

Spontaneous Emission of Dye Molecules, Semiconductor Nanocrystals, and Rare-Earth Ions in Opal-Based Photonic Crystals

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Abstract—Photonic crystals based on silica colloidal crystals (artificial opals) exhibit pronounced stopbands for electromagnetic wave propagation and the corresponding modification of the photon density of states in the visible range. These spectrally selective features can be enhanced by impregnating opals with higher refractive materials like, e.g., polymers. Doping of these structures with dye molecules, semiconductor nanoparticles (quantum dots), and rare-earth ions provides a possibility to examine the challenging theoretical predictions of the inhibited spontaneous emission in photonic bandgap (PBG) materials. First experiments are discussed in which pronounced modification of spontaneous emission spectra and noticeable changes in decay kinetics were observed.

Index Terms—Artificial opal, dye molecules, photonic crystal, rare-earth ions, semiconductor nanocrystals, spontaneous emission.

I. INTRODUCTION

SINCE the pioneering works by Yablonovitch [1] and John [2], the concept of the photonic crystals, i.e., objects which behave with respect to electromagnetic waves like atomic crystals do with respect to electrons, have attracted much attention [3], [4]. Probably the most interesting basic physical phenomenon attainable in a photonic crystal is freezing of the spontaneous decay of excited atoms and molecules. Spontaneous emission of light is not the intrinsic property of the matter but rather a result of its interaction with the field, namely it is essentially the stimulated emission due to presence of zero electromagnetic oscillations, the so-called electromagnetic vacuum. In the weak oscillator-field coupling regime, the rate of the spontaneous emission can be described

by Fermi's Golden rule and is therefore directly proportional to the density of propagating electromagnetic modes available in the space around an atom or a molecule within the frequency range corresponding to the spontaneous emission spectrum. If free space is replaced by a medium with the refractive index modulated on the scale comparable with the spontaneous emission wavelength, the spontaneous emission rate will experience a modification and the spontaneous emission will be either enhanced or inhibited.

The prediction of the controllable spontaneous emission has been advanced for the first time by Purcell [5]. Presently, this phenomenon is a subject of extensive theoretical analysis [6], [7]. Experimental studies in this field include investigations of the spontaneous emission from microcavities [8]–[12], dielectric slabs [13], [14], interfaces [15], [16], water-in-oil micelles [17], phospholipid bilayers [18], and biological membranes [19]. Bykov [20] was the first to outline the possibility of the frozen "excited atom + field" state when a periodic medium offers no propagating mode at the resonance frequency. This was followed by a systematic development of the concept of photonic crystals and experimental investigations in this field.

A one-dimensional (1-D) photonic crystal is nothing but the well-known and widely used dielectric mirror consisting of alternating dielectric layers with different refractive indexes [21]–[23]. Two-dimensional (2-D) photonic crystals (i.e., media with periodic variations of the refractive index in two dimensions) for the optical range can be successfully manufactured using various techniques developed in modern microelectronics (see, e.g., [24], [25], and references therein).

A decade ago, three-dimensional (3-D) photonic crystals for the radio-frequency range have been fabricated and examined [26]. To produce photonic crystals for the optical range, experimenters have concentrated their efforts on the synthesis of artificial media with strong periodic modulation of the refractive index in all three dimensions on the submicrometer length scale. Although modern solid-state technologies presently existing in micro- and nanoelectronics offer several approaches resulting in high-quality 1-D and 2-D dielectric lattices, fabrication of a 3-D periodic superstructure by means of these techniques still remains a challenging problem [27].

In the recent years, self-assembled colloidal structures have been proposed as prototypes for 3-D photonic crystals [28], [29]. Solid-state silica colloidal crystals known as artificial opals have been considered then as promising structures for

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synthesis of photonic crystals for the visible and near-infrared range [30]–[32]. These findings stimulated extensive studies of optical properties of colloidal crystals [33]–[36], their use as templates for fabricating their high-refractive 3-D replicas [37]–[39], and investigations of the spontaneous emission of dye molecules [28], [40]–[48] and semiconductor nanoparticles [49]–[51] embedded in colloidal crystals and their replicas.

In this paper, we review results of our recent experiments on the spontaneous emission of organic dye molecules and semiconductor nanocrystals (the so-called quantum dots) and discuss possible new experiments using rare-earth ions embedded in opal-based photonic crystals. In Section II, we briefly describe the synthesis and optical properties of opals and opal-based photonic crystals. In Section III, we discuss photo-physical properties of light-emitting inclusions (dye molecules, semiconductor nanocrystals, and rare-earth ions) important for the observation of the photonic crystal effect on their spontaneous emission and consider experimental results on the spontaneous emission of these species embedded in opal-based photonic crystals. Section IV contains conclusions and outlook for further research in this field.

II. SYNTHESIS AND PROPERTIES OF OPAL-BASED PHOTONIC CRYSTALS

Opals belong to a class of materials known as colloidal crystals which is an example of a superstructure with organization of matter on the supramolecular level. Most likely, colloidal crystals in nature were first identified in an observation of a crystallizable virus [52]. A recent example of man-made colloidal crystals are 3-D lattices of semiconductor quantum dots, the so-called “quantum dot solids” [53]. Natural and synthetic gem opals with iridescent colors are 3-D periodic colloidal structures consisting of spherical silica globules [54]–[58].

