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UV RADIATION DETECTION USING OPTICAL SENSOR BASED ON Eu^{3+} DOPED PMMA

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Abstract

Progress in UV treatment applications requires new compact and sensor constructions. In the paper a hybrid (organic-inorganic) rare-earth-based polymeric UV sensor construction is proposed. The efficient luminescence of poly(methyl) methacrylate (PMMA) matrix doped by europium was used for testing the optical sensor (optrode) construction. The europium complex assures effective luminescence in the visible range with well determined multi-peak spectrum emission enabling construction of the optrode. The fabricated UV optical fibre sensor was used for determination of Nd:YAG laser intensity measurements at the third harmonic (355 nm) in the radiation power range 5.0–34.0 mW. The multi-peak luminescence spectrum was used for optimization of the measurement formula. The composition of luminescent peak intensity enables to increase the slope of sensitivity up to –2.8 mW^{-1}. The obtained results and advantages of the optical fibre construction enable to apply it in numerous UV detection systems.

Keywords: ultraviolet radiation, UV, optical fibre sensor, lanthanides.

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1. Introduction

The World Health Organization defined the ultraviolet radiation as UV-C (100–280 nm), UV-B (280–315 nm) and UV-A (315–400 nm) ranges and indicated potential risks of uncontrolled exposition of the human body to it [1, 2]. In such circumstances, measurement of UV radiation intensity is an important issue that contributes to fast improvement of the detector technology [3, 4]. The essential influence of UV-B radiation on the human body is well known as it stimulates production of vitamin D and increases calcium and phosphorus assimilability. Additionally, some medical benefits can be also obtained by phototherapy of skin and other tissue diseases [5, 6]. The ultraviolet germicidal irradiation (UVGI, UV-C spectral range) is commonly used to neutralize bacteria and viruses by destroying nucleic acids and disrupting their DNA. This method can be applied in the air, water, and surface treatment [7]. It is also commonly used for scientific research (*e.g.* luminescence-based microscopy for biological and physical applications) and control systems: automatic fire protection, combustion monitoring, biodiesel production [9–12]. The ultraviolet radiation is also used as a chemical reactant (in polymerization, conformal coating technology, photolithography) and a quality inspection marker (*e.g.* in leak testing technology) [13–15]. Moreover, a significant advantage of UV-initiated polymerization is its high process efficiency which is an important parameter in the high-volume production. As a source of UV radiation there are often used Hg, Xe, ^2H lamps as they provide the high power radiation. Nowadays, new designs of UV sources, which offer well-defined radiation parameters (optical power, wavelength, FWHM and long lifetime), are based on semiconductor technology (LEDs and lasers) [16–17]. The sensing

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aspect, therefore, is crucial in numerous applications. There are several techniques of ultraviolet radiation intensity measurement. Although they can use thermal sensors, the band-gap semiconductor devices assure much better sensitivity. Unfortunately, their spectral response is non-uniform and typically falls in the visible or near-infrared spectrum. The well-known luminescence phenomena can be used to overcome this problem. The radiation conversion onto the required detector spectral range in polymeric matrices can be obtained by using organic dyes or lanthanides. The xanthene (*e.g.* Rhodamine, Cumarine) or polycyclic aromatic hydrocarbon (*e.g.* Perylene) are well known for their efficient luminescence but also undesired photo-bleaching effect [18–20]. The efficient luminescence emission of lanthanide ions at high intensity of excitation radiation was frequently reported [21, 22]. Incorporation of rare-earth ions gives an opportunity to use it as UV sensitive markers. The luminescence quantum yield of direct incorporated lanthanide ions in the polymeric host is low because of a narrow absorption band (corresponds to electron transition in the energy level scheme) but can be significantly improved by using organometallic complexes. Some of them (*e.g.* Eu^{3+}, Tb^{3+}, Tm^{3+}, Sm^{3+}, Dy^{3+}) assure luminescence in the visible spectrum range under UV excitation. A benefit of using organic ligand is its much wider absorption spectrum than that of rare-earth ions. The energy transfer of excited ligand antenna to lanthanide ion is used then to sensitize the rare-earth emission. The luminescence spectrum of lanthanides incorporated into an organic host is typically strongly limited to few main peaks because of phonon-mediated non-radiative decay which significantly deactivates the excited states. The polymeric optical fibre technology can be also applied in sensor technology since poly(methyl) methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), fluorinated (CYTOP) and deuterated (ZEONEX) polymers offer excellent optical properties and good processability [23, 24]. A novelty of this paper lies in fabrication of PMMA fibres doped with europium ions (preform polymerization and fibre drawing). The doping process resulted in transparent polymeric disks and fibres. The presented UV detection system uses luminescence of a polymethyl methacrylate host doped with a compound of trivalent europium (Eu^{3+}). The proposed sensor construction has been characterized by its luminescent properties including the spectrum shape and the excited state decay time. On this basis, a fibre optic head for detecting the ultraviolet radiation is proposed and characterized.

