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Instantaneous photoinduced patterning of an azopolymer colloidal nanosphere assembly

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Abstract: Colloidal azopolymer nanospheres assembled on a glass substrate were exposed to a single collimated laser beam. The combination of photo-fluidic elongation of the spherical colloids and light induced self-organization of the azopolymer film allows the quasi-instantaneous growth of a large amplitude surface relief grating. Pre-structuration of the sample with the nanosphere assembly supports faster creation of the spontaneous pattern. Confinement into the nanospheres provides exceptionally large modulation amplitude of the spontaneous relief. The method is amenable to any kind of photoactive azo-materials.

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OCIS codes: (160.4236) Nanomaterials; (190.5940) Self-action effects.

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1. Introduction

Derivatives of azobenzene are candidates for the remote optical control of molecules owing to their efficient and reversible *cis-trans* photoisomerization around the azo-bond [1]. Numerous applications result from the geometric changes happening when azo-chromophores are incorporated into polymers and other materials. Typical examples are the non-invasive remote control of surface properties, photo-patterning, nanofabrication, artificial muscles [2] and directional cell growth [3]. The term photo-fluidization was introduced to account for this repeated photoisomerization phenomenon evidenced in different experiments where a decrease by several orders of magnitude of the local polymer film viscosity was observed [4]. The phenomenon was confirmed by molecular simulation dynamics [5]. The directional photofluidization of azopolymer experienced with two orthogonal canals prepared by holography on an azopolymer film proved strongly dependent on the polarization [6]. Irradiation by linear polarized light demonstrated the anisotropic mechanical behavior. The material filled up in the direction parallel to the light polarization, behaving like a fluid, whereas the canal stayed empty in the direction perpendicular to the light polarization. The same phenomenon also led to the creation of nano-textures using one-beam irradiation on azopolymers [7], to the achievement of a scalable and parallel nano-texturing with a controlled complexity [8] and to new directions in metrology applications [9]. However, expanding these results to large areas, fast patterning, and a deterministic nano-texturing has not been realized yet. This would lead to significant added value in practical applications requiring the extensive use of such periodic nano-textures. None of the methods available today was able to produce surface patterns with easily variable design possibilities while keeping the technique of fabrication simple, fast and cost-effective. This is the reason why we propose to use single beam patterning, with which a scanning of the surface under varying angle of incidence and polarization direction is possible, which cannot be achieved using interferometric techniques. When azopolymer nano-objects with different topological dimensions like nanotubes or nanospheres are illuminated, the spatially confined excitation leads to a unidirectional motion. The photoinduced shape deformation of azopolymer colloidal spheres was recently evidenced using incoherent and unpolarized light [10]. White light flattens the nanospheres and increases their diameter by up to 20%. Besides the usual

spin-coating method, the assembly of colloidal micro- or nano-spherical particles is another technique to produce ultra-thin films. Monolayer or bilayer colloidal crystal films made of self-assembled nanospheres are used in a variety of applications in which their structure can develop into photonic crystals, chemical sensors and anti-reflective coatings [11].

Here we report on the study of mass transport in azopolymer colloidal particles having a dimension in the nanometer range. The azopolymer colloidal spheres are organized into a thin film onto a substrate. Two phenomena occur into the sample: first one is a modification of the nanosphere shape; second one is the enhancement of the modulation depth of the self-induced patterning. We show in this work that the azopolymer nanoparticle assembly can be used as an alternative material to photoinduce a surface relief grating with a single laser light beam. Mechanical stretching of the spherical colloids allows construction of a pattern after a very short time together with exceptionally large depth of photoinduced nano-structuration. Patterning happens faster than in a homogeneous thin film made with the same material and it is as fast as in thin films of an azobenzene-containing epoxy resin [12]. The study offers a physical means for accelerating the formation of surface relief gratings in azopolymer materials without acting on the chemical formulation. The peculiarity of photoinduced mass transport in an assembly of nanospheres allows ultrafast self-organization into a steep surface relief grating.

