Evidence for braggoriton excitations in opal photonic crystals infiltrated with highly polarizable dyes

N. Eradat,[a] A. Y. Sivachenko,[b] M. E. Raikh, and Z. V. Vardeny
Department of Physics, University of Utah, Salt Lake City, Utah 84112

A. A. Zakhidov and R. H. Baughman
UTD NanoTech Institute, University of Texas at Dallas, Richardson, Texas 75083

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We studied angle-dependent reflectivity spectra of opal photonic crystals infiltrated with cyanine dye aggregates, which are highly polarizable media with very large Rabi frequency. We show that, at resonance condition between the exciton-polariton of the dye aggregate and the Bragg gap, the Bragg stop band decomposes into two reflectivity bands with a semitransparent spectral range in between, that is due to propagation of braggoritons inside the gap. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1479197]

Photonic crystals (PC),[1] and, in particular PC with a complete photonic band-gap (PBG)[2] have recently attracted much attention due to their rich physics and possible applications such as lasers, optical communication and tunable, high-reflectivity devices.[3,4] In these systems the periodicity of the dielectric function results in strong diffraction effects.[5] When Bragg conditions are met, a reflectivity plateau occurs within a certain frequency interval, $\pm\Delta\omega_B$ around the Bragg resonance, ω_B, where light propagation is inhibited [see Figs. 1(a) and 1(b)]. Among the main possible applications of PC is the fabrication of low threshold lasers,[6,7] since the photonic density of states can be enhanced for frequencies close to the PBG.[1] Photonic crystals with few planned defects are most suitable for laser action, since for defect-localized intragap photonic states the PC sample acts as a resonator with a very high quality factor.[6] However, photon propagation traffic in and out from the defect resonator has not been well developed.[7–11]

In this work we show that intragap light propagation in 3D PC is possible due to excitations, dubbed here braggoritons,[12] which are present *inside* the PBG when a *highly polarizable* medium with resonance frequency, $\omega_T \approx \omega_B$ is infiltrated into the PC.[13] These excitations are formed due to interaction between the Bragg gap and polariton gap. As a result, the Bragg reflectivity plateau splits into two peaks, with semitransparent spectral region in between. We demonstrate the existence of the braggoriton excitations in a 3D opal PC infiltrated with a cyanine dye that forms aggregates with very large Rabi frequency.[14,15]

The synthetic opal single crystals were cut from a polycrystalline sample obtained by slow sedimentation of a colloidal suspension of silica (SiO_2) spheres (mean diameter $D \approx 300$ nm, dispersion of about 4%) and subsequent sintering at 750 °C to achieve robust mechanical properties.[16] In the formed face-centered cubic (fcc) structure, Bragg diffraction off (*hkl*) crystal planes produces gaps in the photonic spectrum at ω_{hkl}.[17] However, due to the small contrast between the refraction indices of silica and air, opal PC does not possess a complete PBG. In general, the most pronounced stop band in synthetic opals occurs along the fast growing [111] direction,[17] and therefore we conduct our angle-dependent reflectivity measurements off the opal (111) planes.

