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We have observed enhanced photorefractive responses in CdSe doped nematic liquid crystal cells. The effective intensity dependent refractive index coefficients are on the order of $10^{-2}cm^2/Watt$. Using polymer-dispersed mixture of these NLC, 3-D photonic crystals are fabricated by short-exposure direct holographic optical illumination. The resultant structure exhibits 3-D photonic crystal Bragg diffraction and multi-color reflections that can be electronically switched at millisecond speed. Enhanced diffraction efficiency is obtained by doping the liquid crystal with gold nanowires.

Keywords: CdSe nanorods; electro-optics effects; gold nanowires; photonic crystals; photorefractive nematic liquid crystals; tunable diffractions

I. INTRODUCTION

Orientational photorefractive effect in nematic liquid crystals arises under the simultaneous action of an optical and a dc electric field [1–4]. The effect is attributed to photo-induced space charge fields

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[3] as well as the LC's bulk conductivity and dielectric anisotropies [4]), flow [4] and surface interactions [5,6]. The charge producing 'agents' in the NLC cells could come from a variety of materials used in fabricating the NLC cells – trace impurities, ITO coating, surfactants, the LC itself, or deliberately introduced dopants such as C60, dyes and carbon nanotubes [7,8]. Although the nonlinearity of these doped systems [7,8] are quite high, with nonlinear refractive index n_2 approaching unity in some cases, the induced orientational [index] gratings in the NLC tend to assume undesirable [for real time image/signal processing application] permanent and non-erasable nature upon prolonged illumination. Such permanent reorientation of the director axis usually occurs at the cell surfaces, as a result of the laser assisted deposition of the dopants. In this article, we report the observation of *transient* photorefractive response in CdSe doped nematic liquid crystal cells [CdSe-NLC]. The photoconducting nature of CdSe contributes to a larger conductivity difference ($\sigma - \sigma_d$) between the illuminated and the dark region, and therefore a larger space charge field, c.f. the photorefractive space charge field expression [1–3]:

$$E_{ph} = E_{ph}^{(0)} \cos(q\xi) = \left[\frac{mk_BT}{2e} qv \frac{\sigma - \sigma_d}{\sigma}\right] \cos(q\xi)$$

where σ is the conductivity in illuminated state and σ_d the dark state conductivity. This results in an enhanced photorefractive response. More importantly, we found that even under prolonged illumination, no 'permanent' component was observed. CdSe-NLC's are thus promising candidates for real time image processing application.

II. PHOTOREFRACTIVE CD-SE DOPED NEMATIC LIQUID CRYSTALS

The CdSe nanorods are synthesized in the laboratory of Mallouk using the method reported by Bunge *et al*. [9]. The diameter and length of the nanorods are around 7 nm and 30–50 nm, respectively. These nanorods are dispersed in the nematic liquid crystal 5CB. The ITO coated glass cell windows are treated with the surfactant HTAB to yield homeotropic alignment. The linearly polarized 488 nm line of an Argon laser is split into two coherent beams and combined on the sample at an oblique incidence angle [30 degrees from normal] as shown in Figure 1. The beam diameter is 5 mm. Sample thickness d is 35 μm. The overlapping angle of the two beams is 0.28 degree, which gives a grating constant λ of 50 μm. This approaches the optimal

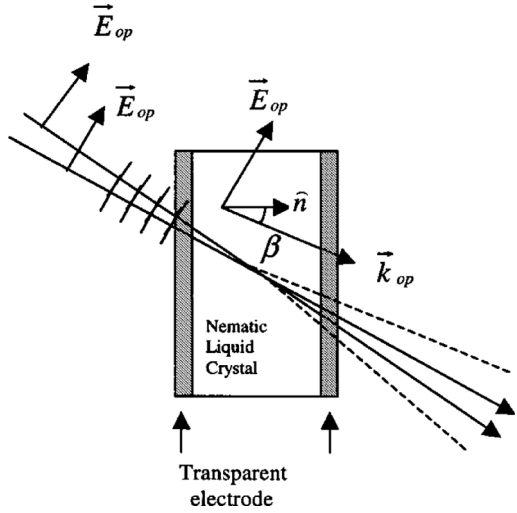

FIGURE 1 Schematic depiction of the four-wave mixing geometry to study the photorefractive effect of a nematic liquid crystal film.

condition of $\lambda \sim 2d$ [4]. At a laser power of 5.22 mW, self diffractions begin to manifest when the applied DC field reach 0.03 Volts/μm, c.f. Figure 2. The general dependence of the diffraction on the applied voltage is similar to other doped [dye, C60, Carbon nanotube] NLC [4,8] as is the dependence of the photorefractive effect on the writing beam power, c.f. Figure 3.

