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Particulate Templates and Ordered Liquid Bridge Networks in Evaporative Lithography

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We investigate the properties of latex particle templates required to optimize the development of ordered liquid bridge networks in evaporative lithography. These networks are key precursors in the assembly of solutions of conducting nanoparticles into large, optically transparent, and conducting microwire networks on substrates (Vakarelski, I. U.; Chan, D. Y. C.; Nonoguchi, T.; Shinto, H.; Higashitani, K. *Phys. Rev. Lett.*, **2009**, *102*, 058303). An appropriate combination of heat treatment and oxygen plasma etching of a close-packed latex particle monolayer is shown to create open-spaced particle templates which facilitates the formation of ordered fully connected liquid bridge networks that are critical to the formation of ordered microwire networks. Similar results can also be achieved if non-close-packed latex particle templates with square or honeycomb geometries are used. The present results have important implications for the development of the particulate templates to control the morphology of functional microwire networks by evaporative lithography.

Evaporative lithography provides a simple, low cost, and energy efficient method of creating large ordered network by the assembly of constituents that are originally in particulate suspensions.[1−4] An important potential application is in the manufacture of large transparent electrodes using a network of fine conducting microwires assembled from conducting nanoparticles on a glass substrate, for example, in photovoltaic cells.[5] Recently, using ideas based on the familiar coffee ring phenomenon,[6] Vakarelski et al.[1] demonstrated a simple method of creating such conducting gold microwire networks by first assembling a monolayer of polystyrene latex particles (50−100 μm in size) onto a glass substrate followed by the deposition of an aqueous suspension of 20 nm gold nanoparticles to cover the latex particles. As the solvent evaporates, a liquid bridge network first develops on the substrate around the base of the 2D lattice of latex particles. Further evaporation of the solvent then leaves behind a conducting network of microwires (1−3 μm thick) formed by the self-assembly of the gold nanoparticles that can span up to few square centimeters in size.

This method of wire lithography uses the slow evaporation of liquid bridge networks that have been formed around a particulate template to assemble conducting nanoparticles in suspensions into connected wire networks on the substrate. This approach avoids the need to fabricate complex physical masks to regulate the spatial variation in evaporation rates to create the desired network topology.[2,3] However, using hexagonal close-packed arrays of monodisperse latex particle crystals without further treatment as templates (Figure 1f), in the final network the wires tend to adopt a random topology (Figure 1h) which is inefficient in terms of fabricating high conductivity network coatings. Here, we demonstrate that, using an appropriately spaced template, instead of a close-packed particle template, it is possible to achieve a variety of fully connected, symmetrical network patterns.

In our earlier work,[1] the gold nanoparticle suspension also contained copolymers whose surfactant properties help stabilize the liquid bridge network. However, we observed that nanoparticle-free aqueous solutions of sodium dodecyl sulfate (SDS) also form the same liquid bridge network. As our goal here is to investigate the relationship between the morphology of the latex particulate template and the liquid bridge pattern, we simply use SDS solutions in the present work. A schematic drawing of the simplified experimental procedure used here is given in Figure 1a and b. The liquid bridge network formed at the late stage of the evaporation process (see, for example, Figure 1e and h) is indicative of the respective microwires network that would be formed if surfactant stabilized nanoparticle suspensions of appropriate concentrations are used.

In Figure 2, we demonstrate the basic unit in the formation of a precursor liquid bridge where two latex particles on a substrate are covered initially by the evaporating solution. To demonstrate the key stages of the process, we use a droplet of 0.2 mM SDS aqueous solution. As the water evaporates and the meniscus falls below the equator of the particles, the pendular rings around the base of each particle remain connected by a thin liquid bridge lying on the substrate (Figure 2b−e). As evaporation proceeds, the shrinking pendular rings form two nodes at the base of the latex particles joined by a thin "liquid thread" lying in contact with the substrate (Figure 2e). According to the theory of capillarity, such a liquid thread should be unstable when its length exceeds its width by about three times.[7,8] The quantitative

