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Introduction

Controlling and manipulating molecular arrangements to vary the physical and chemical properties of materials by an external field, thereby establishing a bridge between the structure of matter and the external stimulation, is a concerned scientific enquiry with tremendous potential applications.^{1–4} Cholesteric liquid crystals (CLCs), a type of versatile soft self-organized helical superstructure, possess multi-responsiveness under various external stimuli, exhibiting an impressive catalogue of potential applications for tuneable photonic devices ranging from optical filters⁵ and mirror-less lasing⁶ to diffraction gratings.⁷ Owing to the remarkable advantage in the ease of spatial, temporal and remote control with high accuracy upon a facile irradiation,⁸ a series of persistent endeavours have been contributed in the past decade.^{9,10}

Light-reconfigured waveband-selective diffraction device enabled by micro-patterning of a photoresponsive self-organized helical superstructure[†]

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A waveband-selective diffraction device, possessing dynamic and reversible light manipulation of its waveband-selectivity within a wide spectral range (~140 nm), was developed by micro-patterning of a photoresponsive self-organized helical liquid crystal superstructure. Distinct from a conventional liquid crystal diffraction device, applied in a wide band from ultraviolet to near infrared wherein the diffracting light is due to the alternate phase modulation caused by the difference on liquid crystal arrangement, herein, the diffraction was mainly induced by an alternate transmittance/reflectance (*i.e.*, amplitude) modulation to an incident light with a certain wavelength located in a selective reflection band of a binary patterned helical liquid crystal layer, producing diffraction both on the transmission and reflection sides of the sample. The waveband-selectivity was determined and manipulated by appropriately controlling the reflection band of the patterned helical liquid crystals. A prominent advantage compared to the majority of other liquid crystal polymer based devices is the electric responsiveness of such a device in addition to its photoresponsiveness. Moreover, an excellent light reconfiguration, exhibiting an erasing of the grating, followed by a rewriting of a Fresnel zone plate was achieved.

The intriguing self-organized helical superstructure, formed by mixing the common nematic liquid crystal (LC) and a chiral dopant, which induces a twisted arrangement in the LC molecules, presents a helical pitch defined as the distance as the molecule rotates at an angle of 2π around the helical axis. The helical pitch is determined by the helical twisting power (HTP, denoted as β) and the doping concentration (c) of the chiral dopant as $P = (\beta c)^{-1}$. In particular, when the helical axis aligns uniformly and parallel to the substrates of the cell (*i.e.*, uniform lying helix), a periodic refractive index modulation is produced along the helical axis. Therefore, embedding the photosensitive moieties or doping some additive with photosensitivity endows the common CLCs with photo responsiveness. Accordingly, with the uniform lying helical arrangement of the photoresponsive CLCs, the light tuneable diffraction grating and its corresponding providential applications in beam steering and widerange spectrum scanning were achieved, resulting from the compression and extension of the helical pitch under light-irradiation.¹¹⁻¹³ Furthermore, light-manipulated two-dimensional¹⁴⁻¹⁶ and even exotic three-dimensional¹⁷ rotations of the helical axis (or grating vector) have been developed. A unique concentric diffraction ring caused by the radial lying helix of the CLCs can be achieved through an accurately controlled photoalignment.¹⁸

On another aspect, the condition, wherein the helical axis is perpendicular to the substrates of a cell (*i.e.*, standing helix),

