Organic phosphor based fiber-optic sensor for detection of UV radiation

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Abstract. The paper presents a simple and low-cost fiber-optic sensor for detection of UV radiation. A sensor construction consists of a silica capillary with a photoactive composition based on an organic phosphor, organic solvent and epoxyacrylate inside and a multimode optical fiber in contact with each other. By adjusting the proportion of components in a photoactive composition, it is possible to obtain a pronounced optical signal at wavelength near 440 nm which is the luminescence emission wavelength of the chosen organic phosphor. The potential of using the construction as a UV sensor is confirmed by the linear dependence of the optical signal amplitude at the fiber output on the optical power supplied to the fiber input.

1. Introduction

Detection of ultraviolet (UV) radiation is a vital challenge in many spheres of anthropogenic activities because being uncontrolled it can be detrimental to human health and environment [1-5]. World Health Organization specifies the following parts of the UV radiation spectrum according to the impact on human health: UV-C (\(\lambda = 100-280\) nm), UV-B (\(\lambda = 280-315\) nm), and UV-A (\(\lambda = 315-400\) nm) [6]. UV-A radiation is harmful to eyes and skin even at low doses due to its deep penetration. UV-B light damages DNA and causes cancer. Natural UV-C radiation is totally absorbed by ozone in the upper layers of the atmosphere, but under extreme exposure from a laser source it destroys some groups of cells despite a small depth of penetration.

On the other hand, UV light also has positive effects. Particularly, UV-A radiation with moderate doses contributes to the formation of vitamin D in humans, facilitates metabolism, and has a therapeutic effect on skin [3, 4]. Using UV-C radiation, it is possible to disinfect air and water, sterilize objects, surfaces and medicines [2, 4, 7, 8].

Moreover, UV light is widely applied to solve technological and industrial problems. Thus, UV-C radiation assists in detection of electric discharge in the presence of strong electromagnetic interference in high voltage equipment and systems of signal intelligence [8]. UV-A radiation is useful in electrical equipment to measure gas parameters of corona discharge [3, 9]. UV radiation also operates in fire protection devices, control systems of flame processes, production of biodiesel, photolithography, technology of polymer coatings, and technology of laser sources [2, 4].

Detection of UV radiation with the use of fiber optic sensors (FOSs) has a number of advantages compared to other types of devices with analogous functionality, mainly thermoelectric [10]. FOSs are compact, lightweight, electrically safe, immune to electromagnetic interference, and provide an
accurate measurement of environmental parameters in a single point or along the whole fiber length.

In recent years, considerable attention is paid to the development of luminescent FOSs which convert UV light into visible one due to photoluminescence. Their benefits are fast response and high sensitivity [11]. There are at least 4-5 groups of such devices which incorporate optical fibers made of polymers with various optically active materials in a cladding or outside it [1, 2, 4, 5, 7, 8, 12, 13], phosphate glasses with rare earth metal ions [14, 15], multicomponent silicate, phosphate and borate glasses with molecular clusters [3], silica glasses and a cladding made of polymers or their modifications with organic dyes in a composition [16].

This work aimed to develop and study a prototype of a simple and low-cost luminescent capillary-type FOS for the UV-A radiation detection. The main idea was to use a combination of a photoactive composition which converts UV light into visible one and a silica optical fiber responsible for capturing and transferring of a spectrally converted optical signal inside a silica capillary.

2. Synthesis and characterization of the photoactive composition

Similar to the methodology described in [17], the photoactive composition was synthesized in two stages. As a first step, an organic phosphor 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole (Sigma Aldrich, mass concentration 98%) and an organic solvent dimethylformamide (EKOS-1, mass concentration 99.9%) were stirred vigorously and exposed to the action of ultrasound waves at normal conditions until a homogeneous and low-viscous (10^3 Pa‧s) solution was formed. At a second step the solution was mixed with a polymer material based on epoxyacrylate DeSolite 3471-3-14 (Royal DSM) under identical conditions in order to provide the viscosity of the final three-component solution (Figure 1a) arising from the following reasons. First, a segment of a silica capillary, which constitutes the basic element of the FOS construction, should be filled in a uniform manner. Second, a silica optical fiber should be rigidly fixed in the solution for subsequent UV curing.

