High-Throughput Generation of Micropatterns of Dye-Containing Capsules Embedded in Transparent Elastomeric Monoliths by Inkjet Printing

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ABSTRACT: We report the high-throughput fabrication of transparent elastomeric monoliths containing customized micropatterns of microcapsules, which might be used as highly flexible identity tags, sensor elements, and photochromic, photonic, or phononic systems. High-throughput replication molding of microsphere monolayers used as sacrificial primary templates via negative secondary replicas and positive tertiary replicas yielded elastomeric specimens containing dense hexagonal arrays of open spherical microcavities. In a subsequent inkjet printing step, some of the open-spherical microcavities were filled with functional materials such as dyes. The subsequent addition of an elastomeric cover layer led to encapsulation of the dyes trapped in the printed microcavities, while empty microcavities were filled with elastomer and vanished.

KEYWORDS: microspheres, monolayers, elastomers, replica molding, inkjet printing, two-dimensional codes
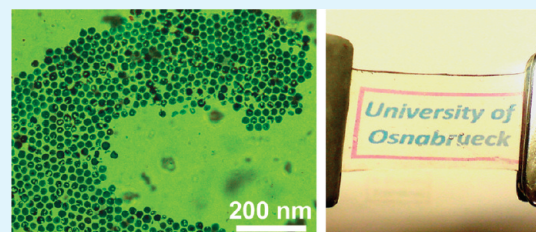
Encapsulating functional materials, such as dyes, photochromic materials,[1,2] magnetic materials, and materials for up-conversion or down-conversion of energy[3] into elastomeric matrices, through which properties of the functional materials can be detected or switched, has remained challenging. However, micropatterns consisting of entities containing a functional material and of voids filled with the matrix material with an edge length of 100 lattice periods (corresponding to 10 000 lattice points) allow the generation of $10000! \approx 10^{35000}$ different lattice configurations. For a lattice constant of 10 μm, the required area would be 1 mm^2. Hence, such micropatterns would be attractive tags containing two-dimensional codes inseparably connected with or incorporated into components or products that need to be unambiguously identified. Tailor-made micropatterns can easily be generated by serial top-down lithographic methods such as electron-beam lithography, which are, however, associated with severe drawbacks regarding throughput and costs. Because the patterns are written pixel by pixel, the patterning speed is low and only small areas can be patterned within a reasonable period of time. Each specimen to be decorated with a pattern has to be processed using cost-intensive devices. Moreover, the pattern has to be transferred into each single specimen by either dry- or wet-etching steps.

Here, we report the high-throughput production of transparent elastomeric monoliths, which contain customized micropatterns of microcapsules filled with functional materials such as dyes and which can be stretched, bent, or rolled up without damage. We applied a high-throughput replication process based on reusable secondary and ternary replicas of sacrificial microsphere monolayers (primary templates) combined with inkjet printing. With this procedure, a high number of monoliths could be obtained from one sacrificial primary template, while problems related to insufficient adhesion and insufficient spatial confinement on smooth elastomer surfaces were circumvented by trapping the printed dye in microcavities.

RESULTS AND DISCUSSION

In principle, primary templates can be produced by standard top-down lithography,[4] which should yield elastomeric poly-(dimethylsiloxane) (PDMS) specimens containing micro-cavities at exactly defined positions. With the conditions that the resolution of the inkjet printer used is not a limiting factor and sufficiently precise sample positioning systems are available, ink could then precisely be deposited into specific cavities. The use of self-assembled primary templates reduces costs and facilitates the production of large-area microcavity arrays. Despite the fact that microsphere monolayers and colloidal crystals, which appear to be the most suitable self-assembled primary templates, may exhibit excellent long-range order,[5] self-assembled arrays are inevitably characterized by a certain density of lattice defects. The presence of lattice defects represents a drawback for the addressability of specific array elements by conventional read-out procedures. However, the development of reliable procedures for the read-out of self-assembled arrays has attracted increasing interest[6] because such robust, defect-tolerant read-out procedures may pave the way for the use of self-assembled array structures in commercial applications.

