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Observation of inhibited spontaneous emission and stimulated emission of rhodamine 6G in polymer replica of synthetic opal

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We report the observation of inhibited spontaneous emission of organic dye rhodamine 6G infiltrated in a polymer replica of synthetic opal as a photonic crystal. The morphology-dependent resonances, superimposed on the broadband emission of rhodamine 6G due to spherical wavelength-sized microcavity enhancement of dye emission, have also been observed. © 1998 American Institute of Physics. [S0003-6951(98)02650-3]

The first observations of inhibited spontaneous emission in a cavity have stimulated great interest in cavity quantum electrodynamics effects.^{1–3} Theoretical prediction of photonic crystals with three-dimensional crystalline structure of the periodicity of the order of optical wavelength^{4,5} and various proposals of applications^{5–7} of their novel characteristics have opened new possibilities in this field from both scientific and practical viewpoints.

We have recently reported on the fabrication of synthetic opals with the periodicity of the order of several hundreds nm utilizing regular array of monodispersed SiO₂ spheres and their characteristics.⁸ We have also demonstrated that these synthetic opals as photonic crystals have nanoscale interconnected voids, and various materials such as fluorescent dyes, photochromic dyes, conducting polymers and liquid crystals can be infiltrated into the void space. Preliminary observations of the characteristics of these infiltrated opals have also been reported. In both the conducting polymer such as poly-(2,5-dialkoxypheylenevinylene) and fluorescent dye, rhodamine 6G infiltrated in opals, spectral narrowing was observed at several wavelengths, one of which is near the photoluminescent (PL) peak. The observed spectral narrowing and lasing were assumed to be due to the effect of the optical feedback in synthetic opal.⁹

The observations of inhibited spontaneous emission of organic dyes embedded in periodic dielectric structures were reported and interpreted in terms of the formation of a photonic pseudogap.^{10–12} On the other hand, the percolated porous structure of opals permits the preparation of a secondary structure—opal replica—by the filling of its voids with the semiconductor¹³ or by infiltration with the polymer.

In this letter, we report the observation of inhibited spontaneous emission of organic dye rhodamine 6G infiltrated in a polymer replica of synthetic opal as a photonic crystal. We have also observed the morphology-dependent resonances (MDR's), superimposed on the broadband emission of

rhodamine 6G due to spherical microcavity enhancement of the dye emission.

Mechanically robust porous opals fabricated by sedimentation of the suspension of monodispersed silica spheres 210 nm in diameter and subsequent annealing at 100–120 °C and sintering at 600–700 °C were cut into plates that were 10 mm in width, 8 mm in length and 1 mm in thickness. The opal prepared by this procedure has a face-centered-cubic (f.c.c.) crystal lattice structure and contains an interconnecting structure of tetrahedral and octahedral voids with characteristic sizes close to ideally structured opal [$(3/2^{1/2} - 1)D = 0.225D = 47$ nm and $(2^{1/2} - 1)D = 0.414D = 87$ nm, correspondingly]. These voids are fully interconnected by channels through hexagonal close-packed layers having the smallest diameter of $[2(3)^{-1/2} - 1]D = 0.155D = 33$ nm. That is, these types of opals have characteristics of highly porous transparent material. The opal replicas were prepared by filling its voids with optically transparent liquid photopolymer (refraction index $n = 1.56$). After polymerization, silica particles were etched in HF. Infiltrated polymer replicas with dye were prepared by dipping the replica into the methanol solution of the rhodamine 6G dye (5×10^{-2} mol/l).

An electron micrograph of the opal's replica was taken with an S-2100 Hitachi scanning electron microscope (SEM). The reflectance spectrum was evaluated using a PMA-11 (Hamamatsu Photonics). For observation of fluorescence emission and spectral narrowing, second harmonic generation light (532 nm) of a Nd:YAG laser (1.064 μm) of 10 ns in pulse width was used as an exciting light source. The emission from the infiltrated opal replica was measured utilizing a MultiSpec257 CCD detector (ORIEL). The spectral resolution of this system is 0.3 nm.

Figure 1(a) shows the SEM microphotograph of noninfiltrated opal replica. The hexagonal-type close packing of the hollow spherical cavities with small holes connecting the neighboring voids is clearly seen. The reflection spectra of the opal replicas filled with methanol showed sharp diffraction peaks at various observation angles [see Fig. 1(b)]. The periodicity of the opal replicas was evaluated from the diffraction peaks and coincided with the structure observed by

