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Orientational holographic gratings observed in nematics aligned by carbon nanotube film

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ABSTRACT In this paper, we present a novel type of nematic liquid crystal cell with carbon nanotube film deposited by electrophoresis as the alignment layer. Self-diffraction was observed without applying a dc voltage across the cell under low intensity optical irradiation of a few milliwatts at 488 nm. The first-order diffraction efficiency increased and the response time of the grating decreased with the applied dc voltage increasing up to the dynamic scattering threshold voltage at 4 V (the corresponding dc electric field was 0.2 V/μm). A diffraction efficiency of $\sim 20\%$, the grating formation time of 0.5 s and an effective refractive index change coefficient of 0.14 cm^2/W were obtained at 3.7 V with a writing beam intensity of 33 mW/cm^2. These observed phenomena were attributed to the photoactive charge layer formed at the interface of the carbon nanotube film and the liquid crystal film.

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1 Introduction

In the pursuit of improved photorefractive (PR) materials, PR liquid crystals (LCs) have been studied systematically [1–6]. Two mechanisms were proposed to explain the formation process of the PR grating in LCs. One was the bulk mediated PR mechanism [1]. In this mechanism, the PR grating was attributed to a light induced modulation of electric charges, in conjunction with an applied dc electric field producing space charges in the bulk of the LC. The other was the surface mediated PR mechanism in which the surface charges played a fundamental role [3–6]. Here surface meant the interface of the nonphotosensitive alignment layer and the LC film. The charges in the bulk aggregated on the surface spontaneously or by applying an external dc electric field. Then, the optical interference pattern modulated the distribution of the surface charges and the modulated electric field reoriented the director of the LC. In addition, the LC cell with photoconductive layer was also studied [7–9]. Ono et al. believed that for this type of cell the charges were generated in the photoconductive layer and trapped on the surface of the insulating layer [7]. However, Kaczmarek et al. [9] believed that the surface charge layer located at the interface of the photoconductive polymer layer and the LC film, and also the incident optical pattern, modulated the photoconductivity of the polymer layer leading to the modulation of the surface charges.

Carbon nanotubes (CNTs) have been known to possess unique mechanical and electrical properties that make them attractive materials for fundamental scientific studies as well as for a wide spectrum of applications including electron field emission sources, nanoscale electronic devices, chemical filters and storage systems, and mechanical reinforcements. By doping CNTs in LCs, the PR performance was enhanced greatly because CNTs dissolved in the LC improved the generation and transportation of photocharges and inhibited the dynamic scattering under the application of a large voltage [10–13]. Khoo et al. obtained an extremely large effective refractive index change coefficient of 7 cm^2/W and rapid buildup and decay times on the order of tens of milliseconds to 100 ms in the LC doped with CNTs and/or C_{60}. However, to achieve those values, very weak optical illumination of 40 μW was needed, which led to a low diffraction efficiency of 1%, and a high applied electric field of 0.8 V/μm was applied for a 1-s duration [10]. Lee et al. [11] also obtained a large effective refractive index change coefficient (0.05 cm^2/W) and the corresponding response time was ~ 30 s in the CNTs-doped nematic liquid crystal (NLC) with two writing beams of equal intensity of 44 mW/cm^2 under application of the electric field at 0.6 V/μm. However, the high diffraction efficiency, large effective refractive index change coefficient and fast response time cannot be achieved simultaneously. In fact, the typical grating formation time when the diffraction efficiency is on the order of 10% for the LC material is in tens of seconds to minutes [14, 15].

Recently Samulski explored the CNT film as a novel alignment substrate [16]. Sparse CNT films composed of CNT bundles deposited with controlled orientation onto indium-tin-oxide (ITO) coated glass substrates were used to induce uniform planar alignment of NLC. In this paper, we report what to our knowledge is the first observation of the Raman–Nath diffraction by the PR gratings recorded in the NLC cell with the CNT film as the alignment layer. This kind of cell exhibits unique optical properties such as self-diffraction occurring without applying a dc voltage, a high diffraction ef-

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ficiency coexisting with the fast grating formation time and a large effective refractive index change coefficient.

