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Photo-responsive suspended micro-membranes

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Light-responsive devices are becoming increasingly relevant in many applications ranging from soft-robotics, energy harvesting, regenerative medicine and tissue engineering. Here we present a two-photon fabrication process based on a photocurable azopolymeric compound that we successfully employed to manufacture suspended micro-membranes. Thanks to the incorporation of azobenzene units, the membranes are shown to exhibit a remarkable mechanical photo-responsivity despite the disordered, amorphous structure of the crosslinked network. When irradiated with a focused laser beam at 532 nm wavelength, a reversible shape modification is observed, with a linear expansion coefficient as large as 28%. This effect is accompanied by a refractive index decrease of about 0.16, as measured interferometrically. The initial state of the membrane is fully recovered when the irradiation is switched off, as the cyclic photoisomerization process is stopped. The presented approach can be extended to light-induce complex modifications of the mechanical features in 3D printed objects by remotely providing arbitrary illumination patterns.

The rapid development in new micro and nano-fabrication technologies over the last decade has driven massive research interests in smart devices based on stimuli-responsive polymers.¹ These are materials whose structural, optical or morphological properties can be reversibly varied upon external stimuli such as environmental pH, temperature, acoustic waves, electric and magnetic fields, electromagnetic waves and radiation.²⁻⁴ In particular, the use of light as a

trigger is very attractive, as it can be remotely provided according to arbitrary spatio-temporal patterns at different wavelengths and polarization states, without the need of direct wire connections on the target device. Light responsivity is typically obtained by using photo-switchable units either chemically bound to the polymer chains or simply dispersed within the network.⁵ Azobenzene-containing chromophores are among the most popular molecular photoswitches⁶ thanks to their ability to undergo a conformational change between two isomeric states, –trans and cis–, upon UV or visible light absorption.^{7,8} By designing proper aromatic ring substitutions or supramolecular environment for the azo-units, such that the two isomers exhibit significantly overlapping absorption bands and short lifetimes,^{9,10} the isomerization process can be made cyclic and triggered by a single wavelength radiation.

Photoisomerization in azobenzene-containing polymers plays a crucial role in phenomena such as athermal directional photofluidization,^{11,12} plastic deformation¹³⁻¹⁶ and mass migration.^{17,18} In those formulation wherein azobenzenes are embedded in crosslinked networks, the trans-cis isomerization can result into a macroscopic mechanical photo-actuation¹⁹ eventually accompanied by a reversible change of the Young modulus.²⁰ Light-induced actuation can be greatly enhanced when Liquid Crystalline Networks (LCN) are used as host matrices for the azo-units. In these cases, the trans-cis-trans isomerization affects the spatial ordering in which LC molecules are packed within the polymeric network,^{21,22} thus giving rise to a long-range contraction-expansion effect along specific directions, depending on the LC molecular alignment.²³⁻²⁵ LCN-based fabrication technology²⁶⁻²⁹ has become particularly effective for the 3D manufacturing of miniaturized soft-transducers and energy harvesters, as recently demonstrated by a number of light-fueled machines³⁰ able to oscillate,^{31,32} walk,³³⁻³⁵ swim,^{36,37} twist,³⁸ grab objects,³⁹ produce electric power⁴⁰ when properly illuminated.

In this work, we manufacture a 3D suspended membrane by means of two-photon lithography, a high-resolution 3D printing technique based on 3D localized polymerization through multiphoton absorption,^{41,42} on an amorphous

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photocurable acrylate resin containing an azopolymer and demonstrate its mechanical photo-responsivity upon single wavelength laser illumination. Differently from LCNs, the light-induced mechanical modification in disordered materials is isotropic and rather localized to the irradiated area, with a limited long-range effect. This aspect is advantageous in applications such as light-responsive scaffolds for cell cultures,⁴³ wherein expansion-contraction is desired only at specific locations. The light-induced mechanical actuation here is generally occurring as a volume expansion,⁴⁴ followed by a contraction due to elastic restoring forces when the illumination is off, as discussed in the following. As a result, local variations of the polymer refractive index are also produced.⁴⁵ Both light-induced volume and refractive index changes under ON and OFF illumination conditions are quantitatively investigated by means of an interferometric characterization, which can be performed thanks to the planar geometry of the membrane. The 3D suspended membrane proposed here represents an ideal platform for investigating the light-responsivity of the polymeric network, as most of the physical interactions with the underlying substrate are minimized.