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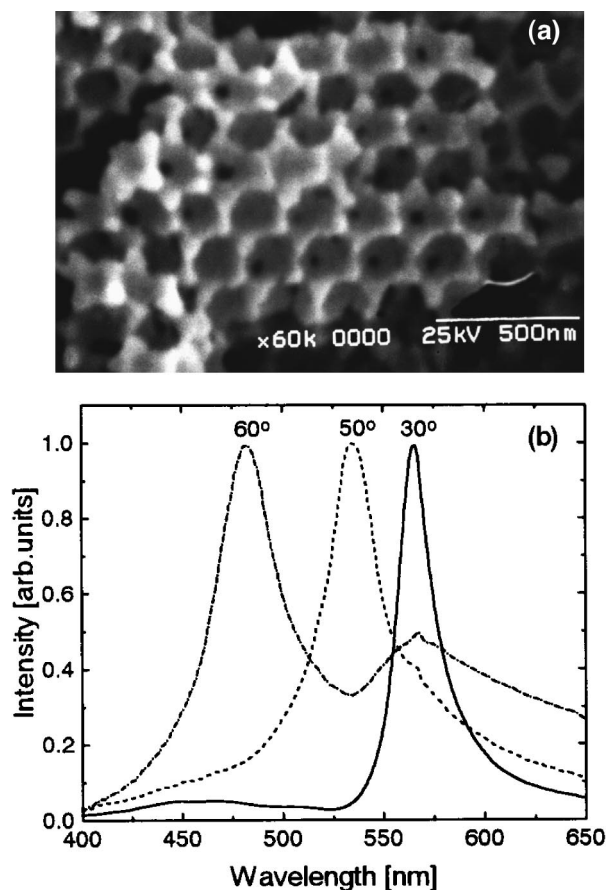


FIG. 1. Electron micrograph of opal's polymer replica (a) and the reflection spectrum of the opal replica filled with methanol at several observation angles: 30°, 50° and 60° (b).

electron microscopy. Two attenuation bands were observed in a polycrystalline sample at 60° due to higher order diffraction from other planes. The synthetic opal replicas were well infiltrated in their nanosize void space with methanol solution of rhodamine 6G.

The photoluminescence spectra of rhodamine 6G in methanol show a broadband at around 580 nm at low excitation intensity and emission spectral narrowing at high ex-

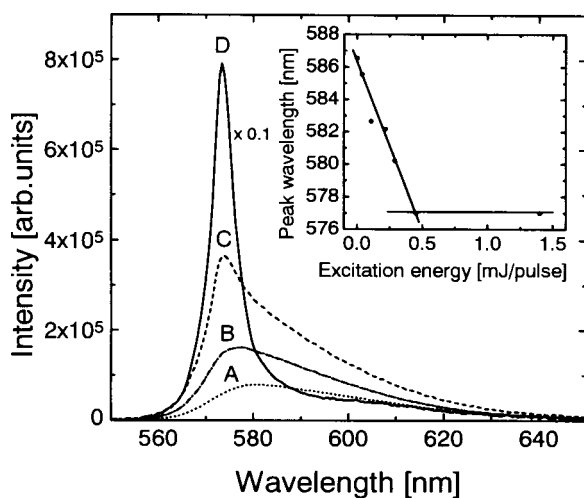


FIG. 2. Emission spectra of rhodamine 6G in toluene solution at various excitation intensities: (A) 0.29 mJ/pulse; (B) 0.45 mJ/pulse; (C) 1.4 mJ/pulse; and (D) 15 mJ/pulse.

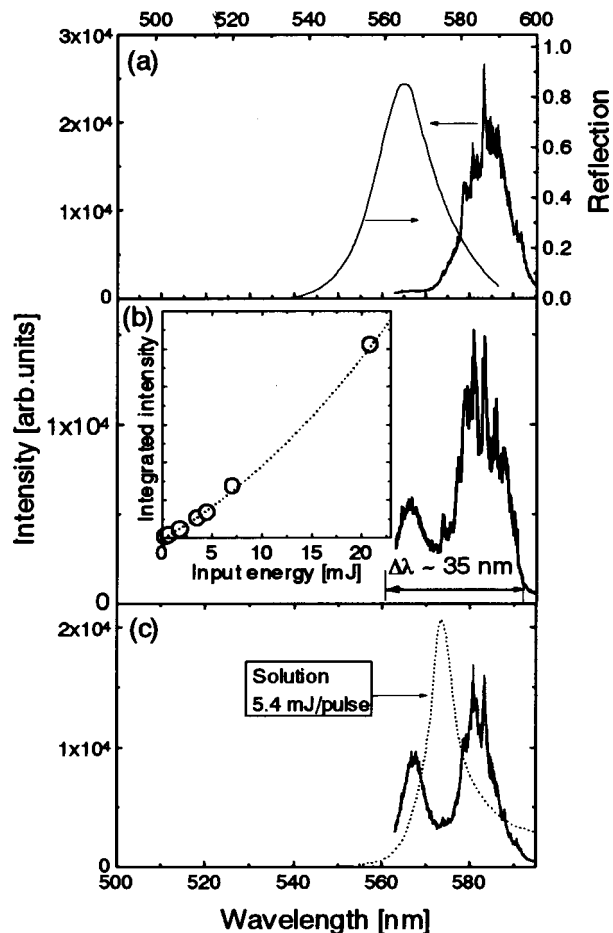


FIG. 3. Emission spectra of rhodamine 6G infiltrated in the opal at various observation angles: (a) 30°, (b) 50° and (c) 60°. Excitation power is 21 mJ/pulse. The inset in (a) shows the reflection spectrum at the same angle. The inset in (b) shows the integrated emission intensity dependence on the absorbed excitation energy/pulse. The inset in (c) shows the emission spectrum of the solution sample at 5.4 mJ/pulse for comparison.

citation intensity occurs at around 575 nm (see Fig. 2). The inset of Fig. 2 shows the dependence of the peak wavelength shift on excitation power. The threshold power was estimated about 0.5 mJ/pulse. This value is much lower than what we used in our experiments.

