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Carbon Nanotube Effects on Electro-Optic Characteristics of Twisted Nematic Liquid Crystal Cells

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Carbon Nanotube Effects on Electro-Optic Characteristics of Twisted Nematic Liquid Crystal Cells

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Twisted nematic (TN) liquid crystal (LC) cells doped with carbon nanotubes (CNTs) were fabricated and their electro-optic characteristics were studied. The CNTs with a minute amount of doping did not disturb the liquid crystal orientation in the off and on state. Effects of CNTs on voltage-dependent transmittance curves and voltage holding ratio were not found to be so strong. The response time however was improved as compared to pure LC.

Keywords: carbon nanotubes; liquid crystal display; response time; twisted nematic

INTRODUCTION

Recently, new approaches such as the doping of nano particle such as MaO [1], BaTiO₃ [2], Sn₂P₂S₆ [3] and carbon nanotube (CNT) into LC were proposed to overcome the limitation of the physical properties of LC [4–9].

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Among several particles CNTs are very interesting because they have anisotropic shape as LC and strongly interact with LC [10]. It is known to prove that the long axis of CNTs is aligned parallel to the LC director without bias voltage and they reorient with a bias voltage especially above a critical voltage [11,12]. Our group have also reported that CNTs not only try to orient along the LC director but also deformed the LC director field due to their motion depending upon the vertical [13] and in plane [14,15] field directions. The effective birefringence (Δn_{eff}) of LC in the presence of an electric field can also be altered by doping a small amount of CNTs in LC [16].

In thin-film-transistor-liquid crystal displays (TFT-LCDs), the LC mixture should show high resistivity such that an applied signal can be held without a leakage current. Otherwise, the flickering of images appears. Therefore, in the TFT-LCDs, high voltage holding ratio is one of the key requirements to exhibit a high image quality. At present, the super-fluorinated LC mixtures show a high resistivity larger than $10^{13} \Omega\text{cm}$ [17]. In this paper, we study how the electro-optic characteristics such as voltage-dependent transmittance (V-T), response time, and voltage holding ratio (VHR) can be affected by doping of CNTs including multi-walled CNTs (MWNTs) and single-walled CNTs (SWNTs) with various concentrations to superflourinated LC mixtures.

EXPERIMENTAL

Fabrication of LC Cell

Figure 1 show the cell structure of the CNT-doped LC cell. For an alignment layer, a homogeneous alignment layer was spin coated on the

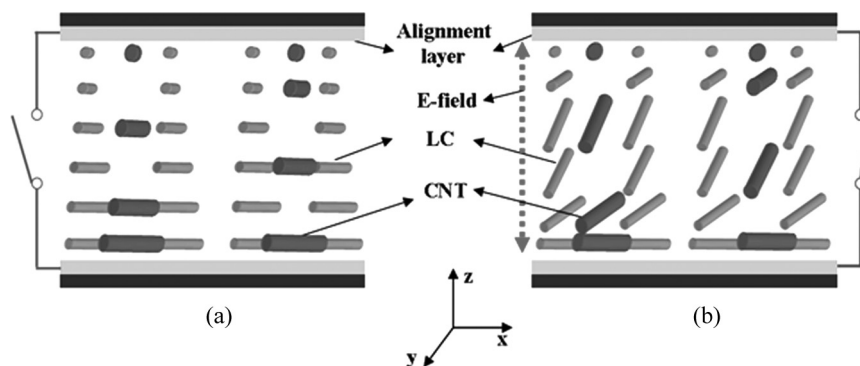


FIGURE 1 Schematic of the cell structure of the CNT-doped TN cells in (a) off and (b) on states.

