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2011 EPL 93 14001

(http://iopscience.iop.org/0295-5075/93/1/14001)

A Letters Journal Exploring the Frontiers of Physics

January 2011

EPL, **93** (2011) 14001
doi: 10.1209/0295-5075/93/14001

www.epljournal.org

Biomimicry of optical microstructures of Papilio palinurus

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received 5 October 2010; accepted in final form 20 December 2010

PACS `42.70.-a` – Optical materials
PACS `42.79.Wc` – Optical coatings

Abstract – The brilliant coloration of animals in nature is sometimes based on their structure rather than on pigments. The green colour on the wings of a butterfly *Papilio palinurus* originates from the hierarchical microstructure of individual wing scales that are tiled on the wing. The hierarchical structure gives rise to two coloured reflections of visible light, blue and yellow which when additively mixed, produce the perception of green colour on the wing scales. We used breath figure templated assembly as the starting point for the structure and, combining it with atomic layer deposition for the multilayers necessary for the production of interference colors, we have faithfully mimicked the structure and the optical effects found on the wing scale of the butterfly *Papilio palinurus*.

The coloration of animals in nature is sometimes based on their structure rather than on their pigments [1,2]. Structural coloration based on diffraction, multilayer reflection, cholesteric analogues or photonic crystal-like structures is pervasive, especially in the world of insects [1–5]. For example, the green colour on the wings of a butterfly *Papilio palinurus* originates from the hierarchical microstructure of individual wing scales that are tiled on the wing. Each wing scale is about 100 μm long and composed of 4–10 μm diameter bowls (fig. 1(a)), which in turn are lined with a multilayer stack of eleven alternating layers of air and chitin [6], each 75 nm thick. Vukusic *et al.* [6] elucidated that the distinct green colour of the wings is the result of additive colour mixing of yellow and blue, involving a combination of two reflections off the multilayer in the bowl; the yellow colour is due to the reflection from the bottom of the bowl at normal incidence (fig. 1(b)) and the blue results from two 45° reflections at the sides of the bowl. (fig. 1(c)). Thus the light incident on the sides of the bowl is retro-reflected due to the double reflection that occurs at the sides of the bowl. The polarization of the ray reflecting from the side is rotated upon each reflection, and thus the sides are visible in a reflection mode microscope under crossed polarizers, while the reflection from the center/bottom is extinguished (fig. 1(d)).

The elegance of this structure has inspired us and others [7] to mimic it, using simple bottom-up self-assembly methods. In this article, we describe the result of mimicking the *Papilio palinurus* structure by atomic layer deposition (ALD) of multilayers of titanium dioxide and aluminium oxide over a polymer film with an ordered array of monodisperse micron size pores formed using breath figure templated assembly [8–12]. On the other hand, one can also use colloidal self-assembly to mimic such structures, as recently demonstrated [7].

The breath figure templated assembly refers to a process that uses the condensation of moisture over an evaporating polymer solution to form an ordered array of pores in the solid polymer film [8–12]. In this process, a dilute ($\sim$0.5–5 wt%) polymer solution in a volatile solvent is exposed to a stream of moist air (relative humidity around 80%). This results in the evaporation of the solvent, which leads to evaporative cooling of the polymer solution, thus allowing the nucleation of water droplets as the temperature close to the polymer solution surface drops below the dew point. The so-formed water droplets grow