The synthesis of opals includes fabrication of a monodisperse silica sol [59], [60], a prolonged sedimentation of a colloidal solution providing self-assembly of globules into a close-packed crystalline structure, and a thermal treatment providing formation of a mechanically robust crystal [55]–[58]. After a hydrothermal treatment and annealing, point contacts between the globules are converted into faceted ones. Thus formed opals have a polycrystalline structure with typical dimensions of single-crystalline domains of order of a few millimeters.

Structures fabricated in such a manner consist of nearly spherical silica clusters with the size ranging from 0.2 to 0.3 μm which are arranged in the face-centered cubic (f.c.c.) lattice (Fig. 1), which was substantiated in the recent study [61]. Under certain synthesis conditions, each silica globule may in its turn have an internal substructure. In this case, depending on the porosity, the effective refractive index $n_{\text{SiO}_2}^*$ of silica globules ranges from the value $n_{\text{SiO}_2} = 1.45$ inherent in bulk silica down to $n_{\text{SiO}_2}^* = 1.26$. Lattices of the type show a dip in the optical transmission spectrum with a spectral position depending on the lattice period a_L and on the $n_{\text{SiO}_2}^*$ value. The nature of the spectrally selective transmission in a

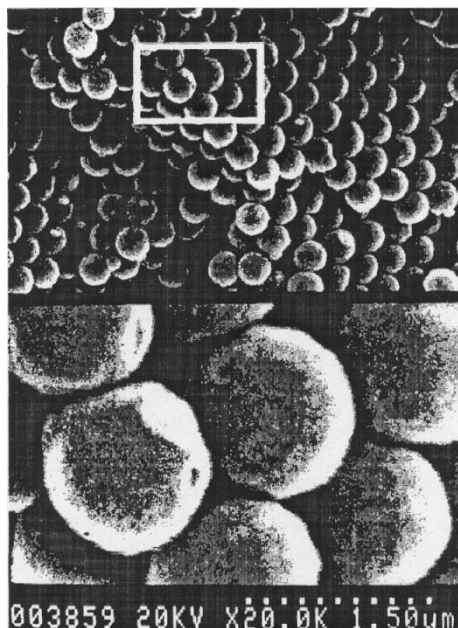


Fig. 1. Electronic micrograph of an opal sample. White rectangle in the upper panel bounds the area of $0.6 \times 1.0 \mu\text{m}^2$. An enlarged fragment of the area is presented in the lower panel.

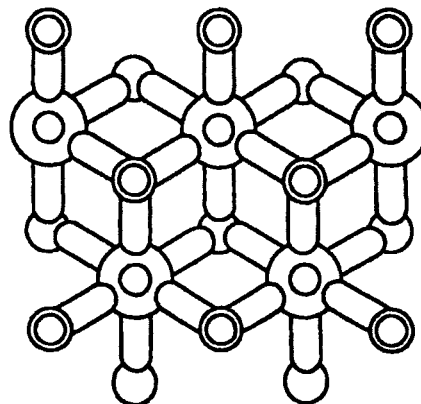


Fig. 2. Lattice of voids of opal presented as a combination of spherical elements. Spheres correspond to tetrahedral and octahedral voids. Diameter of cylinders correspond to the minimum cross-section of channels between the voids. See [57] for details.

refracting medium without dissipation is nothing but multiple scattering and interference of light waves, and can intuitively be understood in terms of Bragg diffraction. From the different viewpoint, formation of a pronounced stopband is indicative of a reduced density of propagating electromagnetic modes [photon density of states (DOS)] inside the structure.

Voids between the globules constituting opal form a regular lattice (Fig. 2). This network of voids can be filled with materials having refraction indexes different from that of the silica globules. By this means, it is possible to control the spectral position and contrast of the optical stopband. Fig. 3 shows spectral characteristics of one and the same 0.5-mm-thick opal sample filled with various liquids. With increasing the refractive index of the substance filling the voids compared to that of the globules forming the opal lattice, the spectral position of the stopband shifts linearly toward

TABLE I
SOME PHOTOPHYSICAL PROPERTIES OF DYE MOLECULES, SEMICONDUCTOR NANOCRYSTALS, AND COMPLEXES OF RARE-EARTH IONS IMPORTANT FOR THEIR USE IN INVESTIGATIONS OF INHIBITION OF THE SPONTANEOUS EMISSION IN PHOTONIC CRYSTALS

Photophysical parameters	Spontaneously emitting species		
	Dye molecules	Semiconductor nanocrystals	Chelates of rare-earth ions
Luminescence quantum yield, η	≤ 1.0	$\sim 10^{-3} \dots 10^{-2}$	≤ 1.0
Luminescence decay time, τ	$\sim 10^{-8} \dots 10^{-9}$ s	$\sim 10^{-3} \dots 10^{-10}$ s	$\sim 10^{-3} \dots 10^{-4}$ s
Dependence of η and τ on chemical environment	Strong	Strong	Moderate
Luminescence decay law	Exponential or nonexponential, depending on the environment	Strongly nonexponential	Exponential
Typical width of spontaneous emission spectrum	$\sim 3000 \dots 5000$ cm^{-1}	$\sim 10^1 \dots 10^3$ cm^{-1}	$\sim 10^2$ cm^{-1} ^{*)}
Direction of emission dipole moment in species	Fixed	Experimental evidence presently not available	Fluctuates on the excited-state lifetime scale

^{*)} Data for solvent-perturbed $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition in $\text{Eu}^{3+} \text{-(HFAC)}_3 \text{-(TOPO)}_2$ complex.

