



Humido-responsive nanostructures prepared by nanoimprinting

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ABSTRACT

The stimulus-responsive polymers have attracted great attentions, because of their deformation ability under certain stimuli like moisture. In this work, the nanoimprinting technique was introduced to fabricate nanostructures (diffraction gratings and hexagonal dots) on poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) stimulus-responsive polymer. The imprinted PVA/PAA polymeric structures show a strong and rapid response to moisture stimulations. The swelling or shrinking of the microstructures lead to the corresponding variations of the grating slit width and array trench depth. The grating structure shows potential application for optical detection of external stimulations, and the hexagonal dot array for piezoelectric detection in combination with ferroelectric materials.

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1. Introduction

One of the most fascinating properties of the hydrogels is its deformations in response to the change of external conditions (stimuli), like heat, electricity, light, magnetic field, moisture/water, and pH value. These deformations include the two-dimensional expansion/contraction as well as the three-dimensional bending/unbending. When a hydrogel is exposed to a moisture-free atmosphere, polymer chains are highly entangled, and the contraction mode is observable, because only cramped space is available. As crosslinked polymers, hydrogels can absorb solvents in aqueous media and swell in a relatively short response time. The swelling continues until the expanding pressure is balanced by the bonding forces between the polymer chains, and maximum volume is reached [1].

Preparing polymer blends is a critical process for controlling the behavior of the hydrogel. Owing to the simplicity of synthesis method of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) blends [2], PAA/PVA polymers arouse the most interest among stimulus-responsive polymers. Through crosslinking PVA/PAA blends, PAA chains can be trapped in PVA network to form new bonds [3]. There are several ways to achieve the crosslinking, e.g. chemical crosslinking agents, gamma-ray radiation, and heat treatment. In our work, the heat treatment that can lead to stable hydrogels was applied to fabricate humido-responsive nanostructures.

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Two different nanostructures based on PVA/PAA hydrogels were investigated in this work. The grating structure was aimed to the application for optical detection of external stimulations, and the hexagonal dot array to the potential application for piezoelectric detection in combination with ferroelectric materials. The nanoimprinting technique was utilized here to fabricate nanoscale structures on the stimulus-responsive polymer, which is not only an economic approach for nanofabrication, but also an efficient way to control the chain orientation and crystal quality of the hydrogels simultaneously. The shape variations of the nanostructures in response to moisture stimulations showed potential applications in actuators, miniature manipulators, cantilever sensors, transducers, robotics, biomimetic devices, micropumps, artificial muscles and switching devices [4].

2. Experimental

2.1. Polymer films preparation

2 wt.% PVA (obtained from Aldrich) was dissolved in deionized water and stirred at 98 °C in a water bath for 2 h. After cooling down to the room temperature, the solution was mixed with 0.5 wt.% PAA (also obtained from Aldrich), and stirred at 60 °C for 1 h, resulting in a transparent PVA/PAA blend solution.

The solution was then spin-coated for 60 s on silicon substrates to form the PAA/PVA polymer films. The relationship between film thickness and spin speed is given by

$$t = A\rho^{0.36}/\sqrt{v}, \quad (1)$$

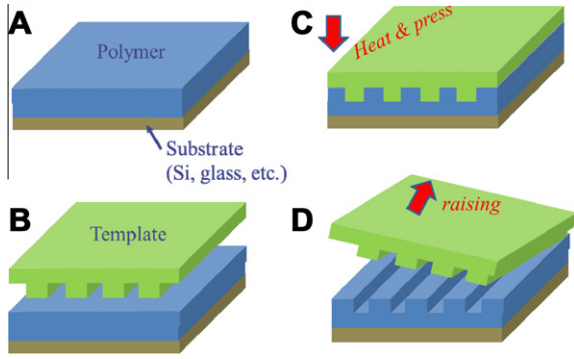


Fig. 1. Schematic representation of the nanoimprinting process for fabricating PVA/PAA nanostructures.

where t is the thickness of the polymer film spin-coated, A is a constant related to solvent-polymer compatibility, ρ is the initial solution viscosity, and v is the angular spin speed [5]. In this work, a spin speed of 1 kr/min was used to obtain polymer films of about 260 nm in thickness. The films were then evaporated by heating at 60 °C for 1 h to avoid formations of bubbles and ripples in the films [6].

