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Color change of Blue butterfly wing scales in an air – Vapor ambient

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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. The optical response of such nanoarchitectures on chemical changes in the environment is determined by the spectral change of the reflected light, and depends on the composition of the ambient atmosphere and on the nanostructure characteristics. We carried out reflectance measurements on closely related Blue lycaenid butterfly males possessing so-called “pepper-pot” type photonic nanoarchitecture in their scales covering their dorsal wing surfaces. Experiments were carried out changing the concentration and nature of test vapors while monitoring the spectral variations in time. All the tests were done with the sample temperature set at, and below the room temperature. The spectral changes were found to be linear with the increasing of concentration and the signal amplitude is higher at lower temperatures. The mechanism of reflectance spectra modification is based on capillary condensation of the vapors penetrating in the nanostructure. These structures of natural origin may serve as cheap, environmentally free and biodegradable sensor elements. The study of these nanoarchitectures of biologic origin could be the source of various new bioinspired systems.

1. Introduction

Dielectric nanoarchitectures composed of materials with different enough optical properties (refractive index) and with a characteristic length scale of a few hundreds nanometers can interact strongly with visible light. Various remarkable optical responses can be designed and tailored depending on the types and parameters of their structures [1]. If having a fully regular, three dimensional (3D) crystalline structure such nanoarchitectures are called photonic crystals (PhC) [2]. However, the alteration of light propagation by nanoarchitectures may take place in disordered systems, too [3]. In a more generalized way, by analogy with semiconductors exhibiting a band gap for certain electron energies, such nanostructures are called photonic band gap (PBG) materials [4]. The PBG is exhibited for certain photon energies, or in a more convenient terminology for a certain wavelength region. This means that the PBG nanoarchitectures if possessing structure with a suitable length scale and sufficient refractive index contrast between the two materials building up the nanostructure, may exhibit color in the visible range in the absence of chemical pigments (i.e., two transparent media like chitin and air may generate color if they form a properly structured nanocomposite). Such colors are called structural colors. The visibility of these colors is supported by pigments, these absorbing the wavelengths that are not reflected by the PBG material. Over the past two decades, the unusual optical properties of the periodic dielectric structures called PhCs have been investigated intensively [4]. For example opal and inverse opal type structures [5] can be produced by various methods of colloidal self assembly. However, not all aspects of the self assembly processes are fully understood [6] and well controlled. On the other hand recently a procedure was developed for the self assembly of nanoparticles with more complex shapes than the spherical one [7].

Interestingly enough, such PBG nanoarchitectures of various shapes and structures were “invented” by biologic evolution about 500 million years ago [8]. The colors of living organism may serve various important purposes from sexual communication (important for the reproductive success of the individual) to cryptic behavior (important for the survival chances of the individual). Most frequently the color of living beings are generated by pigments, but in the insect world one may encounter a particularly rich variety of structural coloration [9].

PhC type structures have been increasingly used in selective chemical sensing [10,11]. Nowadays there is a strong need for low-cost sensors to enable rapid, on-site analysis of biological, biomedical, or chemical substances. The most frequent technical solutions used are various types of hollow core, PhC based optical fibers [12], fibers with suspended solid core [13] or waveguides with, or without side cavities [14]. The main difficulty of these types

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of sensor arises from the need to introduce the gas or vapor to be analyzed inside the fiber of the cavity. To facilitate this, the opening up of PhC based fibers was used [15]. However the reaching of the goal of the photonic nose [16] by this route seems to be less convenient. The surface functionalization of the PBG material [16] and the use of arrays with different functionalization, or the use of arrays of different PBG materials [17] may be a more convenient way.

It was shown recently that butterfly wings colored by PBG type material may exhibit measurable color changes that allow the discrimination of different volatiles [18,19]. Recently we investigated the relation between the color and the PBG type structures of nine closely related lycaenid butterfly (Lepidoptera: Lycaenidae) species [20], all displaying structural blue color in their dorsal wing surfaces. In the present work we compare the optical sensing properties of the scale covered dorsal wing surfaces of three selected butterfly species from the nine Lycaenid species exhibiting similar, quasiordered, "pepper-pot" type photonic nanoarchitectures [21].

