

Azo-dye-doped absorbing photonic crystals with purely imaginary refractive index contrast and all-optically switchable diffraction properties

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Abstract: We demonstrate a two-dimensional absorbing photonic crystal with a uniform real part of the refractive index, but a periodically modulated imaginary part. It was realized through back-filling the voids of a periodic array of azo-dye-doped polymeric disks with the same undoped polymers. The photonic crystals were characterized using the diffraction method. The experimental results showed that only the light in the spectral range where the azo-dye absorbed was diffracted, indicating that a purely absorbing photonic crystal was formed. This absorbing photonic crystal also showed switchable diffraction properties due to the *trans-cis* isomerization of the azo-dye under the light pump.

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1. Introduction

Photonic crystals (PhCs) or photonic bandgap (PBG) materials, which enable the localization of light [1,2], hold promise for an emerging generation of nano- and meso-scale optoelectronic components. So far, most reported PhCs are formed by a periodic modulation of the real refractive index, i.e., the real part of the dielectric constant. However, research effort is still negligible on the PhC structures with periodic modulation of the imaginary

refractive index. By including absorbing features into the structure, various functionalities can be realized. This is particularly interesting for the case of so-called “resonantly absorbing PhCs” [3], where the photonic resonance created by the refractive index contrast overlaps with the absorption feature. Absorbing PhCs have also been exploited to enhance the light absorption in solar cells [4]. Various approaches have been used to fabricate PhC structures, such as electron-beam lithography [5], self-organization of colloids [6], layer-by-layer micromachining [7], and holographic lithography [8–12]. In all of aforementioned approaches, holographic lithography stands out in creating organic structures by combining many desirable characteristics, such as large-area fabrication, lattice tailoring ability, easy defect control, and high repeatability. Based on this method, we have also developed various PhCs [13–15] using holographic polymer-dispersed liquid crystal (H-PDLC) materials [16].

Azobenzene chromophore doped or covalently attached polymer systems [17], in the form of solid films, have been investigated for many potential applications, such as optical switching [18,19], diffractive optical elements (DOEs) [20,21], nonlinear optics [22], and photomechanics [23]. Very recently, we have developed an azo-dye-doped acrylate-based material system for holographic lithography [24]. High efficiency and excellent all-optical switching behavior have been successfully achieved based on such azo-dye-functionalized photonic structures. All the above applications are possible due to efficient photoisomerization and photoinduced anisotropy of the azobenzene groups. Furthermore, azobenzene and its derivatives have strong absorption at their both *trans* and *cis* states—an important feature to form absorbing PhCs. In this letter, we will report the fabrication of a two-dimensional (2D) absorbing PhC with a uniform real part of the refractive index, but a periodically modulated imaginary part, which is based on our newly developed material formulation. This absorbing PhC only diffracts the light in the spectral range where the azo-dye absorbs. Upon the light pump, the diffraction properties of the azo-dye-doped PhC can be switched due to the *trans-cis* isomerization of the azo-dye.

2. Experimental

We used a three-sided pyramid (BK7 Glass) to fabricate the 2D PhC structures [Fig. 1(a)]. This pyramid has a tilted angle of 20° between the sided surface and the bottom surface. Its height and side length of the bottom surface are 1.0 cm and 10.0 cm, respectively. When a collimated laser beam is incident on the pyramid, three separately refracted beams will be generated and then converge together to create a three-beam interference pattern [Fig. 1(b)]. The interference pattern is then recorded in the azo-dye-doped acrylate material system. This single optical element implementation improves the alignment and stability of the optical setup, making it more robust than the multiple-beam setups reported previously.

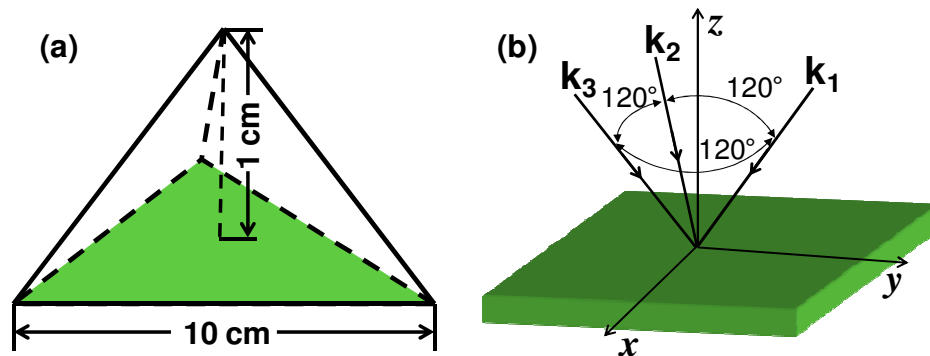


Fig. 1. (a) Schematic of three-sided pyramid and (b) refracted three-beam interference configuration caused by the pyramid.

