NOTE

Fabrication of a gecko-like hierarchical fibril array using a bonded porous alumina template

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Abstract
We report a new method to fabricate a hierarchical microfibril array by using bonded porous alumina templates. The fabrication approach extends a powerful and well-established technique of creating porous alumina to create a polymer multilevel structure, mimicking the hierarchical structure of gecko adhesive foot hairs. The nanoporous alumina (pore diameter \(\approx 60\) nm; interpore distance \(\approx 100\) nm) was generated by the anodization of an aluminum film in an oxalic acid solution. The microporous alumina was produced by exploiting the parallel wafer-scale processing of conventional lithography and anisotropic chemical etching of the thick film of anodic alumina pores. The micro- and nanoporous alumina membranes were subsequently brought into intimate contact and their bonding was accomplished by means of capillary forces and then van der Waals bonding. Hierarchical polymeric microfibrils (fibril diameter \(\approx 10\) \(\mu\)m; fibril length \(\approx 70\) \(\mu\)m) with nanofibril arrays at their tips were obtained after depositing a desired material into the pores and selective etching of the template membranes. The nanofibril has a lateral dimension of approximately 60 nm with length-to-diameter aspect ratios as high as 100:1.

1. Introduction
In nature, some climbing lizards, insects and spiders exhibit remarkable adhesive properties resulting from the intermolecular interaction of micro/nanostructures on their digital pads with the profile of the substrate [1–3]. In the case of geckos, their feet are covered by hierarchical microstructures that provide a sufficiently large contact area with the substrate. Considerable efforts have been devoted to the design and controlled fabrication of gecko micro/nanostructures, including electron beam lithography [4], template synthesis [5, 6], MEMS fabrication techniques [7, 8], colloidal nanolithography [9] and carbon nanotubes based structure [10]. However, in many cases the reported methods aim to produce the terminal bristle component of gecko foot hairs, thereby limiting the applications of artificial structures for smooth substrates [9]. A very different fabrication approach was reported by Northen and Turner [7, 8], who proposed multiscale integrated compliant structures (MICS) to mimic the hierarchical structure of the gecko adhesive system. The MICS was fabricated by silicon
microfabrication technique and it consists of a silicon dioxide platform, supported by a single silicon pillar and covered with vertically aligned polymeric nanorods. Except for this technique, no efficient fabrication method has been reported so far on large-scale arrays of multiscale compliant structures.

A template-assisted nanofabrication strategy, based on the deposition of the desired material into arrays of well-aligned micro- and nanochannels, is one promising method for growing one-dimensional micro- and nanostructures [11]. Among the potential self-assembled templates, porous anodic aluminum oxide (AAO) has drawn much attention because it can give rise to a self-assembled honeycomb array of uniformly sized parallel channels. Thus, by filling the pores of the AAO template, arrays of aligned nanofibrils uniform in diameter and length can be obtained reproducibly and economically. In the past decade, porous AAO films have triggered numerous investigations into their utilization as templates or masks to fabricate various nanostructures (nanotubes [12], nanowires [13], nanoporous films [14] and nanodot arrays [15]) for wide-ranging applications in photocatalysis [12], perpendicular magnetic media [13], DNA sensors [14] and field emission [15]. More recently, a porous template of commercial alumina membranes has also been employed to fabricate a vertically aligned polystyrene nanotube layer, mimicking the terminal structure of a gecko’s foot hairs [6]. The synthesized single-level fibrillar structures, however, do not accurately derive the pattern of multi-branched setae in the feet of a gecko. Although many points of contacts can be made on uneven surfaces by having many small adhesive units to conform to the surface irregularities, without some rigidity or structural stability, the long and thin fibrils will stick together and impair adhesive efficiency. In gecko setae, the design of a solid shaft with branched tips combines the rigidity from the thick setae fibrils, and the flexibility from the fibrillar base and fine spatulae fibrils, to attain the most efficient adhesion without having the problems of matting. It is therefore of great interest to develop methods to create structures with a hierarchical pattern, with the ultimate aim of replicating the complex multi-branched structures in the gecko setae.

Herein, we demonstrate the simple but widely applicable AAO-assisted nanofabrication of a two-level hierarchical fibril array on a flexible substrate over a large area. The central idea of our approach is to fabricate two or more alumina membranes, each containing high aspect-ratios of micro- and nanopores, and bond them together using surface forces. To prepare the microporous alumina, we used a conventional lithography method for selectively closing part of the channels of an ordered array on an AAO film. The pores structure in the exposed area was subsequently etched away in order to create a custom-patterned microchannel array. In the preparation and manipulation of the thin nanoporous anodic film, great care needs to be exercised as AAO is a brittle ceramic film grown on the soft aluminum metal. The key aspect to the nanofabrication process described here is that one could control the aspect ratios of the micro- and nanoporous templates independently before integrating the two together. Following the formation of hierarchical porous template, polymer solution was spun on its surface to fill the channels. An ensemble of hierarchical microstructures protruding from a surface can be obtained after dissolving the template in a wet etchant solution.