2. Experiment

2.1. Azopolymer

The colloidal spheres under study were prepared from a highly photoactive copolymer synthesized by radical copolymerization of an equimolar mixture of photoisomerizable azobenzene group containing 2-[4-[(E)-[4-(acetylsulfamoyl) phenyl]azo]-N-methyl-anilino]ethyl 2-methylprop-2-enoate and isodecyl acrylate. Glass transition temperature determined by differential scanning calorimetry was 89 °C. Average molecular weight of the copolymer was 33 800 g. Extensive details concerning the synthesis and properties of the copolymer will be reported in another publication.

2.2. Colloidal spheres

The colloidal spheres were prepared by a method similar to the one used to obtain micelles and other self-assembled aggregates of amphiphilic polymers [13]. The copolymer was first dissolved into a good solvent tetrahydrofuran (THF). A suitable amount of Milli-Q water was added dropwise into the THF solution. When the water content reached a critical value, uniform colloidal spheres were obtained. When the initial concentration of copolymer in THF changed from 1 to 15.0 mg/mL, the average size of the spheres could be adjusted from 200 to 350 nm.

2.3. Colloidal-crystal films

Colloidal-crystal films are formed by gravity-sedimentation. This method leads to three-dimensional colloidal crystals with (111) plane parallel to the substrate [14]. A few drops of the water suspension of the colloidal spheres (1 mg/mL) was transferred to the surface of a microscope glass slide and dried at room temperature and normal pressure, forming a thin layer by solution casting under gravity. The slides were previously hydrophilized by etching during 1 h in a 30 wt % sodium hydroxide solution. The drying temperature and the colloid concentration were adjusted in order to produce uniform films.

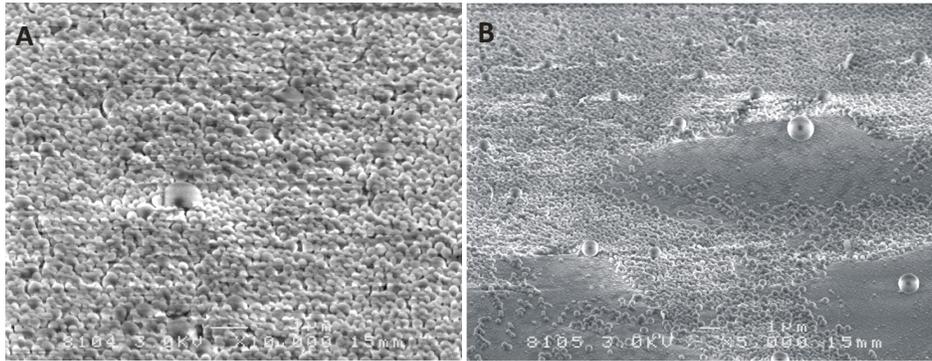


Fig. 1. (a) SEM images of the colloidal film formed by monodispersed nanospheres. (b) Image of the edge of the film showing dispersed nanospheres with 290 ± 10 nm average diameter.

The size (D) of the colloidal spheres was determined from scanning electron microscopy (SEM) images in Fig. 1. The spheres are mostly mono-disperse with an average size centered at 290 ± 10 nm, with values of 200 ± 10 nm and 350 ± 10 nm for the minimum and maximum size, respectively. On the SEM image in Fig. 1, the edge of the film shows that the film consists in 1 - 2 sphere monolayers. In the central part of the sample the film thickness is about 500 nm over a large area.

2.4. Photoinduced patterning

The optical setup consists in a diode pumped solid-state laser beam at $\lambda = 473$ nm with 100 mW maximum power. The laser excites the azopolymer close to its absorption maximum. Absorbance at the 473 nm working wavelength is 0.64. The incoming light intensity is controlled by rotation of a half wave plate before a polarizer. The sample is set perpendicular to the incident laser beam. The laser beam impinging on the polymer sample is collimated into a plane wave and its size is adjusted with a Kepler-type afocal system. The beam diameter is 2 mm at $1/e^2$. The power density at the sample location is attenuated down to 0.7 W/cm². Understanding that the diffraction pattern is the Fourier transform of the surface relief pattern, the first order self-diffraction intensity was used to evaluate the dynamics of the photoinduced structuration [15]. Diffraction from this polymer takes place in the plane of polarization.

