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PAPER

# Holographic fabrication of azo-dye-functionalized photonic structures

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We have developed an azo-dye-doped acrylate-based material formulation for holographic lithography. Volume phase gratings and two-dimensional photonic crystals were demonstrated by recording the interference patterns of two and three coherent beams in this material formulation. The dependence of the first-order Bragg diffraction efficiency of the gratings on the exposure intensity of the writing light was investigated. We have achieved a volume phase grating with a diffraction efficiency of 72%. These azo-dye-functionalized photonic structures showed an excellent all-optical switching behaviour, which was attributed to the imaginary refractive index changes caused by the *trans*–*cis* isomerization-induced absorption changes of the azo-dyes. Such photonic structures are potentially useful in the future development of all-optical devices.

## Introduction

Azobenzene chromophore doped or covalently attached polymer systems, in the form of solid films, have been investigated for many potential applications such as optical information storage and processing,[1–3] optical switching,[4,5] diffractive optical elements (DOEs),[6,7] nonlinear optics,[8,9] and photomechanics.[10,11] All the above applications are possible due to efficient photoisomerization and photoinduced anisotropy of the azobenzene groups. When illuminated with a polarized light of appropriate wavelength, the azobenzene groups undergo a reversible isomerization process between the *trans*-state and *cis*-state and an associated orientational redistribution of the chromophores. This isomerization process can also induce the reorientation of liquid crystal molecules.[12,13] Based on this, researchers have developed all-optical liquid crystal devices.[14–18] The versatility of these photoactive systems is: 1) the azo-dyes can be either simply mixed with a wide class of polymer systems or selectively attached to the side chain, main chain or chain ends of polymers; 2) appropriate substitution of the azobenzene chromophores can be used to tune the chromatic features from UV through to the visible spectrum; 3) efficient optically-induced effects can be achieved with low incident light power.

So far, most of the azo-doped polymer DOEs are surface relief structures induced by the isomerisation-driven surface mass transport at a temperature well below the glass transition temperature.[5] In general, the surface relief DOEs based on azo-dye doped polymers have a low diffraction efficiency (<20%) since the depths of these surface relief structures can only be up to 1 μm, hence limiting their all-optical applications. In addition, when an azo-dye is doped into a polymer matrix with a very high molecular weight or a cross-linked system, it is very hard for the polymer to undergo the photoinduced mass transport,[19] thereby hindering the formation of the surface relief structures and subsequently affecting their diffraction efficiency. To achieve high diffraction efficiency, volume phase type DOEs have to be developed. Zhang *et al.* have reported that holographic volume index gratings with a diffraction efficiency of more than 80% can be achieved in an azo-dye-doped poly(methyl methacrylate) (PMMA) film;[20] however, the film has to be very thick (2 mm thickness in their case) to exert enough phase modulation on the passing light since the refractive index modulation is only $1.1 \times 10^{-4}$. For the thick films, optical loss could be a big concern in a particular wavelength range. Therefore, it is highly desirable to develop high efficiency DOEs in a thin optical film. We previously developed a liquid crystal doped photocurable material formulation for fabricating holographic volume phase gratings.[21] The diffraction efficiency can be up to ~100%.[22] Based on that formulation, we have demonstrated various photonic structures and applications.[23] In this paper, we developed an azo-dye-doped material formulation for fabricating the volume phase DOEs based on holographic lithography. Volume phase gratings and two-dimensional (2D) hexagonal photonic crystal (PhC) structures were demonstrated based on this material formulation. The volume phase grating was holographically fabricated through two-beam interference, while the 2D PhC was fabricated from three-beam interference based on a specially designed prism. The azo-dye-functionalized gratings and 2D PhCs demonstrated an excellent all-optical switching effect, indicating that the

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azo-dye functioned effectively even though it was confined in a highly cross-linked polymer matrix.

## Experimental

The material syrup we developed consisted of 77.2 wt% monomer, dipentaerythritol penta-/hexa-acrylate (DPPHA), 13.1 wt% cross-linking monomer, *N*-vinylpyrrollidone (NVP), 3.7 wt% photoinitiator, Rose Bengal (RB), 6.0 wt% co-initiator, *N*-phenylglycine (NPG), and 1.5 wt% azo-dye, Methyl Red (MR), all from Sigma-Aldrich. RB, NPG, and MR were firstly dissolved into NVP. After that, we mechanically blended all the materials together at an elevated temperature of 50 °C for ~5 h. Finally, a homogenous syrup was formed and ready for experiments.