The main criterion in the choice of a components ratio to synthesize the photoactive composition of the FOS was the condition to register bright visible emission of photoluminescence excited in the coating formed from the composition on a silica glass substrate (Figure 1b). Table 1 shows the characteristics of four synthesized solutions and coatings on their basis. In each case, curing of a solution was performed in the UV furnace under 0.4 J/cm^2 radiation dose during 30 seconds. Photoluminescence excitation and emission spectra were registered using a spectrophotometer LAMBDA 650 UV/Vis (PerkinElmer) and fluorescent/luminescent spectrometer LS-50B (PerkinElmer) respectively.

![Figure 1. Three-component solution based on 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole, dimethylformamide and epoxyacrylate used for the synthesis of the photoactive composition (a) and the photoactive composition UV cured on a silica glass substrate (b).](image-url)
Table 1. Weight of the components in the solutions used for the synthesis of the photoactive composition and luminescence properties of the coatings formed from these solutions.

| N | 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole | Weight, g | Photoluminescence emission of the coating in the visible part of the spectra |
|---|--------------------------------------|----------|--------------------------------------------------------------------------------|
| 1 | dimethylformamide                     | 0.03     | None                                                                          |
| 2 | epoxyacrylate                         | 10       | None                                                                          |
| 3 |                                      | 0.07     | Occurs at λ = 440 nm, the signal cannot be separated from the basic level      |
| 4 |                                      | 1        | Occurs at λ = 440 nm, the signal 5 times higher than the basic level           |

Figure 2 demonstrates photoluminescence excitation and emission spectra of the coating based on the photoactive composition synthesized from the solution 4 with a maximum weight of the organic phosphor. As can be seen from the curves, the measured photoluminescence excitation wavelength locates in the spectral range λ = 365-390 nm, while the photoluminescence emission wavelength falls into the spectral range λ = 425-440 nm. These data correlate with the corresponding bands of pyrazoline derivatives [18]. This fact confirms that noticeable structural conversions of the organic phosphor are absent while stirring the initial components and curing the synthesized solution.

Figure 2. Photoluminescence excitation (a) and emission (b) spectra of the coating based on the photoactive composition synthesized from the solution 4.

Further, the components ratio corresponding to the solution 4 was used to synthesize the photoactive composition for the FOS construction.

3. Construction of the sensor
The FOS prototype consisted of a horizontally oriented silica capillary with 0.8 mm inner diameter and 26 mm length, filled with the photoactive composition from the one end (Figure 3a). The capillary was filled by pumping the composition under pressure through a plastic pipe, hermetically connected to the capillary. The length of the filled capillary segment was about 10 mm. After filling, the pipe was
disconnected and the face end of the capillary was sealed by a cap made of the UV resistant plastic to prevent leakage of the composition during its curing. From the other capillary end a silica optical fiber 100 mm in length was inserted close to the photoactive composition. To provide correct operation, the protective polymer coating from the fiber end was removed and the end face was polished. In order to transfer the converted portion of radiation at wavelength $\lambda = 440$ nm the multimode fiber with a pure silica core and thin fluorosilicate cladding was used. The transmission of the fiber in the visible range exceeds 99% per meter. The core diameter and numerical aperture of the fiber were equal to 200 $\mu$m and 0.22 respectively. Such parameters enabled to simplify focusing of radiation from a xenon lamp on the fiber input end.

**Figure 3.** Scheme illustrating the FOS construction with a purple cone of radiation from a xenon lamp at the input (a) and the FOS view right after UV curing of the photoactive composition (b).

Following the contact of the photoactive composition and the optical fiber, the last one was moved towards the end face of the capillary (Figure 3a) with the use of a specially fabricated tool. The tool represented a system of six silica rods 0.26 mm in diameter fixed close to each other on the inner surface of a capillary identical to the basic one. The fiber with outer diameter 0.27 mm was placed in the center of the mentioned rods system, which automatically provided fiber centering relative to the axis of the FOS capillary. The requirement of positioning the fiber close to the end face of the capillary was caused by the necessity to reduce the optical path length – the distance radiation passes through the photoactive composition towards the fiber input end. Due to a relatively high absorbance of the photoactive composition, photoluminescence was excited in a small volume of the material.

Then the construction with the optical fiber rigidly fixed inside the capillary was subjected to the short-term (less than 10 seconds) exposure in the UV furnace under 0.5 J/cm$^2$ radiation dose. Subsequently, the preliminary installed cap was removed from the end face of the capillary and the centering tool was disconnected from the other one. The capillary once more was placed in the UV furnace for 30 seconds and extracted as the integrated element with the completely cured photoactive composition (Figure 3b).

