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Letter

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Three-dimensional soft material micro-patterning *via* Direct Laser Lithography of flexible moulds

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Three-dimensionally micropatterned surfaces are attracting increasing interest in soft robotics owing to the potential of mimicking natural morphologies at the micro/nanoscale. We employ direct laser lithography to fabricate moulds with complex 3D micrometric features, in positive photoresist on flexible substrates, to pattern curved macroscopic soft surfaces with shapes not achievable with standard methods (e.g. re-entrant angles). We present several 3D intricate microstructures in PDMS, and show a soft cylinder patterned with 3D microstructures with one moulding process. Finally, we deform PDMS-based 3D architectures and show soft microgripping capability, indicating the potentiality of this approach for future application in soft robotics.

KEYWORDS. Micromoulding; direct laser lithography; PDMS; surface patterning; soft robotics.

In recent years soft robotics is emerging as a challenging new approach for developing innovative solutions for engineering issues.[1,2] In particular, roboticists are looking to new soft technologies for designing robots with bioinspired capabilities.[3] Indeed, plants and animals had to develop remarkable capabilities for adapting and interacting with the very complex and unstructured environments they live in. They succeed in such aim by exploiting the advantages offered by soft materials and smart morphologies.[4–6] Properly designed polymeric soft materials can create original solutions for soft robotics: shape and spatial organization of such polymers can add peculiar functionalities to the entire material.[7] An interesting example is surface patterning that provides several functional characteristics such as hydrophobicity, drag reduction, dry adhesion, improved cellular interactions, and many more (like improved mechanical interaction of the material with the outer world by an increased contact area etc.), which occur at both macro- and microscale.[8–11]

Indeed, to fully take advantage of morphological structures, challenges like shaping soft materials at the micro/nanoscale with a three-dimensional (3D) architecture remain to be addressed. In fact, silicone elastomeric materials, widely used in soft robotics, have the disadvantage of not being easily structured in 3D, especially for curved and re-entrant geometries. Moreover, a fundamental aspect is the integrated approach that should be adopted in soft robotics to obtain simple yet functional and robust systems; i.e. new processes and technologies should allow more and more to build sensing, actuation and body of the devices in an integrated manner, instead of fabricating each of them independently and then perform system integration in a second stage. In this sense, it is important to construct the 3D surface micro-morphology together with the bulk of a soft robotic body having a final desired 3D shape.

Finally, the characteristics (physical and/or chemical) of the materials should endow the robotic structure with specific functionalities.

The standard procedure for the microfabrication of patterned silicone elastomeric materials mainly involves the use of moulds prepared by means of standard lithographic techniques.[12,13] These are quite effective in case of 2D or 2D ½ features[14–16], but show some lacks in terms of complex 3D morphologies. This limitation could be overcome by using direct laser lithography (DLL) for the fabrication of three-dimensionally shaped moulds, by microstructuring directly a photocurable silicone[17]. DLL ensures outstanding results in terms of spatial resolution[18], which are not achievable even with 2D multiple lithographic steps.

In this paper we present an innovative micromoulding technique for the fabrication of complex three-dimensional micro-patterned flexible moulds that can be used for shaping mouldable materials (a silicone in our case). Direct laser lithography has been already used for the fabrication of 3D masters to obtain silicone moulds.[19–21] However, in this work we obtain moulds directly on flexible substrates by using direct laser lithography: in this way arbitrarily complex 3D designs can be created, even with cavities and re-entrant geometries like cannot be achieved with previous approaches. Importantly, flexible moulds bring the advantage to allow the patterning of many kinds of surfaces since they are able to conform even to curved ones.[16,22–24] Hence, with the proposed technique, we introduce an integrated approach: micro/nanoscale patterning together with the macroscopic curvatures of the bulk soft material allow to directly fabricate three-dimensional structures with highly complex morphologies that can find useful applications in soft robotics. Soft robots have to gently interact with the external environment by exploiting the compliance of their structural materials; hence, as a case study, we exploit the

hyperelastic behaviour of a silicon rubber to demonstrate the possibility of fabricating surfaces with soft gripping and trapping capabilities.

