

## Spontaneous Emission of Organic Molecules Embedded in a Photonic Crystal

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We report on modification of the spontaneous emission of dye molecules embedded in a three-dimensional solid-state photonic crystal exhibiting a stop band in the visible range. Molecules embedded in artificial opal filled with a polymer show a dip in the fluorescence spectrum and nonexponential spontaneous decay kinetics containing both accelerated and inhibited components compared to the dye fluorescence in a reference polymer matrix. Results are interpreted in terms of redistribution of the photon density of states in the photonic crystal. [S0031-9007(98)06494-1]

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The concept of the control of the spontaneous emission by means of modification of the photon density of states in mesoscopic structures [1] has gained considerable interest during the last decade [2]. The spontaneous decay of visibly emitting species embedded in high- $Q$  microcavities or dielectric slabs, or localized in the vicinity of dielectric interfaces can be modified due to changes in the photon density of states (DOS) as compared to an infinite homogeneous medium, which leads to changes in experimentally observed spontaneous emission spectra and decay rates. The phenomenon is a subject of extensive theoretical investigations (see, e.g., [3] and references therein). Experimental studies in this field include, but are not limited to, investigations of the effect of inhomogeneous optical environments on the spontaneous decay of organic molecules [4], rare-earth ions and their organic complexes [5], and semiconductor quantum wells [6] and nanocrystals [7].

Another approach to the modification of the photon DOS implies fabrication of structures consisting of microscopic light scatterers either arranged in a three-dimensional periodic lattice (photonic crystal) or randomly distributed in space. The ideas of the photonic band engineering were advanced a decade ago [8] and have been investigated extensively in a number of theoretical studies [9]. With certain parameters of scatterers (size, shape, and dielectric function) and types of their spatial arrangement (volume fraction and symmetry), coherent effects in multiple light scattering can result in either localization of light waves or the development of a spectral gap within which the propagation of light is forbidden. These phenomena resemble well-known features of electrons in disordered and crystalline solids, respectively, except for the fact that the phenomena are essentially quantum mechanical in the case of electrons, whereas they have a purely classical origin in the case of electromagnetic waves.

To date, studies of the effect of three-dimensional photonic band gap structures on the spontaneous emission in the visible range are restricted to experiments with dye molecules embedded in ordered aqueous suspensions of polystyrene microspheres, where a slowing down of the spontaneous emission was observed [10]. However, a comprehensive experimental investigation of the same system [11] has shown that intermolecular interactions of dye molecules with polystyrene and a strong overlap of absorption and fluorescence spectra were responsible for a major fraction of the change in the measured lifetime. In the present Letter we report on the photonic band gap effect on the spontaneous emission of organic molecules in a polymer matrix embedded in opal, which manifests itself as a dip in the fluorescence spectrum and nonexponential spontaneous decay kinetics.

Recently, we have proposed artificial opals as promising structures for the photonic band engineering [12,13]. These species are rigid solid-state colloidal crystals consisting of submicrometer-sized amorphous silica globules whose arrangement is favorable to the formation of a pronounced pseudogap in the visible range extending over a region of angles which manifests itself in optical transmission and reflection experiments. The effect can be substantially enhanced by filling opals with highly refractive liquids and solids [12–14].

Artificial opals are produced from a sol of highly monodispersed porous spherical silica globules with the diameter ranging from 200 to 300 nm by means of the hydrothermal treatment and annealing. Silica globules in opals form a self-organized close-packed arrangement similar to the face-centered cubic lattice (Fig. 1), a solid experimental evidence of which has been recently presented in Ref. [15]. Interconnected voids between globules constitute a three-dimensional network, thus providing a possibility to embed light-emitting species therein. We studied an opal sample filled with a solid

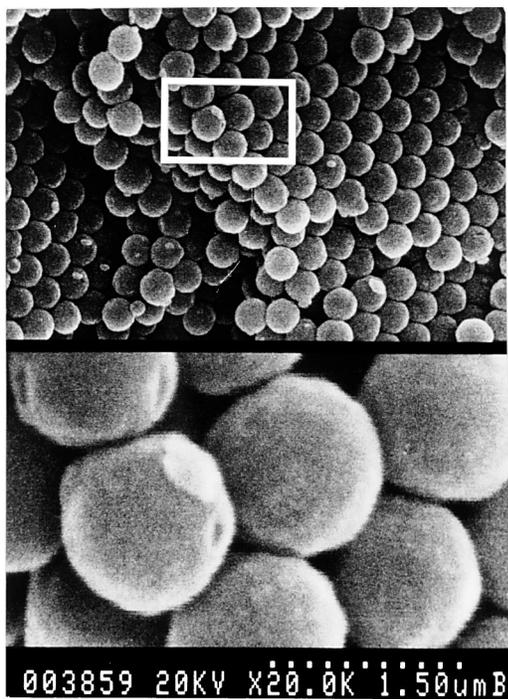


FIG. 1. Electron microphotograph of opal sample. White rectangle in the upper panel bounds the area of  $0.6 \times 1.0 \mu\text{m}^2$ . An enlarged fragment of the area is presented in the lower panel.

