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Selective optical gas sensors using butterfly wing scales nanostructures

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Abstract. Photonic crystals are periodic dielectric nanocomposites, which have photonic band gaps that forbid the propagation of light within certain frequency ranges. This property enables one to manipulate light with amazing facility. Such nanoarchitectures frequently occur in living organism like butterflies and beetles. Butterfly scales are particularly well suited to be used as optical gas sensors as their nanoarchitecture is an open ”sponge-like” type, composed of chitin and air. The open nanoarchitecure allows fast gas exchange. The spectral change of the reflected light depends on the composition of the ambient atmosphere and also on the wing nanostructure. In this work we show the results of recent measurements on nine Polyommatine species with dorsal blue coloration. Their color is generated by similar “pepper-pot” type nanoarchitectures which exhibit species specific characteristics, associated with species specific color. Experiments were carried out changing the concentration and nature of test vapors while monitoring the spectral variations in time. Proper data processing results gas-selective and concentration dependent signals. Our work shows a way to a prospective integrated biological - optical sensor combining light-weight and low power consuming with environmental friendly production.

Introduction

The males of many Polyommatus butterfly species have blue coloration of different hues, arising from complex nanoarchitectures capable of interacting in a spectrally selective way with white light. These type of materials are called photonic crystals (PhC) [1], or photonic band gap (PBG) materials [2] and are constituted from two non-absorbing media having a high enough refractive index contrast and the size of the building elements has to be comparable with the wavelength of the electromagnetic radiation for which the photonic ban gap is expected.

The butterfly wings are covered by scales with the typical dimensions of $100 \times 50 \times 1\ \mu m^3$. The system of the scales is arranged like the tiles on the roof. The photonic nanoarchitecture responsible for the color is located usually in the volume of the scale [3]. In the scales, the nanocomposite is constituted mainly from chitin and air. When the refractive index in the air gaps changes, - for example replacing air by an air / vapor (gas) mixture - the optical properties of the PBG material are altered. Therefore, the natural photonic nanoarchitectures are able to act as selective optical gas / vapor sensors.

The chemical sensing possibilities of butterfly scales were recently shown in the case of Morpho species with a well-known scales structure [4]. Later it was shown that with the simultaneous use of different species, possessing different nanoarchitectures, selective sensing might be possible [5].

The optical response of a butterfly wing on chemical changes in the environment is determined by the spectral changes in the reflected light. These changes depend on one hand on the composition of the ambient atmosphere [4] and on the other hand on the characteristic wing nanostructure [5].

Experimental

The individuals of the nine investigated species were provided by the curated collection of the Hungarian Natural History Museum. The samples represent nine species from the monophyly of Polyommatina (Polyommatini: Polyommatinae: Lycaenidae: Lepidoptera: Arthropoda). After sample preparation [6] the wing scales were investigated by means of scanning (SEM) and transmission (TEM) electron microscopy.

To avoid the sample damage during the optical and gas measurements, wing pieces were mounted in 3 cm × 1.5 cm cardboard frames. These frames fit well in an air-proof aluminium cell with gas inlet and outlet and a quartz glass slide cover to provide UV transmittance. The gas mixing equipment is based on Aalborg digital mass flow controllers. Synthetic air (Messer: 80% N2, 20% O2, others < 20 ppm) was conducted through an ethanol or water containing gas bubbler to obtain saturated vapors. Different concentrations were obtained by mixing the artificial air with the saturated vapors in different ratios. The total flow through the sample cell was set to 1000 ml / min. The calibration of the gas mixing setup was carried out with ethanol vapors at 20°C using standard gas chromatography procedure.

The optical reflectance measurements setup was described in [5]. In gas / vapor detection measurements the reflectance variation is to be followed. Therefore the blue reflectance in pure artificial air was chose as reference, and will be used as a 100% signal for the whole wavelengths range. When using a gas / vapor mixture stream, a difference will appear at certain wavelengths as compared with the pure air case. As we know from our earlier experiments [5], the temporal evolution of the reflectance is also an important factor in the description of the response signal to vapors. Therefore, to obtain a proper time dependent representation, a 3D diagram will be used with wavelength, time and spectral response on x, y, and z axis.

