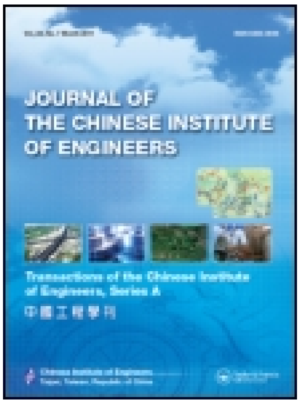

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Dopant effects of photoreactive ZnO nanoparticles on fast response LC materials in optical compensated bend (OCB) mode liquid crystal displays

Hong-Cheu Lin [a], Meng-Dan Jiang [b], Ling-Yung Wang [b], Wei-Hong Chen [b], Szu-Fen Chen [c] & Chi-Neng Mo [c]

[a] Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C. Phone: 886-3-5712121 ext. 55305 Fax: 886-3-5712121 ext. 55305 E-mail:

[b] Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C.

[c] Department of Materials Science and Engineering, Chunghwa Picture Tube, Ltd.tional Chiao Tung University, Hsinchu 300, Taiwan, R.O.C., Taiwan, R.O.C.
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DOPANT EFFECTS OF PHOTOREACTIVE ZnO NANOPARTICLES ON FAST RESPONSE LC MATERIALS IN OPTICAL COMPENSATED BEND (OCB) MODE LIQUID CRYSTAL DISPLAYS

Hong-Cheu Lin*, Meng-Dan Jiang, Ling-Yung Wang, Wei-Hong Chen, Szu-Fen Chen, and Chi-Neng Mo

ABSTRACT

Photoreactive ZnO nanoparticles containing surface-modified acrylate groups were synthesized and applied to improve the threshold voltage in optical compensated bend (OCB) mode liquid crystal display (LCD) cells. The dopant effects of ZnO nanoparticles with or without commercial reactive monomer additives (1 wt% doping ratio) on the values of threshold voltage (V_{th}) and response time in OCB cells were explored by applying different voltages to photo-reactive ZnO nanoparticles during UV curing processes in OCB cells to compare the influences of doped ZnO nanoparticles. As a result, we successfully eliminated or reduced the splay state of OCB mode and thus reduced threshold voltage. However, lower transmissions and higher values of the response time were observed in OCB cells doped with photoreactive ZnO nanoparticles, and the decreasing of V_{th} is independent of various doping materials. Moreover, lower transmission and high response time could be improved through sequential voltage-applied procedures, i.e., bend black mode (10 V) → bend white mode (2.5 V), under the immobile minimum threshold voltage at the bent state during UV curing processes to achieve lower pre-transition and fast response time properties by only doping photoreactive ZnO nanoparticles.

Key Words: fast response, OCB mode cell, ZnO nanoparticle.

I. INTRODUCTION

Optical compensated bend (OCB) mode liquid crystal displays were developed due to their fast response times and wide view angles. However, the exhibition of splay state, which is an unnecessary state existing applied voltage without or in low applied voltage conditions restrains the range of applied voltages for the working state (bend state). Therefore, splay mode suppression or reduction for response time and threshold voltage needs further investigation. Based on the prior literature, many of methods have been developed to improve the response time and stabilize the bend alignment, such as processes of chiral dopants (Huang *et al.*, 2007) and organic reactive monomers to generate polymer walls by UV curing approaches (Kikuchi *et al.*, 2005; Chien *et al.*, 2002; Asakawa et al., 2007). Moreover, nano-sized dopant materials, including nanoparticles (Kobayashi *et al.*, 2004; Kobayashi *et al.*, 2002; Miranda, 2006; Boilot *et al.*, 2007; Kobayashi *et al.*, 2007) and nanotube dopants, (Huang *et al.*, 2006) have also been used to enhance the electro-optical properties of various LCDs. High quality (fast response time and lower driving voltage) properties in OCB cells have also been encouraged by the formation of a pixel-isolating polymer wall and by pre-tilt angle behavior in