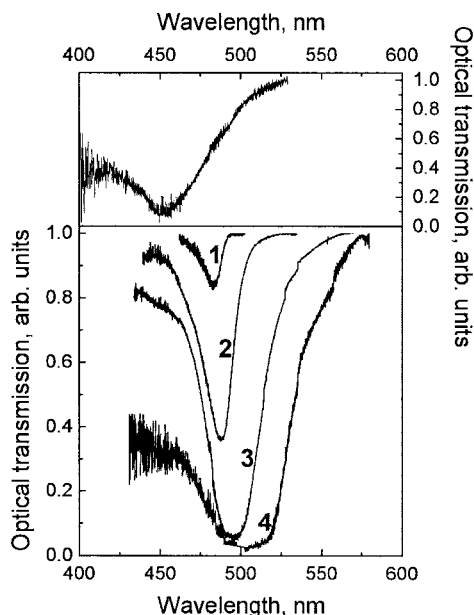


Fig. 3. Optical transmission spectra of a dry opal sample (upper panel) and the same opal sample impregnated with methanol (1), $n = 1.328$; ethanol (2), $n = 1.361$; cyclohexane (3), $n = 1.426$; and toluene (4), $n = 1.497$.

longer wavelengths. Experimentally measured positions of the stopbands for a dry ($n_{\text{voids}} < n_{\text{SiO}_2}^*$) and impregnated samples ($n_{\text{voids}} > n_{\text{SiO}_2}^*$) fit the common straight line [31], [33]. With an increase in the value of the dielectric contrast $n_{\text{voids}}/n_{\text{spheres}}$, a dip in the transmission spectrum becomes deeper and wider. The maximum transmission contrast reached in our experiments was about 10^3 , the spectral width being 40 nm at the 10%-level for the stopband centered at 500 nm (curve 4 in Fig. 3). Enhancement of the stopband in opals filled with high-refractive substances agrees with both a simple consideration based on multiple wave scattering in

a quasicrystalline structure [31], [33] and thorough analyzes of photonic band structures of different 3-D lattices [62]–[64]. These theoretical investigations have shown that 3-D network structures with volume filling factor in the range of 0.2 ... 0.3 possess a stronger modification of the photon DOS than the lattice of closed-packed dielectric spheres in which the volume filling factor is 0.74 (for the f.c.c. lattice).

III. LIGHT-EMITTING SPECIES IN A PHOTONIC CRYSTAL

A. General Features of Dye Molecules, Semiconductor Nanocrystals, and Rare-Earth Ions

It is of principal importance to examine the effect of the photonic crystals on the spontaneous emission of molecules and other resonant inclusions whose emission spectrum overlaps the photonic bandgap (PBG) (or stopband in the case of an imperfect photonic crystal). The three types of light-emitting species can be considered, namely, organic molecules, semiconductor nanocrystals, and rare-earth ions. Each emitter type possesses certain specific features which are important in the context of the modified spontaneous emission under conditions of a relatively narrow electromagnetic stopband covering a finite solid angle, which is typical for opal-based photonic crystals.

Let us consider general properties of spontaneously-emitting species to be used in these studies which are summarized in Table I.

- i) The spontaneously emitting probe should have a high spontaneous emission yield. Otherwise, although in this case spontaneous emission measurements under continuous-wave excitation conditions can reveal a modification of the spontaneous emission spectrum, the probe will exhibit little, if any, changes in the spontaneous emission decay law, since the excited

state will be efficiently depopulated via nonradiative transitions whose rate is insensitive to the presence of the photonic band structure.

- ii) The width of the homogeneous spontaneous emission spectrum should be comparable to that of the stopband (ideally, the homogeneous spectrum should be narrower than the stopband) to maximize the effect of the photonic crystal on the spontaneous emission.
- iii) The photophysics and photochemistry of light-emitting species to be used in experiments must be well-established to avoid unexpected guest-host effects on the spectrum and quantum yield which might be misinterpreted in terms of photonic crystal effects on the spontaneous emission.
- iv) A single-exponential spontaneous emission decay of a species in a bulk medium is highly advantageous from the viewpoint of detecting changes in the spontaneous decay law induced by a photonic crystal.
- v) It is important, whether light-emitting species embedded in a photonic crystal are rigidly fixed in space or may undergo spatial diffusion on their excited-state lifetime scale. As has been shown in calculations [65], [66], the local photon DOS in a photonic crystal, and hence its effect on the spontaneous emission, strongly depends on the position of the emitter within a unit crystal cell. Therefore, if spontaneously emitting probes undergo spatial diffusion on the excited-state-lifetime, they will interact with a spatially-averaging local density of states. On the other hand, species rigidly fixed at random positions within a photonic crystal are expected to show position-dependent interactions with the electromagnetic vacuum in the photonic crystal, which may lead to dispersive spontaneous emission decay laws. When spontaneously-emitting species embedded in the photonic crystal are rigidly fixed in space (e.g., when they are dissolved in a rigid matrix filling the photonic crystal), it is important whether the transition dipole moment has a fixed orientation in the frame of a rigidly fixed species. Indeed, as has been shown in theoretical calculations [65], [66], the spontaneous emission rate in PBG structures depends on the orientation of the emission dipole with respect to symmetry axes of the photonic crystal.

