Enhancement of electro-optic properties in liquid crystal devices via titanium nanoparticle doping

Yong-Seok Ha, Hyung-Jun Kim, Hong-Gyu Park, and Dae-Shik Seo*

Information Display Device Laboratory, department of Electrical and Electronic Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, South Korea
dsseo@yonsei.ac.kr

Abstract: We investigated the properties of nematic liquid crystal device (NLC) doped with titanium (Ti) nanoparticle (~100nm). The electro-optic (EO) properties of LCs changed according to Ti nanoparticle doping concentration. Ti nanoparticles in the NLC cells focused the electric field flux and strengthened the electric field. Further, Ti nanoparticles in NLC molecules may trap charged ionic impurities and suppress the screen effect, leading to a stronger electric field and the van der Waals dispersion interactions between NLC molecules and the alignment layers. We also simulated the boundary conditions of the Ti nanoparticles in the electric field using Ansoft Maxwell software. Our experimental results agreed with the phenomenon predicted by software simulation based on general physical theory. Synthetically, at a 1.0 wt. % Ti nanoparticle doping concentration, the NLC cells showed the best EO properties, such as a low threshold voltage (1.25V), fast response time (13.2ms), and low pretilt angle (3.90°).

© 2012 Optical Society of America

OCIS codes: (160.3710) Liquid crystals; (230.3720) Liquid-crystal devices; (000.2690) General physics; (160.4236) Nanomaterials.

References and links

1. H. G. Park, J. J. Lee, K. Y. Dong, B. Y. Oh, Y. H. Kim, H. Y. Jeong, B. K. Ju, and D. S. Seo, “Homeotropic alignment of liquid crystals on a nano-patterned polyimide surface using nanoimprint lithography,” Soft Matter 7(12), 5610–5614 (2011).
2. A. Glushchenko, C. I. Cheon, J. West, F. Li, E. Büyüktanir, Y. Reznikov, and A. Buchnev, “Ferroelectric particles in liquid crystals: recent frontiers,” Mol. Cryst. Liq. Cryst. (Phila. Pa.) 453(1), 227–237 (2006).
3. O. Kurochkin, O. Buchnev, A. Ilijin, S. K. Park, S. B. Kwon, O. Grabar, and Y. Reznikov, “A colloid of ferroelectric nanoparticles in a cholesteric liquid crystal,” J. Opt. A, Pure Appl. Opt. 11(2), 024003 (2009).
4. K. K. Vardanyan, R. D. Walton, and D. M. Bubb, “Liquid crystal composites with a high percentage of gold nanoparticles,” Liq. Cryst. 38(10), 1279–1287 (2011).
5. G. Zhang, X. Chen, J. Zhao, Y. Chai, W. Zhuang, and L. Wang, “Electrophoretic deposition of silver nanoparticles in lamellar lyotropic liquid crystal,” Mater. Lett. 60(23), 2889–2892 (2006).
6. H. J. Kim, Y. G. Kang, H. G. Park, K. M. Lee, S. Yang, H. Y. Jung, and D. S. Seo, “Effects of the dispersion of zirconium dioxide nanoparticles on high performance electro-optic properties in liquid crystal devices,” Liq. Cryst. 38(7), 871–875 (2011).
7. W. K. Lee, Y. S. Choi, Y. G. Kang, J. W. Sung, D. S. Seo, and C. M. Park, “Super-fast switching of twisted nematic liquid crystals on 2D single wall carbon nanotube networks,” Adv. Funct. Mater. 21(20), 3843–3850 (2011).
8. S. Y. Lu and L. C. Chien, “Carbon nanotube doped liquid crystal OCB cells: physical and electro-optical properties,” Opt. Express 16(17), 12777–12785 (2008).
9. A. Glushchenko, H. Kresse, G. Puchkovs’ka, V. Reshetnyak, Y. Reznikov, and O. Yaroshchuk, “Memory effect and structure of filled nematic liquid crystals,” Mol. Cryst. Liq. Cryst. (Phila. Pa.) 321(1), 15–30 (1998).
10. Y. Shiraiishi, N. Toshima, K. Maeda, H. Yoshikawa, J. Xu, and S. Kobayashi, “Frequency modulation response of a liquid-crystal electro-optic device doped with nanoparticles,” Appl. Phys. Lett. 81(15), 2845–2847 (2002).
11. W. Lee, C. Y. Wang, and Y. C. Shih, “Effects of carbon nanosolids on the electro-optical properties of a twisted nematic liquid-crystal host,” Appl. Phys. Lett. 85(4), 513–515 (2004).
12. W. K. Lee, J. H. Choi, H. J. Na, J. H. Lim, J. M. Han, J. Y. Hwang, and D. S. Seo, “Low-power operation of
1. Introduction

