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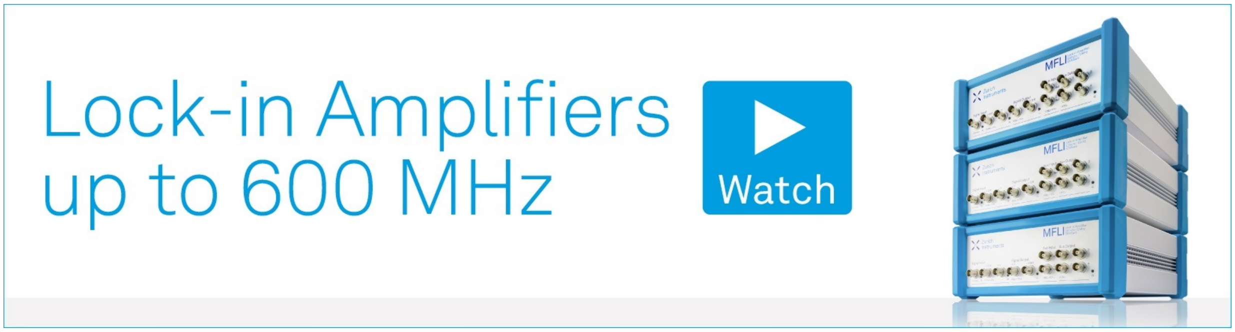

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# Precise replication of antireflective nanostructures from biotemplates

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The authors report herein a new type of nanonipple structures on the cicada's eye and the direct structural replication of the complex micro- and nanostructures for potential functional emulation. A two-step direct molding process is developed to replicate these natural micro- and nanostructures using epoxy resin with high fidelity, which demonstrates a general way of fabricating functional nanostructures by direct replication of natural biotemplates via a suitable physicochemical process. Measurements of spectral reflectance showed that this kind of replicated nanostructure has remarkable antireflective property, suggestive of its potential applications to optical devices.
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After evolution of 3.5 billions of years, biological systems in nature have developed a number of micro- and nanostructures endowed with fascinating functions for tailoring themselves to the elements. The well-known and intensively studied example is the lotus leaf, which has complex micro- and nanostructures responsible for the excellent superhydrophobicity.[1] Other examples involve the dark beetle for collecting dew through hydrophilic/hydrophobic microspots,[2] the gecko's foot hair for wall sticking through elastic nanohairs,[3,4] and so on. Compound eyes of insects present a fascinating object of biomimetic studies because of their well-developed structures responsible for biological optical systems.[5] The typical cornea surface structure of insects' compound eyes is composed of thousands of micrometer scale hexagons. In 1965, Bernhard *et al.*[6] observed nanometer scale nipples on the cornea surface of the night moth's eyes. These round protuberances have an average height and center-to-center distance of ~200 nm, which were found to be highly antireflective from both theoretical and experimental investigations.[6]

Recently we have used nanoimprint lithography to replicate the nanostructures of the cidada's wings.[7] Here we report on the structural investigation and replication of the cicada's compound eyes by a low-cost replica molding process.[8] By using a modified replica molding technique, we replicated the complex micro- and nanostructures with high fidelity for potential functional emulation. Instead of polydimethylsiloxane (PDMS), the harder thermally curable epoxy resin was utilized as the replicating material, which ensured the high-fidelity replication and the atomic force microscopy (AFM) imaging with less distortion. By measurements of spectral reflectance, it is found that this kind of replicated nanostructure has remarkable antireflective property.

Similar to the insects reported previously,[6] the cornea surface of the cicada's compound eye is composed of thousands of hexagons together with a few pentagons and rectangles as shown in the scanning electron microscopy (SEM) image of Fig. 1(a). The side length of the hexagon is 21.31 $\mu$m in average. From the AFM image shown in Fig. 1(c), it can be seen that the hexagons are three-dimensional protuberances and have a dimension of 1.56 $\mu$m in height. The AFM images shown in Figs. 1(b) and 1(d) clearly indicate the nanometer scale nipple structures on the hexagons. The average width of the nanonipples was 98.8 nm from SEM data and the average height was 34.8 nm from AFM data. The nanonipple width estimated from AFM data was $106.1 \pm 12.2$ nm, slightly different from the SEM result, mainly arising from the AFM tip convolution effect. Interestingly the height of the nanonipples for the cicada's eye is only ~1/5 of those of the other insects reported. The center-to-center internipple spacing is approximately 200 nm obtained from two-dimensional fast Fourier transform analysis of the AFM image, similar to the reported value for other insects. Different from the moth's eyes, the nanonipples of which are round and have a regular hexagonal close packing structure, the nanonipples of the cicada's compound eye are not so regular and most of them have a round shape structure. These observations demonstrate that although the cicada's compound eyes have similar hexagon-with-nanonipple structures with other reported insects, the nanonipple structures are considerably different among them, suggesting the different biological needs of individual species tailored to the elements.

