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Generation of Sub-micrometer-scale Patterns by Successive Miniaturization Using Hydrogels**

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Topographically patterned polymer films and surfaces having sub-micrometer- and nanometer-scale resolutions are important to a host of scientific and commercial applications, for example, molecular electronics,[1] optical devices,[2] scaffolds for tissue engineering,[3] biological[4] and chemical sensors,[5] patterned adhesives,[6] carbon microelectromechanical systems (MEMS),[7] and microbatteries.[8] Although photolithography remains the single most popular and widely used method for patterning these different surfaces,[9] it has many limitations; the minimum resolution of the structures is limited by optical diffraction, so that creating small features demands high-energy radiation, which in turn involves the installation of sophisticated and expensive facilities;[10] and these techniques can only produce planar features and can not be easily adopted for generating 3D structures and structures on curved surfaces. Other methods that have been used extensively for patterning polymer surfaces include nanoimprint lithography and its variants,[11–13] replica molding (REM),[14] capillary force lithography (CFL),[15] and micromolding in capillaries (MIMIC),[16] amongst others.[10,17] While these methods are examples of top-down approaches to generating patterns, an other route that is increasingly being probed is directed self-organization. Some examples of this route include, amongst others, dewetting of ultrathin polymer films,[18–20] contact instability of soft elastic films,[21–23] or external-field-induced (e.g., by an electric field[24,25]) instabilities. Both of these routes require fabrication of prepatterned masks or molds on nearly the same scale as the final pattern to be produced. This requires specialized methods, such as electron beam (e-beam) lithography or focused ion beams, for sub-micrometer pattern generation,[17] which are usually limited to a small area (<1 mm^2). One may argue that a right mix of both of these approaches should lead to an inexpensive but high-precision and high-fidelity tool for generating ordered structures over a large area. (>1 cm^2).[26–30]

In this Communication, we explore a novel variant of the top-down approach for the miniaturization of an existing 3D or 2D object or pattern, where the starting pattern to be replicated is much bigger than the final desired size. Thus, engineering of patterns in the size range of hundreds of nanometers becomes possible by starting with a mask or mold that contains micrometer-size features, fabricated easily by photolithography. We generate the patterns in stages, from large to small, by the process of pattern miniaturization using hydrogels, a class of materials that can hold large volumes of water, but shrink in volume in response to changes in the environmental conditions, such as pH,[31] ionic strength,[32] temperature,[33] electric field,[34] and light.[35] We make use of the shrinking characteristic of hydrogels to generate patterns with periodicities as small as 300 nm. In essence, we transfer a large pattern (>1 μm), engraved on a block of poly(dimethylsiloxane) (PDMS) or any other surface, onto a hydrogel by molding. The hydrogel sample is then dried in controlled conditions, resulting in isotropic shrinkage of the pattern. The shrunk hydrogel pattern can then be used again for fabricating a PDMS stamp for a subsequent miniaturization cycle. A reduction in pattern size of almost one order of magnitude is achieved by this method without special efforts and without sacrificing the original pattern geometry and fidelity. We have demonstrated the generality of this process by implementing it for both macroscopic and microscopic structures and by using different types of gels, for example, polyacrylamide gel and resorcinol–formaldehyde (RF) gel.[36]

Figure 1a depicts one complete cycle of the process, for which we used a macroscopic pattern in the shape of the letter "O" of the English alphabet. The gel precursor solution was poured onto this master and was allowed to polymerize for about 15 minutes. The hydrogel sample, having the imprint of the master, was then dried in a controlled environment (temperature 28 °C, relative humidity 60 %), in which the gel sample dried slowly but uniformly without undergoing undulations and distortions at the surface. This pattern with reduced size, referred to here as the second-generation pattern, was then used as the master in the next cycle to achieve subsequent pattern miniaturization. However, this dried piece of hydrogel containing the second-generation pattern could not be directly used as the master because the gel prepolymer solution swells the dry gel and thereby damages the pattern.