2. Experimental details

The fabrication procedure of the binary hierarchical microstructures is schematically shown in figure 1. The porous alumina templates were fabricated through a typical two-step anodization procedure [16]. An aluminum sheet (99.999% purity, 30 mm × 20 mm × 0.25 mm) was first degreased in acetone and annealed in nitrogen ambient at 400 °C to remove mechanical stresses and to recrystallize the samples. Subsequently, the substrate was electropolished under a constant current condition of 100 mA cm⁻² below 10 °C for 4 min in a mixed solution of HClO₄ and C₂H₅OH. The first anodization (step a) was conducted in a 0.3 M oxalic acid solution at 25 °C under a constant voltage of 40 V using a direct current source for 6 h. The electrolyte solution was stirred vigorously using a magnetic stirrer in order to accelerate the diffusion of the heat that evolved from the sample. This treatment is important to prevent the increase in the localized temperature and to maintain the stable growth of the anodic oxide layer. The first porous alumina layer was then removed in a mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid at 60 °C. Following this step, two porous alumina membranes were prepared under different anodization conditions. One was anodized at 25 °C for 8 h (step b) and another was anodized at 2 °C for 15 m (step c) to obtain a thick and thin porous alumina membrane, respectively.
In order to prepare high aspect-ratio microporous alumina template, a 0.15 μm thick Au layer was first sputtered on the surface to block the pores and improve the surface flatness. A photolithography process was then used to define the pattern of micropores. A positive photoresist (Clariant, AZ7220) was spun on the Au-coated alumina substrate and a potassium iodide based etch solution was used to transfer the patterned resist to the Au layer. The exposed area of the porous alumina was then etched down with a chemical etching in an aqueous 5 wt% phosphoric acid solution. And finally, the alumina layers were separated from the Al substrate in the mixture solution of saturated CuSO$_4$ and HCl (step d). The freestanding thin nanoporous alumina template was prepared by placing the 0.1 ml poly(methyl methacrylate) or PMMA solution (5 wt% in anisole, molecular weight: 950,000) on the top side of the template membrane (≈1 cm$^2$ surface area) and heating up the polymer solution above its glass transition temperature at 120 °C for 1 h. Selective removal of the barrier layer and a pore widening treatment were performed by etching in the 5 wt% phosphoric acid solution for 45 m after separation from the Al substrate in the erosive CuCl$_2$ based solution (step e). The thin alumina–PMMA membrane was subsequently wetted with deionized water and placed on the top of the microporous alumina template. The PMMA was then removed using the UV–ozone cleaning system (SAMCO, UV-300H) prior to depositing a desired polymeric material into the hierarchical microporous template (step f). To prove the fabrication concept, we used a more concentrated PMMA (10 wt% in anisole) as the synthetic fibril material. The material was placed on the top surface of the template, spun at 3000 rpm for 30 s, and heated up in the oven at 120 °C for 1 h. The whole template was then dissolved in the phosphoric acid solution to free the fibrils that had been deposited within the pores (step g).

### 3. Results and discussion

Figure 2(a) shows a SEM micrograph of the anodic oxide membrane with the typical self-ordered cell configuration which was formed under the most appropriate conditions in oxalic acid solution. The micrograph was observed from the top side of the membrane after the two-step anodization process. From this figure, an almost ideally hexagonal cell configuration with a cell size of approximately 100 nm was observed. The inset shows a cross-sectional morphology of the ordered nanopore arrays, where straight and parallel long channels are observed. The formation mechanism of these well developed pore systems has variously been studied and described in the literature [17–19]. One of the numerous advantages of this material is the ability to control its pore width and pore length over wide size ranges from a few up to several hundreds nm. The width depends directly on the anodization voltage and the length on the anodization time.

High aspect-ratio microstructures were conventionally fabricated using techniques like deep reactive ion etching or x-ray lithography. By exploiting the built-in anisotropy of nanoporous alumina membrane, such structures can be achieved with a sub-micrometer precision using photolithography and isotropic wet etching, as described in this note. The result of micropatterning process is shown in figure 2(b), where an anisotropic profile can be clearly seen. The pores are about 70 μm long and 10 μm in diameter. A highly anisotropic etch can be expected here as the etchant penetrates into the pores and etching occurs at the whole oxide/solution interface due to the high density of pores of the alumina. By dissolving only half a pore wall, the pores structure in the opened window of the Au layer can be completely removed. In order to achieve steep side walls, it is essential that the etching process is slow enough for the etchant to penetrate deep into the pores. Both the etchant concentration and the etching time are the key factors that determine the profile of the microporous structures. The structure begins to undercut with extended etching time, as shown in figure 3(a). Conversely, etching time that is too short causes an inhomogeneous penetration of the etchant into the pores, resulting in tapered pores as shown in figure 3(b).