2. Materials and methods

The raw materials: Methyl Methacrylate (MMA), Benzoyl Peroxide (BP), Butanethiol (B) with > 99% purity were supplied by Sigma Aldrich. The europium complex was additionally treated to assure its effective embedding into the PMMA chain structure. The free radical polymerization process of poly-methyl methacrylate was used for fabrication of luminescent matrices. The polymerization process had been performed for 48 h at 60–80ºC. The used concentration of europium in the final matrix was 0.7% w/w. It was experimentally verified to obtain efficient luminescence. The PMMA rods (13 mm diameter) were cut into 2.0 mm thick discs. A fabricated sample under UV laser excitation is presented as an insertion in Fig. 1a. Additionally, one of the rods was drawn into the 2.5 mm diameter fibre. The refractive index (1.493) was measured using an optical refractometer (Metricon, 633 nm). The polymeric Eu-doped matrix was excited using a pulsed Nd:YAG laser (Continuum) at the third harmonic 355 nm. Additionally, the excited state lifetime measurements were performed. The spectra were recorded using a Stellarnet Green Wave spectrometer in the range of 400–900 nm (0.5 nm resolution). The obtained results are presented in Fig. 1.

The luminescence was measured at excitation wavelength 355 nm (Fig. 1a). The obtained spectrum exhibits strong emission peaks for energy transitions $^5D_0 \rightarrow {}^7F_1$ (582 nm), $^5D_0 \rightarrow {}^7F_2$ (616 nm) and $^5D_0 \rightarrow {}^7F_4$ (700 nm). The $^5D_0 \rightarrow {}^7F_2$ (616 nm) is dominant in the recorded

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spectrum. It is known as the hypersensitive transition as its intensity strongly depends on the local symmetry of the Eu^{3+} ions and used ligand properties (the peak ratio $^5D_0 \rightarrow {}^7F_2$ / $^5D_0 \rightarrow {}^7F_1$ equals to 4.1 at UV_{exc}=30 mW). The low-intensity transitions can be also noticed. The $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_5$ transitions are forbidden for europium chelate complexes by the selection rules (the $^5D_0 \rightarrow {}^7F_0$ is highly intense only in some β-diketonate europium complexes) [25]. The low-intensity $^5D_0 \rightarrow {}^7F_6$ transition is also rarely observed in europium complexes. A relatively long lifetime (0.569 ms, measured for the transition $^5D_0 \rightarrow {}^7F_2$) confirms efficient luminescent properties of europium chelate in the PMMA host. The deactivation process of excited states in the PMMA host is limited and confirms the ability of effective converting the UV radiation.

