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Photonic crystal type structures of biological origin: Structural and spectral characterization

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Abstract

Photonic crystal type structures of biological origin were investigated by scanning electron microscopy (SEM) and UV–VIS reflectance measurements. It was demonstrated that despite the moderate refractive index contrast between chitin and air, biological evolution developed in the wing scale nanostructures of butterflies representing various families, numerous structures with different hues of blue and very different degrees of directionality. Furthermore, for illustrating the variety of purposes for which nature may use photonic structures, the UV protection mechanism of the high altitude flower Edelweiss has been investigated. We present fully supportive data that the protection mechanism is based on coupling by nanostructured, highly selective couplers the harmful UV radiation in propagating modes along fibers containing UV absorbing pigment.

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Keywords: Photonic crystal; Butterfly; Edelweiss; Guided propagation; Scale micro-structure; Scale nanostructure; Reflectance

1. Introduction

Since 1987 when Yablonovitch [1,2] described a structure with complete photonic band gap and introduced the concept of photonic crystal, the field is more and more in the focus of attention. Photonic crystals are structures in which the refractive index is a periodic function in space. In a certain domain of wavelengths these structures may behave towards electromagnetic radiation in the very same way as the periodic crystal structure of semiconductors and insulators generates band gaps for electrons. In other words, like the electrons cannot exist in a stable state within these regions of forbidden energy, light of a certain wavelength cannot propagate in photonic crystals, respectively. The light within the forbidden gap of an ideal photonic crystal is completely reflected by the structure.

The efforts of the physics and materials science community in understanding and producing photonic band gap materials were motivated mainly by the potential application of these materials in optical computing [3,4], the manufacturing of more efficient lasers [5,6] and other exciting new phenomena. In the same time, a number of papers were published reporting on the occurrence of photonic crystal type structures in the living world [7–10]. Some of these structures have the respectable age of several million years [7]. Indeed, the

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photonic structures of biological origin were optimized during many millennia of biological evolution. These structures are widely available in our natural environment, therefore they can offer very useful and low cost models, for designing new and efficient photonic structures. Moreover, subsequent to detailed structural and spectral characterization, these materials may be used to improve computer models developed for computing properties of artificial photonic structures.

Our paper presents experimental results of structural and spectral characterization of various blue and orange colored photonic crystal type structures found in butterfly scales and nano-structured optical waveguides found in the bracts of the alpine flower Edelweiss. The latter are very efficient in separating the harmful UV part of the solar spectrum from the visible part used for photosynthesis.

Perhaps the most spectacular occurrences of photonic crystals in living organisms are found in the wing scales of the lepidopterous insects—in common language butterflies and moths—having blue and green coloration [8]. In certain butterflies even the yellow and red color may arise by physical mechanism, but the later two colors most frequently are produced by pigmentation, which is often called chemical color [11].

The photonic crystal structures of the wings, beyond their beauty and important role in the behavior of the individual butterfly, may also have a crucial function in thermal management. An example is given by the phenomenon called discoloration described by Bálint and Johnson [12]: the male lycaenid butterflies *Polyommatus marcidus*, living at altitudes of 2000–2500 m, opposite to males of the sister species *Polyommatus daphnis* have no iridescent blue color on their dorsal wing surface but a warm brown. The authors hypothesized that discoloration is the consequence of the adaptation to the harsh climatic conditions at high altitudes. Recently we demonstrated that indeed, the loss of color is associated with the absence of the photonic structure from the scales of *P. marcidus* males and this causes that under identical illumination their temperature may be 5 °C higher than that of the blue males of the *P. daphnis* individuals [9].

Although not so frequently as in the animal world, photonic structures may occur in plants, too. The structuring of optically transparent media on the nanometer scale may be an efficient way not only for generating color by reflection, but for protection against harmful UV radiation, like it will be discussed in the case of edelweiss, *Leontopodium alpinum* (Asteraceae), a well known high altitude plant.

