Key Engineering Materials Vol. 543 (2013) pp 18-21
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doi:10.4028/www.scientific.net/KEM.543.18

Color changes upon cooling of Lepidoptera scales containing photonic nanoarchitectures

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Keywords: photonic crystal, butterfly, condensation, cooling

Abstract. Photonic crystal type nanoarchitectures have an important advantage over conventional displays: they do not fade under solar illumination; on the contrary, more intense illumination generates more intense color. We present a simple method – based on cooling in ambient air - to observe the color change of several butterfly wings colored by various photonic nanoarchitectures. The color change can be attributed to the condensation of atmospheric humidity in the nanocavities of the photonic nanoarchitecture. The effects were investigated by controlled cooling combined with the in-situ measurement of the changes in the reflectivity spectra. For certain species the reflectivity maximum (color) has almost completely disappeared. A correlation was also found between the openness of the nanostructure and the time of the color change. Cooling experiments, using thin copper wires showed that color alteration could be limited to millimeters; this may offer a possible alternative for display technology.

Introduction

There has been a strong interest in photonic crystals (PhCs) since they were first described in 1987 [1,2] for their ability to manipulate and control light propagation. PhCs are composites with a spatially periodic dielectric function, built of two or more materials with different optical properties. Photonic crystals have a photonic band gap (PBG), within which photons with certain energies cannot propagate and are completely reflected by the surface of the photonic crystal. For a 1D PhC the spectral position of the PBG(s) can be approximated by the average refractive index of the structure and its periodicity [3], in the visible range the presence of such a PBG is seen as the color of the structure. The ability of manipulating light by photonic crystals created a wide variety of application ideas [4].

Several reviews showed that similar structures as the above mentioned photonic crystals can also be found in nature. Some colors of animals are generated by photonic crystals. Butterflies, beetles, birds [3,5,6] or even plants [7] have these kind of structures (nanoarchitectures).

Butterflies are diverse and convenient examples of these structures as frequently their color is generated by the combination of pigments and photonic nanoarchitectures [3]. Their essentially flat wings are also practical for scientific examination and for possible applications, such as: solar cells [8], sensors [9] or anti-counterfeiting of banknotes [10]. The wings of butterflies are very complex structures on both the microscopic and macroscopic length scale. The scales, that cover the wings, also contain fine structures down to the nanometer scale. The photonic nanoarchitectures can be found on the top surface or in the volume of the scales if the color of the butterfly is of structural origin. These nanoarchitectures are mainly constructed of a chitinous matrix containing air holes

[11]. The refractive index of the air holes in the structure can be changed by filling them with a liquid, therefore the average refractive index and the position of the forbidden gap (color) changes. We use and investigate this physical mechanism to change the color of the butterflies.

Color change on butterflies due to condensation

It was observed that when butterfly wings are cooled, they changed their color. When the wings were cooled below the dew point, water vapor from air began to condensate into the nanoarchitecture changing its average refractive index and the color. Condensation can also be observed on the cooling surface, water droplets appeared next to the cooled wings. Naturally, water cannot easily penetrate into the butterfly wings because they are mostly superhydrophobic [12], but with condensation this property can be circumvented, the liquid is generated inside the nanocavities.

Small pieces of butterfly wings were placed on top of a Peltier cooler, and were cooled from room temperature (23 °C) to 5 °C, far below the dew point. A few minutes after turning on of the cooling, the color change could be observed on the wing pieces (Fig. 1a.). The pieces were from butterflies: 1. *Albulina metallica* (blue dorsal surface); 2. *Morpho aega* (blue dorsal); 3. *Cyanophrys remus* (green ventral); 4. *Polyommatus daphnis* (blue dorsal); 5. *Cyanophrys remus* (blue dorsal); 6. *Callophrys rubi* (green ventral); and 7. *Eterusia taiwana* (blue dorsal).