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enables a series of fascinating photonic effects from the CLCs, such as the selective reflection of circularly polarized light (CPL) with the same handedness as the CLCs. The central reflection wavelength (λ_c) is determined by the average refractive index $(\langle n \rangle)$ and the helical pitch (P) of the CLCs and expressed as $\lambda_c = \langle n \rangle P$ in the situation of normal incidence. Therefore, most typically, a variety of azobenzene based photosensitive chiral switches, which possess reversible photoisomerization between the trans-isomer with a rodlike shape and the cis-isomer with a bent shape under alternating exposure of ultraviolet (UV) and visible light was doped into the CLCs with a planar texture to induce the shift in the selective reflection band. For instance, some azobenzene based chiral dopants with both a tetrahedrally chiral center and axially chiral binaphthyl center were synthesized to study their influence on the chirality of CLCs,¹⁹ whereas other hydrogen-bonded dopants may induce helicity conversions or phase transitions²⁰ under light exposure and further thermal modulation.²¹ Beyond UV light, commonly adopted to trigger the photoresponsive CLCs by inducing the reconfiguration of the helix, in recent years, the CLCs stimulated by low-energetic and deep-penetrated near infrared (NIR) sources were realized by loading a tiny amount of core-shell upconversion nanoparticles^{22,23} or specifically designed gold nanorods²⁴⁻²⁶ into the photoresponsive CLCs, due to the energetic conversion from NIR to UV for the former and the "photothermal" effect for the latter.

From the viewpoint of photonic applications of the photoresponsive CLCs, some progress had been achieved after consistent efforts. Light-induced metastable two-dimensional gratings in short-pitch CLCs were found, which resulted from the elastic layer undulation caused by the photo-induced change in the helical pitch.²⁷⁻²⁹ On the other hand, taking advantage of the holographic lithography or utilizing a photomask, some diffraction occurred, attributed to the periodic phase modulation conforming to the intensity distribution of light irradiation. Accordingly, through biphotonic irradiation, CLC grating films, presenting a spatially alternate distribution with a homeotropic and planar arrangement of LC molecules, were produced.³⁰ Similarly, a Fresnel-like pattern was formed when the planar texture was destroyed into an irregular multidomain with high scattering and low transmittance.31 The diffraction efficiency of a Fresnel lens would be greatly improved in the case of CPL incidence.³² Diffractions generated from an alternate binary texture of CLCs-planar texture and focal conic states-were developed using patterned light irradiation.33 Moreover, light-induced surface relief phase grating was realized on photoresponsive LC polymer films by decreasing the molecular order parameter through photoisomerization.³⁴ Most recently, stable polarization selective CLC polymer gratings by phototunable modulation of the helix pitch were realized, presenting the diffraction mainly deriving from the periodic phase modulation.³⁵

In this context, we demonstrate a type of waveband-selective diffraction grating achieved upon photo-micro-patterning of photoresponsive CLCs. Different from the common wide-band applicable diffraction grating, diffraction only occurs at the impinged light with the wavelength located in the selective waveband of the patterned CLCs (*i.e.*, the matched wavelength).

Interestingly, rather than the phase modulation induced by the majority of CLCs diffraction devices, the diffraction observed herein is mainly resulted from the periodic amplitude modulation of light between the exposed and unexposed photoresponsive CLC areas. Moreover, owing to the suitable pre-photo-crosslinking, the diffraction performance can be electrically tuned by modulating the transmittance/reflectance ratio of the two areas, enabling a readily multi-stimuli controllability, combining light exposure and electrical excitation. Simultaneously, such fantastic photoresponsive CLCs can be erased and rewritten through reversible photo-isomerization to form diverse photonic micro-patterns by means of a facile photo-patterning. As a representative, a Fresnel zone plate as well as its corresponding focusing performance is exhibited.

