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Biomimetic soft lithography on curved nanostructured surfaces

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ABSTRACT

In this paper a nano-molding process using a nature-created master is demonstrated. The eye of night moth *Agotis exclamationis* having 100 nm-scale structures on a curved surface is used as biomimetic master mold from which nanostructures are replicated onto a flat substrate. Suitable conditions of this simple and cost-efficient process allows for minimal texture damage. The fabrication consists of two steps: first, a negative PDMS mold of the curved eye surface is made, and second, the flexible mold is replicated into a hybrid UV sensitive polymer, on a flat substrate. An accurate copy of the master surface with dense arrays of 200 nm high and 100–120 nm wide posts are generated, thus preserving the integrity of the nanostructures. The known anti-reflecting optical properties of the moth eye were reproduced with a reflectivity reduced by a factor of 2.

1. Introduction

3D and curved surfaces are used in many application areas of micro and nanotechnology e.g. for optical and fluidic elements, MEMS and NEMS. The fabrication of curved prototype surfaces and structures is usually a complex and tedious multistep process, especially when aiming to reach the nanometer scale. These drawbacks encourage the development of replication and molding processes, allowing a fast and simple fabrication [1]. Therefore the ability to replicate curved surfaces with complex patterns into another material and substrate in a repeatable manner helps to significantly decrease the process costs and to add surface functionality.

Pattern transfer techniques are of particular interest in the field of biomimicking, allowing the replication of nature-created functional surfaces with unique properties, such as self-cleaning, wettability or transparency enhancement [2–5]. However, in order to successfully reproduce bio-surfaces some challenges must be overcome: the original bio-molds usually release gases and deteriorate in a short time or contain fragile structures that are difficult to study. As a result, a number of technology tools and methods were developed to mimic and copy surface features and their properties. Costly techniques such as atomic layer deposition (ALD), electroforming or lithographic methods, as well as low cost processes based on self-assembly or etching were exploited to mimic functional bio-surfaces with micro and nanostructures [6–10]. The direct copying of bio-surfaces of cicada wing and various plant surfaces were made using nanoimprint and casting [4,5,11], so far involving only flat and small areas or micrometer-scale structures. In this work we have directly used a nature-created sample as a mold and developed a simple soft lithography template-based approach to transfer curved and nanopatterned features onto a flat surface. An antireflective surface was for the first time copied from nature created sample, providing a no-cost mold suitable for surface reflectivity studies. The nanopatterns having 100 nm size and 2:1 aspect ratio features with antireflective properties were copied.

2. Materials and methods

As proof of concept we have used an eye of *Agrotis exclamationis*, a common European night moth as master. The moth has distinctively black compound eyes, consisting of arrays of 20 μm diameter pentagonal microlenses [7] (Fig. 1). The surface of the microlenses is homogenously covered with arrays of 100–120 nm wide, 200 nm high and 150–200 nm period nanoposts. The nanopatterned surface functions as an antireflective layer and contributes to an enhanced light collection at night. The height and shape of the nanostructures are the critical parameters for the efficiency of the antireflectivity [12]. Therefore, in order to preserve the antireflective effect it is necessary to achieve high resolution molding preserving the nanostructures shape and aspect ratio of 2:1.

The replication process we propose here consists of two steps (Fig. 2): first, the eye structure is transferred into poly-dimethylsiloxane (PDMS), preserving the 3D shape of the eye. In the second step, a drop of Ormostamp (Micro Resist Technology GmbH, Berlin [13]) is dispensed on the curved flexible PDMS-mold and crosslinked in UV light preserving the 3D shape of the eye. In an

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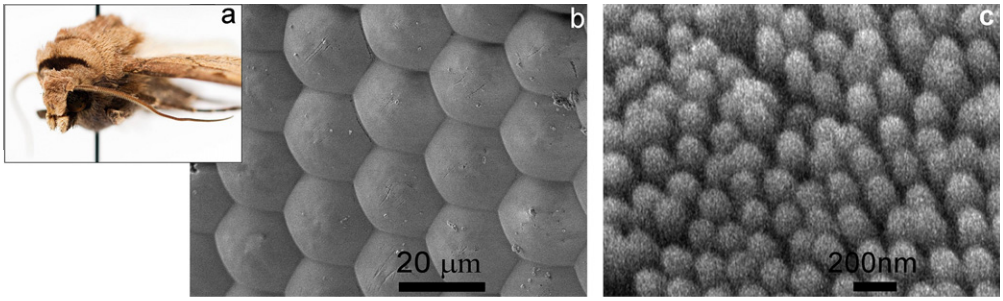

