# FEATURES OF THE FLUORESCENCE SPECTRA OF RHODAMINE 6G DYE IN THE NANOPOROUS STRUCTURE OF SYNTHETIC OPALS

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**The influence of the photonic-crystal structure of synthetic opal on the fluorescence spectrum of the laser dye Rhodamine 6G is investigated. Suppression of fluorescence in the stop-band region and a blue shift of the spectrum are observed.**

**Keywords:** photonic crystal, synthetic opal, stop band, laser dye Rhodamine 6G.

Received 04.11.2025; Received in revised form 03.12.2025; Accepted 10.12.2025

## 1. Introduction

Photonic crystals are a promising class of optical materials characterized by a three-dimensional periodic modulation of the dielectric permittivity with a period comparable to the wavelengths of light in the visible and near-infrared spectral ranges. The concept of photonic crystals independently introduced by Eli Yablonovitch [1] and John Sajeev [2] in 1987 contemplates that they enable control of spontaneous emission due to the presence of a photonic band gap (stop band), i.e., a frequency range, in which photons cannot propagate in a certain direction. This opens opportunities for a wide range of such material applications in optoelectronics and optoinformatics. Therefore, the fabrication and measurement of the spectra of luminescent photonic crystals are important research directions. In several studies, in particular Refs. [3, 4], the fluorescence of laser dyes in the pores of synthetic opals and inverse opals is investigated and the influence of the stop band on the emission spectra characteristics is analyzed. In Ref. [5], a practical application of nanocomposites based on synthetic opals is demonstrated - the fabrication of a fluorescent sensor by infiltrating a porphyrin fluorophore into an inverse opal, which lead to the enhancement of the detected signal and the increase in sensor sensitivity for heavy metal detection.

The aim of this work is to fabricate and investigate the luminescent properties of matrix nanocomposites based on synthetic opals and the laser dye Rhodamine 6G.

## 2. Experimental procedure

Synthetic artificial opals were used as photonic crystals. To fabricate the samples, monodisperse silica spheres were first synthesized using tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS) in a mixture of ethanol, water, and ammonia according to the Stöber method [6]. During prolonged natural sedimentation, the spheres in suspension self-assembled into a three-dimensional photonic crystal. The obtained synthetic opal samples were annealed in a furnace at a temperature of 800 °C for 1 hour to remove possible organic impurities and moisture from the pores and to achieve mechanical strength. Optical spectra were recorded using a DFS-12 diffraction spectrometer and a photomultiplier tube (FEU-79) in the wavelength range of 380 –650 nm. For the characterization of the synthetic opal samples and determination of their parameters, a halogen lamp was used as a broadband light source. The synthetic opal samples were irradiated in both reflectance and transmission geometries. The positions of the maximum in the reflectance spectrum (at an angle of 0°) and the minimum in the transmission spectrum for the samples were expected to coincide, which was observed during the measurements. To determine the parameters of the synthetic opal samples, reflectance spectra were measured. The following relations were used for the calculations:

$$\lambda_0 = 2d\sqrt{n_{\text{eff}}^2 - \sin^2\theta_0}\ , \tag{1}$$

$$d = D\sqrt{2}/3 \tag{2}$$

where $\lambda_0$ is the position of the reflection maximum; $d$ is the interplanar spacing between the planes of globules, at which Bragg diffraction occurs; $D$ is the diameter of the synthetic opal globules; and $\theta_0$ is the angle of incidence with respect to the normal to the (111) plane of the opal sample. The effective refractive index of the synthetic opal was taken as $n_{\text{eff}} = 1.36$ [7]. Reflection from the synthetic opal samples is caused by the presence of a stop band; therefore, the width of the reflection peak is directly related to the width of the stop band. Thus, the stop-band width was determined from the full width of the reflection line at half maximum.

For Rhodamine 6G dye infiltration into the pores of the opal matrix, ethanol solutions with concentrations of $1 \times 10^{-3}$ M and $5 \times 10^{-3}$ M were prepared. The synthetic opal samples were immersed in the solution for 24 hours and then dried in the open air for 24 hours. During the drying process, the solvent evaporated, and Rhodamine 6G was deposited on the surface of the synthetic opal globules, which bound tetrahedral and octahedral voids with sizes of 0.225D and 0.414D, respectively. Narrow channels with a diameter of 0.15D are located between the voids. The total void volume is 25.95%. It was established that the globule surface represents a thin layer composed of primary particles with diameters of 5 – 10 nm and a surface roughness of several nanometers [8]. Excitation of the laser dye in the pores of the photonic crystals was carried out using a high-power laser diode with $\lambda_{\max} = 517$ nm.

## 3. Results and discussion

The obtained parameters of the initial synthetic opal samples are presented in Table 1.

*Table 1*

**The parameters of the synthetic opal samples: the position of the stop band center ($\lambda_{\max}$), the interlayer spacing of the photonic crystal planes where Bragg diffraction occurs (d), the diameter of globules (D), the stop band width (Δλ)**

| Sample | $\lambda_{\max}$, nm | d, nm | D, nm | Δλ, nm |
|---|---|---|---|---|
| PC1 | 589 | 216 | 263 | 35 |
| PC2 | 517 | 190 | 233 | 50 |
| PC3 | 610 | 224 | 274 | 50 |

After Rhodamine 6G infiltration into the pores of the synthetic opal sample PC1, the reflectance spectrum was measured again. The comparison of the reflectance spectra before and after infiltration is presented in Figure 1.