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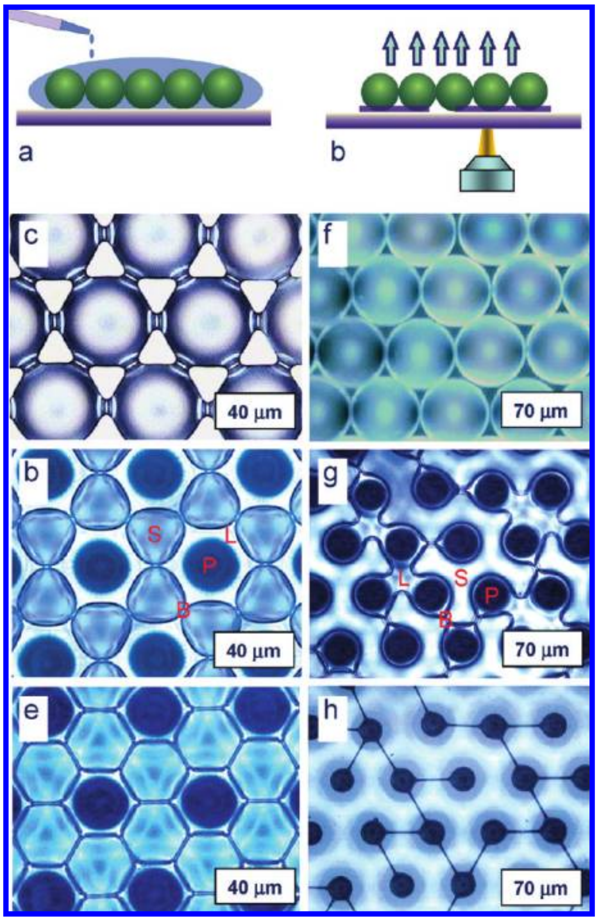

Figure 1. (a, b) Schematic of the experimental procedure (see text). (a) A 2D latex particle array deposited on a glass substrate is covered with surfactant solution, and (b) the progression of the solution evaporation is observed by a microscope through the glass substrate. (c) Top view of a monodisperse 50 μm latex particle array that has been sintered by heat treatment and shrunken by plasma etching. (d, e) Micrograph views through the (c) substrate at progressive evaporation stages of a 0.2 M SDS water film showing the substrate exposed to air (S, shaded), the contact area between the particle and the substrate (P, black), and the liquid pendular ring (L, white) joined by thin liquid bridges (B) (the focal plane is on the glass substrate surface). (f) Top view of a regular close-packed 50 μm latex particle array without treatment. Micrograph views through the (f) substrate of (g) randomly connected exposed substrate/air surfaces and (h) the random liquid bridge network that formed as a result. See the Supporting Information for videos of the entire process.

mechanism by which this stabilization occurs is not clear at present. However, it is the presence of surfactant rather than the lowering of the surface tension that is critical for maintaining the integrity of this liquid thread, because in the absence of surfactants such liquid threads are unstable and always break.[1] While quite low in the original suspension, the surfactant concentration will increase as evaporation progresses, first exceeding the critical micelle concentration when the SDS will form spherical aggregates. As evaporation proceeds further, the surfactant concentration continues to increase and the SDS will form rodlike micelles when the concentrations exceed 1 M.[9] By this stage, the viscosity of the solution also increases rapidly and such solutions eventually become viscoelastic.[10] We believe it is this marked change in rheological properties of the evaporating suspension due to the increasing concentration of surfactants that imparts the required stability in the liquid thread.

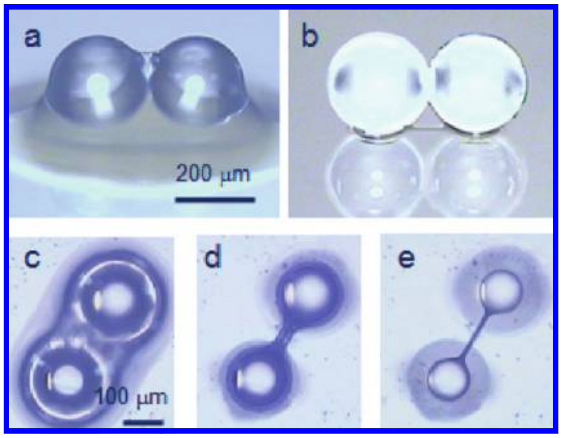

Figure 2. Images of the liquid bridge formed around a pair of 250 μm latex particles at different stages of evaporation of a water droplet containing 0.2 mM SDS: (a) earlier stage with the particle protruding through the receding liquid meniscus; (b) later stage with the thin liquid bridge on the substrate (seen as a dark line) connecting the pendular rings around the base of the particles. (c−e) Microscopic images of the same particle pair taken through the bottom of the glass substrate that shows the formation and the thinning of the liquid bridge on the substrate (the focal plane coincides with the substrate).

A suspension of nanoparticles deposited over a 2D lattice of latex particles deposited on the substrate will evaporate to give a regular wire network provided the disposition of the 2D particulate lattice facilitates the formation of a stable connected precursor liquid bridge network. This network, formed on the substrate, should connect the pendular rings at the base of each latex particle as the solvent level evaporates and falls below the equator of the 2D lattice. The liquid threads joining pendular rings form when the interstitial regions of the substrate between the adsorbed particles "dry out" to expose a substrate/air interface. For a hexagonal close-packed 2D particle lattice, this interstitial substrate/air region is bounded by three spheres whose pendular rings are joined by three liquid threads lying on the substrate. This 2D unit cell of the liquid bridge network will extend over the entire substrate if the interstitial substrate/air region between any three particles does not invade into the neighboring cells, but rather remains separated by the liquid threads that join adjacent pendular rings. Such an invasion event of the substrate/air region can be triggered by random local variations in geometry or in wetting conditions.[1] The optimal condition of the 2D particle lattice that will best facilitate the evolution of a uniform periodic liquid bridge network can be guided by the following considerations.