Self-assembled, ordered monolayers of microspheres typically having diameters of a few hundred nanometers were reported to form via nucleation induced by capillary forces and growth through convective particle flux into ordered areas due to solvent evaporation.[7,8] Extended ordered mesosphere and microsphere monolayers are accessible by dip coating,[9] by use of flow cells,[10] by isothermal heating of evaporation-induced self-assembly,[11] and by spin coating.[12,13] We spin-coated polystyrene (PS) microspheres of 25 μm diameter onto silicon wafers (Figure 1a). Thus, we obtained monolayers of the
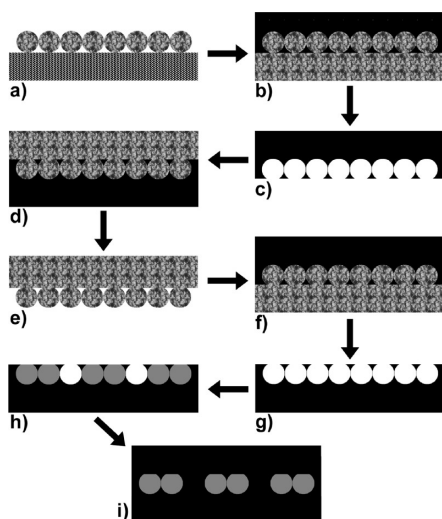

Figure 1. High-throughput generation of micropatterns of dye-containing microcapsules embedded in elastomeric PDMS monoliths. A primary template (self-assembled monolayer of PS microspheres) (a) is covered with elastomeric PDMS (b). (c) Removal of the PS microspheres yields an elastomeric secondary template containing microcavities as a negative replica of the primary template. (d) Molten PS is molded against the secondary template. (e) Nondestructive detachment of the secondary template yields ternary templates (PS microspheres tightly connected with PS substrates) as positive replicas of the primary template. (f) Ternary templates are covered with elastomeric PDMS. (g) After nondestructive detachment, printable elastomeric PDMS specimens containing hexagonal arrays of microcavities are obtained as negative replicas of the primary template. (h) A fraction of the microcavities is filled by inkjet printing. (i) By the addition of elastomeric PDMS cover layers, the materials deposited in the microcavities of the printed areas are encapsulated, whereas the empty cavities are filled with elastomeric PDMS and disappear.

PS microspheres with areas of several square centimeters, thereafter referred to as primary templates, which consisted of ordered hexagonal domains extending up to 20 lattice constants. Replicas of PS microsphere monolayers consisting of elastomeric PDMS containing covalent cross-links between PDMS segments were previously prepared by covering PS microsphere monolayers with PDMS prepolymer mixtures followed by curing. This replication procedure yielded elastomeric PDMS specimens containing hexagonal arrays of concave cavities,[14−16] which served, for example, as microwell arrays for the trapping of cells.[17]

The insufficient mechanical stability of as-deposited microsphere monolayers, even after thermal annealing, prevents their use as master molds in nondestructive replication molding processes. To overcome this problem, we first adapted a double-replication process reported by Nam et al.[14] to prepare ternary templates as positive replicas of the sacrificial primary

templates. While in the first replication step the primary templates are destroyed and only one secondary template is obtained per primary template, multiple ternary templates can be obtained from one secondary template. Subsequently, each ternary template can be replicated multiple times to produce printable PDMS monoliths containing arrays of open-spherical microcavities (Figure 1g). After more than 100 replication processes, both the secondary and ternary templates were still intact so that a large number of printable specimens is accessible from one sacrificial primary template (Figure 1a).

First, we covered primary templates (Figure 1a) with PDMS prepolymer mixtures containing dimethylvinyl-terminated PDMS prepolymer and vinylated siloxane units, allowing conversion of the resin into an elastomer by curing at 65 °C (Figure 1b). The elastomeric PDMS monoliths thus obtained were detached from the silicon wafers serving as substrates for the primary templates, and we could efficiently remove the PS microspheres by rubbing. Thus, elastomeric PDMS secondary templates containing arrays of open-spherical microcavities as negative replicas of the primary templates were obtained (Figure 1c). Then, molten PS was molded against the secondary templates (Figure 1d). After solidification, mechanically stable ternary templates consisting of hexagonal arrays of PS microspheres tightly connected with PS substrates could be nondestructively detached from the elastomeric secondary templates (Figure 1e). The ternary templates were faithful positive replicas of the primary templates. Like the primary templates, the ternary templates could be replicated by covering them with a PDMS prepolymer mixture (Figure 1f) followed by curing. Thus, about 0.3-mm-thick PDMS monoliths containing hexagonal arrays of open-spherical microcavities were obtained and nondestructively detached from the ternary templates (Figure 1g).