Experimental

Materials

The photoresponsive CLCs used in the experiments are composed of a commercial nematic LC (TEB300, $n_e = 1.679$, $\Delta n = 0.168$; 77.9 wt%; provided by Slichem, China), a photo-insensitive chiral agent R811 (19.1 wt%; provided by Merck) and an azobenzene based photosensitive chiral switch with right-handedness (QL55, synthesized in the lab, 3.0 wt%). Different from the previously used photosensitive rod-like azobenzene, in the molecule of QL55 (Fig. 1a), the two azobenzene moieties are connected by a binaphthyl axial chiral center, rendering a significant tunability in the helical twisting power (HTP) of the CLCs upon light irradiation. CLCs transit to a long-helical-pitch state under proper UVirradiation (365 nm) due to the decreasing of the HTP, while recovering to the initial state through thermal relaxation or a visible light-irradiation (532 nm). The HTP value of the chiral switch QL55 was tested through the commonly used Grandjean-Cano wedge method (see ESI[†]). The synthetic routes for QL55 were demonstrated in detail in our prior work. The chemical structure was identified by ¹H NMR spectroscopy (400 MHz), whereas high resolution mass spectrometry was used for analysis; the absorbance spectra were also obtained to demonstrate the photoisomerization of QL55.36 In order to weaken the influence of possible molecular diffusion and long-range interactions on the patterned microstructure, a small amount of acrylate-based liquid crystalline monomers (~6.0 wt%, RM257, provided by Wilshire Tech., Inc.) and photoinitiators (~ 0.5 wt%, Irgacure 784, provided by BASF) were doped for photo-initiated pre-crosslinking, thereby increasing the resolution of the microstructure as well as maintaining the phototunability within a wide spectral range. Such a process is presented in more detail in the Discussion part and ESI.† The whole mixture was homogeneously mixed at a temperature of about 55 °C, and then injected into a 5 µm-thick anti-parallel alignment treated planar cell by capillarity, followed by a slow cooling with the rate of 0.1 °C min⁻¹ to room temperature in dark ambient conditions.

Photo-micro-patterning and spectral measurement

The sample was first exposed to a 480 nm light source (output intensity: 2.5 mW cm^{-2}) for about 30–40 minutes for

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Fig. 1 Photo-micro-patterning and the wavelength-selectivity of the patterned photoresponsive CLCs. (a) Chemical structure of the azobenzene-based binaphthyl chiral switch. (b) Photo-patterning of the CLC layers in the PSS_{UV} state by covering a binary photomask on a LC cell. The visible light (532 nm, 30 mW cm⁻²) impinged along the normal direction after it was collimated by a lens. A corresponding micro-pattern with alternate reflection colours was produced after exposure. At the exposed areas, the pitches were compressed; at the unexposed areas, the pitches were almost invariable. (c) The reflection bands blue-shifted at exposed areas, while at unexposed areas, the reflection band was almost unchanged and maintained the original red reflection colour. Provided that a right-handed CPL with a matched wavelength impinged on the sample, a transmittance/reflectance modulation was generated, therefore enabling the typical diffraction both on the transmission and reflection sides.

pre-photo-crosslinking, and subsequently triggered by a UV mercury lamp (365 nm; 4.0 mW cm⁻²) to the photostationary state (PSS_{UV}) with a longer helical pitch compared to the initial state.

The photo-micro-patterning was implemented by irradiating the sample (at the PSS_{UV} state after UV irradiation) covered by a binary photomask (Fig. 2a) with a collimated 532 nm laser (30 mW cm⁻²), as shown in Fig. 1b. After patterning, the structure was observed through a reflection mode polarizing optical microscope (POM, LV100-POL, Nikon) with a crossed polarizer. The spectral measurement was accomplished under a microscope connected to a spectrometer (Avantes) through a fiber and a backlight as the probe beam, thus the spectra of the exposed and unexposed areas could be detected respectively.

For detecting the diffraction behaviour, three lasers with different output wavelengths (450 nm, 532 nm and 650 nm) were used as the probe beam. The incident beam was converted to a circularly polarized beam by a polarizer and a quarter waveplate with a $\pm 45^{\circ}$ angle to modulate the lasers into a left/ right handed CPL. The intensity of each diffraction order was measured by an optical power meter (Thorlabs).



Fig. 2 Microstructures generated after photo-micro-patterning of the photoresponsive CLCs. (a) Micrograph of the binary photomask for generating intensity modulated irradiation. Microstructures of patterned photoresponsive CLCs produced by the exposure of the 532 nm patterned laser (30 mW cm⁻²) for (b) 15 seconds and (c) 30 seconds. The corresponding reflection spectra of the exposed (denoted as 'I' and 'iii') and unexposed ('ii' and 'iv') areas were respectively shown in (d) and (e). Before the photo-micro-patterning, the sample was in the PSS_{LV} state.

