INVESTIGATION OF NATURAL PHOTONIC CRYSTAL STRUCTURES

PhD thesis summary

KRISZTIÁN KERTÉSZ

SUPERVISOR: Prof. László Péter Biró, doctor of HAS
HAS - Research Institute for Technical Physics
and Materials Science

UNIVERSITY ADVISOR: Prof. Péter Richter, doctor of HAS
BUTE - Department of Atomic Physics

MTA MFA
BUDAPEST
(2009)

Precedents of the work

In the past decade a continuously growing interest was focused on photonic crystal type structures in various scientific communities. These structures are composites made of materials with different refractive index, the propagation of electromagnetic waves within specific wavelength ranges may be forbidden in the nanocomposite, this wavelength range is known as the photonic band gap. In a certain sense, the reasons for the formation of the photonic band gap are similar to the formation of the semiconductor band gap formed between the valence and conduction band. Physics and information technology are interested in the potential application of these materials in optical computing, meanwhile more and more living beings are discovered having photonic crystal like structures developed by biological evolution. These nanostructures (we should call them natural photonic crystals), if the characteristic size of their building elements are in the range of 100 nm, will show different colours for the human eye, the observed hue is a function of the characteristic dimensions in the photonic nanoarchitecture. The biologists name these colours physical, or structural colour. It is possible to combine the structure-related colour with pigments, which generate colours based on molecular absorption. Adding these two effects, we meet the great variety and complexity of natural colours. At the same time the biological photonic structures play a well defined role (sexual signalling, camouflage, etc.), and in certain cases they were optimized during millions of years of evolution. Because these organisms are ready made for us, it is convenient to study these samples to extract new, bioinspired ideas for artificial nanoarchitectures. The biologic nanoarchitectures often do not exhibit a high degree of order as used in artificial photonic nanostructures, on the other hand the scientific literature confirms the existence of photonic band gaps even in strongly disordered (amorphous) or in quasiordered (there is only a local, short distance order) structures.

In my PhD thesis I present three examples from the pioneering investigations on biologic photonic crystals done at MTA MFA Nanostructures Department.

The presented topics

The case studies presented in detail in the thesis were chosen to illustrate by three examples the variety and various functions of natural photonic crystals in different living beings.

In the beginning of the thesis there is a short introduction in the theory of photonic crystals, their fabrication and some of the various applications.

The discussions of the main findings in the presented work are in the final three chapters. First the relation between the wing scale nanostructure, colour and thermal regulation of the males of a Lycaenid butterfly sister species pair is presented. It is shown that the blue colour originates from a so called "pepper-pot" type structure, which is absent from the scales of the discoloured (brown) species. I showed that the existence of the revealed photonic structure can modify the sunlight's heating effect of the wings of the two butterflies, resulting in different butterfly body temperatures.

The next chapter reveals the different appearance and different functions of dorsal (metallic blue), respective ventral (matt green) wing sides of a butterfly. It is remarkable that as far as we know, the *Cyanophrys remus* butterfly is the first and only well studied case where both the dorsal and ventral sides of the wing are coloured by photonic nanoarchitectures. Starting from similar building blocks (photonic nanoarchitectures), a metallic blue coloration is formed on the dorsal side, while on the ventral side a matt green colour is found. The importance of the evolved colours is in sexual signalling for the shiny blue, and in survival strategy for dull green (cryptic colour).

Finally, the structure and the optical properties of the inflorescences of the high-altitude Leontopodium alpinum (edelweiss) are investigated. The submicrometer filaments forming the white, hairy cover layer of the plant acts as a highly efficient and wavelength selective absorber, (guiding and attenuating UV waves along their length) protecting the living tissues from the harmful ultraviolet radiation.

Methods

The research is connecting the field of biology and physics: various physical investigation methods were applied on biological samples: SEM/FIB, TEM, optical microspectrometry, goniometric spectrometry, thermal measurements. The aim was finding the relation between structure, property and function. Concerning the results, materials scientists are delighted on having free samples (in some cases complex photonic nanoarchitectures) which may offer new structural solutions for new types of bioinspired nanoarchitectures, while biologists obtain new answers to the questions related to the spreading, way of life and evolution of the studied organisms.

