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Surface relief grating formation on nano-objects

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We exploit the photoinduced migration effect in azopolymer thin films to induce surface relief patterning of nano-objects. Manipulation and precise control of the molecular order is achieved at the nanoscale. Interaction between a laser beam from an argon laser and the azopolymer nano-objects induces structures on the surface. The self-patterning process is observed to depend on the laser beam polarization. © 2009 American Institute of Physics. [DOI: 10.1063/1.3192359]

Azobenzene is a well-known photochromic compound. It undergoes cyclic photoinduced trans-cis isomerization and is considered as a prototype molecular switch.¹ Azobenzene containing polymers are potentially useful materials in various optical and photonic applications. It was observed^{2,3} that the free surface of Azobenzene polymer films could exhibit induced mass transport if exposed to a light intensity pattern. Absorption of light induces material flow and results in surface relief gratings (SRGs). It is usually formed by the incidence of a periodic optical pattern produced by interference of light beams on the film. The SRG pattern is determined by the geometry and the wavelength of light. More recently, SRGs have been produced in a one-step irradiation process in standard laboratory conditions with a controlled laser beam polarization.⁴ Practically, one single beam with controlled polarization can photoinduce a SRG whose wave-vector direction is parallel to the light polarization. Multi-state addressing by polarization could be achieved in this way.⁵ The driving force responsible for SRG formation is a random molecule migration almost parallel to the polarization direction.⁶ Self-organization is initiated by noisy random fluctuations of the molecular position. The local perturbations are enhanced by interference of the scattered light waves, thus forming regular patterns. Light initiated spontaneous pattern formation arises from the interplay between photoisomerization and diffraction. The final state is self-organized as a coherent grating.⁷ The control of the inscription process of a SRG in the micrometer and submicrometer range has been shown.^{8,9} A scanning near field optical microscope was also used as a means of all-optical polarization encoded information storage with subdiffraction resolution.¹⁰

Periodic structures in the submicrometer scale are in high demand for many applications ranging from electronics to photonics. Up to now, patterning of these structures was possible on the surface of thin films. In this work, we demonstrate the possibility to inscribe a nanostructure on the surface of azopolymer nanotube with laser illumination. Assembly of nanometer-scale building blocks into device configurations is an intensively investigated research field in nanotechnology. Building patterns on the surface of nanometer objects permits optical processing for nanoscale engineering and for biotechnologies.¹¹

Experimentally, an azopolymer solution was prepared from a highly photoactive azobenzene derivative containing heterocyclic sulfonamide moieties;¹² 3-[[4-[(E)-(4-[(2,6-dimethylpyrimidin-4-yl) amino] sulfonyl] phenyl) diazenyl] phenyl]-(methyl)amino]propyl 2-methylacrylate (Fig. 1) with a concentration of 50 mg/ml in tetrahydrofuran.

Tubular nanostructures with controlled diameters are prepared by wetting porous anodic alumina membrane templates consisting in an array of parallel and straight channels. This template method has previously been applied to the fabrication of nanotubes from a range of organic materials.¹³ The Alumina membrane filters (Anodisc) were obtained from Whatman and have a diameter of 13 mm and thickness of 60 μm . The individual cylindrical pores can be viewed as a beaker in which a piece of the desired material can be synthesized. The pores in the membrane have mono-disperse diameters of 200 nm. A nanocylinder of azopolymer can be obtained from each pore. The nanotubes were prepared by filtration of a solution of the azopolymer into the pores of the template membrane. About 1 mL of the azopolymer solution was dropped into a 1 cm^2 area on the top surface of the template membrane. The membrane was left at ambient conditions until the solution was infiltrated through the membrane. It was then placed in an oven for solvent evaporation during one hour at 60 $^{\circ}\text{C}$ temperature. Nanotubes were freed by dissolving the membrane by soaking in 3M aqueous NaOH for 10 min. The tubule material was

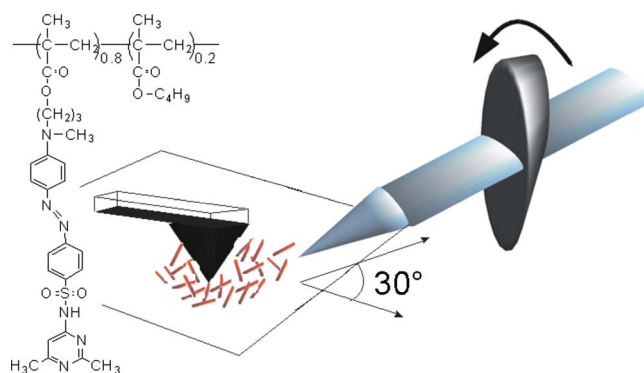


FIG. 1. (Color online) On left: Chemical formula of the polymer; on right: Experimental layout of the patterning experiment showing the AFM tip and the incident focused laser beam.