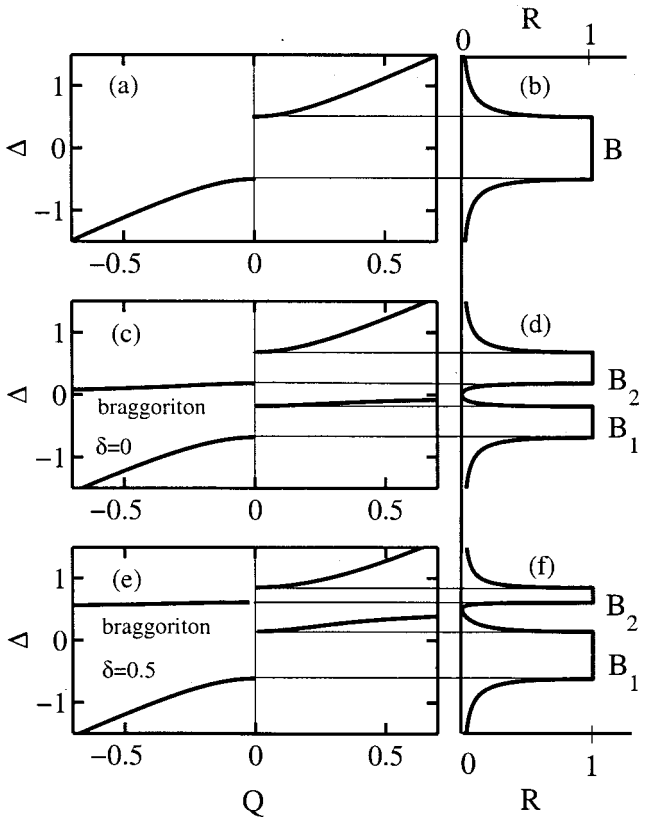

FIG. 1. Calculated dispersion relations $\Delta(Q)$, where Δ and Q are dimensionless frequency and wave vector, respectively and reflectivity spectra $R(\Delta)$ of an uninfiltrated (a) and (b), and infiltrated PC with polarizable medium (c)–(f). The dimensionless detuning between the Bragg and exciton/polariton gaps is $\delta=0$ for (c) and (d) and $\delta=0.5$ for (e) and (f); the coupling parameter $\alpha=0.5$ in both cases.

[a]Present address: Optical Sciences Center, The University of Arizona, 1630 East University Blvd., Tucson, AZ 85721.
[b]Present address: Myriad Proteomics, Inc., 2150 West Dauntless Ave., Salt Lake City, UT 84116.

The treatment of light propagation along the preferred [111] (or z) direction may be simplified by considering a one-dimensional periodicity of the dielectric function, $\varepsilon(z) = \varepsilon_0 + \delta\varepsilon\cos(Kz)$, where $\delta\varepsilon(\ll\varepsilon_0)$ is the modulation amplitude, ε_0 is the average dielectric function, $K = 2\pi/d$, and $d = D\sqrt{2/3}$ is the (111) interplane distance. It is easy to show,[3] that a gap with $\Delta\omega_B = \omega_B\delta\varepsilon/(2\varepsilon_0)$ centered at $\omega_B = cK/(2\sqrt{\varepsilon_0})$ is formed in the photon dispersion relation [see Fig. 1(a)]. The two photonic branches at the light wave vector k away from the Brillouin zone edge $K/2$ acquire the form $\omega^{(1,2)} = \omega_B \pm \sqrt{(2\omega_B/K)^2 q^2 + \Delta\omega_B^2}$, where $q = k - K/2 \ll k$.

These branches are plotted in Fig. 1(a); in Fig. 1(b) we plot the calculated Bragg stop band (B) in the reflectivity spectrum. It is worth noting that if light propagates at an angle θ with respect to z, then the Bragg stop band blueshifts, $\omega_B(\theta) = \omega_B(0)[\varepsilon_0/(\varepsilon_0 - \varepsilon_1\sin^2\theta)]^{1/2}$, where ε_1 is the dielectric constant of the surrounding medium. Our opal PC had a Bragg stop band in air at about 660 nm at $\theta = 0$ and at about 560 nm at $\theta = 45°$.[18]

The photon dispersion relations and the reflectivity spectrum drastically change[12] when a polarizable medium with a dielectric function $\varepsilon(\omega) = \varepsilon_\infty[1 - \omega_{LT}/(\omega - \omega_T)]$ is infiltrated into the opal. Here, ω_T is the transverse frequency, ω_{LT} is the longitudinal-transverse frequency splitting (with a Rabi frequency splitting $\Omega_P = \sqrt{\omega_T\omega_{LT}/2}$), and ε_∞ is the high frequency dielectric constant. In this case, if the dimensionless frequency detuning, $\delta = (\omega_T - \omega_B)/(2\Delta\omega_B)$, is not too large (i.e., $\delta < 1$), then the light dispersion relations near ω_B contain *four* branches given in a concise form by:[12]

$$Q = \sqrt{\left(\Delta - \frac{\alpha^2}{\Delta - \delta}\right)^2 - \frac{1}{4}}, \tag{1}$$

where $Q = (\omega_B/K\Delta\omega_B)q$ is the dimensionless wave vector, $\alpha = \Omega_P/2\Delta\omega_B$ is the Bragg-polariton coupling constant, and $\Delta = (\omega - \omega_B)/(2\Delta\omega_B)$ is the dimensionless frequency. These dispersion relations are plotted in Fig. 1(c) for a detuning $\delta = 0$; the calculated reflectivity spectrum is shown in Fig. 1(d). It is evident from Fig. 1(c) as well as from the formation of the transparent spectral range between the two reflectivity plateaus B_1 and B_2 in Fig. 1(d), that the braggoriton excitations emerge *inside* the original unperturbed photonic gap.