We designed several shapes in order to investigate the potentiality of the presented technique. Moulds have been fabricated in positive photoresist (AZ9260, AZ Electronics materials, GmbH) on Mylar sheets that were chosen both for their flexibility and for their resistance to high temperatures to which the AZ9260 photoresist is subjected during the process. In literature several applications of positive photoresists with DLL are reported, but so far they have required a standard fabrication procedure and DLL configuration since they were exposed only on rigid transparent substrates.[25–28] Our innovative approach allows to work with flexible and non transparent substrates. In particular, we introduced an *ad hoc* upside-down configuration since it is not possible to expose the photoresist through Mylar, which is the material we used that is non transparent to the infrared laser of the 3D lithography system (Nanoscribe GmbH), as shown in Figure 1a. The photoresist is exposed to the femtolaser beam by means of an oil immersion objective. The samples were manufactured by deposition of three different layers. A 100 nm thick layer of Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, Clevios PH1000, Heraeus GmbH) was spin-coated on the Mylar substrate surface in order to facilitate the detection of the Mylar-AZ9260 interface by the laser system, due to its refractive index. A 20 μm thick layer of photoresist was then spin-coated on the PEDOT:PSS thin layer. Finally, a layer of Poly(vinyl alcohol) (PVA, Sigma Aldrich GmbH) with a thickness of about 1 μm was deposited by spin-coating providing insulation between the photoresist and the oil on the lens objective, and an easy removal step in few minutes by immersion in water. The samples were developed in AZ 726 MIF (AZ Electronics Materials GmbH) and rinsed in water (for more details on mould microfabrication see Supporting Information).

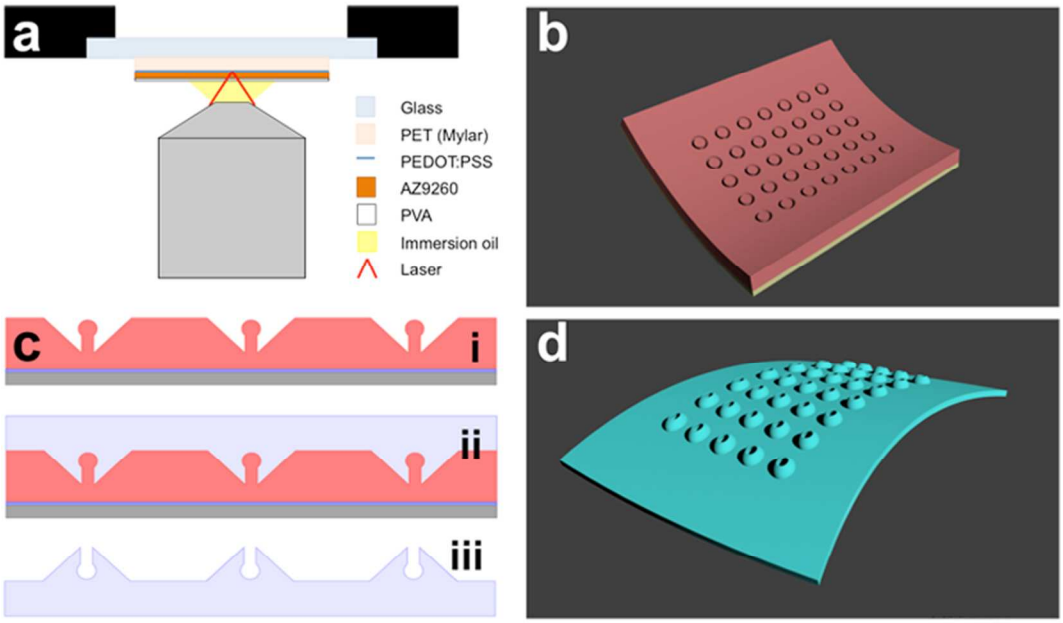

Figure 1. a) Sample configuration in the laser system. b) Sketch of the flexible mould. c) Micromoulding steps: (i) micropatterned photoresist; (ii) Polydimethylsiloxane (PDMS) cast on the mould and cured; (iii) PDMS layer peeled-off and cleaned with photoresist remover and water). d) Sketch of the PDMS layer fabricated by moulding.