2 Experiments

A CNT film was deposited onto an ITO coated glass substrate by electrophoresis. Two ITO-glass slides, which were connected to the positive pole and the negative pole of the dc electric power, respectively, were vertically dipped into the N, N-dimethylformamide (DMF) solution of CNTs (prepared as reported in [17]). The solubilized CNTs were deposited from the solution to the positive electrode under application of the electric field at about 100 V/cm. Then the sample was rinsed by ultrasonication in DMF to remove any weakly adsorbed CNTs. After that, the sample was dried in air for 30 min.

The NLC cell consisted of a layered structure: glass substrate, ITO film, CNT film, NLC film, ITO film and glass substrate as shown in Fig. 1. The planar alignment was verified by a polarizing microscope. The thickness of the NLC film was 20 μm. The NLC used was E7 obtained from Merck. Pure E7 as well as C_{60}-doped E7 was used in this study. The results for pure and C_{60}-doped E7 were qualitatively the same, but doping C_{60} made the cell more sensitive. Unless otherwise noted, the LC used in the sample was doped with C_{60}.

Two-beam coupling setup is shown in Fig. 2. Two p-polarized writing beams from an Ar^+ laser at 488 nm intersected in the cell. The included angle between the normal of the sample and the bisector of the two writing beams I_1, I_2 was 45°, and the LC director was in the incidence plane. The period of the interference pattern was about 40 μm. The power of each writing beams was 3 mW. The diameter of the beams at the intersection was 3 mm. A p-polarized 100-μW He-Ne laser beam I_3 at 633 nm was used to probe the grating recorded in the cell.

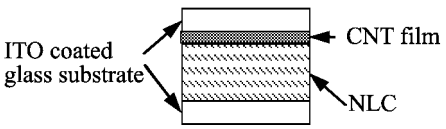

FIGURE 1 The schematic of the structure of the cell

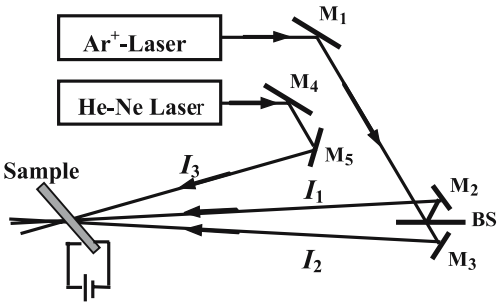

FIGURE 2 The optical setup for two-beam coupling. The grating was recorded by two coherent p-polarized Ar^+ laser beams I_1 and I_2 which intersected in the sample with or without the application of a dc voltage. A weak p-polarized He-Ne laser beam I_3 was used to probe the grating. M_1–M_5 were reflectors, BS was the beam splitter

3 Results and discussion

Under our experimental conditions, the dimensionless parameter $Q = 2\pi\lambda L/n\Lambda^2$ is 0.03 and much smaller than unity, where λ is the wavelength of the writing beams, L is the thickness of the grating, and n is the average index of refraction. It indicates that the grating is in the Raman–Nath regime, where multi-order self-diffractions are allowed in two-beam coupling experiments.

Self-diffraction could be observed without an external electric field in both pure NLC and C_{60}-doped NLC cells. The C_{60}-doped cell had much stronger PR effect than the pure one. The first-order diffraction efficiency could reach 1% without an external electric field. Asymmetric energy transferring between two writing beams was also observed without an external electric field, which substantiated the PR nature of the grating. For all reported pure and C_{60}-doped NLC cells, which used usual alignment materials such as hexadecyl trimethyl ammonium bromide (HTAB), polyvinyl alcohol (PVA), etc., there was no self-diffraction without applying a dc electric field [3, 6, 18, 19]. Therefore, we believe that the adsorption of charges on the surface of the CNT film from the NLC bulk plays the key role in the PR effect, i.e., the CNT film adsorbs charges with a certain sign from the LC bulk through an unknown chemical process and the charge layer is formed on the surface of the CNT film. The adsorbed charges will desorb from the surface under light irradiation, thus the redistribution of the surface charges occurs by the nonuniform irradiation and leads to the formation of the PR grating. Herein the charges in the LC bulk originate from the impurities or dopants.

