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Temperature and saturation dependence in the vapor sensing of butterfly wing scales

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ABSTRACT

The sensing of gasses/vapors in the ambient air is the focus of attention due to the need to monitor our everyday environment. Photonic crystals are sensing materials of the future because of their strong light-manipulating properties. Natural photonic structures are well-suited materials for testing detection principles because they are significantly cheaper than artificial photonic structures and are available in larger sizes. Additionally, natural photonic structures may provide new ideas for developing novel artificial photonic nanoarchitectures with improved properties. In the present paper, we discuss the effects arising from the sensor temperature and the vapor concentration in air during measurements with a photonic crystal-type optical gas sensor. Our results shed light on the sources of discrepancy between simulated and experimental sensing behaviors of photonic crystal-type structures. Through capillary condensation, the vapors will condensate to a liquid state inside the nanocavities. Due to the temperature and radius of curvature dependence of capillary condensation, the measured signals are affected by the sensor temperature as well as by the presence of a nanocavity size distribution. The sensing materials used are natural photonic nanoarchitectures present in the wing scales of blue butterflies.

1. Introduction

Photonic crystals are periodic dielectric nanocomposites capable of interacting with electromagnetic (EM) radiation in a spectrally selective manner [1]. These materials are constructed from two non-absorbing media that possess different refractive indices, and the sizes of the building elements are comparable with the wavelength of the EM radiation for which propagation is forbidden in the nanoarchitecture. Certain frequency ranges cannot propagate inside the structure; they are fully reflected from the surface. This wavelength range is called the photonic band gap (PBG), and the reflected color is called structural color because it is based on the properties of the nanocomposite.

A particularly rich variety of such structural colors can be found in the insect world; many butterflies and beetles show exciting colorations originating from photonic nanoarchitectures [2–4]. In the case of butterflies, the photonic nanoarchitecture responsible for the color is usually located in the wing scales. In the scales, the nanocomposite is constituted mainly from chitin and air, and the nanocomposite may contain a vast variety of different nanoarchitectures. These nanoarchitectures result in a rich variety of colorations that can be used for various communication purposes. Butterflies may use their structural color for sexual communication [5], for cryptic behavior [6] and for warning potential predators [7]. Because the color influences the survival and reproduction chances, it is governed by strong evolutionary pressures developed over millions of years. One can attempt to use this “natural” wisdom that has accumulated over the course of many millennia for potential human applications.

In common gas/vapor sensors, nanostructured materials are often used to increase the specific surface area, but the sensing mechanism is usually based on electric resistance measurements on oxide layers [8]. However, there is a special group among chemical sensors based on artificial photonic crystal structures in which changes in the dielectric constant are detected by the PBG shift effect [9]. As discussed above, natural and bioinspired nanostructures could act as efficient light-tailoring devices. Beyond altering the propagation of light, nanostructures may also change the surface wetting properties [10]. The color change of the butterfly wing as a valuable source of photonic crystal-based sensors was shown for the first time in *Morpho*-type structures [11]. Later, we showed that in the case of Polyommatini butterfly-based sensors, different spectral signals appear for different vapors; therefore, they can be used as a chemical-selective sensor material [12]. Recently, we investigated the relation between the color and the PBG-type structures of nine closely related lycaenid butterfly species, all of which display a structural blue color in their dorsal wing

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surfaces [13]. The Hungarian Polyommatini fauna contains more than 30 species; therefore, we have a ready-made good-quality sensor material, which is a considerable advantage over artificial structures in which the reproducible construction of appropriate macroscopic samples is a slow and expensive process. Moreover, the sample preparation is simple because it only involves the cutting of a wing piece to the desired size. Additionally, these nanoarchitectures are produced in an environmentally friendly manner; if the butterflies are bred under laboratory conditions, the use of their wings does not harm the natural richness of the environment.

In our earlier work [14], we compared the optical sensing properties of the scale-covered dorsal wing surfaces of Polyommatini butterfly species using optical spectrophotometry, and the species with the highest relative spectral change were selected. Furthermore, we investigated the temperature dependence of the relative spectral change and showed that lower temperatures increase the shift of the spectral position, which enhances the spectral response signal [15]. The explanation of the spectral change mechanism when butterfly wings colored by PBG-type materials are exposed to air with vapors of different volatiles concerns the capillary condensation of the different vapors inside the chitin-air nanocomposite [15]. The distribution of pores with small curvatures in the nanostructure (Fig. 1.a) promotes the formation of the ink-bottle effect [16], which results in hysteresis in the condensation of the vapors, whereas lower temperatures enhance the magnitude of the spectral changes. The condensation inside the pepper-pot structure is similar to the condensation in a colloid silica-sphere multilayer [17]. In this paper, a red shift of the reflectance peak similar to that of butterfly wings was reported.

In real sensors operating in an ambient air environment, the changes in temperature (the diurnal or yearly cycle) cannot be completely separated from the changes in vapor concentration. Therefore, it is worthwhile to investigate the possible cross effects that may arise from the temperature and concentration changes, such as:

- The constant concentration gas flow with changing sample temperature
- Testing the effect of the continuously changing vapor concentration on the reflectance measured at a constant temperature

2. Experimental

The Polyommatini and Morpho specimens were provided by the curated collection of the Hungarian Natural History Museum.