The investigated butterfly individuals were obtained from the scientific collections of the Hungarian Natural History Museum, whilst all plant samples used for our investigations originated from cultivated horticultural stocks.

2. Experimental results and discussion

The butterfly samples were prepared for optical measurements by cutting pieces from the forewing of each exemplar. Specular reflectances were recorded using an Avantes 2048 fiber optic spectrometer in the UV–VIS-NIR range. A standard white teflon sample was used to calibrate the reflectance measurements. To check the angular dependence of reflection an integration sphere of 3 cm in diameter was used. Butterfly scales are built of chitin—in the absence of pigmentation—a white colored insulating biopolymer. Pieces cut from the wings were first sputter coated with gold, to avoid charging. The nanostructure of the scales was investigated by scanning electron microscopy (SEM).

Observing blue butterfly wings by naked eye clearly reveals that many hues of blue are produced. For example in the case of several Blue butterflies (tribe Polyommatini in family Lycaenidae) male individuals of different species living in the same type of environment and same geographic location have distinctly colored dorsal wing surfaces, like Common Blue (*Polyommatus icarus*): (“purple blue” called in this paper: blue violet), and Adonis Blue (*Polyomattus bellargus*): (“azure blue” called in this paper: blue). The reflectance spectra of the two above mentioned species are shown in Fig. 1. As the two species are rather similar superficially, this difference is crucial in male–male interactions, and also probably in subsequent mate selection. As male butterflies patrol their territory or perch against competitors of the same species, they have to be able to distinguish between blue males of their own species and blue males of other species. It is interesting to investigate on the micro- and nanoscale in which way the two hues of blue are generated. We presented evidence earlier [9] that the blue color originates from the so called “pepper-pot structure” that fills the windows between the ridges oriented along the longer axis of the scales and the cross ribs linking

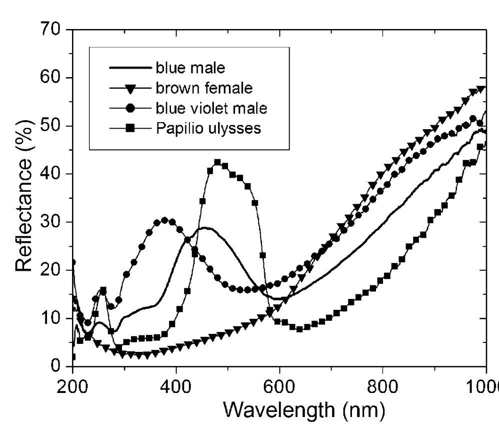

Fig. 1. Normal incidence reflectance spectra of three blue butterfly wings of different hue. The reflectance of a brown female of the same species as the blue violet male was included for comparison.

these ridges. As shown in Fig. 2a and b, indeed, clear morphological differences can be observed in the pepper-pot structures of the two butterfly species. In the scales of the blue violet male the pepper-pot structure has a three dimensional arrangement, with a low filling fraction, in some sense resembling the coral branches (Fig. 2a), while in the scales of the blue male (Fig. 2b) the pepper-pot structure is organized in planar layers running parallel with the plane of the scale. The average geometric dimensions: hole diameter and the width of the walls separating the holes, as measured from SEM images, are given in Table 1. The values of planar filling factor for the pepper-pot structure were estimated from SEM images. First the image was converted into a black/white image, than the regions corresponding to the ridges and cross ribs were excluded and the ratio of white (filled) to black (empty) pixels was measured.

