Ratiometric optical laser power sensor based on polymer luminescent nanocomposite

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Abstract—The fabrication of nanocomposite photonic materials suggests their use in a wide variety of applications. An essential requirement for such materials is their photostability and high photobleaching resistance. Both lanthanides and quantum dots are good candidates for embedding in the polymer matrix to obtain highly luminescent nanocomposites. This paper presents the concept for the ratiometric optical pulsed laser power sensor based on terbium and red-emitting semiconductor quantum dots co-doped polymer luminescent nanocomposite for application in inexpensive laser monitoring systems.

Composite optical materials based on lanthanides (Ln(III)) and semiconductor quantum dots (QD) play an essential role in numerous areas of research. Among others, the development of optical imaging systems, optical sensors, optical switches, and detectors [1‒2], light conversion devices [3], and fabrication of multifunctional materials [4]. Both Ln(III) and QD have their own unique optical properties that make them very useful in co-doped materials. Ln(III) are characterized by: 1) very low specific absorption and, therefore, weak external sensitivity, which can be improved by the appropriate selection of ligands, 2) long excited-state lifetimes up to milliseconds, and 3) emission spectra presented by several narrow bands specific for the emitting ion [5‒6]. QD specifics are: 1) broad absorption spectra with extremely high extinction coefficients, 2) narrow emission bands that can be tuned by varying QD size, shape, and/or composition, and 3) lifetimes of tens of nanoseconds [5‒6]. At the same time, both Ln(III) and QD absorb in the UV range and are photostable and highly resistant to photobleaching.

The Ln(III) and QD embedded into the polymer matrix may be recognized as two simultaneously excited interacting emitters, and their specific emission bands can be clearly distinguished. This opens the possibility of fabricating optical sensors based on the wavelength ratiometry approach. The wavelength ratiometry methods use the concurrently occurring bright luminescence intensity ratio between dual emissions with different behaviors [7]. When using the single-channel luminescence recording, the errors and artifacts may originate from the physical and chemical probe properties, distribution of dopants in the probe, quality of excitation, and measuring systems. The wavelength ratiometry allows the elimination of the mentioned problems, providing more reliable data for measurements [8]. The ratiometric approach's strong advantage is its relatively high resistance to environmental interference [9].

Laser radiation power and energy are usually measured using a photodiode, pyroelectric, or thermal detector. These methods transform incident radiation into measurable physical quantities (current, voltage, or temperature) for measurements [10]. The main goal of the work is to develop the ratiometric optical laser power sensor based on polymer luminescent nanocomposite for application in inexpensive laser monitoring systems.

The co-doped composite optical materials were synthesized by a free radical polymerization method using monomer methyl methacrylate and benzoyl peroxide for the polymer matrixes with terbium(III)-tris(2,2,6,6-tetramethyl-3,5-heptanedionato) (Tb(III)) and CdSe/ZnS core-shell type quantum dots as dopants. All the reagents were characterized by high purity (99%) and supplied by Sigma-Aldrich. The probes' fabrication process in detail was presented in the previous work [11]. Broadly tunable pulsed DPSS Laser NT230 (Ekspla, Lithuania) operated at 100 Hz with pulse duration ~2.6 ns was used as the excitation source at 350 nm with pulse energy ~20μJ; the laser beam was focused on the sample using the reflective objective of an inverted confocal microscope Olympus IX73 (Tokyo, Japan). The steady-state emission spectra were recorded using the setup described in [11]. The average pulsed laser power was measured by Thorlabs power meter equipped with the S120VC standard photodiode power sensor characterized by ±5% measurement uncertainty in the UV range.

Three nanocomposite samples were prepared with a constant Tb(III) concentration of 22.2 mmol/L while the QD concentration varied between 0.106, 0.212, and 0.425 μmol/L. Thus, the ratios QD/Tb(III) [$\times 10^{-6}$] were 4.78, 9.56, and 19.13 for samples 1–3. The fabricated specimens were 4.0 mm thick rod discs (Fig. 1) with no visible polymerization defects and a uniform dopant distribution.

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Fig. 1. Fabricated nanocomposite probes sample 1 (left) and sample 3 (right) under exposition to UV LED (365 nm).

The steady-state emission spectra of the Tb(III)-doped and QD-doped PMMA samples (Fig. 2) are in good accordance with those presented in the literature for both dopants [12−13]. The luminescence bands of the Tb(III) and QD co-doped PMMA samples do not show any shifts for the samples under study. The emission bands at 547 nm for Tb(III) and 606 nm for QD are pretty well separated and selected as the reporter-reference pair excited at the same laser wavelength.

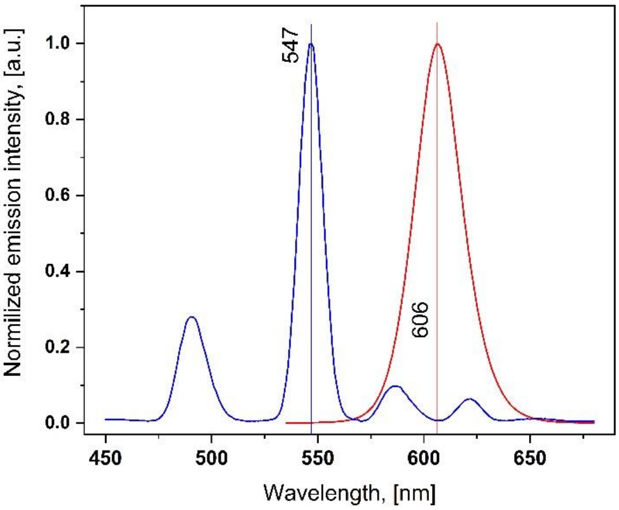

Fig. 2. Normalized emission (excitation 350 nm) of Tb(III)-doped and QD-doped PMMA sample 3.

