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Original article

Controlled fabrication of hierarchically microstructured surfaces *via* surface wrinkling combined with template replication

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ABSTRACT

In this paper, we present a simple method by combining surface wrinkling and template replication to create a series of hierarchical structures on polydimethylsiloxane (PDMS) elastomer. The primary stable lined patterns are formed by duplicating commercialized compact disk and digital versatile disk with PDMS. The secondary microscale patterns are from surface wrinkling, which is elicited by oxygen plasma (OP) treatment of the prestrained PDMS stamp followed with the prestrain release. By systematically varying the OP exposure duration, the prestrain, and the angle (θ) between the primary pattern orientation and the prestrain direction, we obtain highly ordered well-organized composite patterns from different patterning techniques and with different length scales and mechanical stabilities.

1. Introduction

Owing to unique surface morphologies, natural biomaterials exhibit many excellent biofunctionalities, such as self-cleaning ability of lotus leaves [1,2], anisotropic wettability of rice leaves [1,3], antireflection property of cicada wings [4], *etc.* The intimate relation between them attracts considerable interest to fabricate hierarchical micro- and nanostructured materials. To date, the most commonly used techniques for micro/nanostructuring can be roughly classified into two categories: top-down and bottom-up methods [5,6]. Top-down methods are based on creating an organized structure either by etching or by manipulating components into specific locations, such as photolithography and replica molding [7,8]. Bottom-up methods refer to organization of smaller components into lager or more complex assemblies, such as self-assembly [9,10]. Considering internal advantages and limitations (*e.g.*, cost, output, operation conditions) for each method, smart combination of them is one desirable strategy to make best use of them for the controlled fabrication.

Hereinto, replica molding (*i.e.*, template replication) with high fidelity and high precision makes itself a facile technique to fabricate various micro/nano structures [7,8]. Selection of suitable duplicated materials is of importance in the replica molding technique. Polydimethylsiloxane (PDMS) is the most widely used elastomer because of its outstanding properties: excellent elasticity, high thermo-stability, chemical-stability, and low surface energy [11,12].

Surface wrinkling, with typical examples of dried fruits and aging human skin, is a universal and ubiquitous phenomenon in nature [13,14]. As one of the mechanical instabilities, surface wrinkling is derived from the strain mismatch between a stiff skin and the underlying compliant substrate. When the induced compressive stress exceeds the material-defined critical wrinkling stress, wrinkles with typically sinusoidal profiles occur for minimizing the system free energy [15,16]. Evidently, surface wrinkling provides a simple yet versatile efficient bottom-up way to create micro/nanoscale textured surfaces over large areas [17–22].

In recent years, increasing attention has been paid to fabrication of hierarchical micro/nano surfaces based on surface wrinkling [17,23–28]. On the one hand, the resultant microstructures are fully based on the controlled surface wrinkling. For example, Efimenko *et al.* fabricated self-similar multi-generations of wrinkles by release of the pre-stretched UVO-exposed PDMS sheet with a large pre-strain [17]. The similar nested hierarchical wrinkles have also been generated through multi-step plasma treatment/prestrain release [23]. Additionally, Crosby *et al.* used a sequential strain wrinkling process to create a series of biaxial wrinkle morphologies with two distinct wavelengths and orientations [24]. In our group, a variety of well-organized wrinkle patterns have been available *via* the confinement-induced

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wrinkling from the wrinkled template twice [25]. On the other hand, hierarchically composite structures can be realized by means of other patterning techniques combined with surface wrinkling. Namely patterned substrates (or films), which could be prepared from the top-down methods, were introduced into the film/substrate bilayer system for surface wrinkling. The primary patterns were based on the top-down methods, while the secondary ones were from the surface wrinkling. Thus the two-level patterns can be independently manipulated. For instance, Chiche *et al.* utilized the surface wrinkling and template replication to create checkerboard-like patterns [27]. Here the used PDMS stamp was replicated from the wrinkled surface. Recently, Carter *et al.* have combined nanoimprint lithography with chemically induced wrinkling process to fabricate hierarchically wrinkled superhydrophobic surfaces [28]. Of course, in some cases, the primary patterns have an effect on the secondary wrinkling patterns. For instance, in the film/substrate system composed of a planar PDMS substrate and the patterned polystyrene (PS) film, Stafford *et al.* found that the induced wrinkle wavelength strongly depended on the geometry and the orientation of the patterned PS film [26]. Especially, the wrinkle wavelength increased obviously with the decrease of the angle between the film pattern direction and the compression direction, which was originated from the anisotropic property in the effective bending rigidity of the oriented wrinkled film. This intimate relation of wrinkling behaviors with the film pattern could be explained by their provided composite mechanics model. However, few reports have been concerned with the case of patterned compliant substrates. Indeed, the effect of the primary patterns from the patterned substrate on the induced stress field in the film/substrate system should be different from that of the patterned film applied.