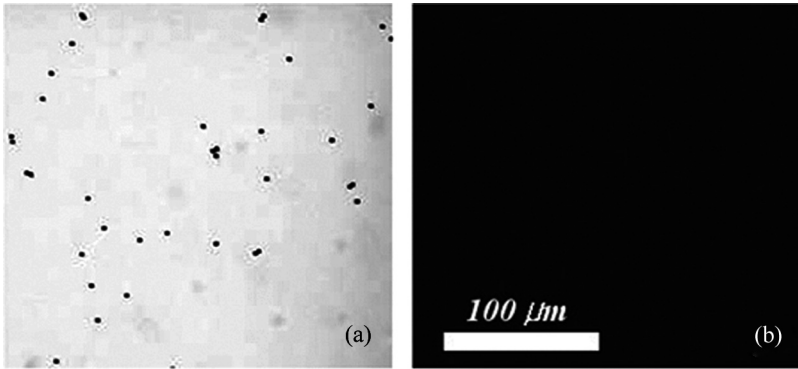


FIGURE 2 Polarization microphotographs of (a) off and (b) on states of the pure and CNT-doped TN cells. The black spots in the off state come from existence of the plastic spacers.

indium-tin-oxide patterned glass at bottom and top glass substrates with a thickness of 800 \AA . The rubbing process on both substrates was performed in perpendicular to each other. The cell was then assembled to give a cell gap (d) of $4.8 \mu\text{m}$ using the plastic balls. The LC with positive dielectric anisotropy from Merck Co. ($\Delta\epsilon = 7.4$, birefringence $\Delta n = 0.088$ at $\lambda = 589 \text{ nm}$, $T_{ni} = 87^\circ\text{C}$, $\gamma = 147 \text{ mPas}$) were used. The CNTs were doped in the LC with different concentrations (MWNTs: 1×10^{-3} , 5×10^{-4} , 1×10^{-4} wt% and SWNTs: 5×10^{-4} , 5×10^{-5} , 1×10^{-5} wt% with LC) and CNTs-doped LC mixture was filled into the cell by capillary action at the room temperature. The crossed polarizers were attached to the TN cell so that the cell shows a white state before applying voltage, realizing a normally white mode. Therefore, we assume that the LC and CNT are aligned with continuous 90° twist from top to bottom substrate and with applied vertical field (E_z), both LC and CNTs try to align along the field direction, resulting in a dark state. In order to confirm our assumption, we first observed the pure and CNT-doped LC cell under the polarizing optical microscopy before and after applying voltage. Pure and CNTs doped LC cells do not show any difference in on and off states, indicating that a small amount of CNTs does not disturb the LC orientation and may follow the LC orientation with bias voltage, as shown in Figure 2.

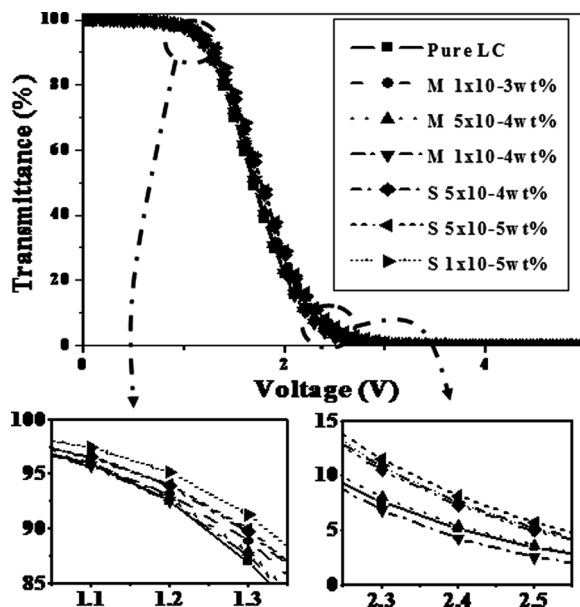
RESULTS AND DISCUSSION

The physical properties of CNT-doped LC mixture were measured and are shown in Table 1. As indicated, the clearing temperature T_{ni} ,

TABLE 1 Change in the Physical Properties of LC by CNT Doping.

