Interaction Nature of Carbon Nanotube Dispersed in Nematic Liquid Crystal

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Abstract

Recently, studies on orientation of carbon nanotubes (CNTs) dispersed in nematic liquid crystal (LC) and CNTs effects on electro-optic characteristics of the LC device have been performed. In this paper, we summarize interaction nature between CNT and LC, local distortion of the LC director field by motion of CNTs, and effects on electro-optic performances of LC device.

1. Introduction

Recently, interactions between CNT and LC have been studied extensively. The ways of approaching are three fold; i) orientation of CNTs in nematic LC media, ii) effect of CNTs on electro-optic performances of LC device, and iii) the LC dynamic patterns generated by motion of CNTs.

First of all, the long axes of CNTs are known to align parallel to the nematic LC director **n**.[1] We also report that a LC orientation is disturbed if the addition ratio of CNTs exceeds a critical weight % due to occurrence of CNT clusters.[2] The conductivity measurement also proves the existence of an electrically controlled reorientation of CNTs from planar (homeotropic) to homeotropic (planar) in nematic LC using a vertical field.[3,4] We also reported interaction nature between CNT and LC by calculation, claiming that the LC is strongly anchored to the long axes of the CNTs by hydrogen bonding.[5,6]

On the other hand, the size of TFT-LCDs becomes larger and larger, recently up to 100 inch, trying to be a major display in large-size display applications. All TFT-LCDs use viscous nematic LC, so that the response time of LCDs cannot be faster than 1ms, which is disadvantageous compared to other emissive displays such as PDP and OLED. In addition, the requirements on reliability of TFT-LCDs become tough and tough. As one of solutions, CNT mixing to nematic LC was performed and the effects have been evaluated.[5-14] According to the reports, the residual dc is suppressed by CNT addition and backflow especially in TN cell is suppressed, thus improving rise response time. However, there are differences in data, especially in decaying time since one[11] claims that it increases with increasing CNT wt. % due to increase in viscosity, and we[8,14] showed the decrease in response time in the CNT-doped cell compared to the pure cells. In other words, the works on CNT/LC system are preliminary stage and thus some are controversial. On the other hands, the CNT effects on physical properties of the LC have not been confirmed yet.

Finally, we also observed that above a critical ac applied field, the CNTs experience translational motion, deforming the LC director field fixed by surface anchoring and electrical field. From polarizing optical microscopy, one can understand motion of CNTs and distribution of CNTs indirectly.[2,14]

In this paper, we describe our works on CNT-LC system comparing with previous works.

2. Interaction nature between CNT and LC

We performed density functional calculations within local density approximation (LDA).[16-18] Figure 1 shows the anchoring of LC molecule on CNTs. The binding was greatly enhanced by maximizing an aromatic ring interaction, as shown in top view of Fig. 1.

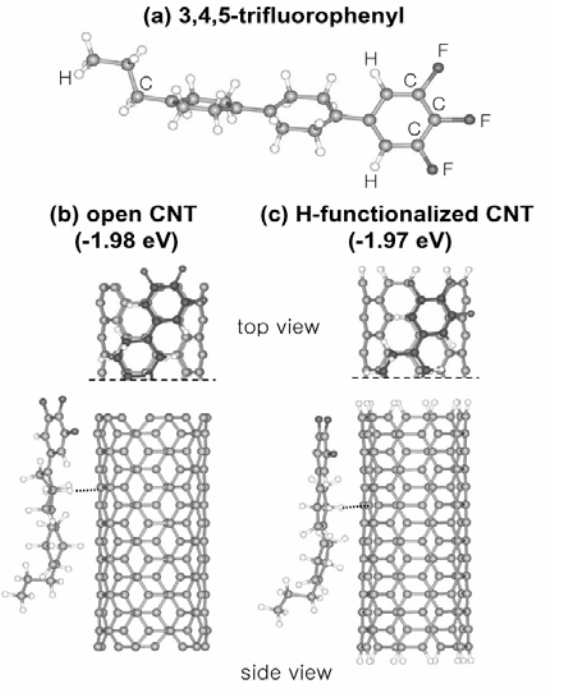


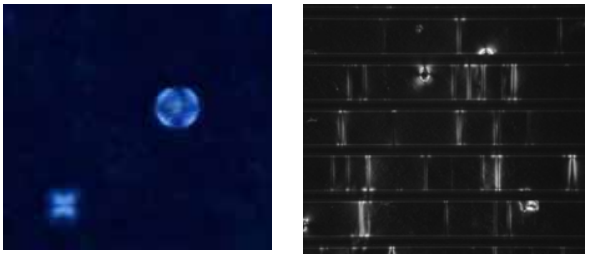
Figure 1. The optimized geometries of (a) 3,4,5-trifluorophenyl LC molecule, and those interacting with (b) open CNT and (c) H-functionalized CNT. The dashed lines in (b) and (c) are the shortest bond lengths of hydrogen atom at LC molecule and carbon atom at CNT.