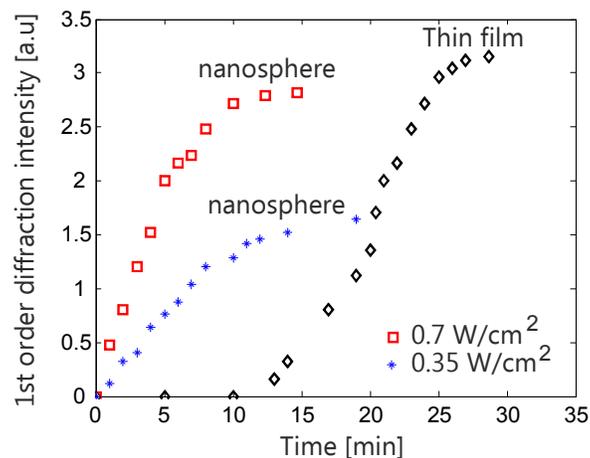


Fig. 2. Comparison between diffraction efficiencies (arbitrary units) recorded during grating inscription for the self-assembled azopolymer nanospheres under two different irradiances and for a uniform thin film of azopolymer irradiated under a single beam of 0.7 W/cm².

3. Results and discussion

Figure 2 shows a typical evolution of the first order self-diffraction intensity from a single-beam surface grating induced on a colloidal nanosphere sample. The curve under 0.7 W/cm^2 has an inverse exponential-like growth with a time constant of about 2 min, reaching a saturation plateau after 10 minutes irradiation. The formation of the grating is about 3 times faster than in previous experiments using uniform spin-coated thin films of a similar polymer [15]. The same experiment performed under 0.35 W/cm^2 laser intensity shows the same growth shape with time constant increased to about 7 min. This must be compared to the single-beam photoinduced structuration of a smooth spin-coated thin film of the same material in which diffraction follows a sigmoidal-like growth, with significant diffraction starting after 15 min irradiation and reaching a plateau after 25 minutes. In past experiments, atomic force microscopy (AFM) study of the spontaneous surface pattern formation on a thin film of a similar polymer also showed a long 15 minutes incubation period before initiation of the growth [15].

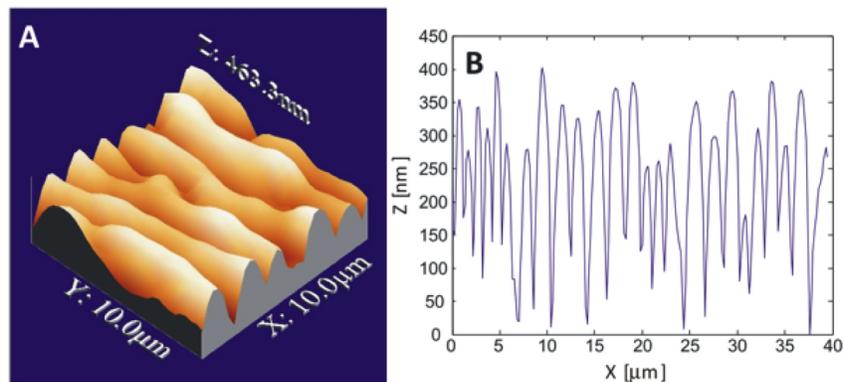


Fig. 3. (a) AFM image of the surface of self-assembled nanospheres after single laser beam inscription of a grating under 0.7 W/cm^2 . (b) Surface relief grating profile: pitch is $1.3 \pm 0.2 \mu\text{m}$, amplitude is $300 \pm 20 \text{ nm}$.