An important point to note is that the observed laser induced orientational (index) grating in CdSe doped NLC cells is transient in nature even under prolonged illumination, i.e., when the either of the input writing beams is blocked, the self diffraction will vanish in about 2 seconds. With the writing beam on, the side diffraction can also be switched on-off with the DC field at milliseconds – sec speed depending on the voltage [4].

To estimate the nonlinearity, we note that a typical first order diffraction efficiency η of 5.36% is observed under an applied electric field of 0.08 Volts/μm. Using the expression $\eta = (\pi \Delta n d/\lambda)^2$, where $\Delta n = n_2 I$ is the laser induced refractive index change and I the optical intensity, the effective nonlinear index coefficient n_2 can be calculated to yield $n_2 = 2.05 \times 10^{-2}$ cm^2/W. This nonlinearity is comparable to C60 or carbon nanotube doped NLC's. In comparison, undoped 5CB's photorefractive response is characterized by an $n_2 \sim 1 \times 10^{-3}$ cm^2/W which is an order of magnitude smaller. Nevertheless, they all rank amongst the highest of all known nonlinear optical materials.

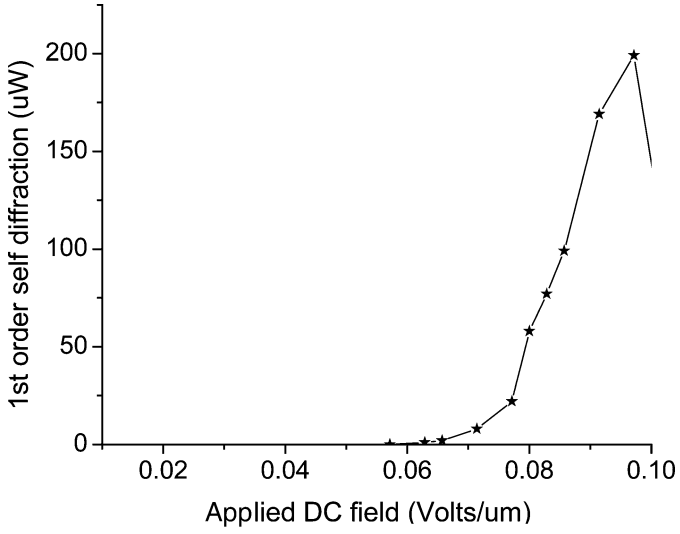

FIGURE 2 Observed dependence of the side diffraction on the applied dc voltage. Homeotropic aligned sample thickness is 35 μm. Laser intensity I = 5.22 mW.

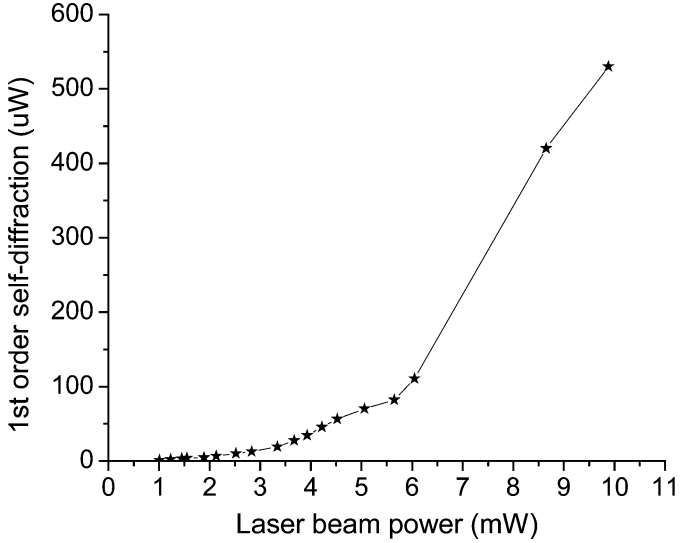

FIGURE 3 Observed dependence of the side diffraction on the writing beam power. DC field is kept at E = 0.08 Volts/μm.