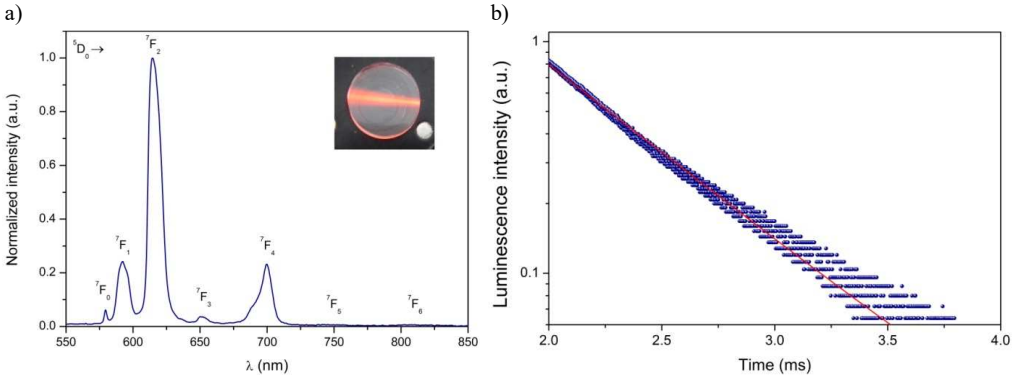

Fig. 1. a) The luminescence spectrum of PMMA doped with trivalent europium compounds at exc. 355 nm with observed transitions (all the transitions start from the $^5D_0$ state);
b) The luminescence decay time measurement results (at 616 nm).

3. Sensor head constructions

The sensor was fabricated using a 2.5 mm diameter PMMA/Eu^{3+} fibre (25 mm length) attached to a commercially available step index optical fibre 980/1000 μm made of PMMA in a fluorinated polymeric cladding (NA = 0.50). The sensor construction is presented in Fig. 2.

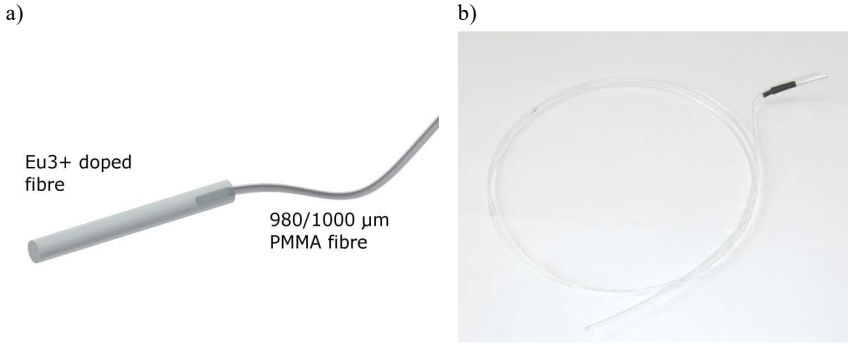

Fig. 2. The UV sensor optrode: a) construction, b) photo.

4. Measurements

A scheme of the measurement setup is presented in Fig. 3. An Nd:YAG laser (355 nm) was employed as the UV radiation source. The 5 Hz repetition rate was used during experiments

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and a build-in diaphragm was used for adjustment of the radiation intensity. To assure proper measurement conditions, the diameter of laser radiation spot was centered in the middle of sensing region and fitted into the sensor diameter. The measurements were done at 21°C temperature and the optrode was protected from ambient light. The emission spectra were measured at the end of fibre using a Stellarnet Green Wave spectrometer which offers a 16-bit digital signal resolution. The reference UV radiation power was measured using a Thorlabs PM-100 optical power meter equipped with a thermal detector.

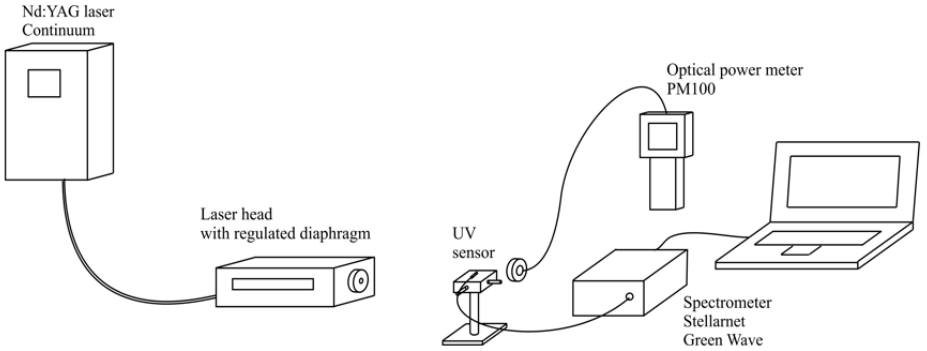

Fig. 3. A scheme of the measurement setup.