In the next step, selected microcavities of the elastomeric PDMS specimens were filled with a functional material (Figure 1h). We used inkjet printing[18] of commercial inks as a cheap high-throughput method to generate micropatterns of filled microcavities, but it is conceivable that, for example, micro-pipetting techniques[19] and electrospraying[20−23] can also be employed to this end. Inkjet printing is a versatile high-throughput approach to create patterns with resolutions up to the micrometer scale by depositing droplets of ink to selectable areas on a substrate. The ink may contain a broad variety of functional materials, such as luminescent polymers,[24] viable mammalian cells,[25] proteins, and hybrid cell-containing materials,[26] or nanoparticles and microparticles.[27] Examples for device structures accessible by inkjet printing include flexible systems for gene expression profiling using arrays of tens of thousands of oligonucleotides,[28] electronic circuits on flexible substrates,[29] ferroelectric active matrix sensor networks,[30] and graphene sheet-based wide-band dipole antennas.[31]

Direct inkjet printing onto smooth surfaces of hydrophobic elastomers like cross-linked PDMS has remained demanding. For example, aqueous inks tend to dewet because they have high contact angles on PDMS,[32] thus resulting in insufficient lateral confinement of the ink on the printed substrates and, consequently, in poor lateral resolution. Moreover, weak adhesion of the deposited material on the elastomer surface and, therefore, abrasion significantly reduces the durability of printed patterns. However, inkjet printing onto PDMS containing dense hexagonal arrays of microcavities allows trapping of the ink within the microcavities of the printed area

(Figure 1h). The diameter of the cavities, which can, in principle, be adjusted to any value between a few hundred nanometers and several tens of micrometers by preparing the primary templates with microspheres having corresponding diameters, determines the maximum resolution of the printed image. Inkjet printers typically generate ink droplets with volumes of approximately 10 pL. We adjusted the lattice period of the microcavity arrays to 25 μm so as to approximately match the typical diameters of ink droplets and, correspondingly, the typical resolution of inkjet printing. Moreover, the volume of a single microcavity of 25 μm diameter is about 8 pL. Thus, taking into account the starting solvent evaporation, the volume of an ink droplet approximately corresponds to the volume of a microcavity.

Because ink droplets impinging on the substrate have considerable kinetic energy, the droplets, or fractions thereof, reach the bottom of a microcavity. If the ink does not wet the substrate, the droplets are trapped in the microcavities by gravity. If the ink wets the substrate, the concave curvature of the microcavities would, in addition, allow for an increased contact area between ink and the substrate. It will be demanding to achieve registration of the microcavity array with the printing device on a micrometer scale in such a way that droplets are precisely directed toward the centers of the microcavities. However, such precise registration during printing appears to be unnecessary as long as the read-out of the printed patterns occurs with a lateral resolution corresponding to two or more lattice periods of the printed microcavity arrays. We assume that, for most of the envisioned applications, a read-out resolution lower than the theoretical maximum resolution imposed by the periodicity of the microcavity array should be sufficient and will even be inevitable in the case of self-assembled microcavity arrays containing lattice defects.[6]

After inkjet printing and drying, the nonvolatile components of the ink were located within the open microcavities of the printed area. Figure 2 shows an optical microscopy image of an approximate 300-μm-thick PDMS specimen corresponding to Figure 1h. The PDMS specimen contained a dense, hexagonal array of open microcavities, which were faithful indirect
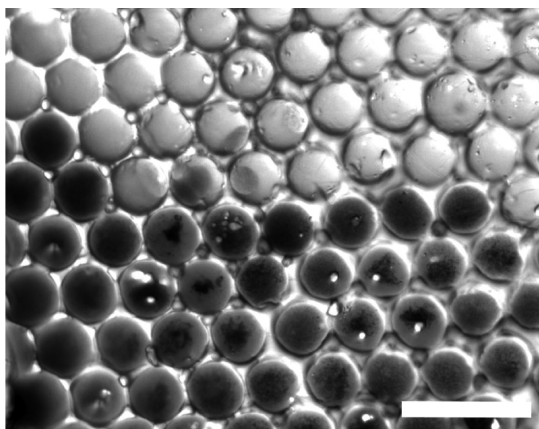

Figure 2. Bright-field optical microscopy image of an approximate 300-μm-thick elastomeric PDMS specimen containing hexagonal arrays of microcavities after inkjet printing (corresponding to Figure 1h). The microcavities at the bottom appearing dark contain ink, those in the upper part of the image appearing brighter are empty. The scale bar corresponds to 50 μm.

