

High Aspect Ratio Polymer Micro/Nano-Structure Manufacturing using Nanoembossing, Nanomolding and Directed Self-Assembly

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Abstract

This paper proposes three methods to fabricate synthetic gecko foot-hair high aspect ratio polymer micro/nano-structures. In the first method, nano-robotically indented templates are molded with liquid polymers, and the cured polymer is peeled off or etched away. Atomic force microscope and scanning tunneling microscope probe tips are used to emboss/indent flat wax surfaces, and silicone rubber micro/nano-bump structures are demonstrated. The second one uses a self-organized polycarbonate nano-pore membrane as the molding template. PDMS is molded into these micro/nano-pores under vacuum, and 1:2 and 1:9 aspect ratio pillar structures with 5 micron and 0.6 micron diameters are manufactured successfully. Finally, a directed self-assembly technique is proposed to grow regularly spaced and oriented micro/nano-pillars. Here, instability of a liquid polymer thin-film under a DC electric field is used to grow nano-pillars, and stretching and shearing of the grown hairs enable high aspect ratio and oriented hair structures. These hair structures will be utilized as novel biomimetic dry adhesives in future miniature space and surgical robot feet.

Keywords

Nano-mechatronics, nano-manufacturing, nanotechnology, smart adhesives.

INTRODUCTION

High aspect ratio micro/nano-structures are becoming very crucial for novel biomimetic dry adhesives [1, 2], smart surfaces, etc. type of revolutionary nanostructures applications. Conventional techniques mostly enable low aspect ratio structures, and this paper investigates the possible novel manufacturing techniques for high and ultra-high aspect ratio micro/nano-structures. As possible methods, three techniques are developed. At first, atomic force microscope (AFM) nano-probes are used to emboss the probe tip shape to a soft wax surface. By this precisely controlled technique, single and arrays of silicone rubber nano-pyramids are manufactured by a step-and-repeat process. This method has the flexibility of fabricating different orientation and non-symmetric nano-structures over almost any surface topography while it enables prototyping of only certain type of low aspect ratio nano-structures, and it is relatively slow due to its serial control process. Therefore, two parallel, easy to mass produce, methods are introduced.

The first parallel technique is based on molding self-organized nano-pore membranes with liquid polymers, curing the polymer, and etching away the membrane, or peeling off the cured polymer from the membrane. As the next technique, micro/nano-structures are grown using directed self-assembly. In this technique, a thin liquid polymer film is coated on a flat conductive substrate, and a closely spaced another metal plate is used to apply a DC electric field on the polymer film. Due to the instabilities on the film, nano-pillars are started to grow until touching to the upper metal plate.

PROBLEM DEFINITION

The main target of the high aspect ratio polymer micro/nano-structure manufacturing is based on mimicking the geometrical and physical properties of synthetic gecko foot-hairs [3, 4]: (1) High aspect ratio *cylindrical* micrometer (1:10-30) and nanometer (1:20-50) scale structure fabrication with diameters of 3-10 μm and 50-500 nm respectively, (2) Maximize micro/nano-hair density (number of hairs in a given area, e.g. 1 cm^2) for higher adhesion, (3) Maximize nano-hair stiffness to prevent matting, (4) Orient the micro- and nano-hairs with 15-60° to enable directional attachment and detachment [3], and (4) Material properties of synthetic hairs: Young's modulus of 0.1-10 GPa, hydrophobic, and high tensile strength.

MICRO/NANO-MANUFACTURING METHODS

Three manufacturing methods are proposed for manufacturing micro/nano-structures with above specifications. At first, a master template with high aspect ratio micro/nano-holes is molded with polymers. These templates are manufactured by nano-embossing or using self-organized nanopores.

