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The fabrication of subwavelength anti-reflective nanostructures using a bio-template

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Abstract
This paper describes a paradigm, a simple, low-cost and conventional approach to the fabrication of large-area subwavelength anti-reflective nanostructures on films directly with a bio-template. Specifically, the nano-nipple arrays on the surface of cicada wings have been precisely replicated to a PMMA (polymethyl methacrylate) film with high reproducibility by a technique of replica molding, which mainly involves two processes: one is that a negative Au mold is prepared directly from the bio-template of the cicada wing by thermal deposition; the other is that the Au mold is used to obtain the replica of the nanostructures on the original cicada wing by casting polymer. The reflectance spectra measurement shows that the replicated PMMA film can considerably reduce reflectivity at its surface over a large wavelength range from 250 to 800 nm, indicating that the anti-reflective property has also been inherited by the PMMA film.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Photonic structures in biology are evolutionary results over millions to billions of years for the needs of adaptation and survival, which can produce astonishing optical effects [1–13]. For instance, *Ophiocoma Wendtii*, a species of brittlestar, by utilizing its skeletal calcite crystals as light-collecting lenses, has a highly sensitive response to light intensity [1]; microstructures and nanostructures that exist on *Morpho Rhetenor* butterfly scales result in an iridescent blue color [2], while photonic structures of reduced dimensions present in certain Colias butterflies give rise to intense UV visibility [2]; arrays of nano-nipple structures on cicada wings and moth eyes can minimize the reflectivity at their surfaces over broad angles or frequency ranges [9]. Biomimetics is the extraction of excellent nature structures for practical applications [14–18]. The common approach is to build biologically inspired artificial analogues based on the principle of biological optical systems [15–17]. One example is that the artificial ommatidia are omnidirectionally fabricated along a hemispherical polymer dome, providing a wide field of view similar to that of a natural insect's compound eye [16]. Recently, Liu and Zhang proposed an alternative way to mimic biological structures [19]. Biological organs, cicada wings therein, have been directly used as stamps in nanoimprint lithography to fabricate replicas of biological nanostructures. Unexpectedly, the cicada wings can endure processing temperatures up to 200 °C during imprinting, and the wing surface nanostructures have been successfully replicated to a polymer film. This overturns a general concept that soft biological organs are hard to serve as the engineering technical templates, which are normally rigid inorganic materials. Subsequently, we also extend this thought to replicate the microstructures and nanostructures on the cicada compound eyes on a material of epoxy resin by a means of a direct molding [20]; Wang *et al* obtained the replica of the fine structures on the wing scales of a Morpho Peleides butterfly by coating a uniform Al_2O_3 film through a low-temperature atomic layer deposition [21].

During the last decade, intensive attention has been paid to make replicas of anti-reflective structures from biology, such as the corneas of moth and butterfly eyes, and the transparent wings of hawkmoths and cicadas [2, 22–24], because the artificial anti-reflective structures have great potential in optical applications [25], such as the surfaces of lenses, solar cells, light-sensitive detectors, displays, and viewing glasses. Therefore, it is of significance that using a simple and low-cost method to replicate these biological structures on multifarious materials. In this work, we use the conventional replica molding technique to fabricate a large-area subwavelength anti-reflective nanostructure on PMMA (polymethyl methacrylate) polymer films directly through a cicada wing bio-template. The results show that the replica preserves not only the photonic structure of the original cicada wing surface but also the anti-reflective property.