In addition, the spontaneously emitting probe must be readily embedded into opal-based photonic crystals by means of existing techniques. The proper choice of the matrix incorporating dye molecules, semiconductor nanocrystals, or rare-earth ions can provide, upon impregnation of opal, formation of a photonic crystal with the network topology which provides, at one and the same dielectric contrast, a stronger modification of the photon density of states [62]–[64].

B. Molecules Embedded in Opal-Based Photonic Crystals

Dye molecules usually have high quantum yields and well-established photophysics [67]. Decay times of singlet excited states of dye molecules typically range from 1 to 20 ns and can be measured to a high accuracy using routinely available

techniques. Dye molecules normally have extremely wide homogeneous emission spectra extending for several thousand cm^{-1} in the visible. As a result of the fast thermalization of the excited state, the homogeneous emission spectrum of a dye molecule is formed by a continuum of vibronic transitions from the lower energy level of the excited state to vibronic sub-levels of the ground state [67], and therefore the fluorescence lifetime of a dye molecule is constant over the entire homogeneous emission spectrum. Intermolecular interactions with the environment can give rise to inhomogeneous broadening of the dye fluorescence. However, the inhomogeneous-to-homogeneous width ratio of fluorescence spectra typically does not exceed 0.2 for polar dye molecules and is more than an order of magnitude smaller for nonpolar ones [68]. Thus, the inhomogeneous broadening of dye fluorescence spectra can be neglected to a good approximation in studies of the photonic crystal effects on the spontaneous emission of dyes. Therefore, the effect of a photonic crystal on the fluorescence lifetime of a dye embedded therein should be essentially independent of the fluorescence detection wavelength (an opposite conclusion has recently been drawn in [48] based on misinterpretation of the dye fluorescence bandwidth as originating predominantly from the inhomogeneous broadening). Another important feature of dye molecules is that the transition dipole moment of spontaneous emission has a fixed orientation in the molecular frame. Dye molecules can be easily embedded into opal-based structures using high-refractive liquid solvents or polymers; however, excited-state lifetimes and fluorescence quantum yields of dye molecules are frequently solvent-dependent.

In our experiments, we observed modification of spontaneous emission spectra of Rhodamine 6G (R6G) and 1,8-naphthoylene-1',2'-benzimidazole (NBIA) dyes by opal-based photonic crystals [33], [41]–[44]: embedding fluorescing dye molecules in normal and inverted opals leads to appearance of pronounced angular-dependent dips in dye fluorescence spectra (Fig. 4) with positions corresponding to those of optical stopbands in the opal-based photonic crystals. Similar modification of the spontaneous emission of organic molecules due to modification of the photon DOS in photonic crystals has also been reported by other groups [45]–[48].

We have also investigated the effect of normal and inverted opals on the spontaneous emission kinetics of dye molecules [41]–[44]. When using dye molecules as probes of the modification of the photon DOS in photonic crystals, one should take into account that dyes with a high fluorescence quantum yield frequently exhibit strongly overlapping absorption and emission spectra. In a strongly scattering environment offered by a photonic crystal this may result in multiple reabsorption and remission of fluorescence photons, which may give rise to an apparent increase in the fluorescence lifetime (see, e.g., [69]) and can be mistakenly interpreted as the photonic crystal effect. As has been pointed out in [40], this may be one of possible explanations of an increase in the fluorescence lifetime of the Kiton Red S dye in an aqueous colloidal crystal observed in [28]. Recently [43], [44], we have observed a similar increase by a factor of ~ 1.5 in the fluorescence lifetime of R6G in a dry opal sample with the stopband overlapping the dye fluorescence compared to fluorescence of