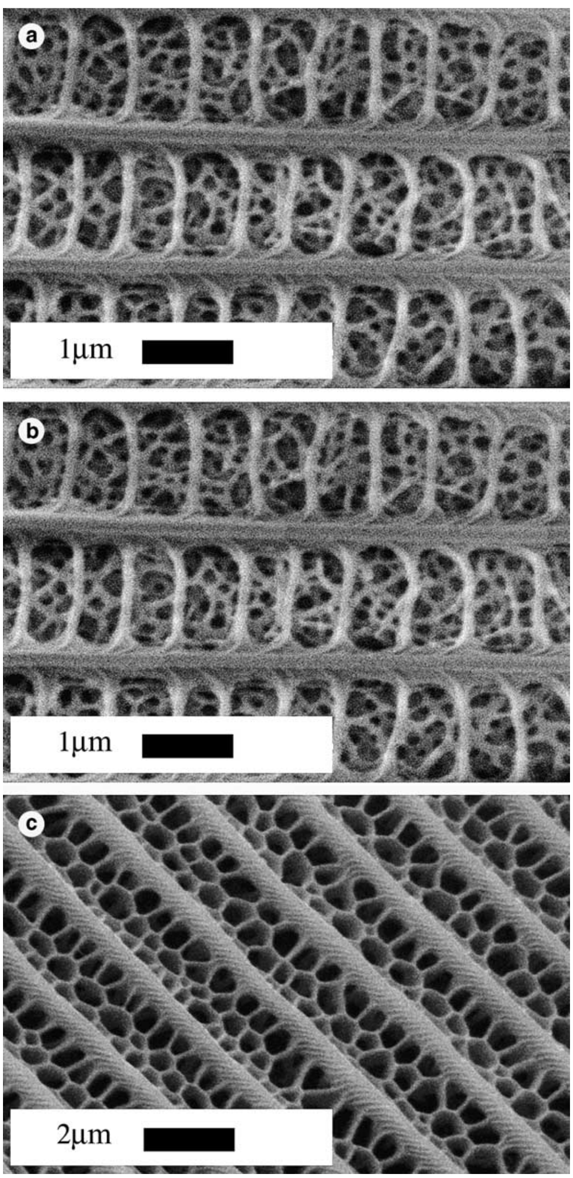

Fig. 2. SEM images showing the nanostructure of blue colored butterfly wing scales: (a) blue violet male (*Polyommatus icarus*); (b) blue male (*Polyomattus bellargus*) and (c) *Papilio ulysses*.

Table 1
Hole diameter, *D*; separation wall width (separating two side by side holes), *W*; planar filling factors and *F*; the spectral position of the reflectance maximum for the pepper-pot type nanostructures

Butterfly name	*D* (nm)	*W* (nm)	*D*/*W*	F	Peak (nm)
Polyommatus icarus	155	77	2.01	2.97	380
Polyommatus bellargus	142	83	1.71	1.046	457
Papilio ulysses	515	164	3.15	0.70	501

A different butterfly species representing the not-so-closely related family Papilionidae, *Papilio ulysses* possesses blue colored marginal spots on the dorsal hind wing surface which have a somewhat greenish hue. The reflectance spectra from these spots are shown in Fig. 1. One may remark that the spectral maximum is shifted towards the green and it has a shape that may suggest the overlap of two closely placed peaks. The SEM image shown in Fig. 2c shows the nanostructure of the scales. In these scales there are no cross ribs and the empty holes occupy a much more significant fraction of the structure (Table 1).

When comparing geometric data of Table 1. with spectral data, no straightforward relation can be established. This clearly indicates that the investigated nanostructures generate color by a complex process, which can be understood only using sophisticated modeling tools [9].

One may also remark (Fig. 1), that irrespective of the position of the blue reflectance maximum, the reflectances in the range of 600–1000 nm are rather similar. The gradually ascending reflectance as a function of the wavelength is attributed to the decreasing absorption of brown melanin [9], a specific pigment of the butterfly wings. It may be pointed out that the melanin content of the scales within related *Polyommatus* species individuals (blue male, brown female, blue violet male) is somewhat similar, the best coincidence is found for males and females of the same species (blue male, brown female), while the *P. ulysses* has a lower melanin content. The melanin found in butterfly wings is a strong absorber in the UV–VIS range [9], therefore the fact that reflectance maxima are produced in the blue, clearly indicates that the reflected radiation was not able to penetrate into the structure, where it would have been absorbed. On the other hand, it has to be emphasized that in the absence of a pigment that is able to absorb effectively those spectral ranges that are not reflected by the photonic structure, no color generation is possible, like in the case of albino peacocks [13,14]. In such a case, when the nanostructures giving rise to physical color have the appropriate structure giving rise to physical color, but lack the absorbing pigment, all wavelengths are randomly scattered and reflected, which yields translucent white coloration. The effect of the melanin on the reflectance in the absence of photonic crystal type structures, with just the ridges and cross ribs present is shown in Fig. 1, the curve corresponding to the brown female (*P. bellargus*), while the characteristic micro- and nanostructure of the scales is presented in Fig. 3a.