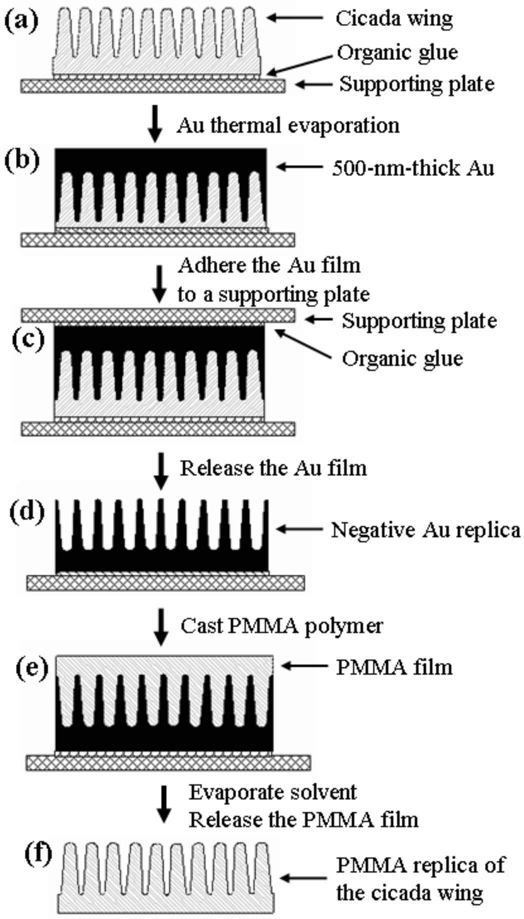
2. Experimental details

The cicadas (Cryptympana atrata Fabricius) were either captured locally or purchased from farms. Cicada wings were cleaned before use. First, the wings were sonicated in deionized water for about 15 min to remove contaminants absorbed physically on the surfaces; the wings were then sonicated in acetone for 20 min to remove the stains that stick the nipples together, and lastly the wings were sonicated in deionized water again for 15 min to remove residual acetone, followed by nitrogen blow-drying. A gold film was thermally deposited onto the wings with a thin-film coating system (Auto 306, BOC Edward, Inc.), with the gold source temperature as high as 1400–1500 °C. PMMA (weight-average molecular weight $M_w = 95\,000$) was purchased from Acros Organics and dissolved in toluene (Acros Organics) to form a 15 wt% solution. Scanning electron microscope (SEM) images were obtained with a LEO 1530 VP (LEO Elektronenmikroskopie GmbH, Oberkochen, Germany).

3. Results and discussion

In scheme 1 is a schematic diagram showing the replication procedure of a subwavelength anti-reflective nanostructure with a bio-template (herein cicada wing). This mainly involves a two-step replica molding: a negative Au mold is prepared directly from the bio-template of the cicada wing by thermal deposition, and then the Au mold is used to obtain the replica of the nanostructures on the original cicada wing by casting polymer. The detailed description of the fabrication process will be given hereinafter.

Figures 1(a) and (b) show typical SEM images of the wing dorsal (or ventral) surface morphology of a locally captured cicada. The transparent wing surface contains a hexagonally quasi-two-dimensional (q2D) ordered assembly of nano-nipples. The nearest-neighbor nipple distance is an approximate 190 nm, derived from the top view of an SEM image (the inset of figure 1(a)). According to the cross-sectional image of figure 1(c), each of the nipples has a height of around 400 nm, and average diameters of about 65 and 150 nm at the nipple top and base, respectively. The anti-reflection function of the wing associated with camouflage is achieved by these subwavelength nipple arrays, which effectively introduce a gradual refractive index profile at the interface between wing and air, and reduce the reflectivity over broad angles or frequency ranges by a factor of about ten [14]. Our previous work [19] shows that, despite it being a biological material, the cicada wing, possessing remarkable properties, is suitable to serve as a mold in the conventional engineering approach. The main component of cicada wings is chitin—a high molecular weight, crystalline polymer—whose Young's modulus is as high as 7–9 GPa [26], which is high enough to maintain the original wing surface structure during the replication process. In addition, a layer of wax present on the epidermis of cicada wings is a low surface tension material [26], and can serve naturally as an antisticking



Scheme 1. Schematic diagram of the replica molding procedure. Using the cicada wing as a bio-template to fabricate a subwavelength anti-reflective nanostructure on a PMMA polymer film. The specification of the fabricating steps (a)–(e) and (f) details in the scheme.