The design of flexible moulds built from AZ9260 on Mylar is shown in Figure 1b. The main stages of the fabrication of micro-patterned surfaces are shown in Figure 1c. Polydimethylsiloxane (PDMS, monomer and reticulation agent in 1:5 ratio, Sylgard 185, Dow Corning) was cast on the mould and cured. The PDMS layer was then peeled-off and the photoresist that remained attached to the silicone surface was dissolved with the AZ100 remover (AZ Electronics materials, GmbH) leaving a 3D micropatterned PDMS layer, which was finally washed with water and dried with air (Figure 1d) (experimental details on fabrication are reported in Supporting Information). Therefore, the specific mould can be used for one moulding process. In order to prove the efficacy of such technique in obtaining structures with

submicrometric resolution, arrays of 10 μm deep and 2 μm spaced holes (whose diameter correspond to a single path of the laser beam) where fabricated and used as moulds (Supporting Information Figure S1a). PDMS nanopillars with high aspect ratio (Supporting Information Figure S1b) were obtained as a result of the micromoulding process. On the basis of this preliminary result, we fabricated a variety of more complex structures having curved and re-entrant geometries. The morphological characterization of the microstructures was performed through optical microscopy, scanning electron microscopy and focused ion beam milling techniques.

The first design (Figure 2a) consists of an array of hollow truncated hemispheres with nominal diameter of 33 μm and height 15 μm; the nominal diameter of the aperture is 15 μm. The mould used for this patterning is reported in Supporting Information (Figure S2a). Owing to the hemispherical geometry and to the elastic modulus of the PDMS, the structures don't collapse, leading to outstanding structures in terms of resolution, surface finish and reproducibility. In particular the internal region of the structures results in being completely clean from any photoresist residual (Figure 2b). A couple of crossed filaments was also fabricated at the top of such hemispheres in order to demonstrate the possibility to obtain suspended high resolution 3D features (Figure 2c-d). The corresponding mould is reported in Supporting Information Figure S2b.

The second type of structures, 3D microgrippers (Figure 2e), consists of couples of sloping walls with trapezoidal shaped sides (major and minor bases with lengths of 20 μm and 10 μm, respectively, and height of 9 μm) and a decreasing thickness from bottom to the top, starting from 3.6 μm at the baseline. The two arms of each gripper are inclined towards each other forming a 60° angle with respect to the base. The mould used for achieving these microstructures

is reported in Supporting Information Figure S2b. Several arrays of microgrippers were fabricated by changing the distance between the top edges of the leaning arms, from an attached to a completely detached configuration (Supporting Information Figure S3). This design was implemented in PDMS to prove the possibility to fabricate slanted self-standing soft micro structures. In particular, this technique enables to accurately reproduce sharp profiles (Figure 2f).

Furthermore, 3D microchannels (Figure 2g-h) composed by a half pipe were fabricated, demonstrating that elements that can cover relative wide areas of hundreds of microns without collapsing can be implemented. We built two types of microchannels having a nominal length of 150 μm, and two different diameters of 10 μm and 12 μm. Cross-sections of the channel, showing the hollow internal region, are shown in Figure 2h and Supporting Information (Figure S4).

At last, structures that consist of two intersecting arches with two different diameter of 37 μm (Figure 2i) and 32 μm (Supporting Information Figure S5a) respectively, were designed in order to investigate the feasibility of tiny self-standing structures. The nominal thickness of the arches is 2.5 μm. The mould fabricated to obtain such microstructures is shown in Supporting Information Figure S2d. The resulting crossed arches have an excellent features resolution (Figure 2j and Supporting Information Figure S5b). The fabrication of such tiny structures requires the careful consideration of the design and the mechanical properties of the materials employed. In fact, if the geometry is not properly designed according to the mechanical strength of the material, it is possible for the structures to collapse. For this reason these structures were fabricated with a more reticulated PDMS (monomer and reticulation agent in 1:2.5 ratio). When the less rigid 1:5 PDMS was employed, during the photoresist removal and the final rinse in water, the structures tend to fall and stay attached to the substrate, changing their morphology

(Supporting Information Figure S6). Actually this behaviour could also be seen not as a weakness, but rather it could enable fabricating structures that passively change the final shape after being exposed to some particular solvents, like shown by De Volder *et al.*[29]