The material syrup consisted of 77.2 wt% monomer, dipentaerythritol penta-/hexa-acrylate (DPPHA), 13.1 wt% cross-linking monomer, *N*-vinylpyrrolidone (NVP), 3.7 wt%

photoinitiator, rose bengal (RB), 6.0 wt% coinitiator, *N*-phenylglycine (NPG), all from Sigma-Aldrich. RB and NPG were firstly dissolved into NVP. Then we blended all these materials together at an elevated temperature of 50°C for ~5 hr to form a homogenous syrup. After that, half of the syrup was further mixed with the azo-dye, methyl red (MR), and the other half was kept as same as the original. The concentration of MR was 1.5 wt%. Finally, two homogenous syrups were formed and ready for experiments.

In our experiments, an Ar⁺ laser operating at 514.5 nm was used to produce the light interference pattern. The MR-doped syrup was spin-coated on a glass substrate with a controlled thickness of ~2 μm and then subject to the light exposure at the intersecting region where the interference pattern happened. Here the exposure intensity before the beam splitting was 20 mW/cm² and the exposure time was 15 min. After exposure, the sample was developed directly in propylene glycol methyl ether acetate (PGMEA) for 1 min, followed by rinsing in isopropanol for 30 s and N₂ drying. Similar to the negative photoresist, the unexposed MR-doped acrylate monomers was removed after the develop process. As a result, a 2D hexagonal photonic lattice of MR-doped polymeric disks was formed. Subsequent back-filling of the voids with the undoped material syrup was carried out and then subject to a uniform laser light exposure. Hereto, the resulted sample gave rise to a pure absorbing PhC with a uniform real refractive index, but a periodically modulated imaginary refractive index. Finally, the sample was further exposed to the UV light to enhance the experimental effect by the following reasons: 1) Since both MR and RB molecules have strong absorption in the range of 450–550 nm, the UV exposure can bleach most of RB molecules to avoid the RB-absorption and hence protrude the MR-absorption; 2) The UV exposure can ensure the complete polymerization by consuming all the left monomers; 3) Since the light for holographic patterning can induce the *trans-cis* isomerization of the MR molecules, the UV exposure can turn most MR molecules of the *cis*-state back to the stable *trans*-state.

3. Results and discussion

As known, due to azobenzene derivatives' reversible *trans-cis* isomerization by photoirradiation, one can manipulate not just optical properties [25], but the optical anisotropy of the surrounding liquid crystals as well [26–28]. However, for most azobenzene derivatives, UV light is needed to trigger the photo-switching, which usually degrades the physical properties of the acrylate-based polymers [29,30]. In order to avoid this issue, it is favorable to choose an azo-dye, whose *trans-cis* isomerization can be triggered by visible light. MR appears to be a good candidate in this case since its absorption band of *trans*-isomer is typically in blue-green range [31], where the blue-green light has neglectable effect on the polymers. Thus far, it has been widely used as a dopant in liquid crystal materials to induce the nematic-isotropic transition for all-optical applications [32–34].

At room temperature, most of the MR molecules are expected to exist in a *trans*-state in our polymer matrix. Blue/green photoirradiation of the molecules causes the *trans*-state to isomerize to the *cis*-state. After removing the light pump, the *cis*-state can go back to the *trans*-state through a thermal relaxation process or UV illumination. The chemical structure of a MR molecule and its reversible *trans-cis* isomerisation were described in our previous report [34]. Upon the photoirradiation, the absorbance above 405 nm decreases, while the absorbance between 305 and 405 nm increases. Figure 2(a) shows the absorption spectra before and after photoirradiation. At a fixed pumping intensity, there is a photostationary state existed between *trans* and *cis* states, at which the prolonged illumination does not change the shape of absorption spectrum any more. It is worth mentioning that in our back-filled absorbing PhCs, the MR concentration was estimated to be less than 0.75 wt%. At this concentration, the absorption was in the linear regime of the Lambert-Beer law, in which the Kramers-Kronig relationship was valid. Using the Kramers-Kronig relationship based on the MR-absorption spectrum, we can determine the refractive index and the refractive index changes before and after pump:

$$\Delta n(\omega') = \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega)}{\omega^2 - (\omega')^2} d\omega \quad (1)$$

where $\Delta \alpha = 2.303A(\lambda)/T$ is the change in the absorption coefficient ($A(\lambda)$ is the molecular absorbance at a given wavelength and T is the effective molecular thickness), c is the speed of light, λ is the wavelength of light, and ω is the angular frequency. The Kramers-Kronig transformation expresses the real part of the refractive indices as an integral of the absorption coefficients. The refractive indices associated with the absorbance before and after pump are shown in Fig. 2(a). As a further step, Fig. 2(b) shows the changes of absorbance and associated refractive index near the absorbance centre of the MR due to photoirradiation.

