

Living Light: Uniting biology and photonics – A memorial meeting in honour of Prof Jean-Pol Vigneron

Vapor sensing of pristine and ALD modified butterfly wings

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Abstract

Butterfly wing scales containing three-dimensional photonic nanoarchitectures exhibit measurable color change when adding to the ambient air different types of volatile vapors. This allows their use as optical vapor sensors. The sensing mechanism is based on the capillary condensation of the vapors into the nanoarchitecture. Using principal component analysis we show that the spectral shift is vapor specific and proportional with the vapor concentration both in the case of pristine and ALD modified butterfly wings.

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1. Introduction

Since its definition, the concept of photonic crystal draws forth a series of new investigations in both experimental and computational materials science. The electromagnetic wave propagation calculations predicts the existence of novel phenomena [1] while the experimentalists tend to produce photonic structures at different scale active at different wavelength: from the radio and microwaves [2] down to the more demanding visible light, with submicron

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size structures [3]. Remarkably, natural evolution, preceded by several million years [4] the few decades of scientific investigation. In nature exists a large variety of living organisms completing their chemical coloration with physical colors of a photonic crystal (or crystal-like structures) of one two or three dimensions [5, 6]. Intensive reflectance or iridescence are the strongest indication of a biological photonic crystal, but there are several exceptions [7]. Such photonic nanoarchitectures are most frequent present between the arthropods, in the nanometer size features of the chitinous scales covering the insect. The conspicuous aspect as a consequence of the photonic structure helps different behavioral functions [8]. From the point of view of a material scientist these structures offer two approaches: it is important to understand the mechanism of light interaction with the structure, and to use this knowledge in the design of new structures, similar to the natural ones. In this work we present a couple of aspects in the use of butterfly wing as a vapor sensor which was first introduced by Potyrailo et al. [9]. The change of the refractive index in the chitin nanoarchitecture by placing the wing into an atmosphere with different vapor content generates a measurable difference in the reflectance of the wing. Reversely, analyzing the optical reflectance spectra variation one can obtain information on the properties of the surrounding medium.

2. Materials and methods

The *Chrysidia rhipheus* and *Polyommatus icarus* butterflies which were used as sensor material were obtained from the curated Lepidoptera Collection of the Hungarian Natural History Museum. For the vapor sensing measurements a home-built setup was used [10]. This contains a vapor sensing cell which is an air-proof aluminum box ($65 \times 15 \times 10 \text{ mm}^3$) with a quartz window for the optical reflectance measurements. Through its gas inlet and outlet different concentrations of volatile vapors were passed. The required vapor concentration were set by diluting the saturated vapors obtained from gas bubblers containing the pure solvents with artificial air in different ratios [10] using digital mass flow controllers (Aalborg). The spectral change of the butterfly wing samples were measured through the quartz window of the gas flow cell with the use of Avantes HS 1024*122TEC spectrometer. Normal incidence illumination was used, while the reflected light was collected at about 45° of angle of detection adjusted so to get the highest reflectance signal.

The data from the vapor sensing experiments were analyzed by principal component analysis (PCA). PCA is the most widely implemented pattern-recognition technique for multivariate signals. The basic idea of the PCA is to reduce the dimensionality of the dataset consisting of a large number of interrelated variables, while retaining as much as possible of the variation present in the dataset. This is achieved by transforming the initial set of variables to weighted sums, called the principal components, and ordered so that the first few retain most of the variation present in all of the original variables [11].

3. Results

Before the vapor sensing measurements the optical reflectance spectra of the specimens inside the sensing cell were recorded by using a white diffuse standard as a reference [12, 13]. The vapor sensing experiments were carried out in the vicinity of room temperature and atmospheric pressure. For the comparability of the measurements we elaborated a protocol in the following way: in the beginning a few minutes of constant air flow was set to save the measured reflectance of the wings as optical reference. Then the vapor concentration was set from 10 to 100 % in 10 % steps while the reflectance change of the spectra was recorded continuously. Between the steps and after the 100 % (saturated) vapor concentration artificial air purging was required to reset the reflectance to its initial (reference) value.