Membranes have been fabricated by two-photon lithography according to the 3D geometry shown in Figure 1a, whereby a squared top slab, with nominal 120 μm -long sides and 4 μm thickness, lays on four squared pillars 28 μm tall and 15 μm side. The curable resin employed consists of a diacrylate monomer, Bisphenol A Ethoxylate Diacrylate, Mn 512 (BEDA), a photoinitiator, phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPOs), and an azopolymeric compound, Disperse Red 1 Methacrylate (DR1M), as shown in Figure 1b. The diacrylate

monomer provides a passive crosslinked mesh, once polymerized, while the azopolymer provides light-responsivity based on the well-known photo-isomerization effect.⁷ In Figure 1c an electron microscope image of an illustrative fabricated membrane is presented. More details on the fabrication process can be found in the Experimental section.

[FIGURE 1]

Figure 1. (a) Sketch of the membrane layout; (b) electron microscope image of a fabricated suspended membrane; (c) molecular structures of the azopolymer and UV-curable resin used for fabrication.

Membranes are investigated by means of an optical setup able to provide white light and laser interferometric imaging. As shown in Figure 2a, the interferometric imaging system is based on a Mach-Zehnder scheme. By this means, a quantitative estimation of the optical path length travelled by the transmitted light on a pixel-by-pixel basis can be retrieved.⁴⁶ As an example, from measured wrapped and unwrapped⁴⁷ phase distributions shown in Figure 2b and Figure 2c respectively, it is possible to appreciate thickness inhomogeneities of the fabricated membranes, as confirmed by phase-contrast white-light images (Figure 2d). The setup is also equipped with a frequency doubled Nd:YAG laser at $\lambda = 532$ nm wavelength, used to trigger photo-actuation effects in the polymer. After being spatially filtered, expanded and focused, a confined spot is produced onto the membrane as shown in Figure 2e.

[FIGURE 2]

Figure 2. (a) Scheme of the interferometric imaging system; (b) wrapped and (c) unwrapped phase distribution of an exemplary membrane and (d) corresponding phase-contrast optical image highlighting thickness inhomogeneity; (e) white-light image of another exemplary membrane under laser illumination.

Light-responsivity is investigated after switching on and off the focused $\lambda = 532$ nm laser beam onto the membrane. A proper fitting of the laser intensity recorded on the camera allows us to estimate the laser distribution as a Gaussian function $I(x, y) = I_0 \exp \left[-2 \cdot \frac{(x-x_0)^2 + (y-y_0)^2}{\sigma^2} \right]$, where I_0 is the maximum light intensity, x_0 and y_0 identify the spot center in the membrane plane coordinates and $\sigma = 17$ μm .

Due to the expansion of many azopolymer-containing compounds⁴⁸ upon light irradiation, pushing forces result to be exerted over the membrane in radial and vertical directions. The amount of deformation is proportional to the illumination light intensity and the overall volume of the irradiated polymer region. When observing the membrane from a top view during laser irradiation, a reversible lateral expansion can be readily appreciated both in the interferometric images and in the white-light images (see Movie M1). Once the laser is switched on/off, a corresponding expansion/contraction of the membrane occurs on time scales of about 1 second. Figure 3a and Figure 3b show the interferometric images of an

illustrative membrane at dark and under laser irradiation, respectively.

[FIGURE 3]

Figure 3. Top-view interferograms of a membrane at dark (a) and laser-illuminated (b). Membrane edges are reversibly displaced by about 2.5 μm during irradiation of the membrane center (see Supporting Movie M1).