*Corresponding author. (Tel: 886-3-5712121 ext. 55305; Fax: 886-3-5724727; Email: linhc@cc.nctu.edu.tw)

H. C. Lin, M. D. Jiang, L. Y. Wang, and W. H. Chen are with the Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C.

S. F. Chen and C. N. Mo are with the Chunghwa Picture Tube, Ltd., Taoyuan 330, Taiwan, R.O.C.

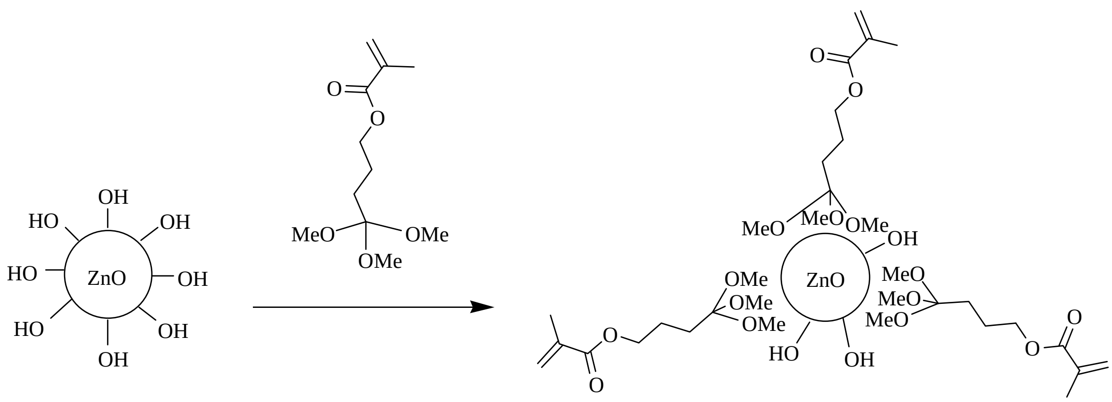

Fig. 1 Structures of surface-modified ZnO nanoparticles

vertical alignment layer by ion beam exposure (Kim *et al*., 2008; Kim *et al*., 2007). However, there have been few examples of the applications and effects of nanoparticles with photoreactive groups on the improvement of the threshold voltage and the response time in OCB mode displays.

For our investigation, we focused on the combination of nanostructure with photo-curing technique for electro-optical properties in OCB cells. Hence, surface-modified ZnO nanoparticles bearing photoreactive acrylate groups (Whang *et al*., 2005) were developed as shown in Fig. 1, and three kinds of LC mixtures consisting of a host nematic liquid crystal material (LC) and a guest commercial reactive monomer (RM) and photoreactive ZnO nanoparticles (NPs) were prepared. Furthermore, the values of threshold voltage and response time of OCB mode LC cells containing these LC mixtures were also studied. Firstly, the influences of the various doping ingredients (with or without RM), such as (1) LC + RM, (2) LC + RM + ZnO nanoparticles and (3) LC + ZnO nanoparticles on electro-optical properties at the same doping ratios and UV curing process were surveyed. Afterward, various doping ratio of NPs and UV curing processes were carried out to optimize their electro-optical properties in OCB cells.