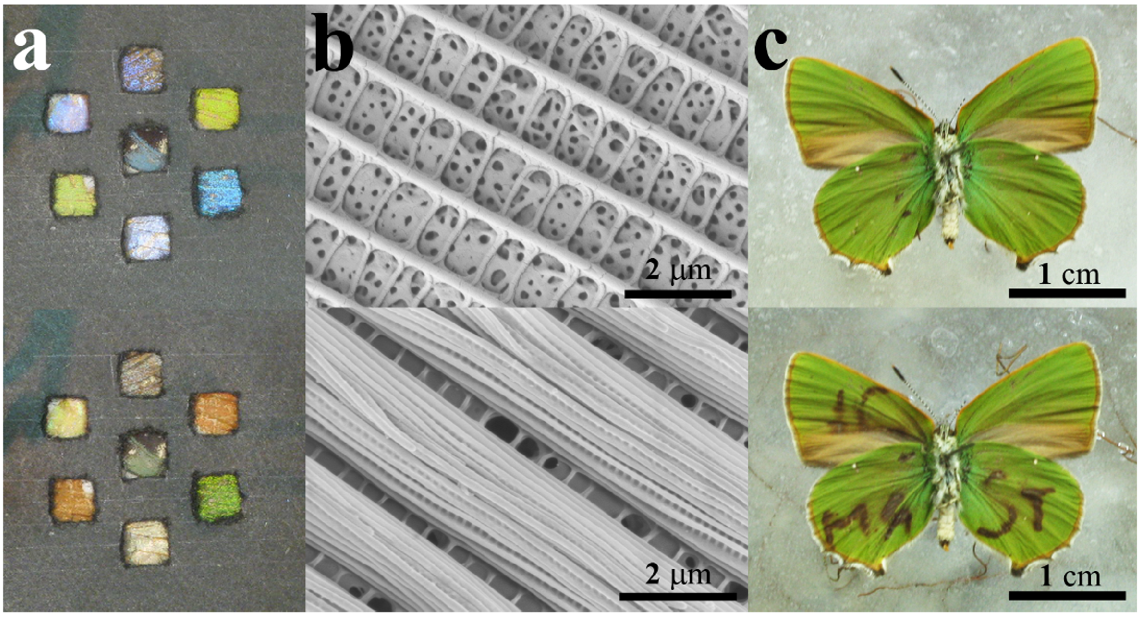

Figure 1. a) Pieces of butterfly wings on top of a Peltier cooler. The color change can be easily observed. b) Scanning electron microscopic images of nanoarchitectures found in butterfly wings (top: *A. metallica*, green ventral side; bottom: *M. aega*, blue dorsal side). c) The butterfly (*C. rubi*) on top of cooled wires. One end of the wires were used to form characters, the other were frozen into ice blocks. (top: after placing the butterfly onto the wires, bottom: after about a minute). The characters began to appear after a few seconds).

If cooled locally, the color change can be limited to millimeters or less, making it possible to write onto the wing surface (Fig. 1c.). In our experiments, small copper wires were used. One end of the wires was frozen into an ice block; the other end was used to form horizontal characters. Special care has to be taken for the best thermal contact of the wires with the surface of the wings. The butterfly (*C. rubi*) was then put to these characters, cooled by the ice block. The wires cool a small area around them and if the temperature of this area is below the dew point, the water from air begins to condensate and the color changes. The temperature of the wires and therefore the thickness of the cooled area around the wires can be adjusted by the distance of the characters from the ice block. This area also widens slightly in time as condensation progresses.

Controlled cooling

Cooling experiments were done on the previously mentioned butterfly species while the temperature and reflection spectra were measured in every second. An example can be seen on Fig. 2, where the shift of the reflection maximum can be seen during condensation and evaporation. The shift of the reflection maximum to the longer wavelengths and the decreasing of the intensity were observed on every experiment, but the magnitude and the time scale of these changes varied from species to species. It was also observed that after prolonged cooling the reflection spectra needed about a day or more to recover its original shape because chitin absorbed water. The absorption of water by chitin was also observed as the wings became malleable. Due to the availability of only a few individual samples from one species, a statistical comparison could not be made. However it was observed that the change during cooling of the reflection spectra was characteristic from species to species. The duration of the change during condensation is found to be very varied, on the other hand the duration of the change during evaporation was found to have much less variation. These characteristic properties can be related to particular nanostructure of the color generating nanoarchitectures that are characteristic to a species.