Electrical modulation

A driving voltage with 1 kHz frequency was applied to the sample through the planar indium tin oxide (ITO) transparent electrodes using a signal generator (AFG-3022, Tektronix) to investigate the electrical modulation of diffraction and the corresponding response behaviours. The optical signal of the +1st-order diffraction was received by a photoelectric convertor connected with an oscilloscope (Tektronix) for exploiting the response behaviour.

Results and discussion

Phototuning of grating

The sample exhibited a conspicuous, fast and continuous redshifting of the reflection band during UV irradiation from the initial state (Fig. S2b-i, ESI[†]) with a green reflection colour ($\lambda_c = 533$ nm; band width $\Delta\lambda = 35$ nm) to the PSS_{UV} state (Fig. S2b-iv, ESI[†]) with a red reflection colour ($\lambda_c = 644$ nm; band width $\Delta\lambda = 45$ nm) within 160 seconds (Fig. S2a, ESI[†]). It was found that a 140 nm band-shifting range for the CLCs was well maintained even after the pre-photo-crosslinking. As demonstrated in prior works, the widening of the band width was related to the elongation of the helical pitch.^{37,38}

As shown in Fig. 2b, a well-defined stripe-pattern, presenting an alternate red and earth yellow reflection colour, was developed very fast (within 15 seconds) under the irradiation of a 30 mW 532 nm laser through the photomask (Fig. 2a). Such earth yellow stripes were caused by the recovery of the helical pitch under the irradiation of the visible laser at exposed areas. Continual irradiation led to a further compressing of the helical pitch until reaching the PSS_{vis} state (*i.e.*, photo stationary state under the irradiation of visible 532 nm laser) at 30 s, exhibiting alternating red and green stripes (Fig. 2c). The corresponding reflection band at the exposed areas (i.e., green-colour stripes) showed a significant blue-shifting from the position at $\lambda_c = 644$ nm (PSS_{UV} state), passing through the intermediate state with $\lambda_c = 585$ nm (Fig. 2d, spectrum i), to approximately the original state with $\lambda_{\rm c}$ = 537 nm (Fig. 2e, spectrum iii); nevertheless, there was almost no obvious band-shifting in the unexposed areas (Fig. 2d, spectrum ii; Fig. 2e, spectrum iv) due to the dynamical weakening of the photosensitive molecules. The typical Grandjean texture (Fig. 2c and d) revealed that the vertical arrangement of the helical axes of the CLCs (i.e., standing helix) was well maintained after photo-patterning. It can be noted that by virtue of the suitable pre-photo-crosslinking of the monomer RM257 before the patterning, the sharp boundaries between the exposed and unexposed areas were formed. In comparison, a lower monomer concentration ($\sim 4.0 \text{ wt\%}$) would lead to an unsharp boundary between two adjacent stripes because of the unconfined molecular diffusion of QL55 during the photo-patterning (Fig. S2, ESI^{\dagger}). Similarly, a high monomer concentration (~8.0 wt%) would narrow the phototuning range, degenerating the tunability of the CLC diffraction device.

Waveband selectivity and the diffraction

Distinct from the ordinary gratings that are applicable in a wide range of light wavelengths, diffraction of the CLC grating presented herein only occurs when the wavelength of the impinged light lies in a certain narrow reflection band of the patterned CLCs. In particular, such diffraction appears in a situation wherein the impinged right-handed CPL is reflected by one CLC stripe area but passes through the adjacent one, *i.e.* from the spectrum wherein the wavelength is located in the reflection band of one area but out of its adjacent area. However, no diffraction would be generated if the incident wavelength "jumped" out of the reflection band (i.e., a mismatched wavelength) such as 450 nm (Fig. S6a-i and a-ii, ESI⁺), which confirmed the waveband-selectivity of the CLC grating. Such waveband selectivity derives from the transmittance/ reflectance modulation between the adjacent areas, resulting in the amplitude regime both on the transmission and reflection sides, as schematically shown in Fig. 1c.