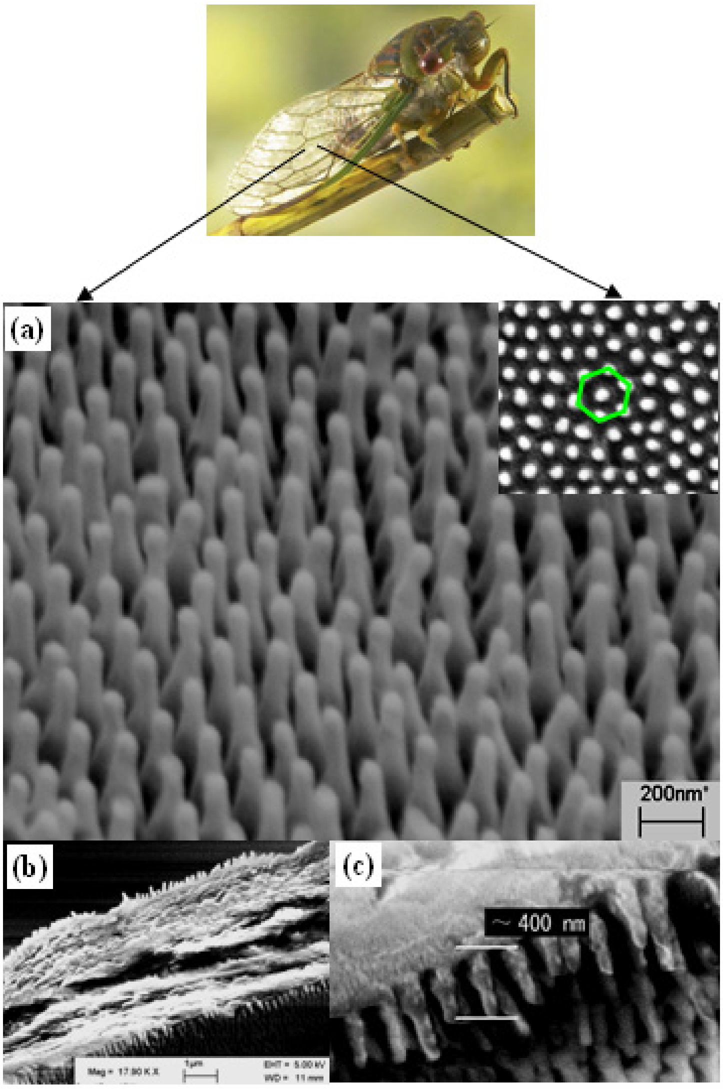


Figure 1. SEM images of a cicada wing. (a) Large-scale perspective view. The inset is a top view. (b) Cross-sectional view showing the dorsal and ventral surfaces full of nano-nipples. (c) Higher-magnification cross-sectional view.

coating during the replication process. This is in contrast to the cases of artificial molds, where the antisticking treatment has to be carried out by self-assembling a monolayer of fluorine- or methyl-terminated organic molecules to avoid adherence [27, 28].

As shown in scheme 1(a), a section (1 × 1 cm^2) cut from the cicada wing was adhered to a supporting plate with organic glue (EPO-TEK 377, Epoxy Technology Inc.). Then, a 500 nm-thick film of gold was deposited on the wing surface by thermal evaporation at a rate of 0.1–0.5 nm s^{-1} (scheme 1(b)). Subsequently, as another supporting plate was adhered onto the Au film with the organic glue, the film can be released from the cicada wing with small tweezers (schemes 1(c) and (d)), while keeping the wing surface structure intact. Figure 2 shows a large-scale SEM image of the Au film. It can be seen that the negative replica of the wing surface structure has been perfectly fabricated, exhibiting hexagonally q2D arrays of nano-holes that are the inverse of the nano-nipples. The higher-magnification image (the inset in figure 2) gives the average structural parameters of the negative replica as follows: the separation is 195 nm; the depth 390 nm (obtained from an atomic force microscope; not shown here); the top and base of a nano-hole 155 nm and 60 nm, respectively. These values are in close agreement with those from the nano-nipple arrays on the surface of the original cicada wing, which indicates that the direct nano-molding process involves no significant distortions, and the surface nanostructures on the original cicada wing can be precisely transferred to the Au film.