Figure 3 shows the emission spectra of rhodamine 6G infiltrated in the polymer replica at various observation angles: (a) 30°, (b) 50° and (c) 60°. The excitation power is 21 mJ/pulse. The inset in Fig. 3(a) shows the reflection spectrum of the polymer replica at the same angle. The spectral narrowing in the methanol solution of the rhodamine 6G with a concentration of 5×10^{-2} mol/l is also shown for comparison at an excitation power of 5.4 mJ/pulse in Fig. 3(c). It is evident from Fig. 3 that the dye emission is strongly inhibited in the range of 550–580 nm. Instead of a spectral narrow peak at 575 nm at high excitation power [see Figs. 3(c) and 2] we have observed a dip. The observed narrow peaks superimposed on the broadband fluorescence spectrum in the range of 580–595 nm can be attributed to morphology-dependent resonances of spherical microcavities and reflect the distribution of sizes and shapes of spherical voids in the opal replica.^{14,15} The inset in Fig. 3(b) shows the nonlinear integrated emission intensity dependence on the absorbed excitation energy/pulse. The threshold input power

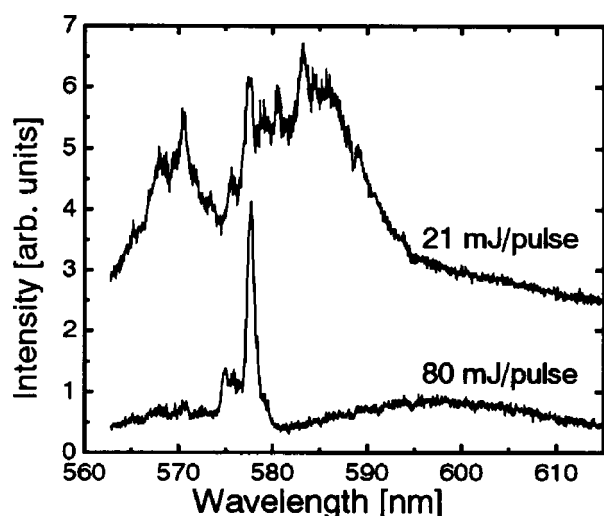


FIG. 4. Emission spectra of rhodamine 6G infiltrated in the opal's replica at high excitation power.

was estimated ≥ 0.5 mJ/pulse. The optical feedback in the polymer replica is provided by the reflection at the spherical liquid-polymer boundary. However, in our case the reflectance of the methanol/photopolymer interface is very low (0.65%) and the refraction index of the photopolymer ($n = 1.56$) is higher than that of the methanol solution ($n = 1.328$). So, the optical confinement factor is very low. This accounts for the very high excitation powers we used in our experiments. From the wavelength distribution of the MDR's ($\Delta\lambda \approx 35$ nm) we can estimate the range of diameters of spherical microcavities 210–225 nm that is a little bigger than the diameter of the original silica balls (210 nm). It should be mentioned that we could not properly resolve the MDR's superimposed on the broadband emission of rhodamine 6G due to the spherical cavity enhancement of the dye emission because of the low spectral resolution of our measuring system. As can be seen in Figs. 3(b) and 3(c), with an increasing observation angle the new attenuation band can be observed at about 575 nm. We suppose it is because of the polycrystalline nature of the polymer replica [see Fig. 1(b)].

In Fig. 4 we show the emission spectra of rhodamine 6G infiltrated in the polymer replica at high excitation power. The spectral narrowing at 578 nm was observed and accompanied by a total decrease of intensity. The position of this peak coincides with that of the solution (see Fig. 2). We suppose that this effect is caused by damage of the regular

polymer replica structure. Such structural damage was also observed visually under an intense electron beam in the scanning electron microscope. However, this effect supports the important role of the regular three-dimensional structure of the opal's replica in the inhibition of spontaneous emission.

In conclusion, the inhibited spontaneous emission of organic dye rhodamine 6G solution in methanol infiltrated in a polymer replica of synthetic opal as a photonic crystal was observed. We have also observed the MDR's superimposed on the broadband emission of rhodamine 6G due to the spherical cavity enhancement of the dye emission. The polymer replica presents a very interesting system of spherical wavelength-size microcavities regularly packed in the photonic crystal structure. The observation of inhibited spontaneous emission of the organic dye infiltrated in the polymer replica of the synthetic opal is a step toward the formation and study of real photonic crystals using a nanoscale supramolecular architecture of photonic crystals by sequential templating. A detailed study of the MDR's in polymer spherical microcavities of a higher quality factor is underway.

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