The evaporating front of the liquid suspension moves down through the 2D particle lattice as a surface of near zero mean curvature on the length scale of the particles. Thus, the minimization of regions of high curvature in the local geometry of the 2D particle lattice will facilitate the even evolution of the evaporating front. Local regions of high curvature in the 2D lattice can be avoided with the following treatment. After depositing a 2D close-packed lattice of spherical particles on the substrate[1,11] (50 μm polystyrene latex particles, microParticles GmbH), we subject the system to heat treatment by placing the glass substrate on a

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heating plate at 100 °C for 3−5 min. This procedure has three beneficial effects: (1) the contact area between each particle and the substrate will increase as the latex particles are "partially melted" onto the substrate, and this eliminates regions of high curvature at the base of the particles and shortens the length of the liquid thread needed to join neighboring pendular rings; (2) sintering of the particle−particle contact zone at the equator to eliminate possible large variations in gaps between the particles; and (3) shrink the particle diameters slightly by up to 5% to further open up the interstitial region between the particles. This heat treatment is then followed by oxygen plasma etching[12,13] to reduce the particle diameters while ensuring that all latex particles in the 2D lattice are still connected by the sintered necks formed during the heat treatment stage. The plasma etching is performed in a Harrick PDC-002 plasma cleaner device. Four to six hours of oxygen gas plasma etching will reduce the particle diameter by 15−20% when the power applied to the radio frequency coils is about 30 W. This preparation method created the optimal particle lattice structure shown in Figure 1c which facilitated the formation of a stable regular substrate/air area in the interstitial region between the particles (Figure 1d) and the subsequent formation of a stable, regular liquid bridge network (Figure 1e) formed in this instance using a 0.2 mM aqueous solution of SDS. The increase in the size of the interstitial region between the particles by the plasma etching has a critical role in improving the "breathability" of the template through enlarging the space between the particles which allows the lowering liquid meniscus to contact the substrate at the center region between each three neighboring particles. In contrast, a close-packed 2D lattice of latex particles without any treatment has regions of high local curvature (Figure 1f) and a smaller interstitial region between the particles. As a consequence, initially exposed substrate/air areas occur much earlier at locations outside the regularly packed region of the crystal where there are missing or dislocated particles.[1] These then invade into neighboring cells during the evaporation process (Figure 1g, see also movie 1 in the Supporting Information) and give rise to a random liquid bridge network (Figure 1h).

If the heat annealing and etching procedure results in some of the particles in the crystal being disconnected from some of its neighbors, the corresponding network that forms will not have the symmetric structure observed for connectivity defect-free crystals. Figure 3a shows a larger area of a liquid bridge network, and Figure 3b and c details how the absence of one connection opens a wider gap in the space between four particles, resulting in the formation of the rhombic unit cells in the respective liquid bridge networks (see movie 2 in the Supporting Information). However, this example demonstrates the possibility of producing different microwire network structures by regulating the connectivity of the particulate network template. The occurrence of disconnected particle defects will depend on the monodispersity of the latex particles and the method of 2D crystal deposition. In the present study, our focus is on the general dependence of the liquid bridge network on the template structure and we deposit our template by simple drying of a droplet of the latex particle suspension over the glass substrate.[1,11] Using more sophisticated deposition methods such as spin coating (applicable only for smaller particles),[14] continuous deposition procedures,[15] or template guided deposition[16] could result in lower defectivity networks.