As shown in schemes 1(e) and (f), the second-step replication process is to transfer the structure of the Au film to a PMMA film. A 15 wt% PMMA solution in anisole was cast on the Au mold, and then kept at room temperature for 10 min for degassing. Following heating in an oven at 90 °C for 30 min, the PMMA film was mechanically peeled off from the Au mold with tweezers. Figure 3(a) shows the replicated nano-nipples free-standing on the PMMA film, exhibiting a

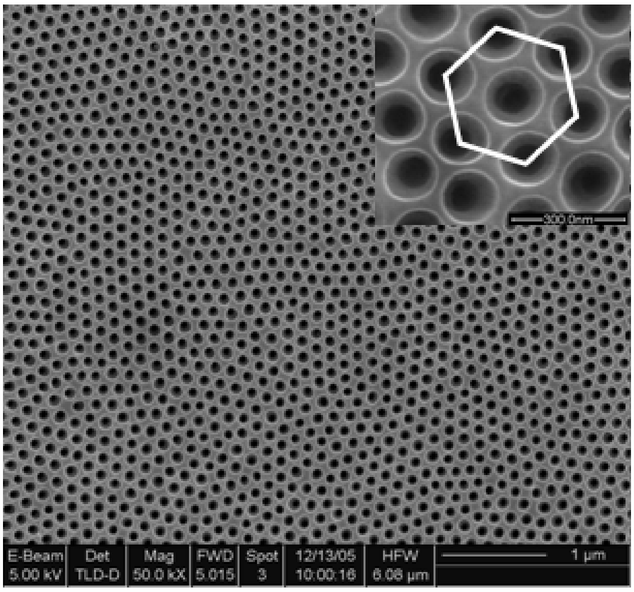


Figure 2. SEM images of the nano-hole arrays on a 500 nm thick Au film after replication from the cicada wing by thermal evaporation. The inset is a higher-magnification top view showing the hexagonal pattern.

good hexagonally q2D ordered pattern (figure 3(b)). The PMMA polymer was chosen because of its high resolution, optical transparency in the wavelengths between visible and near-infrared regions, and a higher compression modulus (∼2–3 GPa) [19]. In addition, since thin PMMA films are flexible, the obtained anti-reflective structures can be mounted on curved optical components for practical applications. The average structural parameters of the nano-nipple arrays on the PMMA films are as follows: the separation is 185 nm; the height 440 nm; the top and base of a nano-hole 55 nm and 140 nm, respectively. These values indicate that the nano-nipple arrays on the surface of cicada wing can be precisely replicated to PMMA film by direct mold-replica processes. Note that the heating temperature is a key factor for the stability of the PMMA nano-nipples. When the heating temperature is below 60 °C, severe structural deformation was observed in the replicated nano-nipples, as shown in figure 3(c). Subsequently, using this Au mold, we carried out three cycles of such replication process at the heating temperature of 90 °C. Almost identical replicated nanostructures were obtained in each cycle, indicating that the Au mold is highly reusable. In this process, we have not found any PMMA sticking on the Au film, although no antisticking treatment was performed. This implies that the wax on the surface of the cicada wing may have been transferred to the Au film during the first mold process.

Figure 4 shows the measured reflectivity as a function of wavelength for the replicated PMMA film and a flat PMMA film without the nano-nipple structure. The incident light was randomly polarized and the incident angle was 8°. Our measurement clearly shows that, compared with the flat PMMA film, the reflection on the PMMA surface with nano-nipple arrays decreases reflection drastically. The reflectivity of the PMMA surface with nano-nipple arrays is on average less than 30% (1.8%/5.9%) of that of the unpatterned flat PMMA surface at wavelengths in the UV and visible regions. As an example of application, we deposited a layer of Cr on the subwavelength anti-reflective PMMA film. As a comparison, a layer of Cr was also deposited on the flat PMMA film. Figure 5 shows the optical microscope image of the structured (left) and unstructured (right) PMMA films with a Cr layer deposited on the surfaces. The completely dark region on the left indicates that the visible light with less reflection and more transmission on the structured PMMA film was adsorbed by the Cr layer. In contrast, the bright region at the right shows that more visible light was observed due to the stronger reflection on the surface. Obviously, this subwavelength anti-reflective PMMA film can be used as an ‘absorber’ component, which may have applications in solar cells, high-power laser windows and even prescription glasses.