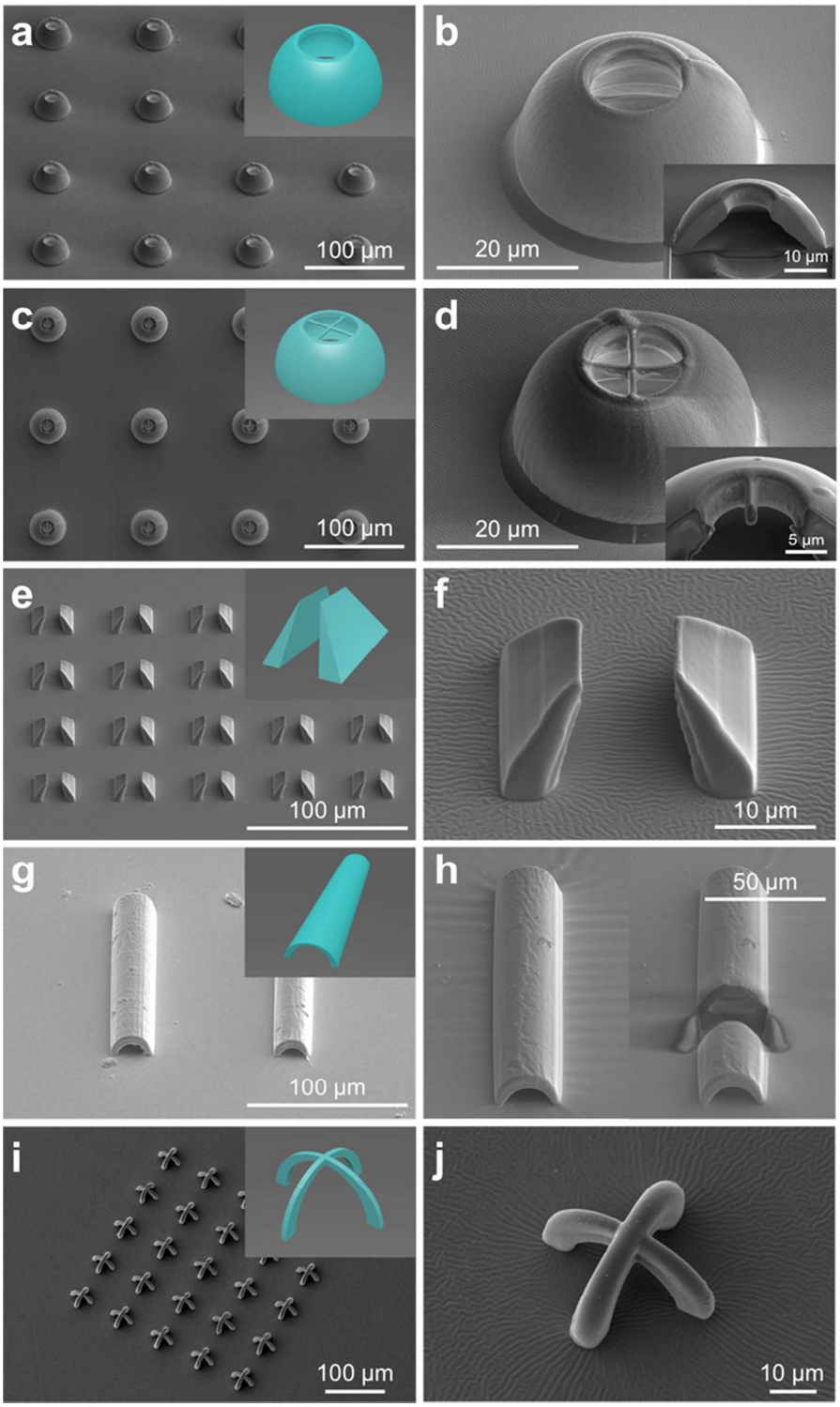

Figure 2. SEM images of a) an array of hemispheres in PDMS (design in the inset); b) a single hemisphere (section in the inset); c) an array of hemispheres with filaments in PDMS (design in the inset); d) a single hemisphere with filaments (with section shown in the inset); e) an array of microgrippers in PDMS (design in the inset); f) a single microgripper; g) channels in PDMS (design in the inset); h) a single channel and its transversal section; i) an array of crossed arches in PDMS (design in the inset); and j) single couple of crossed arches.