III. ELECTRO-OPTICAL RESPONSE OF CdSe DOPED NEMATIC LIQUID CRYSTALS

Doping the NLC with photoconducting CdSe also leads to interesting electro-optical properties. Figure 4a shows a standard set up to evaluate their electro-optical response. A 25 μm thick planar aligned CdSe-NLC cell is placed between two crossed polarizer with its director axis at 45 degrees to the input polarizer direction, c.f. Figure 4a. An ac voltage [1 KHz] is applied on the film and the transmission of a linearly polarized He–Ne laser through the system is monitored. Above an ac applied voltage of 0.8 Volts, the transmission drops dramatically to less than 10% of the initial transmission, c.f. Figure 4b, as a result of the field induced reorientation of the director axis towards homeotropic alignment [perpendicular to cell window]. The transmittance can be reversibly switched on and off with this ac voltage with a response time of about 1 second. Much faster response can be achieved at higher applied voltage, or using dual frequency NLC. It is noteworthy that the Freedericksz transition voltage required for these CdSe doped NLC's are quite low [$<$0.03 Volt/μm] compared to the pure

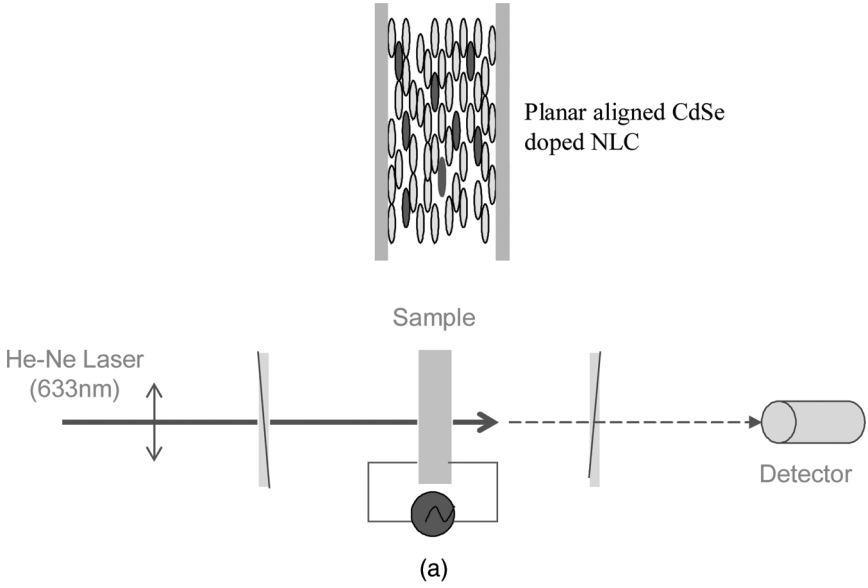

FIGURE 4 a) Experimental set up to monitor the electro-optical response of a planar aligned CdSe doped (25 μm thick) nematic liquid crystal cell. b) Observed transmission through the output polarizer as a function of the applied ac (1 kHz) voltage.