Liquid crystal (LC) alignment methods and alignment materials have been extensively studied to fabricate high-quality liquid crystal devices (LCDs). However, these methods are rather more difficult than conventional methods due to additional complicated processing and equipment [1]. In recent years, nanoparticle (NP) doping with LCs has been actively studied for enhancing LC properties, because NP doping with LCs is easier than other methods and can be applicable in the conventional process.

A variety of NPs in LCs have been investigated. Ferroelectric particles were used for increasing the dielectric anisotropy [2, 3]. NPs of metals such as Au [4] and Ag [5] change the elastic parameter and the rotational viscosity of LCs. For suppressing the screen effect, ZrO₂ oxide particles were doped with LCs [6], and carbon nano-tubes (CNTs) were doped into the alignment layer [7]. CNTs in LCs make LCs mixture operate more rapidly [8]. In addition, LCs mixed with NPs showed new properties, such as memory effects [9], frequency modulation [10], fast response [11], and low driving voltage [12]. In other studies, another group used ferromagnetic metal, diamagnetic metal, and metals with a functional group to investigate the phenomenon of LCs doped with NPs [13, 14]. Overall NPs result in minor changes the physical and chemical properties of LCs, and enhance the function of LCDs.

In this report, we experimented with nematic LCs (NLCs) doped with pure metallic titanium (Ti) NPs. Pure metallic Ti NPs without functional groups have not been used for enhancing the properties of NLC cells to date. Metallic Ti is paramagnetic and has a relatively low conductivity. We dispersed Ti NPs of various doping concentrations in NLC cells. We measured EO characteristics to confirm the enhancement of LCDs properties, and then investigated the changes of LCD properties.

2. Experimental

Ti NPs (~100 nm) dispersed in mineral oil were purchased from Sigma Aldrich Korea. Ti NPs are basic to 98.5% trace metal. In order to disperse NPs s in NLCs, Ti NPs were mixed in NLCs and the mixture was ultrasonicated for 10 min, and then was left to sit for 5 min at room temperature. This process was repeated three times to obtain a uniform dispersion. Homogeneous polyimide (PI, SE-150, 50 nm thick) was prepared by coating onto an indium-tin oxide (ITO) deposited glass substrate using a spin coater. Films were prebaked at 80 °C for 15 min and were then imidized at 230 °C for 1 hour. We implemented the unidirectional rubbing method using velvet on the PI layer to obtain homogeneously aligned LCs. The NLC
mixtures were prepared at various Ti NP doping concentrations at weight ratios of 0.1 wt. %, 0.5 wt. %, 1.0 wt. %, 1.5 wt. %, and 2.0 wt. % and were injected into each cell via capillary force at room temperature. A pure NLC cell was prepared for comparison. Positive NLCs (MJ001929, Merck), which have a reflective index (Δn) of 0.077, an isotropic transition temperature of 72 °C, and a dielectric anisotropy Δε (ε∥-ε⊥) of 8.2, were used during cell fabrication. X-ray diffractrometer (XRD) analysis was performed using a DMAX-III A (Rigaku) and Cu-Kα radiation to verify the crystallinity of the NPs in NLCs. Anti-parallel and EO cells were fabricated for measuring the pretilt angles and EO characteristics with cell gaps of 60μm and 4.5μm, respectively. The LCs alignment was investigated using a photomicroscope (Olympus BXp 51). Pretilt angles were measured by the crystal rotation method (TBA 107 tilt-bias angle evaluation device: Autronic). EO measurements of the voltage-transmittance (V–T) characteristics and response times in various doping concentrations of NPs were confirmed using an LCD evaluation system (LCMS-200). We simulated the physical phenomena of the electric field in the LC mixed with NPs by using Ansoft Maxwell software.

3. Results and discussion

The average crystalline sizes of Ti NPs can be calculated via full width at half maximum (FWHM) using the Debye-Scherrer equation [15],

$$\tau = \frac{K \lambda}{\beta \cos \theta}$$

where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. According to the equation, the diameter of the Ti NPs was approximately 100nm.