According to the nature of the specimens – nanocomposites on 100 nm scale – the experimental work necessitated the development of novel measurement setups, like for example the spectro-goniometer. The light reflecting properties of complex three dimensional nanoarchitectures strongly differ from the specular reflectors or the diffuse (Lambertian) surface. A significant part of the reflected light emerges on under well defined angles, often the backscattered (incident and reflected directions are the same) component dominates, even under incidence angles different from normal. Therefore, an instrument able to map the reflected light in the whole upper hemisphere was needed and the illumination angle also had to be a free parameter. Carrying out thermal measurements in ambient atmosphere – the normal environment in which the butterfly wings work as solar collectors – rises difficulties in handling the nascent air flows when illuminating samples at atmospheric pressure with light intensities comparable to the sunlight. The air flows arises from the warming of the illuminated sample, and power meter, and human presence also influences the thermal measurements by air currents and breathing. These factors and the very small heat capacity require extremely carefulness during the measurements. In certain cases SEM, TEM images, spectrogoniometer reflectance measurements and theoretical modelling had to be consistently combined for the correct interpretation of the structural data and of the optical properties.

Statements of the thesis

1a. By the investigation of the blue Polyommatus daphnis and the brown Polyommatus marcidus butterfly sister species I have shown that the origin of the blue wing colour is associated with the so called "pepper pot" nanostructure which is absent from the brown wing scales. The pepper pot acts as a natural photonic structure, and increases the light reflectance in blue and near UV range. [T1]

1b. Using thermal measurements I showed that the brown wing's light absorption is more efficient than the absorption of the blue one. This is can be attributed to the colour change occurred in the case of high altitude population. The colour change from blue to brown offers higher survival chances for the males of the high altitude butterfly population. [T1]

1c. I pointed out that the pepper-pot structure on blue Polyommatus daphnis scales are far from being as perfect as artificially produced photonic crystal type structures still they generate colour in an efficient way and have effects on the thermal management. I proposed that the manufacturing conditions are less strict for photonic structures to be used in thermal applications and photonic type colorants. My results confirm the possibility of using photonic crystal coated surfaces for thermal management. [T1]

2a. Using scanning electron microscope (surface information), transmission electron microscope (cross-section data) and spectral reflectance results, I revealed the structure of the complex three-dimensional nanoarchitecture found in Cyanophrys remus butterfly wing scales. [T2], [T3]

2b.Tthe metallic blue colour of the dorsal Cyanophrys remus wing originates from photonic single crystals which cover the entire wing scale. [T2]

2c. The ventral side matt pea-green coloration arises from the cumulative effect of randomly oriented, blue, green, and yellow, bright (locally well ordered) photonic crystallites. The structure is a photonic polycrystal. [T2]

2d. I pointed out two component of the dorsal wing colour:

- *reflectance form the two sides of the wide ridges (that contain photonic nanoarchitecture) (λ = 480 nm)*

- reflectance from the structure visible through the windows determined by ridges and cross ribs (λ = 422 nm)
Because their different width and structure, the ridges does not play significant role in the reflectance of the ventral side. [T2]

3a. The filamentary cover layer found on Leontopodium alpinum has a tubular structure, with longitudinal waveguides on their surface. The incident UV waves are transferred into guided modes propagating along the filaments and absorbed. [T4]

3b. I performed spectral transmittance measurements on foliaceous bracts. According to these measurements and the theoretical model, the entire visible range is able to pass through the hairy cover, making possible the photosynthesis, but the UV light is efficiently filtered, offering a shielding for the living cells. [T4]

Usage and further prospects

All results presented in this thesis are part of EU6 BIOPHOT NEST „Complexity and evolution of photonic nanostructures in bio-organisms: templates for material sciences” (2005-2008) programme, and of the Hungarian OTKA grant T042972 “Comparative physiomorphologic and thermodynamic investigations on the scales of monophyletic and non-monophylethic lycaenid butterfly (Insecta, Lepidopetra, Lycaenidae) species-groups with special regard to the convergent phenomenon of discolouration (2003-2006)”.

The nanoarchitectures revealed in photonic crystals of biological origin could give inspiration for novel methods of producing similar, bioisnpired artificial structures [D15]. In contrast with the well known crystals of the solid state physics, in the field of photonic crystals does not exists other natural models but the opal and inverse opal structures, respective the rich variety of biological systems. Most of the artificial structures are designed on the basis of theoretical calculations, and often these calculations result in hardly realizable 3D nanoarchitectures, or require complex infiltration and dissolution methods in several steps to achieve the desired high refractive index contrast. The significance of the results presented in the thesis is illustrated by the number of citations.

