

Notes

Patterned Colloidal Coating Using Adhesive Emulsions

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Received October 24, 2000.

In Final Form: January 23, 2001

Colloidal particles can serve as very convenient building blocks for fabricating new materials. They can be synthesized from a wide range of materials and can be highly uniform and controllable in size; this allows them to be patterned into a variety of regular structures which can be useful in themselves or can serve as templates for making more complex structures. Achieving this controlled organization of the colloidal particles can be accomplished by different means. External fields can be used to induce anisotropic interactions. For example, electromagnetic fields induce chain formation in electro- or magnetorheological fluids.¹ Alternatively, patterned substrates can be used to direct colloidal crystallization, with gravitational settling² or depletion interactions³ promoting the growth of three-dimensional (3D) structures, starting from a template on the surface. Strictly two-dimensional (2D) ordering of colloidal particles is also of great interest; it can provide a means of creating highly useful surface templates or structures, while also presenting growth mechanisms of considerable fundamental interest. Such 2D structures can be produced for instance with charged colloids using electrostatic interactions to guide their deposition onto oppositely charged zones of a patterned substrate.^{4,5} For practical purposes, however, the use of charged particles limits the range of materials that can be used as the building blocks, and the possibility of extensively varying the chemistry with a more versatile range of materials would be highly desirable. In this Note, we describe a new approach to colloidal coating that overcomes some of these limitations. This technique exploits the adhesion properties of emulsions droplets to create 2D patterns of these droplets. The interactions involved in the process depend exclusively on the surfactant film coating the droplets but do not depend on the nature of the dispersed phase. As a result, a large variety of materials can be used, making this novel technique potentially valuable for applications involving colloidal

coatings. Selective wetting^{6,7} on a decorated surface constitutes another versatile process; however it results in a pattern of totally dried material while our process leads to the formation of a 2D pattern of a liquid material in a 3D liquid medium.

The key to our new technique is the adhesive properties of emulsions. Under appropriate conditions, two surfactant layers can experience strong attraction and adhere to each other. This is convincingly demonstrated by the adhesion between surfactant monolayers adsorbed at the oil/water interface of emulsion drops.⁸ In the case of oil-in-water emulsions stabilized by ionic surfactants, addition of salt or the decrease of temperature, or a combination of both, can cause a transition from a state where the surfactant monolayers repel each other to a state where they attract one another.^{8–10} This same effect can be used to selectively adhere emulsion particles onto a surface. In contact with a hydrophobic substrate, some of the surfactant molecules present in solution coat the substrate (with their tails adsorbed to the hydrophobic surface),¹¹ thus forming a surface that is similar to a surfactant monolayer. This surface will interact with emulsion droplets in solution in a similar fashion, leading to adhesion of the droplets to the surfactant-covered surface.¹² In the case of a sticky emulsion, the droplets, which adhere each other, will therefore also adhere to a hydrophobic surface. This mechanism has already been observed for macroscopic hydrophobic surfaces.¹⁰ In this Note, we demonstrate that it holds also for much smaller surfaces, such as hydrophobic patches of micrometer scale on a hydrophobic surface. The droplets of a sticky emulsion adhere exclusively to the hydrophobic patches of an otherwise hydrophilic field. This allows us to use a microscale patterning technique to generate hydrophobic patches on a hydrophilic surface and to control the adhesion of the droplets to form well-defined, patterned surfaces. We demonstrate this behavior here by investigating the interactions between a patterned surface and an emulsion comprised of liquid-crystal droplets in water.

A standard method is used to pattern the surface.^{13,14} A glass coverslip is coated with a thin layer of negative photosensitive resin by spin-coating. Standard lithographic techniques are used to prepare a mask consisting of a periodic square lattice (periodicity 20 μm) of square holes of 10 $\mu\text{m} \times 10 \mu\text{m}$. This pattern is transferred onto the photoresist by exposing the coverslip to UV radiation through the mask. The photoresist is then developed, so

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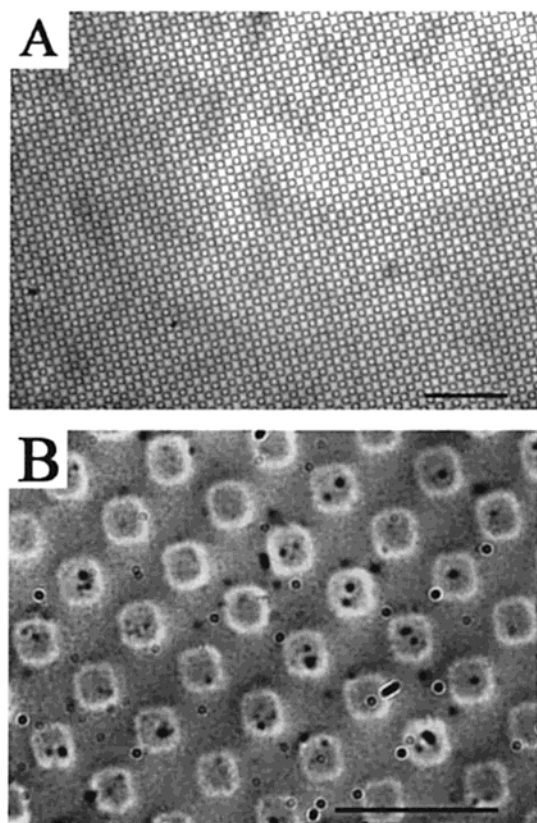