2.2. Nanostructures fabrication

The thermal cross-linking of PVA/PAA was conducted by prebaking the films at 160 °C for 30 min. The hot embossing process was performed at the same temperature, as soon as the prebaking was done. The molds were pressed on the hydrogel films in a conformal contact manner with a pressure of 11 MPa for 20 min. After the systems cooled down to the room temperature, the molds were peeled off and the structures were formed on the films. Schematics of the nanoimprinting processes on the hydrogel films are illustrated in Fig. 1.

Fig. 2a shows a typical atomic force microscope (AFM) image of a grating structure with period of 4 μm and depth of ~ 100 nm. Fourier Transformed Infrared (FT-IR) spectroscopy was carried out to characterize the degree of cross-linking of the PVA/PAA microstructure. In the transmission spectrum (Fig. 2b), the peak around 1710 cm^{-1} is attributed to the carbonyl groups produced by the degradation of the hydroxyl group in PVA, the carbonyl in PAA, and the carbonyl in the ester linkage indicating that PVA/PAA was well crosslinked [7].

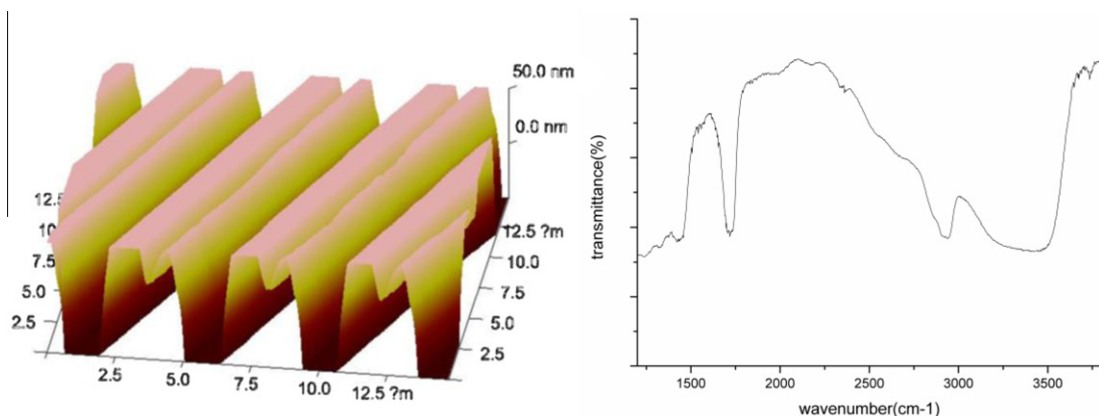


Fig. 2. (a) AFM image of PVA/PAA polymer grating with spatial period of 4 μm , (b) FT-IR spectrum of imprinted PVA/PAA polymer.

3. Results and discussion

The responses of the PVA/PAA polymeric nanostructures to humidity were studied by optical microscope (Keyence VHX-600) and atomic force microscope (AFM). The PVA/PAA hydrogel films were exposed to environments of different humidity to investigate the response behaviors of the hydrogel structures to the stimuli. The deformation of the hydrogel samples was found reversible through the swelling-shrinking cycle as expected [8].

3.1. Diffraction gratings

Fig. 3 displays the ongoing change of the shape deformation on the polymer surface reacting to increasing ambient humidity captured by a digital optical microscope. At room temperature (25 °C) with a humidity of 20% RH, the grating structure was clearly observed through the microscope. When the polymeric grating was exposed to a moisture flow, resulting in an increase of the humidity from 20% RH to $\sim 80\%$ RH, the grating structure was gradually blurred without readjusting the microscope focus, due to the expansion of the polymeric PVA/PAA film upon moisture adsorption.