In our experiments, the MR-doped syrup was firstly spin-coated on a glass substrate with a controlled thickness of ~2 μm and then subject to light exposure at the intersecting region where the interference pattern happened. Photopolymerization occurs during the exposure. In brief, the photopolymerzation route for the acrylate monomer-based photocurable materials is: 1) the photoinitiator RB absorbs the light energy to produce enough free radicals; 2) the free radicals initialize the polymerization and cross-linking of the acrylate monomers; 3) the polymerization process finally terminates when all the monomers are consumed. In our experiments, we varied the exposure intensity before the beam splitting and fixed the exposure time at 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 $N_2$ drying. The unexposed MR-doped acrylate monomers were removed during the developing process. As a result, a desired MR-doped polymeric pattern was formed.

## Results and discussion

To choose a suitable light wavelength for the photopolymerization, the absorption spectra of MR and RB are plotted in Fig. 1. From Fig. 1, MR has a much broader absorption than RB in the UV-Vis range. It is worth mentioning that there is an obvious overlap from 450 nm to 600 nm in the visible range for both MR and RB absorption spectra. This could hinder the initialization of the photopolymerization process because RB has to compete with MR to absorb enough light energy to initialize the photopolymerization process. In our experiments, an $Ar^+$ laser operating at 514.5 nm was used to produce the light interference pattern given its excellent coherent properties. Although MR has a strong absorption for this wavelength, we have successfully achieved the patterned MR-doped polymeric structures by choosing suitable concentrations of MR and RB.

Firstly, we fabricated a one-dimensional (1D) grating by exposing the material to a double-beam interference pattern. The exposure intensity of each beam is approximately same. The two interfering beams were symmetrically introduced into the sample at an angle of 19°. In our experiments, we found that there existed a critical range for the exposure intensity to form an excellent grating structure. The performance of a grating can be characterized by its diffraction efficiency. Fig. 2 shows the diffraction efficiency for the first-order diffraction of the grating as a function of the exposure intensity. Here, we define the critical range as the full width at half maximum (FWHM) by a Gaussian fit. The diffraction efficiency was measured using a p-polarized He–Ne laser operating at 632.8 nm. From Fig. 2, the critical range is from 16 mW $cm^{-2}$ to 29 mW $cm^{-2}$. It clearly shows that outside of this range, the diffraction efficiency drops dramatically, indicating that the grating structure is not well formed. This can be attributed to the competition of the light absorption between the photoinitiator RB and the azo-dye MR. At the low exposure intensity, MR absorbs most of light energy and the remaining light energy absorbed by RB is not enough to initialize the polymerization. Fig. 3(a) shows a blurry grating structure observed under an optical microscopy with the exposure intensity of 9.4 mW $cm^{-2}$. We have noticed that the DPPHA monomer cannot even polymerize at an exposure intensity less than 5 mW $cm^{-2}$. While at a high exposure intensity, the MR absorption induces a strong thermal effect. The thermally induced polymerization takes over the photo-induced polymerization. As a result, only a uniform polymer film is formed.