The eventual angular dependence of the four butterfly wings discussed was checked by comparing measurements carried out with integration sphere with those done under specular conditions. No characteristic differences were found.

Opposite to the coloration by pepper-pot-type structure, the morpho type scales in which the ridges have a complex structure [15] (typical for the brilliantly blue colored South American morphine nymphalids (family Nymphalidae: subfamily Morphinae) the most intensely investigated species being *Morpho rhetenor* [15]) is characterized by a very high degree of directionality of the reflected light. We examined a male individual of *Morpho aega* displaying similar metallic blue coloration to that of *M. rhetenor*. The reflectance at normal incidence is shown in Fig. 4. The reflectance peak, with magnitude larger than 100%, is caused by the fact that in the particular wavelength range of the reflection maximum the butterfly wing reflects more light than the white standard used to calibrate the spectrometer. Using a goniometric setup in combination with the fiber optic spectrometer we were able to map the reflectivity both in wavelength and angle. Natural solar light was used for illumination at normal incidence, the reflected light was picked up at a fixed angle of 45° with respect to the wing plane, while rotating the analyzing optical fiber in polar angle range from 0° to 360°. The resulting three dimensional (3D) plot is shown in Fig. 5. One may notice a rather narrow angular and wavelength range in which the reflectivity is two orders of magnitudes stronger than in the plateau region for the spectral range of the reflection maximum.

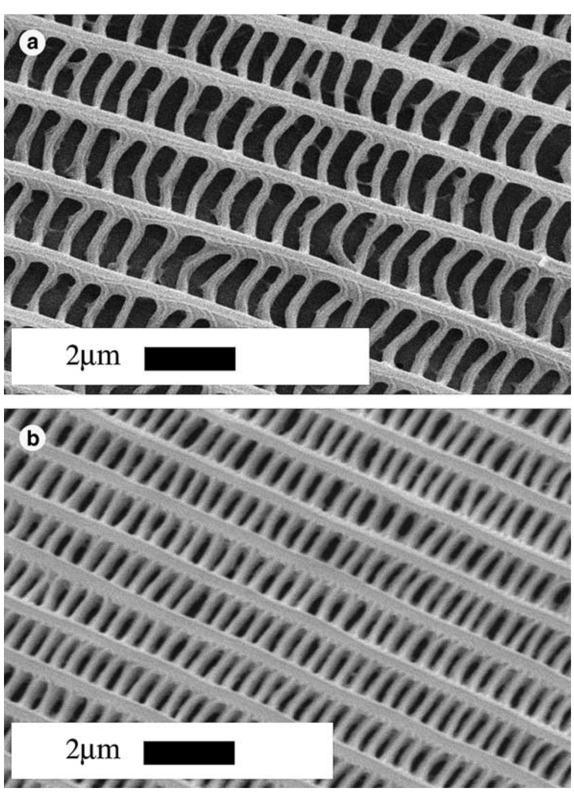

Fig. 3. SEM image showing the scale nanostructure of: (a) brown female (*Polyommatus icarus*) and (b) male copper butterfly (*Lycaena virgaureae*).