The interaction energy is close to -2 eV, independent of the presence of the functional groups at the edge of CNTs. This strong binding energy is attributed to a charge transfer (0.45 e and 0.23 e for open and H-functionalized CNTs, respectively) from LC molecule to CNT due to strong electron affinity of CNTs. The shortest bond length is 2.2 Å for H at LC molecule and carbon atom at CNT. The binding nature is therefore a hydrogen-bonding rather than a simple van der Waals interaction. This strong anchoring in fact induces a self alignment of CNT molecules in LC medium. Furthermore, the charge transfer indicates that the CNT has a net charge.

3. Distrotion of LC director field by CNTs

According to our calculations, the CNT has a net charge. If this is true, the CNT should experience translational motion under ac electric field instead of only orientational ordering by induced dipole moment[18] like the LC in the electric field. To confirm this, we fabricated CNT-doped cells withe the vertical field-driven vertically aligned (VA) and in-plane field-driven homogenously aligned (HA) ones. To evaluate this, we doped single wall CNT by 10^{-4} wt% to a superfluorinated LC mixtures from Merck Co. ($\Delta\varepsilon$ = +7.4, Δn = 0.088 at λ = 589 nm). For the VA cell, the cell gap was 60 ㎛, and for the HA cell, the electrode width and distance between them were 10 ㎛ and 30 ㎛, respectively, with initial LC alignment parallel to the in-plane field direction. The CNT-doped LC mixture was filled at room temperature by the capillary action.

As clearly seen in Fig. 2, both cells exhibit some LC textures under polarizing optical microscopy above a critical ac electric field with 60 Hz. In these experiments, the LC with positive dielectric anisotropy is used so that the vertically and homogenously aligned LC director should be more stabilized by vertical and in-plane electric field, respectively. Therefore, under crossed polarizers, the cell should show a perfect dark state. Nevertheless, such textures appear in the CNT-doped cell while the pure LC cells do not show these. The number of these textures increases with increasing field strength, uniformly distributed over whole cell area. To understand the LC textures, we applied voltage 15 V_{rms} with 1 Hz in the HA



< Vertical field driven cell> **<In-plane field driven cell>**

Figure 2. LC textures generated by motion of CNTs under polarizing optical microscopy.

cell and could observe that the texture starts at one electrode, then reaches opposite electrode, and comes back to original position according to the frequency, as shown in Fig. 3. We analyzed the LC orientation of two vertical stripes between electrodes by rotating the sample under crossed polarizers and found out that the LC director at two vertical stripes with dark line between them is distorted symmetrically along the dark line from initial alignment like a sailing boat in a sea. In this cell, the transmittance is proportional to $sin^2 2\psi(V)\ sin^2(\pi d\Delta n_{eff}(V) / \lambda)$ where ψ is a voltage-dependent angle between the LC director and the crossed polarizer axes, and $d\Delta n_{eff}$ is also a voltage-dependent effective cell retardation value. Therefore, the occurrence of transmittance indicates the LC director is deviated from the initial alignment. Interestingly, the ψ at different cycles is different each other. This indicates that the ψ is function of time and we are observing time averaged-transmittance. Due to time-dependent LC director, we could not find any angle that shows dark texture when rotating the in-plane driven cell under crossed polarizers in Fig. 3.[19] Again, this experiment prove that the CNT dispersed in nematic LC medium has a net charge.

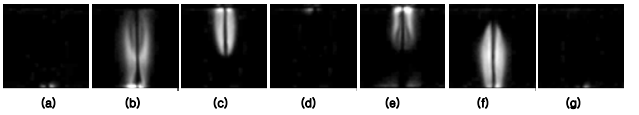


Figure 3. Time evolution of the LC texture in the in-plane field driven cell for 1 second. Positive cycle (a-d) and negative cycle (d-g).

