Evidence for Braggoriton Excitations in Opal Photonic Crystals Infiltrated with Highly Polarizable Dyes

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We studied angle-dependent reflectivity spectra of opal photonic crystals infiltrated with cyanine dyes, which are highly polarizable media with very large Rabi frequency. We show that when resonance conditions between the exciton-polariton of the infiltrated dye and Bragg frequencies exist, then the Bragg stop band decomposes into two reflectivity bands with a semi-transparent spectral range in between that is due to light propagation inside the gap caused by the existence of braggoriton excitations. These novel excitations result from the interplay between the Bragg gap with spatial modulation origin and the polariton gap due to the excitons, and may lead to optical communication traffic inside the gap of photonic crystals via channel waveguiding.

Photonic crystals (PC) and in particular PC with a complete photonic band gap (PBG) have recently attracted much attention due to their rich physics and possible applications such as lasers, optical communication and tunable, high reflectivity devices. In these systems the dielectric function is periodically modulated and consequently light diffraction effects dominate their optical properties. When Bragg diffraction conditions are met then light scattering is very strong so that a reflectivity plateau occurs within a certain frequency interval, \( \Delta \omega_B \) around the Bragg resonance, \( \omega_B \), 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, since the photonic density of states can be enhanced for frequencies close to the PBG. Photonic crystals that contain few planned defects are most suitable for laser action, since defects cause localized intragap photonic states for which the PC sample acts as a resonator with a very high quality factor, \( Q \). However, photon propagation traffic in and out from the defect-resonator has not been well developed for three-dimensional (3D) PC. In fact there has been only little experimental progress on light propagation inside the PBG and mostly for line defects in 2D PC.

In this work we demonstrate a way by which light can, in fact communicate with a high \( Q \) laser resonator with frequency inside the gap of a 3D PC. In particular we show that intragap light propagation in 3D PC may be controlled by wave-guiding due to novel excitations, dubbed here braggoritons, which are present inside the PBG when the PC is infiltrated with a highly polarizable medium having strong coupling to light. PC’s infiltrated with polarizable media having weak light coupling were treated in Ref. [13]. The braggoriton excitations are formed through the interaction between the Bragg gap due to spatial modulation and polariton gap due to the excitons, when their characteristic frequencies (\( \omega_B \) and \( \omega_T \), respectively) are close to each other. As a result, a semi-transparent spectral region is formed inside the gap, which splits the Bragg plateau in reflectivity into two peaks such that intragap light propagation becomes possible for frequencies in between the peaks. We demonstrate the existence of the braggoriton excitations in a 3D opal PC infiltrated with a cyanine dye that has very large Rabi frequency and hence is highly polarizable. In contrast to recent experiments where the infiltrated dye and Bragg reflectors do not spatially overlap and thus the braggoriton excitations are not formed, in our case the polarizable medium and the Bragg reflectors coexist, giving rise to the novel excitations. We show that the angle-dependent reflectivity spectra of the infiltrated opal contain a split Bragg- polariton stop band with a semi-transparent band in between where braggoriton excitations can propagate for impinging angles, \( \theta \) at which the unperturbed Bragg stop band, \( \omega_B(\theta) \) is close to \( \omega_T \). The correlation of the two reflectivity bands to each other is further demonstrated when, due to a strong light bleaching effect of the cyanine molecules the two reflectivity bands collapse together as the cyanine molecules are progressively bleached with the illumination time.

The synthetic opal single crystals used here were cut from a polycrystalline sample obtained by slow sedimentation of a colloidal suspension of silica (\( \text{SiO}_2 \)) spheres (with a mean diameter \( D \approx 300 \text{ nm} \) and dispersion in \( D \) of about 4\% [16]). Since the as-grown opals are weakly bound, sintering at \( 750^\circ \text{C} \) was used to achieve robust mechanical properties. This sintering process provides inter-sphere necks joining neighboring silica spheres in a face-centered-cubic (fcc) structure of the opal. Weak iridescence in air results from Bragg diffraction off \( (hkl) \) crystal planes, which produce gaps in the reflectivity spectrum at \( \omega_{hkl} \). However due to the relatively small contrast between the dielectric constant, \( \varepsilon \) of the silica and air, the opal PC do not possess a complete PBG; instead the various \( \omega_{hkl} \)
Fig. 1. The dispersion relations [\(\Delta(Q)\), where \(\Delta\) and \(Q\) are normalized frequency and wave-vector, respectively (see text)] and reflectivity spectra [\(R(\Delta)\)] of an uninfiltated (a) and (b), and infiltrated (c)-(f) PC with a highly polarizable dye, for wave-vector \(Q\) close to the Brillouin edge (\(Q = 0\)). For the infiltrated opal the normalized detuning between the Bragg and exciton/polariton gaps is \(\delta = 0\) for (c) and (d) and \(\delta = 0.5\) for (e) and (f), whereas the normalized coupling parameter is \(\alpha = 0.5\) in both cases. \(B\) is the Bragg stop band in reflectivity, whereas \(B_1\) and \(B_2\) are the split stop bands due to Bragg-like and polariton-like gap, respectively.