For a detuning $\delta \neq 0$ the branches lose their symmetry[12] [Fig. 1(e)]; this can also be seen in the reflectivity spectrum [Fig. 1(f)]. By changing the light impinging angle θ with respect to the [111] direction, the detuning δ between the Bragg and polariton gaps may be easily changed in opals since $\omega_B(\theta)$ changes with θ (see above), whereas ω_T remains unaffected.[19] We use this mechanism for measuring the dispersion of the braggoriton excitations with θ.

For these measurements we infiltrated a large single crystal opal with the cyanine dye NK-2567, or 2,2′-dimethyl-8-phenyl-5,6,5′,6′-dibenzothiacarbocynine chloride, the chemical structure of which is shown in Fig. 2(b), inset. When a thick chloroform solution of NK-2567 is casted into films on glass substrates, then the dye molecules readily form J aggregates characterized by a redshifted absorption (or reflectivity) band at $\omega_T \approx 700$ nm and by greatly diminished photoluminescence band. Under these conditions

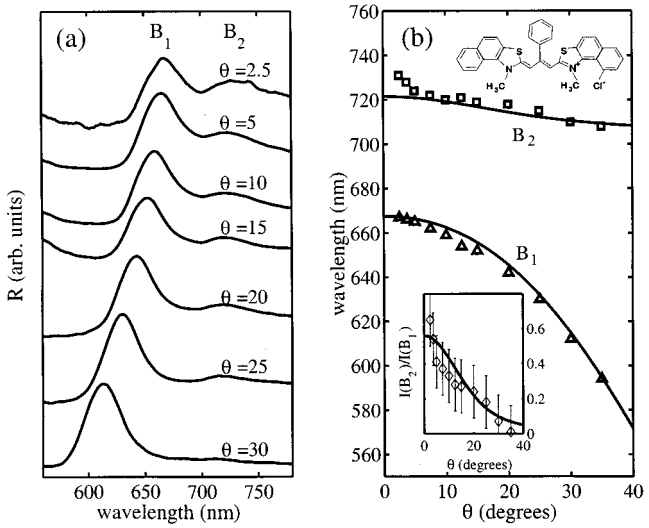

FIG. 2. (a) Evolution of bands B_1 (Bragg-like) and B_2 (polariton-like) in the reflectivity spectra of an opal PC infiltrated with J aggregates of NK-2567 cyanine [inset (b)] with the light impinging angle, θ respect to the opal [111] direction. The frequency dispersion and relative strengths of B_1 and B_2 bands with θ are summarized in the (b) and (b) inset, respectively, where the lines through the data points are calculated using the braggoriton model.

the reflectivity spectrum can be measured with little or no interference from the emission band.[15] The cyanine molecules were infiltrated inside the opal PC and J-aggregate formation was achieved by repeated pulling of the sample through a thick dye solution in chloroform.[18] Uninfiltrated molecules were washed out from the sample surface to eliminate their reflectivity peak in the spectrum, which interferes with the braggoriton bands.[19] The crystal was embarked on a θ–2θ homemade goniometer, where an incandescent, well-collimated light beam was directed at an angle θ with respect to the [111] direction. The reflected beam at 2θ was dispersed by a monochromator (0.25 m) and its intensity was measured by a Si photodiode and a lockin amplifier.[18] At $\theta = 0$ the uninfiltrated opal showed a [111] Bragg stop band in the reflectivity spectrum at $\omega_B(0) \approx 660$ nm; this band redshifted to $\omega_B(0) \approx \omega_T \approx 700$ nm after infiltration due to the increase in ε_0.