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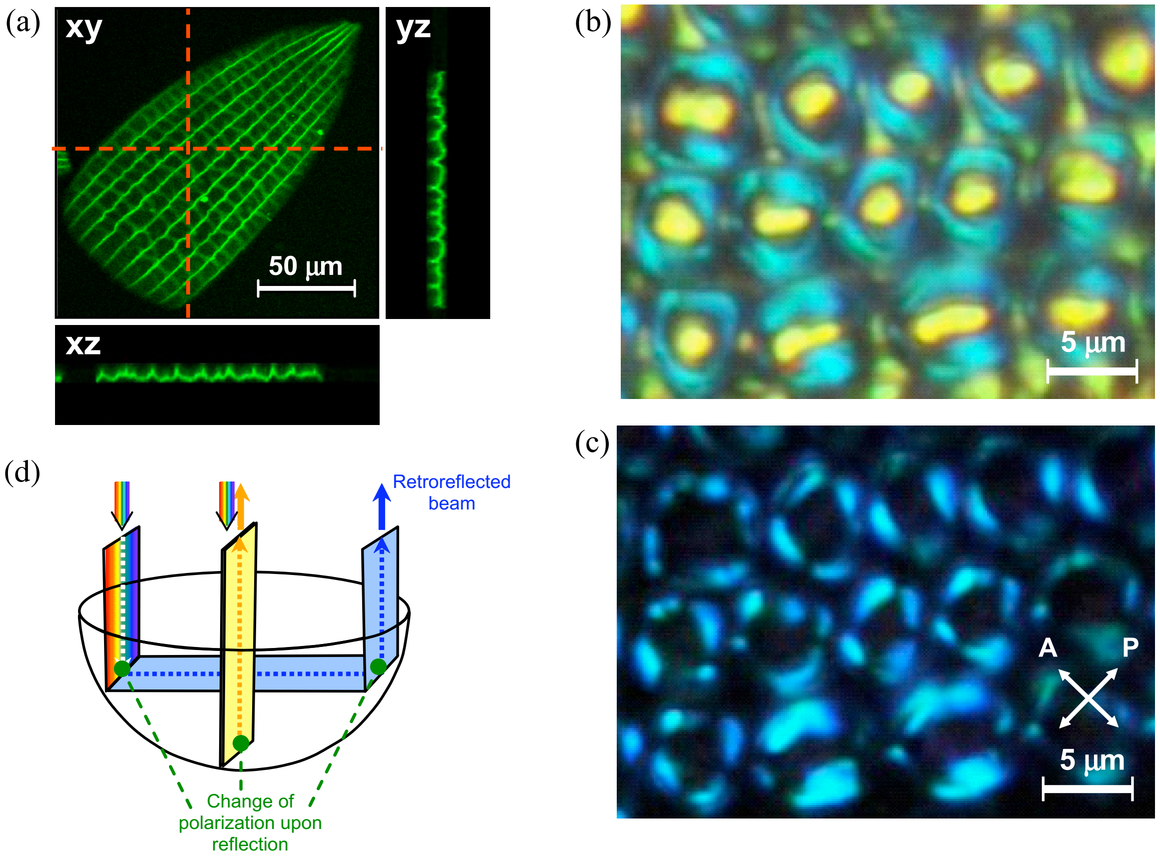
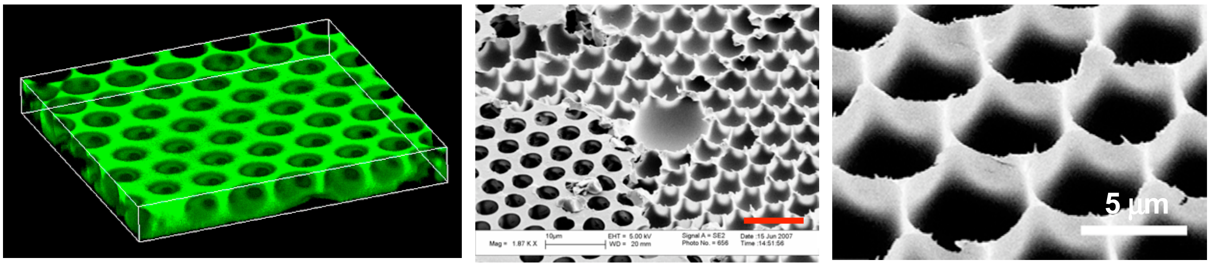


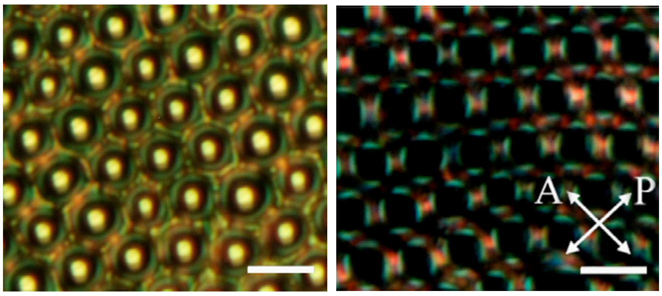
Fig. 1: (a) Confocal pseudo-2D micrographs of *Papilio palinurus* in fluorescence reflection mode, showing the individual wing scale in *xy*, *yz*, and *xz* sections. The *yz* and *xz* images correspond to the area along the red dotted lines in *xy* image. Real-color optical micrographs of *Papilio palinurus* in reflection mode with a polarizer (b), and under crossed polarizers (c), using white light as illumination. The reflection from the center/bottom of the bowls is extinguished under crossed polarizers. (d) Schematic diagram to show the ray tracing and reflections from the center or sides of the individual bowl, leading to dual colors when white light is used as an incident beam.



(a) (b) (c)

Fig. 2: (a) Three-dimensional micrograph of a macroporous PS film, reconstructed from a series of *xy* images obtained using laser scanning confocal microscope in the fluorescence mode. The dimensions of the 3-D image are $29.7 \times 29.7 \times 3.7$ (μm). (b) SEM image of a macroporous polymer film partially peeled (top and right), and (c) SEM image of a peeled part of the film shown in (b), at a larger magnification, showing bowls of 6-sided walls, which was used to mimic the coloration of the butterfly wing. The scale bars in (b) and (c) represent 10 and 5 μm, respectively.