300 nm with \(\varepsilon_0 \approx 1.55\); these parameters determine the Bragg stop band in air to be close to 660 nm at \(\theta = 0\). This stop band, however could be easily shifted with \(\theta\) to about 560 nm for \(\theta = 45^\circ\) (Eq. (2)) [19].

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

\[
Q = \sqrt{\left[\Delta - \frac{\alpha^2}{\Delta - \delta}\right]^2 - \frac{1}{4}},
\]

where \(Q\) is the normalized wave-vector, \(Q = (\omega_B/K\Delta\omega_B)q\), \(\alpha\) is the Bragg-polariton coupling constant given by \(\alpha = \Omega_p/2\Delta\omega_B\), and \(\Delta\) is the normalized frequency given by \(\Delta = (\omega - \omega_B)/(2\Delta\omega_B)\). These dispersion relations are plotted in Fig. 1(c) for a detuning \(\delta = 0\); the resulting calculated reflectivity spectrum is shown in Fig.1(d). It is seen that the interaction between the Bragg gap and the exciton/polariton gap leads to light propagation inside the photonic gap via novel type excitations, dubbed here braggoritons. This is evident in the dispersion relations (Fig. 1(c)) as well as in the transparent spectral range that is formed in between the two reflectivity plateaus in Fig.1(d).
absorption (or reflectivity) band that peaks at $\omega_T \approx 700$ nm; simultaneously, the photoluminescence band greatly diminishes so that clean reflectivity measurements could be completed with little or no interference from the emission band $^{13}$. The aggregate formation is not as straightforward when the cyanine molecules are infiltrated inside the opal, since the opal voids are not aligned properly to promote aggregation. However repeatably pulling the opal sample from the thick solution provided better aligning to form the J-aggregates inside the opal $^{19}$. In addition, the aggregated cyanine molecules on the opal surface were carefully washed out so that an extra reflectivity peak in the spectrum $^{20}$, which is due to the uncoupled excitons/polaritons, does not form to further complicate the spectrum. The opal sample was embarked on a homemade goniometer, where an incandescent, well-collimated light beam was directed at an angle $\theta$ respect to the [111] direction of the opal. The reflected beam at $2\theta$ was dispersed by a monochromator (0.25 m) and its intensity measured by a Si photodiode and a lockin amplifier $^{13}$. At $\theta = 0$ the uninfiltred opal showed a [111] Bragg stop band in the reflectivity spectrum at $\omega_B(0) \approx 660$ nm; this band red-shifted when infiltrated with the cyanine aggregates due to the increase in $\varepsilon_0$ upon infiltration so that the new $\omega_B(0) \approx \omega_T \approx 700$ nm.

Fig. 2(a) shows the angle-dependent reflectivity spectra of the cyanine-infiltrated opal for $\theta$ ranging from 2.5° to 30°. At large $\theta$ when $\omega_B(\theta) > \omega_T$ the Bragg/polariton interaction is small. Then due to the large detuning $\delta$, only one reflectivity band ($B_1$), which is the Bragg stop band, dominates the spectrum. However as $\theta$ decreases, $\omega_B(\theta)$ red shifts towards $\omega_T$ so that the detuning $\delta$ decreases and consequently the Bragg/polariton interaction increases. It is then apparent that another band ($B_2$) is formed at small $\theta$, with increasing relative intensity at smaller $\theta$ (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)). This behavior is exactly as expected from the bragggoriton model above if there is strong coupling between the Bragg and polariton gaps when they are close to each other $^{12}$. The reason that a deeper dip in between the split reflectivity bands is not observed in the reflectivity spectra at small $\theta$ is the unavoidable disorder that exists in the opal sample, which tends to smear out sharp spectral features $^{21}$.