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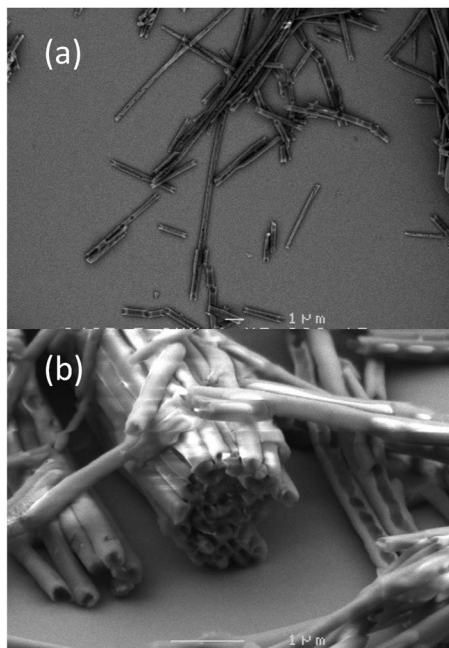


FIG. 2. (a) SEM of azopolymer nanotubes prepared from the 200 nm diameter pores of the Anodisc membrane. (b) High magnification image of an azopolymer nanotubule bundle on glass.

extracted from the resulting mixture by three 30 s cycles of centrifugation at 8000 rpm, followed by two more cycles in distilled water. Nanotubes were then dispersed into water by sonication. The water suspension of dispersed nanotubes was then dropped on the surface of clean microscope glass slides, which were subsequently placed in an oven for water evaporation.

In order to pattern the surface of the nanotubes, we configured an atomic force microscope (AFM) with a laser beam illuminating the sample. An Argon laser with 477 nm wavelength in the absorption band of the azopolymer was used. It delivers 7 mW power with 2.8 mm beam diameter. A Mitutoyo M plan $\times 20$ (0.45 NA) microscope objective with 20 mm working distance focuses the laser beam into a $1.3 \mu\text{m}$ full width at half maximum spot on the sample surface with a 60° incidence angle (Fig. 2). We scan the sample surface at the beam spot in a noncontact AFM mode every 10 min. During the AFM scan of the surface, the laser beam is blocked to avoid multiple reflections from the scanning head. Polarization is changed from vertical to horizontal using a half-wave plate.

Figure 2(a) shows a scanning electron microscopy (SEM) image of typical nanotubes dispersed on the surface of a microscope glass slides. We can estimate by statistical analysis of the images the frequency distribution of the external nanotubule diameter. It is 220 ± 20 nm which is slightly larger than the stated nominal pore diameter value of the membrane. Figure 2(b) is a higher magnification SEM image of the nanotubule showing their tubular morphology with smooth side walls. Wall thickness is estimated as 30 ± 5 nm. Nanotubule length depends on the dispersion process through sonication and large length dispersion from a few to several μm could be observed.

Figure 3 shows an AFM image of a nanotubule before and after irradiation of the sample surface with horizontally polarized laser beam [transverse electric (TE) excitation]. Absolute resolution is actually limited by the tip size. After

