The Effect of Chemically Modified Multi-Walled Carbon Nanotubes on the Electro-Optical Properties of a Twisted Nematic Liquid Crystal Display Mode

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Abstract: In this study, we have chemically modified multi-walled carbon nanotubes (MWNTs) with different side chains for better dispersion in liquid crystal solutions, and fabricated twisted nematic liquid crystal cells doped with such MWNT derivatives. The introduction of MWNT derivatives affects the alignment of LC molecules with or without external electric fields. Electro-optical property tests showed that the contrast ratio changed slightly with the sharp decrease in drive voltage, improving the drive ability of the twisted nematic liquid crystal display (TN-LCD) mode.

Keywords: multi-walled carbon nanotubes; liquid crystal; electro-optical properties

1. Introduction

Ever since they were discovered, the extraordinary properties of carbon nanotubes (CNTs), such as excellent mechanical behavior [1–3] and special electric properties [4,5], have been triggering enormous interest in many scientific fields. Carbon nanotubes, divided into multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs), have large potential in being applied to reinforced composites due to their high strength and elasticity [6–8], and to field emission devices for their electric properties [9–12].

Their special electrical performance and high aspect ratio of $10^3$, like those of liquid crystal, have drawn much attention from researchers in the liquid crystal fields [13–16]. The effects of the interaction of carbon nanotubes and liquid crystals on their own properties have been studied in several ways for improving the characteristics of both materials. It has been reported that carbon nanotube dispersed in liquid crystals is parallel to the director of liquid crystals, and such an LC-parallel state is maintained even when the director of the LC changes under an external field. Liquid crystals are also used as precursors in the processing of carbon nanotube arrays. These demonstrate that the orientation of carbon nanotubes is improved by the liquid crystals [17–19]. Additionally, the properties of liquid crystal are changed by doping the carbon nanotubes. The effects of carbon nanotubes on the phase transitions of nematic liquid crystal have been studied; it has been found that the isotropic–nematic phase transition temperature of the liquid crystal component is enhanced by the incorporation of MWNTs within a small composition gap [20]. For the twisted nematic (TN) mode, one of the liquid crystal display modes, the doping of raw carbon nanotubes could apparently reduce the drive voltage [21–25].

It must be noted that there is very little research on the effect of doping carbon nanotubes on the contrast ratio of the TN mode. In our previous study [23], we found that the contrast ratio of the TN mode was reduced sharply with a reduction in drive voltage by doping raw carbon nanotubes, by even less than $1/3$ of the values of the neat LC cells; we speculated that this phenomenon was brought on by the uneven dispersion
and aggregation of carbon nanotubes. Based on this presumption, the carbon nanotubes were chemically modified with the molecules, which have a typical liquid crystal structure, and prepared for uniform dispersion in liquid crystal solutions to achieve less of a contrast ratio decrease in the TN mode with a reduction in drive voltage.

2. Experiments

2.1. The Materials

The chemicals, 4′-hydroxy-biphenyl-4-carbonitrile and 4-(4-propyl-cyclohexyl)-phenol (purity > 99%), were purchased from Shanghai Aladdin Bio-Chem Technology Limited Company (Shanghai, China). The raw multi-walled carbon nanotubes (purity > 90%; outside diameter, 10–20 nm; length, 1–2 µm) were purchased from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). The nematic liquid crystal, SLC 7011-100, was purchased from Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd. (Shijiazhuang, China), China (nematic phase at temperatures from −30 °C to 68 °C).

2.2. The Preparation of Samples

Figure 1 shows the chemically modified synthetic routes for MWNT-1 and MWNT-2. The synthesis was performed by following the steps in [26]. Then, 0.01 wt%, 0.02 wt%, 0.03 wt%, and 0.05 wt% of MWNT-1 and MWNT-2 were added to the SLC 7011-100, respectively, to obtain different liquid crystal–carbon nanotubes solutions. Sonication was applied to each mixture for 2 h to achieve fine dispersion. The simple cells were fabricated by two ITO glass substrates, with the thickness (16 µm) controlled by spacers. PVA was used as the alignment layer was spun on the ITO surface, which was rubbed to make the LC molecules parallel to the substrate. The rubbing directors of substrates on one cell were placed perpendicular to each other. Then, the mixtures were filled into the cells by capillary action. A cell filled with pure liquid crystal was also prepared as a reference.