4. CNT effects on electro-optic performances of twisted nematic (TN)-LC device

To confirm CNT effects on physical properties of the LC and electro-optic characteristics of the LC device, we fabricated many different kinds of cells with homogenous, vertical, and twist alignment.

As mentioned before, other reports claim that the increase in CNT wt. % increases dielectric anisotropy and viscosity. However, since the CNT contents either multi or single wall, is less than 10^{-3} wt. % in our study, with such low concentration, the effect on dielectric anisotropy is minimal but the rotational viscosity is quite affected. When measuring rotational viscosity with transient-current method using HA cells, it is lowered by 5 ~ 10% depending on CNT concentration and types.[20] In addition, elastic constants of the LC is also affected by CNTs within 10%.

With understanding of change in physical properties of the LC by CNT doping, we made TN test cells to evaluate electro-optic performances. Figure 4 shows optical microphotographs of the CNT-doped TN cell with normally white mode. The cell gap was 4.5 ㎛. The white state shows uniform textures except some spots, which were originated from the existence of ball spacers. With increasing voltage, the transmittance of the cell decreases

and appears to be black at 4.5V. There are no differences in texture between pure and CNT-doped LC cells. However, when a high voltage is applied to the cell, only CNT-doped cell shows some turbulent textures (see Fig. 4(c)). This texture covers whole electrode area, indicating that this is related to motion of CNT and CNTs are well distributed over whole cell area. Understanding these texture associated with CNT motion is under studying.

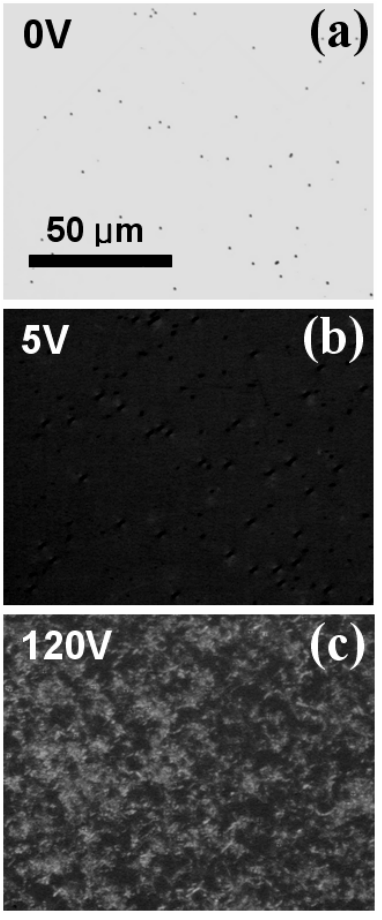


Figure 4. Microphotographs of a MWNT-doped TN cell at (a) 0 V, (b) 4.5 V and (c) 117 V.

From above experiments, we know that the voltage-dependent LC dynamic is also the same even in the CNT-doped cell within driving range of TFT-LCDs. Now, we measured voltage-dependent capacitance (V-C) and transmittance (V-T), as shown in Fig. 5. As presented, there is only little difference between pure and CNT-doped cells, which is consistent with change ratio of physical properties of the LC. Nevertheless, according to other's reports,[7,11] the threshold voltage is quite strongly shifted under dc applied voltage, while our works do not show this behavior at all[6]. The discrepancy between results may come from either that other's material has denser ion density than ours since they use nematic LC 5CB or E7 which has high dielectric anisotropy (>10) or that the CNT wt. % is much higher in theirs (~0.02 wt. %) than ours. According to our observations, such high concentration of CNTs disturbs LC orientation by CNT clusters with size larger than 1 ㎛. The CNT cluster with 0.1 wt. % doped cell is also observed in other's work.[12] If CNT clusters exist in the LC device, this deforms LC orientation defined by surface treatment so that measuring voltage-dependent electro-optic characteristic such as V-T, V-C and hysteresis is rather meaningless since the data is not repeatable. Conclusively speaking, at moment, doping of CNTs with high concentration is not applicable to LC devices but minor doping of CNTs to LC mixture causes change in physical properties within 10%, so that V-T change by CNT is little.