We then used the experimental setup as shown in Fig. 2 to observe the diffraction from the NLC cell at different applied dc voltages. The electrode with the CNT film was connected to the positive pole. Data were obtained by applying voltages ranging from 2 to 4 V. When the applied dc voltage was below 2 V, the diffraction was weak. Strong dynamic scatterings due to the dc field induced flow occurred at about 4 V. Figure 3 demonstrates the asymmetric coupling dynamics of the two writing beams under an applied voltage of 2.5 V, which substantiates the PR nature of the grating recorded in the presence of the dc electric field. Figure 4 shows the typical recording and erasing dynamics of the grating at 3.3 V. The first-order diffraction efficiency increased almost linearly with the applied voltage increasing from 2 to 3.7 V, and the grating for-

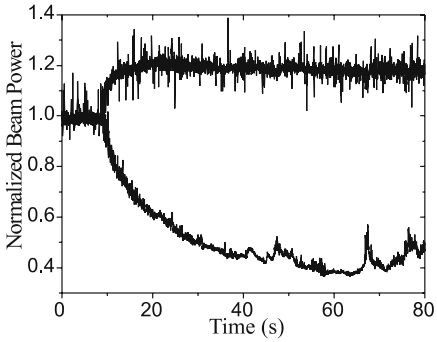

FIGURE 3 Dynamics of the asymmetric beam coupling under an applied dc voltage $V = 2.5$ V

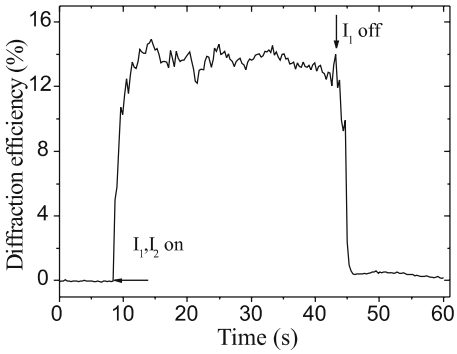

FIGURE 4 Time evolution of the first-order diffraction efficiency under an applied dc voltage $V = 3.3$ V

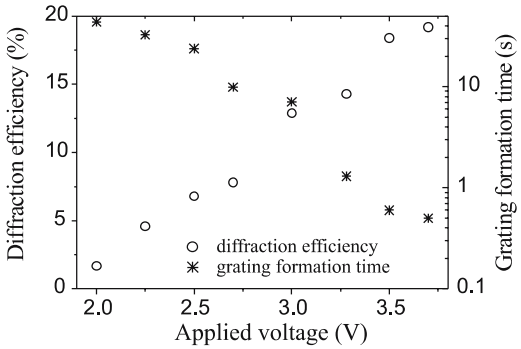

FIGURE 5 Dependence of the first-order diffraction efficiency and the grating formation time on the applied dc voltage

mation time decreased with the applied voltage, as shown in Fig. 5. At 3.7 V, a first-order diffraction efficiency of $\sim 20\%$ and the grating formation time of 0.5 s were obtained. Here, the grating formation time is defined as the period in which the diffractive signal reaches $(1 - 1/e)$ of the steady state value. Since the first-order diffraction efficiency $\eta = (\pi \Delta n d/\lambda)^2$, we obtained $\Delta n = 4.5 \times 10^{-3}$, and therefore an effective refractive index change coefficient $n_2 = \Delta n/I \approx 0.14\,\mathrm{cm}^2/\mathrm{W}$ with a writing beam intensity of $33\,\mathrm{mW/cm}^2$. So the grating recorded in the C_{60}-doped NLC cell with the CNT film as the alignment layer exhibits unique optical properties, such as self-diffraction, which occurs without applying a dc voltage, a high diffraction efficiency, which coexists with the fast grating formation time and a large effective refractive index change coefficient.

