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A novel composite alignment layer for transfective liquid crystal display

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Abstract

A novel composite photoalignment layer for transfective liquid crystal displays is explored. The key technique is to introduce a functional photo-crosslinkage into a rewritable azodye material with proper mixing. Bearing good alignment quality derived from the azodye material, the composite layer provides strong azimuthal and polar anchoring energy comparable to that of rubbed polyimide layers. The capability of dual modes fabrication in one cell exhibited by azodyes could be well retained and the new alignment film exhibits a display resolution of up to 2 μm . Furthermore, after exposure to strong LED unpolarized light the composite layer shows much better stability than that with a pure azodye material.

(Some figures in this article are in colour only in the electronic version)

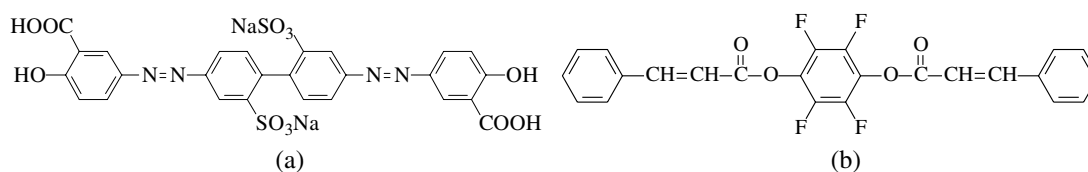
1. Introduction

Liquid crystal displays (LCDs) are used extensively in many applications due to their small thickness, low power consumption, portability and so on. An alignment layer plays a crucial role in controlling the orientation of liquid crystal molecules and is indispensable in practical display fabrication. Commonly, a rubbed polyimide film is used as the alignment layer. However, this method always brings dust and static electricity with friction and deteriorates the image quality [1, 2]. Liquid crystal photoalignment is a promising technology for manufacturing a variety of LCDs, which avoids many drawbacks of the traditional rubbing technique for LC alignment, such as sample contamination, static charge generation and mechanical damage [3, 4]. The technique is attractive as a promising alternative to the rubbing process to be used in the next generation of displays, such as multidomain, vertically aligned and/or in plane switching mode displays. Linearly polarized light, non-polarized light and coherent light of lasers are used as irradiation light. Photoinduced anisotropy in the absorption property was first reported in 1977 using polyvinylcinnamate. However, polyvinylcinnamate was not

that suitable as an alignment layer for LCDs because of its poor thermal stability and anchoring energy [5]. Photodegradation of polyimide films was also explored, but has not drawn much attention due to its side product after photodegradation [6]. As for azobenzene materials, reversible change between homeotropic and planar alignment of nematic LC triggered by the *trans*–*cis* photoisomerization of azobenzene molecules was first introduced to silica substrates by silylation [7]. Recently, the potential ability of azobenzene materials for molecular rearrangement based on photoisomerization has drawn much attention. It has been reported that photoaligning diazodyes, which can be easily rotated with blue light, could provide anchoring energy as strong as a commercial polyimide film and show potential for applications as optical rewritable liquid crystal devices and alignment layers for transfective liquid crystal devices [8, 9]. The rewritable property could show tunable control of alignment for LC and further change the displayed information of the LCD easily. However, the disadvantage is that the information generated by the azodye material is not stable enough against light in the visible spectral range for long-time display applications.

Attempts to improve the photostability of azodyes have already been made, in which a reactive group capable of

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Scheme 1. Chemical structure of SD1 (a) and 4F-BADE (b).

polymerization is added to the dye molecule, but resulting in poor anchoring energy [10]. Moreover, a dual photo-reactive group in one copolymer structure was also explored by introducing a photo-crosslinking group [11]. However, these ideas led to long time and high cost of synthesis and the alignment of LCs was usually degraded due to additional groups. Recently, a polymer liquid crystal (PLC) layer has also been used to deposit on top of an azodye film, but it needed critical control of the thickness of the PLC layer and did not result in strong stabilization of the azodye material either [12]. Hence, a more efficient and easier method to stabilize dye materials should be explored.