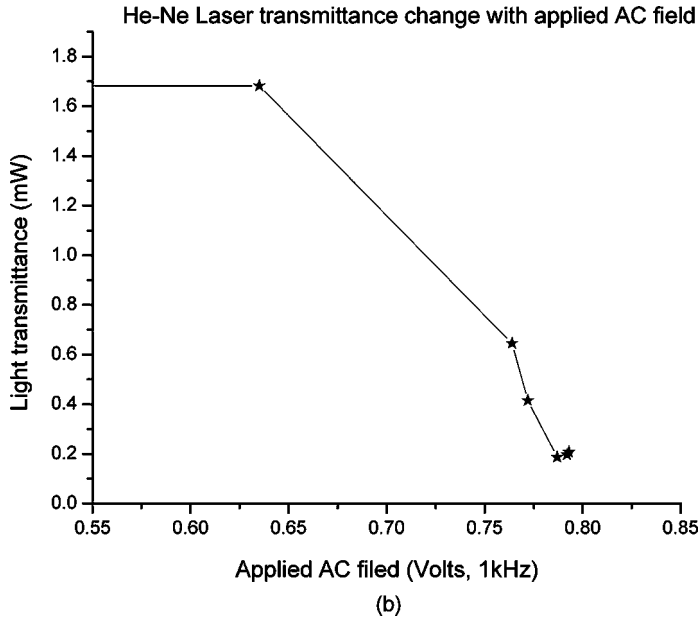

FIGURE 4 Continued.

undoped NLC. The exact mechanism responsible for such lowering of the threshold voltages remain to be ascertained. Most likely and plausible explanation is the modification of the dielectric constant, conductivity and dielectric anisotropies....etc. Such low-switching-voltage and photorefractive NLC's are promising candidates for electro- and nonlinear-optical image processing and switching application.

IV. NANO-PARTICULATE DOPED LIQUID CRYSTAL PHOTONIC CRYSTALS

Another means of enhancing the optical properties of liquid crystal is to fabricate novel structures by infiltration of LC's into photonic crystalline structures such as opals and inverse opals [10], and holey fibers [11]. These procedures are tedious and the alignment of the liquid crystal on the surfaces within the opal or holey fiber is difficult to control. Direct one step holographic interference methods [12–16] circumvent many of these fabrication problems. In particular, Bunning *et al.* [15,16] demonstrated the possibility of optically writing switchable 3-D photonic crystals in polymer-dispersed liquid crystals [PDLC] using a set up that involves three pairs of intersecting laser beams.

The resultant structure exhibits good reflection switching but relatively low transmission/reflection diffraction efficiency and very large scattering loss in the unclear [voltage-off] state.

In this article, we report similar holographic writing process, but with a much shorter exposure time. As a result of such partial polymerization, the resultant samples are optically transparent [very little scattering compared to fully cured PDLC] yet exhibit fairly high bulk diffraction efficiency and multi-color surface reflection.

In our experiment, a single expanded UV [wavelength 351 nm] Argon laser beam (about 6 cm diameter) is split into 4 coherent laser beams by a compact beam splitting device [16], which intersect at the desired incoming angles on the sample, c.f. Figure 5. The configuration eliminates the complexity and instability of a multiple beam configuration [14]. The optical intensity imparted on the sample consists of a 3-d array of intensity maxima and minima. According to Cai *et al*. [17], these four non-planar beams could create all fourteen crystalline symmetries. The set up we used gives a hexagonal lattice. The incident angle of the 3 side beams [measured with respect to the

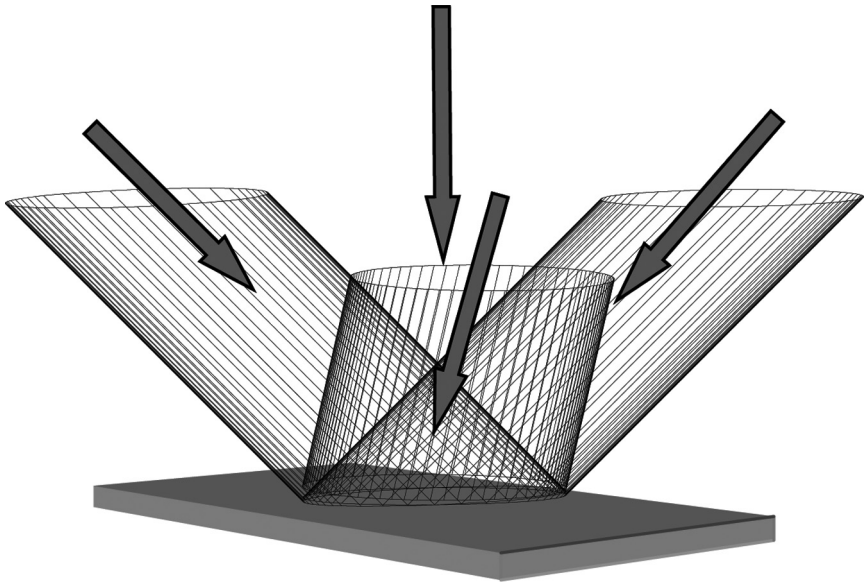

FIGURE 5 Schematic depiction of the 4 [coherent]-beam holographic writing set up to generate 3-D periodic optical intensity pattern on the polymer-liquid crystal mixture. The central beam is symmetrically surrounded by three outer side beams.