![Figure 1. The chemically modified synthetic routes of MWNT-1 and MWNT-2.](image)

2.3. The Measurements

The electro-optical properties were measured by an LCT-5016 (Changchun Liaocheng Instrument Co, Ltd. (Changchun, China)), equipped with two crossed polarizers, to make the cells exhibit the TN display mode. Moreover, the voltages at which the transmittances are 90% and 10% are defined as the threshold voltage ($V_{th}$) and saturation voltage ($V_{sat}$), respectively.
respectively. The contrast ratio (CR) is defined as the ratio of maximal transmittance to minimal transmittance. The data of the electro-optical properties of the SLC 7011-100 with raw carbon nanotubes were obtained from our previous study [23].

3. Results and Discussion

It is easy for MWNTs to aggregate due to their strong van der Waals forces, especially at high concentrations, but the dispersion of MWNTs in LC was improved by chemical modification as shown in Figure 2. It is clearly seen that the dispersion of the chemically modified MWNTs was greatly improved.

![Figure 2](image-url)  
*Figure 2.* The TEM images of the MWNT forms: (a) raw MWNT; (b) oxidized MWNT; (c) MWNT-1; and (d) MWNT-2.
Table 1 shows the exact data about the CR, $V_{th}$, and $V_{sat}$ of each sample. The $V_{th}$ and $V_{sat}$ were lower than those of pure LC cells, but higher than those of raw MWNT-doped TN cells [23], which were less than about 1/3 of pure LC cells produced by the same materials and process. From former research, we knew the reason that CNT doping reduced the drive voltage of the TN mode was due to the special electrical abilities of CNTs; the raw CNTs in the LC host could trap the ion charges and restrain their movement, reducing the screening effect, which made the actual drive voltage decrease. However, the MWNT-1 used in this experiment was chemically modified, the structure of the CNT was destroyed, and the electrical properties were changed, so the interaction between CNTs and ion charges became lower, the trapping and restraining effect became weak, and the drive voltages became higher than those of the raw CNT-doped TN cells.

Table 1. The contrast ratio, threshold voltage, and saturation voltage in different concentrations of MWNT-1-doped TN cells.

| MWNT-1 Concentration (wt%) | Contrast Ratio | Threshold Voltage (V) | Saturation Voltage (V) |
|---------------------------|----------------|-----------------------|------------------------|
| 0                         | 91.43          | 0.765                 | 1.582                  |
| 0.01                      | 64.10          | 0.516                 | 0.774                  |
| 0.02                      | 58.25          | 0.523                 | 0.810                  |
| 0.03                      | 49.67          | 0.579                 | 0.955                  |
| 0.05                      | 41.78          | 0.431                 | 1.088                  |

Figure 3 shows the voltage-transmittance curves obtained from the experiments, with the percentage of MWNT-1-doped cells from 0.01 wt% to 0.05 wt%; the black spots could be found in the cells with the naked eye when the concentration was above 0.05 wt%. From Figure 1, we found that the transmittance of MWNT-1-doped cells at the null voltage (off stage) was less than that of the pure LC cell, and the transmittance at the null voltage decreased as the concentration of MWNT-1 increased, from 89% at 0.01 wt% to 83% at 0.05 wt%, compared with 92% in the pure LC cell. When the voltages were above 2 V (on stage), which was usually used as the drive voltage, the transmittance of each sample was slightly larger than that of the pure LC cell at the same voltage, and the intensity of light through the cell increased with the more MWNT-1-doped cells in the LC host.