The strong increase of the diffraction from the nanosphere sample happens with the formation of a sinusoidal grating on the surface of the film. This is confirmed by topographic profiling with an AFM in the contact mode in Fig. 3. The modulation amplitude of the topographic profile achieved at saturation in Fig. 2 reaches $300 \pm 20 \text{ nm}$, with a pitch $\Lambda = 1.3 \pm 0.1 \mu\text{m}$. In order to evaluate its coherence, the surface relief grating in Fig. 3 was compared to the holographic surface relief grating obtained from illumination with two-beam interference on a smooth spin-coated thin film of the same azopolymer. The spatial Fourier transform of the AFM scans is given in Fig. 4. It characterizes the diffraction pattern and gives information on the spatial coherence of the surface grating. The two-beam grating printed on the spin-coated film in Fig. 4(a) is highly coherent; it shows bright and narrow harmonics of the fundamental grating. The grating grooves in single beam irradiation are oriented perpendicular to the laser beam polarization direction. In contrast, the grating printed on the colloidal thin film is partly disordered; it shows two spots with about $0.3 \mu\text{m}^{-1}$ width characteristic of the jitter on the pitch recorded from Fig. 3(b); it shows also $0.1 \mu\text{m}^{-1}$ width horizontal stripes characteristic of the average size ($\approx 10 \mu\text{m}$) of the coherent domains on the colloidal surface. The jitter on the pitch is attributed to the size of the individual nanospheres that cannot be divided into smaller grains. The larger scale disorder is a usual feature of single-beam surface relief gratings. Grating grooves for the single beam irradiation are oriented perpendicular to the laser polarization direction.

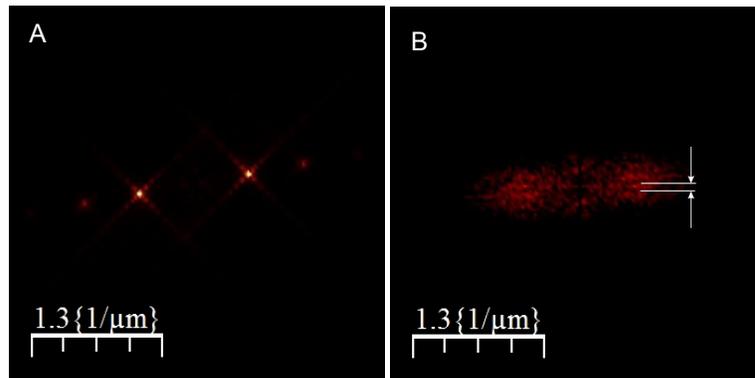


Fig. 4. Computer generated spatial Fourier transform of the surface relief patterns of: (a) grating formed by two beam interference printed on an azopolymer thin film, (b) single beam illumination of the azopolymer nanospheres under horizontal polarization. Horizontal stripes discussed in the text are highlighted with white lines in the figure. Full bar length given by the software is $1.3 \mu\text{m}^{-1}$.

In order to visualize the photo-fluidic nano-structuration effect, additional characterization of the nanospheres was performed. Well-dispersed nanospheres with different diameters were illuminated with the same polarized laser. As shown in Fig. 5(a), the nanospheres are elongated after exposure. Elongation occurs in the direction of the laser polarization, as expected according to previous measurements by Wang et al. [16]. Figure 5(b) shows the elongated length L as a function of the initial nanosphere diameter D . Length stretching is almost linear, it follows $L [\mu\text{m}] = 2.3 \times D [\mu\text{m}] + 0.38$. The strain $\varepsilon = \delta L / D$ on the nanospheres is almost uniformly equal to 1.3. Previous studies on photo-modification of nanospheres didn't report on the maximum length measured after illumination of the nanospheres [16]. The deformation is more important in the nanospheres than in thin films in which viscous interaction between the film and the substrate limits the mass transport. The strain on the spheres is related to the freedom of lateral deformation without interaction with the substrate.