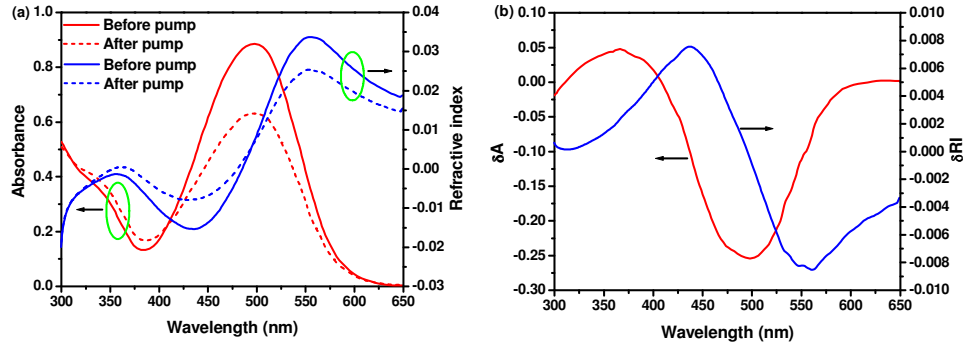


Fig. 2. (a) Absorption spectra and associated refractive indices before and after photoirradiation, and (b) Absorbance change ΔA and associated refractive index change ΔRI induced by photoirradiation.

The morphologies of PhC structures were observed under an optical microscope (Fig. 3). Figure 3(a) shows the microscopic image of the patterned MR-doped polymeric disks through holographic lithography. A clear 2D hexagonal lattice is observed and the lattice constant is $\sim 2.6 \mu\text{m}$. By back-filling the same syrup without MR-doping, the back-filled voids and the original disks are assumed to have the same real refractive index but different imaginary one in the PhC structures. Figure 3(b) shows the microscopic image of the back-filled sample. Compared to Fig. 3(a), the back-filling sample shows a very low contrast due to the uniformity of the real RI. The original polymeric disk array appears as blurred reddish dots, which indicates that the wavelength-dependence of the periodic corrugation.

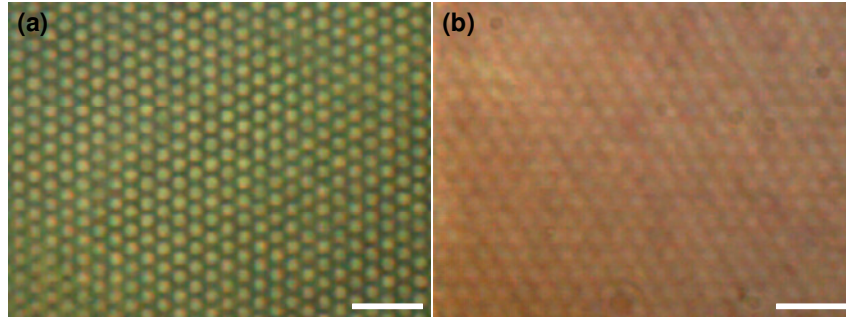


Fig. 3. Microscopic images of the patterned polymeric disks through holographic lithography before (a) and after (b) back-filling. Scale bar: $10 \mu\text{m}$.

The diffraction patterns of the PhCs were checked and compared before and after back-filling. Figure 4(a) shows the diffraction pattern of the PhC structure before back-filling, which is given by the dielectric modulation that exists for all wavelengths. As a result, the light dispersed from inside to outside is from deep blue to near infrared. By contrast, blue-green light diffraction is more obvious once the structure has been back-filled [Fig. 4(b)]. It is

worth mentioning that volume shrinkage (5–10%) generally happens during the polymerization process for the back-filled acrylate monomers [35], which could result in a small air gap between the MR-doped polymeric disks and the back-filled undoped polymers, hence forming a small real refractive index modulation. Therefore, weak diffraction of red color light is still observed from Fig. 4(b).

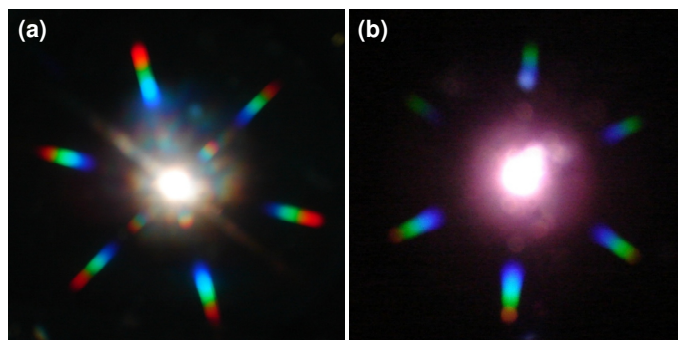


Fig. 4. Diffraction pattern of the PhC structure before (a) and after (b) back-filling.