In a second phase of our work, once the structures were fabricated, we focused on exploiting the hyperelastic behaviour of the PDMS material[30] that can be deformed when subjected to strain. In particular, because of both their design and of the strains induced in the 3D microstructures by external mechanical stimuli, such structures can be enabled of some function, and specifically, in our case, the object trapping capability. To this aim we demonstrated the feasibility to grasp and trap microparticles in fluids by using two different kinds of 3D microstructures: hemispheres and microgrippers. An uniaxial strain was applied to the patterned PDMS layers by means of two manual micro-translation stages (see Supporting Information for details), in order to obtain conformation changes in both hemispheres and microgrippers. In particular, in case of hemispheres, a dispersion of polystyrene microbeads in water with 7μm diameter (Sigma Aldrich GmbH) was cast on the PDMS patterned layer, allowing particles to enter into the hollow open structures. All the steps are described in Figure 3a. During the application of the strain, the openings of the hemispheres were elongated of about 50% of their initial diameter along the axis parallel to the stretching direction, while along the perpendicular axis the width of the same decreased. This way, the microparticles were trapped inside the hollow hemisphere (Figure 3b-c).

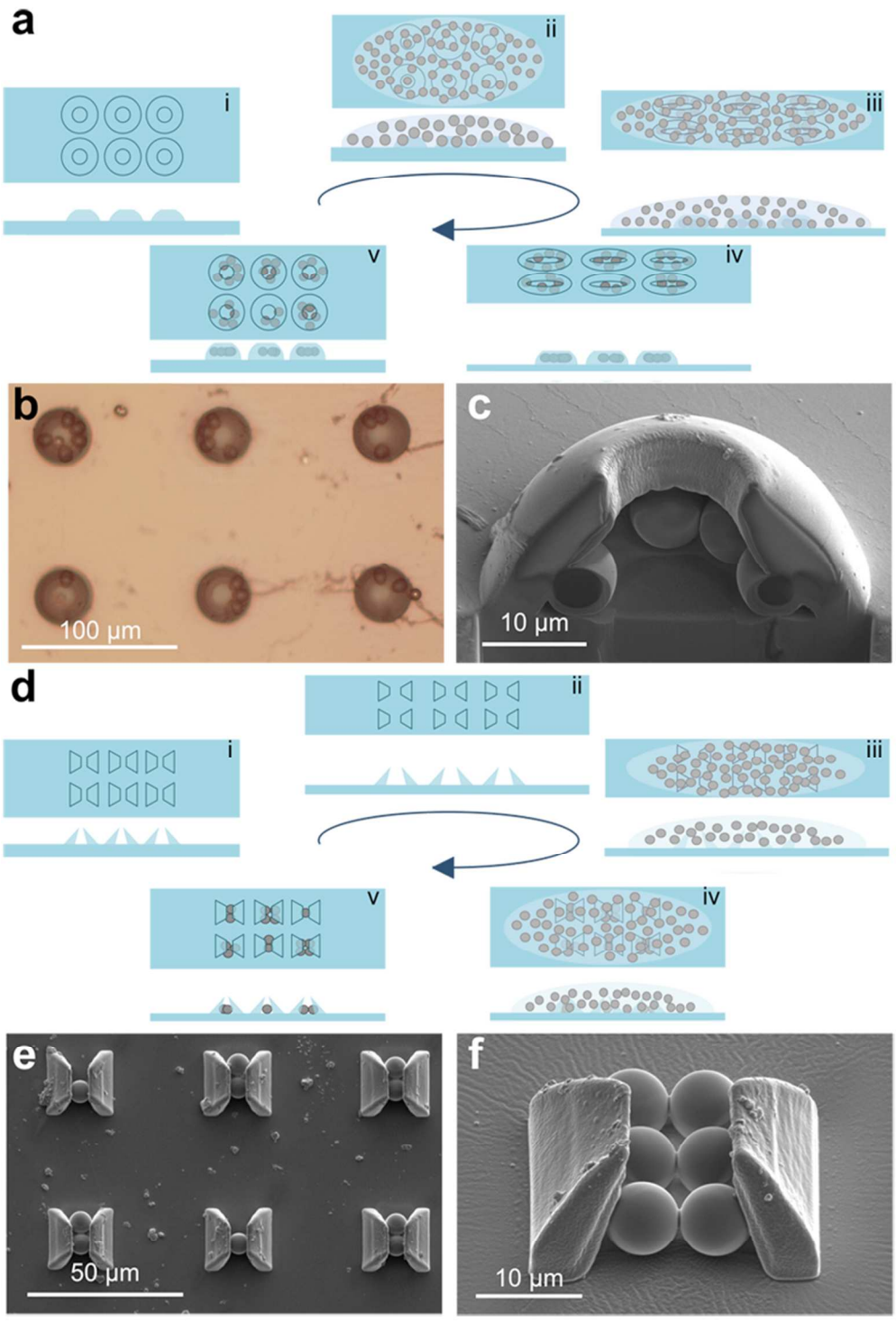

Figure 3. a) Schematic representing particles trapping by hemispheres: (i) relaxed PDMS sheet; (ii) solution of microparticles poured on the pattern; (iii) the axial strain applied to the sheet to trap the particles in the hemispheres; (iv) the sample is rinsed with water; (v) the strain is

released, and particles remain trapped. b) Microparticles, entrapped in the relaxed hemispheres, visible in transparency with optical microscope. c) SEM image of the section of a hemisphere containing microparticles. d) Schematic representing particles microgripping procedure: (i) relaxed PDMS sheet; (ii) the axial strain is applied to the sheet increasing the gap between the edges of the grippers; (iii) the solution of microparticles is poured on the pattern; (iv) the strain is released; (v) the sample is rinsed with water, leaving the particles trapped by microgrippers. e) SEM image of an array of microgrippers holding microparticles. f) SEM image of a single microgripper holding two rows of microparticles.