II. EXPERIMENTAL

Surface-modified ZnO nanoparticles were synthesized following previous reports. The commercial nematic LC host (**ZCE-5096**) and reactive monomer (**RM257**) were purchased from Chisso Chemical Co and Merck Chemical Co, individually. The LC mixtures were prepared by blending LC host and ZnO modified nanoparticles directly (no solvent used) with various doping ratios (0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%), and all samples were stirred by vibration caused by ultrasonicwaves at 0°C (in dark environment). The electro-optical properties of LC materials were determined in commercially available OCB cells (from Mesostate Corp., thickness = 4.25 μm, active area = 1 cm^2) coated with rubbing polyimide alignment layers (parallel rubbing direction). The test cells were prepared by the following processes. First, 3 min of holding at a square waveform of ±10 V under a frequency of 60 Hz was given, then the test cell could be cured by UV light with a wavelength of 365 nm for 60 min in OCB cells under different voltages (5 V, 4 V, 3 V, 2.5 V, and 0 V). *V*-*T* measurements were performed under AC fields of square waveform from ±10 V to ±0 V decreasing gradually at a frequency of 60 Hz, and the threshold voltage (V_{th}) is determined by the voltage with the highest transmittance. Switching time measurements were started with 3 minutes of holding at a square waveform of ±10 V under a frequency of 60 Hz (from splay to bend), and followed by 3 minutes of holding at an arbitrary waveform of ±7 V or ±29.5 V under a frequency of 60 Hz in order to avoid going back to the splay state. Then, the field-on response time (τ_{on}) was determined from an arbitrary waveform of voltages ±7 V (in dark state) to ±2 V (in bright state), and the field-off response time (τ_{off}) was decided by a reversed voltage process (from ±2 V to ±7 V), correspondingly. Switching time measurements were determined by the time period for 90 % change of transmission. Finally, the value of total response time (τ_{total}) was determined by the summation of the field-on response time (τ_{on}) and the field-off response time (τ_{off}), i.e., $\tau_{\text{total}} = \tau_{\text{on}} + \tau_{\text{off}}$. As shown in Fig. 2 (a) and 2(b), one set of data regarding *V*-*T* and switching time measurements of the pure LC host (**ZCE-5096**) were given values of 1.93 V (V_{th}) and 4.57 ms (τ_{total}), respectively.

III. RESULTS

Based on the SEM patterns, synthesized ZnO nanoparticles with or without surface modification

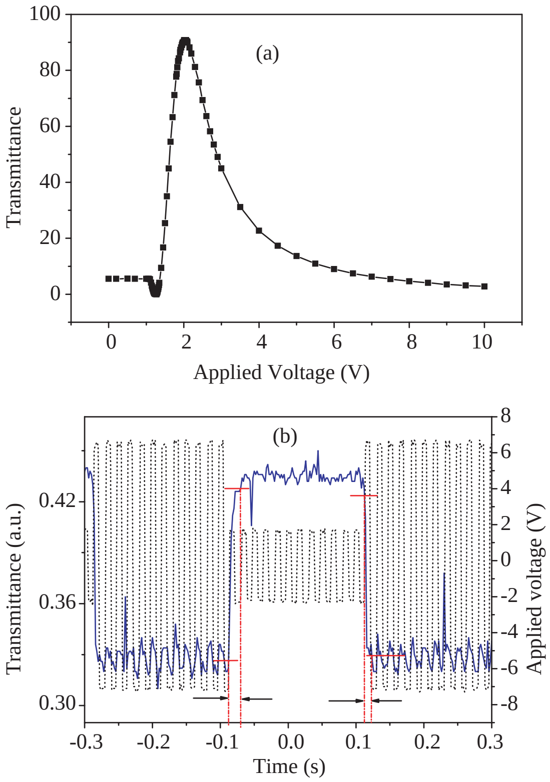

Fig. 2 Electric-optical measurements of the pure LC host (**ZCE-5096**) (a) *V-T* measurements and (b) switching time measurements of the field-on response time (τ_{on}) and the field-off response time (τ_{off})