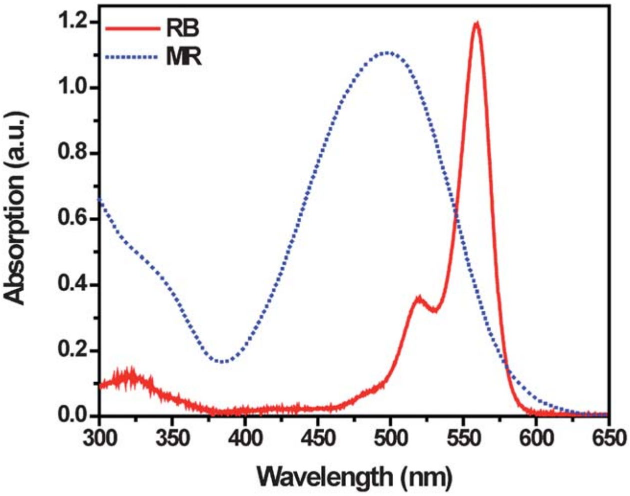

**Fig. 1** Absorption spectra of MR (dashed) and RB (solid) in IPA solutions.

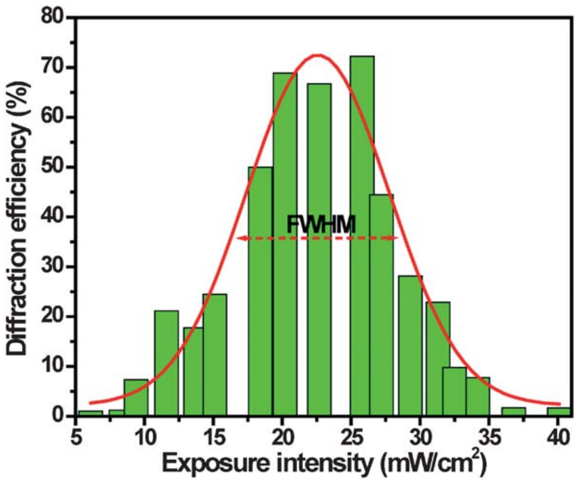

**Fig. 2** The first-order diffraction efficiency of the grating as a function of the exposure intensity. The solid curve showing a Gaussian fit.

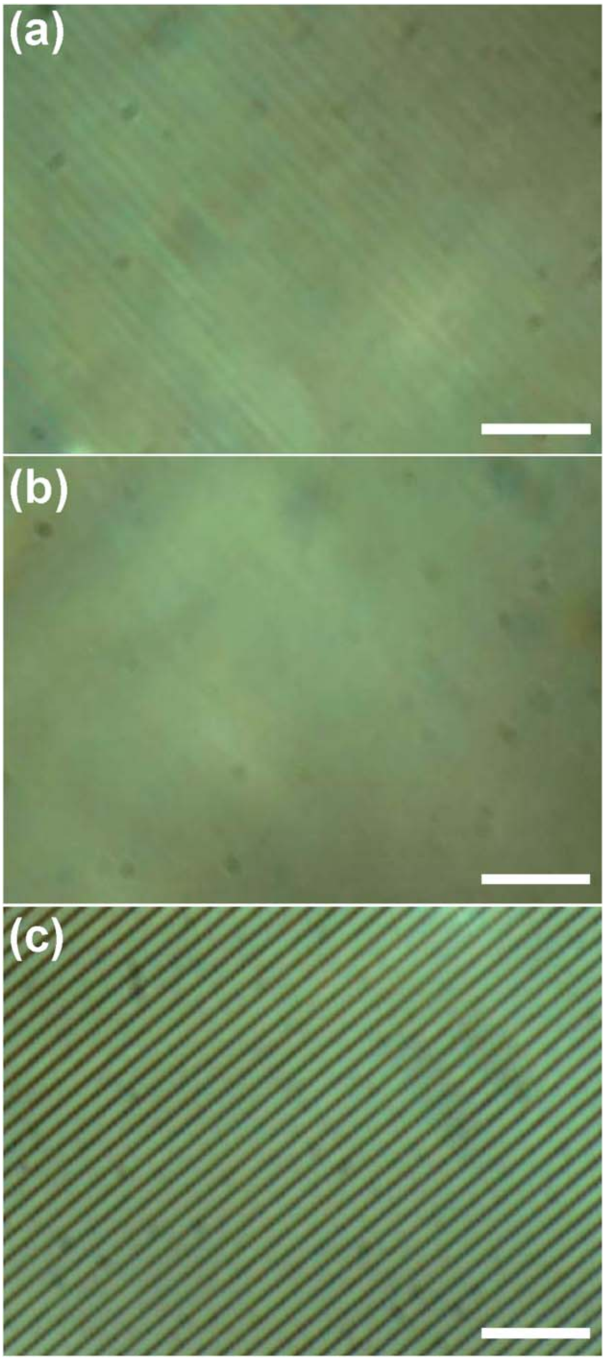

**Fig. 3** The observed grating morphologies under an optical microscopy with the exposure intensities of (a) 9.4 mW cm$^{-2}$, (b) 40 mW cm$^{-2}$, and (c) 26 mW cm$^{-2}$. Scale bars: 10 μm.

Fig. 3(b) shows the case with an exposure intensity of 40 mW cm$^{-2}$. From Fig. 2, gratings with high diffraction efficiency can be achieved with an exposure intensity only in between the critical range. As a further verification, Fig. 3(c) shows the observed 1D grating pattern with an exposure intensity of 26 mW cm$^{-2}$. A periodic grating structure can be clearly observed, indicating excellent performance. It is obvious that due to the competition between the thermally- and photo-induced polymerization, there exists a resolution limit for our material formulation. Our experimental results reveal that this can be down to ~1 μm.