To be more persuasive about the particular amplitude grating, apart from the disappearance of the diffraction with respect to the 450 nm impinged light, we checked the diffraction when the incident wavelength was between the reflection bands of two adjacent CLC areas. Similarly, no obvious diffraction was observed owing to the very low phase difference between the two areas measured through interferometry (see ESI[†]). The calculated 0th-order and +1st-order diffraction efficiencies of the grating using the common scalar diffraction theory by assuming no phase differences in the system showed to be quite conformed to the measurements, proving the amplitude regime of the CLC grating from other aspects. Furthermore, we investigated the diffraction of a CLC grating with diffused boundaries (Fig. S5a, ESI[†]), exhibiting only the diffraction pattern with the missing order at the $\pm 2nd$, but no other diffraction patterns were observed (Fig. S5b, ESI[†]), which was another confirmation of the amplitude regime of the grating (see ESI⁺).

Diffraction of the sample shown in Fig. 2 was detected subsequently. The alternating reflection colours of the patterned CLCs with sharp boundary implied a non-overlapping of the reflection bands between the adjacent exposed and unexposed areas. Fig. 3a-i and a-ii exhibit the diffraction patterns of the corresponding sample exposed for 30 seconds (corresponding micro-pattern was shown in Fig. 2c) received on the transmission and reflection sides, respectively, through the optical setup shown in Fig. S3 (ESI[†]), in the case of normal incidence of a right-handed 532 nm CPL (wavelength matched the reflection band of green-colour stripes as shown in the spectrum iii, Fig. 2e). A similar diffraction effect can be observed provided that the wavelength matched the reflection band of red stripes, e.g., 650 nm, as shown in Fig. 3b-i and b-ii. The missing even orders in Fig. 3 indicated a well-defined rectangular distribution with a width ratio of 1:1 between the exposed and non-exposed areas. Similarly, the 5nth (n is integer) diffraction orders were also indiscernible when such width-ratio became 1:4 or 4:1 (Fig. S7, ESI⁺), thereby implying the effectiveness of appropriate pre-photo-crosslinking. Moreover, as shown in prior reports, 33,34 such grating possessed an evident polarization dependency as well. In the case of the left-handed polarization of an incident CPL, light diffractions almost disappeared both on the transmission and reflection sides regardless of the incident wavelength (Fig. S6b-i, b-ii, c-i and c-ii, ESI⁺) because the opposite handedness of the impinged light.

The matched wavelength of the impinged light can be accurately tuned by virtue of a patterned-irradiation through the same photomask due to the reflection band-shifting in the exposed area, thus enabling the dynamic light manipulation of the waveband selectivity. For example, a diffraction effect can be generated after a right-handed 585 nm CPL is impinged on the grating formed by 15 second irradiation (as the micro-pattern shown in Fig. 2b), *i.e.*, the matched wavelength was manipulated



Fig. 3 Diffraction patterns with the corresponding selective wavelengths of (a) 532 nm and (b) 650 nm on the transmission (a-i and b-i) and the reflection (a-ii and b-ii) sides, respectively. The diffraction order of each pattern was labelled. A significant diffraction missing at the even orders was exhibited, due to the 1:1 width ratio between the exposed and unexposed areas.

by light. Notably, such waveband selectivity of the grating is completely different from the previously reported colour-filtered diffraction obtained by adjusting the cross-angle between the transmission axes of the polarizer and the analyzer settled at the front and rear surfaces of the LC cell.³⁹

The stability of the CLC gratings is essential for potential photonic applications. As the QL55 molecules were sensitive to the wavelength of the probe beam, their diffraction performances were evaluated. It was found that the +1st-order diffraction efficiency of the CLC grating can be kept almost invariable for about 1 hour when the intensity of the 532 nm probe beam was about 10 μ W; however, such stability would be more or less degraded under high-intensity irradiation (maintained for only tens of minutes). If the incident wavelength was replaced by an insensitive wavelength of QL55, the stability was predicted to be more satisfying. However, such grating is more suitable to be applied in many low-intensity systems such as quantum optics, optical calculations, Fourier optics, and light coding and spectrometers.