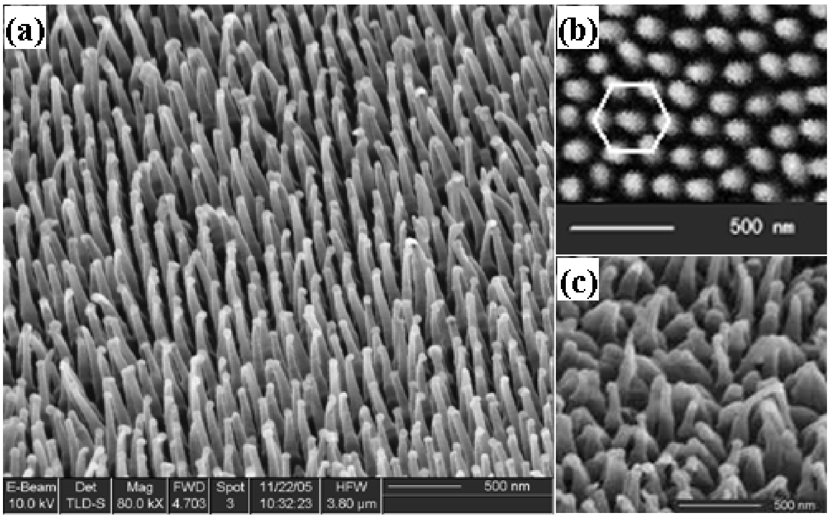


Figure 3. SEM images of the replicated PMMA films with nano-nipple arrays on the surface from the negative Au mold. (a) Large-scale perspective view. (b) Higher-magnification top view showing a hexagonal pattern. (a) and (b) were obtained after the PMMA film was heated at 90 °C for 30 min. (c) Perspective view after the film was heated at 60 °C for 30 min.

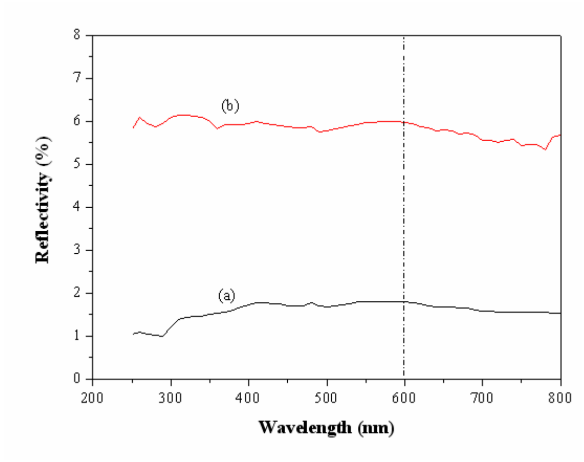


Figure 4. Wavelength dependence of the measured reflectivity of the replicated PMMA film with nano-nipple arrays on the surface (a), and an unpatterned flat PMMA film (b).

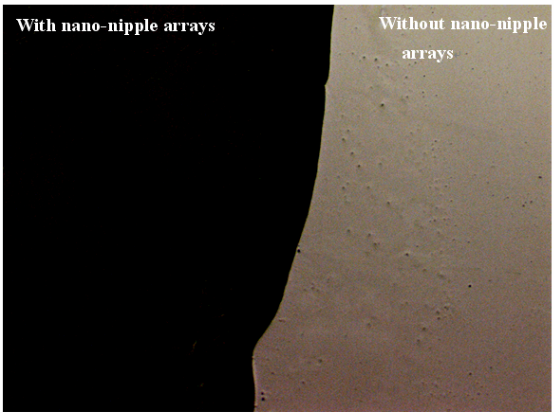


Figure 5. Optical microscope image of the structured (left) and unstructured (right) PMMA films with a Cr layer deposited on the surfaces.

4. Conclusion

We have demonstrated that cicada wings can be used as a bio-template to fabricate large-area subwavelength anti-reflective nanostructures by means of replica molding. The nano-nipple arrays on the surface of cicada wings have been precisely replicated to the surface of a PMMA film. At wavelengths from 250 to 800 nm, the reflectivity of the replicated PMMA film with nano-nipple arrays on the surface decreased from about 5.9% for an unpatterned flat PMMA film to lower than 1.8%, suggestive of the potential applications on optical devices. This also provides a general strategy of biomimetic fabrication of functional devices.

Acknowledgments

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