**4. Results and discussion**

Figure 4 demonstrates the output end of the optical fiber in the process of the FOS operation. For clarity, two drops of the phosphor-free polymer material PC-3745AP (Fospia Efiron) were applied close to the fiber end that has been cleaned from the protective polymer coating and polished. The FOS was fixed in a mechanical 5-axis positioner in a way that radiation from a xenon lamp XBO 150 W/4 (OSRAM) was focused on the input end of the fiber after passing a monochromator MDR-23 (LOMO) and the capillary filled with the photoactive composition. The use of the 5-axis positioner allowed focusing UV radiation more precisely in order to provide visually intensive blue emission at the fiber output ($\lambda \sim 440$ nm). As can be seen from Figure 4a, the drop of the fluoroacrylate PC-3745AP transparent in the visible part of the spectra applied close to the fiber output became blue. This indicates that the optical signal at the FOS output has a relatively high intensity. The efforts to
focus UV radiation in the plane of the capillary end face or space between the capillary end face and the fiber input led to the absence of the optical signal at the FOS output.

Figure 4. Visualized spectral conversion of the UV-A radiation by the FOS fixed in a mechanical positioner under daylight (a) and in a semi-dark room (b). In Figure 4a: 1 – optical fiber end face, 2 – silica capillary.

To quantitatively confirm the visually registered effect of photoluminescence, spectral characteristic of optical signal at the FOS output was measured. The measurement was performed on the experimental setup described in [17]. The optical scheme was supplemented by an optical amplifier eLockIn 204 (Anfatec Instruments) and an optical power meter AQ-1135E (Ando Electric Corporation) connected with a silicon photodetector FPD510-FV (Menlo Systems). Figure 5a demonstrates the measured characteristic. Note that validity of photodetector indications was influenced by the extrinsic radiation. For that reason, the measurement was performed in a semi-dark room with a minimum noise level.

The character of the curve in Figure 5a indicates an increase of the optical signal at least on 3 dBm above the basic transmission level of the FOS near the photoluminescence emission wavelength excited in the phosphor-based photoactive composition. In the authors’ view, this fact confirms the conversion of $\lambda \approx 365$ nm radiation focused on the optical fiber input into $\lambda \approx 440$ nm radiation after passing the capillary segment filled with the photoactive composition. The absence of the optical signal in the wavelength range $\lambda < 400$ nm in the spectral characteristic is related to the sensitivity of the silicon photodetector functioning in the spectral range $\lambda = 400-900$ nm.

Figure 5. Measured spectral characteristic of the FOS transmission (a) and dependence of the FOS optical signal amplitude on the UV radiation power (b).
Experimentally, the FOS potential to be implemented as a UV-A radiation sensor was evaluated by measurement of the optical signal amplitude at wavelength of 440 nm with an increase of the UV radiation power at wavelength of 365 nm. For this purpose, the optical power meter in the optical scheme was replaced with a digital oscilloscope Infinium HP54830 (Agilent Technologies). As a result of experimental testing, it was revealed that dependence of the FOS optical signal amplitude on the UV radiation power has a linear character with a 98% approximation confidence interval (Figure 5b). Thus, based on the determined linear dependence it is possible not only to detect UV radiation in the environment but also to qualify changes of its relative power.

5. Conclusions
An experimental study of the luminescent sensor for the UV-A radiation detection was reported. The device comprised of a silica capillary partially filled with the organic phosphor 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole containing photoactive composition which contacted the silica multimode optical fiber. Functioning of the sensor was driven by the spectral conversion of the UV-A light (λ = 365 nm) delivered by the fiber to the phosphor-based photoactive composition. The results demonstrated the possibility to register an optical signal of the sensor at the photoluminescence emission wavelength of the phosphor λ = 440 nm by choosing a components ratio in the initial solution used for the synthesis of the photactive composition (1 g organic phosphor, 5 g organic solvent, 5 g epoxyacrylate) and conditions of the fiber input end excitation. The potential of the developed sensor to be used for the UV-A radiation detection was confirmed by the linear dependence of the optical signal amplitude at the sensor output on the UV radiation power. Among the benefits of the sensor there are an availability of raw materials and simplicity of fabrication, no need to change a construction of the fiber by partial removal of the cladding and/or deposition of coatings based on optically active materials, as well as an opportunity to function at considerably long distances far from sources of UV radiation.

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