The *Chrysidia rhipheus* (figure 1a) has multilayer type nanoarchitecture in the wing scales with various structural colors from blue-green to purplish yellow [12]. For the vapor sensing experiments the orange-red hind wing region was used. The results of the experiment can be seen in figure 1b. The graph shows the relative reflectance signal of the wing for seven different saturated vapors. As can be clearly seen from the curves, all signals are in the well measurable range and they are distinct, which means that the nanoarchitecture occurring in *Chrysidia rhipheus* wing shows vapor-specific optical response. Furthermore, it is worth to emphasize, that the signal develops in very short time, of the order of seconds [12].

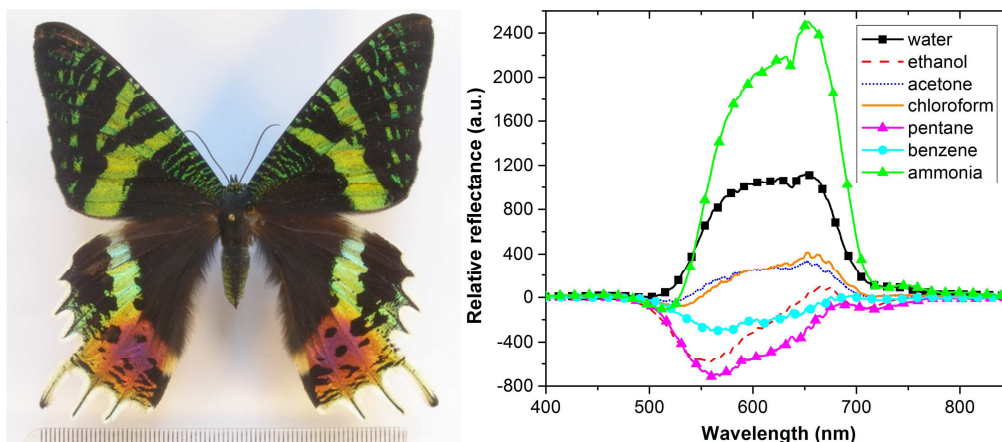


Fig. 1. (a) Ventral side of a male *Chrysiridia rhipheus* butterfly, photo by Gergely Katona (HNHM); (b) Reflectance signal change of the *Chrysiridia rhipheus* hind wing for seven different vapors (the wing in artificial air was used as reference).

It was shown earlier [14], by calculating reflectance spectra of nanoarchitectures for different surrounding atmosphere compositions, that the substance specific coloration modifications cannot be explained only by the variation of the refractive index of the surrounding atmosphere because the magnitude of the refractive index differences of the various volatile vapors is not large enough for this. Therefore it was suspected that the origin of substance specific coloration modifications may be the combination of two phenomena: the swelling of the photonic structure and the condensation of the volatile vapors inside the nanoarchitecture, on the inner surface of the nanopores. To verify the results of the simulations we carried out temperature-dependent vapor sensing experiments [9].

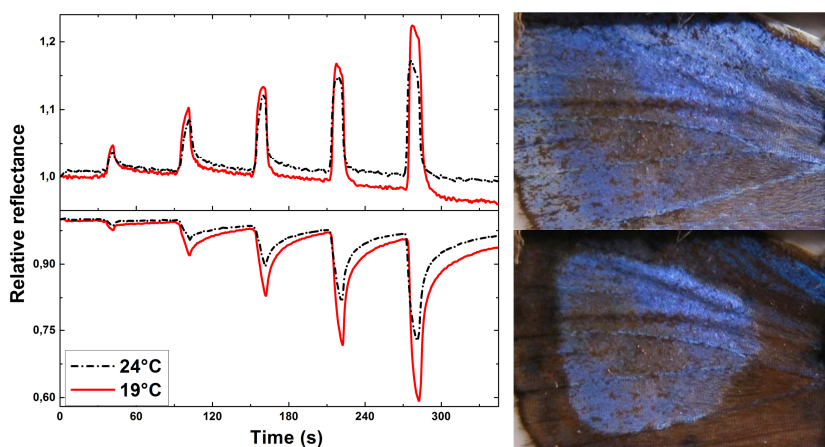


Fig. 2. (a) *Polyommatus icarus* (spectral range of maxima: response signal integrated over the spectral range of the maximum 480–510 nm (top), response signal integrated over the spectral range of minima 300–330 nm (bottom)) response curves for saturated ethanol vapor at the two investigated temperatures; (b) wing in air (top), wing in ethanol vapor at lower temperature, see the outer ring filled completely with liquid ethanol which causes the local color change (bottom)

