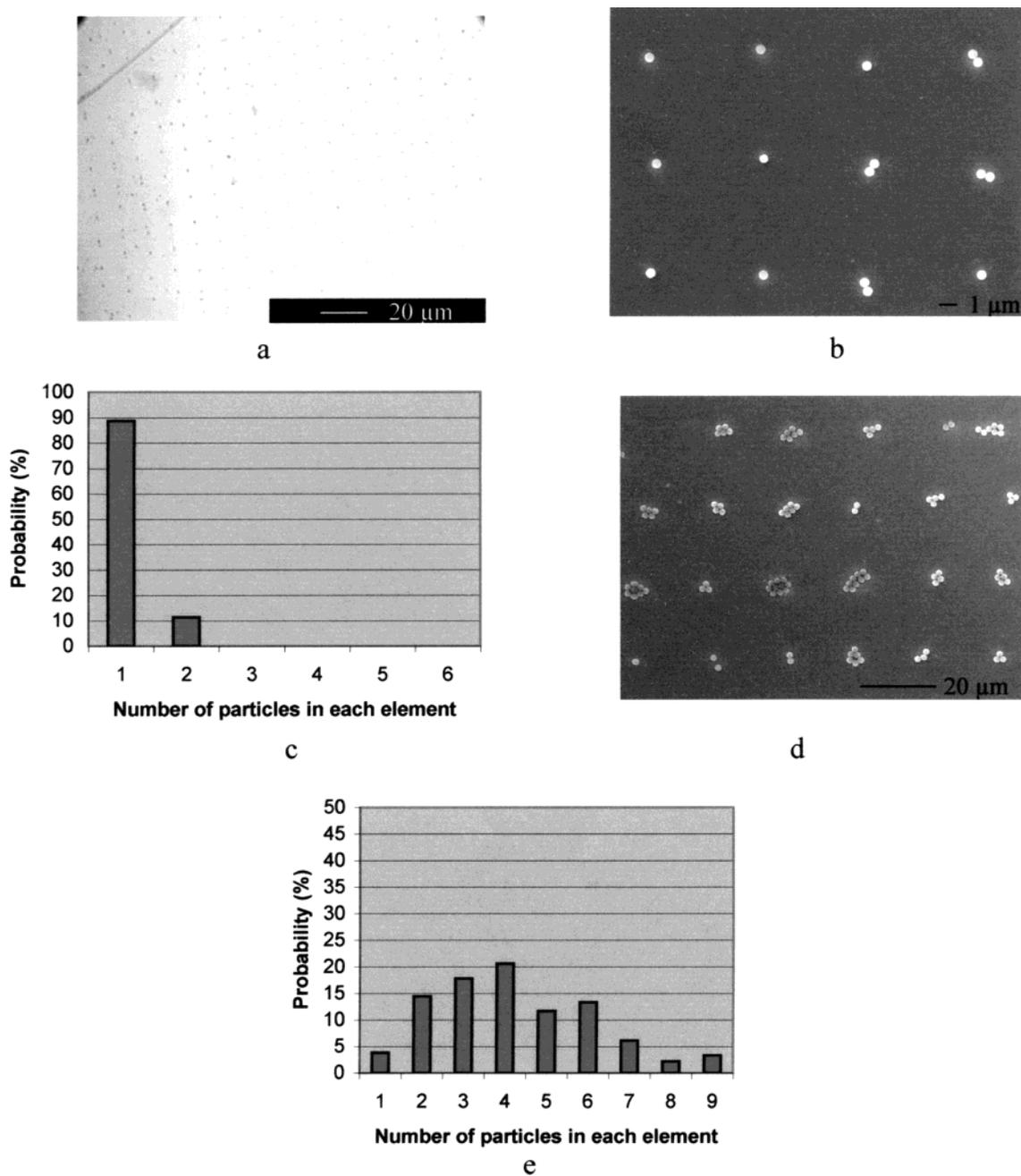
Figure 5. 800 nm particles assembled on 5 μm carboxylic acid terminated square patterned surfaces on a continuous methyl-terminated surface at pH 2, 24.5 °C, 21% humidity at 0.01% volume fraction. (a) An optical micrograph of nearly zero-dimensional distribution of single particles on each feature. (b) Corresponding SEM image. (c) A histogram of particle distribution in (a). (d) SEM image of particle assembly deposited under apparently similar conditions. (e) Histogram of particle distribution in (d).