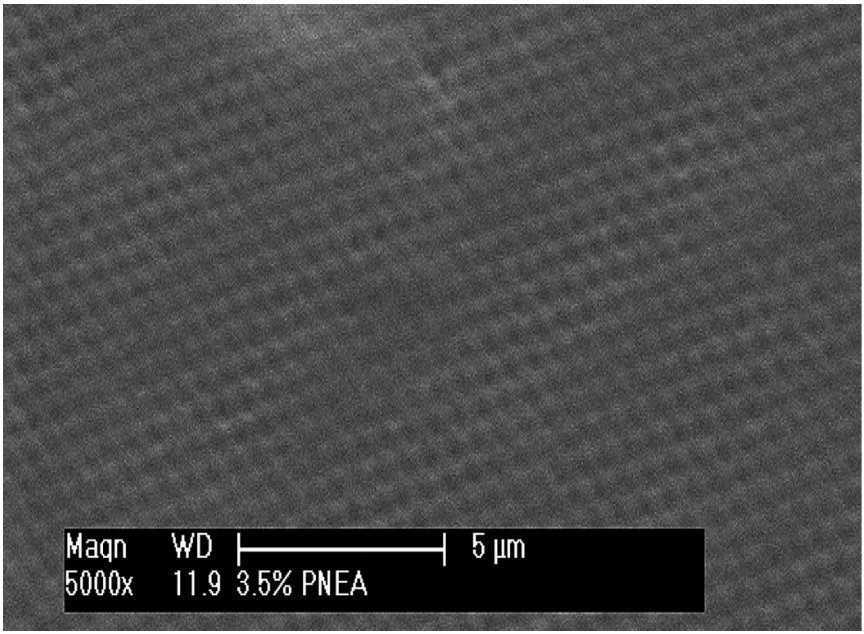

FIGURE 6 Scanning Electron Microscope picture of the 3-D polymer dispersed liquid crystal structure.

normally-incident central beam] is 45 degree [in air]. This gives rise to an optical interference grating constant of about 0.5 μm inside the polymer-liquid crystal mixture. The beam intensity is about 9 mW at the sample. The overlap area is 0.13 cm^2. A 5 μm thick homogenous [50:50] mixture of the liquid crystal E7 [from Merck) and the UV curable optical polymer glue NOA65 from Norland is sandwiched between two ITO-coated glass slides and is exposed to the 4-beam interference pattern.

In general, we found that exposure duration of 3 to 5 seconds will suffice, when multiple-orders 3-D diffractions from the sample are generated. Figure 6 is an SEM picture of the resultant structure which shows a periodic array of (partially) cured polymer and phase-separated liquid crystals. The lattice constant of periodic structure is about 500 nm, consistent with the incident angles of the 3 side beams and the laser wavelength used. Figure 7 shows the transmission spectra for different orientations of the structure. In this un-optimized sample, the peak transmission dip observed is about 20%. When viewed under white light, the structure shows multi-color reflections