2. Materials and methods

The investigated butterfly species (Lepidoptera, Lycaenidae) *Polyommatus icarus*, *Polyommatus bellargus* and *Polyommatus coridon* were obtained from the curated scientific collection of the Hungarian Natural History Museum. Recently we worked [20] on the structural and spectral comparison of nine species representing the monophyletic subtribe Polyommatina [22] (Polyommatinae: Lyceanidae) including these three species selected for the current study. Methods for the optical and electron microscope investigation of the samples were carried out as described previously in [20].

Gas sensing measurements were done fixing a piece of butterfly wing of about 0.5 cm^2 in an air-proof aluminum cell covered with a quartz glass window. To decrease the wing temperature, a miniature Peltier element was placed under it, in this way a $\pm 10\,^{\circ}C$ difference can be achieved relative to the room temperature. Full sets of measurements were carried out at 17, 19 and at room temperature (24 °C). During the measurements a constant gas flow of 1000 ml/min through the cell was maintained. The vapor concentration was set by switching digital mass flow controllers (Aalborg) to let pass synthetic air (Messer: 80% N_2, 20% O_2, others < 20 ppm) and saturated volatile vapor in the required ratio. The calibration of the gas mixing equipment was done with gas chromatography using five ethanol concentrations. One complete cycle of measurement contains 10 s of vapor flow followed by 50 s of synthetic air flow to clean the cell, repeated 5 times with increasing the vapor concentration in 20% steps.

The optical measurements were based on an Avantes HS1024*122TEC fiber optic spectrophotometer. An UV/VIS/NIR light source was used to illuminate the sample. The incoming light and the light collecting fiber were oriented at an angle yielding a maximum signal reflected from the butterfly wing and avoiding the collection of the light reflected from the cell quartz window [17]. Due to the fact that the wing scales, as elemental reflectors, make a certain angle (different for species) respective to the wing membrane [23], and the light reflected from these scales has a well defined reflectance direction, in order to obtain the maximum intensity of the reflected light, the illuminating and collecting fibers usually have to be positioned under angles different from the directions of specular reflection from the wing. In the beginning of each cycle, the color of the wing in synthetic air was chosen as a reference. This means that the relative reflectance in air will be 100% for the full wavelength range. Mixing a certain amount of vapor to the air results a change in the optical properties of the wing, and this generates a deviation of the reflectance spectra from the 100%. This deviation was recorded as a function of time to follow the temporal evolution of the response signal during the experiment.

3. Theory

It was shown recently by optical simulation based on a scalar-wave approximation model, that the predicted optical responses during vapor condensation in colloidal photonic crystals agree well with experimental results [11]. Capillary condensation is the process by which multilayer adsorption from the vapor phase into a porous medium proceeds to the point at which pore spaces become filled with condensed liquid from the vapor phase [24]. The phenomenon of capillary condensation is governed by the Kelvin equation: $\ln(P_v/P_{sat}) = -(2H\gamma V_l/RT)$, where P_v is the equilibrium vapor pressure, P_{sat} is the saturation vapor pressure, H is the mean curvature of meniscus, γ is the liquid/vapor surface tension, V_l is the liquid molar volume, R is the ideal gas constant, T is the temperature.

The capillary condensation takes place below the saturation vapor pressure, P_{sat}, of the pure liquid in containers of extended volume. Meaning that if at a given temperature vapors are flowing from a reservoir containing non-saturated vapors, when flowing over a surface with suitable small pores, like those seen in Fig. 1 may condensate inside the pores to liquid phase. If the pores are the pores of a PBG material, the change on the refractive index contrast – due to the presence of liquid by condensation of the vapors – will shift the spectral position of the PBG. In this way measuring the reflectance spectra – the color – of the PBG material, one can obtain information on pore filling liquid, and moreover, we show that the measured spectral change is dependent on the flowing vapor concentration.