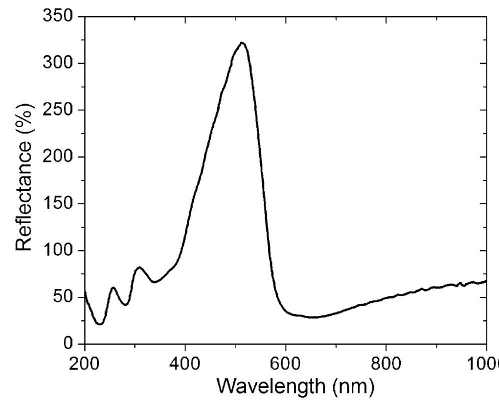

Fig. 4. Normal incidence reflectance spectra of blue *Morpho aega* male wing. The reflectance values higher then 100% are produced by the higher reflectance of the sample in a certain wavelength range than the reflectance of the white calibration standard.

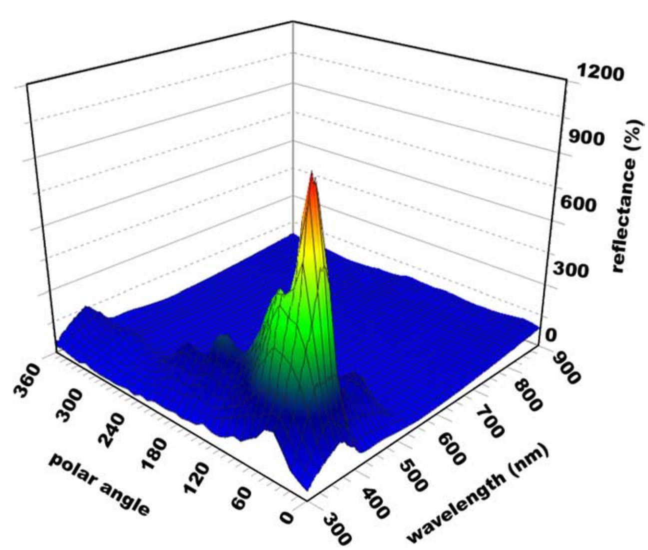

Fig. 5. Reflectance values at normal incidence natural solar illumination with reflected light picked up at 45° from the wing plane versus wavelength and polar angle value (the rotation axis is normal to the wing plane) for *Morpho aega* male.

We carried out a similar measurement on the wing of a male individual of the copper lycaenid Scarce Copper (*Lycaena virgaureae*) (family Lycaenidae, subfamily Lycaeninae). The representatives of the subfamily are commonly called as "Coppers" because of their orange coloration with metallic or coppery aspect. The resulting 3D reflectance spectrum is shown in Fig. 6, while the corresponding micro- and nanostructure of the scales is presented in Fig. 3b. Although a certain directionality—to which the metallic aspect may be associated—can be seen in Fig. 6, the ratio of reflectance values in the reflectance peak region and in the plateau region for the same spectral range does not exceed 2. Still, it is worth pointing out that even this level of directionality makes that by naked eye observation one has a metallic impression opposite to the dull (brown) coloration of the structure shown in Fig. 3a. corresponding to a brown female of Adonis Blue butterfly. The exact physical mechanism by which the metallic aspect is produced needs further investigation.