Figure 2(a) shows the reflectivity spectra of the aggregated cyanine-infiltrated opal for θ ranging from 2.5° to 30°. At large θ, when $\omega_B(\theta) > \omega_T$, the detuning δ is large and the Bragg stop band (B_1) dominates the reflectivity spectrum. However, as θ decreases, $\omega_B(\theta)$ red shifts towards ω_T so that the detuning δ decreases and consequently the Bragg/polariton interaction becomes important. Thus, at decreasing θ another band (B_2) is formed with increasing relative intensity [Fig. 2(b), inset]. At the same time the dispersion of peak B_1 slows down, whereas the dispersion of peak B_2 increases [Fig. 2(b)]. The reason that only a moderate dip between the split reflectivity bands is observed [Figs. 1(d) and 1(f)] is the unavoidable disorder in the opal sample, which tends to smear out sharp spectral features.[20]

Using Eq. (1),[12] we fit the frequencies of the Bragg-like (B_1) and polariton-like (B_2) reflectivity peaks and their relative intensities versus θ. Far from resonance the Bragg–polariton interaction is weak and the reflectivity peaks are governed by ε_0 and δ. The apparent split between the reflectivity peaks at resonance condition critically depends on α,

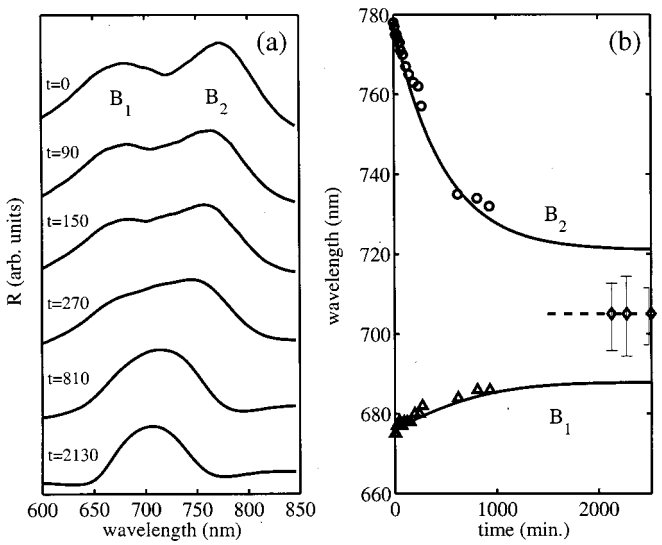

FIG. 3. (a) Reflectivity spectra of aggregated NK-2567 dye infiltrated into opal measured at $\theta=0$ and different illumination times, t (minutes) using a strong incandescent light to gradually bleach the dye molecules. (b) The dependence of B_1 (triangles) and B_2 (circles) peak wave lengths on t; the diamond symbols stand for the collapsed band at large t, when B_1 and B_2 cannot be separated any more. The lines through the data points are calculated.

and their relative intensity is very sensitive to δ [see Figs. 1(d) and 1(f)]. The calculated curves are shown in Figs. 2(b) and the 2(b) inset. The excellent agreement of the braggoriton model with the experimental data was achieved using $\omega_B=684$ nm, $\Delta\omega_B=20$ nm, $\omega_T=703$ nm ($\delta=-0.46$ at $\theta=0$), and $\varepsilon_0=1.4$. The relatively strong Bragg–polariton coupling $\alpha=0.57$ that we obtained results in a Rabi splitting $\Omega_P=60$ meV for the infiltrated density of NK-2567 J aggregates, in good agreement with that of Ref. 15.

The coupling α can be readily varied by changing the density, N of the infiltrated cyanine molecules,[18] since the Rabi splitting, Ω_P is proportional to $\sqrt{\omega_{LT}}$, with $\omega_{LT}\propto N$. We directly demonstrate the correlation between the bands B_1 and B_2 by observing the temporal evolution of the reflectivity spectrum of the infiltrated opal at $\theta=0$ illuminated with a strong incandescent light source, which is used here to gradually bleach N and consequently reduce α with time, t [Fig. 3(a)]. It is seen that peaks B_1 and B_2 approach each other with time [see Fig. 3(b)]. At long times they collapse into a single broad Bragg reflectivity band centered at about 700 nm [Fig. 3(a)]. This time resolved reflectivity spectrum can be fit [Fig. 3(b)] using an exponentially decaying density, $N(t)=N(0)\exp(-t/\tau)$ with $\tau=425$ min, and $\alpha(0)=0.75$. The excellent fit shown in Fig. 3(b) was achieved when we considered the time dependent dielectric function, $\varepsilon_0(t)=1.5+0.16\exp(-t/\tau)$; we also used $\omega_B(0)=742$ nm and $\Delta\omega_B(0)=31$ nm at $t=0$. The good agreement between experiment and theory unambiguously shows that the two reflectivity bands are correlated, and therefore the braggoriton approach used here is the correct model.

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