As one may observe from the Kelvin equation for a given vapor and a given temperature the value of P_v increases with the increase of the mean curvature of the meniscus, i.e., with decreasing pore size. If the pores are narrow enough – like in the case of the pores of a few tens of nm in radius – the pore may be approximated with a cylinder geometry and the interface between two fluids (air and liquid) forms a meniscus that is a portion of the surface of a sphere with radius R_{cyl}, so that the $H = 1/R_{cyl}$. Given that in the scales of the butterfly wings (see Fig. 1) one may find a distribution of pores around a certain characteristic value of pore size, there will be also a well definite range for the P_v values. As we reported earlier [20], we used the structural characteristics of the "pepper-pot" nanoarchitectures on a large number of exemplars for species discrimination. We showed for the nine investigated species that their discrimination on the basis of the structural parameters in unambiguous [20]. The hole center distance for the nine studied blue species varies in a range of 320–420 nm. The layer thickness mean is 140–240 nm. The pore volume which can be filled with the condensed liquid is defined by these values and also the filling factor of the structure. To specify the real geometry of the 3D structure in full detail is not straightforward even when trying to combine the SEM and TEM images [23]. As a first approximation cylindrical cavities in a layer can be adopted.

Although is not within the scope of the present paper to give a detailed mathematical discussion of the real experimental case, where a dynamic equilibrium will be established between the streaming gas–vapor mixture and the PBG nanoarchitecture (with a distribution of pore sizes), one may easily infer that the filling of the pores of different sizes in time will generate a time and vapor concentration (partial pressure) dependent signal as seen in Fig. 2. The shape of the curve for a given scale nanostructure and gas combination, characterizing the modification of the reflectance curve recorded under streaming synthetic air should depend on the vapor concentration in the air–vapor mixture, the time for

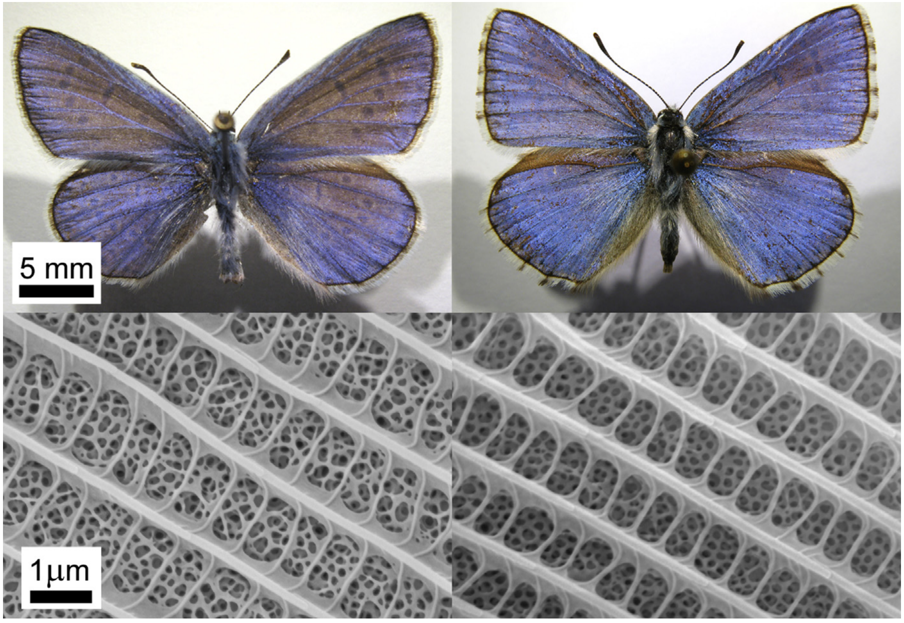

Fig. 1. The violet *Polyommatus icarus* (left) and the sky-blue *Polyommatus bellargus* (right) imago and scanning electron microscope image of a wing scale (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

which the mixture flows through the cell and the temperature of the butterfly wing.

In certain cases, when high concentration of vapors were used hysteresis was observed. Non-uniform pore geometries often lead to differences in adsorption and desorption pathways within a capillary. For example, if a capillary's radius increases sharply, then capillary condensation (adsorption) will cease until an equilibrium vapor pressure is reached which satisfies the larger pore radius. However, during evaporation (desorption), liquid will remain filled to the larger pore radius until an equilibrium vapor pressure that satisfies the smaller pore radius is reached [25]. This effect may have a strong influence in the case of "pepper-pot" like structures, where besides the average hole diameter in the range of visible light wavelength, also exists smaller pores.

