Programmable surface anisotropy from polarization-driven azopolymer reconfiguration

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Abstract

The ability to accurately realize complex textures is of great relevance for tailoring surface-driven functionalities as wettability, adhesion and light diffraction. The fabrication of superficial micro-textures, in a simple and cost-effective way, is high desiderable in this framework. A versatile technique for surface micropatterning is based on reconfiguration of photosensitive azobenzene-containing polymers, in which a macroscopic light-induced motion of polymer chains, fueled by the photo-isomerizing azobenzene molecules, allows the controlled optical reshaping of prestructured superficial micro-textures. Here, azopolymer surfaces, prepatterned with an array of discrete cylindrical micropillars, are reconfigured through a polarization-driven large-scale surface deformation until achieving superficial gratings with programmable amplitude, orientation and periodicity. The high degree of structural surface anisotropy, the possibility to program the directionality of such anisotropy from the reconfiguration of basic pristine surfaces, and the simplicity of the optical setup, make the proposed structuration method attractive for versatile and cost-effective surface patterning.

1. Introduction

The engineering of surface geometry of polymeric materials is of great interest for several application fields. Examples include light diffraction, adhesion properties, bio-interfaces for substrate-influenced cell cultures, tuning of the wetting effects [1–8]. A high degree of control over surface properties and their tuning, can be achieved through the fabrication of surface geometries with a significant degree of complexity and anisotropy [9]. Standard lithographic techniques, including photolithography, electron beam and focused ion beam lithography, self-assembly, and soft lithography [10–13], are extensively used in this framework but require high costs and complex equipment [11]. Furthermore, the need of designing the desired final surface before the manufacturing process even starts, without the possibility of modifications of the realized geometries post-fabrication, represents an additional limit for these techniques.

Overcoming some of these limits has led to research efforts toward the development of new microfabrication methods. A promising photolithographic approach is based on the light-induced mass transport occurring in azobenzene-containing polymers (briefly named azopolymers) under irradiation of their surface with spatially-structured UV/visible light [1, 14]. In these materials, the absorption of a photon with suitable energy (λ = 300–550 nm) induces cyclic structural transitions of the photo-active azobenzene molecules between their trans and cis isomerization states. The isomers have different chemical, physical and geometrical properties, which can affect the properties and the functionalities of materials in which they are embedded, acting as molecular photo-switches.
The trans-cis structural photo-switch is of great interest in several scientific fields. Some examples of technological applications in which the suitability of azomaterials photo-switch has recently been investigated, are the photo-responsive biosensors for antiproliferative activity against cancer cells [15, 16], or as alternatives data storage devices in electronics, where traditional phase-change materials are widely used [17, 18]. Additionally, the propagation of the molecular azobenzene dynamics at macroscopic level induces the photo-actuation effect observed in azo-LCEs (azobenzene-containing liquid-crystalline elastomers) [11]. Such phenomenon is very attractive for direct optical-to-mechanical energy conversion devices, aimed at the realization of light-driven soft-robots and energy-harvesting devices [19]. An example is the chaotic self-oscillation induced by the sunlight in azo-LCEs films, permitting the conversion of the solar energy in controlled isomerization-initiated mechanical motion [20, 21].

When the azomolecules are embedded in amorphous materials, the cyclic azobenzene photoisomerization, through intricate interactions with the material matrix, gives rise to a macroscopic light-driven material movement (known as mass migration phenomenon), which results in the appearance of topographic reliefs at the free surface of thin films [22–24]. The photoinduced surface structuration is very attractive for surface patterning technologies because, unlike traditional lithographic techniques, is a cost-effective method that can require simple illumination schemes and even allows to reconfigure previously structured surfaces. Taking advantage of the strong dependence of the phenomenon on the irradiated intensity pattern and the peculiar anisotropic response to the polarization distribution of the optical field over the surface, a wide range of large-scale topographical textures can be produced by tuning few illumination parameters. The largely investigated anisotropic structuration of a flat azopolymer surface is achieved with a sinusoidal intensity pattern produced by two interfering beams, that generates large-scale sinusoidal surface reliefs (the surface relief gratings, SRGs) [25]. Different degrees of surface complexity and anisotropy can be achieved acting on the illumination scheme. For example, quasicrystal surface reliefs are obtained by means of sequential inscriptions of SRGs with different orientation across the surface [6, 26, 27], and 3D topographic reliefs can be made using holographic structured intensity patterns [28, 29]. Furthermore, periodic and complex superficial topographies can also be obtained by using the light-induced material motion to reconfigure a properly structured azopolymer surface. The photo-driven reconfiguration of controlled prestructured surfaces is typically investigated for the tuning of anisotropic wetting effects (such as controlled directionality or unidirectional spreading) [30–32] or cell culture influencing [4, 33].