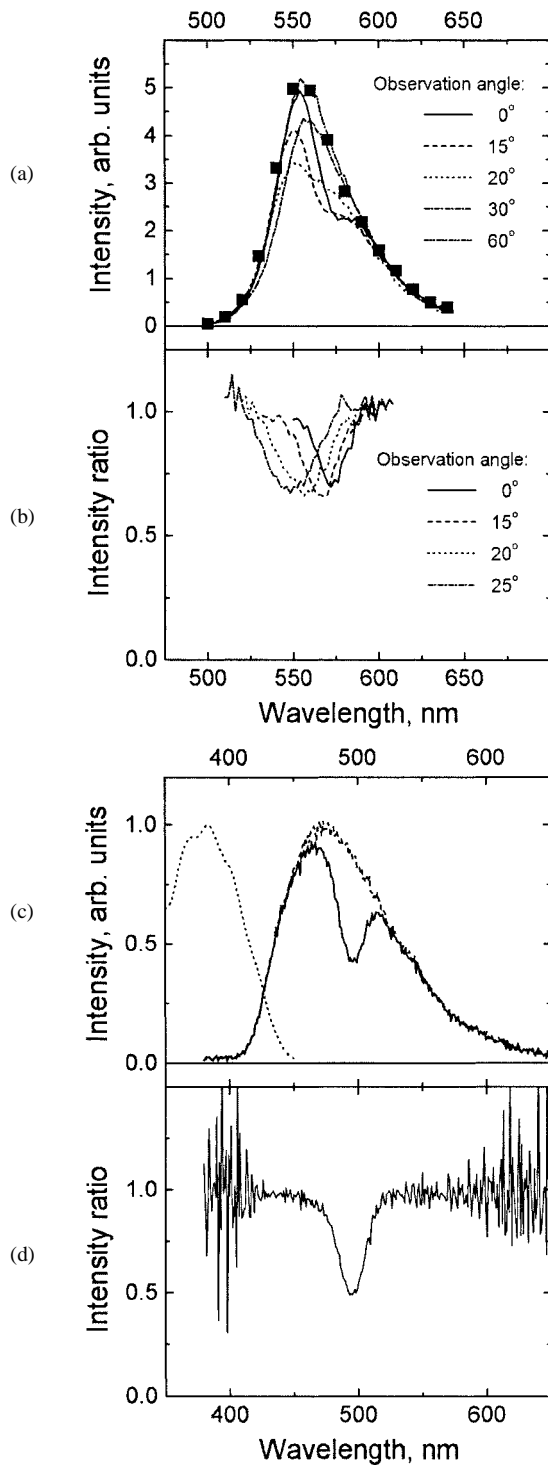


Fig. 4. Fluorescence of molecules embedded in opal-based photonic crystals: (a) Spontaneous emission spectra of R6G in an opal sample with the stopband overlapping dye fluorescence measured at different observation angles with respect to the normal to the sample surface and the "vacuum" spectrum (squares) recorded in an opal sample with the stopband located well to the blue from R6G fluorescence, and (b) their ratios; (c) fluorescence emission (—) spectrum of NBIA in PMMA-filled opal, and excitation ($\lambda_{em} = 500$ nm) (---) and emission (\cdots) spectra of the dye in a reference polymer film, and (d) ratio of fluorescence intensities of NBIA in PMMA-filled opal and in a free-standing PMMA film: $\lambda_{ex} = 337.1$ nm. The spectra were detected within an aperture of 0.09π sr.

the same dye embedded in a reference dry opal sample with the stopband located well to the blue from the dye fluores-

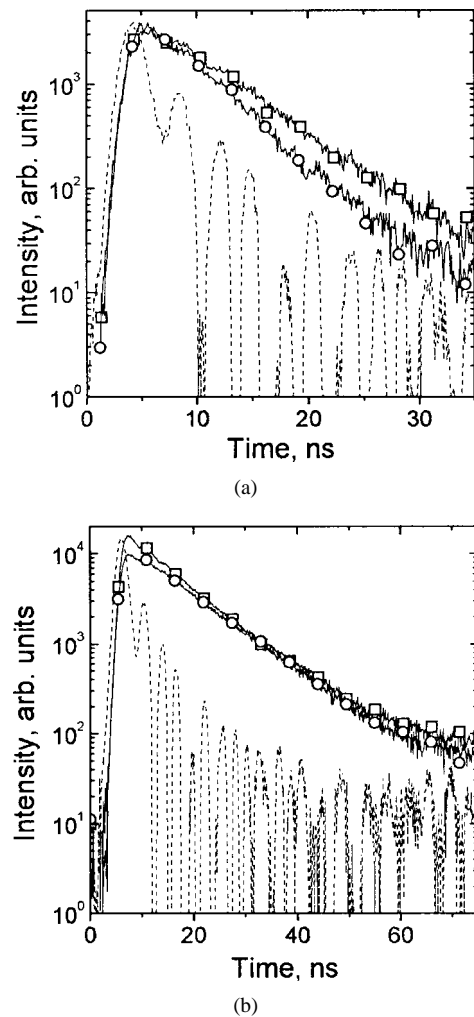


Fig. 5. Fluorescence decay kinetics of dyes in opal-based photonic crystals: (a) R6G in dry opal sample with the stopband overlapping dye fluorescence (-□-) (mean lifetime 4.9 ns) and in dry opal sample with the stopband located well to the blue from R6G fluorescence (-o-) (mean lifetime 3.3 ns); (b) NBIA in PMMA-filled opal (-□-) and in the reference PMMA film (-o-). Dashed curves show impulse response function of the fluorimeter. $\lambda_{ex} = 337.1$ nm: (a) $\lambda_{em} = 575$ nm and (b) 510 nm.

cence [Fig. 5(a)]. This increase in the fluorescence lifetime was tentatively explained by the multiple reabsorption and remission of fluorescence photons by R6G molecules having strongly overlapping excitation and emission spectra. The reabsorption effect was most likely enhanced in the photonic crystal due to a substantial increase in the effective photon path in the vicinity of the stopband. Uncontrollable intermolecular interactions with the environment of dye molecules can be considered as an alternative explanation of the fluorescence lifetime modification.

