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Photoinduced doughnut-shaped nanostructures

A.M. Dubrovkin [a,b], R. Barillé [a,*], E. Ortyl [c], S. Zielinska [c]

[a] LUNAM Université, Université d'Angers/UMR CNRS 6200, MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers, France
[b] Division of Physics & Applied Physics, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[c] Department of Polymer Engineering and Technology, Wroclaw University of Technology, Faculty of Chemistry, 50-370 Wroclaw, Poland

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ABSTRACT

We show that an incoherent unpolarized single-beam illumination is able to photoinduce nano-doughnuts on the surface of azopolymer thin films. We demonstrate that individual doughnut-shaped nano-objects as well as clusters of several adjacent nano-doughnuts can be formed and tailored with wide range of typical sizes, thus providing a rich field for applications in nanophotonics and photochemistry.

Azopolymer nanostructures are recognized as an excellent choice for a broad range of fundamental and applied research in modern nanotechnology. Owing to unique photomechanical properties [1,2] of azopolymers, these nanostructures show the perfect performance in photoinduced nanopatterning and reshaping by tailored light fields [3,4]. Unprecedented flexibility of recently reported photofluidization lithography allows producing well-defined lines, ellipsoids, rectangles and circles on azopolymer surface with structural features of several tenth nanometers [5]. Self-organization is also one possible solution to obtain nanostructures. Micro-droplets of polystyrene solutions on surfaces were used to obtain typical structures like micro-size domes [6]. Other experiments have shown the possibility to create meso-patterning of thin film polymers by controlled dewetting [7]. A 2-D array of femto-litter beakers best described as nano-membrane were investigated by the dewetting of PS film on complex patterned surfaces and exposition to toluene vapor. However the size of the holes is a function of the dimensions of the holes on the underlying substrate. Azopolymer nanostructures are created by illumination with a laser or laser pattern, and an incoherent light from UV-lamp or LED is most frequently used for optical erasing [8]. Another related experiment was performed by illuminating the azobenzene film by a strip-like uniform light pattern formed due to the use of an optical mask [9]. Depending on the polymer architecture either peaks or trenches were observed in the illuminated strips. Laser induced surface deformations were investigated in azobenzene functionalized polymers with one [10] or two-photon isomerization [11] but the obtained patterns were highly dependent of the laser polarization. A good efficiency was obtained with a circular polarization. The width of the deformation induced by the laser was around 2 μm and difficult to overcome with current conventional optics. Moreover two-photon isomerization needs a high power peak laser. Nano-structures were obtained by near-field light generated by an optical fiber probe with a very small aperture diameter of about 50 nm [12] or 120 nm [13]. However the particular set-up for generating near-field light is suitable for evaluation of the response of materials to nano-processing but not for large scale patterns.

Examples of quite rare utilization of incoherent white-light for thin film regular photopattering and reshaping of a single azopolymer nano-sphere has been recently demonstrated [14]. In the last case the size of the nano-objects is sufficiently small to limit the random directions of molecular movements. The use of incoherent light is a promising technique in the case of formation or patterning of nano-objects with dimensions in the order of the coherence property of light. Moreover this technique requires only cheap optical sources. By an exposure of light, azopolymers can produce complex nanostructures such as directed nanoparticle assemblies [15].

In this work we experimentally demonstrate a simple bottom-up approach to form doughnut-shaped nanostructures at the tailored surface of an azopolymer film by an incoherent unpolarized light illumination. The key difference in our approach is the use of an incoherent light for growing nanostructures rather than for optical erasing, and simultaneously directing the final shape of a nanostructure by the initial seed of tiny nanoscale holes.

Doughnut-shaped nano-structures (including nano-doughnuts, nano-rings, nano-toroïds and in particular the example of nano-wells), being a reach object for fundamental study of light localization at nanoscale, have also recently attracted attention due to their efficient use in nano-plasmonics, photochemistry, nano-rectors and sensors. Several successful approaches were developed to produce organic and inorganic doughnut-shaped nanostructures by chemical synthesis and self-assembling [16] as well as colloidal [17] and

* Corresponding author.
E-mail addresses: alexandre.dubrovkin@univ-angers.fr (A.M. Dubrovkin), regis.barille@univ-angers.fr (R. Barillé).