While a freestanding thick alumina membrane (>30 μm) is simple to be prepared, it is not so straightforward to prepare a thin membrane with a thickness in the sub-micrometer range. Due to the handling difficulty, the reported thinnest freestanding alumina is 120–150 nm in thickness [20]. Prior to selective etching of aluminum in copper (II) chloride solution, it is essential that one infiltrates polymer into the pores to act as a supporting layer. In our experiment, PMMA was coated.
Figure 3. SEM micrographs of (a) undercut structures due to the extended etching time and (b) tapered pores due to the non-homogenous penetration of the etchant solution into the pores.

Figure 4. Intimate contact between two membranes (inset shows clean nanoporous alumina template after the UV–ozone treatment).

onto the alumina surface and heated above its glass transition temperature so that it can easily move into the pores. After cooling down to room temperature, the sample was immersed into the erosive CuCl₂ solution and within few minutes the ∼200 µm thick aluminum was completely removed. The ∼0.5 µm alumina was found floating on the surface and was still intact with the thin PMMA film. The alumina–PMMA membrane was subsequently rinsed with deionized water and carefully transferred onto the top surface of the microporous alumina membrane, which has been prepared previously. Figure 4 shows that both surfaces adhered closely by means of van der Waals bonding when the water dries out. Such technique of bonding alumina with another surface using van der Waals interaction has been previously employed to produce nanodot arrays using alumina templates as masks [21, 22]. Utilizing a combination of ultraviolet light, a high concentration of ozone and controlled heating, the PMMA was stripped from the bonded template to obtain a clean porous template, as shown in figure 4 (inset).

The final fabrication step involves the infiltration of a solution of the desired material into the pores of alumina membranes. Here we used low-viscosity polymeric solutions (10 wt% PMMA) to fill the pores. PMMA, a thermoplastic material, has Young’s modulus of approximately 2400 MPa [23]. The relatively low processing temperature and low shrinkage properties make PMMA easy to process in casting and molding. Other prominent physical properties of PMMA, such as good mechanical strength and dimensional stability, along with high tensile and flexural strength, also provide a reasonably good approximation to the material properties of natural gecko foot hairs. Under optimum conditions, PMMA flows into the pores by the capillary action, creeps along the inner pore walls and fills them, resulting in fibril structures. As discussed in section 2, the alumina membrane was dissolved away to expose the polymeric fibrils prepared in the pores. This fibril preparation method is applicable to any polymer that can be dissolved in a solvent that does not attack the template membrane. Water soluble polymers might not be suitable for this application as the polymeric fibrils would dissolve in the aqueous solutions used to dissolve the template. Figure 5 shows SEM images of hierarchical microstructures composed of PMMA after dissolving the alumina membrane in phosphoric acid solutions. An ensemble of hierarchical microfibrils that protrude from a surface like arrays of gecko
Figure 5. SEM micrographs of (a) hierarchical microfibril array featuring \(\approx 10 \mu m\) wide and \(\approx 70 \mu m\) long microfibrils, each branches into an \(\approx 60 \text{nm}\) wide and \(\approx 0.5 \mu m\) long nanofibril array; (b–c) magnified top view and (d) oblique view of the nanofibril array.

foot hairs is obtained. The lengths of these microfibrils show that they span the complete thickness (\(\approx 70 \mu m\)) of the template membrane. The diameter of the fibrils is about 10 \(\mu m\), as determined by the opening diameter of the Au transfer layer. At the tip of these fibrils, closely packed arrays of smaller and thinner fibrils are observed. The fibril diameter reflects the pore diameter (\(\approx 60 \text{nm}\)) of the template, and the fibril length is equivalent to the thickness (\(\approx 0.5 \mu m\)) of this template.