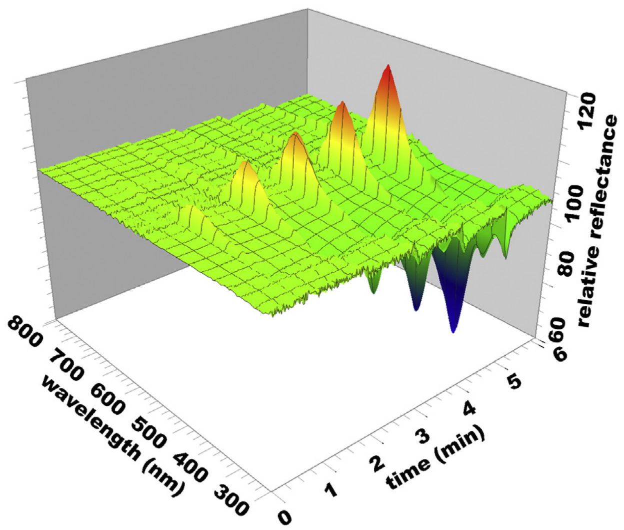

Fig. 2. Optical reflectance variation in time of *Polyommatus icarus* when the wing in synthetic air was used as reference (100%). Increasing concentrations of ethanol vapor flow were applied for 10 s followed by 50 s synthetic air flow for cleaning the cell.

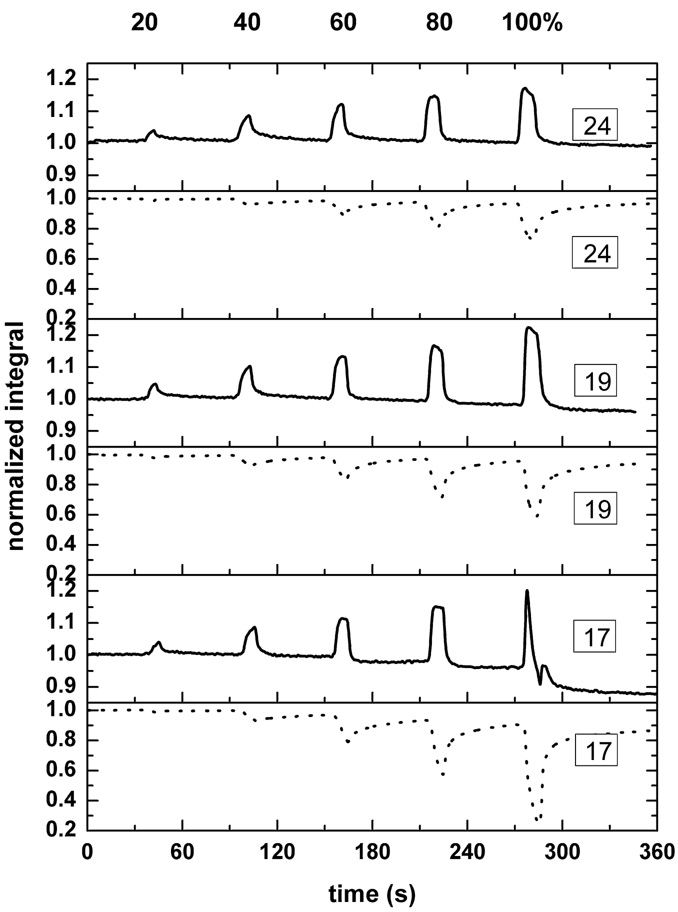

Fig. 3. Minima (dotted line) and maxima (continuous line) of the integrated response signal variation in time in selected spectral ranges (480–510 nm for maxima, and 300–330 for minima) from the previous 3D graph. During the measurements the *Polyommatus icarus* wing scale was kept at 17 °C, 19 °C respective 24 °C. For better comparison, the *y* axes of the three pairs of graph are the same. See the horizontal upper axis for ethanol vapor concentrations.

