Optical properties of globular photonic crystals with different particle sizes

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Abstract. The article reports the results of experimental studies of the optical properties of globular photonic crystals filled with various chemical liquids. It opens up the possibility of creating highly sensitive refractive sensors of chemical compounds based on the introduction of these substances into the pores of opal matrices. The optical properties of opal matrices with different sizes of globules have been analyzed. Different spectral positions of the stop bands are present in the reflectance spectrum of globular photonic crystals, depending on the size of the particles. The sharp increase in the density of photonic states in photonic crystals opens up the possibility of increasing the efficiency of Raman scattering and nonlinear-optical processes in materials of this kind.

1. Introduction
Currently, one of the most promising optical materials is photonic crystals. There are so-called stop bands—the spectral regions of strong reflection of optical radiation in reflectance spectra of photonic crystals [1–3]. A well-known example of photonic crystals are opal matrices created on the basis of amorphous SiO\textsubscript{2}—silica [4–7]. Figure 1 shows photographs of the growth surface (111) of the opal matrix, obtained using a camera (see figure 1(a)) and an electron microscope (see figure 1(b)). Opal matrices are characterized by high softening temperature, chemically inertness, and resistance to intense laser radiation. For the [111] direction, these crystals can be considered as one-dimensional periodic structures. Opal matrices are constructed in the form of a face-centered cubic lattice from spherical globules of amorphous SiO\textsubscript{2} of close sizes [5]. The diameters of the globules of opal matrices depend on the conditions of synthesis and can vary in the range of 200–600 nm. The use of photonic crystals with large globule sizes is of interest due to the presence of stop bands in the infrared region of the spectrum, as well as the possibility of increasing the scattering efficiency in such structures provided the excitation radiation wavelength is close to the diameter of the corresponding globules. In this case, the Anderson localization of electromagnetic radiation inside globules, the transition from a ballistic photon to diffusion trajectory from radiation localizations, and a change in the scattering indicatrix according to the Mie scattering theory are possible [8]. Up to now, the optical properties and laws of the dependence of the optical properties on the size of particles forming a globular photonic crystal have not been sufficiently studied.
This paper reports the results of experimental studies of the optical properties of globular photonic crystals and provides information on the possibilities of using globular photonic crystals for applications.

2. Experimental methodology

Samples of artificial opal matrices were synthesized by the method of Stober [9,10], based on the hydrolysis of tetraethoxysilane in an aqueous-alcoholic medium in the presence of ammonium hydroxide as a catalyst. By changing the ratios of chemical reagents, opal matrices were obtained with various particle sizes of 200—350 nm.

Figure 2 shows a setup diagram for recording the reflectance spectrum from the (111) surface of opal matrices. A sample of the opal matrix (1) was stirred on a
Teflon plate (2). The light from the halogen lamp (3) was fed to the light guide (4) and directed perpendicular to the surface (111) of the sample. Reflected radiation from the second light guide (5) was transmitted to a mini-spectrometer (6). Computer (7) was designed for digital signal processing. In this case, the spatial resolution on the surface of the photonic crystal was 100 μm. It allows the construction of reflectance spectra from different parts of the (111) surface of globular photonic crystals.

3. Experimental results and discussion

Figure 3 shows the registered broadband radiation reflectance spectra of a halogen lamp from the surface (111) of globular photonic crystals with different particle sizes.

![Figure 3](image)

**Figure 3.** The reflectance spectra of globular photonic crystals with different particle sizes, obtained by changing the ratios of chemical reagents.

As can be seen from figure 3, in the reflectance spectra of globular photonic crystals, distinct reflection bands (curves 1–4) with an intensity maximum are observed. These maxima correspond to the spectral positions of the stop bands, which are determined from the well-known Wulff-Bragg relation [11]:

$$m\lambda_m = 2n_{ef}(\lambda)a.$$  \hspace{1cm} (1)

Here, \(\lambda_m\) is the wavelength corresponding to the spectral position of the \(m\)-th stop band; \(a\) is the period of the crystal lattice of the opal matrix; \(n_{ef}(\lambda) = \sqrt{(1 - \eta)n_{SiO_2}^2(\lambda) + \eta n_{Air}^2}\) is the effective refractive index of the opal matrix, where \(\eta = 0.26\) is the porosity of the opal matrix, \(n_{SiO_2}(\lambda)\) is the refractive index of silica at different wavelengths, \(n_{Air} = 1\) is the refractive index of air.

For photonic crystals at the edges of the stop bands, the group velocity of the electromagnetic wave tends to zero. This corresponds to an effective “stop” of light and a sharp increase of the density of photonic states [12, 13]. High densities of photonic states and deceleration of electromagnetic radiation near the edges of the stop bands of photonic crystals open up the possibility for the excitation of low-threshold stimulated Raman scattering (SRS) and an increase of the probability of excitation of Raman scattering of chemical compounds when introduced into the pores of photonic crystals. When
the wavelength of the exciting radiation for Raman scattering approaches the edges of the stop bands of photonic crystals filled with various chemical compounds, the intensity of the Raman spectra of the corresponding compounds may abnormally increase.

In opal matrices consisting of spherical particles, it is possible to observe Mie scattering when the dimensionless parameter of particles \( x \) corresponds to the relation [8]:

\[
x = \frac{\pi d n}{\lambda} : 1.
\]

Here \( d \) is the diameter of spherical particles of opal matrices; \( \lambda \) is the wavelength of the exciting radiation; \( n \) is the refractive index of the environment. In this case, for the original opal matrix, the environment is air (\( n_{\text{Air}} = 1 \)). As a result of the interference effect in the scattering of Mie, the density of photonic states increases sharply and Anderson localization of light is possible. As the particle size increases, the conditions for localizing light shift to the long-wavelength region. With the localization of electromagnetic radiation in a photonic crystal filled with molecular structures, the efficiency of Raman scattering and nonlinear optical processes in such structures increases.

![Figure 4](image-url)

**Figure 4.** Broadband reflectance spectra of the original globular photonic crystals (1) and photonic crystals filled with various liquids (2): (a)—benzene, (b)—ethyl phenol solution, (c)—nitric acid, (d)—alpha-bromonaphthalene.

Figure 4 shows the reflectance spectra of globular photonic crystals filled with various organic or inorganic liquids. As can be seen from these figures, with the introduction of various chemical substances into the pores of globular photonic crystals, the spectral positions of the stop bands are shifted to the long-wavelength region and their shapes are deformed. This indicates a change in the
effective refractive indices due to the introduction of various substances into the pores of the globular photonic crystals. On the basis of measurements of the shift of the stop bands, it is possible to determine the corresponding refractive indices and to perform an analysis of the refractive properties of various chemical substances introduced into the pores of the opal matrices. When using the original photonic crystals with different sizes of globules, it becomes possible to create nanocomposite photonic structures based on them that meet the conditions for enhancing Raman scattering and nonlinear optical processes.

4. Conclusions
Thus, in this work, the possibility of creating highly sensitive refractive sensors of organic and inorganic compounds based on the introduction of these substances into the pores of opal matrices is established. A sharp increase of the density of photonic states near the edge of the stop bands of photonic crystals and the localization of electromagnetic radiation during Mie scattering in photonic crystals open up the possibility to increase the efficiency of Raman scattering and nonlinear optical processes in materials of this kind.

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