solution of the 1,8-naphthoylene-1',2'-benzimidazole (7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one) dye (referred to in what follows as NBIA) in poly(methyl methacrylate) (PMMA). The sample was fabricated by impregnating opal with an NBIA solution in methyl methacrylate with subsequent polymerization. An optically thick ( $\sim 0.5$  mm) polymer film prepared from the same dye solution was used as a reference sample. The resulting concentration of NBIA in PMMA was about  $10^{-5}$  M. The polymer provides a reasonably high dielectric contrast between the filler and silica globules (refractive index of 1.490 for PMMA versus  $\sim 1.3$  for opal silica clusters [12,13]), and makes it possible to avoid undesirable interactions of dye molecules with the silica surface [16]. In nonpolar solvents, the NBIA dye has a high quantum yield [17] and a substantial Stokes loss that provides a weak reabsorption of fluorescence. The opal sample used in our experiments demonstrated a pronounced stop band in the region of 500 nm (Fig. 2) lying within the fluorescence emission band of NBIA.

Thus, a photonic crystal was fabricated from a 3D polymer network with the volume filling fraction of about 25% separated by nearly spherical silica globules with a lower refractive index. Numerical simulations [18] have shown that the network topology of the high-refractive material is favorable to the formation of gaps in the photon DOS, which can lead to modification of the spontaneous emission of species embedded in the photonic crystal.

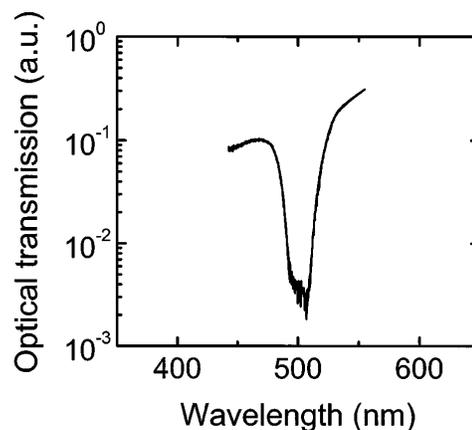


FIG. 2. Optical transmission spectrum of opal sample with voids filled with poly(methyl methacrylate).

Fluorescence experiments were carried out on an automated laser fluorescence spectrometer with the sub-nanosecond time resolution described in detail elsewhere [19]. A TEA  $\text{N}_2$  laser with the pulse duration of about 500 ps was used for excitation at 337.1 nm. Fluorescence was collected in the direction normal to the surface of the sample within a solid angle of  $0.09\pi$  sr. To ensure reliable interpretation of time-resolved emission data, both the conventional two- and three-exponential nonlinear fitting method and the decay time distribution analysis technique (see, e.g., [20]) based on the numerical inversion of the Laplace transform were used in the analysis of fluorescence decays. A model-free analysis of fluorescence decay traces of NBIA embedded in the photonic crystal and reference polymer film was carried out using an efficient regularized method for the recovery of fluorescence decay time distributions recently proposed by one of us [21]. Fluorescence decay time distributions were computed subject to non-negative constraints since no fluorescence buildup is expected in the system under investigation.

Fluorescence spectra of NBIA in a separately standing polymer film and polymer network filling voids in opal are shown in Fig. 3a along with the fluorescence excitation spectrum of NBIA in PMMA. Embedding the dye and polymer system in opal clearly leads to a modification of the spontaneous emission: a dip in the emission spectrum is formed with the position close to that of the dip in the optical transmission spectrum of the opal sample. The ratio of emission intensities of systems with the modified (opal sample) and "vacuum" (optically thick polymer film) photon densities of states is shown in Fig. 3b.

Results of the analysis of fluorescence kinetics of samples are presented in Fig. 4. We have found that fluorescing impurities with characteristic decay times approximately an order of magnitude shorter than the NBIA excited-state lifetime are present in the polymer and opal. However, the substantial difference between the dye and impurity lifetimes makes it possible to analyze the