As reported in [23], in a certain percentage range, the MWNT-doped cells align along the director of the LC host. Because of the imperfect dispersion and entanglement, a number of MWNTs could not be parallel to the director of the LC host. On the other hand, the interaction between MWNTs and LC molecules makes the LC molecules tend to rotate to the axial direction of the MWNTs, resulting in the disordered arrangement of the LC molecules. At the off stage, this destroyed the twisted structure, making less light pass through the cell; at the on stage, the MWNTs would not rotate with the LC molecules totally and immediately under the external electric field. Thus, the acting force between the MWNT and LC molecules makes some LC molecules’ long axes not vertical to the substrates of the cell, the leakage of light accrues, and so the intensity of the light passing through the cell increases at this stage. The diminishment in the ratio of maximum transmittance to minimum transmittance induced the drop in contrast ratio values. We also found that the more MWNT doped, the more aggregation and entanglement accrued, and the more the values of the contrast ratio dropped. Compared with raw MWNTs, MWNT-1 have a finer dispersion and less aggregation in the LC host, and due to their shorter long axes, they can align and rotate with LC molecules easily. All of these factors made the MWNT-1-doped TN cells have a better contrast ratio than the raw MWNT-doped TN cells.
ion charges became lower, the trapping and restraining effect became weak, and the drive voltages became higher than those of the raw CNT-doped TN cells.

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Figure 3. The voltage dependence of the transmittance curves of the TN cells with different concentrations of MWNT-1 doping.

Table 2 and Figure 4 show the electro-optical properties of MWNT-2-doped TN cells, with the concentration range corresponding to the concentrations of MWNT-1. The $V_{th}$ and $V_{sat}$ were also smaller than those of the pure LC TN cells. Compared with MWNT-1, the MWNT-2-doped TN cells had a larger transmittance at the null voltage and a smaller transmittance at the same drive voltage in each concentration, so the value of the contrast ratio is higher. This was likely due to the effect of the side chain attached to the MWNTs on the arrangement of the LC molecules. MWNT-1 have an affinity to cyano- groups, more similar to LC molecules, while MWNT-2 have an alkyl side chain, so the affinity between the side chain of MWNT-1 and LC molecules is larger. This affinity makes the MWNTs perpendicular to the director of the LC host, making the directors of MWNT-1 and the LC host interact less favorably, which is exhibited by the values of the contrast ratios being smaller than those of MWNT-2-doped TN cells. Meanwhile, it was found that the $V_{th}$ and $V_{sat}$ of TN cells with MWNT-2 were larger compared with MWNT-1, however the reason needs more investigation. As Figures 3 and 4 show, the slopes of the voltage-transmittance curves of MWNT-1- and MWNT-2-doped TN cells are much larger than the slope of the pure LC cell. A restriction of the further application of the TN mode is that it is not suited for multi-drives in modern displays due to its slow transmittance change under an applied external electric field. However, doping with MWNT-1 and MWNT-2 made the voltage-transmittance curves much sharper, conforming to the requirements of the multi-drive
display. This improvement is also expected to be used in the TFT display mode, which is much like the TN mode.

Table 2. The contrast ratio, threshold voltage, and saturation voltage in different concentrations of MWNT-2-doped TN cells.

| MWNT-2 Concentration (wt%) | Contrast Ratio | Threshold Voltage (V) | Saturation Voltage (V) |
|----------------------------|----------------|-----------------------|------------------------|
| 0                          | 91.43          | 0.765                 | 1.582                  |
| 0.01                       | 69.60          | 0.530                 | 0.993                  |
| 0.02                       | 64.13          | 0.677                 | 0.970                  |
| 0.03                       | 56.06          | 0.605                 | 1.297                  |
| 0.05                       | 47.59          | 0.645                 | 0.876                  |

Figure 4. The voltage dependence of the transmittance curves of the TN cells with different concentrations of MWNT-2 doping.

4. Conclusions

In this work, chemically modified MWNTs with two types of side chains, respectively, were synthesized, in order to achieve finer dispersion in LC. The electro-optical properties of the TN cells doped with these MWNT derivatives were investigated. Compared with raw MWNT, the doping of MWNT derivatives not only reduced the threshold voltage and saturation voltage, but also kept the contrast ratio at a relative high value. It was found that the contrast ratio declined as the concentration of MWNT derivatives in the LC
host increased. The improvement of the contrast ratio and drive voltage is be expected to promote MWNT derivatives being applied in TN and TFT display areas.

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