The recorded spectra are presented in Fig. 4a. The experiments confirm that the UV radiation can be measured in the range from 5.0 to 34.0 mW. The lower and upper UV limits are caused by a low signal intensity at $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_4$ transitions. The maximum level was limited by the laser power, since no saturation of luminescence signal has been observed.

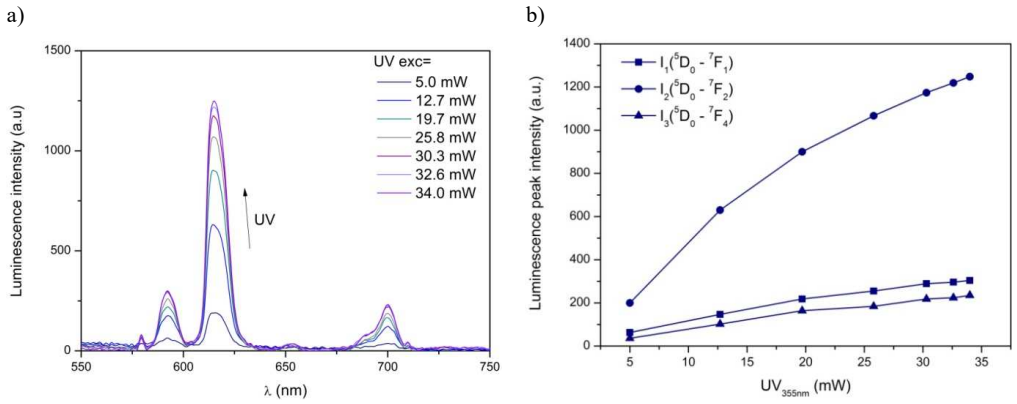

Fig. 4. a) The luminescence spectrum obtained for the sensor type A at exc. 355 nm;
b) The maximum peak for the main emission transitions.

The main aim of experiments was to determine the dependency on the UV power. The obtained characteristic (maximum of peaks for emission transitions) is presented in Fig. 4b. A well-defined shape of the emission enables to eliminate the ambient light disturbance that can be detected in low luminescence signal wavelengths. A common way in intensity-based optical fibre sensors is determination of the maximum intensity change. Unfortunately, the accuracy and repeatability of measurements strongly depend on undesired signal changes in the optical system (*e.g.* attenuation or bending losses in the optical fibre). The advantages of using

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them are their low cost and easy-to-install equipment. The sensor sensitivity can be calculated using the equation:

$$S = \frac{dI}{dUV}, \tag{1}$$

where I is the peak intensity and UV is the ultraviolet radiation power. The experiments showed that the fabricated optrode exhibits a high slope of the maximum luminescence peak for ($^5D_0 \rightarrow {}^7F_2$) vs. UV intensity (Fig. 4b). A multi-peak spectral luminescence shape of europium can be used for optimization of the measurement procedure. One possibility is using a combination of intensities of main luminescence peaks ($I_1 + I_2 + I_3$) to increase the sensitivity in comparison with that calculated for a single dominant luminescence peak (I_2). The slopes of sensitivity for linear fitting are equal to –2.3 mW^{-1} (Ra = 0.94) and –2.8 mW^{-1} (Ra = 0.92) for I_2 and I_1+I_2+I_3 intensity additive methods, respectively (Fig. 5).