When the direction of the electric field was reversed, i.e., the electrode with the CNT film was connected to the negative pole, the dynamic scattering threshold voltage lowered to below 1.5 V. When the substrate with the CNT film was connected back to the positive pole, the typical operating voltage and dynamic scattering threshold voltage decreased permanently. The large diffraction efficiency and rapid response time could no longer be observed. We speculate that this phenomenon is due to irreversible changes in the CNT film induced by the reverse electric field. Since CNTs are deposited onto the positively charged ITO film surface from the CNTs solution under the application of the electric field, the reverse electric field may desorb CNTs from the ITO film partially or induce other unknown process.

To further verify the surface mechanism of the grating recorded in the cell, we investigated the light induced change

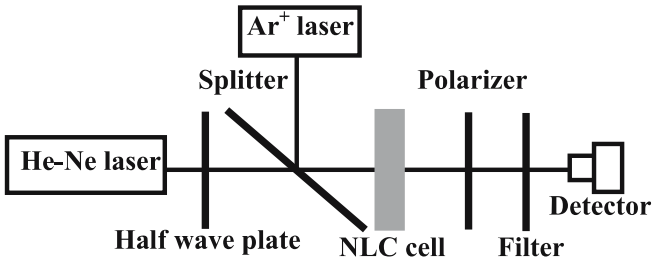

FIGURE 6 Optical setup for investigation on the light induced birefringence change

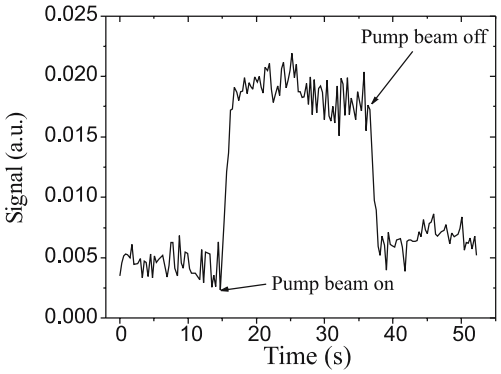

FIGURE 7 Probe beam signal versus time during the pump beam turning on and then subsequently turning off

in birefringence of the LC film, which had been used to study the surface charge effect previously [5, 20]. The optical setup is shown in Fig. 6. The lower power, linearly polarized probe He-Ne laser beam ($\lambda = 633$ nm) and the pump Ar^+ laser beam ($\lambda = 488$ nm) co-propagated at normal incidence on the sample. The director of NLC was oriented along 45° to the polarized direction of the probe beam. A filter filtered the pump beam entirely after the cell. Then, a crossed polarizer was located in front of the detector. Under the applied electric field perpendicular to the LC wall, the director was toward the field direction, i.e., homeotropic. The resulting birefringence changes induced probe beam phase retardation due to the different propagating velocities of the ordinary and extraordinary rays in the NLC film. Figure 7 shows the typical data, showing the detected signal versus time during the pump beam turning on and then subsequently turning off. In this experiment, the applied voltage was 2.4 V, and the power of the pump beam and the probe beam were 5 mW and 100 μW, respectively. The experimental data are consistent with the above postulation that the surface of the CNT film can adsorb charges from the bulk of NLC. The surface charge layer adsorbed on the surface of the CNT film screens the electric field partially. The light can desorb the charges from the CNT film surface and consequently the electric field acting on the NLC film increases. Thus the director reorients and the signal behind the polarizer is changed. When the pump beam is turned off, the director is relaxed and the signal is restored. Similar phenomena were obtained at voltages from 2 to 4 V.

4 Conclusion

In conclusion, the grating recorded in the CNT film aligned NLC cell exhibits unique optical properties,

such as self-diffraction occurring without applying a dc voltage, a high diffraction efficiency coexisting with the fast grating formation time and a large effective refractive index change coefficient. These results are of benefit to the applications of PR LCs in holography and image processing.

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