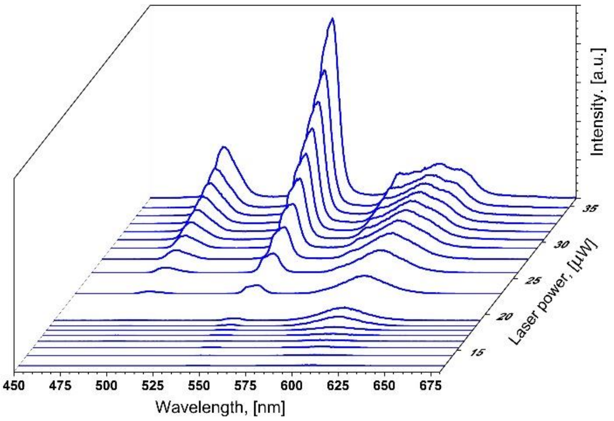

Fig. 3. The emission spectra evolution of sample 3 versus the power of the exciting laser radiation (350 nm).

Figure 3 shows the evolution of the composite sample 3 emission spectra with excitation power change in the 11–36 µW range. Similar evolution behavior may be observed for samples 1 and 2 (not presented). The spectra clearly demonstrate a significant emission intensity increase for both Tb(III) and QD dopants with increasing laser excitation power. However, the dynamics of the observed changes differ significantly. Saturation is noticeable in the emission of QD, starting from about 18 µW, while the emission of Tb(III) steadily increases. At the lower exciting powers, the emission of QD dominates, but after QD signal saturation at higher powers, the Tb(III) signal dominates.

The QD signal would serve as the reference, so the intensities ratio was calculated in two ways:

a) intensities at peaks $R_A = \frac{I_{547}}{I_{606}}$ and integral intensities,

b) $R_B = \frac{I_{\Delta 547}}{I_{\Delta 606}} = \frac{\int_{545nm}^{549nm} I_{Tb}(\lambda)d\lambda}{\int_{604nm}^{608nm} I_{QD}(\lambda)d\lambda}$.

Figure 4 presents the results for both ratios for sample 3 (with the highest QD concentration) as a function of excitation power.

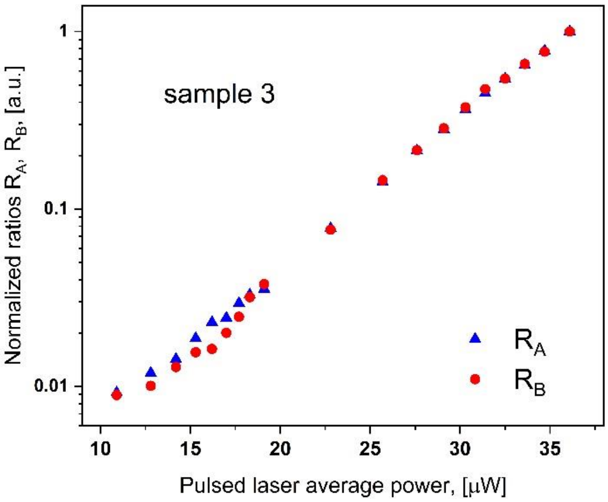

Fig. 4. Ratios dependencies versus excitation laser power.

An excellent agreement between both dependences can be observed at laser radiation power of 18 µW and higher up to 36 µW. In this case, the emission of QD is close to their saturation signal. This means that the nanocomposite allows for similarly effective intensity measurements both integrally near the band maxima and at the peak of the emission bands. Similar dependencies are observed for samples 1 and 2 (not presented).

Exponential functions fit the intensity ratio's dependence on the higher laser power. This allows us to plot the specified dependencies on a logarithmic scale, as shown in Fig. 5. A linear fit ($R^2 = 0.99$) can be observed for all three samples, which means the logarithm of the intensities ratio is a linear function of power.

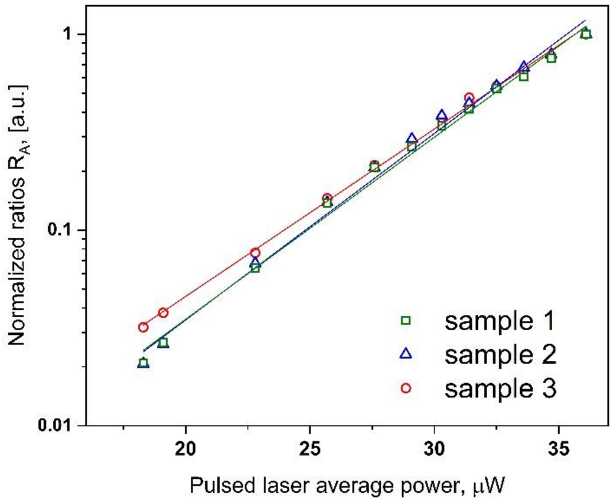

Fig. 5. A linear fit of the logarithm of the intensities ratio as a function of laser power.

Based on the obtained dependences and providing calibration, co-doped Tb(tmhd)$_3$-CdSe/ZnS quantum dots-PMMA nanocomposites can be used as a sensor for the power of pulsed exciting laser radiation. The selection of dopant concentrations can also optimize the sensing material and, consequently, expand the power measurement range depending on the requirements of a specific application. The perspective of the fiber-integrated sensor device fabrication opens even more possibilities for using the proposed sensor.

In summary, this work presents a concept for a ratiometric pulsed laser power sensor based on polymer nanocomposites co-doped with Tb(III) and QD. The proposed sensor's advantage is noticeable photostability and high resistance to photobleaching. It can be used in inexpensive laser monitoring systems.

The capability of the effective energy transfer (FRET) between Tb(III) and QD was reported earlier [11], making the fabricated composite a multifunctional material.

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