One of the essential biomimetic efforts to implement a biologically inspired system is to develop the precise replication technique of target structures. A two-step direct molding technique was proposed for replicating the complex micro- and nanostructures of the cicada's compound eyes. The replication process involves two main steps: the first-step replication at room temperature using PDMS and the second-step replication using epoxy resin at 150 °C. Figure 2 shows the SEM and AFM images of the epoxy replica of the cicada's compound eye obtained by the two-step direct molding technique. The general features of the epoxy replica are in nice accordance with the original cicada's eye template. Using a similar data analysis method, we obtained the three-dimensional data of the epoxy replica, which were 20.85 and 1.57 $\mu$m for the side length and height of the hexagon, and 104.6 and 36.6 nm for the width and height of

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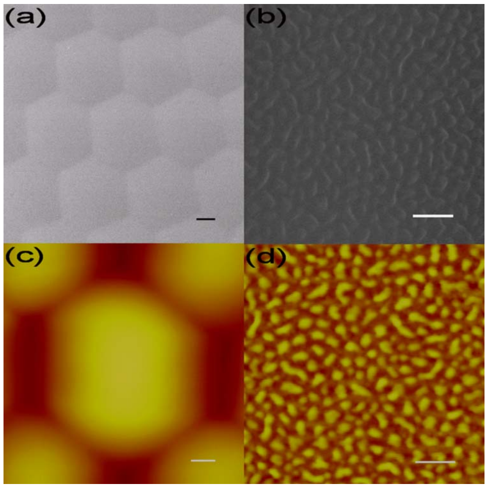

FIG. 1. (Color online) Structural identification of the cicada's cornea surface. (a) SEM image of the micrometer scale hexagons (Scale bar: 10 $\mu$m). (b) SEM image in low vacuum mode of the nanonipple structure (Scale bar: 500 nm). (c) AFM image of the hexagons (Scale bar: 5 $\mu$m). (d) AFM image of the nanonipple structure on the hexagons (Scale bar: 500 nm).

the nanonipples, respectively. For the micrometer scale hexagon structures, the deviations of the epoxy replica from the biotemplate are −2.2% and 0.64% for the side length and height, respectively. On the other hand, in the case of the nanonipple structures, the deviations from the original template are 5.2% and 5.9% for the height and width, respectively. The structural fidelity of replication is better than 94% for the complex micro- and nanostructures of the cicada's compound eyes. These results demonstrate that the two-step direct molding technique using epoxy resin enables a reliable replication of the sophisticated natural structures of the cicada's compound eyes.

The high fidelity of replication achieved in this work originated from our meticulous processing and the thermally curable epoxy resin used. There are a number of advantages of the epoxy resin over the reported replicating materials such as hard PDMS (h-PDMS),[9,10] polyurethane,[11,12] polymethylmethacrylate (PMMA),[13] and UV-curable SU-8.[14] Firstly, the liquid epoxy prepolymer has a low viscosity and good wettability to PDMS, which allows for an improved filling to the porous structures of the templates especially under vacuum condition. Secondly, the prepolymer does not involve any solvent or thinner, and therefore there is no outgassing problem during the thermal curing process. This merit helps to eliminate the solvent swelling effects to PDMS and decreases the shrinkage of epoxy resin after curing. Thirdly, the solidified epoxy resin has an elastic modulus of 6895 MPa, much harder than those of PDMS, h-PDMS, NOA 63, PMMA, and SU-8, which have elastic modulii of 1.5, 9,[10] 1655,[12] 3000,[15] and 4400 MPa,[16] respectively. Therefore the epoxy replica can be directly used as a template for imprinting and embossing operation. Moreover the epoxy resin is chemically very stable, resistant to alcohol, nitric acid, ammonia, and most solvents, which is of importance for practical applications. The density of nanonipples on the epoxy replica showed a slight decrease as compared to the biotemplate. This would be a consequence of incomplete wetting of PDMS to the original cicada's eye and epoxy prepolymer to the PDMS negative replica and of thermal expansion effect.