To date, however, the reported experimental situations have been focused on small deformations of the pre-patterned surfaces (typically with microvolumes arranged in square arrays) reaching asymmetric geometries, while maintaining, even if deformed, the discrete nature of the pristine texture [34–39].

In this work, we show the ability to reconfigure prepatterned azopolymer film surfaces in a large deformation regime. In this reconfiguration scheme, the single microvolumes of the initial 2D discrete texture are deformed until they are joined together to form continuous structures with 1D symmetry. We demonstrate that different grating-like structures, with a very high degree of anisotropy and programmable amplitude, periodicity and orientation, can be produced with this approach by simply acting on light polarization direction and light exposure dose.

The evolution of the light diffraction patterns, produced by the obtained surface textures, is used as a prototype of possible programmable functionalities achievable through our light-driven surface reconfiguration method.

The proposed approach allows remarkable flexibility in fabrication and a high degree of control over achievable surface geometries and their anisotropy.

2. Methods

2.1. Sample fabrication

Azopolymer films with prestructured surfaces were fabricated by means of a soft-lithography technique (replica molding process) as schematized in figure 1(a). The process involves two steps of fabrication: first the preparation of a polydimethylsiloxane (PDMS) mold that reproduces the negative of the desired surface pattern, and then the use of the mold to transfer the texture on azopolymer films.

2.1.1. PDMS mold

A silicon wafer, lithographically patterned with an array of micro-pillars (arranged in a square lattice of pitch $p = 10.0 \mu m$, diameter $d = 4.5 \mu m$ and height $h = 10.0 \mu m$), was used as the master template for making the PDMS molds. First, a surface antistacking treatment was performed on the master using a silanization process. The silicon wafer was exposed to the silanizing vapors (trichloro(1 H,1 H,2 H,2 H-perfluorooctyl) silane in our case) in a hermetically sealed glass box, kept at $125^\circ C$ for 90 min. Afterwards, the box was opened, and the temperature was increased to $150^\circ C$ for 90 min to remove the vapor excess. PDMS (Sylgard
Figure 1. Samples fabrication and light-induced reconfiguration of azopolymer surfaces. (a) Replica molding manufacturing steps used to produce prestructured azopolymer surfaces. The fabrication of PDMS mold starts from a silicon master lithographically fabricated (top panel). In the bottom panel, the azopolymer patterning process to reproduce the same superficial structure as the silicon master; (b) schematic of the optical setup used to reconfigure the micro-posts. The laser beam, incident on the sample surface (placed in the x–y plane) at normal incidence, is first circularly polarized using a waveplate and then reconverted to arbitrary linear polarization by a linear polarizer mounted on a rotational stage; (c) SEM image of the as-prepared array on a 1 × 1 cm$^2$ area of cylindrical micro-pillars fabricated by soft imprinting from the PDMS stamp; (d)–(e) SEM images of the azopolymer microposts reconfigured by the linearly polarized laser beam in x axis direction for 1 and 3 min of exposure, respectively. The material displacement follows the polarization direction of the incident light. The SEM images were collected with 5000× of magnification and scale bars reported in each panel are 5 µm.

184, Dow Corning) mixture was prepared by mixing the precursor and the curing agent in a 10:1 ratio by weight. After degassing in a vacuum chamber, the mixture was gently poured over the silicon master and cured at 80 °C for 120 min. At the end of the process, the PDMS mold was accurately detached from the master (see the top of the figure 1(a)) and directly used for azopolymer patterning.