Publications used in the statements of the thesis

T1. Biró L. P., Bálint Zs., **Kertész K.**, Vértesy Z., Márk G. I., Horváth Z. E., Balázs J., Méhn D., Kiricsi I., Lousse V.and Vigneron J. P.: Role of photonic-crystal-type structures in the thermal regulation of a Lycaenid butterfly sister species pair. **Phys. Rev. E** 67. art. no. 021907 (2003)

Virtual Journal of Nanoscale Science & Technology 7, March 03, 2003 (**www.vjnano.org**)
Virtual Journal of Biological Physics Research 5, March 01, 2003 (**www.vjbio.org**)

Number of citations: 25

T2. **Kertész K.**, Bálint Z., Vértesy Z., Márk G. I., Lousse V., Vigneron J. P., Rassart M., Biró L. P.: Gleaming and dull surface textures from photonic-crystal-type nanostructures in the butterfly Cyanophrys remus, **Phys. Rev. E** 74, 021922, (2006)

Virtual Journal of Nanoscale Science & Technology 14, September 11, 2006 (**www.vjnano.org**)

Number of citations: 6

T3. Biró L. P., Bálint Zs., Vértesy Z., **Kertész K.**, Márk G. I., Lousse V., Vigneron J. P.: Living photonic crystals: nanostructure of the scales of Cyanophrys remus butterfly, **Nanopages** 1 195–208, (2006)

T4. Vigneron J. P., Rassart M., Vértesy Z., **Kertész K.**, Sarrazin M., Biró L. P., Ertz D., Lousse V.: Optical structure and function of the white filamentary hair covering the edelweiss bracts, **Phys Rev E** 71, 011906, (2005)

Number of citations: 5

Publications related to the topic, but not used in the statements of the thesis

D5. Bálint Zs., Vértesy Z., **Kertész K.**, Biró L. P.: A lepkék színeváltozása. **Természet Világa** 135, 311 – 313, (2004)

D6. Vértesy Z., Bálint Zs., **Kertész K.**, Méhn D., Kiricsi I., Lousse V., Vigneron J. P. Biró L. P.: Modifications to wing scale microstructures in Lycaenid butterflies, **Microscopy and Analysis** 18, 25-27, (2004)

Number of citations: 1

D7. **Kertész K.**, Bálint Zs., Vértesy Z., Márk G. I., Lousse V., Vigneron J. P., Biró L. P.: Photonic crystal type structures of biological origin: structural and spectral characterization, **Current Applied Physics** 6, 252- 258, (2006)

Number of citations: 9

D8. Bálint Zs., Boyer P., Dahners, H. W., Salazar-Escobar J. A., **Kertész K.**: Comments on the systematics and natural history of Aveexcrenota, a genus of rare andean Eumaeine Lycaenidae (Lepidoptera), **Acta Zoologica Academiae Scientiarum Hungaricae** 52 (3), 331–352, (2006)

Number of citations: 1

D9. Vértesy Z., Bálint Zs., **Kertész K.**, Vigneron J. P., Lousse V., Biró L. P.: Wing scale micro- and nanostructures in butterflies - natural photonic crystals, **Journal of Microscopy**, Vol. 224, Pt 1 October, 108–110, (2006)

D10. Bálint Zs, **Kertész K.**, Wojtusiak J., The description of Atlides halljasoni n. sp. from Ecuador and its spectrographic characterization with some notes on the genus (Lepidoptera: Lycaenidae: Eumaeini), **Genus** 17 (3), 409-415, (2006)

D11. Biró L. P., **Kertész K.**, Vértesy Z., Márk G. I., Bálint Zs., Lousse V., Vigneron J. P.: Living photonic crystals: Butterfly scales – Nanostructure and optical properties, **Materials Science and Engineering C** 27, 941-946, (2007)

Number of citations: 1

D12. Márk G. I., Bálint Zs., **Kertész K.**, Vértesy Z., Biró L. P.: A biológiai eredetű fotonikus kristályok csodái, Fizikai szemle, 2007. április, 116-121

D13. Bálint Zs., Wojtusiak J., **Kertész K.**, Biró L. P.: The description of Theritas Gozmanyi from the andes and its spectroscopic characerization with some notes on the genus (Lepidoptera: Lycaenidae: Eumaeini), **Acta Zoologica Academiae Scientiarum Hungaricae** 53 (Suppl. 1), 211-224, (2007)

D14. Bálint Zs., Horváth Z. E., **Kertész K.**, Vértesy Z. Biró L. P.: Observations on scale structures and spectroscopic properties of Polyommatus lycaenid butterflies (Lepidoptera: Lycaenidae), **Annales historico-naturales musei nationalis hungarici** 99, 115-127, (2007)

D15. **Kertész K.**, Molnár G., Vértesy Z., Koós A. A., Horváth Z. E., Márk G. I., Tapasztó L., Bálint Zs., Tamáska I., Deparis O., Vigneron J. P., Biró L. P.: Photonic band gap materials in butterfly scales: A possible source of “blueprints”, **Materials Science and Engineering B**, 149, 259-265, (2008)