We also measured the polarization dependence of the first- and second-order Bragg diffraction efficiencies by changing the incident angle of the read-out beam. Fig. 4 shows the diffraction efficiencies measured for p- and s-polarized light, respectively, for the optimum grating. From Fig. 4, we can see that the p-polarized light has a slightly higher diffraction efficiency than the s-polarized one. There are ~9% and ~6% differences for the first- and second-order diffraction, respectively. The polarization dependence could be attributed to the anisotropic distribution of azo-dye molecules induced by the writing laser beam during the grating formation process. Blanche *et al.* have discussed that the anisotropy arises from three main mechanisms:[24] 1) angular hole burning—the polarized writing beam preferentially isomerizes *trans* molecules with their transition axes oriented along the light polarization; 2) angular redistribution of the azo-dye molecules when they relax from *cis* to *trans*; 3) angular diffusion due to the thermal agitation.

We further demonstrated the fabrication of 2D hexagonal PhC structures using the same material formulation. A specially designed prism, which divided a collimated beam into three beams, was used to generate the interference pattern. Fig. 5 shows the observed structures of the sample fabricated at an exposure intensity of ~20 mW cm$^{-2}$ for each beam. It reveals a clear hexagonal morphology with a lattice constant of about 2.6 μm. A rainbow-like diffraction pattern (R–G–B color dispersion from the outmost to the innermost) can be clearly observed for an incident white light, as shown in the inset of Fig. 5. Here, it is worth mentioning that the fabrication of 3D structures is also possible in principle based on this material formulation; however, it is very challenging in practice because the strong absorption of the MR causes an uneven distribution in exposure intensity along the film thickness direction.

For the azo-dye-doped optical materials, a distinct advantage is that they can be optically controlled, an important factor in the future development of all-optical devices. Therefore, we investigated the dynamic changes of diffraction for both 1D and 2D structures. We irradiated the grating with a pulsed Ar$^+$ laser beam (514.5 nm) with a duration of ~5 s. The diffraction change of the grating was monitored and compared using a photodiode

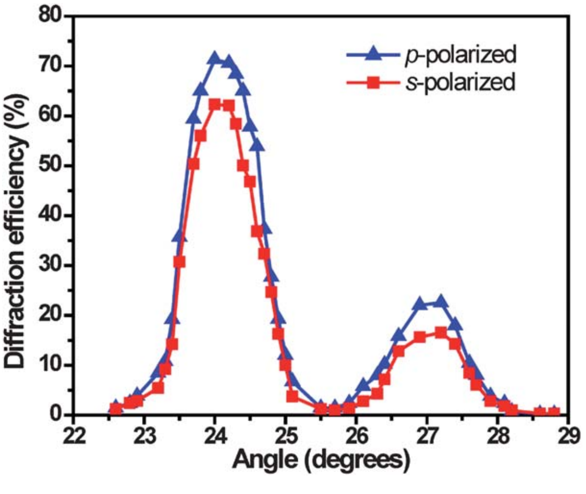

**Fig. 4** The polarization dependence of the first- and second-order Bragg diffraction efficiency.

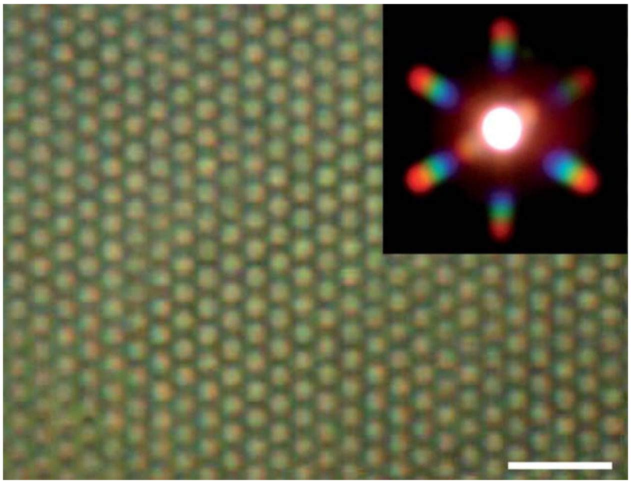

**Fig. 5** The optical image showing the 2D hexagonal PhC structures. Scale bar: 10 μm. The inset showing the rainbow-like diffraction pattern of a white light beam.