Further confirmation was carried out by checking the diffraction intensity changes using a pump-probe configuration. The pump light is a pulsed Ar^+ laser beam working at 514.5 nm with a duration of 25 s, which is used to induce the *trans-cis* isomerization of MR molecules. Two He-Ne lasers with different working wavelengths were used as probe light to monitor and compare the diffraction changes of the absorbing PhC detected by a photodiode. One is working at 633 nm, which is out of strong absorption range of the MR-dye. The other one is working at 543 nm, which is in MR's strong absorption range. Figure 5 shows the comparative results of the optical switching effect in diffraction at the pumping power of 80 mW. It is obvious that under the light pump, there is almost no change for 633 nm, but a distinct change for 543 nm, which indicates that the sample has a much higher refractive index modulation for 543 nm than that for 633 nm. In our experiments, the *trans-cis* isomerization of the azo-dye caused a dramatic change in the absorption spectra, indicating a change of the imaginary refractive index according to the Kramers-Kronig relations. As a result, the imaginary index modulation in this 2D structure and subsequent diffraction were changed. From Fig. 2(a), the spectral change of the absorption before and after photoirradiation is below 600 nm and the biggest change happens at ~500 nm. The larger the spectral change in absorbance, the higher the modulation in imaginary refractive index. Therefore, the probing green light (543 nm) used in our experiments experienced a much larger imaginary refractive index modulation than the red light (633 nm). As a result, we observed a dramatic difference in diffraction for the green and red light, as shown in Fig. 5. For azo-dyes, after removing the light pump, the *cis*-state can go back to the *trans*-state through a thermal relaxation process, which indicates that the optical switching behaviour is reversible. Under the pump with a period of 25 s, the rising time was ~2.8 s and the falling time was ~3 s at the pump intensity of 80 mW. Such a slow response speed originates from the azo-dye molecules' reorientation through *trans-cis* isomerization and accommodating motions of polymer chains [36]. The slow relaxation of the azo-dye also causes a pronounced offset in the dynamic response curve for the 543 nm probe light (red curve) since the azo-dye molecules do not have enough time to completely relax to their original state before the next excitation pulse is applied. Furthermore, from Fig. 2(a), the refractive index decreases at 543 nm upon photoirradiation, indicating a decreased refractive index modulation. Therefore, we observed gradually decreased diffraction intensity (red curve) during the pumping process. Depending on the wavelength of light pump, the photoisomerization of azobenzene from *trans*-state to *cis*-state could undergo the pathway of either π - π^* rotation or n - π^* inversion with different response speeds [37]. Khoo *et al.* have reported that an optimized response time

can be microseconds in MR-doped liquid crystals [38]. Therefore we believed that much faster response times in our PhCs can be achieved.

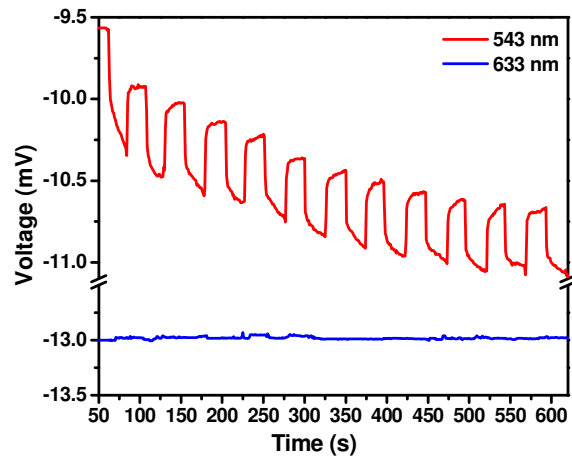


Fig. 5. Comparison of the optical switching effect for the red and green light diffraction.

4. Conclusion

We have demonstrated 2D absorbing PhCs that are based solely on the imaginary part of the refractive index. The azo-dye absorbance-associated refractive index was analyzed using the Kramers-Kronig relationship. The experimental results confirmed that only the light in the spectral range where the azo-dye absorbed was diffracted, indicating that purely absorbing PhCs were formed. Such absorbing PhCs also showed all-optically switchable diffraction properties due to the *trans-cis* isomerization of the azo-dye under the light pump. We believe that this fabrication technique can be extended to 3D fabrication and such kind of absorbing PhCs can find many photonic applications, such as optical switching, coherent and incoherent PhC structure manipulation, and soliton generation.

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