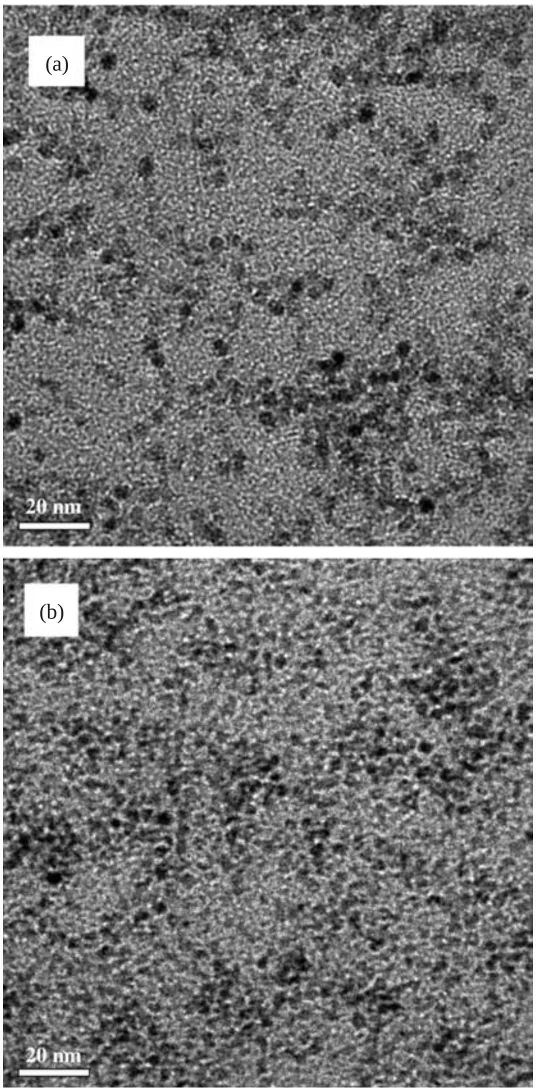

Fig. 3 TEM micrographs of (a) unmodified ZnO nanoparticles and (b) modified ZnO nanoparticles

revealed an average diameter of 3 nm shown in Fig. 3(a) and 3(b). For the functional group studies of the photoreactive NPs, almost 15% of surfactants were detected, indicating surface-modified acrylic derivatives as shown in Fig. 4(a). In addition, the methylene protons could be confirmed as the cause of the NMR characteristic peaks at 6.02 ppm and 5.47 ppm (Fig. 4(b)). According to the previous descriptions, the acrylic surface-modified LC dopants on NPs improved the electro-optical properties of LC OCB cells.

In order to compare the influence of applied voltages under UV curing, LC mixtures composed of nematic LC host (**ZCE-5096**) doped with photoreactive ZnO nanoparticles were cured under two different voltages of 3 V and 5 V, individually, which were higher than the threshold voltage (V_{th} = 1.9 ~ 2.0 V) of pure LC host (**ZCE-5096**) so as to fall into the range of the bend state during UV curing. After the LC mixture (i.e., LC + NP) had a voltage of 3 V applied under UV curing, the threshold voltage was decreased from 2.03 V (for pure LC host) to 1.47 V (for LC + NP) as shown in Fig. 5(a). It is suggested that the bend state may be restricted by the polymerization of photoreactive ZnO nanoparticles.

Moreover, the splay state of the LC mixture could be completely suppressed at a higher applied voltage of 5 V under UV curing. However, a larger reduction in the highest transmittance was observed as the applied voltage was increased from 3 V to 5 V under UV curing. It is conjectured that even in the off state the LC arrangement after UV curing under electric fields would be partially perpendicular to the ITO surface to cause light blocking. To evaluate the effects of reactive monomers, three kinds of LC mixtures: (1) LC + monomer (1 wt%), (2) LC + NP (1 wt%), and (3) LC + NP (1 wt%) + monomer (1 wt%) were compared and their *V-T* (transmittance vs. voltage) measurements with the same applied voltage of 5 V under UV curing for 60 min are illustrated in Fig. 5(b). In general, decreased transmittances and lower threshold voltages (V_{th} = 0.59 ~ 0.75 V) were observed after the photoreactive step, and the splay mode was suppressed or eliminated even if at low applied voltages under UV curing.