To illustrate the great variety of functions the photonic structures may play in living beings, the Edelweis (*Leontopodium alpinum*) (family Asteraceae), a perennial which lives in adverse circumstances such as extremely exposed cliffs or steep rocky swards, most often in high altitudes, (eg. in the Alps, 3400 m altitude) was chosen, Fig. 9. This plant has a characteristic "inflorescence" covered by white wooly hair, Fig. 7. As a matter of fact the reproductive parts of the flower are situated in the centre and are surrounded by the protective petals and leaves covered by white filament, which are not elements of the reproductive organ. The lower leaves are also covered by a not so dense white hair. Although at high altitudes the atmosphere is rare, thus the intensity of harmful UV radiations is increased, the Edelweiss does not suffer UV damage. In searching the ways in which this UV protection is achieved, we come to study the white filament. The examination by optical microscopy revealed entangled translucent fibers of 10 μm in diameter [16]. The SEM investigation at medium magnification showed that the surface of the hollow fibers is covered by a fine nanostructure (Fig. 8a), which is shown in more detail in Fig. 8b. These parallel fibers have an average diameter of 180 nm. Computer modeling supported [16] that such a structure can selectively couple the UV light in propagating modes along the fiber, while the visible light is mostly reflected or transmitted trough the fiber. Indeed, the reflectance of the white hair measured (without removing it from the leaves) both at normal incidence and with the integration sphere shows a plateau like profile in the range of 400–1000 nm, with a sharp drop at wavelengths below 400 nm. The transmission measurements through a carefully removed filamentary layer showed a similar, plateau like behavior as found in the reflectance measurements. Transmission of about 80% was found in the visible region with a sharp drop at wavelengths below 400 nm. Thus, apparently the UV light was neither reflected, nor transmitted. Following a recently published patent [17] we prepared an extract of the Edelweiss bract in alcohol, a colorless solution was obtained after filtration and chlorophyll photo-degradation, which could be reversibly dried and redissolved without changing its spectral behavior, shown in Fig. 10. The transmission measurements of Fig. 10 show that the solution contains a strong UV absorber. Therefore the combined action of coupling the UV radiation in a guided mode along the fiber, and the UV absorption of the fiber results in the harmless dissipation of the

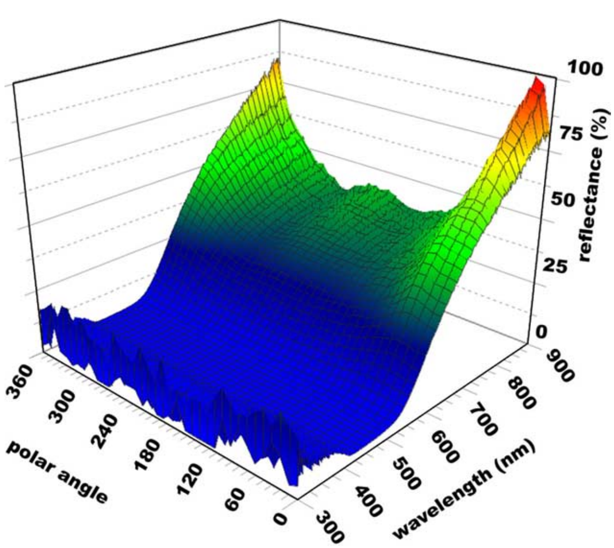

Fig. 6. Reflectance values at normal incidence natural solar illumination with reflected light picked up at 45° from the wing plane versus wavelength and polar angle value (the rotation axis is normal to the wing plane) for *Lycaena virgaureae* male.

Fig. 7. Photograph of the Edelweiss (*Leontopodium alpinum*) flower. The investigated white filamentary wool is shown on the bracts.