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ADVANCED MATERIALS

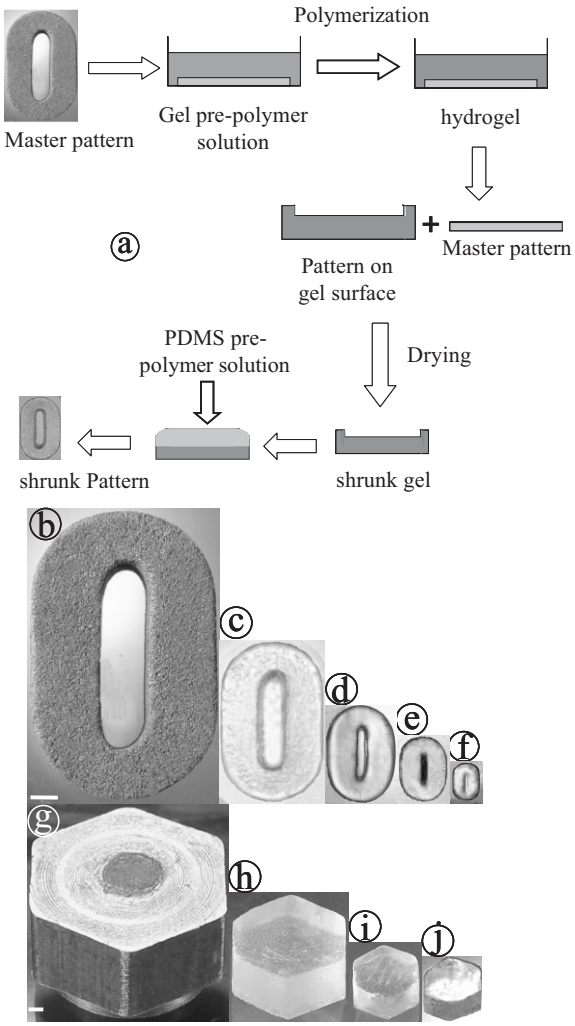

Figure 1. a) Schematic illustration of the pattern miniaturization process for a macroscopic pattern. b–f) A macroscopic pattern of the letter "O" was miniaturized following the procedure depicted in (a). In each cycle, the pattern could be shrunk by ca. 38 %. After four cycles, the overall reduction in size was 86 % of the original size. g–j) Miniaturization of a 3D object, demonstrating that the size reduction is isotropic. The scale bars in all images are 1 mm.

Instead, a nonpolar crosslinkable Sylgard 184 elastomer (PDMS) was first used to develop the master for the next cycle. The Sylgard 184 elastomer, mixed with the curing agent (10:1 v/v) and de-aerated in vacuum, was poured onto the dried sample and cured for ca. one hour at 80 °C. After peeling off, the crosslinked block of PDMS, having the imprint of the second-generation pattern, was used as the master for the next cycle. However, the PDMS surface was not wettable by the prepolymer solution, which led to poor fidelity of the imprinted patterns, particularly near the sharp corners. Hence, to ensure complete wetting the PDMS stamp was plasma-oxidized at a pressure of 0.05 Torr (1 Torr = 1.333×10^2 Pa) for ca. one minute inside a plasma chamber. The gel precursor solution was allowed to polymerize on this hydrophilic master, and the cycles were continued to generate progressively smaller patterns.

Figure 1b–f shows patterns that were obtained in successive cycles of the above process. Whereas Figure 1b, having a characteristic length scale of 15 mm, represents the master, or the first-generation pattern, Figure 1c–f represents the subsequent cycles. A reduction in size of 35–45 % (by length) was achieved in each cycle, which finally resulted in a reduction from the initial size of the master of ca. 86 %. Furthermore, the reduction in size was isotropic, which is essential for miniaturizing 3D objects. This is demonstrated in Figure 1g–j, in which a hexagonal block was miniaturized while the angle between any two planes remained unaltered.