Fig. 1. (a) Optical image of *Agrotis exclamationis* and electron micrograph images of (b) pentagonal microlens array on the moth eye, and (c) close-up to the surface of microlenses showing 100–120 nm wide posts covering the entire microlens surface.

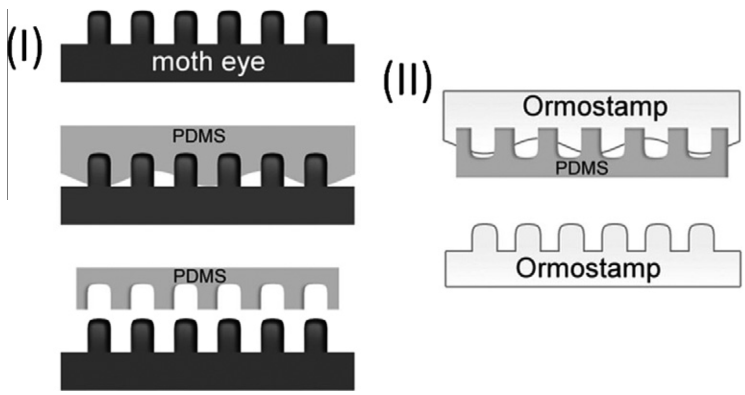

Fig. 2. Schematic presentation of the nanopost replication process: (I) the original moth eye is immersed into PDMS-mixture and cured at 80 °C; PDMS mold is removed and cleaned in IPA; (II) a drop of Ormostamp is dispensed on the PDMS mold and cured in UV light either pressed to the substrate (2D) or in the original shape (3D).

alternative process we also pressed the PDMS-mold onto a substrate to render it flat. Thus, both 3D and flat 2D functionalized surfaces can be created by this method. Using a soft primary mold and a UV cross-linkable hard final copy allows us to change their curvature and realize final copy in a stabile and hard material offering optical properties close to the biological sample.

3. Results

PDMS elastometer is extensively used as versatile molding material for micro and nanostructures [14,15]. In order to make the most accurate PDMS copies of the nanoposts we have tested several PDMS solutions and its treatment in vacuum. 5:1, 10:1, 20:1 mixtures of PDMS base elastometer and curing agent solutions, and 10:1 mixture with hexane were prepared. The curing was performed in an oven at 80 °C for 1 h. It was found that the standard 10:1 solution results in the best replicated pattern (Fig. 3a). The harder and more stabile cross linked PDMS made of 5:1 solution was too brittle for further surface shaping, while the 20:1 solution, expected to improve the elasticity, was too viscous to penetrate between the posts for fine pattern transfer. The more liquid PDMS solution can be made by adding 50% weight hexane to the standard PDMS prepolymer [16]. The positive PDMS copies made with hexane indeed resulted in highest posts, nevertheless the posts were irregular and collapsing possibly due to residual hexane effects on Ormostamp. Additionally, we have tested various vacuum levels to help PDMS penetration into sub-50 nm gaps between the posts. When mixed, PDMS base elastometer and curing agent solutions were placed into vacuum with pressures from 10^{-2} to 10^{-5} mbar. The PDMS preparation in vacuum at the pressure of 10^{-5} mbar resulted in significantly improved post height.

The following final nanopost pattern transfer was made by placing a drop of Ormostamp on PDMS mold and covering it with a primed glass substrate for the transfer, and after cross linked in UV light (Fig. 3b). In order to obtain the copy on a flat surface, before and during the UV curing a slight pressure was applied on the glass slide. The copied posts on the curved surface were well replicated over the whole sample area. Flat or 2D copies of the posts have been also obtained on the area of several square millimeters. Applying pressure to the PDMS mold during the second step of the process resulted in distortion of the microlenses with minimal damage to the nanoposts (Fig. 3c).