Electrical modulation

As one of the advantages of CLCs, electrical modulation of the diffraction, which was difficult for the LC polymer, was exploited. The results indicated that the CLC grating can be modulated by a relatively low applied voltage (less than 8.0 V) and recovered to the original state quickly after the voltage was removed. Fig. 4a showed the +1st-order diffraction intensity modulation as a function of enhancement of the external field, and the turn ON and OFF of the diffraction driven by the gradually strengthened applied voltages were detected simultaneously (Fig. 4b). It can be discovered that the modulation range of the diffraction was widened by increasing the voltage.

The mechanism of the electrically modulated diffraction is based on the electrically controllable transmittance/reflectance



Fig. 4 Electrical modulation of the CLC grating. (a) The +1st-order diffraction intensity modulation as the external field was enhanced and (b) electrically controlled ON and OFF of the diffraction. The transmittance spectra of (c) the unexposed area and (d) exposed area after patterning indicated a gradual declining transmittance contrast to a 650 nm probe beam (the matched wavelength) with an increasing electric field.



Fig. 5 Microstructures of a Fresnel zone plate, rewritten with a patterned visible light (532 nm, 30 mW cm⁻²) for about a (a-i) 15 second and (b-i) 30 second exposure time after UV-erasing of the grating. The conspicuous focuses were shown, corresponding to the incident right-handed CPL with the wavelength of (a-ii) 650 nm and (b-ii) 532 nm. In the case that a left-handed CPL impinged on the sample, uniform light patterns were present (a-iii and b-iii), regardless of the wavelength.

ratio between the exposed and unexposed CLC areas, due to the electrically induced reorientation of the LCs. The transmittance spectra of both the two areas are shown in Fig. 4c and d. The helical structure was gradually unwound with the enhancement in the electric field, leading to a decrease in the transmittance/reflectance ratio between the adjacent exposed and unexposed areas, *i.e.*, the amplitude modulation was decreased, which led to a decrease in the +1st-order diffraction efficiency.

Dynamical erasable and rewritable diffraction device

A preferable feature of such a photoresponsive CLC based diffraction device is dynamical erasability and rewritability, *i.e.*, the grating can be developed and erased in real time by a uniform irradiation and reconfigured to another diffraction device such as the Fresnel zone plate shown in Fig. 5. A collimated red-colour right-handed CPL was focused (650 nm, Fig. 5a-ii) after passing through a Fresnel pattern with alternate red-and-earth-yellow reflection rings (Fig. 5a-i) formed by 15 second irradiation by a 532 nm laser. The prolongation of the irradiation to 30 seconds reconfigured a Fresnel pattern with alternate red-and-green reflections (Fig. 5b-i), which were sensitive to the green-colour right-handed CPL, as the focusing effect shown in Fig. 5b-ii. Similarly, the Fresnel zone plate exhibited a polarization-dependency, showing a transmission of left-handed CPL independent of wavelength (Fig. 5a-ii) and b-iii).

Conclusions

In conclusion, a light-reconfigured waveband-selective diffraction grating was developed by micro-patterning photoresponsive CLCs through a photomask. Distinct from the conventional phase modulated CLCs grating, herein, a periodic transmittance/ reflectance modulation (*i.e.*, amplitude modulation) was achieved when the wavelength of the impinged light was located in the reflection band of patterned CLCs. Therefore, diffractions both on

the transmission and reflection sides were produced. Wavebandselectivity can be reversibly tuned by virtue of patterned light irradiation within a wide spectral range (~140 nm). Attributed to the suitable pre-photo-crosslinking, electrical modulation of diffraction is achieved by controlling the transmittance/ reflectance contrast between the exposed and unexposed CLC areas. Moreover, owing to the reversible photoisomerization of the azobenzene-based chiral switch, such grating can be erased under uniform light exposure and rewritten to other patterns, such as a Fresnel zone plate, through a corresponding photomask. Furthermore, one of the prominent advantages is the electric responsiveness. Such a light-manipulated waveband-selective diffraction device accompanied by rewritability and electrical tunability is not only a step towards LC based stimuli-responsive devices but also provides a new concept on the light-directing reconfigured and redeveloped soft superstructure with a charming prospect on materials, photonics, and mechanics.

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