In order to minimize both the reabsorption and uncontrollable chemical interactions of the dye with its environment, we have investigated fluorescence of NBIA in poly(methyl methacrylate) (PMMA) filling voids in opal [42]–[44]. The NBIA dye has a small overlap of absorption and emission spectra, whereas the PMMA matrix provides an identical chemical environment for dye molecules. Filling opal with a higher refractive polymer ($n_{PMMA} = 1.490$ versus $n_{SiO_2}^* \approx 1.30$) provides a transition from the lattice of high-refracting

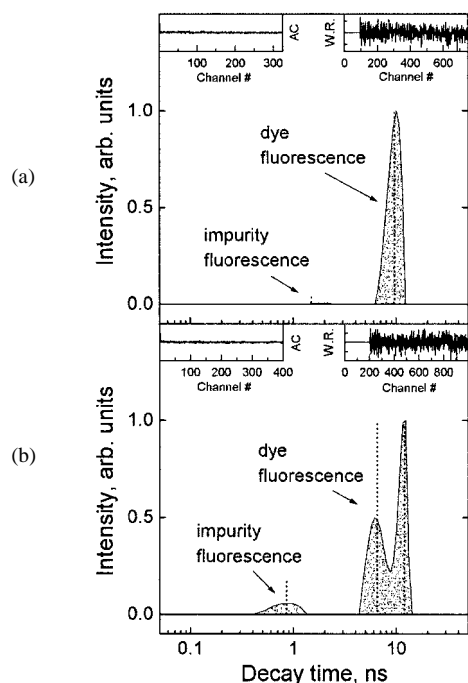


Fig. 6. Decay time distributions (gray shapes) recovered from NBIA fluorescence kinetics presented in Fig. 5(b): (a) in free-standing polymer film and (b) in opal-polymer photonic crystal. Results of (a) two- and (b) three-exponential analysis of the same decay curves are shown by dotted lines. Insets show plots of weighted residuals (W.R.) and their autocorrelation functions (AC). $\lambda_{ex} = 337.1$ nm, $\lambda_{em} = 510$ nm.

spheres to its replica (Fig. 2) which is important for obtaining a stronger modification of the photon DOS [62]–[64].

A modification of the spontaneous emission kinetics of NBIA molecules embedded in this opal-polymer photonic crystal was observed [Fig. 5(b)]. A comprehensive analysis [70]¹ of the fluorescence kinetics presented in Fig. 5(b) shows that the excited-state decay of the NBIA dye is exponential in the reference polymer film [Fig. 6(a)], whereas both accelerated and inhibited decay components appear in the spontaneous emission kinetics of dye molecules embedded in the opal sample [Fig. 6(b)].

The nonexponential behavior of the excited-state decay of the dye embedded in the photonic crystal has a reasonable explanation in terms of a modification of the photon DOS in the photonic crystal. According to the sum rule for the spontaneous emission rate derived for an arbitrary optically inhomogeneous environment [71], a photonic crystal just redistributes the spontaneous radiation power over the spectrum. Indeed, numerical simulations [65] have shown that the radiation power of a dipole embedded in a photonic crystal undergoes a spectral and angular redistribution compared to free space and depends strongly on the position and orientation of the emitter with respect to a unit crystal cell. In addition, the fluorescence spectrum of the dye used in the investigation

¹To ensure reliable interpretation of time-resolved emission data, both the conventional two- and three-exponential fitting and the decay time distribution technique based on the numerical inversion of the quasi-Laplace transform were used in the analysis of fluorescence decays. The decay time distributions presented in Fig. 6 were computed using a regularized method described in [19] of the present article.

is substantially wider than the stopband. As has been shown in the theoretical investigation [72], either acceleration or inhibition of the spontaneous decay of a molecule with a wide spontaneous emission spectrum can be observed in a photonic crystal, depending on the mutual position of the PBG and fluorescence spectrum. Taking into account that polymer-filled opal shows an angular-dependent stopband, and dye molecules assume random orientations and positions with respect to the unit crystal cell, the above considerations can well explain the observed nonexponential spontaneous emission decay of organic molecules embedded in the photonic crystal. It should be emphasized that dye molecules in a rigid environment have fixed directions of emission dipole moments, and therefore, the modification of the spontaneous emission rate of a particular molecule should depend not only on its position but also on the orientation as well. In the case of random molecular position and orientations the effect of an imperfect photonic crystal will result in a distribution of modified radiative rates possibly containing both inhibited and enhanced spontaneous emission probabilities.