Figure 1. (A) Optical micrograph of a photosensitive resin pattern on glass. Scale bar is 100 μm . (B) Optical view by differential interference contrast of a breath figure, formed by the adsorption of water on a surface with dewettable hydrophobic patches (lighter on the picture). Scale bar is 50 μm .

that the area that has not been exposed is removed by the developer. This leads to a pattern of resin and glass (Figure 1A). The glass parts of the pattern surface are then made hydrophobic by immersing the surface for a few seconds in a solution of octane containing 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane molecules and subsequently letting the solvent evaporate. The silane molecules are known to form dense grafted monolayers on glass that make it hydrophobic.¹⁵ Finally, the photosensitive resin is dissolved in acetone. The resulting surface consists of a square lattice of hydrophobic patches on glass, as evidenced by the adsorption of a thin layer of water on the pattern surface (breath figure, Figure 1B). This technique for creating hydrophobic/hydrophilic patterns is used for convenience; other chemical methods can also be used.^{16–18}

The liquid-crystal emulsions are prepared by adding a nematic liquid crystal, consisting of a mixture of cyanobiphenyls, to an emulsifier solution, composed of sodium dodecyl sulfate, which is the surfactant, in water. The resulting crude emulsion is extruded several times through a Millipore membrane with a pore size of 1 μm . This technique leads to an emulsion with nematic droplets of average size 1 μm . The nematic volume fractions used are typically a few percent. The stickiness of the emulsion is tuned by the addition of salt (NaCl) at different concentrations, ranging from 0 to 0.5 M. The emulsions are

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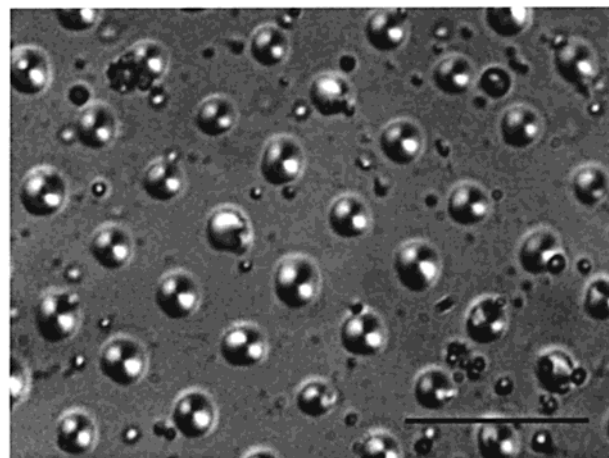


Figure 2. Optical view by differential interference contrast of liquid crystal droplets adsorbed on the hydrophobic patches of a patterned surface. In the bulk, one can distinguish isolated and aggregated (upper left and lower right) freely suspended emulsion droplets. Surfactant concentration is 8 mM. Scale bar is 50 μm .

