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Theoretical predictions of photonic properties of nanoporous copolymer films as photonic band gap materials using FDTD

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ABSTRACT Block copolymers (BCPs), which self-organize into ordered 1-, 2- and 3-dimensional periodic equilibrium structures, can exhibit photonic band gaps (PBGs). In this paper, cylinder microdomain nanoporous films are proposed to be treated as a new kind of 2-dimensional BCP based photonic crystal. The minor component of the nanoporous films has been removed chemically with only pores left in order to enhance their dielectric constant contrast, which provides a new solution to achieve necessary PBG properties with BCPs. The finite-difference time-domain (FDTD) method is used to investigate band features of this kind of photonic crystal theoretically. It is noted that the complete band gaps for the *H* polarization are obtained, although for the *E* polarization only the incomplete gaps exist. In addition, the gap map of the PBG materials is presented and its characteristics are analyzed.

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1 Introduction

Photonic crystals, a new class of dielectric materials that have periodic spatial modulation of the refractive indices and are able to mold the flow of light in a controlled fashion, have attracted wide attention [1–3]. There is currently a variety of ways of making photonic crystals, such as lithography and etching, electrochemistry, vertical selection oxidation, etc., most of which impose periodicity on a photonic scale onto the otherwise uniform material. Very recent work has introduced self-assembly as a method of making photonic crystals with periodicities suitable for frequencies in the visible part of the spectrum. Materials used include colloidal crystal arrays, artificial opals and inverse opals and hollow spherical micelles [4–6].

Block copolymers (BCPs) can self-assemble into spatially periodic 1-, 2- and 3-dimensional ordered equilibrium structures [7, 8]. There are several essential challenges to overcome in order to achieve desirable photonic crystal properties employing block copolymers. These include obtaining the correct size of domains for the optical frequencies of interest, at-
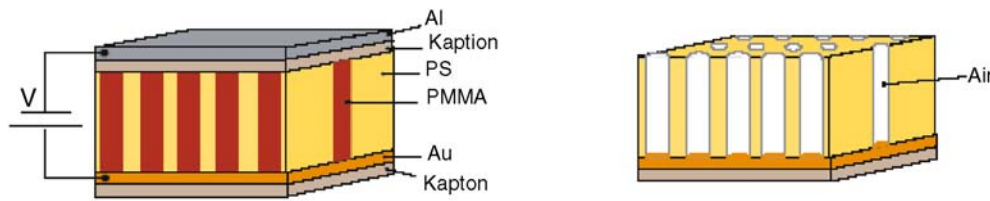
tainment of long-range domain order and appropriate orientation, as well as providing sufficient dielectric contrast between the domains. Studies have been carried out theoretically and experimentally concerning a one-dimensional (1D) BCP multilayer stack [9, 10]. But, very little research has been done in the two-dimensional (2D) BCP based photonic crystals.

In the present paper, cylinder microdomain nanoporous films [11, 12] are proposed to be treated as a new type of 2D BCP based photonic crystal. Substituting air for the minor component of the film, its dielectric constant contrast is enhanced. This is very important for the 2D hexagonally packed cylindrical photonic crystals, for, with sufficient dielectric constant contrast, hexagonally packed cylindrical photonic crystals are able to produce a complete photonic band gap for both *E*-polarization and *H*-polarization modes [8, 9]. In addition, the domain orientation is controlled by applying an electric field across the top electrode and the bottom electrode through the film and the domain sizes of the films are able to be tailored by the addition of a homopolymer to the neat block copolymers [13]. So, the nanoporous film is a kind of interesting platform material for BCP based photonic crystals. In Sect. 2, the finite-difference time-domain (FDTD) method [13, 14] is used to obtain the band-gap features of the photonic crystals.

2 The FDTD simulation and analysis of the photonic band structure

The nanoporous copolymer films have mainly been applied for nanoscopic templates before [11]. Figure 1 is a schematic representation of the technique of forming this kind of film [12]. The nanoporous films can be produced using diblock copolymers composed of polystyrene (PS) and polymethylmethacrylate (PMMA), denoted P(S-b-MMA). First, the asymmetric diblock copolymer P(S-b-MMA) is spin coated and annealed above the glass-transition temperature of the copolymer between two electrodes under an applied electric field, forming a periodic hexagonal array of cylinders oriented normal to the film surface. After removal of the minor component (PMMA), a nanoporous film is formed. Since the matrix of this nanoporous film is the 2D ordered periodic structure that is self-assembled by the diblock copolymer, it naturally can be treated as a 2D photonic crystal. And, its di-

electric constant contrast has been enhanced from 1.44 : 1 to 2.5 : 1 ($\varepsilon_{PS} = 2.5$, $\varepsilon_{PMMA} = 3.6$, $\varepsilon_{air} = 1$).