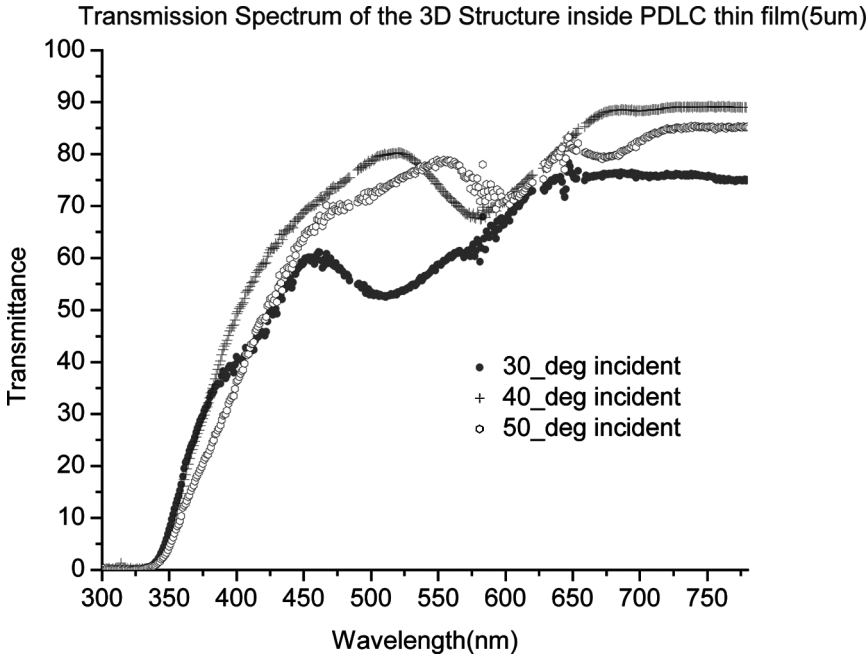

FIGURE 7 Transmission spectra of the PDLC photonic crystals obtained above at various orientation showing dips in the transmission. Sample is 5 μm thick.

as it is tilted. These properties are due to the small index difference between the (partially) cured polymer and the encapsulated liquid crystal. For E7, $n_o = 1.5211$, and $n_e = 1.7464$. The effective refractive index n_{eff} of the liquid crystal droplet as 'seen' by the incident light lies somewhere between n_o and n_e. For the UV curable optical polymer NOA65, the index of the cured polymer is $n = 1.524$.

Figure 8 shows the forward diffraction of a UV probe laser at 375 nm. Strong diffractions in the original directions of the three side beams, and weaker second order diffractions are observed. The measured diffraction angles agree with the writing beam angles of 44.5 degree and the peak 1st order diffraction efficiency [for the UV probe beam] is over 10%. By applying an ac (800 Hz) voltage to the PDLC photonic crystal, the side diffraction can be switched off when the applied voltage is sufficiently large to realign the liquid crystal along the applied field, and the probe beam 'sees' an effective index of LC close to the polymer matrix. The response times for these field reorientation range from 40 ms (at lower voltage) to 20 ms (higher voltage),