	Pure LC	MWNT 1×10^{-4} wt% doped LC	SWNT 1×10^{-4} wt% doped LC
T_{ni} (°C)	87	87.5	86.5
$\Delta\epsilon$	7.4	7.41	7.41
Δn	0.088	0.0882	0.0881
ν	146	140	136

dielectric anisotropy, and birefringence of the CNT-doped cell were almost the same as pure LC although it was measured only for specific amount of CNTs. However, the rotational viscosity measured by transient current method [18] shows decrease of rotational viscosity to some degree and however, the effect was large in the SWNT-doped cell. Next, we measured electro-optic characteristics of the cells. The measurement applied a square wave voltage of 60 Hz with an increasing step of 0.05 V. The incident light used a halogen lamp and the light intensity was measured using a photodiode. Figure 3 shows the voltage-dependent transmittance curves between pure LC cell and CNT-doped LC cell as a function of CNT concentrations. Instrumental

**FIGURE 3** Measured voltage-dependent transmittance curves according to CNTs concentration. Here, M and S represent MWNT and SWNT, respectively.

uncertainty in the determination of threshold/operating voltage is $\pm 1\%$. The threshold voltage (V_{10}) at which the transmittance changes by 10% from its maximal value, increases slightly in all CNT-doped cells, and the operating voltage (V_{90}) at which the transmittance changes by 90% from its maximal value does also follow the behavior of V_{10} . However, the effect of CNTs on V-T curves is not so strong. Nevertheless, in order to understand the dependency clearly, V_{10} and V_{90} are plotted in terms of CNT concentrations, as shown in Figure 4. As indicated, both V_{10} and V_{90} increase in the relatively high amount MWNT-doped LC cell, however, with decreased doping amount of MWNT to 1×10^{-4} wt% effect of CNT on V-T seems minimal. Unlike the MWNT-doped cells, both V_{10} and V_{90} increase clearly in the SWNT-doped LC cells although the increasing level is within 0.2V. Because the CNT is mixed in terms of weight percent, the lighter weight of SWNT than that of MWNT allows relatively more amount of SWNT than MWNT into the pure LC although the same weight percent of MWNT and SWNT is mixed into the LC.

In the TN cell, the threshold voltage V_{th} can be written as $V_{th} = \pi(K_{eff}/\epsilon_0\Delta\epsilon)^{1/2}$, where $K_{eff} = K_{11} + (K_{33} - 2K_{22})/4$. The K_{11} , K_{22} and K_{33} are splay, twist and bend elastic constants respectively. Previously we have shown that existence of CNTs in LC increases the physical parameters of the LC layer such as twist elastic constant and hence the threshold voltage (V_{th}) of CNT doped LC cell was found to be slightly larger than that of pure LC for in-plane cell [16], as for in plane LC cell, V_{th} depends only on K_{22} . However in TN cell, the V_{th}

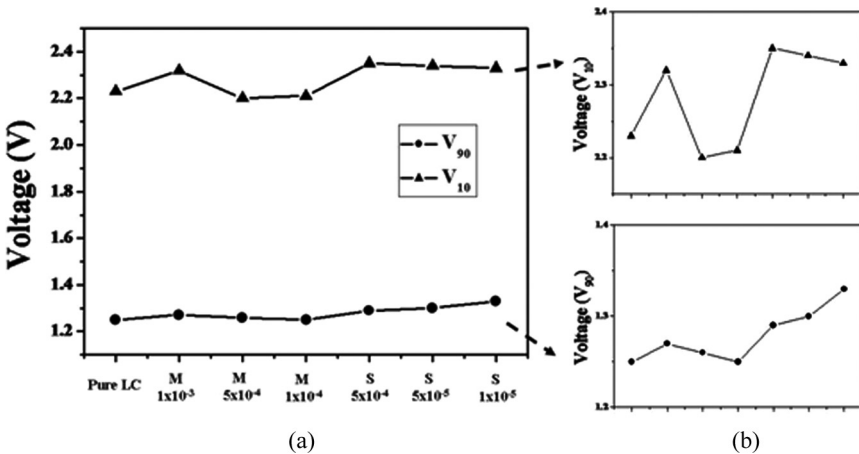


FIGURE 4 (a) V_{10} and (b) V_{90} as a function of the CNT concentrations.

depends upon $K_{\text{eff}} = K_{11} + (K_{33} - 2K_{22})/4$. In general K_{11} and K_{22} increase [16,19] and K_{33} decreases [19], in CNTs doped LC cell. Therefore K_{11} would cause to increase K_{eff} , however K_{22} and K_{33} would cause to decrease K_{eff} in CNTs doped LC cell. Hence K_{eff} would not change appreciably in CNTs doped LC cell and thus the effect of CNTs on threshold voltage is not so strong but might affect the response time.