2.1.2. Azopolymer thin film patterning
To obtain polymer films with prestructured surfaces, few drops of 10 wt% solution of the azo-polymer in N-methyl-2-pyrrolidone were casted onto a glass slide and then covered by the fabricated PDMS stamp. The whole system was maintained at 45°C for 12 h in order to allow the complete evaporation of the solvent, taking advantage of the porous nature of the PDMS mold. Once the process was completed, the PDMS stamp was carefully removed and a replica of the silicon master texture was realized onto the polymer film (bottom of the figure 1(a)). Details about azopolymer synthesis and its thermal and chemical characterizations are reported in previous works [34, 40].

2.2. Optical setup for azopolymer surface reshaping
In figure 1(b), the experimental configuration used to reshape the azopolymer prepatterned surfaces is schematically reported. The illumination source was a solid-state diode laser emitting at the wavelength of 405 nm. The linear polarization direction of the laser beam in the azopolymer film plane (x–y plane) is properly controlled by a quarter waveplate and a linear polarizer mounted on a rotational stage. The micropillar reconfiguration was obtained at normal incidence with intensity of approximately 200 mW cm$^{-2}$.

2.3. Morphological characterization
The 3D shape of the reconfigured grating structures was analyzed by means of scanning electron microscope (SEM) and atomic force microscope (AFM) and corroborated by the observation of the light diffraction patterns produced by the reconfigured surfaces.
2.3.1. Structural analysis
The pillar structural characterization was performed by SEM using a FEI Nova NanoSEM 450 system. The samples were previously sputtered with a nanometric layer of an Au/Pd alloy using a Benton Vacuum Desk V deposition system. The 3D topographies of the reconfigured surfaces were characterized by means of an AFM (WITTEC Alpha RAS300) [41] operating in tapping mode using a cantilever with 75 kHz resonance frequency. The AFM scans were performed over a sample area of 60 × 15 μm² with resolution of 512 × 128 pixels. The image analysis was accomplished by means of the open source software ‘Gwyddion’.

2.3.2. Diffraction light patterns
To confirm different orientations and grating pitches of the anisotropic structures produced, photographs of diffraction patterns related to reconfigured surfaces were collected. As schematized in figure 2(q), the azopolymer films were illuminated with a p-polarized He–Ne laser at λ = 633 nm at normal incidence, and the patterns were projected onto a screen placed at distance d ≈ 11.5 cm from the surface.

3. Results
The prepatterned azopolymer surfaces were prepared using the standard replica molding technique through a PDMS stamp, as schematically shown in figure 1(a) (see 'Methods' section). This structuration method produced 1 × 1 cm² azopolymer area, homogeneously patterned with a square array of cylindrical micropillars. Figure 1(c) presents the SEM image of the typical as-prepared textured polymer surface.

The first analysis involved the evaluation of the deformation regime for the micro-posts illuminated by the laser with different exposure doses. Whereby, in the initial experiment, the light intensity and the linear polarization direction, oriented along the x-axis direction of the sample plane (here defined as horizontal polarization), were kept fixed and the deformation of the pillars was analyzed as the exposure time increased. Figures 1(c)–(e) show SEM images of the sample surface collected before the illumination starts and after 1 and 3 min of film exposure, respectively. It is immediately evident that, after just 1 min of exposure, the material displacement at the top surface of the pillars produced a transition from the initial circular section to a pseudo-elliptic section [34], with the major axis oriented in the polarization direction. The increase in the exposure time resulted in an elongation of the pillars top layers, which came in contact after 3 min of irradiation. Starting from this point, the deformation at longer exposure times was so large that the pillars were definitely connected.