Method I: Molding Nano-Embossed Templates

At first, an atomic force microscope (AFM) and scanning tunneling microscope (STM) nano-probe tip, high aspect ratio micro/nano-pillars fabricated using optical or electron-beam lithography type of methods, or an array of ultra sharp glass pipettes are embossed mechanically on a soft wax surface to copy their negatives on to the surface. Then, this template is molded with a liquid polymer such as silicone rubber, and the polymer is cured and peeled off from the surface. Previously, nano-tip arrays are used as templates

for imprint patterning of a polystyrene surface with $0.8\ \mu\text{m}$ diameter and $3\ \mu\text{m}$ depth holes [5]. Also, PMMA is indented by an AFM probe for data-storage applications [6] or by a micro-fabricated tip array and molded with a metal layer for patterning down to $40\ \text{nm}$ metallic contacts [7].

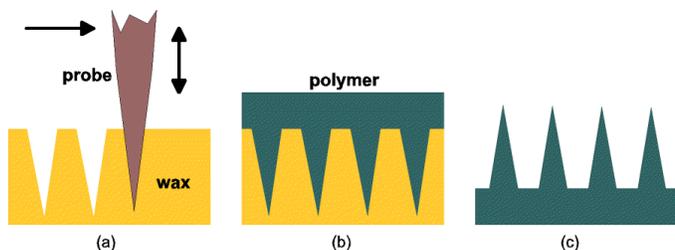
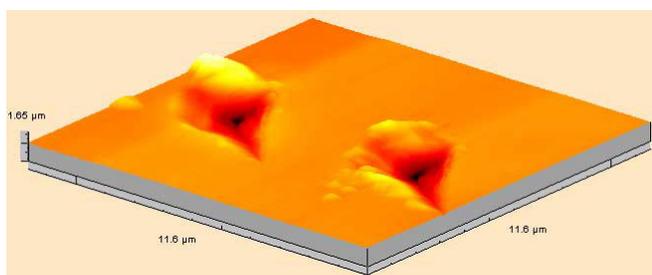
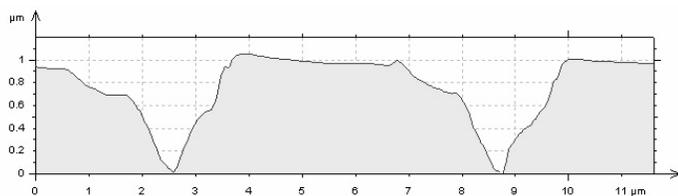


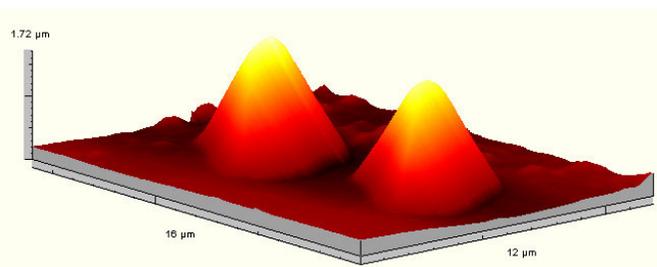
Figure 1. Synthetic hair fabrication by the Method I: (a) Indenting a flat wax surface using a micro/nano-fabricated probe or structure, (b) molding it with a polymer, and (c) separating the polymer from the wax by peeling.



(a)



(b)



(c)

Figure 2. 3-D AFM tapping mode image of (a) the AFM probe based indented flat wax surface, (b) profile of the indented wax surface, and (c) molded and peeled off silicone rubber nano-bumps.

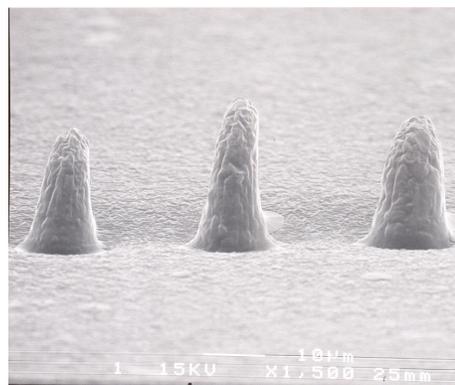


Figure 3. Scanning electron microscope (SEM) micro-graph of micro-bumps (around $10\ \mu\text{m} \times 20\ \mu\text{m}$ size) molded from the STM probe based indented wax surface.