Figure 5 shows measurements of rising time and decaying time of TN cells by applying a 60 Hz square wave ac voltage. The uncertainty in the determination of response time is $\pm 1.5\%$. In case of rising time, all CNT-doped cells react faster than the pure LC cell and it was improved by more than 5% at least. However, at higher voltages, the difference in rising time of pure and CNTs doped LC cells becomes smaller. Also, the decaying time of the CNT-doped cell is faster than that of the pure LC cell, like those in rising time measurement. Decaying time is inversely proportional to the elastic constants of LC and proportional to rotational viscosity of LC. The cell gap of pure and CNT doped LC in the present study were nearly equivalent and hence its affect would be minimal. Therefore, we regard as that improvement of response characteristics is due to reduction of rotational viscosity or slight increase in elastic constant.

The voltage holding ratio (VHR) was also measured in pure and CNTs doped LC. Figure 6 shows the schematic representation of applied waveform for the measurement of VHR. The VHR is defined as $\text{VHR} = \int_0^T V dt / V_0 T$, where V_0 is the applied voltage for certain period of time T . Frequency of 60 Hz (16.6 ms) was applied to measure the VHR in which on time was 1 ms and the holding time was 15.6 ms. The results are shown in Figure 7. The VHR value for pure LC cell was

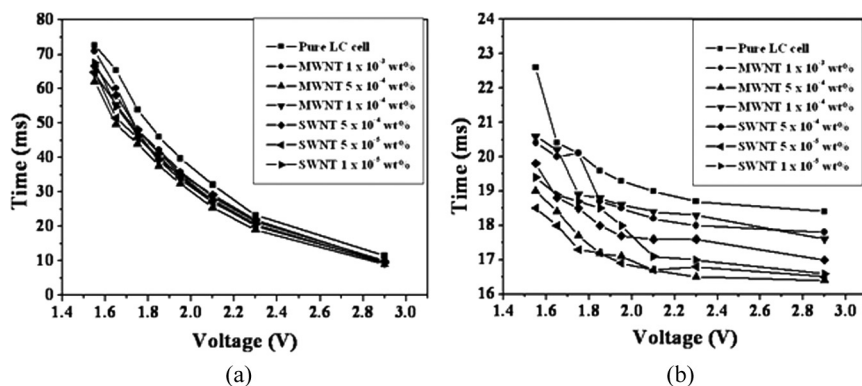


FIGURE 5 Measured (a) rising and (b) decaying time for pure and CNTs doped TN cells.

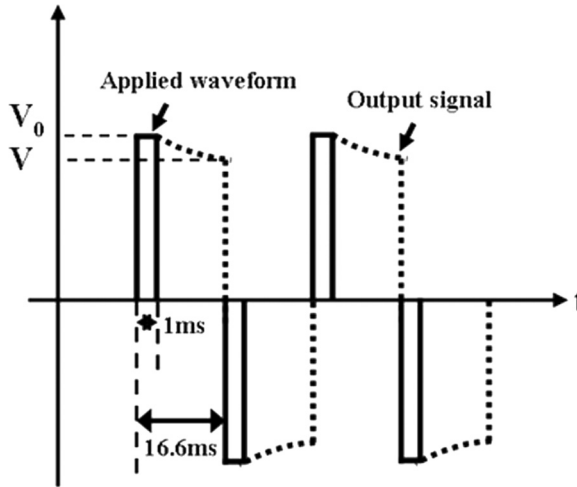


FIGURE 6 Schematic applying a 60 Hz square waveform and output signal of the measurement.

96.8%. However for MWNTs doped LC, the VHR values were found to be 96.3% (1×10^{-4} wt.%), 98.2% (5×10^{-4} wt.%) and 98.3% (1×10^{-3} wt.%). Hence VHR values were slightly increased by $\sim 1.5\%$ for 5×10^{-4} wt.% and 5×10^{-3} wt.% of MWNTs concentrations and its value was decreased $\sim 0.5\%$ for 1×10^{-4} wt.% of MWNTs con-