By decreasing the sample temperature during the experiments with saturated ethanol vapor we observed the redshift of the reflectance signals. We integrated two wavelength domains where the highest variation of the reflectance spectra was observed due to the redshift of the main reflectance peak. It was found that the reflectance

change signal during the vapor sensing experiments of *Polyommatus icarus* butterfly wing scales is proportional with the vapor concentration and it shows temperature dependent intensity as it can be seen in figure 2a. But this proportionality is corrupted at a certain concentration-dependent sample temperature threshold at which the entire volume of the nanoarchitecture is completely filled with the liquid phase of the volatile vapor which results the redshift and the desaturation of the wing coloration (figure 2b). This clearly shows that the observed temperature dependence of the coloration modifications is connected to the capillary condensation of the vapors inside the nanoarchitecture.

Similar vapor sensing experiments with seven volatiles, like in the case of *C. rhipheus* were carried out using *Polyommatus icarus* wings, too. It was shown earlier this species provides the highest reflectance change signal from 9 investigated Lycaenid species during the vapor exposure, therefore the further detailed investigation is appropriate [10]. The results of the measurements when the vapor concentration was set from 10 to 100 % in 10 % steps were analyzed using principal component analysis (with Origin 8.6 software). In figure 3a the individual trajectories of each volatile can be seen. The good separation of the curves represents the vapor selectivity, while the points representing different vapor concentrations follows each other in ascending order (from right to left) confirms the sensitivity of the sensor. One can clearly see that the good separation of the trajectories is based on their curvature at higher concentrations which suggests a reversible interaction between the chitin and the vapors.

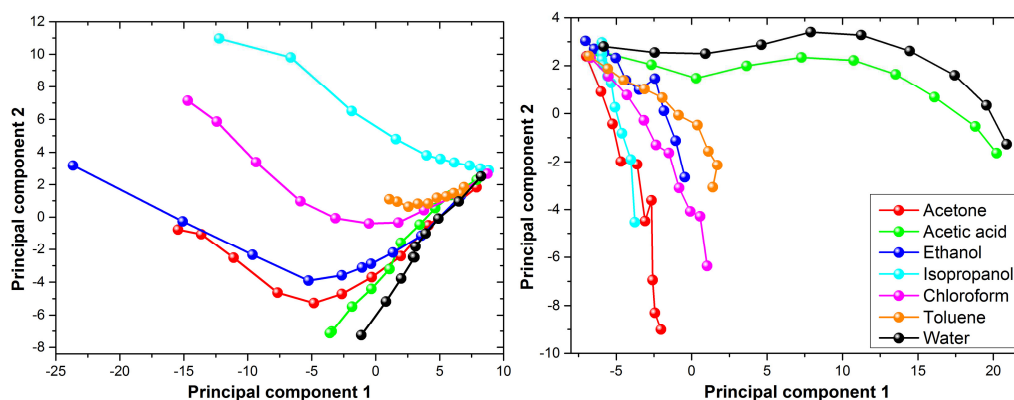


Fig. 3. (a) PCA result of the pristine wing where the characteristic vapor trajectories can be seen; (b) and the characteristic vapor trajectories of the wing conformally covered by 5 nm Al_2O_3 .

To test our hypothesis regarding the possible effects contributing to the selective vapor sensing we prepared a butterfly wing sample with 5 nm conformal Al_2O_3 coating which isolates the chitin from the vapors. After the same seven vapor experiment and the data evaluation with PCA the trajectories in figure 3b results. One can see that the characteristic aspect of the vapor-specific trajectories undergoes a strong modification. It is worth to point out that the two substances which for the pristine wing produced almost straight trajectories with large negative slopes, exhibit for the alumina covered wing an almost horizontal trajectory, with clearly seen curvature. In the same time the substances exhibiting curved trajectories with positive slope in the case of the pristine wing, exhibit almost straight trajectories with strong negative slope for the alumina covered wing. This means that the reversible interaction could be tuned using the Al_2O_3 coating. Further investigations are needed to fully reveal the opportunities offered by the controlled modification by ALD, or other similar materials science related methods of the butterfly wings.

4. Conclusions

We showed chemical selectivity in the optical sensor based on the photonic nanoarchitecture of butterfly wings. The signals are also proportional with the applied vapor concentration. PCA was used for signal analysis. We compared pristine and surface-modified samples. We showed that conformal modification of the wing surface offers

a handy tool in tuning the response signal of sensors based on butterfly wings containing photonic nanoarchitectures.

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