It should be noted that the length of the fibrils cannot be too long as there is an instability leading to fiber bunching as the aspect ratio of the fibrils increases. The surface adhesive forces may cause the neighboring fibrils to bundle together, significantly reducing the adhesion forces. Spolenak et al [24] have previously derived an anti-condensation criterion for fibrils with the radius \(R\), the length \(L\) and the interfibril spacing \(2\Delta\) as follows:

\[
R \geq \frac{8\gamma h(f)\lambda^2}{E} \frac{1}{\lambda^3}
\]  

where \(\lambda\) is the length-to-diameter aspect ratio of a fibril, \(E\) is Young’s modulus, \(\gamma\) is the work of adhesion between two fibril tips and \(h(f)\) is given by

\[
\frac{1}{h(f)} = \left(\frac{(2R + 2\Delta)^2}{4R^2} - 1\right)^{\frac{1}{2}}.
\]

For a given fibril diameter \(2R \approx 60 \text{nm}\), aspect ratio \(\lambda \approx 10\), work of adhesion \(\gamma \approx 60 \text{mJ m}^{-2}\) and Young’s modulus \(E = 2.4\) GPa, we get the minimum value of the interfibril spacing \(2\Delta \approx 400 \text{nm}\) to prevent fibril condensation. In order to obtain such a wide interpore spacing, a more sophisticated and promising technology, involving prepatternning of the substrate surface, can be adopted [25]. This is because naturally occurring self-organized alumina membrane, in general, has a very high density of pores with a very small interpore distance. With the prepatternning method, it is possible to control the interfibril spacing and therefore minimize the clumping effect between fibrils.

Although we have artificially created the binary-branched gecko setae and unraveled the long time challenge in replicating the hierarchical pattern in gecko foot hairs, more detailed studies are needed to help understand their adhesive property as a result of the hierarchical patterns. In addition, two factors have yet to be incorporated in the design of our artificial structures; future work will pursue these issues. First, the gecko foot hairs are built at an inclined angle other than 90° to the backing surface and second, at a much smaller scale, there exist triangular-shaped compliant pads at the tips of gecko spatulae. Both have been reported to have considerable influences on the adhesion strength of ‘hairy’ attachment structures [26]. Other application, considered to be of significant technological impact, is to make ‘self-cleaning surfaces’ by using hierarchical fibrillar structures, such as gecko’s feet that remain clean despite their surroundings. Such surfaces have distinctive superhydrophobic characteristic, that is, water droplets form spheres with a very little adhesion to the surface and roll off very quickly even at small inclinations, due to the roughness on the micro- and nanometer scales. Water droplets as well as dirt particles only lie on the tips of these structures and develop low adhesion forces to such rough surfaces.

In the present study, we determined the wetting property of three types of surfaces. All samples are made of polymer, have the same surface chemistry, allowing the comparison of the effect of different micro- and nanostructure geometries on water repellency and self-cleaning. Figure 6 shows the equilibrium water contact angle on these surfaces. It can
be seen that the measured contact angles of the non-patterned PMMA surface is the lowest of all surfaces presented here. The water contact angle was measured to be about 70° (figure 6(a)). The second specimen was prepared from a ≈0.5 µm thick alumina membrane, resulting in ≈ 60 nm wide fibrillar structures with interfibrillar spacing of ≈ 100 nm. Figure 6(b) shows the water contact angle of ≈ 85° on the patterned surface, a mere ≈ 15° increment from that on the non-patterned surface, in view of the fact that the nanostructures are closely packed arranged on the surface and there is a very little air enclosed between the structures. The third specimen, which is our hierarchical fibril array (figure 5), has a combination of micro- and nanostructures on different length scales. On this surface, the water droplet is almost spherical with a contact angle of ≈ 150° (figure 6(c)). It appears that the combined structures lead to a considerable reduction of the contact area between the surface and the water droplets.

Our experimental analysis above indicates that the hierarchical structure could be contributing to the amplification of the apparent contact angle. More importantly, it helps in understanding the optimal surface pattern to develop ‘self-cleaning surfaces’. This is in good accordance with the calculations of Patankar [27] who proposed the significance of double roughness structures in the lotus ‘self-cleaning effect’.

4. Conclusions

In summary, we have employed conventional lithography to selectively close nanochannels on an AAO film and performed an isotropic chemical etching to partially remove the exposed pore structures, thereby creating custom-designed templates containing high-aspect ratio microchannels. In contrast to the anisotropic microporous structures fabricated by, e.g., deep reactive ion etching, x-ray lithography, our samples can be prepared by using a simple experimental setup without the need of high cost equipments. We have successfully obtained a free-standing thin AAO film with a thickness of ≈ 0.5 µm and demonstrated the convenience of bonding two membranes using capillary forces and van der Waals interactions to produce the hierarchical porous template. The binary-branched fibril arrays closely copy the hierarchical pattern of the bonded AAO templates. Since the fibrils are regulated by the micro- and nanochannels of AAO template, there is basically no limitation to the materials for the fibril arrays. We believe that the reported process has a strong impact on the prospect of developing multi-branched structures of gecko setae for future design of a remarkably effective adhesive.

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