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Fluorescence of Dye Molecules Embedded in a Photonic Crystal

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Abstract. Modification of fluorescence spectra and decay kinetics of dye molecules embedded in artificial opals is interpreted in terms of redistribution of the photon density of states.

1. Introduction

In is well known that the spontaneous emission can be modified in inhomogeneous optical environments such as interfaces, dielectric slabs, microcavities, etc., and can be strongly suppressed in periodic dielectric structures (photonic crystals) due to changes in the photon density of states (DOS) as compared to the free space (see, e.g., [1]). Despite a number of works devoted to modification of the spontaneous emission in 1D and 2D structures, effects of 3D photonic band structures were left almost unexplored, except for Ref. [2], where inhibition of the spontaneous emission of dye molecules in a 3D aqueous colloidal polystyrene crystal was observed. However, it has been found in [3] that the fluorescence lifetime modification observed in [2] is mainly due to intermolecular interactions of dye molecules with polystyrene and reabsorption of fluorescence.

We have recently shown that artificial opals consisting of submicrometer-sized amorphous silica globules arranged in an fcc lattice are promising structures for the photonic band engineering [4]: they exhibit a pronounced stop band in the visible range which manifests itself in optical transmission and reflection experiments and affects fluorescence spectra of embedded dye molecules. In the present paper, we report on the effect of 3D solid-state photonic crystals on the spontaneous emission of dye molecules.

2. Experimental Methods

Artificial opals were fabricated using a standard technology described elsewhere [5]. In the first set of experiments [4], Rhodamine 6G (R6G) dye molecules were embedded in opals by impregnating samples with an ethanol dye solution and
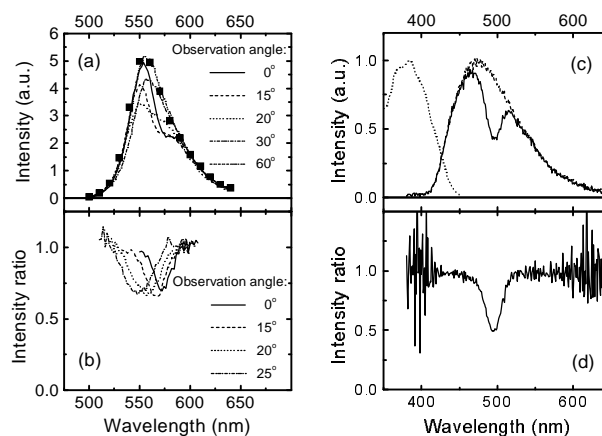
Fig. 1. (a) Fluorescence of R6G molecules embedded in opal sample measured at different observation angles and the "vacuum" spectrum (squares) recorded in an opal sample with the stop band located well to the blue from R6G fluorescences (a), and (b) their ratios; (c) fluorescence emission of NBIA in PMMA filling voids in opal (–) and fluorescence excitation (λ_{em}=500 nm) (···) and emission (---) spectra of the dye in a reference polymer film, and (d) ratio of fluorescence intensities of NBIA/PMMA solution in opal and free-standing film. λ_{ex}=337.1 nm.

subsequent evaporation of the solvent. In the second set of experiments [6], a photonic crystal was fabricated by filling voids in opal by a solid solution of 1,8-naphthoylene-1′,2′-benzimidazole (NBIA) dye in poly(methyl methacrylate) (PMMA). An optically thick polymer film was prepared from the same solution to perform reference measurements. Dissolution of the dye in the polymer eliminates uncontrollable dye–silica interactions and thus makes it possible to study the fluorescence of molecules in an identical chemical environment. In addition, NBIA fluorescence and absorption spectra overlap insignificantly, which makes it possible to avoid multiple reabsorption and reemission of fluorescence.

3. Results and Discussion

Steady-state fluorescence spectra of both R6G and NBIA dyes embedded in opal samples with stop bands overlapping the dye fluorescence show pronounced angular-dependent dips (Fig. 1) with positions corresponding to those of stop bands.

Time-resolved fluorescence investigations revealed a slowing down by a factor of ~1.5 of the fluorescence decay of R6G molecules in an opal sample with the photonic stop band overlapping the fluorescence spectrum compared to the sample with the stop band located well to the blue from the R6G fluorescence. We concluded, however, that the effect is most likely explained by an interplay of modification of the photon DOS, reabsorption and reemission of fluorescence due to the strong overlap of absorption and emission spectra of the R6G dye, and possible differences in intermolecular interactions of dye molecules with the silica surface in different opal samples.
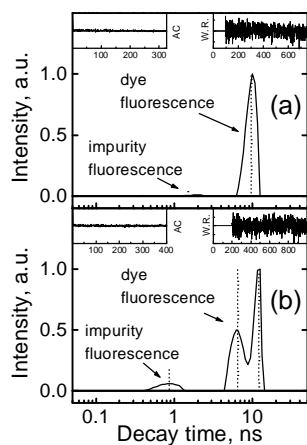
Fig. 2. Decay time distributions of NBIA fluorescence: (a) in free-standing polymer film and (b) in polymer network filling voids in opal. Results of two- (a) and three-exponential (b) analysis of the same decay curves are shown by dotted lines. Insets show plots of weighted residuals (WR) and their autocorrelation function (AC). $\lambda_{ex}=337.1$ nm, $\lambda_{em}=510$ nm.

An analysis of fluorescence kinetics of the solid solution of NBIA in PMMA filling voids in opal revealed both accelerated and inhibited components as compared to the dye fluorescence in the reference polymer film (Fig. 2). Taking into account that dye molecules are randomly oriented within opal and that opals show angular-dependent stop bands, one can expect that the spontaneous emission rate of a molecule will depend on its orientation with respect to the elementary crystal cell due to the angular dependence of the photon DOS, which is supported by numerical investigations [7].

4. Conclusions

Thus, we conclude that modification of the photon density of states can lead to both inhibition and acceleration of the spontaneous emission of dye molcules embedded in in photonic crystals.

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