A closer look to the membrane edges allows to directly evaluate a spatial shift of about 2.5 μm of each membrane side, leading to an overall linear expansion $\Delta t \approx 5$ μm along each perpendicular direction, when both opposite edges are taken into account. Correspondingly, the surface area S is roughly expanded by $\Delta S = 1225$ μm^2 . This value is likely overestimated, as the membrane expansion is more limited at the corners, where the pillars introduce strong mechanical constraints. It should be observed, however, that the membrane is only partially illuminated, as the laser intensity follows the spatial distribution $I(x, y)$ described above. Due to

the small thickness of the membrane, we assume the Gaussian beam intensity as invariant along the (longitudinal) z-direction. It is then possible to estimate a surface expansion coefficient α_s , such that a corresponding surface increase $\Delta S = \iint \alpha_s \cdot w(x, y) dx dy = 1225 \mu\text{m}^2$ is obtained over the membrane plane. The function $w(x, y) = I(x, y)/I_0$ is a normalized dimensionless weighting function conformal to the laser intensity distribution used for illumination. A numerical solution of the integral leads to $\alpha_s = 0.566$, for an overall laser power of about 50 mW. This simplified model considers surface and thickness expansions as decoupled, leading to independent linear expansion coefficients $\alpha_L = \frac{1}{2}\alpha_s = 0.283$ along each of the three orthogonal Cartesian directions. More interestingly, the photo-induced expansion also occurs perpendicularly to the membrane plane. The interferometric approach presented here can provide a quantitative measurement of the optical path length change across the membrane thickness. However, as the optical path depends on both the physical path length and the refractive index of the medium travelled by light, such a measurement takes into account both the photo-induced expansion previously discussed and the photo-induced refractive index changes, which are known to be common in azopolymeric compounds.^[45,49] The two effects are both present in our samples and cannot be decoupled without using additional a priori information. In Figure 4, phase images of two representative membranes are shown.

At dark (laser off), the measured (unwrapped) phase maps $\Phi_{OFF}(x, y)$ show a concave light wavefront (Figure 4a and Figure 4e), meaning that the transmitted light through the membrane experiences an increasing delay as it passes closer and closer to the membrane center. This observation indicates that the membrane thickness is inhomogeneous, the membrane being thicker at the center as compared to the edges. When the green laser illumination is switched on (50 mW, corresponding to a 3.8 kW/cm² peak intensity), the membrane expands rapidly and reaches a mechanically stable, steady state allowing a further phase mapping $\Phi_{ON}(x, y)$ to be performed, as shown in Figure 4b and Figure 4f. Remarkably, the phase change $\Delta\Phi(x, y) = \Phi_{ON}(x, y) - \Phi_{OFF}(x, y)$ is positive with a convex shape (Figure 4c and Figure 4g), thus indicating that the irradiated area has been (reversibly) made optically thinner. The Nd:YAG ($\lambda=532$ nm) beam and the interferometer ($\lambda=633$ nm) beam are both linearly polarized, with electric fields reciprocally perpendicular. Cross-sectional profiles along the x direction, passing through the laser spot, reveal a maximum phase change $\Delta\Phi_{MAX} = 1.37\pi$ (Figure 4d) and $\Delta\Phi_{MAX} = 1.43\pi$ (Figure 4h). Additional measurements on similar membranes lead to similar variations in measured phase. Birefringence effects, which have been shown to occur in similar systems,⁵⁰ involve a typically lower refractive index variations in such amorphous materials and are neglected here.

[FIGURE 4]

Figure 4. Unwrapped phase distributions of light transmitted through two representative membranes (a,e) kept at dark and (b,f) under focused laser illumination; (c,g) light-induced phase difference distribution across the membrane surface; (d,h) cross-sectional phase profiles along an horizontal cut passing at the membrane center. The membrane considered in (a-d) is the same membrane presented in Figure 3 and Figure 5.