In this work, a composite layer based on mixing a crosslinking monomer with an azodye material was proposed as an alignment layer for transmissive LCDs. With the proper concentration of the mixture, we could obtain a dual functional alignment film. The fine alignment quality derived from azodyes was actually retained and good photostability against strong blue light from cinnamate was indeed achieved. The azimuthal and polar anchoring energies of the composite layer were high and comparable to that of rubbed polyimide layers. Also, the composite layer could produce pattern alignment information based on a mask with a two-step exposure process to polarized light. The display resolution of the composite layer for transmissive LCDs was up to $2\ \mu\text{m}$, which is good enough for real applications.

2. Experiment

Azodye material SD1 was provided by Dainippon Ink and Chemicals, and crosslinking material 4F-BADE, denoted as 4F in the following, was synthesized by Changchun Institute of Optics, Mechanics and Physics, Chinese Academy of Sciences, according to [13]. SD1 and 4F material were dissolved separately in dimethylformamide of concentration 1% and then mixed together in different ratios. The composite alignment film was prepared following the pretilt angle generation process reported in [14] with a two-step exposure process (normal exposure with polarized LED light for 60 s: high power $4 \times 3\ \text{W}$ blue LED lamp; $450\ \text{nm} \pm 20\ \text{nm}$; $70\ \text{mW cm}^{-2}$, and subsequently 5 min oblique irradiation of unpolarized UV lamp: Oriel 6925NS; $365\ \text{nm}$, $6\ \text{mW cm}^{-2}$; $300\ \text{nm}$, $3.5\ \text{mW cm}^{-2}$). A parallel or 90° twisted cell with $5\ \mu\text{m}$ cell gap was fabricated and a commercial liquid crystal (E7, Merck) was used. Microscopic photos were taken using an Olympus microscope (BH3-F04T). The optical property and transmittance versus voltage curve of the cell were studied using a crossed polarizer with He-Ne laser ($632\ \text{nm}$) with a photodetector. The

anchoring energy was measured by a method developed by our group [10].

3. Results and discussion

Scheme 1 is the chemical structure of the azodye material SD1 and crosslinking material 4F-BADE. The composite alignment film was obtained by mixing two solutions in different ratios. Azodye materials are restricted in many application fields due to their poor photostability; this disadvantage is extremely distinct for SD1 material. In experiments it was seen that when SD1 was exposed to oblique unpolarized light during a pretilt angle generation process, its anisotropy decreased, which was caused by its rotation nature [15]. Here, in order to retain its high anisotropy in the film, photo-crosslinking material 4F was used to stabilize SD1. A blue LED was used to bring about the orientation in SD1; and a UV lamp with a wide wavelength range ($365\ \text{nm}$ for SD1 to tilt; $300\ \text{nm}$ for 4F to crosslink) was used to generate pretilt angles, simultaneously stabilizing the azodye with the crosslinking reaction. Both materials show similar rod-like structures, and this allows better miscibility when they are mixed together. Furthermore, in the composite film, similar structures would exhibit similar orientation properties; after photo-orientation the SD1 molecule could align the adjacent 4F molecule in its alignment direction. This could retain good anisotropy of pure SD1 film and provide a high chance of exact position fix for SD1 molecules by a network generated by 4F material after crosslinking. To investigate the practical effect of 4F material for stabilization, dichroic ratio (DR) in the film after oblique unpolarized light exposure was measured. The DR before/after unpolarized light exposure and retaining level to that before exposure are shown in figure 1. Before exposure, due to the dilution effect of 10% 4F, interaction between SD1 molecules is weakened, which reversely promotes its rotation performance. Hence, more molecules are rotated by the polarized light and this causes a higher DR value than for pure SD1. With increase in concentration, 4F molecules are too many for SD1 to align all of them in its orientation direction and anisotropy is decreased gradually. After exposure, lower stability is obtained for the 10% film because a concentration of 10% is not enough for all molecules to undergo crosslinking reaction. When only one C=C bond in a 4F molecule gets a chance to crosslink with the adjacent C=C group in another 4F molecule, both molecules will tilt from the initial position to become closer for a successful reaction. Correspondingly, the neighbouring SD1 molecules are affected and also tilted from the initial position; hence anisotropy is destroyed and the DR value is smaller than that of pure SD1. When the concentration is above 10%, full photo-crosslinking reaction