The alignment characteristics of the NLC cells dispersed with various concentrations of Ti NPs were investigated. Figure 1 shows the alignment of NLC cells doped with 0.0 wt. % to 2.0 wt. % Ti NPs. NLC cells doped with 0.1 wt. % and 0.5wt. % Ti NPs were similar to the pure NLC cell. The photomicrograph images showed uniformly homogeneous alignment without local defects, and Ti NP aggregation was not observed. This indicates that Ti NPs were well dispersed within the NLC molecules. Little or no aggregation was observed at a 1.0 wt. % Ti NPs doping concentration. However, in 1.5 wt. % and 2.0 wt. % doping concentrations, many Ti NPs aggregates were observed in the photomicrograph images. Ti NPs were not well dispersed within the NLC molecules. Therefore, we did not proceed with the next experiment at 1.5 wt. % and 2.0 wt. % Ti NP doping concentrations.
The pretilt angles of the NLC cells doped from 0.0 wt. % to 1.0 wt. % with Ti NPs were analyzed by the crystal rotating method using the transmittance measurement with a latitudinal rotation of ± 70° at room temperature. Calculated pretilt angles of 0.0 wt. %, 0.1 wt. %, 0.5 wt. % and, 1.0 wt.% Ti NP doped samples were 5.3°, 4.6°, 4.4° and, 3.9°, respectively, as shown in Fig. 2(a). The pretilt angles were affected by the concentration of Ti NPs, resulting in decreased values as the concentration of Ti NPs was increased.

In fact, the mechanism of pretilt angle formation is still not completely understood. Many mechanisms have been studied to explain the pretilt angle [16–18]. In this report, the pretilt angle formation and decrease may be explained via the mechanism mentioned below. Specifically charged ionic impurities intermittently induced electrification of the Ti NPs. The electric charge-induced Ti NPs in NLC molecules may make the charged ionic impurities separate from the alignment layer by gathering the impurities around Ti NPs under no applied voltage. This occurs because of molecular interaction between the electric charge-induced Ti NPs and the ionic impurities, as shown Fig. 2(b). Therefore, the van der Waals dispersion interactions between NLC molecules and the alignment layers become stronger and the pretilt angle decreases [19].
Fig. 2. Pretilt angles of NLCs with different Ti NP doping concentrations. (a) Plots of the pretilt angle value. (b) Schematic diagram to illustrate the operation of the interaction between the NLC molecules and the alignment layers.

Fig. 3. V-T curves of the Ti NPs doped NLC. The weight percent of the Ti varies from 0.0 wt.% to 1.0 wt.%.

The characteristics of voltage-transmittance are shown in Fig. 3 under applied voltages of 0V to 4.0V at room temperature. Voltage transmittance curves demonstrated that the threshold voltage values decreased as Ti NP doping ratio increased. The pure NLC cell exhibited the highest threshold voltage of 1.72V. For 0.1 wt. %, 0.5 wt. %, and 1.0 wt. % Ti NP doping, the threshold voltages were 1.65V, 1.42V, and 1.25V, respectively. The threshold voltage of the NLC cell doped at 1.0 wt. % Ti NPs was 1.25V, and this threshold voltage was reduced by 27% as compared with the pure NLC cell.
Figure 4 shows the response times of the mixed and non-mixed NLC cells and NLC operating mechanisms with Ti NPs. The rise time (fall time) is defined as the time taken for transmittance to change from 90% (10%) to 10% (90%) with a supplied voltage. As shown in Fig. 4(a), for 0.1 wt. %, 0.5 wt. %, and 1.0 wt. Ti NP doping, the rise times (RTs) were 3.9ms, 3.7ms, 3.1ms, and 1.9ms, respectively. The fastest RT was observed in 1.0 wt. % doped Ti NPs, 1.9ms, while the lowest RT was observed in the pure NLC, 3.9ms. The fall times (FTs) were 14.5ms, 13.0ms, 12.7ms, and 11.3ms, respectively, as shown in Fig. 4(b). The fastest FT of 10.7ms was observed in 1.0 wt. % doping concentration and the slowest FT of 17.1ms was observed in the pure NLC cell. All response times decreased as Ti NPs doping increased.

Synthetically, at a 1.0 wt. % doping concentration, Ti NPs are well dispersed, and the EO characteristics were enhanced. The response time was 13.2ms (RT 1.9ms / FT 11.3ms), the threshold voltage was 1.25 V, and the pretilt angle was 3.90°.