Here, we report a simple low-cost method to create a series of hierarchical structures on polydimethylsiloxane (PDMS) elastomer, which is based on the combined bottom-up/top-down strategy. Firstly, PDMS stamps with line gratings are formed by duplicating the commercialized compact disk (CD) and digital versatile disk (DVD). Secondly, the replicated PDMS stamps are pre-strained for oxygen plasma (OP) exposure, followed with the slow release of the pre-strain. Consequently, the secondary microscale patterns are produced *via* surface wrinkling. We systematically investigate the effect of experimental factors (*e.g.*, plasma exposure time, the prestrain, and the angle between the two-level pattern directions) on the well-organized composite patterns. Since the thin oxidized layer and the bulk PDMS substrate are essentially from the same material, we can avoid potential delamination at a large strain, which is one serious problem in the previous reports [26,28]. More importantly, the replicated PDMS stamp is utilized to provide the first-level patterns, which is different from the previously reported patterned film [26,28]. Thus the influence of the substrate geometry on the induced wrinkling wavelength has been considered. Furthermore, the applied structured templates from the well commercialized and cheap CD and DVD endow our combined strategy with low cost and high output in the controlled surface patterning. Evidently, our work presents a new perspective to fabricate hierarchically functional structured surfaces for advanced and extended applications.

2. Experimental

Materials: Polydimethylsiloxane (PDMS) elastomer kits with the base/curing agent (Sylgard 184) were purchased from Dow Corning. Commercialized compact disk-recordable (CD-R) and digital versatile disk-recordable (DVD-R) were purchased from the market.

Fabrication of PDMS stamps from CD/DVD: PDMS was used to duplicate the surface structure of CD/DVD by replica molding. CD/DVD with recording layer was used as the original template in the replication step. The mixture of PDMS base and its curing agent (10:1, mass ratio) was cast onto the recording layer of the CD/DVD templates, followed with thorough degassing. After heated at 70 °C for 4 h, the flexible negative stamps were obtained by peeling of the cured PDMS sheet from the CD/DVD template.

Fabrication of the secondary wrinkle patterns: Rectangular specimens (flat PDMS and PDMS stamps) were cut into 4 cm × 1 cm with a razor blade and mounted onto a home-made manual screw-driven stage. Uniaxial strain ranging from 5% to 30% was exerted by mechanical uniaxial stretching. Then the pre-strained specimens undergo oxygen plasma (OP) treatment (Harrick PDC 32G) at a pressure of 0.02 mbar for 10–30 min. Finally, the pre-strain in the OP-exposed PDMS substrate was slowly released to induce the surface wrinkling.

Characterization: Atomic force microscope (AFM) images were obtained in tapping mode on an Agilent 5500 AFM/SPM microscope with silicon cantilevers (NC-W, the typical frequency of 285 kHz). Optical microscope images were recorded using an inverted Observer A1 microscope (Zeiss, Germany) equipped with a charge-coupled device camera.

3. Results and discussion

Scheme 1 shows our combined strategy to fabricate hierarchically composite patterns. It is composed of three steps: (I) fabrication of PDMS stamps (②) by replication of the structured CD/DVD templates with PDMS (①) to obtain the primary patterns; (II) OP exposure of the pre-strained PDMS stamps to generate the SiO_x/PDMS bilayer; (III) release of the pre-strain to induce surface wrinkling for formation of the secondary wrinkle patterns, resulting in the hierarchical structures with different relative orientations (③ and ④). In order to successfully realize the replication, thorough degassing needs to remove trapped air and promote PDMS pre-copolymer to fill the microstructures of the CD/DVD templates. Fig. 1a shows the atomic force microscope (AFM) image of the as-replicated PDMS stamp. It is seen that the PDMS stamp has highly ordered line-to-space microstructures. The corresponding cross-sectional profile indicates that the stamp replicated from CD has a pitch of ~1.2 μm and a height of ~200 nm (Fig. 1b), while the stamp from DVD has a pitch of ~750 nm and a height of ~100 nm (Fig. S1 in Supporting information).

In the following steps, the replicated PDMS stamp that is uniaxially stretched for a given prestrain (ε_{pre}) is exposed to oxygen plasma (OP), followed with slow release of the prestrain. During the OP treatment, the PDMS surface is oxidized and converted into a rigid thin silicate-like (SiO_x) layer, which has been well characterized previously [29–31]. Consequently, the film/substrate system composed of the SiO_x/PDMS bilayer is formed with the thickness and modulus of the oxidized layer being dependent on the OP exposure time (t_{OP}) [32]. During the prestrain relaxation, the compressive stress (σ) is increasingly induced due to the different stiffness between the SiO_x layer and the underlying PDMS substrate. Once σ is higher than the bilayer-defined critical stress (σ_c), the surface wrinkling takes place with sinusoidal waves perpendicular to the prestrain direction. It is noted that the strain release rate has a major impact on the overall quality of wrinkle patterns [17]. For example, releasing the strain at a high rate always results in structural defects coupled with weak regularity. In order to avoid these undesired disadvantages, the pre-strain is released at quite a slow rate in our experiment.

Just as expected, two-level well-organized composite patterns are obtained (Fig. 2). It is easy to differentiate them based on the periodicity and orientation. For the primary ones, they correspond to the lined gratings of the replicated PDMS stamp with the constant periodicity of ~1.2 μm (marked with yellow line in