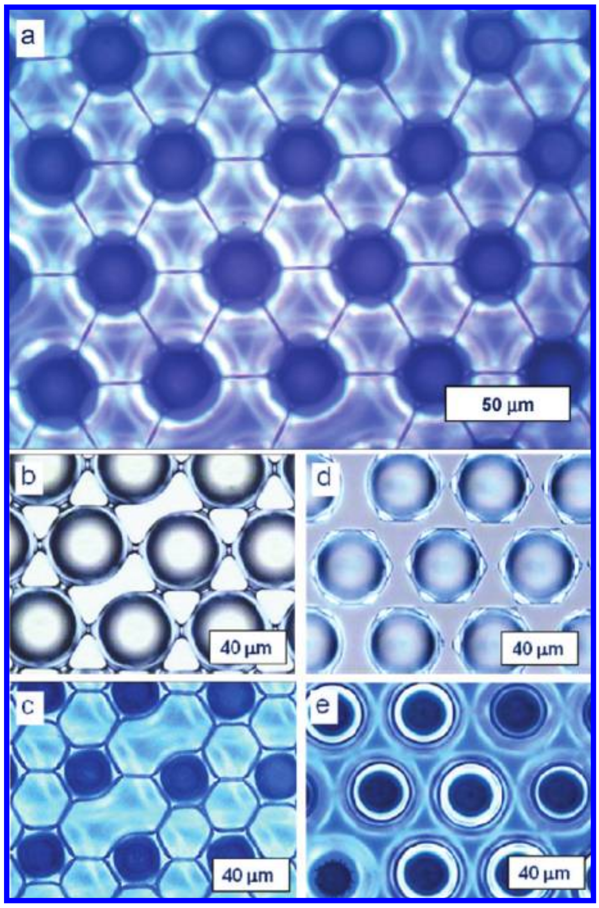

Figure 3. (a) Micrograph view through the glass substrate showing a selected area of liquid bridge network forming during the evaporation of 0.2 M SDS solution using heat treated and plasma etched 50 μm latex particle array. (b) Top view of the latex particle array with missing neck connection defects and (c) micrograph view through the substrate of the liquid bridging network formed under the same template section. (d) Top view of the latex particle template after prolonged plasma etching destroying all neck connections and (e) corresponding macrograph view through the substrate showing the drying out of the pendular rings around the particle bases.

Another important finding is that when particulate templates have been subjected to prolonged etching (more than 8 h), which reduces the particles to about 30% of their initial diameter, all connecting necks between the particles will be destroyed (Figure 3d) and connected liquid bridge networks can no longer form. The resultant disconnected meniscus pattern at the late drying stage can be seen in Figure 3e. In this case, the larger interparticle space and lack of neck connections did not allow stable bridges to form and the receding menisci simply break up into circular pendular rings around each particle/substrate contact.

Close-packed or hexagonally ordered particles crystals are the most natural and easy to produce two-dimensional particle templates.[11,15] However, there are also various literature methods for producing non-close-packed two-dimensional latex particle crystal patterns.[16−18] To demonstrate liquid bridge networks that

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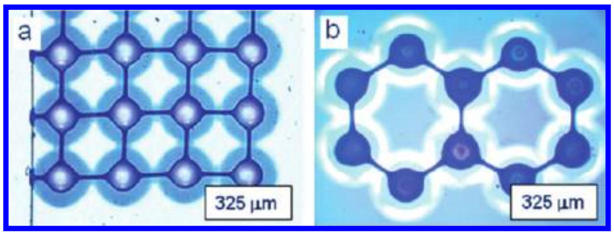

Figure 4. Micrograph views through the glass substrate showing (a) square and (b) honeycomb examples of liquid bridge networks formed using directly assembled 250 μm latex particle clusters with the respective geometry.

can result from different particulate packing, we used larger latex particles (250 μm polystyrene latex beads, Sigma) that allowed manual manipulation and assembly of small particle clusters with the desired lattice types under the direct view of a stereomicroscope. We give examples of liquid bridge networks formed around such particle clusters with square (Figure 4a) and honeycomb symmetries (Figure 4b). The larger interstitial space between particles facilitated the formation of stable exposed substrate/air areas that are clearly separated by stable liquid bridges on the substrate that join the pendular rings around the base of the particles.

In summary, using connected structures of non-close-packed latex particle templates, we demonstrate how to create stable regular liquid bridge networks that are precursors to the formation of large connected and regular networks of microwires. One key factor critical to the formation of stable liquid threads on the substrate is the presence, even at low concentrations, of surfactants in the evaporating suspension. Stable liquid bridges are never observed experimentally using surfactant-free distilled water, in accordance with the theory of capillarity.[1,7,8] The stabilizing polymers that are always present in the gold nanoparticle solution used to form the wire networks act as the surfactant. As the solvent evaporates, the surfactant concentration in the liquid thread will increase by 2−3 orders of magnitude. This has the effect of modifying significantly the rheological properties of the suspension and stabilizing the liquid threads on the substrate.[10] The second factor required for the formation of regular liquid bridge networks is to optimize the disposition of the latex particles in the template (1) by increasing the contact area between the particles and the substrate through heat treatment which also sinters the particles and maintains a regular interparticle spacing, and (2) by decreasing the sintered particle size by 15−20% using oxygen plasma etching. Both steps have the effect of eliminating regions of high curvature in the particulate lattice and opening up a larger area between the particles to allow stable regions of substrate/air interface to develop as the drying proceeds. The use of different packing lattices such as square or honeycomb with larger void fractions also achieves the same outcome.

This advance in our understanding of the key factors that underpin the formation of regular microwire networks to maximize connectivity and hence conductivity[1,19] has a major implication for the deployment of evaporative lithography to fabricate functional networks.

Supporting Information Available: QuickTime videos of the evaporation process shown in the case of close-packed (movie 1) and heat and plasma treated templates (movie 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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