By this precisely controlled technique, a silicon AFM probe (with around $20\text{-}30\ \text{nm}$ tip size) and tungsten STM probe (with around $30\text{-}40\ \text{nm}$ tip size) are used to indent a flat wax surface. A single probe indenting can give the flexibility of even fabricating oriented hair. By indenting the wax surface as can be seen in Figure 1a, the template given in Figure 2a was obtained. The profile of the indented wax surface can be seen in Figure 2b. By molding the wax template with silicone rubber (Dow Corning Inc., HS II), curing the rubber and separating it from the template by peeling, synthetic nano-bumps of Figure 2c were obtained. Moreover, a wax surface indented using the STM probe by a step-and-repeat process gave the high aspect ratio micro-bumps shown in Figure 3.

This nano-robotic method has the flexibility of fabricating different orientation and non-symmetric nano-structures over almost any surface topography and area. However, it enables prototyping of only certain type of low aspect ratio nano-structures, and it is relatively slow due to its serial control process. Therefore, parallel and higher aspect ratio manufacturing methods are proposed below.

Method II: Molding Self-Organized Nano-Pore Membranes

For the second method, a membrane with self-organized high aspect ratio polycarbonate micro/nano-pores (Poretics, Osmonics' Lab Inc) is used as the master template and molded with a liquid polymer as illustrated in Figure 4. This membrane can have pore size of $0.02\text{-}20\ \mu\text{m}$, thickness of $5\text{-}10\ \mu\text{m}$, and pore density of $10^5\text{-}10^8\ \text{pores}/\text{cm}^2$. Moreover, these membranes have a random orientation of the nano-pores ($\pm 15^\circ$) created by a nuclear track etch. The SEM micrograph of a polycarbonate membrane is displayed in Figure 5. 5 and $0.6\ \mu\text{m}$ diameter polycarbonate membranes were molded with polydimethyl siloxane (PDMS, Sylgard 184, Dow Corning Inc.) under vacuum and the PDMS hairs are peeled off from the membrane after curing

at 65 C° for 4 hr. Resulting hairs with 5 and 0.6 μm diameters and 10 and 5 μm lengths, respectively, are shown in Figure 6.

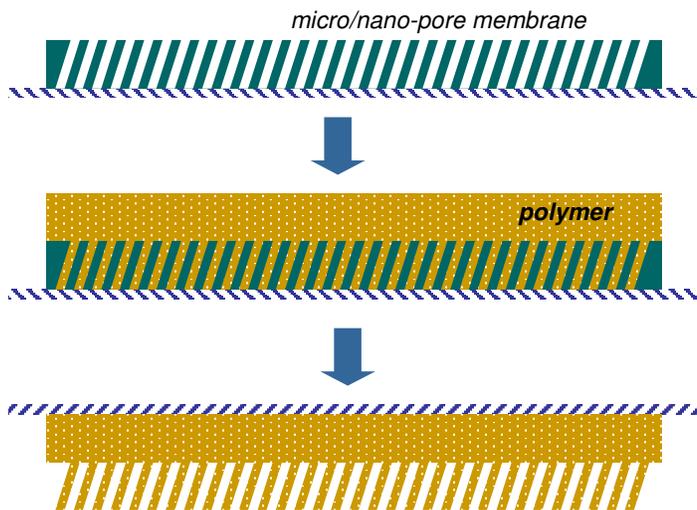


Figure 4. Molding a micro/nano-pore membrane template: bonding the membrane to a substrate, molding the liquid polymer under vacuum, and peeling off the cured polymer or etching away the membrane.