The refractive index of the final nanopost copy in Ormostamp is 1.48, while the refractive index of the cornea of the moth eye lens reported in the literature varies in the range 1.38–1.52 [17,18]. The close values of refractive indexes of both, the original moth eye and the copy as well as the accurate geometrical copy of the eye surface allow us to reproduce the optical surface performance of the eye. The preliminary measurements of the moth eye reflection intensity ratio from the surface with and without the nanoposts reach the value of 2.1 (Fig. 3d), showing the efficiency of the nature created antireflective surface. The moth is active at night and profits to a great extent from this nanostructured surface phenomena.

Numerical optical simulations done using the FIMMWAVE and FIMMPROP software (Photon Design, Oxford, UK) have shown that the replicated nanostructures exhibit reduced reflection intensity by a mean value 2.8 in the visible spectrum. Differences between experimental results and simulations may be due to the fabricated nanostructure size uncertainty, as well as incomplete area coverage with nanostructures. However, this demonstrates enhanced transmission of light on the surface having the moth eye-transferred nanostructures, as it was expected.

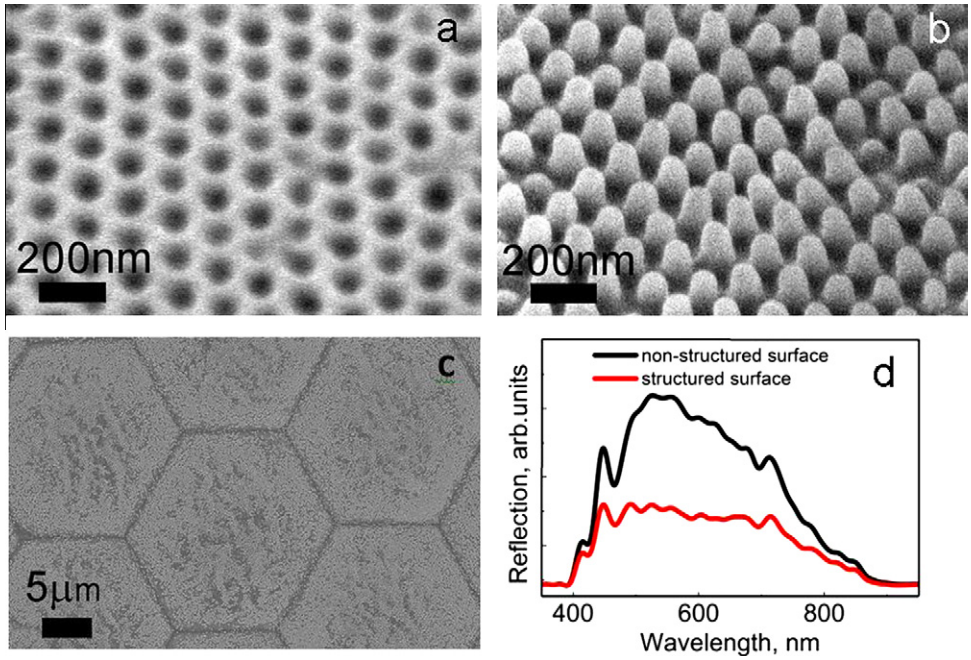

Fig. 3. Soft lithography molding process from a curved surface of the moth eye covered with nanoposts on a flat substrate: (a) a positive-PDMS mold of the nanoposts replicated from the surface the moth eye obtained in a step I, (b) Ormostamp copy of the 200 nm dense post arrays obtained in the step II, (c) a flat Ormostamp copy of the moth eye microlenses covered with nanoposts transferred onto a glass substrate and (d) reflectivity of nanostructures surface decreases by a factor of 2.1 compared to non-structured surface.

In conclusion, we have demonstrated a simple pattern transfer technique from a biological sample, both curved and flat surfaces having micro and nano-patterns by using a biomimetic template. The results obtained using this bio-inspired nano-molding technique proved that the proposed technology can be used to replicate complex functional surfaces and integrated into PDMS-based fabrication process of small area micro-optical and microfluidic and upscalable systems.

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