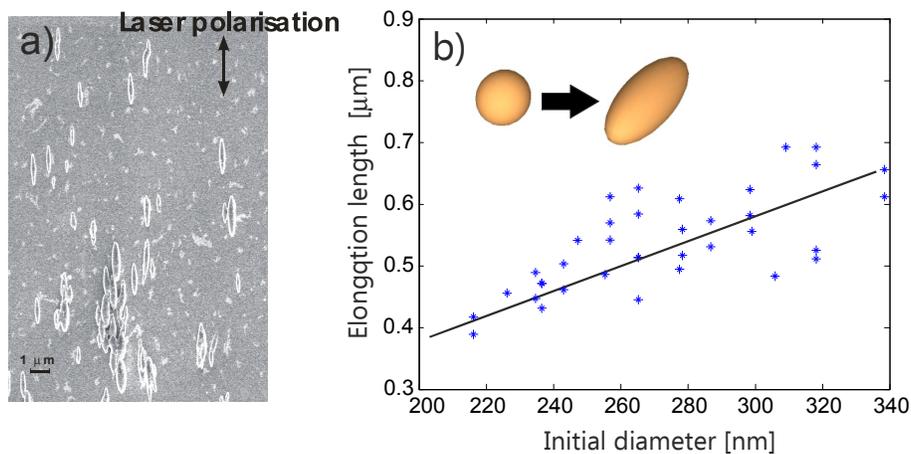


Fig. 5. (a) SEM image of colloidal spheres of the azopolymer after 10 min exposition to a vertical polarization beam. (b) Elongated length L as a function of the initial diameter D of the nanospheres.

The intensity distribution of the electric field around 100 nm polystyrene nanospheres has been calculated [17]. It was shown that the electric field is enhanced at the edges of the spheres along the polarization directions of the light beam. In such case, the nanospheres act

as nano-lenses with enhanced cross-section in which the anisotropic movement of the azopolymer is amplified. The combination of the two effects: the light polarization and the field enhancement, amplifies the anisotropic photo-induced deformation. It justifies the large amplitude strain monitored in Fig. 5(b).

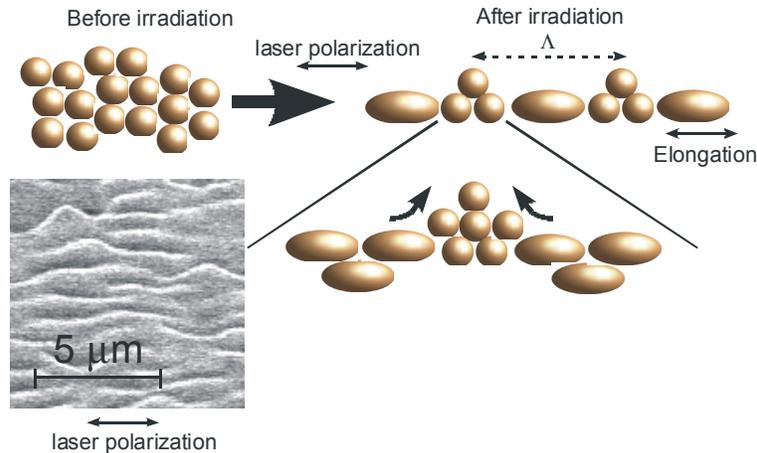


Fig. 6. Schematic evolution from the assembly of colloid nanospheres into the surface relief grating during elongation of the nanospheres along the polarization direction. Vertical direction in the figure is the direction perpendicular to the substrate. The zoom in the scheme illustrates the subduction mechanism responsible for the large amplitude relief happening in the direction of the oblique arrows. Insert is a zoom on a SEM image of the grating fringes on top of which the spherical particles emerge.

In the standard model of the single-beam formation of self-assembled gratings, three mechanisms take place successively under photo-fluidic anisotropic mass-transport [18]. Mass transport amount is proportional to the rate of excitation of the molecules [19]. The three mechanisms are sequentially: an incubation period in which a surface roughness develops on the thin film owing to random photo-fluidic mass transport; a coherent growth period in which the wave amplitudes scattered on top of the roughness interfere to initiate a surface grating; a saturation period in which the most efficient diffraction grating takes over all the other ones. Evidence is that the incubation period is suppressed in the present experiment owing to the natural roughness of the colloidal surface. This is not equivalent to reported pre-patterned surface roughness that did not increase the rate of growth of the laser-induced periodic surface structures on a polycarbonate film [20]. The two other processes, which are driven by photo-fluidic mass transport, are enhanced by the nanospheres. It is to be noted that the relative orientation of the light polarization direction with the crystal axis of the colloidal lattice did not significantly influence the rate of growth of the structures. This may be attributed to the short-range order ($\leq 10 \mu\text{m}$) of the lattice in the colloidal assemblies under study.