It is prospective that the hydrogel gratings can be used to optically detect the ambient humidity by means of the variation of Fraunhofer diffraction patterns caused by the changes of the hydrogel volume. The grating diffraction phenomenon can be regarded as the interaction of the single slit diffraction and the multi slits interference phenomenon [9]. It is well known that the light intensity of single slit diffraction pattern at a diffraction angle θ is given by

$$I'_0 = I_0 \left(\frac{\sin \alpha}{\alpha} \right)^2, \tag{2}$$

where I_0 is the central main maximum, and α is half of the diffraction ray phase difference of the single slit edge. When the incident light is vertical to the grating,

$$\alpha = \pi a \frac{\sin \theta}{\lambda}, \tag{3}$$

where a is the slit width of the hydrogel grating, and λ is the wavelength of the incident light. In Fraunhofer diffraction, through a focusing lens, the diffraction patterns of each slit with the same diffraction angle are superposed. As the result of the mathematical integral, the gross light intensity with the diffraction angle θ resulting from multi slits diffraction has the following relationship with α ,

$$I_\theta = I_0 \left(\frac{\sin \alpha}{\alpha} \right)^2 \left[\frac{\sin(N\delta/2)}{\sin(\delta/2)} \right]^2, \tag{4}$$

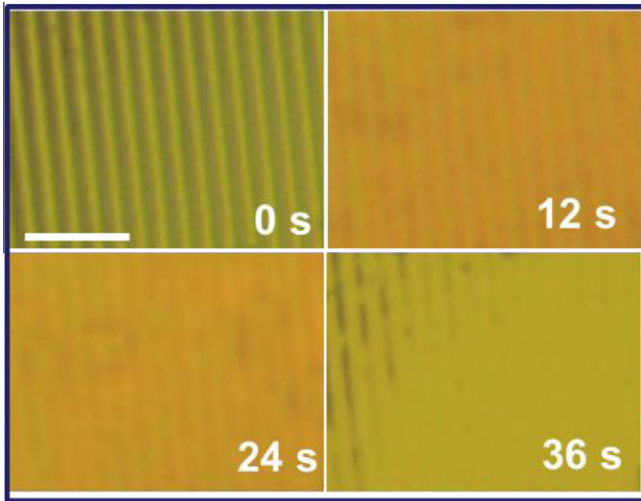


Fig. 3. Time lapse optical images of the shape deformation of a PVA/PAA grating with humidity change. The length of the scale bar shown in the upper left picture is 10 μm .

where N is the amount of the slits, δ is the phase difference of the adjacent single slit, expressed as

$$\delta = \frac{2\pi}{\lambda} d \sin \theta, \quad (5)$$

where d is the spatial period of the grating.

For a typical hydrogel grating (N and d are constants), at a fixed diffraction angle θ and wavelength λ , the gross light intensity I_θ is only determined by the slit width a , which is sensitive to the ambient humidity in case of the PVA/PAA grating. The dependence of the gross light intensity I_θ on slit width a can be calculated using Eqs. (3) and (4). As is shown in Fig. 4a, at the diffraction angle $\theta = 15^\circ$, the gross light intensity I_θ decreases monotonically with increasing slit width a , for a smaller than 3λ . It can be seen that the light intensity I_θ shows the best sensitivity for the slit width a at about 1.7λ (Fig. 4b).

The gross light intensity I_θ can be well correlated to various slit width a , and thus to various ambient humidity for the humidity-responsive grating. Therefore, the environmental change can be detected by the light intensity variation of the Fraunhofer diffraction patterns in response to the external humidity. Such stimulus-responsive grating might find broad applications in smart optical devices.

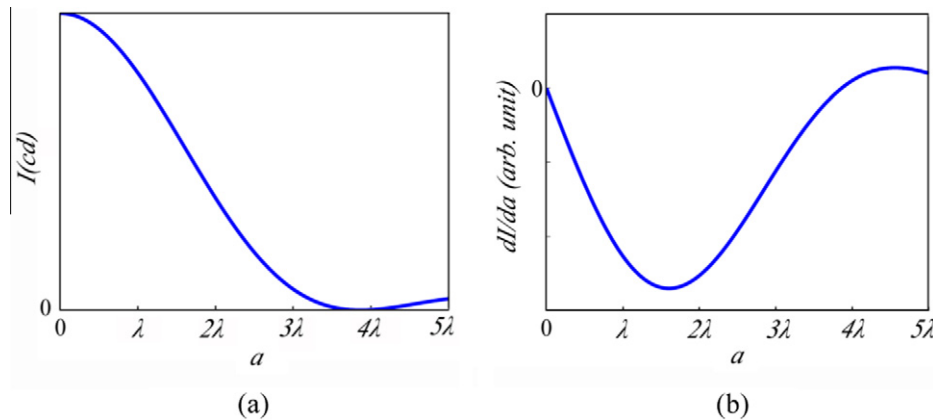


Fig. 4. The relationship between the gross light intensity I_θ and slit width a , with all the other parameters fixed (supporting the diffraction angle θ is 15°).