Results and discussion

The general layout of the structures is similar, but the colors generated by the specific nanoarchitectures are species specific [6]. The fine differences in the structure are revealed only by a detailed examination of the structural dimensions of the “pepper-pot” type structure. This can be done using in combination the SEM and TEM images. Processing size-related data by the specially developed BioPhot software [7], a correlation was found between the structure and species, and in this way the structure and the characteristic wing color [6]. Before the gas sensitivity measurements the optical reflectance spectra of the samples were recorded, inside the mounted sensing cell in the conventional way. In this case, the white diffuse reference reflector was used as reference. The reflectance plots were normalized to the highest blue maxima, this provides an easier comparison of the characteristic reflectance of the nine species. See for an example three species compared in Fig. 1.

Earlier we showed [8] that the blue wing coloration is species-specific: using a proper artificial neural network analysis of the reflectance spectra, the discrimination of the nine species is possible with more than 90% accuracy. Even if the butterfly individuals were collected from different places and different years, the spectral characteristics are stable. Given the biologic role of the coloration in sexual communication, the species-specific blue colors have to be stable [9].

The sensing experiments were carried out at room temperature in the following way: in the beginning a few minutes of constant air flow was set to clear the connecting tubes and the cell from residual ambient atmosphere and to ensure the wing samples to be filled with air. This state was saved as optical reference. Then, to obtain comparable datasets, the following sequence was executed for all nine samples with ethanol and water vapors: 1 minute of air flow, 1 minute of 100%

ethanol or water vapor flow, 3 minutes of air flow. Within this five minute sensing experiment one can see the starting value of 100%, the change produced as a consequence of the vapors and the returning to the initial value when the mixture is purged from the measuring cell.

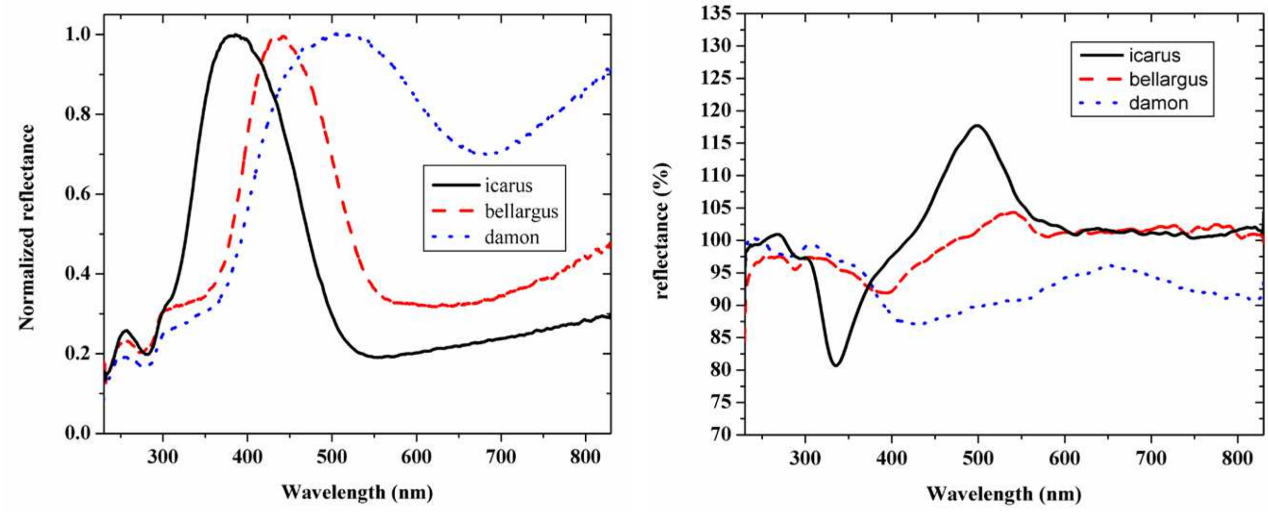

Fig. 1 Reflectance (a.) and spectral response after 100% ethanol vapor exposure (b.)

In Fig. 1a as an example from the nine samples we show the reflectance of *P. icarus* (violet), *P. bellargus* (blue) and *P damon* (greenish) butterfly. One may observe with the naked eye they have characteristic colors with well individualized reflectance maxima. During the gas exposure there is a wavelength shifting, and a signal intensity variation. Curves extracted at 1 min 55 sec. analyte exposure (just before switching back to air) are plotted in Fig. 1b. The changes occurring by the vapor exposure show positive and negative peaks.

The nine investigated species may be divided in three groups: the violet group (*P. thersites*, *P. icarus* and *P. semiargus),* the blue group *(P. bellargus, P. dorylas* and *P. daphnis)* and the greenish group *(P. amandus*, *P. damon* and *P. coridon).* Within each group the response signals are similar, the three characteristic responses for each group are shown in Fig. 1b.