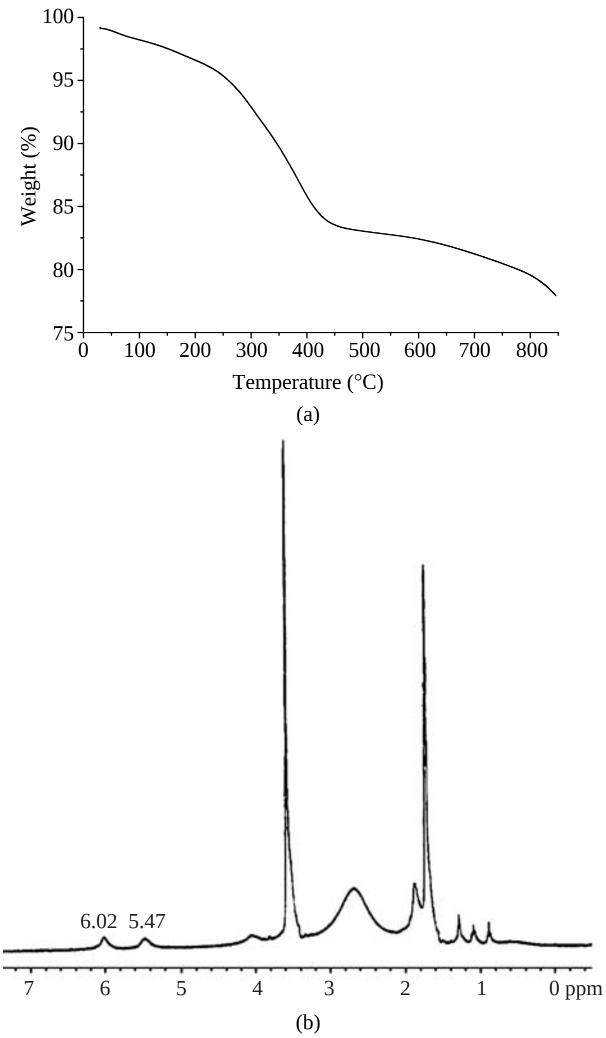

Fig. 4 (a) TGA measurements and (b) NMR determinations of modified ZnO nanoparticles

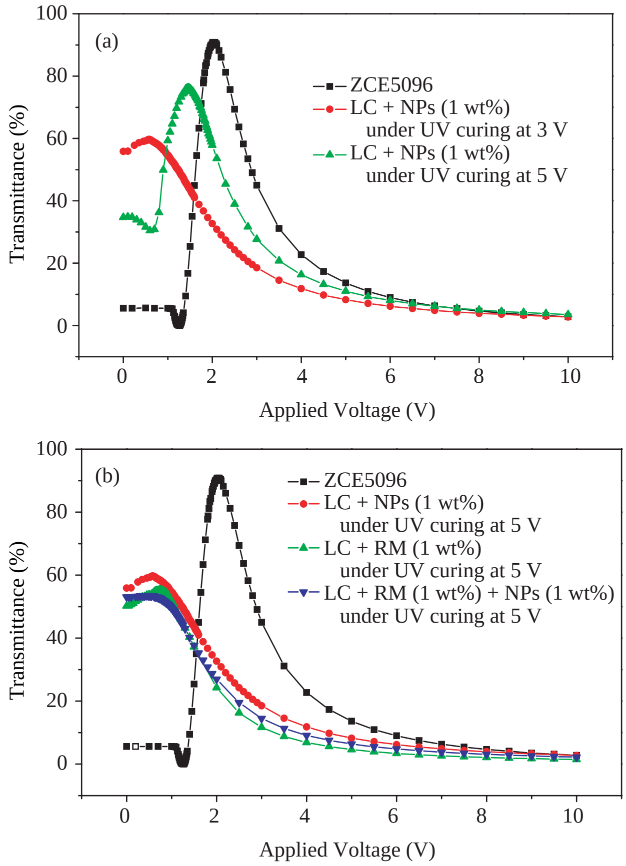

Fig. 5 *V-T* measurements of (a) pure LC and LC mixtures (i.e., LC + NP) being applied voltages of 3 V and 5 V under UV curing, (b) Pure LC and LC mixtures (i.e., LC + RM, LC + NP, LC + RM + NP) being applied a voltage of 5 V under UV curing