Moreover, in the case of the microgrippers (Figure 3d), the abovementioned dispersion was cast on pre-stretched PDMS layers, as the distance between the two arms increased with the application of the stretching. This way, when the sample relaxed, the arms became closer again, thus entrapping the particles (Figure 3e). The initial value of the gap between the baselines of the two leaning sides of each microgripper plays a key role in determining the amount of particles that can be trapped according to their dimensions. If they are closer they can reach a relative small final distance for a certain maximum deformation with respect to broader microgrippers, leading to a minor amount of trapped particles. As an example, microgrippers with a gap of 4 μm can trap only one row of microparticles (Supporting Information Figure S7a) while those with a gap of 10 μm can trap two rows (Supporting Information Figure S7b). As an example, microgrippers with a gap of 4 μm (Figure 3e) or 6 μm (Supporting Information Figure S7a) can trap only one row of microparticles, while those with a gap of 10 μm can trap two rows (Figure 3f and Supporting Information Figure S7b).

Finally, the possibility to merge macroscopic shaping of materials with microscopic patterns was investigated (Figure 4a). Exploiting the flexibility of the mould, the latter was attached and conformed to the concave surface of a hollow cylinder with 3.5 mm radius of curvature, which was used as the macroscopic part of the mould (Figure 4b). PDMS was cast in the cylinder, and all the fabrication process steps were followed as previously described, obtaining a macroscopic 3D object with a micropatterned surface. For this purpose, both hemispheres and microgrippers were patterned on the cylinder surface (Figure 4c-f). The results show that the presented technique allows obtaining outstanding three-dimensional patterns at the microscale even on curved surfaces with radius of curvatures in the order of few millimetres. Hence, our integrated approach (3D micro-patterns fabricated directly on macro-curvatures) proves the possibility to obtain 3D modelled flexible materials with truly 3D microscopic surface features that can find a wide range of applications in soft robotics.