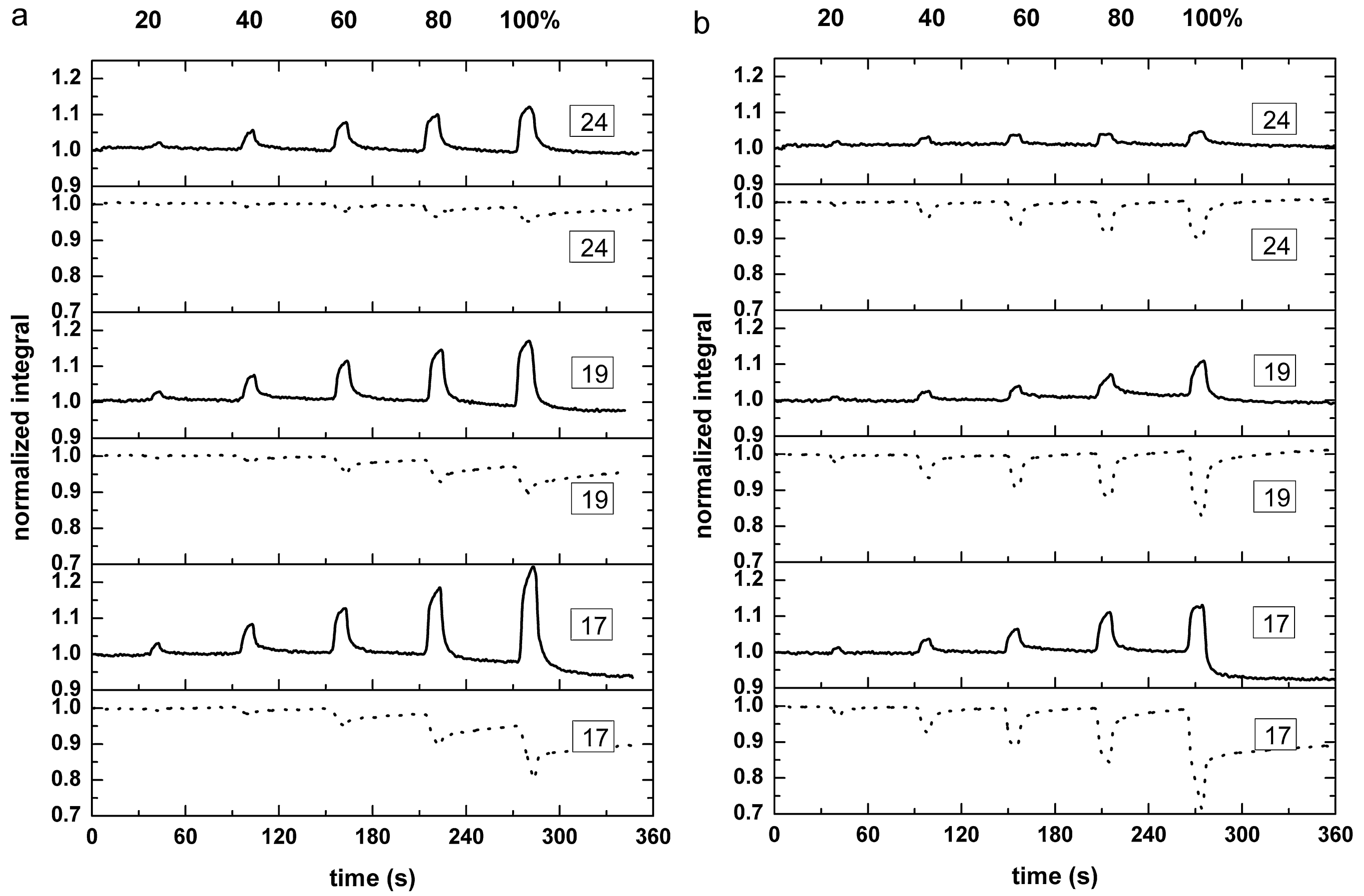

Fig. 4. *Polyommatus icarus* (left, spectral range of maxima: 480–510, spectral range of minima 300–330) and *Polyommatus bellargus* (right, spectral range of maxima: 500–530, spectral range of minima 350–380) response curves for water vapors at the three investigated temperatures.

4. Results and discussion

To exemplify the colors of the butterfly wings used in the experiments and the nanoarchitectures generating them, in Fig. 1 photos of the *P. icarus* and of the *P. bellargus* are shown together with the characteristic nanoarchitecture of the scales covering their dorsal wing surfaces. These two butterflies have saturated colors, with well-defined maxima [20]. On the contrary, the coloration of *P. coridon* is less saturated than that of the other two species; it is used as test specimen in order to see the effect of the shape of the reflectance curve on the sensing properties. Under the experimental conditions used in the gas sensing cell [17] *P. icarus* and *P. bellargus* exhibited a strong reflectance maximum at 380 nm and at 435 nm respectively. Under the same conditions the *P. coridon* exhibited a broad and shallow maximum at 550 nm.