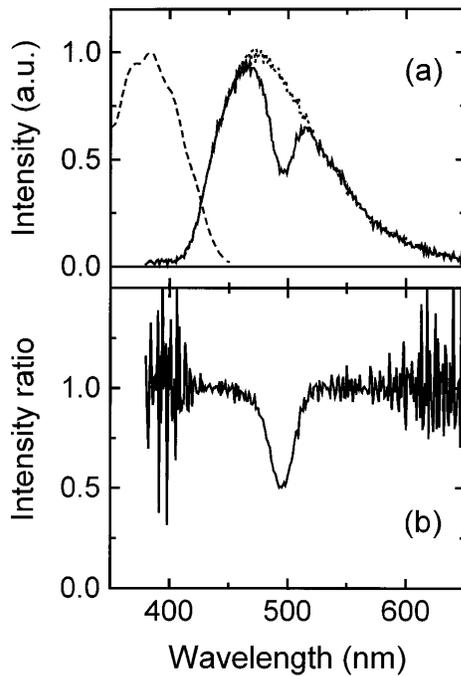


FIG. 3. (a) Fluorescence emission spectrum of NBIA solution in a PMMA polymer network filling voids in opal (—), and fluorescence excitation (---) and emission (· · ·) spectra of NBIA in a freestanding PMMA polymer film (impurity fluorescence subtracted). Fluorescence was excited at 337.1 nm, and the excitation spectrum was detected at 500 nm. (b) Ratio of fluorescence intensities of NBIA/PMMA solid solution in the opal sample and freestanding film.

excited-state decays of the dye even in the presence of the fluorescing impurities.

The analysis of the fluorescence kinetics shows that the excited-state decay of the NBIA dye is exponential in the reference polymer film (Fig. 4a), whereas both accelerated and inhibited decay components appear in the spontaneous emission kinetics of dye molecules embedded in the opal sample (Fig. 4b). The nonexponential behavior of the excited-state decay of the dye embedded in the photonic crystal has a reasonable explanation in terms of a redistribution of the photon DOS. According to the sum rule for the spontaneous emission rate derived for an arbitrary optically inhomogeneous environment [22], the photonic crystal just redistributes the spontaneous radiation power over the spectrum and, we believe, over directions. Indeed, numerical simulations [23] have shown that the radiation power of a dipole embedded in a photonic crystal undergoes a spectral and angular redistribution compared to the free space and depends strongly on the position and orientation of the emitter with respect to an elementary crystal cell. In addition, the fluorescence spectrum of the dye used in the investigation is substantially wider than the stop band. As has been shown in the theoretical investigation [24], either acceleration or inhibition of the spontaneous decay of a molecule with a wide spontaneous emission spectrum can be observed in

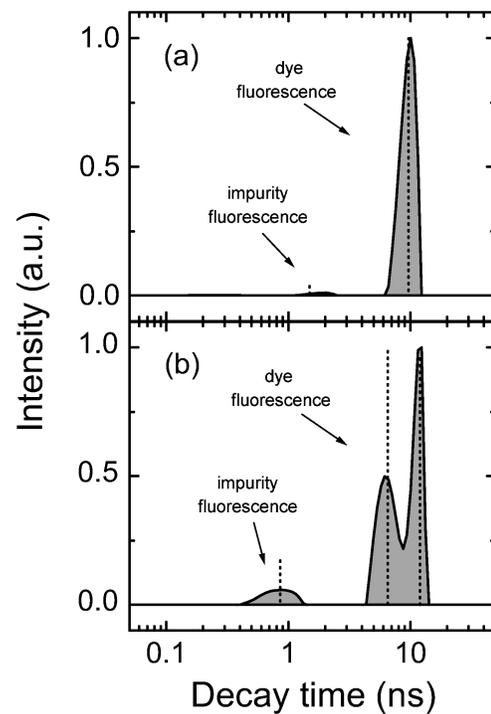


FIG. 4. Decay time distributions of NBIA fluorescence: (a) In freestanding polymer film and (b) in polymer network filling voids in opal. Results of (a) two- and (b) three-exponential analysis of the same decay curves are shown by dotted lines. Excitation wavelength 337.1 nm, emission wavelength 510 nm. Decay curves were recorded in 1000 time channels with 0.1 ns/channel; 100 exponential terms with decay times logarithmically spaced within the interval 0.05 to 50.0 ns were included in the decay time distribution analysis.

a photonic crystal, depending on the mutual position of the photonic band gap and fluorescence spectrum. Taking into account that opal filled with the polymer shows an angular-dependent stop band, and dye molecules assume random orientations and positions with respect to the elementary crystal cell, the above considerations can well explain the observed nonexponential spontaneous emission decay of organic molecules embedded in the photonic crystal.

Thus, we conclude that two competitive processes of inhibition and acceleration of the spontaneous decay resulting from a redistribution of the photon density of states contribute to the observed fluorescence decay giving rise to a nonexponential spontaneous decay kinetics of dye molecules embedded in a photonic crystal. To observe the pure inhibition of the spontaneous emission in a photonic crystal, one should use narrow-band emitting species, e.g., rare-earth ions or semiconductor nanocrystals, to avoid effects connected with the redistribution of the photon DOS across the spontaneous emission spectrum. In addition, absorption and emission spectra of decay inhibition probes should have a minimum overlap to avoid effects of multiple reabsorption or reemission on the observed fluorescence decay time. Experiments with probes of this type

are in progress and will be the subject of our forthcoming papers.

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