C. Nanocrystals Embedded in Opals

Nanoparticles of II–VI, V–III, and other semiconductor compounds (quantum dots), emit visible light upon optical excitation and can be embedded in opal-based photonic crystals upon dissolution in liquids or polymers. Optical properties of these species are determined by quantum confinement effects on the energy and probability of optical transitions [73], [74]. Typically, quantum yields of quantum dot luminescence do not exceed a few percent, and decay kinetics are strongly nonexponential due to a number of nonradiative relaxation processes. Ensembles of semiconductor nanocrystals, depending on the material and synthesis conditions, exhibit luminescence spectra with widths ranging from tens to thousands cm^{-1} [73]. However, as opposed to fluorescence spectra of dye molecules, nanocrystal photoluminescence is substantially inhomogeneously broadened due to a size distribution and some other factors: typical inhomogeneous-to-homogeneous width ratios for nanocrystal ensembles are of the order of ten or higher. Because of the substantial difference between electron de Broglie and photon wavelengths, the electron and photon densities of states can be engineered separately within one and the same mesoscopic structure. In addition to quantum dots or quantum wells in microcavities, simultaneous confinement of electrons and photons with separately controllable electron and photon energy bands can be realized in photonic crystals doped with quantum dots [49]–[51]. Interplay of electron and photon confinement within one and the same structure opens up a way toward novel light sources with controllable spontaneous emission.

In [49], we experimentally realized overlapping size-dependent electron resonance in nanocrystals and structural optical resonance in a photonic crystal by filling opal with an aqueous colloidal solution of CdTe nanoparticles. Due to the size restriction, the absorption spectrum of CdTe nanocrystals shifts by more than 1 eV compared to the bulk semiconductor (from 827 nm in bulk CdTe to 460–500 nm in nanocrystals)

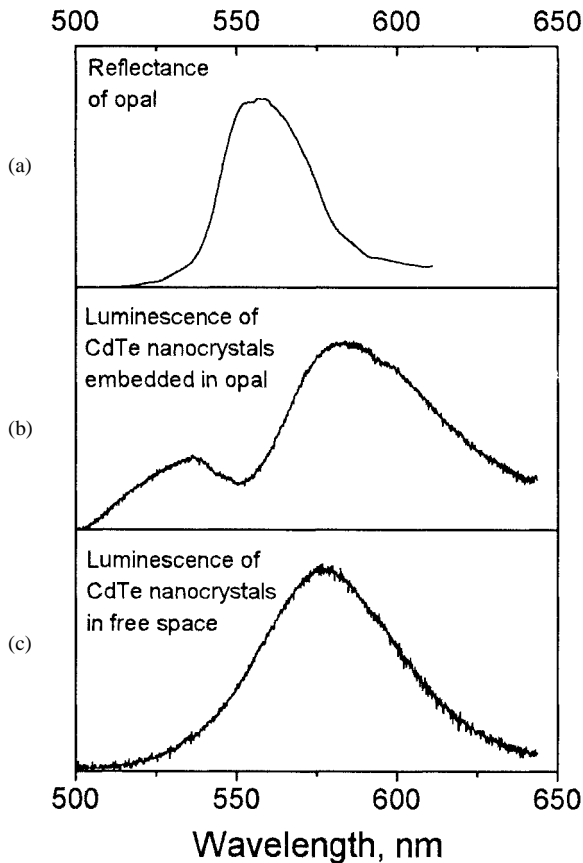


Fig. 7. Modification of the spontaneous emission of CdTe nanocrystals embedded in opal. (a) Optical reflection spectrum of opal sample, (b) modified spontaneous emission spectrum of CdTe nanocrystals in opal, and (c) reference emission spectrum of CdTe nanocrystals in free space.

[75]. In the context of quantum-size effects, this is a typical strong confinement regime when kinetic energies of electrons and holes are substantially larger than the energy of the electron-hole Coulomb interaction. Because of the pronounced size dependence, the emission spectrum of quantum dots can be tuned to overlap the stopband of a photonic crystal. The intrinsic emission band peaking at 575 nm dominates in the luminescence spectrum of CdTe nanocrystals which exhibits a substantial inhomogeneous broadening and shows strongly nonexponential decay kinetics with lifetimes spanning the range from 10^{-10} to 10^{-7} s [76].

Quantum dots embedded in a photonic crystal exhibit a noticeable change in the luminescence spectrum when the latter overlaps the optical stopband in opal (Fig. 7). Our experiments clearly show a dip in the emission spectrum correlating with the spectral position of the stopband, i.e., inhibition of the spontaneous emission of semiconductor nanocrystals embedded in opal takes place as result of a modified photon DOS within this spectral region. An increase in the numerical aperture of optics used for collecting CdTe luminescence in the photonic crystal from 0.25 (as in Fig. 7) to unity, leads to disappearance of the dip in the emission spectrum due to the angular dependence of the stopband [77]. Although the shape of the emission spectrum of quantum dots in the photonic crystal is modified at the edges of the stopband as