We worked with butterflies collected from 1900 to the present. The wing is composed of a dry material made of chitin with a complex structure. The photonic crystal-type structure located in the wing scale defines the wing color, and this is a constant species-characteristic value: identical reflectance spectra can be measured from a wing that is 100 years old and from a modern wing. When used as a gas detector, a bottleneck can be the contact with chemicals that damage the chitinous nanostructure. However, all the specimens we have currently used fully recovered after exposure to vapors of various volatiles.

To obtain insight into the nanostructures, detailed scanning (SEM) and cross-section transmission (TEM) electron microscopy images were taken. To avoid charge buildup during the SEM observations, 15 nm of sputtered gold was deposited onto butterfly wings mounted on conducting carbon tape. For TEM sample preparation, wing pieces measuring a few millimeters were embedded in a resin, and 70 nm thick sections were cut using an ultramicrotome. These slices were placed on a copper TEM grid. The vapor-sensing experiments were conducted using computer-controlled gas/vapor-mixing equipment and an airproof gas cell. The mixing equipment consists of two digital mass flow controllers (Aalborg) that provide a constant gas flow output of 1000 ml/min. The vapor concentration was set by switching the flow controllers to allow synthetic air (Messer: 80% N_2, 20% O_2, others <20 ppm) and saturated volatile vapor pass in the required ratio. The prepared vapor mixture was placed into the aluminum, airproof gas cell with the butterfly wing. The cell has a quartz glass-slide cover to allow UV transmission.

Optical spectroscopy was performed using an Avantes HS 1024*122TEC fiber optic spectrophotometer. A UV/Vis/NIR light source was used to illuminate the sample. The incident light was perpendicular to the sample, and the reflected light was collected by an off-normal optical fiber that was oriented to an angle yielding a maximum signal reflected from the butterfly wing. To analyze the temporal-spectral dataset, a MATLAB code was implemented that allowed us to create 3D surfaces and colored maps. In addition, using the MATLAB code, we were able to create 2D line-cuts from the 3D datasets that describe the temporal evolution of the reflectance signal at a given wavelength.

To change the sample temperature, a miniature Peltier element was placed under the wing inside the gas cell. The current of the Peltier element was controlled by a NI DAC card and a Labview code.

Based on our earlier investigations [14], the *Polyommatus icarus* butterfly species was selected to examine the selectivity, thermal dependence and sensitivity as a gas-sensor material. We also examined *Morpho aega* wings because this species has a narrow and intense reflectance maximum and because their photonic crystal-type nanostructure is well described [18].

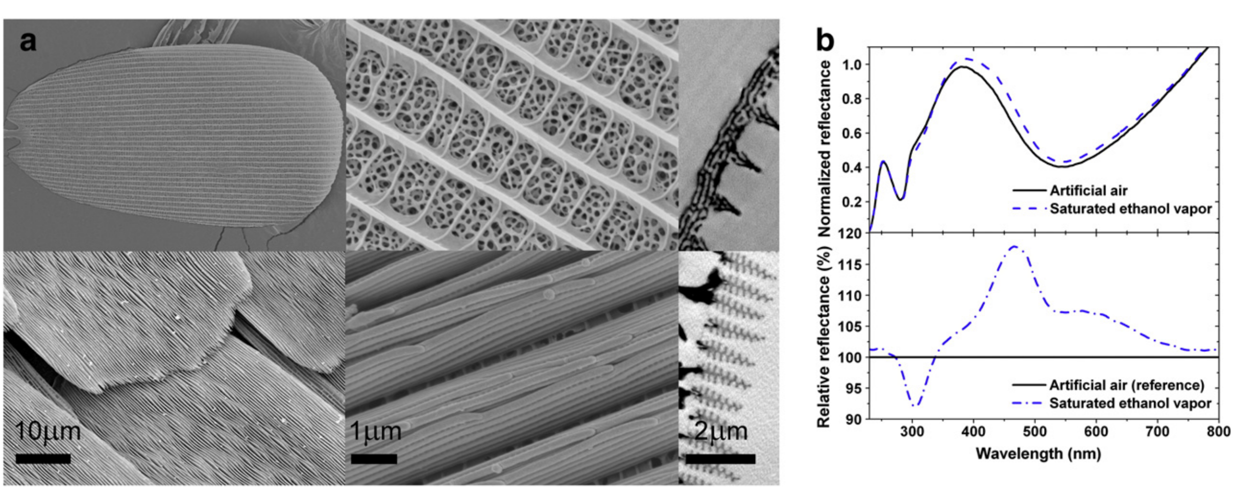

Fig. 1. a) Scanning and transmission electron micrographs of *P. icarus* (top) and *M. aega* (bottom) wing scales. b) Transforming the shift by recording the relative reflectance using the wing in artificial air as a reference (in (b) the lower panel).