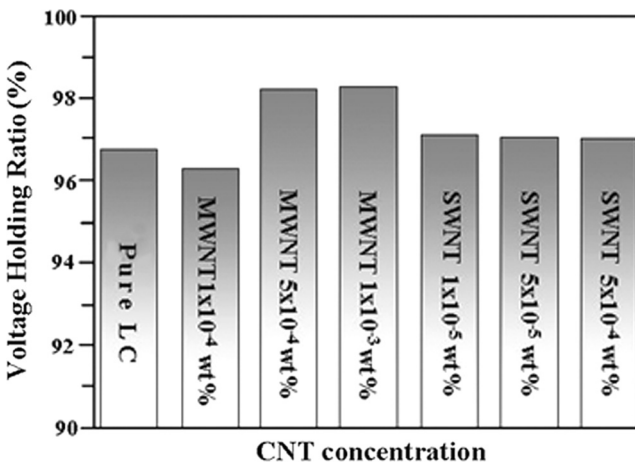


FIGURE 7 Measured voltage holding ratio characteristics according to CNT concentration.

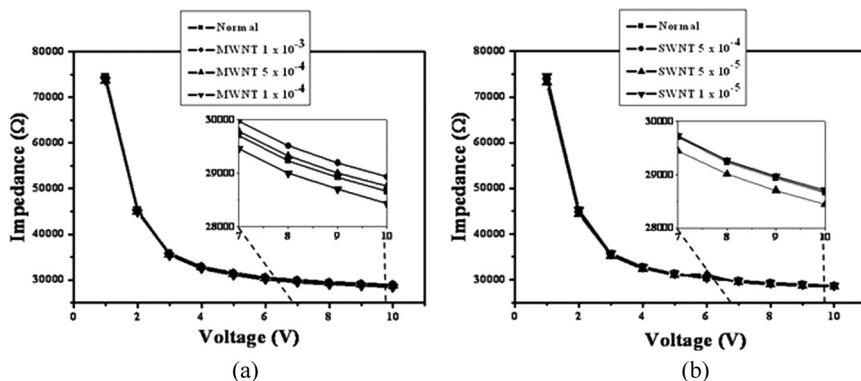


FIGURE 8 Measured voltage dependent impedance curve, (a) MWNT doped cells and (b) SWNT doped cells.

centration with respect to the pure LC cell. For SWNTs doped LC, the VHR values were found to be 98.0% (1×10^{-5} wt.%), 97.2% (5×10^{-5} wt.%) and 97.0% (5×10^{-4} wt.%). Therefore in case of SWNTs doped LC cells, the differences in VHR values of different SWNTs concentrations are much smaller and less than 0.5%. It is noteworthy to mention here that the uncertainty in the measurement of VHR values was less than $\pm 0.2\%$. Hence VHR's values do not seem to be changed appreciably in CNTs doped LC.

VHR can be approximately described, with an assumption of a single discharge process, as follows, $VHR = \exp(-t/C_{lc}R_{lc}) = \exp(-t/\epsilon_{lc}\rho_{lc})$, where C_{lc} , R_{lc} , ϵ_{lc} and ρ_{lc} are the capacitance, the resistance, the dielectric constant and the resistivity of LC, respectively. The cell gap of pure and CNT-doped LC cell was same. Therefore from the above equation VHR value of LC cell will increase with increase in capacitance and resistance values. We measured voltage-dependent impedance curve to confirm VHR characteristic of CNT doped LC. The result is appeared in Figure 8. The measured impedances of CNTs doped LC cells were found to be changed within $\pm 1\%$ for different CNTs concentrations and pure LC. However, the instrumental error in the measurement of impedance was $\pm 2\%$. Hence impedances of CNTs doped LC cells are almost same as to pure LC. Therefore VHR values are almost according to their impedances values.

CONCLUSIONS

In this study, a CNT-doped twisted nematic LC cells were fabricated. The CNTs were well aligned with the LC director in the off and on

stage. The physical properties of the LC such as the elastic constant and the rotational viscosity were modified by the minute doping of CNTs, which helps to improve the response time of the TN cell. Threshold and operating voltages were increased slightly compared with that of pure LC cell. The VHR values in CNTs doped LC does not change appreciably. Our study opens a possible application of the CNT-doped LC to the LCD mode to improve the response time by modifying the physical properties of the LC by CNTs.

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