The conventional 2D FDTD algorithm is applied in our simulation. The photonic crystals are periodic structures, so naturally a single unit cell will be analyzed by applying appropriate periodic boundary conditions. The computational domain contains 100×100 grid points (see Fig. 2; a is the lattice constant). The eigenmode's electromagnetic field in the photonic crystals should satisfy the Bloch theory, which means that at a fixed instant of time the only difference of the eigenmode's fields between corresponding points in different cells is the phase. Consequently, Bloch boundary conditions can be enforced to all four sides of the computational domain. When Bloch periodic boundary conditions are applied, the electromagnetic field will reach a steady state after some time and its spectrum, which contains peaks at frequency values corresponding to the eigenmodes compatible with the wave vector K chosen to enforce the periodic boundary conditions, could be obtained via a fast Fourier transform (FFT). The selection of the excited source is essential to the computation. There are two ways to be chosen here for this eigenmode problem, either some initial field distribution or a Gaussian pulse in time whose spectrum must be wide enough to cover the frequency range of interest. Here, an initial field distribution is established at first in the computational domain. The forms of initial field distribution are diverse; even a random distribution can be chosen. But, an appropriate choice means a saving in CPU time, which is usually a disturbing problem in the FDTD simulations. An initial distribution that satisfies the Bloch theory has proved a more efficient one [15].

Shown in Fig. 3 is the schematic of a unit in the hexagonal array of the nanoporous copolymer, where a is the center-to-center pore distance (lattice constant) and r is the cylinder column radius. Since the volume fraction range of 2D hexagonally packed cylinders is about 13–30%, the cylinder radius to lattice constant r/a ratios can be tuned from 0.19 to

0.29 [9]. Using the algorithm discussed, we simulated the E-polarization and H-polarization band-gap structures of the 2D BCP based photonic crystals for their r/a ratio from 0.2 to 0.3 (every 0.0125 interval), respectively. Two photonic band structures of the copolymer (P(S-b-MMA)) films are shown in Figs. 4 and 5, respectively. Figure 4 shows the band structure of the nanoporous BCP film. The band structure of the neat BCP film whose minor component has not been removed is shown in Fig. 5. The radii of the cylinder columns are both $r = 0.625a$.

One sees from Fig. 4b that a narrow band gap for H polarization appears between band 1 and band 2. This bandgap is around 0.44 ($\omega a/2\pi c$) with $\Delta\omega = 0.0164(2\pi c/a)$. Usually, the band structure for the hexagonal lattice has complete photonic band gaps for both the E polarization and the H polarization [3]. However, as shown in Fig. 4a, for the E-polarization case the complete band gaps do not exist. Further research shows that no band gaps for E polarization can be found in the whole r/a ratio range we simulated. Further experiments have been carried out to identify that for E polarization a band gap exists from $r/a = 0.325$ to 0.3875. But usually in these situations the copolymer films cannot form the 2D ordered equilibrium structures.

In contrast to Fig. 4, we do not find a complete band gap for both polarizations in Fig. 5. The only difference of the two kinds of BCP films in Figs. 4 and 5 is the dielectric constant contrast. This shows that the removal of the minor domain of the copolymer films is an essential and effective way to the achievement of the 2D BCPs as the PBG materials.