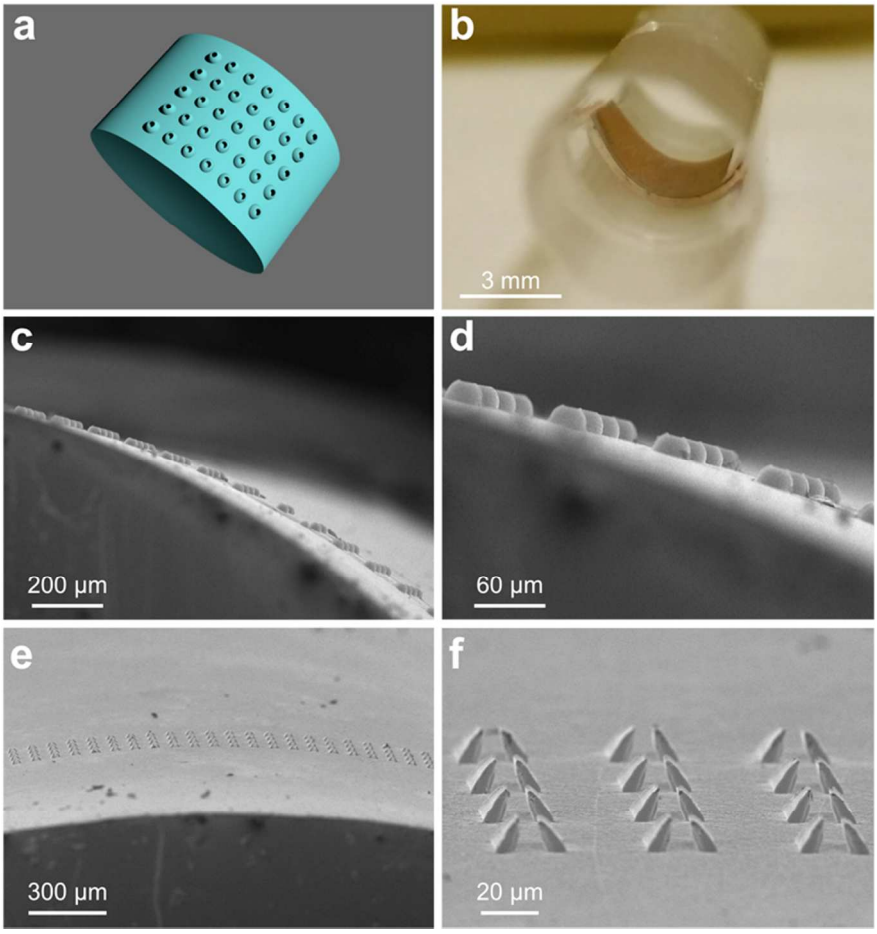

Figure 4. a) Sketch of the combined approach of patterning a curved macroscopic surface (a cylinder) with three-dimensional features in the microscale. b) Flexible mould fitting the internal part of a hollow cylinder, to be filled with PDMS. c) SEM image of the profile of the cylinder patterned with hemispheres. d) SEM image of the detail of the hemispheres on the curved surface. e) SEM image of the profile of the cylinder patterned with microgrippers. f) SEM image of the detail of the soft microgrippers on the curved surface.

In conclusion, we propose a micromoulding technique for the fabrication of complex three-dimensional micro-patterned surfaces in PDMS, but that can be extended also to the use of any

other mouldable compatible material. The technique proved to be effective in terms of resolutions and reproducibility. In particular the dedicated DLL setup is fundamental for the fabrication of moulds with three-dimensional re-entrant features at the microscale. Our flexible moulds can be used through a single moulding step to shape materials at the macroscale, yet with 3D complex surface morphologies at the microscale, and also specific functional characteristics can be provided. All these are remarkable aspects that are not easily achievable with other microfabrication techniques.

ASSOCIATED CONTENT

Supporting Information. More details about microfabrication processes are provided in sections 1 and 2, and about experimental procedures are given in section 3, with related results. Figure S1: SEM images of a) array of holes in AZ9260 used as mould to fabricate b) PDMS nanopillars. Figure S2: Optical images of a) hemispheres and b) microgrippers moulds. Figure S3: SEM images of microgrippers with different gaps. Figure S4: SEM image of the lateral section of a PDMS microchannel. Figure S5: SEM images of crossed arches with 32 μm diameter. Figure S6: SEM images of collapsed PDMS arches. Figure S7: SEM images of different amount of microbeads depending on microgrippers gap.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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