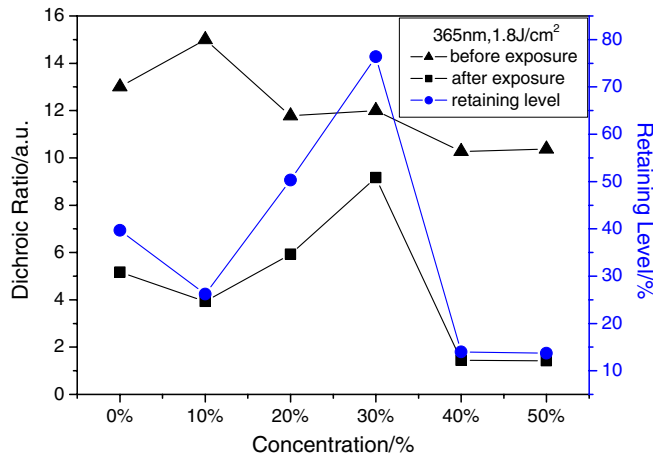


Figure 1. Change in DR and retaining level in films with different concentrations.

can happen easily and a network after crosslinking is formed by the polymer structure of the crosslinked 4F molecules. SD1 molecules are fixed inside the network and its photo-rotation with light is limited. This results in a high DR value after unpolarized exposure, retaining 80% extent of the original DR value. This means 4F indeed helps to protect SD1 from photodegradation. However, when the concentration is above 30%, the number of 4F molecules is very large, and the aligning capability of SD1 is not strong enough to induce orientation of all the 4F molecules in the same direction as its direction. Part of 4F acts like that in the film of 30% concentration. However, some 4F molecules form random domains without any induced direction of SD1 and SD1 inside is fixed in random directions simultaneously. Correspondingly, the anisotropy in the film is decreased, and it becomes even worse than that of 10% concentration. As the measured DR shows, larger concentration ($>30\%$) exhibits worse anisotropy. In summary, it is concluded that 30% concentration is the optimized condition to stabilize the azodye molecule.

To further investigate the LC performance on the 30% alignment film, both parallel and twist cells were fabricated. Figures 2(a) and (b) show the photos taken under the microscope in dark and bright states in parallel and 90° twisted cells. The disclination lines in figure 2(b) are the boundary of the two domains. When the twist angle in the LC cell is close to 90° , turning left or right from the normal direction to the substrate will appear identical for them. Hence both domains of turning left or right will exist at the same time. And due to the small pretilt angle of the composite layer, LC molecules at the boundary will tilt slightly from the normal direction and some light can pass through the cell. That is why under the crossed polarizer the disclination lines appear not as dark as the other domain without disclinations. Hence, the existence of disclination lines just proves good anchoring strength but not defect of alignment. Hence, figure 2 shows that the alignment is good without any obvious defect. This means the introduction of 30% 4F to the SD1 material does not degenerate its alignment quality. Furthermore, the azimuthal anchoring energy and polar anchoring energy were also measured for this

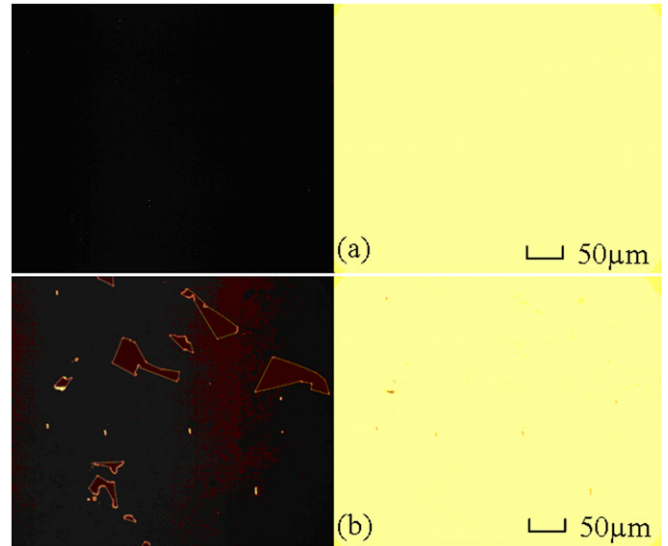


Figure 2. Photos of dark/bright states of LC alignment in parallel (a) and twisted mode (b).