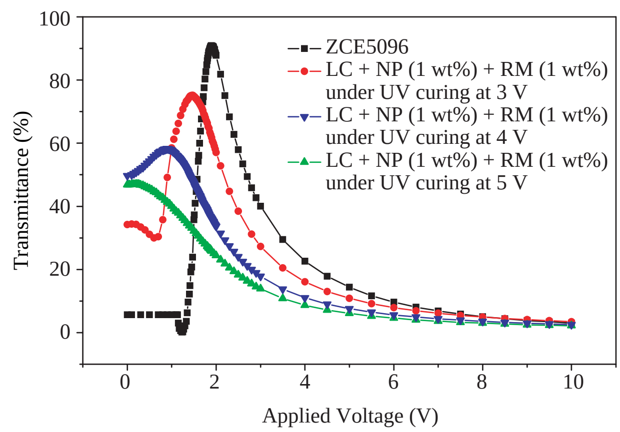

Fig. 6 *V-T* measurements of LC mixtures, i.e., LC + NPs (1 wt%) + RM (1 wt%), at different applied voltages (3 V, 4 V, and 5 V) under UV curing

The *V-T* and *R-T* (transmittance vs. response time) measurements for LC mixtures (LC + RM + NP) were examined at different applied voltages (3 V, 4 V, and 5 V) under UV curing as shown in Fig. 6 and Table 1. Similar *V-T* results of LC mixtures in (LC + RM + NP) and (LC + NP) were acquired. The values of transmittance and V_{th} were reduced by increasing the applied voltage under UV curing. Regarding *R-T* measurements of LC mixture at different applied voltages (3 V, 4 V, and 5 V) under UV curing, photoreactive ZnO nanoparticle and reactive monomer dopants led to increases of τ_{off} values, especially in the condition of a lower applied voltage of 3 V. However, there were no clear variations in τ_{on} values at different applied voltages (3 V, 4 V, and 5 V) under UV curing. In general, the values of the total response time (τ_{total}) in OCB cells using LC mixtures (LC + RM + NP) became a little larger in contrast to those using pure LC host (ZCE-5096). Photoreactive ZnO nanoparticles were doped into LC mixtures to improve the electro-optical performance of OCB mode cells. The effects of various dopant formulations (NP and RM) and different applied voltages

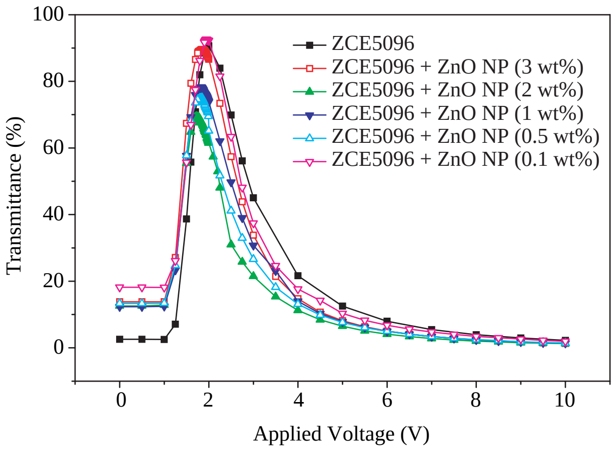

Fig. 7 *V-T* measurements of pure LC and LC mixtures doped with ZnO NPs (0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%)

under UV curing were investigated in this report. Above all, the LC mixtures of (LC + NP) or (LC + NP + RM) at low applied voltages (3-5 V) under UV curing could suppress or reduce the splay state (and thus reduce the threshold voltage) effectively.

