Fabrication and investigation of biological and bioinspired photonic nanoarchitecture based vapor/gas sensors

OTKA K 115724

– final report –

Generals and facility improvements

During the whole time of the project we performed general tasks covering the management of the newly included specimens. For the exemplars stored at the Nanostructures Department we executed preparative activities: correct taxonomic identification of the new butterfly samples of certain specimens, photo-documentation by optical imaging and optical, scanning and transmission electron microscope investigations of the wing surfaces, sample preparations for the previous techniques. As our samples are mostly colored by photonic nanoarchitectures the optical spectroscopy characterization of wings by different techniques was done.

The obtained financial support together with other resources was used to extend the instrumentation facilities. The most important is the update of spectral measurement devices. A new high sensitivity and high resolution spectrophotometer, AvaSpec-HERO was purchased and installed. The installed UV/VIS/NIR grating covers the spectrum required for our measurements on photonic nanostructures. As a very important option, with the slit-kit there is the possibility to change the opening slit size, in this way matching the sensitivity and the resolution in the best way to the application, e.g. gold nanoparticles [1].

A new computer-controlled power supply was purchased with high output current suitable to be used as Peltier element driver. This is needed to maintain the precise temperature control of the sensing element during measurements. It was completed by writing a LabView application to control the Peltier element (the samples are directly attached to it) in the gas measuring cell to keep a constant temperature even when the gas flow rate is changed. This is achieved by a special thin thermocouple, using its amplified signal as a PID controller input.

An “artificial sun” light source was installed and tested. As the spectral distribution of the emitted light is broad enough and of high intensity, we plan to perform long time irradiation experiments on butterfly wings to investigate the changes occurring in the nanostructure integrity and the pigmentation of the wings. Both factors determine the visible color, and with this the sensing properties.

An XY stage with motorized driver was purchased and installed. Using this, in combination with the Avantes bifurcated perpendicular fiber optic probe, automated optical multispectral mapping is possible on flat surfaces. It was implemented the software control of the scan and the spectral data acquisition in LabView. Obtaining a large number of reflected spectra is important in the investigation of the wing scale variability, impossible to carry out manually on thousands of sampling points. Using these results and other several optical spectroscopy measurement methods we demonstrated on the species *Polyommatus bellargus* as a test case how different techniques support and extend each other [2]. This kind of approach promotes the understanding the complex optical behavior of biological or artificial surfaces structured at multiple size levels.

Vapor sensitivity measurements

We showed that the conformal modification of the scale surface by atomic layer deposition and by organic volatile pretreatment can significantly alter the optical response and chemical selectivity [3], which points the way to the efficient production of sensor arrays of different butterfly wings in parallel to "fingerprint" a certain volatile. This is a cheap way of altering the surface properties, at the same time, this procedure can be easily scaled up for practical applications. After the vapor-sensing measurements, the ethanol pretreatment provided the most significant results–more than doubling the maximal spectral response–while the chemical selectivity increased at lower vapor concentrations (<50%) and remained almost unchanged at higher (>50%) concentrations. The treatment of the wings resulted in the functionalization of the epicuticle layer covering the photonic nanoarchitecture, which has become sensitized that way. The marked differences found between the increase in selectivity and sensitivity after soaking in ethanol and the loss of selectivity due to soaking in chloroform and isopropanol clearly indicate that careful choosing of the soaking liquid offers a wide range of tuning options for the optical response of butterfly wings. The reduced spectral response measured on ALD coated samples convincingly shows that not only the structure of the nanoarchitecture is relevant, but the chemical composition of the material from which the nanocomposite is built is also important. Most of the chemical selectivity arises from the characteristic chemical interaction of chitin with the condensed volatiles, namely the swelling of the chitin nanoarchitecture which was eliminated by applying the ALD coating.