From the concave shape of the measured phase profile at dark, an overall phase difference $\Delta\Phi_{conc} = \Phi_{edge} - \Phi_{center}$ between membrane edges and center can be evaluated as $\Delta\Phi_{conc} = 7\pi \pm \pi$ for both membranes. This translates into a thickness change $\Delta t = \frac{\lambda}{2\pi(n-1)} \Delta\Phi_{conc} \cong 4.2 \mu\text{m} \pm 0.6 \mu\text{m}$, where $\lambda=633$ nm is the interferometer beam wavelength and $n=1.53$ is the BEDA refractive index (from Sigma Aldrich specifications). Such a thickness variation is confirmed by side-view electron microscope images, as shown in Figure 5, referred to the membrane characterized interferometrically in Figure 4.

[FIGURE 5]

Figure 5. Side-view electron microscope images of an exemplary membrane showing the thickness inhomogeneity along the side edge, in accordance with the interferometric measurements.

Since the membrane is expanding and the phase variation $\Delta\Phi_{MAX}$ is positive upon laser illumination, the refractive index of the polymer needs to decrease, in order to compensate for such an expansion. Taking into account a simultaneous variation of the membrane thickness and refractive index, it is possible to express the maximum phase variation as $\Delta\Phi_{MAX} = \frac{2\pi}{\lambda} [(n-1) \cdot t_{off} - (n-\Delta n-1) \cdot t_{on}]$, where Δn is the absolute value of the refractive index change, t_{off} and t_{on} are the membrane thicknesses at dark (not expanded) and under illumination (expanded) respectively. After a little algebra, the maximum refractive index change can be written as $\Delta n = \left[\frac{\lambda}{2\pi} \Delta\Phi_{MAX} + (n-1) \cdot (t_{on} - t_{off}) \right] \cdot t_{on}^{-1}$. Worth to observe that membrane expansion along the z-direction can be calculated as $t_{on} - t_{off} = \int \alpha_L dz = \alpha_L \cdot t_{off}$, as the integral is extended over the whole membrane thickness. In Figure 6, the refractive index change $\Delta n(\alpha_L, t_{off})$ is plotted as a 3D surface as a function of the linear expansion coefficient α_L , and the membrane thickness t_{off} , with a constant phase variation equal to the measured $\Delta\Phi_{MAX} = 1.37\pi$.

[FIGURE 6]

Figure 6. Iso-surface representing a light-induced membrane deformation corresponding to $\Delta\Phi=1.37\pi$, as a function of the linear expansion coefficient α_L and the maximum thickness t_{off} of the membrane. For $\alpha_L = 0.283$ and $t_{off} = 9 \mu\text{m}$, a maximum refractive index (negative) variation is found as $\Delta n=0.16$.

On this surface we can find all possible Δn values resulting in a phase change equal to the measured $\Delta\Phi_{MAX}$, for different combinations of α_L and t_{off} . Recalling that the linear expansion coefficient has been previously determined as $\alpha_L = 0.283$, and

the membrane thickness at the center is $t_{off} \cong 9 \mu\text{m}$, we estimate a maximum refractive index decrease $\Delta n \cong 0.16$ upon irradiation with a 50 mW beam focused down to a Gaussian spot as wide as about $30 \mu\text{m}$. Such a value is consistent with previous observations on azopolymeric compounds.⁵¹

Conclusions

In conclusion, we demonstrate the fabrication of light-responsive suspended micro-membranes by successfully employing two-photon lithography on an azopolymer-containing photocurable acrylate formulation. Despite the disordered, amorphous structure of the crosslinked network BEDA-DR1M, we observed relevant light-induced deformations and refractive index changes. When irradiated with a 50 mW green laser, membranes show a volume increase followed by a relaxation to the initial state when irradiation is switched off. Expansion/relaxation processes occur over time scales of seconds, similarly to other crosslinked compounds containing DR1M.⁴⁵ During the expansion, the refractive index along a direction parallel to the polarization of the green laser is observed to decrease by an amount estimated as $\Delta n = 0.16$. Such expansion/contraction behavior is reversible and can be repeated several tens of times, till the azo-dyes are bleached. Our finding can be particularly useful in the emerging domain of smart, light-responsive scaffolds for cell cultures,^{52,53} wherein local mechanical cues have to be arbitrarily provided with minimally invasive external stimuli.