In this deformation regime, that we refer as large deformation regime as opposed to the deformation regimes reported so far [34–37], it is reasonable to assume that the pristine 2D array of discrete pillars is gradually transformed in a continuous and periodic 1D grating structures, with properties similar to the SRG observed when an azopolymer thin film with flat surface is structured via an interference light pattern [25, 42]. This hypothesis has been experimentally demonstrated by 3D characterization of the morphology of the azopolymer micropillars in the large deformation regime performed by means of SEM and AFM. To this aim, a study of the deformation dynamics of the pillars has been accomplished as function of the exposure time. The results are presented in figure 2. In this experiment, the light-induced pillar reconfiguration was repeated at 5, 10, 20, 30 and 60 min of exposure, while maintaining fixed the light intensity and polarization direction (vertical). The resulting superficial morphologies are shown by the SEM images in figures 2(a)–(e). After 5 min of illumination (figure 2(a)), the reconfigured pillars were already stretched along the direction of polarization with their ends in close contact, but the original positions of each pillar were still recognizable. Increasing the illumination time to 10 min (figure 2(b)), the microposts began to merge together in a single linear structure oriented along the light polarization direction, until their geometry as single discrete pillar was no longer recognizable after 20 min of illumination (as shown in figure 2(c)). SEM characterization confirms that as the exposure time increases (figures 2(c)–(e)), the reconfigured pattern becomes more and more similar to 1D superficial gratings. Additionally, to analyze the 3D properties of the reconfigured structures, we performed an AFM analysis with the aim of studying the illumination time-dependence of the structure heights. The collected AFM images for the different illumination times are reported in figures 2(f)–(j), while the figures 2(k)–(o) show the cross-section surface profiles traced along gray dashed lines. The relief heights were measured as indicated by the black arrows drawn on each topographic profile and reported as function of the exposure time in the plot shown in figure 2(p). As expected from azopolymer volume conservation during the reconfiguration process, the height of the structures decreased as the exposure time, and the resulting structural deformation, increased. The collected AFM images for the different stages of the reshaping process (figures 2(r)–(t), for pristine, and reconfigured structures at 10 and 60 min, respectively) allow a deeper insight in the dynamic of 3D structural reconfiguration of the pillars. The height...
of the pristine micropillars showed a substantial reduction in the first few minutes of the light-induced reconfiguration process, changing from the pristine 10.0 to 5.0 \( \mu m \) after 5 min of illumination. In this condition, however, while the upper layers of the pillars were largely deformed to have adjacent structures merging together, the pillars bases remained less deformed (figure 2(s)). At longer illumination times, the volume reconfiguration produced a further reduction in the amplitude of superficial architectures following a non-linear trend, until a saturation condition was reached after 30 min of exposure. SEM image in figure 2(t) shows that at this reconfiguration stage the transition from the discrete pristine 2D array to a continuous 1D grating was completed. The analysis of the 3D reconfiguration dynamics was further supported by the evolution of light diffraction patterns that the azopolymer surfaces produced at each reconfiguration step. To this aim, as schematized in figure 2(q), a camera was used to acquire the photographs of the light pattern projected, in the illumination of the azopolymer surfaces with a He–Ne laser, on an opaque screen placed at distance \( d \approx 11.5 \) cm from the sample. According to the discrete 2D geometry of the initial square array of pillars, pristine surfaces were characterized by a square 2D arrangement of diffraction spots (inset, figure 2(r)), emerging at angles predicted by Bragg’s diffraction law. For the first diffraction orders in both horizontal and vertical directions, the diffraction angles \( \theta \) in respect to the surface normal were directly related to the periodicity \( p \) of the pristine pillar array \( (\sin \theta = \lambda / p) \). However, as the pillar reconfiguration proceeded in one direction, the vertical diffraction spots of the initial 2D square pattern gradually faded (inset, figure 2(s)), until the diffraction pattern turned, in the final reconfiguration stage, into the typical one produced by a 1D diffraction grating of periodicity \( p \), oriented vertically (inset, figure 2(t)). Due to the peculiar polarization-driven directionality of the mass migration in azopolymers, the anisotropic reconfiguration of the pristine pillar pattern was repeated also for directions other than the principal ones (horizontal and vertical for the square array). In this case, the large light-induced deformation demonstrated above have produced grating structures with different orientation and periodicity, by a simple polarization rotation of the reconfiguring light beam. As an example, six gratings structures, with different periodicities and/or grating orientation, were fabricated starting from the square lattice of azopolymer micropillars. In order to select the directions for pillar reconfiguration, we considered the periodic pristine square array of pillars and we identified the positions of first, second and fourth nearest neighbors, each lying
Figure 3. Realization of programmed polarization-driven gratings. (a) SEM image of the pristine pillar lattice with a schematic representation to identify relative rotation angles to connect pillars in different directions. Dashed colored rings indicate the position of the first (in red), second (in green) and fourth (in light blue) nearest neighbors of the central micropost. Their related colored arrows indicate the directions along which microvolumes can be connected by the light-driven material motion simply by rotating the linear polarization. In particular, knowing the pitch of the array $p = 10 \, \mu m$ and choosing the vertical direction as the reference as $\theta = 0^\circ$, angles calculated from simple geometric considerations are $\theta_{I,1} = 0^\circ$, $\theta_{I,2} = 90^\circ$; $\theta_{II,1} = 45^\circ$, $\theta_{II,2} = 135^\circ$; $\theta_{IV,1} = 26^\circ$, $\theta_{IV,2} = 116^\circ$; (b) detail of the optical setup scheme reported in figure 1(b). Circularly polarized incident light passes through a linear polarizer mounted on a rotational stage. The direction of output linear polarization is determined by the orientation of the transmission axis. Polarization states are indicated by the yellow arrows; (c)–(h) SEM images collected with magnification of 5000× on reconfigured surfaces obtained by rotate the light polarization by angles calculated and using a laser intensity approximately of 200 mW cm$^{-2}$ for 16 min of exposure time. The polarization directions are indicated by the yellow arrow shown in each panel. For all SEM images the scale bars are 5 µm. (i)–(n) Photographs of diffraction patterns produced by illumination of the azopolymer films reconfigured shown in (c)–(h) at normal incidence with an He–Ne laser at $\lambda = 633$ nm. The scale bars are 1 cm.

