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Invited Paper

Spontaneous emission of organic molecules and semiconductor nanocrystals in a photonic crystal

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Abstract

Photonic crystals based on artificial colloidal silica crystals (opals) exhibit pronounced stop bands for electromagnetic wave propagation and the corresponding modification of the photon density of states in the visible range. Doping of these structures with dye molecules and semiconductor nanoparticles (quantum dots) provides a possibility to examine the predictions of the inhibited spontaneous emission in photonic band-gap materials. First experiments are reviewed in which pronounced modification of spontaneous emission spectra and noticeable changes in decay kinetics were observed. © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Spontaneous emission of light is not an intrinsic property of the matter but rather a result of its interaction with the field, i.e. it is essentially the stimulated emission due to the 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 will be either enhanced or inhibited. Since the first prediction of inhibited spontaneous emission in a periodic medium [1] and the development of the photonic crystal concept [2,3], many experimental efforts have been made by various groups to develop threedimensional dielectric structures with a period of the order of optical photon wavelengths and to investigate spontaneous emission of light by molecules embedded therein [4-14]. In these experiments, self-assembled colloidal structures are used as prototypes for three-dimensional photonic crystals. In the present contribution, we summarize experimental results [5-9] on spontaneous emission of organic dye molecules and semiconductor nanocrystals embedded in silica-based colloidal structures providing a photonic pseudogap within the intrinsic spontaneous emission spectrum of the probe species.

2. Experimental

Natural and artificial silica colloidal crystals (gem opals) possess three-dimensional periodicity on the

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Fig. 1. Lattice of voids of opal presented as a combination of spherical elements. Spheres correspond to tetrahedral and octahedral voids. The diameters of cylinders correspond to the minimum cross section of channels between the voids.

submicron scale resulting in well-known iridescent colors related to interference of light. The synthesis of opals includes fabrication of monodisperse spherical silica globules, prolonged sedimentation of a colloidal solution providing self-assembling of globules into a close-packed crystalline structure, and a thermal treatment providing formation of a mechanically robust crystal. After a hydrothermal treatment and annealing, point contacts between the globules are converted into faceted ones. Voids between the globules form a regular sublattice (Fig. 1) which can be filled with liquid or solid inclusions.

Structures fabricated in such a manner consist of nearly spherical silica clusters with size ranging from 0.2 to 0.3 mm which are arranged in the face-centered cubic (FCC) lattice. 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 of silica globules ranges from the value n = 1.45 inherent in bulk silica down to $n_{\rm eff} = 1.26$. Opals show a dip (stop band) in the optical transmission spectrum with the spectral position depending on the lattice period and on the *n* value. This can be understood in terms of Bragg diffraction of optical waves. From a different viewpoint, formation of a pronounced stop band is indicative of a reduced density of propagating electromagnetic modes (photon density of states (DOS)) inside the structure.

The network of interconnected voids in opals can be filled with materials having refractive indices different from those of the silica globules. Therefore, it is possible to control the spectral position and contrast of the optical stop band. With increasing the refractive index of a substance filling the voids compared to that of the globules forming the opal lattice, the spectral position of the stop band shifts linearly toward longer wavelengths. 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 10³ for a 0.5mm-thick sample, the spectral width being 40 nm at the 10% transmission level for the stop band centered at 500 nm. Enhancement of the stop band in opals filled with high-refractive substances agrees with both a simple consideration based on multiple wave scaterring in a quasicrystalline structure [5,6] and thorough analyses of photonic band structures of different three-dimensional lattices [15,16]. These theoretical investigations have shown that three-dimensional 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 FCC lattice). The spectral position and the magnitude of the stop band also depend on the angle between the direction of propagation of light and crystal axes.

Luminescence of opal-based photonic crystals was investigated using pulsed nitrogen and continuous-wave argon laser excitation. The angular aperture of luminescence collection was adjusted by means of different objectives, the numerical apperture being in the range of 0.25–1. Time-resolved measurements were performed in the analog mode using a fast-response photomultiplier and a boxcar integrator for fluorescence signal detection. To ensure a 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.

3. Molecules embedded in opal-based photonic crystals

We have observed modification of spontaneous emission spectra of Rhodamine 6G (R6G) and 1,8-naphthoylene-1',2'-benzimidazole (NBIA) dyes by opal-based photonic crystals [7,8]. Embedding fluorescing dye molecules in normal and inverted opals leads to the appearence of pronounced angular-dependent dips in dye fluorescence spectra (Fig. 2) with positions corresponding to those of optical stop bands in the opal-based photonic crystals.