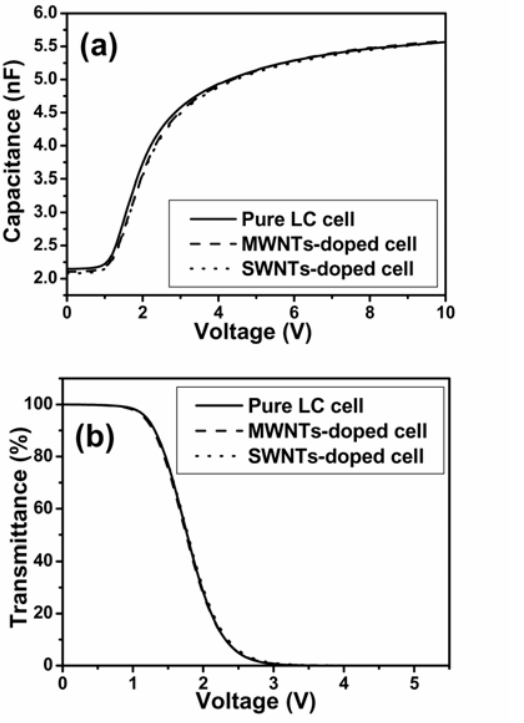


Figure 5. Measured voltage-dependent (a) capacitance and (b) transmittance curves by applying ac voltage.

Next, the response time of TN cells is evaluated, as shown in Fig. 6. According to our results, both rising and decaying response time is reduced. For a rising time, all CNT-doped cell exhibit a faster response time than that of pure LC cell up to about 3 V. At applied voltage of 5V, the response time becomes about the same, indicating that the CNT is more effective in improving grey scale response time. For a decaying time, it is proportional to K_{eff}/γ where K_{eff} is effective elastic constant and γ is rotational viscosity. Since the rotational viscosity decreases with CNT-doping, the decaying time also decreases. According to other's report again[7,11], the CNT depresses backflow in the TN cell, thus improving switching time but nevertheless, it is increased due to increase in viscosity by CNTs. We believe that the switching time is improved by

reduced rotational viscosity associated with change in elastic constant, rather than backflow effect, at the moment.

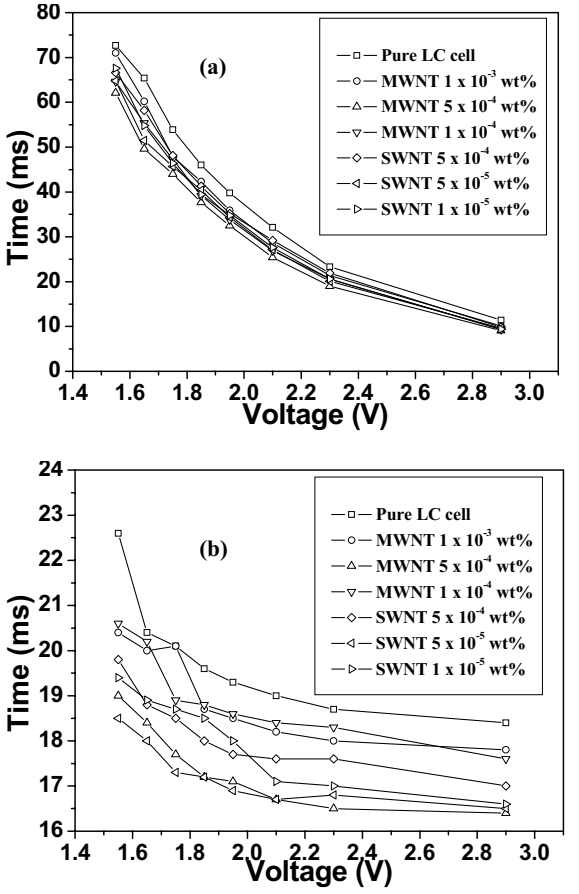


Figure 6. (a) Rising and (b) decaying times for both pure and CNT-doped TN cells.

Finally, many experimental results[6,7,21] report that the CNT-doped cell reduces residual dc; nevertheless, one[21] claims that the behavior is rather different depending on type of CNTs. We attribute this to the charge trapping effect by CNT since the CNT has a dipole moment by interaction with LC; nevertheless, more detail understanding is under progress.

6. Summary

We have reviewed recent works on CNT-LC system. A lot works need to be performed further to understand interaction nature of CNTs with LC. Finally, we hope that the anisotropic nano rod CNT helps improve the LC device by overcoming intrinsic limitation of nematic LC.

7. Acknowledgements

This work was partly supported by grant No. R01-2004-000-10014-0 from the Basic Research program of the Korea Science & Engineering Foundation.

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