The molecules are irradiated under resonance by the polarized laser beam; they undergo repeated *trans-cis* isomerization cycles. This induces a continuous anisotropic molecular migration that is confined into the spheres. Densely packed spheres onto the surface of the film push each other into a kind of subduction mechanism, creating the deep relief observed in Fig. 3. When significant light is diffused into the polymer film, the interfering waves propagating into the film get coupled [21]. The interfering waves then create a surface relief grating in the usual manner. A schematic explanation is presented in the Fig. 6. The insert in Fig. 6 is a zoom on the grating fringes revealing a few nanospheres, which were pushed by the deformed spheres up to the top of the fringes of the self-induced surface relief grating. The $\Lambda = 1.3 \mu\text{m}$ grating pitch corresponds to first order diffraction at an angle $\theta = 21^\circ$ verifying $\sin \theta = \Lambda / \lambda$. As predicted by theory [21], multiple order diffraction, the third in that

case, is coupled into the plane of the film. A smaller pitch grating is not obtained owing to the finite nanosphere size.

In view of these results it is possible to estimate the mechanical force that would be needed to induce the same deformation on an azopolymer nanosphere. The uniaxial compression of polymer spheres was studied previously [10]. The force F needed to exert an elastic deformation $\varepsilon = \delta L / D$ on an incompressible sphere of diameter D is given by Hertz theory of elasticity:

$$F = \frac{4}{3} ED^2 \varepsilon^{1.5}. \quad (1)$$

in which E is the Young modulus of the copolymer. Considering polymethylmethacrylate (PMMA) as the main component of the nanospheres, Saphiannikova took $E = 1$ GPa [22]; using the same, we get the force $F \approx 170 \mu\text{N}$. Toshchevnikov et al. [23] calculated the stress that should be exerted on a polymer during surface relief grating formation, they found $F \approx 2 \mu\text{N}$, which illustrates the difference between nanospheres and the usual surface relief gratings. Light may also induce a radiation pressure on nanospheres [24], but that one falls into the pN range. Using the force F , we obtain the vertical deformation of the nanosphere δL given by [25]:

$$\delta L = \left(\frac{9F^2}{16DE^2} \right)^{1/3}. \quad (2)$$

We get $\delta L \approx 56$ nm, which is consistent with the deformation. 170 μN on the surface of a nanosphere corresponds to a pressure of 3.5 GPa. That is larger than the largest photo-irradiation force measured in liquid-crystalline azo-materials [26]. That justifies qualitatively the subduction mechanism illustrated in Fig. 6. It may be interesting in the future to study the transduction of light into a mechanical force using colloidal azo-nanospheres as mechanical actuators.

4. Conclusion

An assembly of colloidal azopolymer nanospheres was used for fast and efficient photopatterning of a surface relief grating. Anisotropic photofluidization by polarized light deforms the nanospheres along the polarization direction. The phenomenon is amplified by the self-lensing effect of the nanospheres. Single beam surface relief grating formation is itself accelerated by the initial roughness of the colloidal assembly, suppressing the long incubation time usually observed in spontaneous grating organization. The subduction mechanism of nano-spheres pushing each other along the polarization direction enhances the grating modulation amplitude. Altogether, exceptional large and fast surface relief grating is self-organized using single beam irradiation in the colloidal nanosphere assembly. The technique allows printing high contrast holograms as fast as with liquid crystal materials. It can be easily implemented with any kind of azo-material: polymer or glass. The study also suggests that pre-nanopatterning of an azopolymer film could accelerate spontaneous photo patterning under a single beam.

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