Table 1. Summary of anchoring energy for SD1 and S/4F.

Anchoring energy	$W_a (10^{-4} \times \text{J m}^{-2})$	$W_a (10^{-4} \times \text{J m}^{-2})$
SD1	1.004	9.43
S/4F	9.78	21

composite alignment film and are summarized in table 1. It is seen that the azimuthal anchoring energy and polar anchoring energy of the composite alignment film indicate stronger anchoring ability than pure SD1 film. This value is consistent with the result in figure 1. The 4F material limits the photo-rotation of the SD1 molecule against random unpolarized light irradiation, and hence maintains the high orientation order and possesses stronger anchoring energy. The values of anchoring energy confirm the practical ability of 4F material to protect the composite alignment film in liquid crystal cells.

Furthermore, transmittance versus voltage curve (TVC) is a key parameter for LCDs; hence the stability against unpolarized exposure was investigated. A blue LED was used as the light source (450 nm , 70 mw cm^{-2}), in which there is no UV light, but instead more powerful blue light close to real life environment. After fabricating 90° twisted nematic LC cells, the powerful blue LED was used for exposure. The TVC curves for both SD1 and S/4F alignment films were measured before and after 21 J cm^{-2} exposure, as shown in figure 3. It is seen that after unpolarized exposure, the TVC in the SD1 cell shows obvious deviation from that before exposure shown in figure 3(a). After exposure the threshold of the LC changed due to the change in pretilt angle, and the contrast ratio decreased because of the degradation in alignment quality. This means 21 J cm^{-2} exposure can easily destroy the alignment quality inside the SD1 cell. However, the TVC of the S/4F cell fits very well before and after exposure except for a small floating, which is possibly the birefringence variation of the LC caused by the heating effect of light. This means that the alignment performance of the LC in the composite alignment film, pretilt angle and anchoring energy

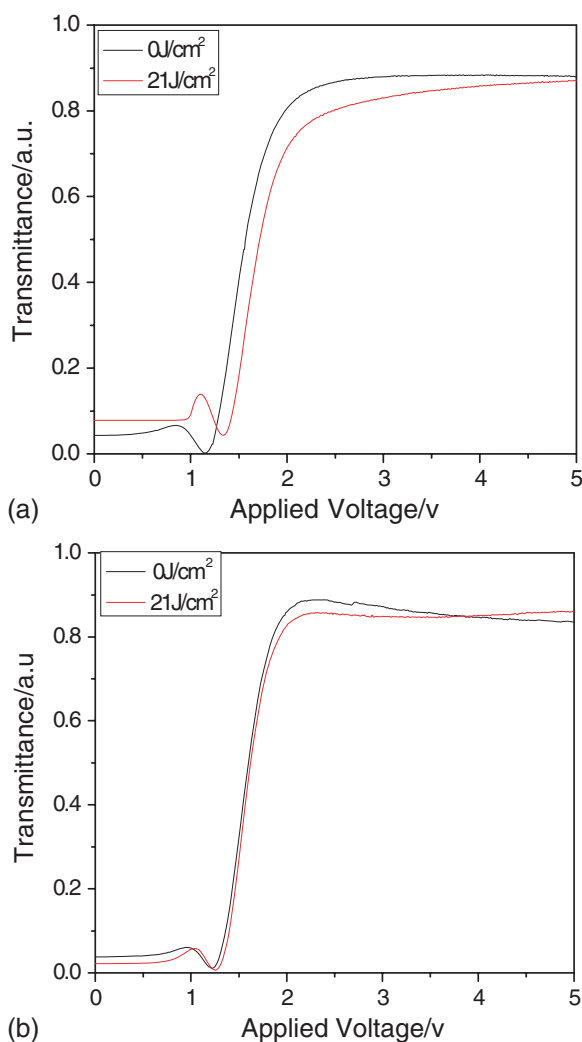


Figure 3. TVC curves against blue light irradiation in twisted nematic cells on SD1 (a) and S/4F (b).