A decrease in intensity and a red shift of the reflectance spectrum were observed after dye infiltration. This can be attributed to changes in the dielectric contrast, absorption of radiation by Rhodamine 6G, and the dye’s fluorescence.

When fluorescence was recorded in the reflection geometry, the first fluorescence peak of the dye was observed, while the second peak was “suppressed” by the stop band of the synthetic opal. In the transmission geometry, the second fluorescence peak of Rhodamine 6G was significantly reduced by the stop band, and the first peak disappeared. This behavior is explained by scattering processes and self-absorption of the dye’s emission. Figure 2 shows the fluorescence spectra of the samples PC2 and PC3 in the transmission geometry.

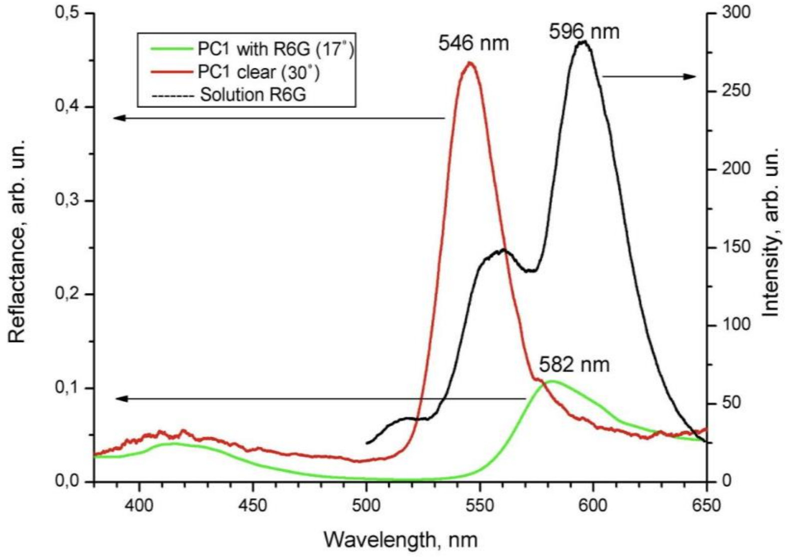

**Fig. 1. The reflectance spectrum of the sample PC1 before infiltration with Rhodamine 6G (red, θ = 30°) and after it (green, θ = 17°). The fluorescence spectrum of Rhodamine 6G in ethanol solution with the concentration of 5×10$^{-3}$ M is shown in black.**

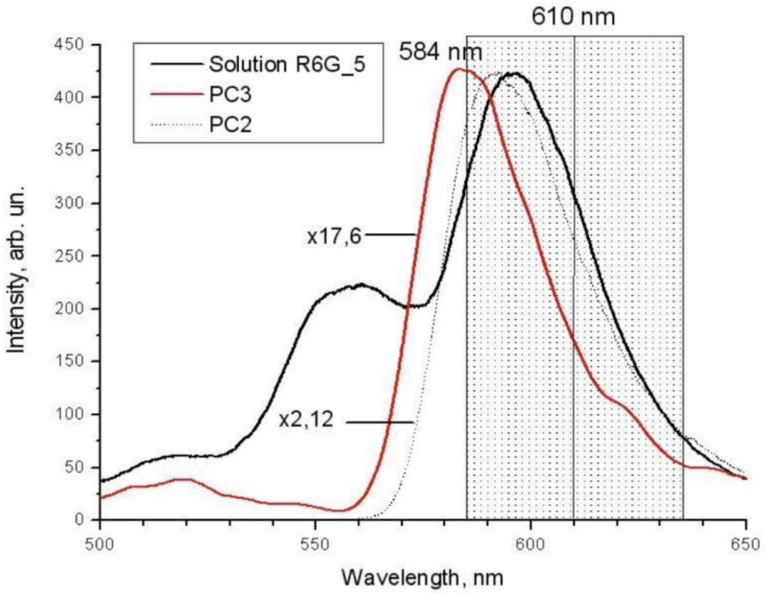

**Fig. 2. Fluorescence spectra of the sample PC2 (dashed line) and the sample PC3 (red line) in the transmission geometry. The emission spectrum of R6G dye in solution is shown in black. The stop band of the sample PC3, centered at 610 nm, is indicated by the rectangle.**

For the sample PC3, suppression of emission by the stop band and a blue shift of the fluorescence spectrum were observed. This is explained by the overlap of the stop band of the selected synthetic opal (610 ± 25 nm) with the spectral emission range of Rhodamine 6G, demonstrating the direct influence of the stop band on the propagation of emission in this spectral region. For the sample PC2, whose stop band is sufficiently shifted toward the blue region of the spectrum (517 ± 25 nm) relative to the dye's fluorescence maximum, no such effect is observed. The mechanism of suppression of the first fluorescence peak of R6G is similar to that described above.

## Conclusions

1. Suppression of the dye's emission is observed when the fluorescence spectrum of Rhodamine 6G overlaps with the stop band of the synthetic opal.
2. A blue shift of the fluorescence spectra of Rhodamine 6G infiltrated into the pores of the synthetic opal is detected, occurring when the dye's emission region overlaps with the opal's stop band. It is also shown that no such shift occurs when the stop band of the synthetic opal does not overlap with the fluorescence spectrum of the laser dye.

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