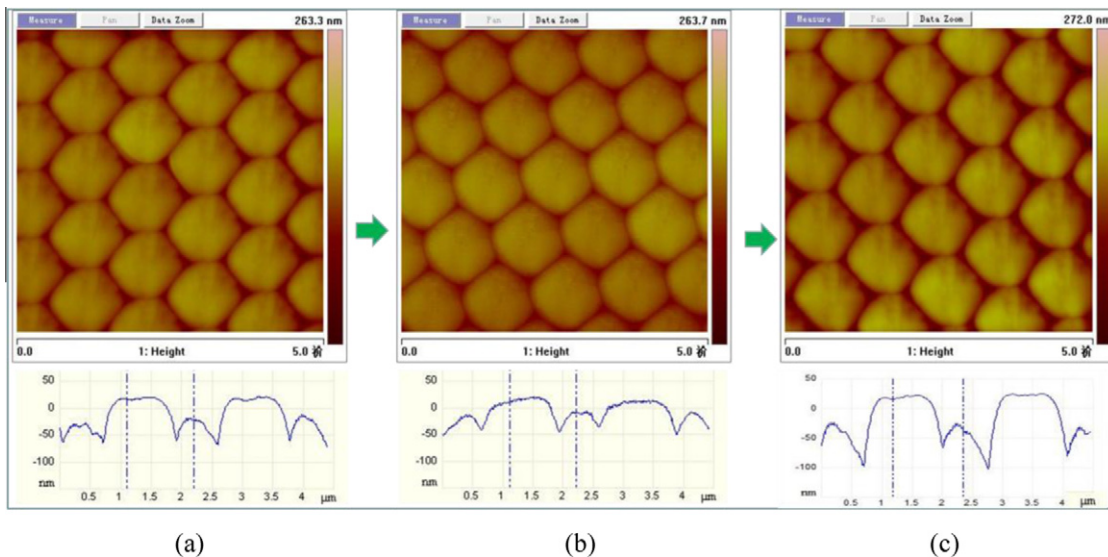


Fig. 5. AFM images and profiles of PVA/PAA nanostructures after being exposed to different humidity conditions. (a) Initial humidity of 20% RH, (b) after being exposed to a moisture flow of the humidity of 80% RH, (c) dried to the humidity of <5% RH.

3.2. Hexagonal dot arrays

Fig. 5 shows the AFM images of a PVA/PAA hexagon nanoarray under different humidity. The trench depth of the hexagon array was ~ 80 nm under a humidity of 20% RH (Fig. 5a), and after being exposed to a moisture flow of the humidity of 80% RH, its depth decreased to ~ 60 nm (Fig. 5b). The sample was then dried in an oven at 130 °C for 30 min to reduce the humidity down to under 5% RH, the array structure relaxed back and the trench depth became ~ 110 nm (Fig. 5c).

It can be observed in Fig. 5 that most significant deformation of the hydrogel occurs in the trench area, as it can accommodate larger volume change and stress relaxation. Compared with the pristine state, much bigger deformation should thus be achieved with the patterned structures. On the other hand, the volume change of the hydrogel is typically driven by the diffusion, so the response rate of the hydrogel deformation is inversely proportional to the square of its smallest dimension [10]. The micro/nanoscale hydrogel structures can significantly reduce the response time without changing mechanical properties of the polymers. The nanoimprinted PVA/PAA hydrogel structures have, therefore, the higher sensitivity towards humidity with bigger deformation rate and shorter response time. Integrated with the piezoelectric material, the hydrogel nanostructure might be one of the ideal choices in fabricating electrical humidity sensors for accurate and timely measurement.

4. Conclusions

In summary, we have used the nanoimprinting approach to pattern micro/nanostructures on a humido-responsive polymer.

The imprinted PVA/PAA polymeric structures show a strong humido-response. The swelling or shrinking of the microstructures lead to the corresponding variations of the grating slit width and array trench depth. It is believed that such stimuli-responsive polymer structures can be used as optical sensors or versatile transducers, and our nanoimprinting approach offers a simple and efficient way for fabricating such devices.

Acknowledgements

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