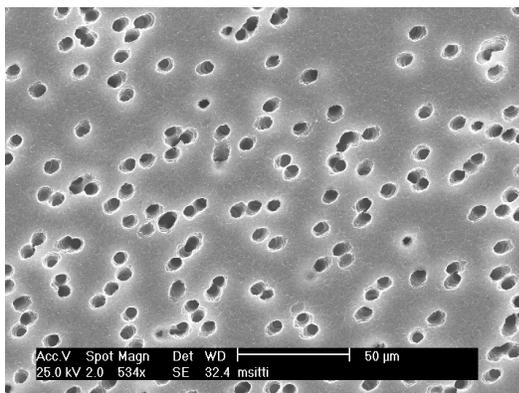


Figure 5. SEM micrograph of a polycarbonate micro/nano-pore membrane top-view image (5 μm pore size here).

The real gecko foot-hairs are hierarchical integration of micron and nanometer diameter high aspect ratio structures for adapting to micron and nanometer scale surface roughness. For enabling the similar hierarchical geometry, two micron and nanometer size pore membranes are bonded, and molded with the liquid polymer as shown in Figure 7. This proposed method would enable high volume, low cost and large area manufacturing of synthetic gecko foot-hairs.

Here, the molded micro/nano-hairs are randomly spaced and oriented on the surface due to the random distribution

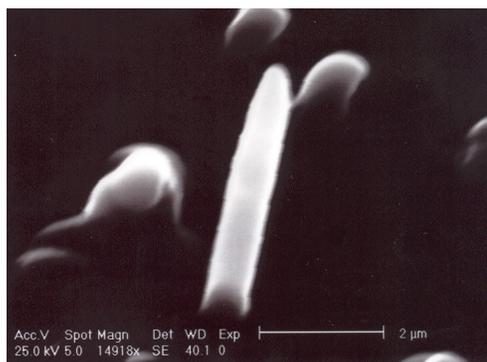
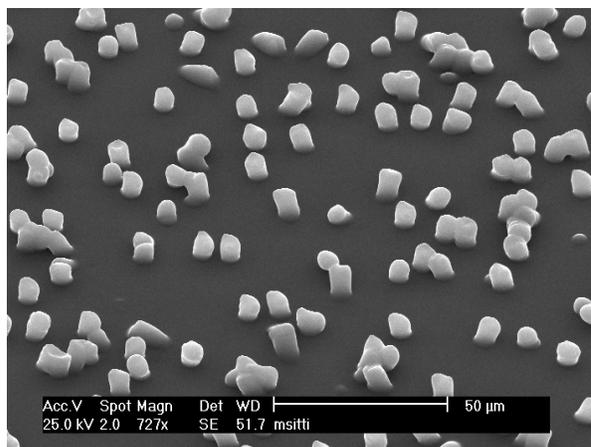


Figure 6. Side view SEM micrographs of PDMS micro/nano-pillars with 5 μm (upper image, 1:2 aspect ratio) and 0.6 μm (lower image, 1:9 aspect ratio) diameters, respectively, fabricated by the Method II.

of the self-organized pores, and regularly spaced and oriented hairs are hard to get.

Method III: Directed Self-Assembly based Micro/Nano-Hair Growth

As a possible solution to the regularly spaced and oriented micro/nano-hairs, a directed self-assembly manufacturing technique is proposed. In this technique, a thin liquid polymer film is coated on a flat conductive substrate, and a closely spaced another metal plate is used to apply a DC electric field on the polymer film. Due to the instabilities on the film, micro/nano-pillars are started to grow until touching to the upper metal plate. By precise timing control using optical microscope feedback, micro/nano-pillars are stopped on the top plate. This technique is proposed in [8, 9]. As an extension of this technique, the self-organized micro/nano-pillars are stretched in z-direction and sheared along x-direction after soft-baking the polymer in this paper. These tensile and shear forces are applied by moving the upper electrode plate precisely for controlling the expected aspect ratio and orientation of nano-pillars. The growth and stretch/shear schemes are illustrated in Figure 8. Then, the desired structures are held by hard-baking the

final structures, and peeling the polymer from the upper electrode. Pulling length is limited by the volume of the nano-pillar, surface energy of the polymer, and the pulling speed.