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optical [18] lithography. However they are limited to fabrication of non-reshapeable nanostructures that makes them inefficient for the study of size-dependency of optical and photochemical properties of these structures and their applications to nanoreactors. It remains that a method to produce doughnut-shaped nanostructures with a photoinduced material as azopolymer has not been suggested in the literature. Furthermore all mentioned approaches require relatively complicated fabrication procedures. An example is the fabrication of polymer dot arrays with Electron Beam Lithography [19] that requires a multistep process with dewetting of e-beam exposed film immersed in a mixture of liquids and is considered slow for large area nanopatterning without possibilities to zreshape the structures. Polymer thin films are made from a highly photoactive azobenzene derivative containing heterocyclic sulfonamide moieties (ISO1). The details of synthesis of 2-[{4-[(E)-(4-{[(2,6-dimethyl pyrimidin-4-yl)amino]sulfonyl}phenyl)diazen yl]-phenyl}-(methyl)amino]ethyl2-methylacrylate (Figure 1a) are reported elsewhere [20]. The thin films are prepared by dissolving 75 mg of azopolymer in 1 ml of THF (Tetrahydrofuran), spin-coated on clean glass substrate and let in an oven at 60 °C during one night to eliminate residual solvent. The film thickness was determined with a Dektak profilometer and was around 550 nm. The molecular weight of the polymer determined by GPC was between 14000 and 19000. The glass transition temperature (T_g) was 71 °C. Figure 1a and c shows topography images of the film obtained with different resolution by atomic-force microscope (AFM, Veeco Instruments Inc.) in the tapping mode. The surface of the film is covered with randomly placed nano-holes with a mono-dispersed diameter but with different depths. A typical height cross-section of the film corresponding to dashed lines on AFM images is presented in Figure 1b, d. The topography analysis shows that 'big depth' nano-holes have heights of 10–35 nm with full widths at a half minimum (FWHM) of 350–500 nm. 'Small depth' nano-holes have heights of 5–10 nm with FWHM of 60–100 nm. The appearance of nano-holes at a polymer film can be achieved by different methods. One is the use of several disturbing factors in the spin-coating procedure such as a non uniform evaporation of a solvent, a presence of small air bubbles and traces of a different solvent (water) in the polymer solution [21]. These methods are difficult to control and the final result is non reproducible. Here we address the issue to create nano-holes easily reproducible with a monosize diameter on a surface of an azopolymer film. The method chosen is a solvent-droplet-induced-dewetting of thin azopolymer films on glass substrates. The contact of a thin polymer film to a solvent droplet reduces the glass transition temperature to below the room temperature as the solvent molecules penetrate into the film matrix. The stable polymer thin film is destabilized by the introduction of polar interactions. More informations on the surface topology observed with spontaneous hole development in thin polymeric films can be found elsewhere [22]. A 3 µl droplet of THF (Tetrahydrofuran) is dropped off on the

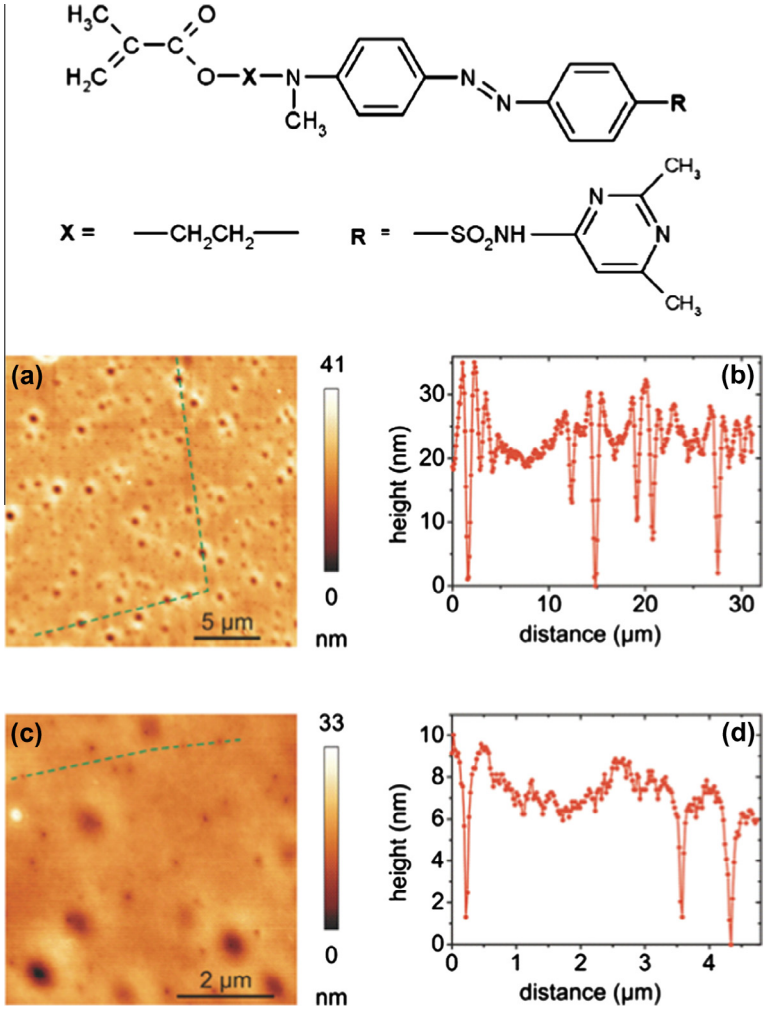

Figure 1. Chemical structure of azopolymer thin film and AFM characterization of the surface. (a, b) A typical topography and corresponding height cross-section shown by the dotted line. (c, d) Zoom of the topography obtained by AFM scanning in the centre part of the region presented in the image (a) and corresponding cross-section.