on the respective colored ring drawn on the SEM image shown in figure 3(a) (the third nearest neighbors are not mentioned since they lay in the same directions identified for the first neighbors). For each nearest neighbor, the relative arrows indicate the directions of the shortest distances between adjacent structures. The micropillars can be elongated and connected together along the identified directions using the light-induced reshaping, resulting in 1D architectures with three different periods.

In each reconfiguration experiment, the linear polarizer was rotated to match the desired polarization direction for the reconfiguring laser beam, as schematically represented in figure 3(b). The laser intensity (200 mW cm$^{-2}$) and the illumination time (16 min) were kept fixed for all the reconfiguration experiments. The SEM images of the surface at the end of the different directional reconfiguration processes are reported in figures 3(c)–(h), together with their He–Ne diffraction patterns (figures 3(i)–(n)). In each panel, the reconfiguring polarization direction is represented by the yellow arrow. This direction is orthogonal to the grating vector of the 1D periodic pattern obtained as result of the reconfiguration of the micro-posts. As expected, according to the geometry of the pristine array, the obtained gratings presented the three different periodicities $p_1 = 10 \, \mu m$, $p_2 = p_1 / \sqrt{2}$ and $p_3 = p_1 / \sqrt{5}$, and two sets of grating orientations as confirmed by SEM analysis and light diffraction patterns in figures 3(i)–(n), which quantitatively reproduced the diffraction angles predicted for the first diffraction orders by Bragg’s relation with the relative grating periodicity ($\sin \theta_i = \lambda / p_1$).
4. Conclusions

We have demonstrated that the light-induced reconfiguration of prestructured surfaces of materials containing azobenzene molecules is a suitable approach to produce a high degree of superficial structural anisotropy. This technique is relevant for several application fields in which the topography controls surface functionalities.

Here we reported the experimental analysis of the process of the light-induced reconfiguration of an array of azopolymer cylindrical micropillars, which produce structured surfaces with controlled degree and orientation of structural anisotropy, exploiting the polarization sensitivity of azopolymer structuration. In particular, morphological analysis conducted on the reshaped surfaces has shown that, after a reasonable exposure time of a few minutes, the transition from small to large deformations regime allows to reconfigure a discrete texture in a continuous and periodic grating, characterized by few microns in height and high degree of structural anisotropy.

Additionally, by simply varying the direction of the reconfiguring light polarization, even different grating periodicities are easily achievable starting from the same prestructured array, bringing to a versatile and cost-effective surface structuration technique.

This approach could even be generalized to achieve higher degrees of anisotropy and complexity of textured surfaces, for example by multistep sequential irradiations of the same prepatterned surface, changing the polarization directions, or even using more complex polarization states (such as radial or azimuthal polarization), besides different pre-structuration configurations.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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