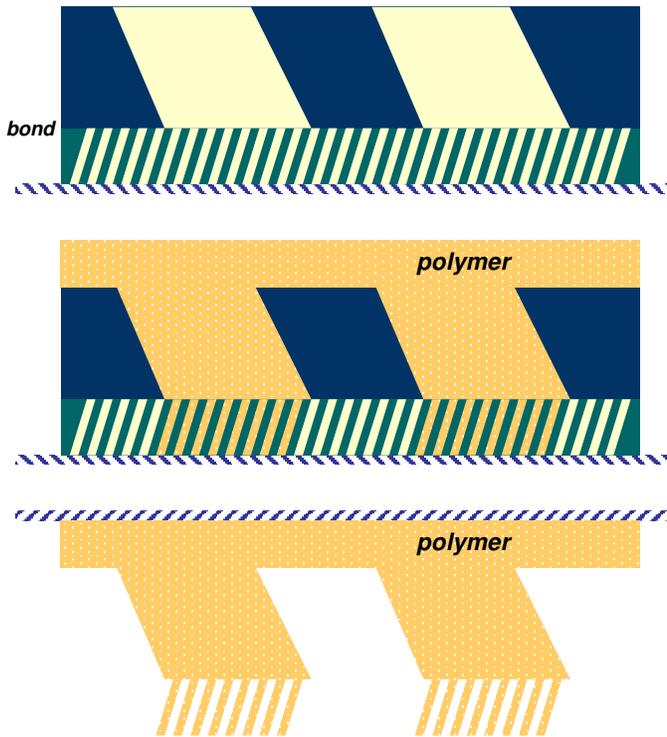


Figure 7. Integration of micro- and nanometer size structures for manufacturing hierarchical high aspect ratio gecko foot-hairs: bonding the micron and nanometer size pore membranes (uppermost), molding with the liquid polymer through the micro-pore membrane site (middle), and curing the polymer and etching away the both membranes (lowermost).

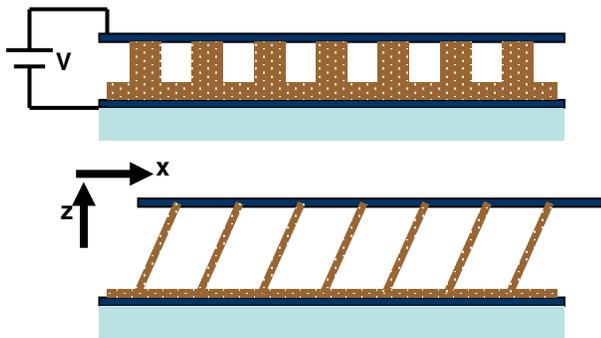


Figure 8. Directed self-assembly based growing of high aspect ratio micro/nano-hairs scheme: (a) Growing low aspect ratio micro/nano-pillars by applying a DC electric field to a thin-film polymer, and (b) stretching and shearing the pillar structure stuck to the upper gold electrode using a precision stage.

CONCLUSION

High aspect ratio micro/nano-structures inspired from biological gecko foot-hairs were fabricated by three different manufacturing techniques. AFM probe-based indented flat wax surfaces in the Method I and self-organized polycarbonate micro/nano-pore membranes in the Method II were used as the master templates as the first molding approach. Micro/nano-bumps and 1:2 and 1:9 aspect ratio micro/nano-hairs are fabricated using PDMS as the molding polymer, and the preliminary results are very promising for mass production, even for integrated hierarchical micron and nanometer hairs. The proposed Method III is still under progress while it is the best method since the aspect ratio and orientation are controlled very precisely and spacing and orientation of all the hairs are very regular.

Fabricated hairs will be characterized by measuring their adhesion and friction on various rough and flat surfaces to show the dry adhesion property of the synthetic gecko foot-hairs. These synthetic hairs will be utilized for future novel miniature space and surgical robot feet.

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