of the film do not change after unpolarized irradiation. In summary, it may be concluded that the composite alignment films exhibit much better stability than the SD1 cell; the 4F material actually stabilizes SD1 against 21 J cm^{-2} exposure. Hence, when used in real environment where light intensity is much weaker than the LED light, the lifetime of the LCD on composite alignment S/4F must be much longer and could meet the requirement of transfective device applications.

For the transfective device developed by our group [9], dual modes fabrication inside one cell is the crucial technology. As shown in figure 4(a), a transfective LCD prototype with a composite layer was successfully fabricated. In the experiment, one composite layer of the cell was patterned with a mask using a two-step exposure process, and the other layer was just given a uniform alignment in one direction. Hence, dual mode with different twist angles inside one LC cell could be fabricated together easily. This shows that the composite layer can be easily written with pattern information before the photo-crosslinking reaction. After crosslinking, the layer also has fine alignment quality comparable to that of a pure dye layer. In addition, the resolution of pattern display for the composite alignment layer is investigated. A mask with line

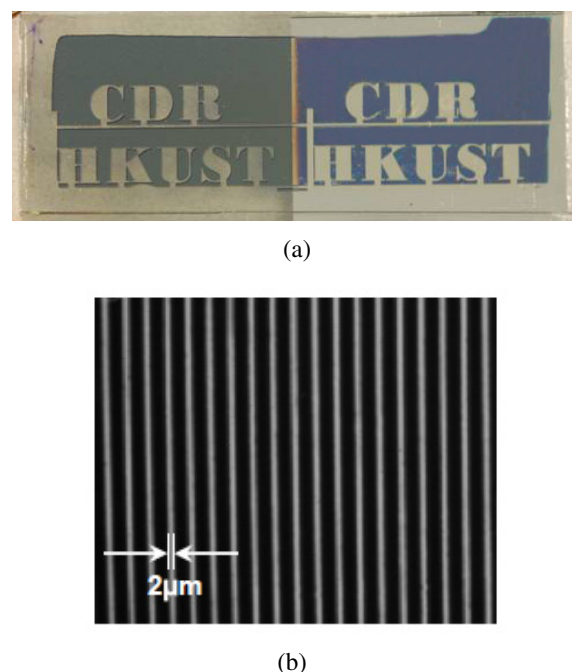


Figure 4. Prototype (a) and display resolution (b) of transfective LCD on composite layer.

shape was used with a two-step exposure process to form the pattern structure. As shown in figure 4(b) under the crossed polarizer, parallel mode of dark lines and 90° twist mode of bright lines were obtained in one cell, and the size of bright lines was $2 \mu\text{m}$. We can see that the profile of bright lines is clear and sharp. This means that the composite alignment film also shows high resolution as with pure SD1 [16]. Hence it is concluded that mixing 4F material does not degenerate the pattern ability of SD1 and can be successfully used as an alignment layer for stable transfective LCDs in outdoor or more rigorous environments.

4. Conclusions

A new stable alignment film for transfective LCDs is proposed in this work. The key point is mixing a crosslinking material with an azodye material. The novel alignment film shows as good a quality as that with a pure azodye material. Since no additional layer is needed and no complicated structure is involved in the synthesis, this method explores an easy way to fabricate a stable alignment film. Photostability against unpolarized light is obviously improved compared with a pure SD1 layer. Even after 21 J cm^{-2} powerful blue light irradiation, the TVC of the novel layer could fit well with the curve without exposure. A high display resolution of $2 \mu\text{m}$ is successfully achieved for the novel layer. This novel method provides a promising alignment layer for transfective LCD applications.

Acknowledgments

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