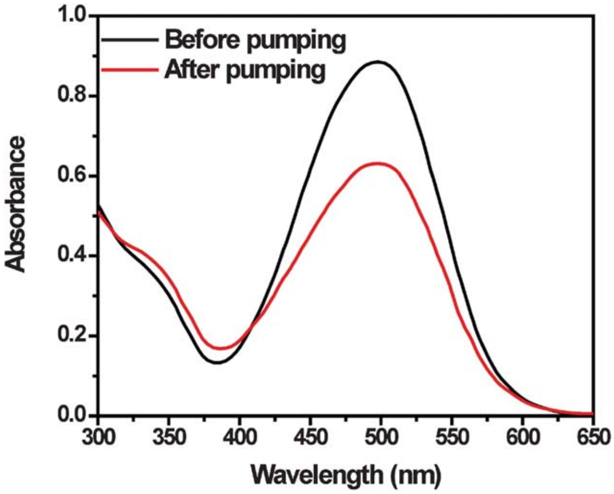

**Fig. 7** The absorption change of the azo-dye due to its *trans–cis* isomerization under the light pump.

for a green and red probe beam respectively. An aluminium foil with a small aperture (~0.5 mm in diameter) was used to cover the photodiode, thus allowing only a small portion of diffracted light to reach the photodiode and blocking most of the scattered light. Fig. 6 shows the comparative results of the optical switching effect in diffraction at the pumping power of 80 mW. We can see that the green light diffraction has much stronger changes than the red one. Considering the experimental errors, there are nearly negligible changes for the red light diffraction. For the green light, the response times for the "ON" and "OFF" photo-switching processes were roughly estimated to be ~3.4 s and ~2.6 s, respectively. Such a slow response speed originates from the azo-dye molecules' reorientation through the *trans-cis* isomerization and accommodating motions of the polymer chains.[25] The slow relaxation of the azo-dye also causes a pronounced offset in the dynamic response curve for the green probe light (see Fig. 6) since the azo-dye molecules do not have enough time to completely relax to their original state before the next excitation pulse is applied. In some previous reports, the azo-dye-doped material systems can have a very fast optical response ranging from microsceconds to femtoseconds.[26,27] We believe a faster response speed could be achieved with further optimization of our material formulation.

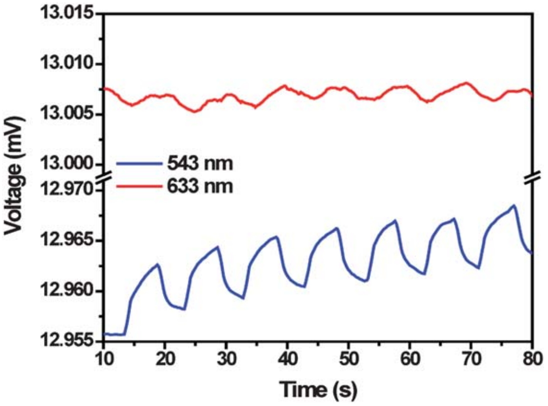

**Fig. 6** The optical switching effect of the diffraction for the red and green probe light.

The observed optical switching phenomenon in Fig. 6 was mainly attributed to the *trans–cis* isomerization of the azo-dye. At room temperature, most of the MR molecules are expected to exist in a *trans*-form in our polymer matrix. The photoirradiation of the molecules at this band causes the *trans*-form to isomerize to the *cis*-form. The *trans–cis* isomerization of the azo-dye will cause a dramatic change in the absorption spectra (Fig. 7), indicating a change of the imaginary refractive index according to the Kramers–Kronig relations.[28] As a result, the imaginary refractive index modulation in our 1D or 2D structure will change and the diffraction is subsequently changed. From Fig. 7, the spectral change of the absorption before and after photoirradiation is below 600 nm and the biggest change happens at about 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 larger imagninary 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. 6. For azo-dyes, after removing the light pump, the *cis*-form can go back to the *trans*-form through a thermal relaxation process or a UV illumination, which indicates that the optical switching behaviour is reversible.

## Conclusions

We have developed an azo-functionalized material formulation for holographic lithography and have successfully demonstrated two different structures by optimizing the exposure intensities: volume holographic gratings and 2D hexagonal PhC structures. The diffraction efficiency can reach more than 70% for the gratings. In addition, these azo-functionalized photonic structures showed an excellent all-optical switching behaviour. The physical mechanism for the switching effect is attributed to the imaginary refractive index changes caused by the *trans–cis* isomerization-induced absorption changes of the azo-dyes. The azo-dye functionalized photonic structures are potentially useful for future all-optical devices.

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