The above-described procedure for a macroscopic object could be easily adopted for transferring and miniaturizing microscopic patterns having a length scale (ca. 1 μm) several orders of magnitude smaller than that of the macroscopic patterns (ca. 1 cm). Figure 2b and e shows atomic force microscopy (AFM) images of the periodic stripes on the protective aluminum foils of commercially available compact discs (CDs) and digital versatile discs (DVDs), which were transferred and miniaturized by the method described in Figures 2a and 1a. For pattern transfer, a piece of the foil was gently peeled off the polycarbonate backing of the CD/DVD, attached to a rigid support, and placed on the gel prepolymer solution in a container. The polymerization reaction was complete within 15 minutes. The crosslinked block of gel was cooled to room temperature and the aluminum foil was removed from the surface of the hydrogel, leaving behind an imprint of the pattern. This block of hydrogel was then dried in controlled conditions, similar to the procedure used for miniaturization of macroscopic patterns. Figure 2 also shows typical patterns that were obtained in two successive cycles of the above process performed on the patterns of CDs and DVDs, which resulted in a 30–50 % reduction in size, depending on the initial content of water in the gel. For example, we used gel prepolymer solution containing 55 % water on a CD foil having stripes with a periodicity of 1500 nm and a height of (110 ± 5) nm. After implementing the above miniaturization process, the periodicity of the second- (Fig. 2c) and the third-generation (Fig. 2d) patterns were (961 ± 17) nm and (628 ± 12) nm, respectively. Thus, the extent of miniaturization in the two consecutive cycles was ca. 36 % and ca. 34.5 %, respectively. During this process the height of the stripes was also reduced, from the original 110 nm to (74 ± 6) nm and (49 ± 3) nm, respectively. Similarly, using the pattern on a DVD as the master (periodicity 800 nm; height (65 ± 5) nm), the periodicity and height of the second-generation patterns were (531 ± 14) nm and (44 ± 4) nm (Fig. 2e), respectively, which decreased to (359 ± 7) nm and (30.2 ± 3) nm, respectively, after the next cycle (Fig. 2f). Thus, the overall reduction in length scale of the patterns was ca. 56 %. Importantly, this reduction in size could be easily achieved within an area of 1 cm × 1 cm.

The extent of pattern miniaturization could be enhanced by increasing the initial water content in the prepolymer solution, but not without a limit because an increase in the quantity of water in the prepolymer solution results in a decrease

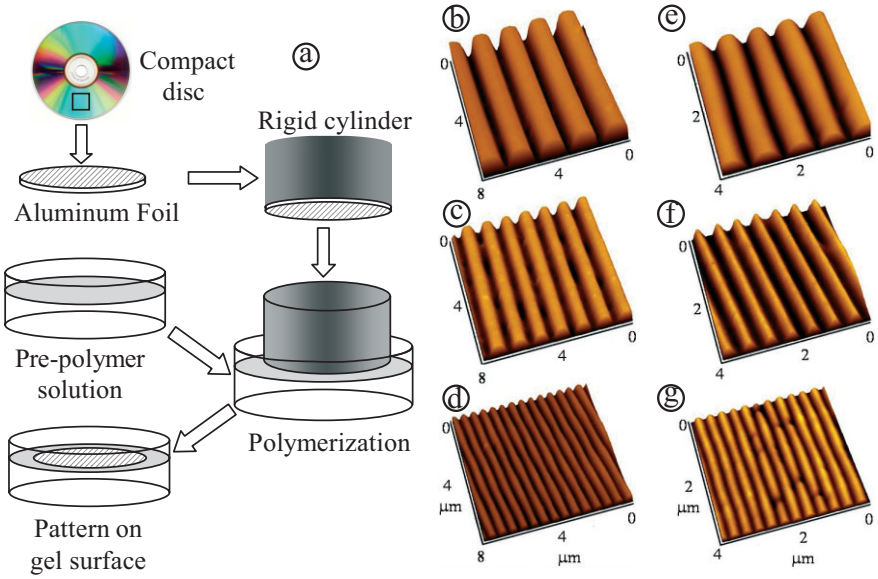

Figure 2. a) The process of transferring the pattern from the back of a CD/DVD onto a block of hydrogel. b,e) AFM scans of the patterned aluminum foils of a CD and DVD, respectively, used as stamps. c,d,f,g) The first generation and the second generation miniaturized patterns using CD (c,f) and DVD (d,g) foils as stamps, respectively.

of the strength of the gel, which then tends to deform and rupture, thus rendering it difficult to handle. Besides, the polymerization reaction is accompanied by the release of small amount of water that forms a film at the contact of the cross-linked gel and the surface of the pattern, thus preventing pattern transfer from the master to the gel. The amount of water expelled, although not quantified, increases with an increase in the initial water content of the prepolymer solution. As a result, the patterns from either the CDs or the DVDs do not get transferred onto the hydrogel when prepolymer solutions with a water content higher than 85 % are used. This result is summarized in Figure 3, in which the pattern on a CD was reduced in size by gels with different initial water contents. Figure 3a–c represents typical examples of second-generation patterns developed by using gels with a water content of 55 %, 70 %, and 85 % . Where the reduction in size was larger for the gel containing 85 % water, the pattern transfer was somewhat unsatisfactory as it led to the appearance of a small number of defects. However, the pattern transfer and its reduction were perfect when gels with lower water content, 50–70 %, were used. Furthermore, the plot in Figure 3d shows that, at any water content, the percentage reduction in periodicity and height of the stripes was nearly identical for both the CD and the DVD patterns, emphasizing the isotropic nature of the shrinkage.