As already discussed in Ref. [17] the most convenient reference that can be used in a gas sensing experiment, is the sensor (butterfly wing covered by scales containing PhC) itself in a synthetic air environment. If this signal is used as the 100% reference of the spectrometer, in subsequent steps only the modification of the spectrum in the presence of the mixture to be analyzed will be recorded. Such curves are presented in Fig. 2 as a 3D, time and wavelength dependent signal. One may note that during each gas mixture admission step, followed by a washing step (when only synthetic air is circulated through the measurement cell) the difference signal forms and drops off in a few seconds, but it is clearly a time dependent signal. Another observation is the clearly seen concentration dependence. Both maxima and minima form on the 3D graph in different wavelength ranges. In both wavelength ranges a region of 30 nm width is selected and the integrated reflectance value in the selected range is presented as a time dependent signal in Fig. 3 for the measurements carried out with a *P. icarus* wing piece and ethanol vapors as analyte. The three different panels in the figure correspond to the measurements carried out at three different wing temperatures. One may clearly see that the magnitude of the increasing (maxima) response signal to the presence of alcohol vapors in air shows clear linear dependence with the concentration of ethanol. Similar results were obtained for water and acetone vapors. *P. bellargus* exhibits a much similar behavior, but the maximum (minimum) of the response signal is situated in different spectral ranges as compared with *P. icarus*. In case of *P. coridon*, which in pure synthetic air does not exhibits a well developed reflectance maximum, but has a more plateau-like reflectance, despite the fact that it showed a certain level of response signal, the signal was of low magnitude and affected by noise. For the decreasing response (minima) the concentration dependence is not linear, especially at 17 °C and at 100% concentration a distorted peak is found. Also both signals show a higher drift at lower temperature. These two features could be attributed to the temperature dependence of the capillary condensation described in the previous section.

The wing scale nanoarchitectures are built up from branching submicron size features that promotes the formation “ink-bottle effect”. Characteristic hysteresis appears in such a system, resulting in different adsorption desorption paths. This effect decreases at higher temperatures [26].

Performing the same experiment for water vapors for *P. icarus* and *P. bellargus* (Fig. 4) looking at the maximum response curves one may note the near linear dependence of the intensity with the concentration, and for both the maximum and minimum curves a temperature dependent behavior. The signal intensity is increasing with the decrease of the sample temperature. This implies the sensitivity increase with the use of lower temperatures, which is a benefit when using such a structure as a gas sensor. However, at lower operating temperatures the recovery of the sensors will last longer, which may be disadvantageous for the applicability as a fast instrument. Similarly as in the case of ethanol, a nonlinear minimum appears at 17 °C sample temperature and 100% vapor concentration. Being present also at the experimental curves with acetone vapors and for all tested butterflies, we consider this nonlinearity as a part of the hysteresis of the capillary condensation. We plan to investigate this phenomenon in more details in the future.

5. Conclusion

We report the temperature dependence of optical gas sensing on wing scale nanostructure in the case of three selected polyommatine butterfly species. It was found that the “pepper-pot” structure is open enough to allow fast response time of the order of seconds. Each species was found to exhibit a characteristic response to the tested water, ethanol and acetone vapor, but the sample with less saturated color (*P. coridon*) produces weaker signals. The concentration dependence of the signal amplitude is close to linear, except the highest concentration, where the alteration of the shape of the response curve is found. This nonlinearity can be attributed to the hysteresis of the capillary condensation taking place in the scale nanostructure. The ability of capturing different signals for different species (scale structures) and different vapors shows the possibility of a selective gas sensing device. The short range order of a scale nanostructure, may prove important for the engineering of similar bioinspired artificial materials where the design and manufacture of each particular structure is time consuming and of high-cost. Developing the manufacturing process for a proper photonic nanoarchitecture of the type found in the scales of the investigated butterflies could be helpful as a standard pattern for preparing similar structures with various sizes of the building elements, in this way one can tune the response signal. As the pepper-pot type structure exhibits only a short range order, simple techniques like those based on foam production may prove sufficient for the bioinspired manufacturing of such structures. Another route is to use the biologically produced nanoarchitectures as they are cheap, reproduced with high precision and environmentally friendly.

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