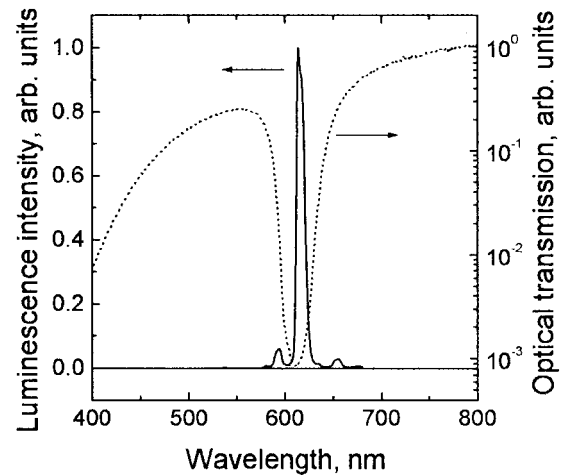


Fig. 8. Luminescence spectrum of $\text{Eu}^{3+}\text{-(HFAC)}_3\text{-(TOPO)}_2$ complex in toluene superimposed with the optical transmission spectrum of a toluene-filled opal sample.

well (see Fig. 7), additional studies are necessary to make an unambiguous conclusion on the presence of an enhanced spontaneous emission at the edges of the stopband.

Other aspects of semiconductor-doped opals including enhancement of the stopband and optical gain are discussed in [78], [79].

D. Doping of Opal-Based Photonic Crystals with Rare-Earth Ions

Rare-earth ions have high quantum yields and in the absence of quenching show single-exponential decay kinetics with lifetimes lying in the milli- or microsecond range. They exhibit narrow spontaneous emission lines, which is favorable for their use as spontaneously emitting probes for investigation of opal-based photonic crystals. Rare-earth ions can be embedded in porous structures either by sol-gel reactions [80] or in the form of complexes with organic ligands [81], the latter providing an efficient shielding of the rare-earth ion from quenching effects of the environment.

Recently, we started investigations of the spontaneous emission of rare-earth ions embedded in opal-based photonic crystals. In our experiments, we use the $\text{Eu}^{3+}\text{-(HFAC)}_3\text{-(TOPO)}_2$ complex consisting of a Eu^{3+} ion with three hexafluoroacetylacetonate ligands and two trioctylphosphine molecules as synergistic agents [81]. The complex has an intense absorption band at about 300 nm due to the organic ligands. The energy absorbed by the ligands is nonradiatively transferred to the Eu^{3+} ion which exhibits a strong narrow luminescence line in the vicinity of 613 nm due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electric dipole transition (Fig. 8). Due to the shielding of the Eu^{3+} ion from the environment by the ligands, the $\text{Eu}^{3+}\text{-(HFAC)}_3\text{-(TOPO)}_2$ complex in hydrocarbon solvents exhibits a high luminescence quantum yield (of about 0.95 [14]) and a single-exponential luminescence decay in the submillisecond range closely following a single-exponential law over the intensity range exceeding three decades. Thus, the $\text{Eu}^{3+}\text{-(HFAC)}_3\text{-(TOPO)}_2$ complex is an attractive probe for investigating the effect of opal-based photonic crystals on the spontaneous emission.

First, preliminary experiments with opals impregnated with solutions of Eu^{3+} -(HFAC)₃-(TOPO)₂ in solvents with refractive indexes close to 1.50 did not reveal substantial changes in the decay kinetics of the complex, in contrast to our experiments with the NBIA dye in the polymer-filled opal (vide supra). However, two following reasons may be responsible for this effect. First, as has been pointed out above, the direction of the emission dipole moment of the Eu^{3+} ion fluctuates on its excited-state lifetime scale (see, e.g., discussion in [13]), and thus this probe senses only the angular-averaged local photon DOS which undergoes substantially smaller changes in the photonic crystal compared to the free space than the angular-dependent local photon DOS [66]. Second, the spatial diffusion of the europium complex in the liquid solution on its excited-state lifetime scale may smear out the effect of strong spatial variations [66] of the local photon DOS in the photonic crystal on the spontaneous decay kinetics.

An increase in the dielectric contrast between the silica opal and the filling liquids should lead to a stronger modification of the local density of photon states in the photonic crystal, and modification of the spontaneous emission of europium ions may be observed in this case despite the fluctuating orientation of the emission dipole moment and spatial diffusion of the probe in the solution. Experiments on the spontaneous emission Eu^{3+} -(HFAC)₃-(TOPO)₂ in higher-refracting solvents filling opals are in progress.

IV. CONCLUSIONS AND OUTLOOK

First experiments with opal-based structures as prototypes of 3-D photonic crystals can be summarized as follows. Opals possess a stopband in the visible range which can be enhanced by impregnating with high-refractive materials and by making high-refractive replicas using opals as templates.

Modification of the spontaneous emission of dye molecules embedded in opal-based photonic crystals does take place. Molecules embedded in opal-based photonic crystals exhibit dips in spontaneous emission spectra. Dye molecules embedded in opal-polymer photonic crystal show 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.

Novel mesoscopic structures with separately controllable densities of photon and electron states can be developed when opal-based photonic crystals are doped with semiconductor nanoparticles. Spontaneous emission of nanocrystals which is controlled at large by the quantum confinement effect experiences strong modification due to modified photon density of states in opal-based photonic crystals.

Further progress toward observation of the modified spontaneous emission in 3-D photonic crystals can be foreseen with the use of high-refractive opal replicas and narrow-band light emitters, e.g., rare-earth ions.

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