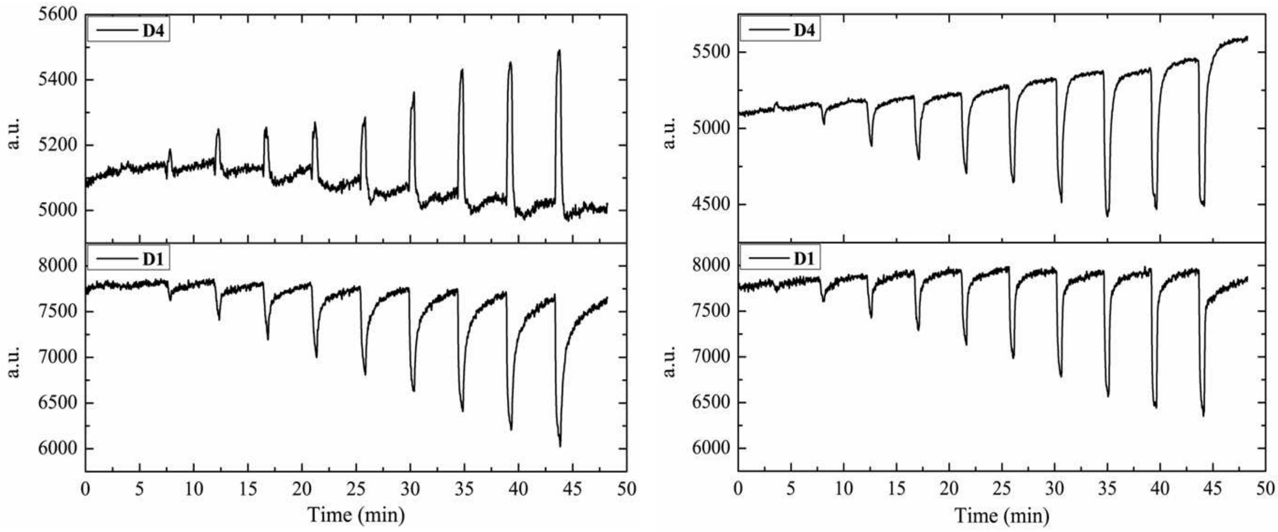

Fig. 2 Ethanol (a.) and water (b.) signals when increasing concentrations were applied from 10% to 100%.

To investigate the concentration dependence, a series of increasing ethanol and water concentrations were measured in a time-span of cca. 50 minutes using the wings of *P. icarus*. The ratio of vapor - saturated air to pristine air was increased in steps of 10%. Thus, 10 values were set, each for 0.5 minutes, with 4 minutes of pure air stream in between. We represented integrated wavelength intervals in the ranges 250 nm – 332 nm (D1) and 700 nm – 750 nm (D4). Both D1 and D4 show a close to linear dependence with the applied vapor concentration (Fig. 2). A clearly different behavior was found for ethanol and water vapors. The main difference is clearly visible in the D4 range. While the increasing concentrations of ethanol vapors produced positive peaks of increasing amplitude, the increasing concentrations of water vapors produced negative peaks of increasing amplitude. A minor but significant difference appears in the D1 range, too: the cell emptying part of the ethanol measurements shows a longer and smoother decay while in the case of water there is an abrupt decrease, followed by a slow relaxation. These types of variances are at the basis of an efficient gas discrimination: describing them with numerical values, automated data processing could be developed and used to find correspondence between the measured features and the sort of gas or vapor present in the unknown mixture. Higher reliability could be obtained by using in parallel wings with different nanostructures. It is worth to emphasize that as seen in Fig. 2, the butterfly wing sensors show a minute scale recovery without external heating.

Summary

We reported optical gas sensing of the wing scale nanostructure in the case of nine related polyommatine species. It was found that the "pepper-pot" structure is open enough to allow fast response time. Each species was found to exhibit a characteristic response to water vapor and ethanol, but the structures, which are similar to a certain extent – the groups with violet, blue and green hue – exhibit similarities in their response signals.

The measurements show that the increasing concentration of water or ethanol in the gas mixture results in higher signals with linear concentration dependence.

From the point of view of materials science and materials design it is important that based on the same type of nanostructure with difference only in the size of the characteristic building elements it is possible to get characteristic responses to gas / vapor exposure.

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