Comparative gas sensing measurements on the blue and greenish wing sides of *Albulina metallica* butterfly species were carried out. Both wing sides are colored by similar type photonic nanoarchitectures (pepper-pot type), but the structural parameters differ, this is also the reason of the difference in coloration. Based on our earlier experience in executing vapor sensing experiments we used a well-defined protocol to register the wing color variations while applying 10 different volatiles in 10 concentration steps from 0 to 50%. The sample temperature was kept constant by a Peltier element-based thermostat built in the sensing cell for this special purpose. To check for the reproducibility of the data, the measurements were performed two times on each wing surface. The whole experiment was repeated two times by two operetors disassembling the measurement setup between the measurement cycles to avoid systematic errors. These experiments resulted in a large amount of raw data the easiest way to represent is the plot of most significant components of a PCA [4]. On the two sides (dorsal blue and ventral gold-green) of the wing we obtained qualitatively similar results. Using artificially stacked several layers of dorsal wing scales in transmittance setup under an optical microscope, we demonstrated for the first time that the magnitude of the sensing signal can be increased. This is important as the thickness of these scales barely exceeds one micrometer.

We carried out measurements investigating the effect of mixed volatiles on the vapor sensing signal using wings with different type of nanoarchitectures [5]. With the installed mass flow controllers we have the possibility to manage the computer controlled mixing of two vapors in different concentration to the carrier air. Five different butterfly species were investigated with mixtures of ethanol, water, isopropanol and acetone vapors at different concentration. Processing the whole set of reflectance spectra with principal component analysis shows improved results, enhancing the selectivity and the sensitivity characteristics. It was found that optical responses of the mixtures are the linear combination of the optical responses of the pure solvents, showing that the biological photonic nanoarchitecture-based sensor materials can differentiate between vapor mixtures, as the optical response was found to be characteristic for each of them. Also, the influence of the order of exposure upon the wings was shown, a "memory effect" attributed to different volatilities.

For real applications it is important to develop sensors that can work in atmospheric humidity similar to our everyday living and working conditions, can endure repeated vapor exposures, and can be used for real-time analysis while remaining sensitive and chemically selective. Earlier exposure times in order of seconds were tested, now we performed long time measurements in the presence of water vapors to explore the differences from mixtures of the inert atmosphere and one pure vapor setup [6]. Selective signals similarly to the measurements without water vapors were obtained. Also, to test the durability and repeatability, it was found that a long (50 min.) series of short vapor pulses resulted in similar optical responses, and after a long exposure the wings preserved their initial sensing properties [6].

Computer simulations

To be able to exploit the possibilities of these photonic nanoarchitectures the modeling of the complex physical-chemical process involved in the vapor sensing by photonic nanoarchitectures is very important. We built a parametric simulation model for the *Albulina metallica* butterfly wings that matched the measured spectra. The reflectance spectra were calculated by ab-initio methods by assuming different amounts of condensed liquid in the air voids, as well as vapor concentration-dependent swelling of the chitin. We found similar swelling on both side of the wing surfaces, but more liquid was found to concentrate in the smaller air voids for each vapor concentration value measured [7].

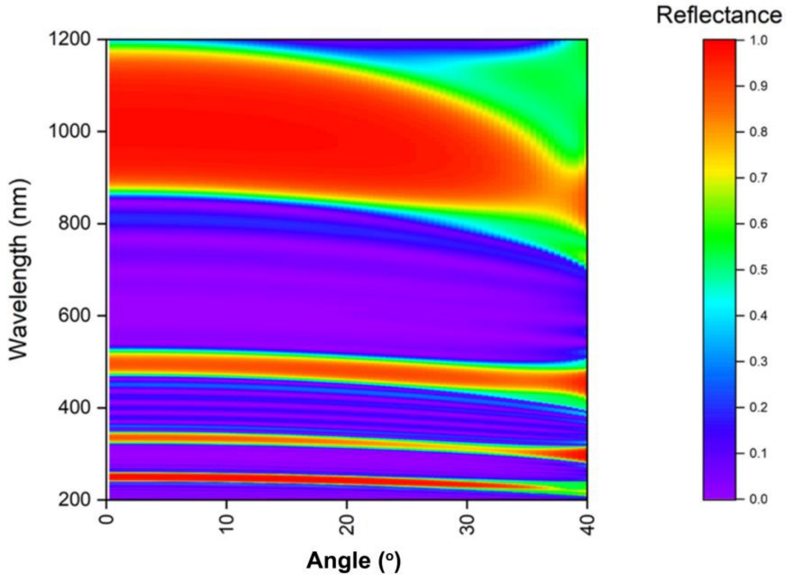
In the formation of reflectance on ordered submicron structures we created a model taking into account the second order scattering. Our simulations showed that different scattering processes determine the spectrum in different wavelength ranges. For large wavelengths (>350 nm) the optical reflection can be well described by a corresponding effective multilayer model and the peak positions are well represented by a simple first Born approximation. In order to correctly reproduce the small wavelength side of the spectrum (<350 nm) one has to include second order scattering processes [8]. This means that the shape of the air voids inside the layers determine the small wavelength spectrum. These calculations on perfect lattices are premise for the model on a real photonic crystal on butterfly wing scales with a certain degree of disorder.