While we have so far described the process using a polyacrylamide hydrogel, the above method of successive miniaturization could be implemented with other types of gels as well. For example, we have used resorcinol–formaldehyde (RF) gels in a similar manner as in Figure 2. Again, we used the aluminum foil of a CD as the stamp, the pattern from which was transferred to the surface of the gel. Slow drying of the wet gel over three days resulted in miniaturized striped patterns having a periodicity and height of (743 ± 11) nm and (53 ± 5) nm respectively, that is, isotropic shrinkage on the order of ca. 50 % could be achieved in one cycle.

To summarize, we have demonstrated a novel, simple, and robust method for faithfully duplicating and miniaturizing patterns on hydrogels and PDMS over a wide range of length scales: from a few hundred nanometers to tens of nanometers and over a large area in the range of 1–10 cm^2. Here, patterning is implemented under gentle conditions without any pressure, temperature, radiation, or chemical treatment, which makes it especially suitable for various biological applications, such as gels with embedded biomaterials and cells in tissue engineering. While transfer and miniaturization is perfect for curved patterns, as observed with the patterns on the CD or DVD and also the macroscopic objects, there is the possibility of nucleation of nano- to microscopic air bubbles where very sharp corners are located, which may result in some loss of information. The isotropic nature of the shrinkage is, however, especially useful for minimizing 3D objects, which is difficult to achieve through lithographic routes. In addition, the extent of miniaturization can be controlled simply

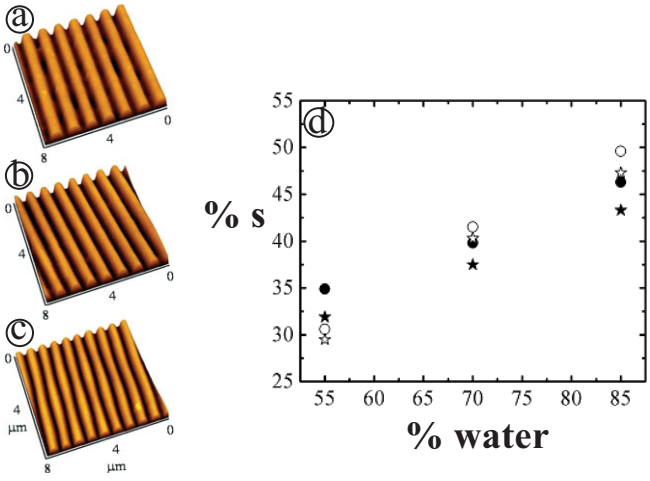

Figure 3. Atomic force microscopy images of second-generation shrunk hydrogel patterns with an initial prepolymer water content of a) 55 %, b) 70 %, and c) 85 %. In all cases, the first-generation stamp used was a CD foil, as shown in Figure 2b. d) Plot of the percentage reduction in the periodicity (stars) and height (circles) of the stripes in the second-generation patterns. Open and filled symbols represent data obtained from a CD and a DVD foil, respectively.

by using gels of varying water content and shrinking them to a desired extent. Thus, the process alleviates the need of multiple masks or stamps of different feature sizes. Furthermore, the intermediate miniaturized PDMS patterns can also be used as moulds, masks, stamps, and templates for processing of many other materials by established techniques.[7–14] For example, this procedure can be used for generating monolithic microchannels embedded in the soft platforms of PDMS or hydrogels.[37] Besides, this "do-it-yourself" method is particularly useful to research that routinely requires patterned hydrogel surfaces as substrates, templates, and molds for rapid prototyping and experiments.

Experimental

The polyacrylamide hydrogels were prepared by the polymerization of acrylamide (AA) and *N,N*-methylene bis-acrylamide (MBAA, crosslinking agent) in aqueous phase. A solution of AA (10 % w/v) and MBAA (4 % w/v) in water was prepared, to which *N,N,N,N*-tetramethyl ethylene diamine (TEMED, 1.25 % w/v) was added as catalyst and ammonium persulfate (0.5 % w/v) as initiator. The gelation time was about 5 min. The polymerization reaction of resorcinol (R) and formaldehyde (F) was carried out in the presence of a base catalyst (K_2CO_3) [33]. The molar ratio of R:F:C:H_2O (H) was maintained at 1:0.335:0.137:1.45 so as to obtain ca. 80 % of water (by weight) in the final gel sample. The gelation reaction was complete in ca. 10 h.

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