Experimental Section

Membrane fabrication. Membranes are squared, with nominal $120 \mu\text{m}$ -long sides and $4 \mu\text{m}$ thickness. They lay on four squared pillars $28 \mu\text{m}$ tall and $15 \mu\text{m}$ side. In order to improve adhesion onto the glass substrate, a thin squared-holed base is fabricated beneath the pillars. The curable resin consists of a diacrylate monomer, Bisphenol A Ethoxylate Diacrylate, Mn 512 (BEDA), a photoinitiator, phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPOs), and an azopolymeric compound, Disperse Red 1 Methacrylate (DR1M). In order to overcome issues associated to the formation of aggregates, it is possible to either dissolve the azopolymer into the resin by means of a magnetic stirring or dissolve the azopolymer into a proper solvent first and then add the dissolved azopolymer to the resin. However, the use of a solvent in the blend preparation should be avoided, as it can result in the formation of nanocavities during the lithography process. DR1M has been employed because of the absorption tail in the green region and the good solubility into the BEDA monomer, resulting in a complete and homogeneous blend. The commercially available DR1M azopolymer and the BAPOs photoinitiator are directly added to the liquid monomer BEDA in a ratio of 1:2:97. All materials are purchased from Sigma-Aldrich. The solution is magnetically stirred for several hours at 400 rpm, maintaining a constant temperature at 40°C . As a result, a clear and transparent light red solution is obtained.

The suspended membranes are fabricated by means of a commercial two-photon lithography system (Photonic Professional GT, Nanoscribe GmbH, Germany), equipped with a high magnification oil immersion objective (Zeiss 100X NA 1.4). Immersion oil is index-matched to the glass substrate and, hence, allow for ideal focusing in the photoresist, which is casted on top of the glass substrate. Immersol 518 F immersion oil (Thermo Fisher Scientific, USA) is used as index-matching medium. The fabrication is carried out with the following optimized parameters: Laser Power 50 mW, Scan Speed $15000 \mu\text{m/s}$, Slicing $0.3 \mu\text{m}$, Hatching $0.1 \mu\text{m}$. The shape of the structures is designed with a CAD software (SolidWorks). Once fabricated, structures are developed in tetrahydrofuran (THF) by rinsing for 5 minutes.

Raman Spectroscopy Characterization. Raman micro-spectroscopy (Aramis, Horiba, France) is employed to check the homogeneity of degree of polymerization crosslinking across the suspended membranes. The characteristic peaks of the monomer, the azopolymer and the photo initiator can be easily identified in the reference spectra (see Figure 7).

[FIGURE 7]

Figure 7. Raman spectra of the three components of the photocurable resin; b) overlay of the Raman spectra measured at 3 different points across a representative membrane.

The crosslinking homogeneity of the suspended membrane is evaluated by comparing spectra in several different points, taken across the membranes (three illustrative points are considered in Figure 7). A decrease of the vinyl C=C stretch peak intensity at $\sim 1635 \text{ cm}^{-1}$ after polymerization is considered as representative of a successful crosslinking. As the peak intensity is almost constant, we conclude that the suspended membrane is rather homogeneously crosslinked during the writing process. Therefore, no further UV irradiation has been generally provided.