Modification of biological and inorganic samples

We performed experiments in modification of wings by means of oxygen plasma treatment and atomic layer deposition. Chemical surface properties play a significant role in the vapor sensing selectivity. In its original state the butterfly wings are superhydrophobic, according to the external skin layer and the submicron size structure. By changing these properties we expect sensor material with different properties, in this way extending the possibilities for sample "library" in sensing experiments. Controlled modifications were performed on photonic nanoarchitectures of structurally colored butterfly wings: of biological origin, built mainly from chitinous materials; and of bioinspired samples fabricated using the Langmuir-Blodgett method from silica spheres. Two distinct methods were used, thinning by oxygen plasma treatment and thickening by ALD, to obtain a series of optically modified sample sets. We found that by carefully applying the plasma treatment it is possible to reduce in a controlled way the dimensions of the photonic nanoarchitecture, which was associated with a corresponding shift of the spectral position of the reflectance maximum. And by ALD deposition of Al_2O_3 layer we were able to increase the dimensions of the photonic nanoarchitectures, which was associated with a red-shift of the reflectance maximum. These two structural modification methods offer fine and controllable shifting of the reflected light spectrum [9]. The principles and instrumentation of the two methods are completely different, they are complementary in term of spectral modification they produce. In terms of surface chemistry, one builds up the substrate with a conformal, chemically inert coating, and the other removes the original superhydrophobic superficial layer. These modifications open new routes to potential applications.

Forthcoming results

Due to the epidemic that lasted longer than was imagined, the experimental work remained in the background, we advanced rather with theoretical aspects. To calculate the reflected light intensities from the surface of a multilayer structure, we developed the extension of an earlier built software based on the transfer matrix method. It can be easily parameterized, and in this way highly exceeds in throughput the manual work demanding single data set introduction – single spectrum calculation process. The former can be very time-consuming when dealing with multiple variables. Thus, the natural variability of the biological samples can be more easily approached with a theoretical background. As an example, the following figure is the result of a computation in which the two variables are the wavelengths of the reflected light, the other is the incidence / reflected angle. It is possible to perform similar batch calculations according to several variables automatically, which speeds up searching the structure-color relation and understanding changes during vapor exposure. The results will be published later.



Intensity of the reflected light of different wavelengths in function of the incident/reflected angle. The structure consist of 7 pairs of 200 nm thin films (air and refractive index = 1.5). Angular resolution: 0.5°, wavelength resolution: 1 nm.

During the extended period of the proposal, the performed experimental work turned towards miniaturization. Since wings with a homogeneous surface structure are typically used for sensing, a small area of them is also suitable for sensing, as we have shown earlier, whether a single detached wing scale is used individual or layered on top of each other [4]. Thus, the following work will be focused firstly on eliminating the optical microscope to measure the spectrum while using the approx. 70*150 micron scales with the help of fiberglass. On the other hand, to replace the light source and the spectrometer with small semiconductor devices. The preparation of the amplifier with the right sensitivity was done, I performed preliminary tests but the results are not yet to be published.

Effect in education

During the whole period of the support, in total five inland and Transylvanian undergraduate students attended to the summer school of the Institute of Technical Physics and Materials Science working on the basics of natural structural colors investigation.

Gábor Piszter working on this topic since 2009, performed relevant experimental work, obtained MFA Youth Price 2017, and scholarship of ÚNKP-17-3-IV New National Excellence Program of the Ministry of Human Capacities. In 2018 he obtained PhD degree at the Budapest University of

Technology and Economics. One chapter in his thesis was the investigation of gas sensing properties on butterfly wings.

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