In Figure 4a SEM images of patterns formed by 40 nm gold particles (0.01 vol %) deposited on these substrates form a multilayer filling the feature. In Figure 4b, a more dilute suspension of the same particles (0.0001 vol %) deposits primarily at the edges of the feature to form a "coffee ring".

In parts a and b of Figure 5, results obtained with suspensions of 0.8 μm particles (0.01 vol %) on 5 μm squares are shown. Each feature contains only one or two particles. In Figure 5c, a histogram of the particle distribution over 100 features is shown, with a preponderance of the features containing only a single particle. These results are extremely sensitive to variations in laboratory conditions. Distributions of particles under apparently similar condi-

tions can differ strongly, as shown in the figure and histogram reported in parts d and e of Figure 5. These results demonstrate that under appropriate conditions, lattices of single particles can form but that subtle differences in laboratory conditions can strongly alter the patterns.

Other surface patterns can be studied. When a striped patterned surface is used, with alternating hydrophilic stripes (5 μm wide) and hydrophobic stripes (5 μm wide), discontinuous lines of the 0.8 μm particles form in a manner that mimics the wetting patterns of the substrate, as shown in Figure 6.

Note that in all of the cases in this work, the discrete fluid elements form in geometries dictated by the underlying wet/nonwet topography. However, in certain cases,
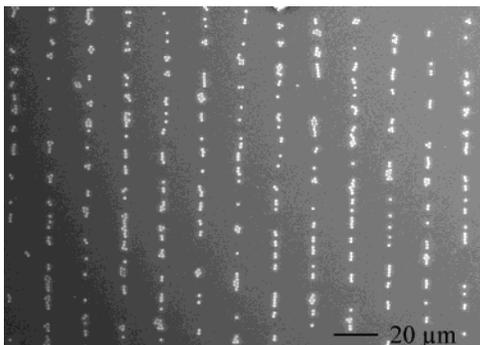
Figure 6. An SEM image of 0.8 μm microspheres assembled on a surface patterned with alternating 5 μm carboxylic acid terminated stripes and 5 μm methyl terminated stripes at pH 2, 24.5 °C, 21% humidity, and 0.01% volume fraction.

the minimum free energy for the fluid element is not a shape dictated by the underlying surface energies of the solid but is defined by shapes that traverse wet/nonwet boundaries.[21] For example, a substrate patterned with concentric rings will form a nodoid that respects the underlying wetting topography until a critical volume, above which a bulge state occurs with fluid bulging out of the annular rings, placing fluid on the nonwet surface.[22] If the height of the fluid in these bulges were too small to accommodate a particle of the diameter of interest, they

(21) see, e.g. Gau, H.; Herminhhaus, S.; Lenz, P.; Lipowsky, R. *Science* **1999**, *283*, 46.
(22) Lenz, P.; Lipowsky, R. *Phys. Rev. Lett.* **1998**, *80* (9), 1920.

would not effect the method presented here. If they were comparable to the particle diameter, however, they could limit this technique.

Conclusions

Ordered arrays of particles were created spontaneously by evaporative deposition of colloidal suspensions on surfaces of patterned wetting from parent drops with diameters large compared to the length scale of the underlying pattern. For particles with diameters far smaller than the feature length scale, a variety of patterns were realized depending upon the volume fraction. At high volume fractions, particles pack to form ordered colloidal crystal multilayers. As volume fraction was reduced, ordered sparse monolayers and "coffee rings" decorating the edges of the features were created. The apparent receding contact angle of the drop can be related to the height of liquid in each fluid element. This determines the upper bound on the diameter of the particles that can be deposited on each feature. Thus, particles above a certain diameter were excluded from the features, receding backward with the parent drop. Under certain conditions, particles could form zero-dimensional arrays of a single particle per feature on wetted squares or one-dimensional stripes on wetted stripes. These results indicate that wetting patterns provide a highly parallelizable means of tailoring the geometry of particle distributions to create patterned media. Any particle can be deposited by this technique, provided that it is well-wet by the evaporating liquid.