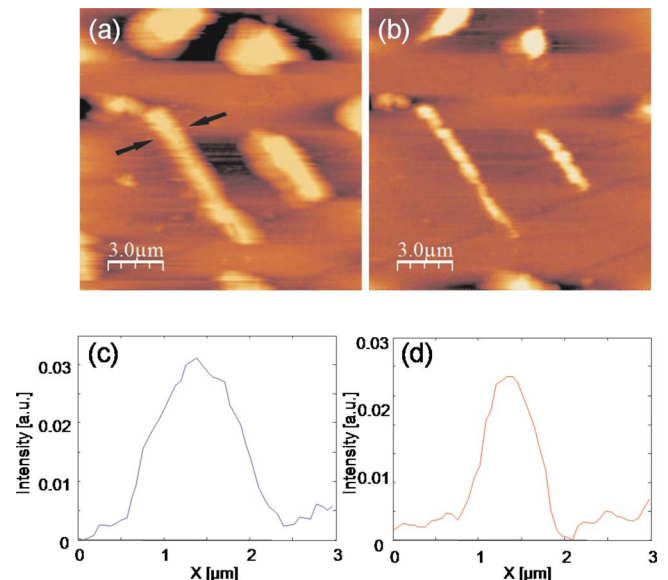


FIG. 3. (Color online) (a) Noncontact AFM image of individual nanotubules before laser light excitation with a horizontal (TE) polarization. (b) Noncontact AFM image of the same nanotubules after laser light excitation. (c) and (d) Surface line profile of the nanotubule before and after optical excitation; the scanning direction is indicated by arrows in (a). Vertical unit is 10^{-5} m.

irradiation, the nanotubule width has shrunk. Using the AFM profiling, shrinkage is estimated to about 60% of the initial width. We also note in the top of Fig. 3 crumbs on the nanotubules. They come from the dispersion process during nanotubes preparation. They follow the same shrinking process during illumination. Interestingly, TE excitation of the nano-objects follows the same trends as the excitation of a surface by the evanescent wave of a near-field microscope.¹⁴ The light pulls the polymer upwards.

The same experiment was repeated with a vertical polarization [transverse magnetic (TM) excitation]. At the beginning of the process, the surface profile of the nanotubule measured in Fig. 4 in the longitudinal direction as indicated

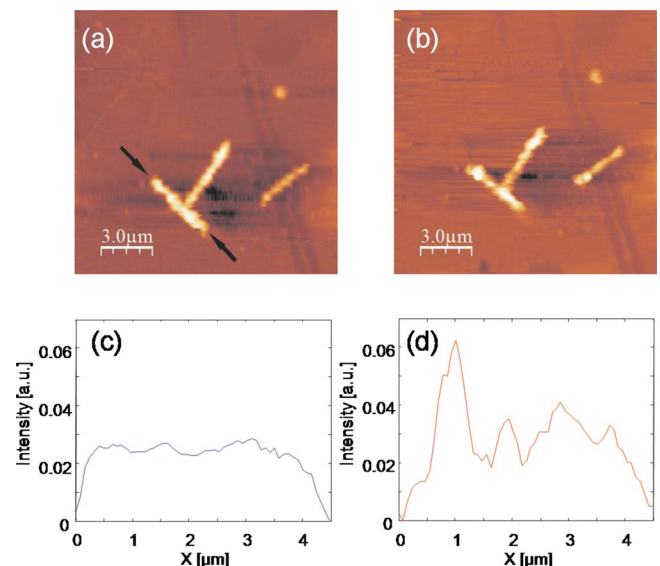


FIG. 4. (Color online) (a) Noncontact AFM image of individual nanotubules before laser light excitation with a vertical (TM) polarization. (b) Noncontact AFM image of the same nanotubules after laser light excitation. (c) and (d) Surface line profile of the nanotubule before and after optical excitation; the scanning direction is indicated by arrows in (a). Vertical unit is 10^{-5} m.

by arrows is flat. After 30 min irradiation, the nanotubule presents a quasi periodically structured surface. The mean distance between the peaks is $0.9 \pm 0.1 \mu\text{m}^2$. That distance is about the same as the grating pitch measured in the case of self-structured thin films of the same azopolymer.⁵ Different measurements carried on different isolated nanotubules using the same TM polarization lead to the same patterning, which confirms the robustness of the structuration method. To make sure that the process is induced by light and not by some heat induced softening, we increased the laser beam power up to the degradation limit; the nanotubules then spread on the glass surface and become distorted but no such structure is formed. Further studies are in progress to investigate eventual modifications of the inner surface of the nanotubules.

In conclusion, we have demonstrated controlled optical patterning of the surface of nano-objects. The pattern on the nanotubule revealed with an AFM clearly indicates spatially confined excitation of unidirectional motion of molecules; in agreement with previous works where the angular distribution of molecular motion is anisotropic.^{15,6} Photoinduced structuring of the azopolymer is realized with the recording of a SRG on the nanotubules. The process is a photoinduced molecular motion where the molecules push or pull the polymer chains giving rise to the corrugated surface. This work is a demonstration of optical nanostructuration on the surface of nano-objects. We can already foresee applications as an engineering technique in the field of nanotechnologies.

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