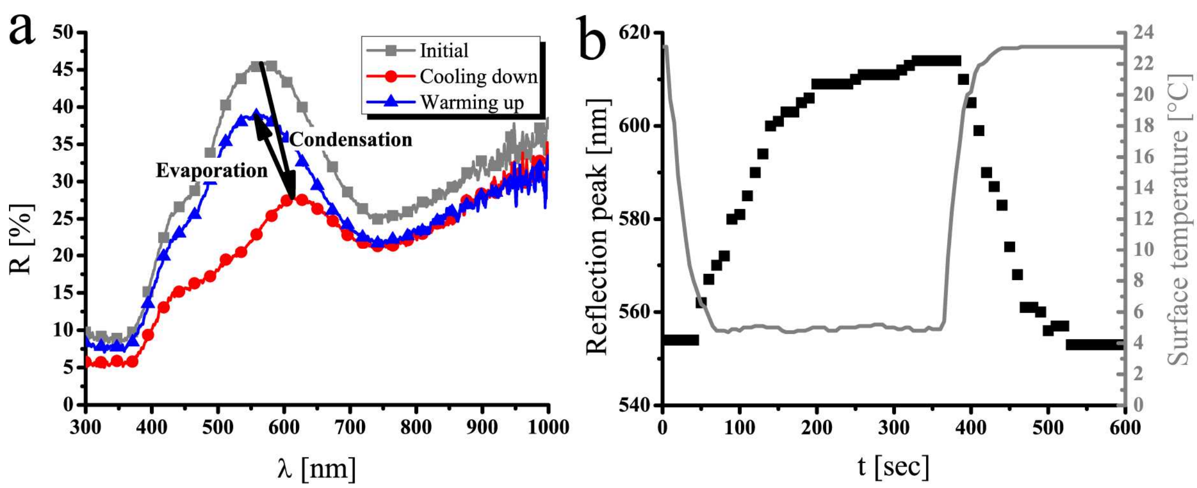

Figure 2. a) Change of the reflection spectrum during cooling on the green (ventral) side of *A. metallica* butterfly. b) The change of the surface temperature (gray, continuous line) and the position of the reflection maximum (black, dotted line) during cooling.

Table 1. Time of the color change during evaporation compared to the proportion of surface holes (openness) of the nanoarchitecture (see text for details). Butterflies with a more closed nanoarchitecture changed color in a longer time during evaporation.

Butterfly	Color/side	Evaporation time [s]	Hole proportion
C. remus	green/ventral	19	0.45
	blue/dorsal	30	0.3
P. daphnis	blue/dorsal	46	0.37
C. rubi	green/ventral	49	0.3
M. aega	blue/dorsal	68	-
A. metallica	blue/dorsal	73	0.24
	green/ventral	103	0.15
E. taiwana	blue/dorsal	150	0.11

The photonic nanoarchitecture responsible for the color generation is very similar, a chitin matrix with holes in it, for every investigated species except the *M. aega*. The condensation and evaporation of water in the nanoarchitectures depends on the available holes on the surface where humidity can be exchanged with the environment. To test this hypothesis, measurements were done on scanning electron microscopic images from every (several) species, where the area of the surface holes was measured in proportion of the whole surface area. It was found that there is a very good correlation between the openness and the duration of the reflection spectra (and color) change during evaporation (see Table 1.).

Summary

Cooling butterflies is not only non-destructive but also allows an easy method for identification of butterflies colored by photonic nanoarchitectures. It was found that the change of the reflection spectra is characteristic for every species. This can be interpreted by the difference of the nanoarchitectures as compared with other butterfly species. It was shown that the duration of the change during evaporation can also be correlated with the openness of the nanoarchitecture.

The color change due to cooling, caused by the condensation of humidity from air, was shown to be suitable for a new type of displays. Because condensation and the color change depend on the dew point, this method can be used as humidity sensor, too. By measuring the temperature of the cooled surface when the color changes, the dew point and therefore the relative humidity can be determined.

Acknowledgments: The work in Hungary was supported by OTKA grant PD83483.

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