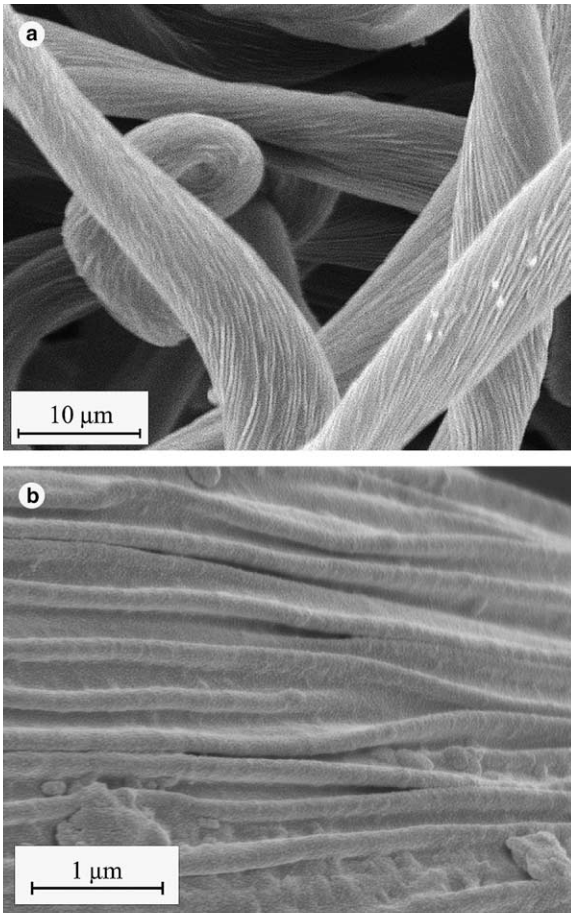

Fig. 8. SEM images of the white filamentary wool: (a) low magnification image of entangled fibers and (b) high magnification image showing the nano-relief responsible for the selective coupling of the UV light.

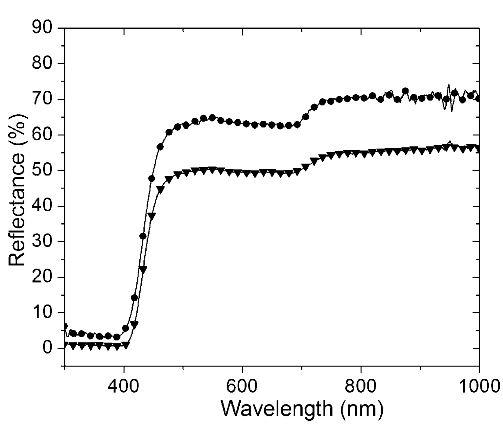

Fig. 9. Reflectance of the white filamentary wool: normal incidence (heavy triangles); integration sphere measurement (heavy circles).

UV part of solar radiation in the white wool, while the useful visible part penetrates to contribute to photosynthesis. It is worth pointing out that the reduction of intensity the UV radiation would suffer when transmitted through a 10-μm thick filament would be negligible

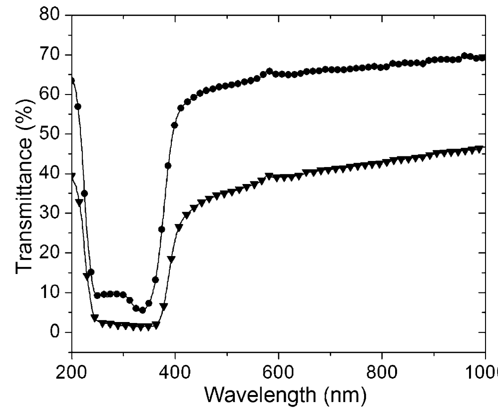

Fig. 10. Transmittance of the filament extract in ethanol: concentrated (heavy circles); after dilution (heavy triangles). One may remark that in the range below 400 nm, where the UV absorber pigment is active, the dilution had a much weaker effect than in the visible range.

while the attenuation suffered after several millimeters of propagation along the fiber is orders of magnitude stronger. Evolution in nature designed a highly selective and efficient UV protection based on the use of guided modes along fibers containing UV absorbing material which have nano-metric photonic structures acting as wavelength selective couplers.

3. Conclusion

Photonic crystal type structures of natural origin were characterized structurally and spectrally. It was demonstrated that such structures optimized during several millennia of evolution may have various uses for living beings: from sexual signaling via thermal regulation to UV protection. Nature has developed a remarkable variety of photonic structures using the very same low refraction index material chitin for generating various hues of blue and with different degrees of directionality. This gives insight in the flexibility to be expected from photonic crystal type materials once the technology to produce them at low cost will be mastered. Although all the investigated structures contain many structural defects and the refractive index contrast is relatively low, these structures showed to be very effective in achieving certain "tasks" like a very finely tunable coloration, high directionality, selective coupling and attenuation. These features of the photonic structures have a great potential of practical applications, too.

Our results clearly show that in a similar way like in the case of the real crystals despite their point defects, dislocations and impurities they were suitable to produce micro-electronic devices, photonic crystal type material with defects may also find many practical applications before technology will mature to the level at which it can produce photonic crystals with good enough quality needed for optical computing.

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