Interferometric Imaging system. The interferometric imaging system is based on a Mach-Zehnder setup. A He-Ne laser beam ($\lambda = 633 \text{ nm}$) is expanded and split into a reference beam and an object beam by means of a polarizing beam splitter (PBS). The intensity and polarization of the reference beam can be controlled by means of a neutral density (ND) filter and a Half Wave Plate (HWP). The object beam is reflected by a piezo-actuated mirror (Physik Instrument), which sequentially provides five $\pi/2$ -phase shifts for phase retrieval.^[46] The object beam illuminates the sample and the transmitted light is collected by a high-NA objective (Olympus, 100x 0.95 NA). An image of the object is then produced onto a CMOS camera (Thorlabs DCC14p35M) by using a tube lens (TL). Thanks to the high magnification of the high Numerical Aperture (NA) objective, it is possible to observe individual membranes completely filling the field of view. On the image plane, the superposition of the object and reference beams results in interferograms that are recorded for each phase shift provided by the piezo-mirror. Phase maps are obtained by combining the collected interferograms. Since the phase calculation is

performed by means of an inverse tangent operation, the resulting phase values are typically ranging between $-\pi$ and π (the so-called wrapped phase). A suitable algorithm based on the Goldstein method is then used to unwrap phase maps,^[47] which allows a quantitative estimation of the optical path length travelled by the transmitted light on a pixel-by-pixel basis. The system is also equipped with a frequency doubled Nd:YAG laser emitting a TEM₀₀ Gaussian beam at $\lambda = 532$ nm wavelength, with power up to 200 mW. After it has been spatially filtered, expanded and focused by means of a 10x objective (Focusing stage), a confined spot is produced onto the membrane. The maximum incident power onto the sample can reach 100 mW. Transmitted green light is blocked by an edge filter (Semrock RazoEdge MaxLine 532) positioned along the optical path of the image formation system, in such a way as to not affect the resulting collected interferograms

Conflicts of interest

There are no conflicts to declare.

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Figure 1. (a) Sketch of the membrane layout; (b) electron microscope image of a fabricated suspended membrane; (c) molecular structures of the azopolymer and UV-curable resin used for fabrication.

67x39mm (300 x 300 DPI)

Figure 2. (a) Scheme of the interferometric imaging system; (b) wrapped and (c) unwrapped phase distribution of an exemplary membrane and (d) corresponding phase-contrast optical image highlighting thickness inhomogeneity; (e) white-light image of another exemplary membrane under laser illumination.

38x22mm (300 x 300 DPI)

Figure 3. Top-view interferograms of a membrane at dark (a) and laser-illuminated (b). Membrane edges are reversibly displaced by about 2.5 μm during irradiation of the membrane center (see Supporting Movie M1).

48x48mm (300 x 300 DPI)

Figure 4. Unwrapped phase distributions of light transmitted through two representative membranes (a,e) kept at dark and (b,f) under focused laser illumination; (c,g) light-induced phase difference distribution across the membrane surface; (d,h) cross-sectional phase profiles along an horizontal cut passing at the membrane center. The membrane considered in (a-d) is the same membrane presented in Figure 3 and Figure 5.

68x101mm (300 x 300 DPI)

Figure 5. Side-view electron microscope images of an exemplary membrane showing the thickness inhomogeneity along the side edge, in accordance with the interferometric measurements.

23x9mm (300 x 300 DPI)

Figure 6. Iso-surface representing a light-induced membrane deformation corresponding to $\Delta\Phi = 1.37\pi$, as a function of the linear expansion coefficient α_L and the maximum thickness t_{off} of the membrane. For $\alpha_L = 0.283$ and $t_{\text{off}} = 9 \mu\text{m}$, a maximum refractive index (negative) variation is found as $\Delta n = 0.16$.

42x31mm (300 x 300 DPI)

Figure 7. Raman spectra of the three components of the photocurable resin; b) overlay of the Raman spectra measured at 3 different points across a representative membrane.

38x65mm (300 x 300 DPI)

Table of Contents

A light-responsive 3D micro-membrane capable of mechanical photo-actuation is fabricated by means of high-resolution two-photon lithography on an azopolymer-doped acrylate resin.