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 reemission of fluorescence photons, which may give rise to an apparent increase in the fluorescence lifetime and can be mistakenly interpreted as the photonic crystal effect. An increase in the fluorescence lifetime of R6G in a dry opal with the stop band overlapping the emission spectrum of the dye was tentatively explained by multiple reabsorption and



Fig. 2. Fluorescence of molecules embedded in opal-based photonic crystals: (a) emission (-) spectrum of NBIA in PMMA-filled opal, and excitation ($\lambda_{em} = 500 \text{ nm}$) (- -) and emission ($\cdot \cdot \cdot$) spectra of the dye in a reference polymer film, and (b) ratio of fluorescence intensities of NBIA in PMMA-filled opal and in a free-standing PMMA film. $\lambda_{ex} = 337.1 \text{ nm}$. The spectra were detected within an aperture of 0.09 π sr.

reemission of fluorescence photons by R6G molecules having strongly overlapping excitation and emission spectra.

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. 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 the polymer ($n_{PMMA} = 1.490$ versus 1.30 for silica globules) provides a transition from the lattice of high-refracting spheres to its replica (Fig. 1) which, as has been pointed out above, is important for obtaining a stronger modification of the photon DOS.

We have observed modification of the spontaneous emission kinetics of NBIA molecules embedded in this opal-polymer photonic crystal (Fig. 3). The excited-state decay of the NBIA dye is exponential in the reference polymer film, whereas both accelerated and inhibited decay components appear in the spontaneous emission kinetics of dye molecules embedded in the opal sample.

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 in the photonic crystal. According to the sum rule for the spontaneous emission rate derived for an arbitrary optically inhomogeneous environment [17], a photonic crystal just redistributes the spontaneous radiation power over the spectrum. Furthermore, the radiation power of a dipole embedded in a photonic crystal depends strongly on the position and orientation



Fig. 3. Decay time distributions (gray shapes) recovered from NBIA fluorescence kinetics: (a) in free-standing polymer film and (b) in opal-polymer photonic crystal. 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 functions (AC). $\lambda_{ex} = 337.1$ nm, $\lambda_{em} = 510$ nm.

of the emitter with respect to a unit crystal cell [18]. In addition, the fluorescence spectrum of the dye used in the investigation is substantially wider than the stop band. Either acceleration or inhibition of the spontaneous decay is expected depending on the mutual position of the photonic band gap and fluorescence spectrum. These considerations can explain the observed nonexponential spontaneous emission decay.

4. Nanocrystals embedded in opals

Three-dimensional spatial confinement of electrons in nanocrystals ("quantum dots") results in size-dependent energies and probabilities of optical transitions [19,20]. Because of the substantial difference between electron and photon wavelengths, the electron and photon DOS can be engineered separately within one and the same mesoscopic structure.

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 of diameter ranging from 1.8 to 2.4 nm shifts by more than 1 eV compared to the bulk semiconductor. In the context of quantum-size effects, this is a typical strong confinement regime when kinetic



Fig. 4. Modification of the spontaneous emission of CdTe nanocrystals embedded in opal. Nanocrystal mean diameter is 2.4 nm. (a) Optical reflection spectrum of opal sample; (b) modified spontaneous emission spectrum of CdTe nanocrystals in opal; (c) reference emission spectrum of CdTe nanocrystals in free space.

energies of electrons and holes are substantially higher than those of the electron-hole Coulomb interaction. Because of the pronounced size dependence, the emission spectrum of quantum dots can be tuned to overlap the stop band of a photonic crystal. The intrinsic emission band peaking at 575 nm dominates the luminescence spectrum of CdTe nanocrystals which exhibits a substantial inhomogeneous broadening and shows strongly non exponential decay kinetics described by distributions of lifetimes spanning the range of 10^{-10} - 10^{-7} s.

Nanocrystals embedded in a photonic crystal exhibit a noticeable change in the luminescence spectrum when the latter overlaps the optical stop band in opal (Fig. 4). Our experiments cleary show a dip in the emission spectrum correlating with the spectral position of the stop band, i.e., inhibition of the spontaneous emission of semiconductor nanocrystals embedded in opal takes place due to 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. 4) to unity, leads to disappearance of the dip in the emission spectrum due to the angular dependence of the stop band. Although the shape of the emission spectrum of quantum dots in the photonic crystal is modified at the edges of the stop band as well, additional studies are necessary to make an unambiguous conclusion on the presence of an enhanced spontaneous emission at the edges of the stop band. Because of the strong inhomogeneous broadening, complicated intrinsic decay law and low quantum yield of luminescence, the effect of the photonic pseudogap on decay rate of nanocrystals remains a challenging experimental problem.

5. Conclusion

Opals possess a stop band in the visible range which can be enhanced by impregnating these structures 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. The molecules exhibit dips in spontaneous emission spectra and nonexponential spontaneous decay kinetics containing both accelerated and inhibited components compared to the dye fluorescence in a reference homogeneous matrix. The results are interpreted in terms of redistribution of the photon DOS 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.

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

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