as a function of time, closely pack, and crystallize to form an ordered array of droplets, which sink into the solution and are held in the solid polymer film. The water droplets eventually evaporate thus leaving their imprint as air pockets which are organized in a hexagonal fashion [12]. In our experiments, we used a dilute (1 wt%) solution of polystyrene ($M_\mathrm{w} = 50000$, mono-carboxy terminated) in a volatile solvent (carbon disulfide). A stream of moist air was passed over the solution, which eventually generated an ordered array of holes with an average pore size of about 4 to 5 μm. The three-dimensional reconstruction of the morphology using a laser scanning confocal microscope is shown in fig. 2(a). It is clear that the ordered array of holes have thin polymer walls between them. In order to



(a) (b)

Fig. 3: (a) Optical micrograph of ALD coated polymer microbowls in reflection mode. The center is much brighter than the edges and therefore the edge reflections appear duller. Polarized light was used to enhance the edge reflection, and the polarizer direction is the same as in image (b). (b) Optical micrograph of ALD coated microbowls under crossed polarizers. The red reflections between the bowls are due to imperfect edges of the peeled microbowls. All scale bars are 5 μm.

mimic the optics found on the wing scale of the butterfly, we used the ordered array of holes as a template. To create the bowls necessary to emulate the optical effects on the wing scales, we simply peeled off the top of the polymer film using an adhesive tape which ruptures the film in the midplane of the ordered array of holes, as this is the thinnest part of the film: fig. 2(b) and fig. 2(c) show a partially peeled and peeled array, respectively.

To replicate the optical effect of the individual wing scale, we first simulated the reflectance of a multilayer stack composed of alternating layers of titanium oxide, TiO_2 (refractive index $n = 2.5$) and aluminium oxide, Al_2O_3 ($n = 1.5$). The calculations showed that 5 alternating 20 nm layers of TiO_2 and Al_2O_3 were necessary to best mimic the optical effects seen on the *Papilio palinurus*. The layers were deposited using the ALD technique with a custom designed instrument [13–16]. During ALD, the volatile precursors are pumped through at reduced pressure. The precursor ($TiCl_4$ or $Al(CH_3)_3$) reacts with nucleophilic groups on the surface to form a thin layer of the corresponding oxide. In our case, since we were using a microstructured polystyrene film as the template, the nucleophilic groups were water molecules adsorbed on the surface or the carboxylic end groups of the polystyrene used. A second pulse of water was then introduced to complete the transformation to the corresponding oxide layers [Al_2O_3, TiO_2]. A pulse of nitrogen was used between precursors to remove unreacted precursors and by-products, and the whole process was repeated for as many layers as needed.

We examined the optical effect of the resulting structure in a light microscope in reflection mode, equipped with a spectrophotometer, using a 50×0.8 NA dry objective. As demonstrated in fig. 3(a), the bowls reflect most of the white light from the center, *i.e.*, from the bottom of the micro-bowls. This light is yellow in color. Light reflected from the sides of the bowls is blue-green in colour and less intense. There appears to be a third colour present, a red colour reflected from the jagged edges of the peeled bowls. Under crossed polarizers, as shown in fig. 3(b), the intense yellow light from the center of the bowls is extinguished, while the blue-green from the sides and red from the edges remain. The optical effect is analogous to that seen on the *Papilio palinurus* scales (fig. 2(b)). In obtaining the image in fig. 3(b) under crossed polarizers, the incoming light intensity was increased, because the reflected light intensity was greatly reduced due to the presence of the crossed polarizers.

The spectral analysis shows a blue shift for the spectrum taken under crossed polarizers. This shift can be explained by the different incident angle of the ray reflected from the side of the bowl. The reflection from a multilayer is blue shifted with the angle increasing from the surface normal [17]. The light reflected from the edge of the bowl is reflected twice at 45°, whereas the reflection from the bottom of the bowl is at normal incidence as previously mentioned.

In summary, using breath figure templated assembly as the starting point for the structure, and using ALD to simulate the multilayer structure with bicomponent refractive indices, we were able to faithfully mimic the optical effect of the individual wing scales of *Papilio palinurus*. The prepared microstructured and (TiO_2/Al_2O_3) ALD coated polystyrene film showed double reflection, polarization and polarization effects exactly analogous to the microbowls in the scales of the butterfly *Papilio palinurus*. The intense reflection, yellow in color, is from the center/bottom of the microbowls and disappears under crossed polarizers. Meanwhile, the weaker reflection, blue in color, from the edge of the bowls, still remains even under crossed polarizers. The additive mixing of the yellow and blue leads to the apparent green colour of this butterfly, as experienced by the human eye. It remains to be determined if this optical effect can be perceived by fellow *Papilio palinurus* butterflies and potential predators, and if the structural colour offers any evolutionary advantage to the butterflies.

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This work was partially supported by NSF through the grant to MS and JOP (DMR-097529 and DMR-0603026). The authors would like to thank Prof. L. Tolbert for useful discussions. MS would also like to acknowledge support by WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R32-2008-000-10142-0).

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