We used the bragggoriton model $^{12}$ to fit the experimental data. For this fit we calculated the Bragg-like ($B_1$) and polariton-like ($B_2$) reflectivity peaks in the angle-dependent spectra to derive the peaks frequency and relative intensity at each $\theta$. The calculated frequencies and relative intensities versus $\theta$ are shown in Figs. 2(b) and 2(b) inset, respectively and compared with the data. The good agreement between theory and experiment seen in Figs. 2(b) and 2(b) inset was achieved using Eq. (1) with the following free parameters: $\omega_B = 683$ nm, $\Delta\omega_B = 53$ meV (or 20 nm), which are slightly shifted compared to the values of uninfiltred opal: $\omega_T = 705$ nm, which is directly determined from the reflectivity peak in the aggregated films outside the opal; and $\varepsilon_0 = 1.45$: this results in a detuning parameter $\delta = 0.55$ at $\theta = 0$. In addition, we used a Rabi frequency splitting

For a detuning $\delta \neq 0$ the photon dispersion relations lose their symmetry $^{12}$ (Fig. 1(e)) and this can be also seen in the reflectivity spectrum (Fig. 1(f)), where the reflectivity peak due to the polariton-like branch in the dispersion relations ($B_2$ in Fig.1(f)) diminishes with increasing $\delta$. By changing the light impinging angle $\theta$ respect to the [111] direction, the detuning $\delta$ between the Bragg and polariton gaps may be easily changed in opals since $\omega_B(\theta)$ changes with $\theta$ according to Eq. (2) above, whereas $\omega_T$ remains unaffected when $\theta$ is varied $^{20}$. We use this mechanism of changing $\delta$ in the infiltrated opals for measuring the dispersion of the bragggoriton excitations with $\theta$.

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, of which chemical diagram is shown in Fig.2(b), inset. In chloroform solution these cyanine molecules weakly absorb in the yellow part of the spectrum (at approx. 600 nm) and have a moderately strong photoluminescence band in the red $^{13}$. However when a thick chloroform solution of NK-2567 is casted into films on glass substrates, then J-aggregates are readily formed from the cyanine molecules. The cyanine J-aggregates are characterized by a red shifted
The infiltrated polarizable medium in opal may serve as a channel wave guide for in and out light traffic from the PC, for frequencies inside the gap. In general, even in the absence of the Bragg grating effect a channel structure along \( x \) with an attenuation length, \( L_x \), which is determined by the ratio \( \varepsilon_1/\varepsilon_2 \). In the presence of Bragg grating along \( z \) and for frequencies inside the PBG, however a waveguide mode exists only if \( L_x < L_x^0 = (L_B/K)^{1/2} \), where \( L_B = 2\omega_B/(K\Delta\omega_B) \) is the Bragg attenuation length for \( \omega = \omega_B \). If the channel is filled with a polarizable medium then for \( \omega \approx \omega_T \), \( \varepsilon_1 \) is large and consequently \( L_x \) substantially decreases. At some frequency, \( \omega_0 < \omega_T \), however \( L_x \) becomes so small that a waveguide mode is formed in the structure along \( z \).

We calculated \( L_x \) for a channel with lateral dimension \( d << L_x^0 \). We found in the case \( \omega_T \approx \omega_B \), \( \omega < \omega_T \) and \( (\omega - \omega_B) << \omega_B \), that

\[
L_x \approx \frac{8(\omega_T - \omega)}{\omega_T K^2d}.
\]  

Using the condition for the existence of a wave-guide mode, namely \( L_x < L_x^0 \) we find the waveguide/braggorton...
frequency in the PBG to be: \( \omega > \omega_0 = \omega_T - (1/8)\omega_T K d \sqrt{2\omega_B / \Delta \omega_B} \). We note that \( \omega_0 < \omega_T \) and therefore the waveguide-braggiton mode can propagate for relatively long distances along \( z \) with little attenuation due to absorption.

In conclusion, we showed that a highly polarizable medium that is infiltrated into a PC can induce a transparent spectral region inside the gap when the coupling, or Rabi frequency is strong and the unperturbed polariton frequency is close to the gap frequency. This is caused due to the strong interaction between the Bragg and exciton-polariton gaps that results in the existence of intragap braggiton excitations, which promote light propagation inside the gap. Although the braggiton-induced transparency was demonstrated for cyanine dye aggregates infiltrated in an opal PC that does not possess a complete PBG, we expect that our conclusions would also hold in case of a PC with a complete PBG. The induced intragap transparency may then serve to direct light traffic in and out of a defect laser resonator inside the PC via a braggiton type waveguide.

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