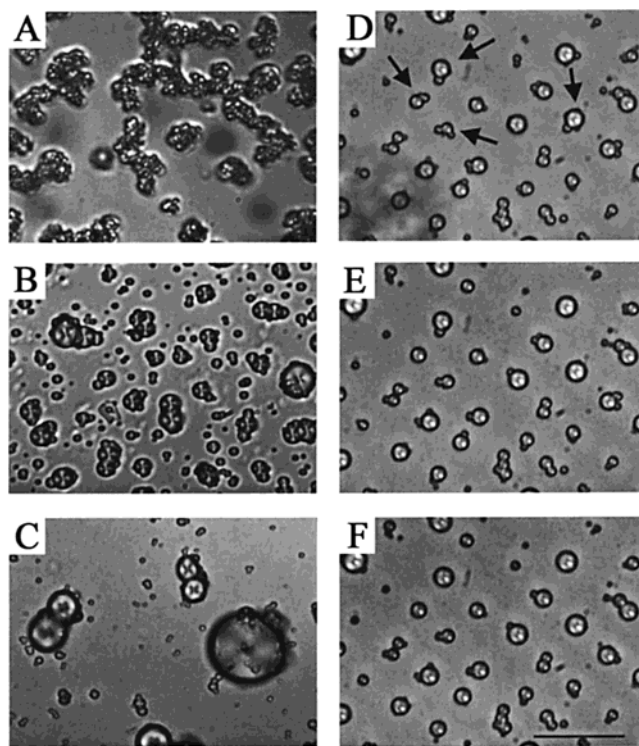


Figure 3. Optical view by differential interference contrast of a liquid crystal emulsion. Initial aggregated emulsion in the bulk, at $T = 24^\circ\text{C}$ (A), same emulsion, at $T = 35^\circ\text{C}$, on a purely hydrophobic (B), purely hydrophilic (C), and pattern (D, E, F) surface. The droplets undergo coalescence (see for instance the droplets marked by arrows at different times (D) $t = 0$, (E) $t = 1$ min and (F) $t = 2$ min). Note the differences between coalesced drops on conventional surfaces (B, C) and the emulsions on the pattern surface (D, E, F). Surfactant and salt concentrations are 2 mM and 0.3 M, respectively. Scale bar is 50 μm .

introduced in closed cells of approximate thickness 2 mm formed by two coverslips separated by an O-ring, with the lower coverslip being patterned. They are observed using an inverted microscope.

The feasibility of this approach is illustrated in Figure 2. While the bulk solution displays conventional weakly adhesive droplets dispersed in water, the observation of the solution close to the patterned surface reveals a well-defined symmetry for the liquid crystal droplets, with a

periodicity of $20\ \mu\text{m}$, equal to the periodicity of the template surface. The absence of any Brownian motion for the droplets indicates that they are adsorbed on the hydrophobic patches. Interestingly, their average diameter is $9 \pm 1\ \mu\text{m}$, slightly smaller than the size of the patches ($10\ \mu\text{m}$) but much larger than that of the initial droplets. This demonstrates that the droplets wet the hydrophobic surface, reflecting a very strong adhesion between the liquid crystal droplets and the surfactant-covered hydrophobic surface. The adhesion between the droplets and the surface is sufficiently strong to induce coalescence between the droplets. This allows us to build surface structures of arbitrary size and shape, as the droplets will adhere and coalesce, forming a coating that follows the contours of the pattern, independent of the shape of the initial droplets. Thus, we have shown the possible use of a bulk emulsion to direct the adsorption of liquid droplets on predetermined sites.

Coalescence effects present unusual features in the vicinity of the pattern surface. The coalescence between the droplets is enhanced by using a solution with a rather weak surfactant concentration and by slightly increasing the temperature, from 24 to $25\ ^\circ\text{C}$. As can be seen in Figure 3D–F, at the pattern surface, the coalescence events are confined to the hydrophobic patches. The pattern surface is found to induce controlled coalescence of the droplets adsorbed on the hydrophobic patches, leading to fairly homogeneous sizes of the final droplets. This should be contrasted with the observations made using a purely hydrophobic (Figure 3B), or purely hydrophilic surface (Figure 3C), where coalescence of the droplets yields highly polydisperse drops.¹⁹

This Note presents a validation of the concept of using the adhesion properties of emulsions to create a 2D pattern of the dispersed phase of an emulsion. To make the observations by optical microscopy easier, a pattern of several micrometers in size was used; however, much smaller, or larger, feature sizes could be used. The

interactions relevant to this process are governed by the properties of the surfactant film covering the liquid droplets. The major difficulty of this method is that aggregation of the droplets in the bulk and their adsorption on hydrophobic patches are strongly correlated, since both are controlled by analogous interactions between surfactant monolayers. This requires a delicate adjustment of the experimental conditions to prevent attractions that are too strong between droplets in the bulk, while still maintaining sufficient attraction between the droplets and the patterned surface. Nevertheless, one of the main advantage of this technique is that, in principle, these interactions do not depend on the nature of the dispersed phase. This separation of the function of the coating agent and the contents of the droplets allows a much wider variety of materials to be used for the coating, greatly increasing the flexibility of the technique. Examples include polymerizable species, suspensions of magnetic colloids, or liquids with various optical indices. This makes this coating technique potentially useful for creating 2D ordered structures that may find applications as Bragg gratings. In addition, because the droplets coalesce to follow the contour of the pattern, this technique may serve as the basis of a very simple and inexpensive means of coating patterned surfaces, and could, for example, provide a very inexpensive and simple means of wiring a surface. In addition, the use of liquid crystalline or magnetic microdomains could be used to investigate interactions between defects in liquid crystals or interactions between magnetic dipoles, while simultaneously controlling the geometry. This method combines both simplicity and versatility, suggesting that it could provide an important addition to the methods for patterning or coating surfaces.

Acknowledgment. We thank Paul Umbanhowar for stimulating discussions and Vikram Prasad for help in preparing the emulsions. This work was supported by NASA (NAG3–2284), NSF (DMR-9971432) and the Ministère Français des Affaires Étrangères (Lavoisier grant).

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