negative replicas of the PS microspheres of the primary template and direct negative replicas of the spherical entities of the ternary template. The microcavities appearing dark in the lower part of Figure 2 were filled with ink, whereas the microcavities appearing bright in the upper part of Figure 2 remained empty. As is obvious from Figure 2, the 25-μm resolution typical of inkjet printing was by-and-large retained in the printed pattern. It should be noted that the printing process was performed with a standard office printer commercially available for less than $100 (cf. the Experimental Section). However, it is straightforward to assume that the methodology reported here is also compatible with commercially available industrial printers having droplet throw distances of several centimeters.[33]

For real-life applications, the durability of the printed micropatterns, resistance against abrasion and chemicals and protection from manipulation can be optimized by encapsulation of the printed material located in the open microcavities. To this end, after drying of the ink, the printed elastomeric PDMS specimens were covered with an approximate 700-μm-thick PDMS prepolymer layer. Apparently, the density of the unreacted vinyl groups at the surfaces of the elastomeric PDMS specimens containing the open microcavities was sufficient for the development of a tight and stable cohesive connection between existing and newly formed elastomeric PDMS layers during the subsequent curing step. No additional activation of the PDMS surface, for example, by oxygen plasma treatment, was required. Empty microcavities were filled with PDMS and became part of the elastomeric PDMS matrix, whereas the dye in the printed microcavities was encapsulated (Figure 1i). As a result, we obtained transparent elastomeric monoliths containing patterns of embedded microcapsules filled with ink (Figure 3). An approximate 1-mm-thick PDMS specimen extending 2.3 $\times$ 1.4 mm containing micropatterns of dye-filled microcapsules is shown in Figure 4a. The elastomeric PDMS monolith was stretchable, as is obvious from Figure 4b. When subjected to tensile stress and stretched to about 150% of its initial length, the printed micropattern, albeit elongated, retained its sharpness. After release, the elastomeric PDMS monolith relaxed completely, and the printed micropattern regained its original shape and size.

■ EXPERIMENTAL SECTION

Self-assembled monolayers constituting the primary templates (Figure 1a) were prepared using microspheres consisting of cross-linked PS obtained by copolymerization of styrene and divinylbenzene with a diameter of 25 μm and monodisperse diameter distribution (Polybead; Polysciences, Inc.). We adapted procedures previously applied to nanospheres with a diameter of 500 nm.[13] Pieces of silicon wafers with areas of about 4 $\times$ 4 cm^2 were treated with a piranha solution [3:1 (v/v) H_2SO_4/H_2O_2] for 3 min and then covered with a thin surfactant layer (Trition X-100, CAS 9002-93-1, Sigma-Aldrich) by spin coating at 3500 rounds per minute (rpm) for 30 s. Then, a few droplets of an aqueous suspension of the PS microspheres having a concentration of 2.91 $\times$ 10^6 microspheres/mL were deposited onto the surfactant-treated silicon wafer pieces, followed by a multistep spin-coating program (60 s at 150 rpm, 60 s at 200 rpm, 60 s at 300 rpm, 60 s at 600 rpm, 60 s at 3600 rpm, and 10 s at 60 rpm). The deposition/spin-coating cycles were repeated, typically 3−4 times, until the entire wafer pieces were covered with dense hexagonal PS microsphere monolayers. Excess PS microspheres on top of the
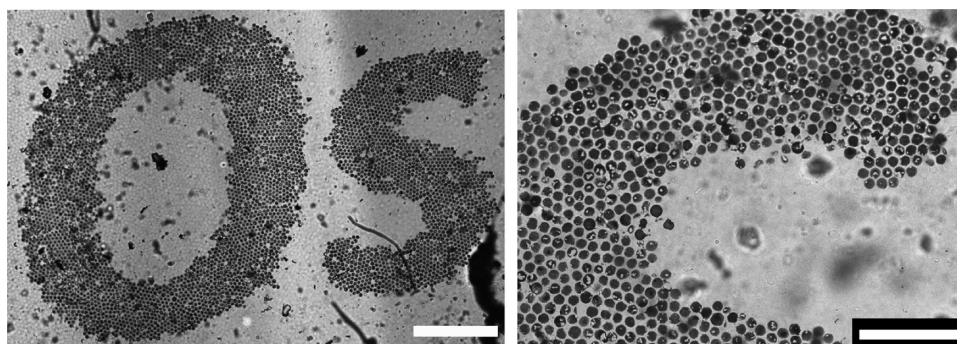
Figure 3. Bright-field optical microscopy images of an approximate 1-mm-thick elastomeric PDMS monolith containing micropatterns of dye-containing microcapsules encapsulated in a PDMS matrix: (a) overview with a scale bar corresponding to 500 μm; (b) detail with a scale bar corresponding to 200 μm.