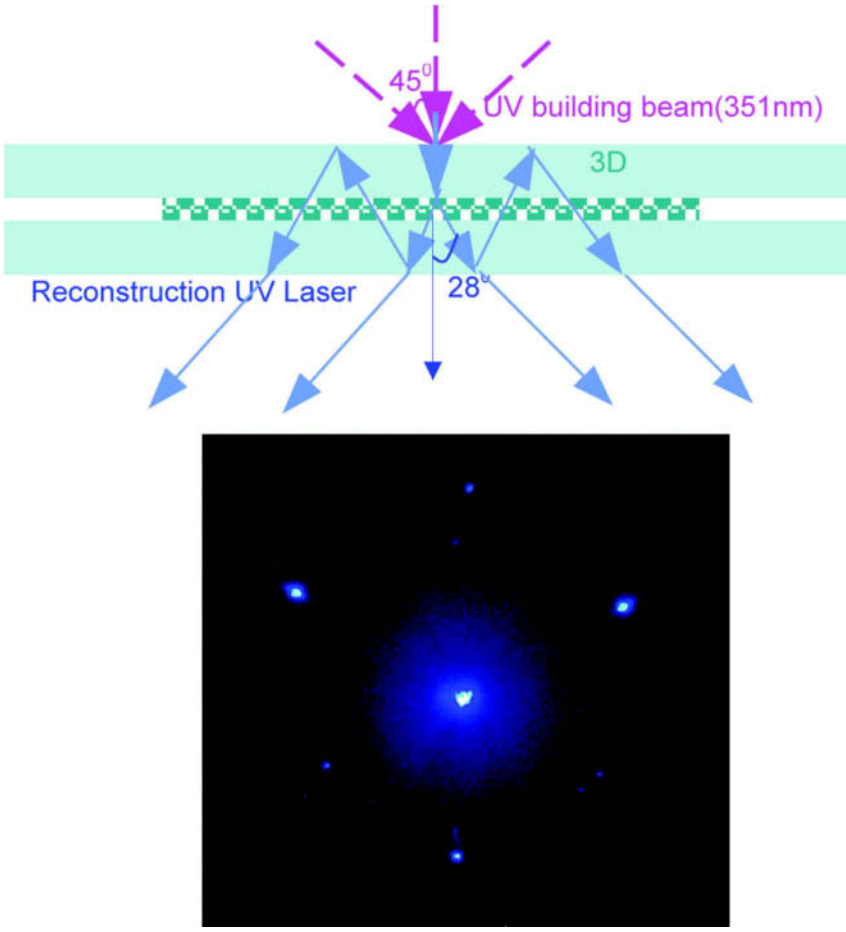

FIGURE 8 Bragg diffractions from the UV probe beam.

c.f. Fig. 9. When the ac field is turned off, the orientation grating recovers in $\sim$50 ms.

In some recent experiment, we found that these diffraction efficiencies can be enhanced by several folds [to >35%] if the liquid crystal is doped with gold nanowires. The exact responsible mechanism remains to be ascertained, but the results clearly indicate the feasibility of fabricating good optical quality tunable/switchable 3-D PDLC based-photonic crystals.

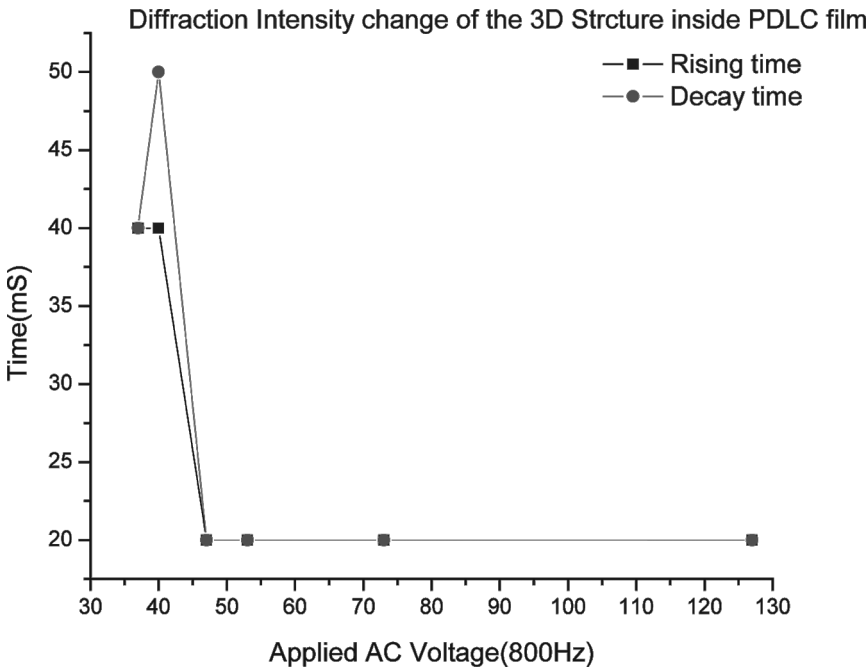

FIGURE 9 Switching dynamics of the photonic crystal.

V. CONCLUSION

In conclusion, we have demonstrated two promising avenues to further develop the nonlinear- and electro-optical properties of liquid crystals. In CdSe doped nematic liquid crystals, we found that the orientational photorefractivity is comparable to other previously investigated C60-, Fullerene, or dye-doped systems. But unlike these other doped systems, the photorefractive effect obtained here is purely transient, thus enabling real time image processing application. Furthermore, the switching voltage required for electro-optical modulation of these CdSe doped NLCs is considerably lowered than undoped NLC. We have also demonstrated direct holographic 3-D photonic crystal fabrication with polymer dispersed nematic liquid crystal mixture. The resultant structures exhibit switchable/tunable transmission, reflection and diffraction properties, with response times typical of PDLC. We are currently exploring the possibility of fabricating 3-D photonic crystals with CdSe doped liquid crystals, and creating electronically and [nonlinear] optically tunable structures.

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