Shown in Fig. 6 is the gap map for H polarization of the nanoporous film based PBG materials as the r/a ratio is varied. There are two points deserving attention. First, the
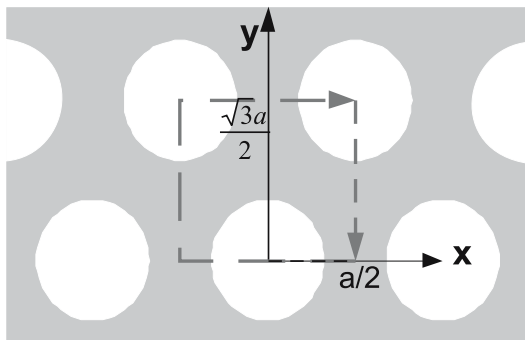
FIGURE 2   The computational domain in real space
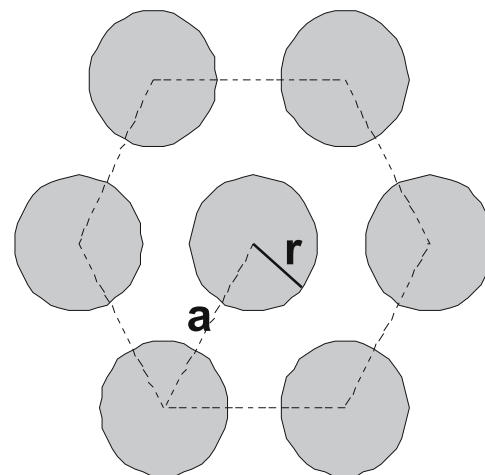
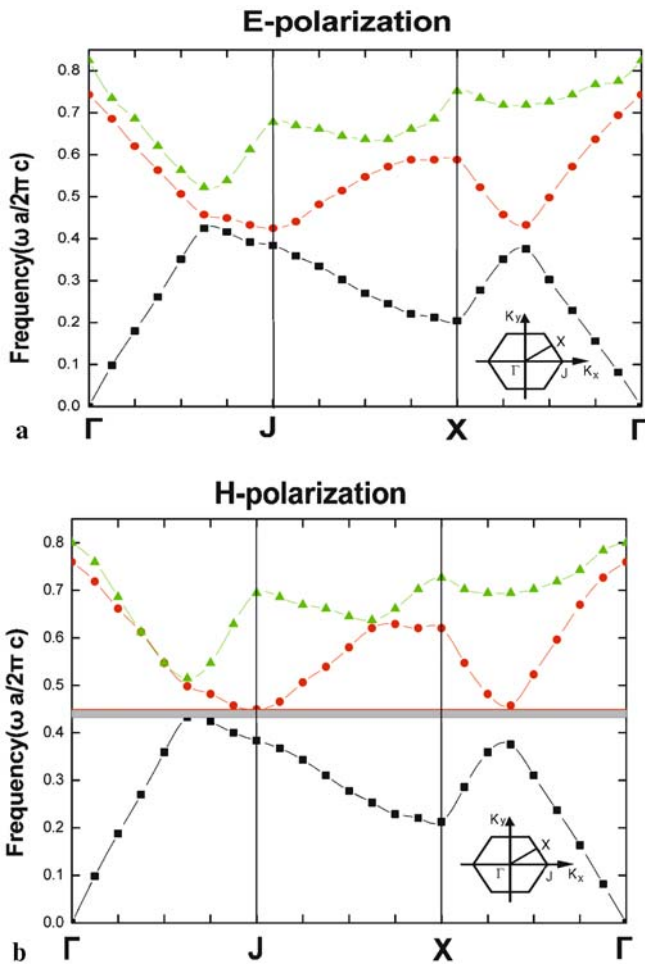FIGURE 3   The schematic of the hexagonal array of the nanoporous copolymer

E-polarization

H-polarization

FIGURE 4 The photonic band structure of nanoporous film based PBG materials. (**a**) *E* polarization, (**b**) *H* polarization

E-polarization

H-polarization

FIGURE 5 The photonic band structure of neat BCP film based materials. (**a**) *E* polarization, (**b**) *H* polarization

location of the band gap for the *H* polarization rises as r/a increases. This is the consequence of the ready increase of the average dielectric constant of the medium [3]. Second, the band-gap widths become broad with the increase of the r/a ratio. The two points are consistent with the gap map regularities of conventional photonic crystals with air columns in dielectric [3]. These also indicate that the macromolecular architecture and the composition of the copolymers play a key role in the photonic band structure, for the r/a ratio is mainly controlled by the copolymers' macromolecular architecture and composition [12].