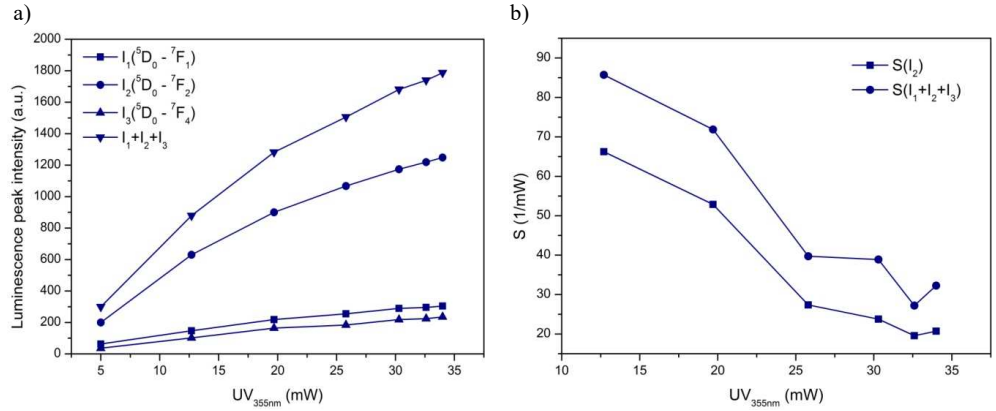

Fig. 5. a) The maximum peak intensity for sensor A at exc. 355 nm; b) the calculated sensitivity.

The efficiency of emission transitions and their dependence on the UV excitation can be used for increasing the measurement repeatability. Fig. 6 shows the $^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_4$ intensity ratio. It is noticeable that the ratio assures the linear dependence (slope 0.070 mW^{-1}, Ra = 0.998) in the UV range of 5.0–20.0 mW. The calculated sensitivity plot is presented in Fig. 6b. An additional advantage of using this method is immunity of measurements to changes of the optical signal losses in the optical fibre. Those properties significantly improve the repeatability of measurements.

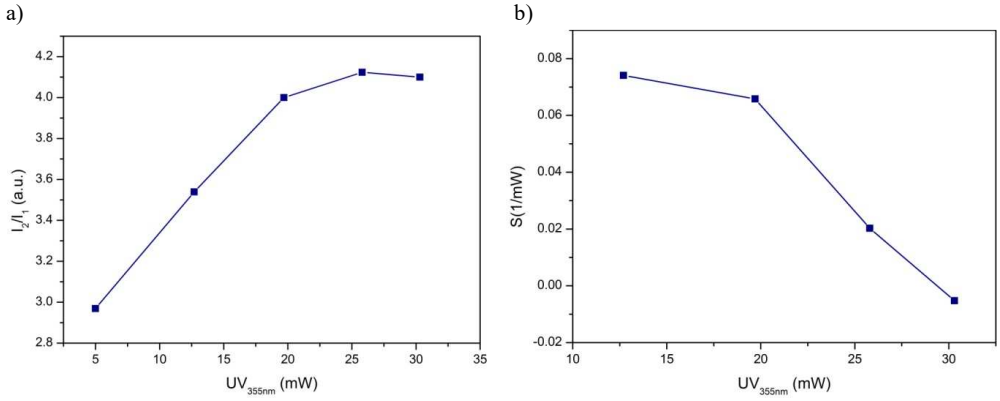

Fig. 6. The intensity ratio method: a) $^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_4$ intensity ratio; b) sensitivity plot.

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Determination of the UV power based on luminescent properties of europium ions incorporated in the PMMA matrix enables to modify the measurement procedure. The different phenomena can be applied to improve both sensitivity and repeatability. The proposed sensor construction was calibrated using a 355 nm radiation source. Therefore, the sensor can be used as a calibrated single-wavelength radiometer in the UV-A range after its calibration in the required spectral range. The advantages of the fabricated sensor, such as its UV sensitivity, high environmental compatibility, small size/weight and galvanic isolation enables to use it in numerous applications for monitoring the UV radiation.

5. Summary

A hybrid construction of a polymeric UV sensor based on the organic-inorganic europium complex was presented. The efficient luminescence of europium in the PMMA host was characterized using a 355 nm excitation source. The measured relatively long excitation state decay time 0.57 μs confirms a low deactivation of the excited state by non-radiative processes and the possibility of efficient UV conversion. The used lanthanide complex assures a high luminescence signal in the visible range with a well-determined spectrum shape according to luminescence of europium ions. The intensity-based measurement of UV radiation (in the range of 5.0–34.0 mW) using different measurement procedures was presented. The advantages of using a combination of the intensity (improvement of the sensitivity up to $-2.8\ mW^{-1}$) and the peak ratio (immunity to changes of signal losses) were shown. The obtained results prove the capability of using the presented sensor in a wide range of applications.

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