D16. Vigneron J. P., **Kertész K.**, Vértesy Z., Rassart M., Lousse V., Bálint Zs., Biró L. P.: Correlated diffraction and fluorescence in the backscattering iridescence of the male butterfly Troides magellanus (Papilionidae), **Phys. Rev. E** 78(2), 021903, (2008)

D17. Bálint Zs., Boyer P., **Kertész K.**, Biró L. P.: Observations on the spectral reflectances of certain high Andean Penaincisalia and Thecloxurina, with the description of a new species (Lepidoptera : Lycaenidae : Eumaeini), **Journal of Natural History** 42(25-26) 1793-1804, (2008)

D18. Bálint Zs., Wojtusiak J., **Kertész K.**, Biró L. P.: Description of Penaincisalia biophot with emphasis on the optical properties of the wing dorsal surfaces, **Genus** 19 (3), 343-353, (2008)

Publications not related to the topic of the thesis

19. Biró L. P., Horváth Z. E., Szalmás L., **Kertész K.**, Wéber F, Juhász G., Radnóczi G., Gyulai J.: Continuous carbon nanotube production in underwater ac electric arc, **Chemical Physics Letters** 372 399-402 (2003)

Number of citations: 22

20. Biró L. P., Horváth Z. E., Koós A. A., Osváth Z., Vértesy Z., Darabont A., **Kertész K.**, Neamțu C., Sárközi Z., Tapasztó L.: Direct synthesis of multi-walled and single-walled carbon nanotubes by spray-pyrolysis, **J. of Optoelectronics and Advanced Materials** 5. 661-666 (2003)

Number of citations: 5

21. Biró L. P., Márk G. I., Horváth Z. E., **Kertész K.**, Gyulai J., Gruenberger Th., Fulcheri L., Nagy J. B. Lambin Ph.: Carbon nanoarchitectures containing non-hexagonal rings: „necklaces of pearls", **Carbon** 42. (12-13) 2561-2566 (2004)

Number of citations: 4

22. Tapasztó L., **Kertész K.**, Vértesy Z., Horváth Z. E., Koós A. A., Osváth Z., Sárközi Zs., Darabont Al., Biró L. P.: Diameter and morphology dependence on experimental conditions of carbon nanotube arrays grown by spray pyrolysis, **Carbon** 43. 970–977 (2005)

Number of citations: 13

23. Darabont Al., Nemes–Incze P., **Kertész K.**, Tapasztó L., Koós A. A., Osváth Z., Sárközi Zs., Vértesy Z., Horváth Z. E., Biró L. P.: Synthesis of carbon nanotubes by spray pyrolysis and their investigation by electron microscopy, **J. of Optoelectronics and Advanced Materials** 7, 631-636 (2005)

Number of citations: 3

24. Horváth Z. E., **Kertész K.**, Pethő L., Koós A. A., Tapasztó L., Vértesy Z., Osváth Z., Darabont Al., Nemes-Incze P., Sárközi Zs., Biró L. P.: Inexpensive, Upscalable Methods For Nanotube Growth, **Curr. Appl. Phys**. 6, 135-140, (2006)

Number of citations: 4

25. Horváth Z. E., Koós A. A., **Kertész K.**, Vértesy Z., Molnár Gy., Ádám M., Dücső Cs., Gyulai J. Biró L. P.: Mats of Functionalized Carbon Nanotubes for Gas/Vapor Sensing, **Nanopages** 1, 209 – 217, (2006)

26. Nemes-Incze P., Daróczi N., Sárközi Z., Koós A. A., **Kertész K.**, Ţiprigan O., Horváth Z. E., Darabont Al., Biró L. P.: Synthesis of bamboo–structured multiwalled carbon nanotubes by spray pyrolysis method, using a mixture of benzene and pyridine, **Journal of optoelectronics and advanced materials** Vol. 9, No. 5, May 2007, 1525 – 1529

Number of citations: 2

27. Sárközi Zs., **Kertész K.**, Koós A. A., Osváth Z., Tapasztó L., Horváth Z. E., Nemes-Incze P., Jenei I. Z., Vértesy Z., Daróczi N. S., Darabont Al., Pana O., Biró L. P.: Synthesis of carbon nanotubes from liquid hydrocarbons using a spray-pyrolysis method, **Journal of Optoelectronics and Advanced Materials** 10(9), 2307-2310, (2008)

28. Horváth Z. E., Koós A. A., **Kertész K.**, Molnár Gy., Vértesy G., Bein M., Frigyes T., Mészáros Z., Gyulai J., Biró L. P.: The role of defects in chemical sensing properties of carbon nanotube films, **Applied Physics A** 93(2), 495-504, (2008)