Another aspect of BCP-based PBG materials that needs to be considered is the absorption of the materials for frequencies that are in the gap [8]. The practical short-wavelength limit for the use of polymers is around a wavelength of 300 nm due to their strong absorption in the ultraviolet (UV) regime. Achieving large enough domain sizes is the way to solve the problem. In terms of our FDTD results, lattice constants that are greater than 150 nm are enough to avoid the UV absorption for the nanoporous copolymer films. We can increase the domain sizes by incorporating homopolymer in the films. The dependence of the lattice constant of the films on molecular weight and volume fraction of added homopolymer has been studied [13]. By this means, the lattice constant can be increased by over 50%. The selections of the proper copolymers
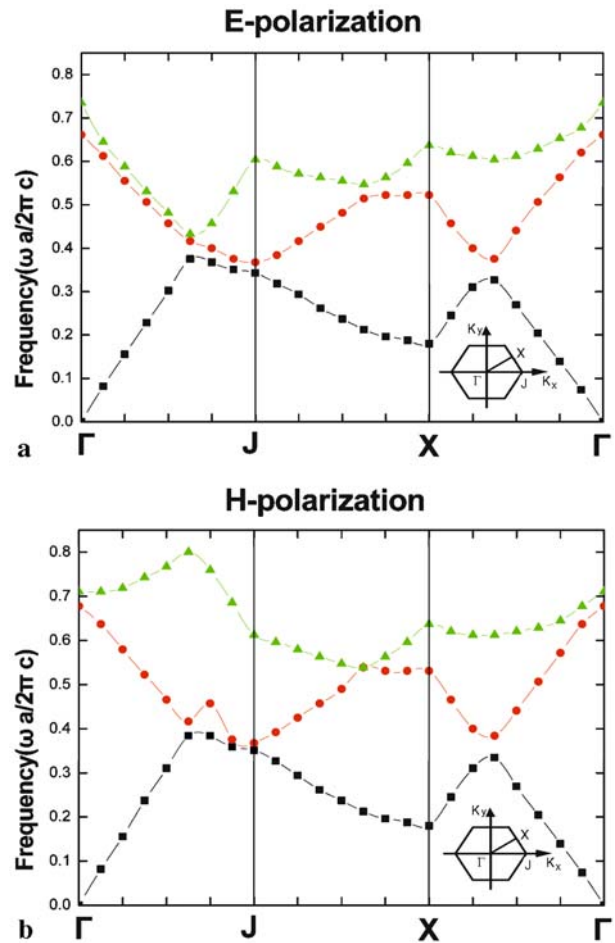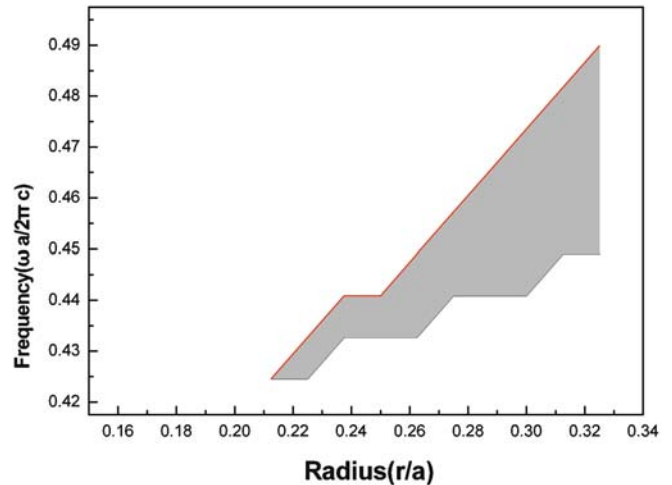

FIGURE 6 Gap map for *H* polarization of the nanoporous BCP film based PBG materials as the r/a ratio is varied

and non-volatile solvents [8] and the variation in the molecular weight of the copolymers provide two means to increase the domain sizes. Cylindrical domains with relatively large periodicity ($r \approx 60$ nm) and controlled orientation have been produced through roll casting of a polystyrene-polyisoprene (PS-PI, 3 20/ 680 kg/mol) BCP with a molecular weight of

1.0 Mg/mol [16]. In conclusion, through applying these approaches synthetically the necessary domain sizes can be easily obtained.

3   Conclusions

Cylinder microdomain nanoporous films are proposed to be treated as a new kind of 2D BCP based photonic crystal. The band structure of the photonic crystals is studied theoretically using the FDTD method. After removing the minor domain of the copolymer films to enhance the dielectric constant contrast, the complete band gaps for the H polarization can be obtained and the features of the gap map are consistent with conventional photonic crystals with air columns in dielectric, although there are not complete band gaps for the E polarization. The domain sizes of the films are able to be increased with the addition of a homopolymer to the neat block copolymers, by which absorption of the materials for frequencies that are in the gap will be avoided. In addition, other means such as multiphoton polymerization [17] or femtosecond laser hole drilling [18] also deserve to be considered to achieve the necessary domain sizes and fabricate 2D polymer based PBG materials.

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