Based on the previous description, larger reductions in the highest transmittance were produced in NP-doped mixtures because of the large holding applied voltage under UV curing. Hence, in order to prevent the decreasing of the transmittance value, the holding voltage was changed form high voltages (5V and 3V) to 2.5 V, which is close to the lowest voltage of the bend state. Furthermore, their *VT* and *RT* results were checked to compare the effect of various nanostructure doping ratios (0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%) as shown in Fig. 7, Table 2, and Table 3. According to our measurements, similar V_{th} and transmittance values could be obtained for mixtures with a low doping ratio (0.1 wt%), indicating less influence of splay type suppression due to fewer photoreactive ZnO NPs. However, decreasing V_{th} values, as revealed in table 2 were observed, where the doping ratios were increased to 0.5 and 2 wt%, so higher photoreactive compositions were supplied to prevent the existence of the splay state or extend the bend state without more loss of transmittance. Finally, a little rise of threshold voltage and transmittance at 3 wt% doping ratio was due to the overloaded ZnO doping ratio.

Based on the previous examination, LC mixtures with conditions of lower V_{th} values and smaller decrease of transmittance were more suitable to apply in practical OCB displays. With regard to *RT* measurements, all response time values with different ZnO nanoparticle doping ratios are listed in Table 3. Slight decreases; field-on response times (τ_{on}) for LC mixtures with all ZnO NP compositions and clearly reduced field-off response times (τ_{off}) could be perceived in OCB cells, where the lowest τ_{off} value was obtained in LC mixtures with 2 wt% doping ratio. Hence, according to the results for values of total response time (τ_{total}), in table 3, i.e. $\tau_{total} = \tau_{on} + \tau_{off}$, similar trends of τ_{off} and τ_{total} values were acquired, and the best doping ratio of 2 wt% NPs was achieved.

Table 1 ***R-T* results of LC mixture, i.e., LC + NP (1 wt%) + RM (1 wt%), at different applied voltages (3 V, 4 V, and 5 V) under UV curing**

Sample	τ_{on} (ms)	τ_{off} (ms)	τ_{total} (ms)
ZCE5096	1.29	2.74	4.03
LC + NP + RM (3 V)	1.48	4.58	6.06
LC + NP + RM (4 V)	1.45	3.44	4.88
LC + NP + RM (5 V)	1.14	3.23	4.37

Table 2 ***V-T* measurements of pure LC and LC mixtures doped with ZnO NPs (0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%)**

Sample	V_{th} (V)	Tran. (%)
ZCE5096	2.03	90.8
0.1%	1.98	92.6
0.5%	1.85	75.1
1%	1.83	78.3
2%	1.73	70.1
3%	1.85	89.6

Table 3 ***R-T* measurements of pure LC and LC mixtures doped with ZnO NPs (0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%)**

Sample	τ_{on} (ms)	τ_{off} (ms)	τ_{total} (ms)
ZCE5096	1.22	3.72	4.94
0.1%	1.1	3.47	4.57
0.5%	0.86	3.76	4.62
1%	1.03	4.07	5.1
2%	1.16	2.61	3.77
3%	0.99	3.37	4.36

IV. CONCLUSION

We successfully developed LC mixtures containing photoreactive ZnO nanoparticles with several doping ratios in OCB mode LCDs. The effects of different doping ratios of ZnO nanoparticles and commercial reactive monomer in LC mixtures, which were UV cured by sequential voltage procedures, on the values of response time and threshold voltage were analyzed. In summary, photoreactive ZnO nanoparticle dopants in LC mixtures were useful to suppress the splay state by photo curing process to extend the existing range of the bend state, which is similar to commercial RM dopants. The suppression of reduced transmittance values and decrease of *VT* and *RT* values were controlled by the doping ratio of ZnO NPs. The optimal electro-optical properties of LC mixtures, doping 2 wt% of ZnO NP dopants yielded almost 23% reduction of τ_{total} values. To sum up, the values of response times and threshold voltages in OCB mode cells can be reduced by doping photoreactive ZnO nanoparticles into LC hosts, and the values of τ_{total} and V_{th} can be tuned by the UV curing holding voltage and the doping ratio of ZnO nanoparticles.

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