Figure 4. Photographs of an approximate 1-mm-thick elastomeric PDMS monolith containing micropatterns of embedded dye-containing microcapsules: (a) relaxed elastomeric PDMS monolith; (b) elastomeric PDMS monolith subjected to tensile stress.

microsphere monolayers were removed by rinsing with distilled water.

To prepare the secondary templates corresponding to Figure 1c, primary templates consisting of self-assembled microsphere monolayers on surfactant-coated silicon wafer pieces were covered with commercially available two-component PDMS prepolymer mixture (SYLGARD 182 supplied by Dow Corning). Both components [5:1 (w/w) base/curing agent] were well mixed for 3 min and then kept under ambient conditions until the air bubbles formed during the mixing had vanished. The PDMS prepolymer mixture was then poured onto a primary template in such a way that the whole substrate was covered with an approximate 0.3-mm-thick layer of the PDMS prepolymer mixture (Figure 1b). After curing at 65 °C for 2 h, the thus-obtained secondary template consisting of elastomeric PDMS was mechanically peeled off from the silicon wafer. The microspheres embedded in the elastomeric PDMS secondary templates were mechanically removed by rubbing.

The ternary templates consisting of PS microspheres attached to PS substrates corresponding to Figure 1e were prepared by pressing molten PS (Polysciences, Inc.; broad molecular weight distribution, molecular weights ranging from 800 to 5000 g/mol; polydispersity index 28) onto secondary templates using a commercially available Hot Melt Applicator (HB 710 manufactured by Bühnen). After cooling to room temperature, the PS ternary templates were nondestructively detached from the secondary templates. Thus, about 1.0−1.5-mm-thick PS substrates decorated with dense hexagonal arrays of PS microspheres (Figure 1e) were obtained.

Micropatterns of dye-containing microcapsules embedded in elastomeric PDMS monoliths corresponding to Figure 1i were obtained as follows. Elastomeric negative PDMS replicas of the ternary templates were prepared in the same way as the

elastomeric PDMS secondary templates but were non-destructively detached from the ternary templates (Figure 1g). For inkjet printing (Figure 1h), a commercially available HP Deskjet 980Cxi inkjet office printer and commercially available standard ink cartridges (black ink: HP 45; colors: HP 78) were used. However, we increased the printhead height (distance between printer nozzle and paper) by placing washers in the cartridge rails. At first, patterns were printed on sheets of standard A4 paper. The ≈0.3-mm-thick elastomeric PDMS specimens containing hexagonal arrays of microcavities were fixed on the printed areas with adhesive tape and then fed into the inkjet printer. The printed elastomeric PDMS specimens were covered with a two-component PDMS prepolymer mixture and cured in the same way as the secondary templates so that a 0.7-mm-thick elastomeric PDMS cover layer formed.

Optical microscopy images were taken with an optical microscope Zeiss Axio Imager 2 equipped with an Axio Cam MRC4 camera in transmission mode.

■ CONCLUSIONS

A procedure for the high-throughput fabrication of large-area micropatterns of embedded microcapsules containing dyes encapsulated in transparent elastomeric monoliths was reported (the samples presented here have lateral dimensions of up to 2.5×2.5 cm^2). A single sacrificial primary template consisting of a hexagonal microsphere monolayer was used to prepare a large number of printable elastomeric specimens containing dense hexagonal arrays of microcavities, which were faithful negative replicas of the primary template. Selected cavities were filled with dyes by inkjet printing. The ink was trapped in the printed microcavities and was encapsulated by the addition of an elastomeric cover layer, while microcavities outside the printed area were filled with matrix elastomer and vanished. Elastomeric specimens obtained in this way could be stretched, bent, or rolled up without damaging the micropatterns of embedded dye-filled microcapsules. The procedure reported here should be applicable to a broad range of thermosets and photo-cross-linkable polymers, such as epoxy, polyurethanes, rubbers, and polyisoprene. Likewise, a broad range of functional materials including photochromic, magnetic, Raman-active, IR-active, and upconverting materials may be deposited into the microcavities so that the spatial arrangement of the resulting embedded microcapsules can be read out by suitable microscopic methods. We anticipate that optical or magnetic switching of the materials located in the embedded micro-capsules through the transparent elastomeric matrix is possible.

Potential applications of monoliths containing micropatterns of encapsulated functional materials, which can be inseparably connected to or incorporated into a broad range of components, parts, or devices, include their use as identity tags, as sensor elements, and as photochromic, photonic, or phononic systems.

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Notes
The authors declare no competing financial interest.

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