The EO enhancement may be explained via two mechanisms. Figure 4(c) shows the operation of NLCs under an applied voltage, and Fig. 4(d) shows the operation of NLCs under no applied voltage. For the first mechanism, if there is a metallic conductor in an electric field, the tangential component of the electric field on a conductor is zero, and the normal component of the electric field at the conductor surface is equal to the surface charge density on the conductor divided by the permittivity of space. No electric field exists in the conductor. The equation for this phenomenon is

$$E_N = \frac{D_N}{\varepsilon} = \frac{\rho_S}{\varepsilon}$$

where $E_N$ is the normal component of the electric strength, $D_N$ is the normal component of the electric flux density, $\varepsilon$ is permittivity of space, and $\rho_S$ is surface charge density. The surface
charge density of Ti NPs thereby changed the electric field strength in the NLCs. As shown in Fig. 4(c), the metallic Ti NPs changed the path of the electric flux, and then they focused the electric flux around the Ti NPs surface between the top substrate and bottom substrate. Due to the focusing of the electric flux around Ti NPs, the electric flux density increased and the electric field strength is increased around Ti NPs. At the same voltage level, the voltages of the substrates increased the electric field strength. The stronger electric field made NLC molecules rise quickly, and then the desired transmittance was obtained. This phenomenon may also lead to a lower threshold voltage and a faster RT.

A second mechanism explaining the enhanced performance is the suppression of the screen effect [20]. Ion impurities adsorbed on the alignment layer until a voltage was applied across the NLC cell. The screen effect induced by the adsorbed ion charges on the alignment layer creates an inner direct current field and decreased the effective voltage of the NLC layers. Ti NPs in NLC molecules may trap the ions, as shown in Fig. 4(c), leading to an effective decrease in impurities on the alignment layers, thereby abating the screen effect.

Under no applied voltages, FT enhancement can be explained by the change of interaction between LC molecules and alignment layer by Ti NPs as shown Fig. 4(d). Under no applied voltage, charged ionic impurities intermittently induced electrification of the Ti NPs. And the electric charge-induced Ti NPs in NLC molecules may make the charged ionic impurities separate from the alignment layer by gathering the impurities around Ti NPs. Therefore, the force of alignment layer, that pulled liquid crystal, increased. In other words, the van der Waals dispersion interactions between NLC molecules and the alignment layers become stronger. Stronger van der Waals dispersion interactions allow rapid responses in the NLC molecules under no applied voltage.

The two mechanisms described that the lower threshold voltage and faster response times can be attributed to the Ti NPs.

![Fig. 5. Plots of the results of Ansoft Maxwell software simulation. (a) Plots of the electric flux density in NLC cell doped with Ti NPs. (b) Plots of the electric field strength in NLC cell doped with Ti NPs.](image)

To confirm the boundary conditions of the conductor in the electric field, we simulated the Ti NPs and NLC in an electric field using Ansoft Maxwell software. PI, electrode, and Ti NPs were assigned by default material properties. The dielectric anisotropy (MJ001929, $\varepsilon_\parallel = 12.3$, $\varepsilon_\perp = 4.1$) was used as the setting parameter. Applied voltages were 0V and 5V. Figure 5 shows the change in the electric field under an applied voltage. As shown in Fig. 5(a), the electric flux density was changed and became strong around Ti NPs. However, in the Ti NP free area, the electric flux density was not changed. The orientation of the electric field changed to the same orientation of the electric flux density and became stronger than in the Ti NP free area, as shown in Fig. 5(b). We ensured that our experimental results matched the
results of the software simulation based on general physical theory. Thus, NLC molecule operations are enhanced by stronger electric field strength.

4. Conclusion

In conclusion, we investigated the alignment properties and EO characteristics of NLC cells doped with Ti NPs. Homogeneous alignment of Ti NP doped NLCs at various concentrations were prepared by the rubbing method. We verified high-quality LCDs as control of the doping concentrations of Ti NPs in NLCs at specific conditions. As the Ti NP concentration increased, lower threshold voltages, faster response times, and a lower pretilt angle were obtained. Therefore, we verified that LCDs performance can be controlled by changing the NP concentration in Ti NPs doped with NLCs to improve EO characteristics. The results of Ti NPs doping in NLCs show high performance optical properties necessary for LCD devices, and are suitable for LCD applications by simple, physical mixing of Ti NPs with NLC.