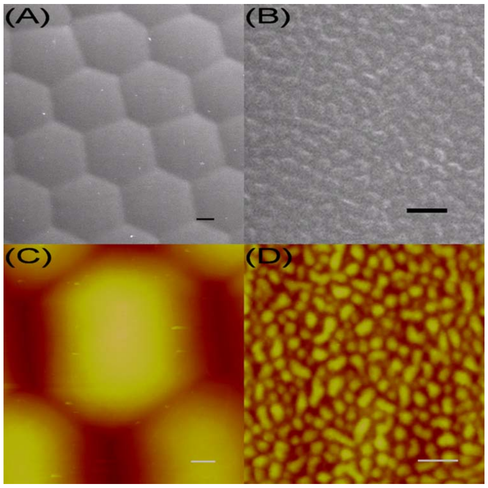

FIG. 2. (Color online) Epoxy replica of the cornea surface of the cicada's compound eye. [(A) and (B)] SEM images of the replicated micrometer scale hexagons and nanonipple structures. Scale bars are 10 $\mu$m and 500 nm, respectively. [(C) and (D)] AFM images of the hexagons and nanonipple structures. Scale bars are 5 $\mu$m and 500 nm, respectively.

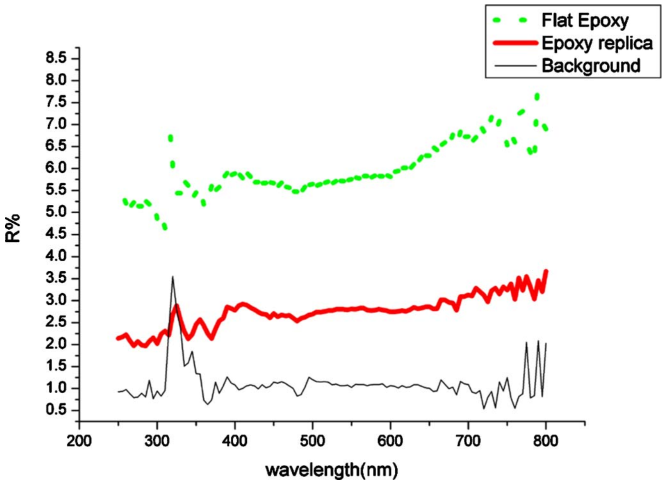

FIG. 3. (Color online) Reflection spectra of the samples. The thin black line (solid curve) at the bottom represents the reflectance of the background (sample holder). The other two solid and dotted curves represent the reflectance of the epoxy replica with nanostructures and the flat epoxy sheet without any surface structure, respectively.

The cornea of insects' compound eyes is mainly composed of wax, chitin, and protein, in which chitin takes the largest part, up to 60% in dry weight of the procuticle.[17] Chitin is a fairly completely acetylated polysaccharide akin to cellulose. The elastic modulus of crystalline regions of $\alpha$-chitin in the direction parallel to the chain axis was measured to be 41 GPa at 20 °C by x-ray diffraction.[18] For the experimentally used samples, the elastic modulus is at the level of gigapascals, large enough for tolerating the replication operation.[19] The results obtained in this work proved that such kinds of cicada compound eyes can serve as natural biotemplates for fabrication of functional nanostructures.

After precise replication of the complex micro- and nanostructures of the cicada's eyes, we used a Lambda 950 spectrophotometer to check its optical performance. As shown in Fig. 3, this kind of nanostructures shows a remarkable antireflective property. For the black background, the reflectance is at the level of 1%. After attaching the flat epoxy sample without any surface structure on this sample holder, we got a reflectance at the level of ~5.5%. In contrast, when using the epoxy replica with the complex micro- and nanostructures, the reflectance dropped to the level of 2.5%, remarkably different from the flat epoxy sample. This demonstrates the possibility of using natural biotemplates to fabricate antireflective optical devices via a simple low-cost replica molding technique.[20]

In summary, we demonstrated a new approach for fabricating various nanostructures by directly using natural biotemplates via a replica molding technique, which provides a new pathway of biomimetic fabrication of functional devices. The cicada's compound eye is proven to be a typical example of such kinds of biotemplates, which can be replicated in high fidelity by a two-step direct molding process using the thermally curable epoxy resin. It is also found that although the cicada's compound eyes have similar hexagon-with-nanonipple structures with other reported insects, the nanonipple structures are remarkably different among them, suggesting the different biological needs of individual species tailored to the elements. A preliminary biomimetic investigation has demonstrated the nice antireflection performance of such kinds of replicated complex micro- and nanostructures, suggestive of their potential applications on unique optical devices.

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[20] See EPAPS Document No. E-APPLAB-90-071711 for schematic diagram, data table, and experimental details. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).