Carbon-Nanotube Doping in Liquid Crystals of Display Interest

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Abstract

Recent studies in the literature have shown that it is possible to overcome the limitations of the physical properties of liquid crystals by the doping of carbon nanotubes. Although still in its infancy, the potential of such a new approach for opportunities in display applications should not go unnoticed.

1. Introduction

Current liquid-crystal-display (LCD) technology demands the suppression of field screening (and the resulting residual dc) as well as the shortening of response time to ensure a high quality of performance of a TFT-driven display. The field-screening effect is an ion effect induced by charges adsorbed on the interfaces between the alignment layers and liquid-crystal (LC) layer, which may cause serious problems such as image sticking, unreproducible gray levels, hysteresis of the transmission–voltage curve, and prolonged response time from the voltage decay over an active-matrix-addressed pixel. Because the electro-optical (EO) performance of a LC device can be degraded by the accumulation of ion impurities on the alignment layers, it is significant to understand how the transport of ionic charges in the LC device generates a change in distribution of the electric field and, in turn, influences the LC director orientation under an applied voltage. On the other hand, the response time is related to the relaxation process of the LC molecules and governed by the viscoelastic coefficient: the lower the rotational viscosity and the higher the effective elastic constant, the faster the response. Previous experimental investigations have revealed that adding carbon nanotubes (CNTs) into LCs has an impact on the modulation of physical properties of the LCs and of EO characteristics of the device [1–15]. In this paper, we briefly review the associated results, with an emphasis on how CNTs as a nanodopant repress the ion effect via charge transfer (CT) [11, 16–18], which leads to a reduced threshold (dc) voltage and dc offset, and how they invariably lower the rotational viscosity in nematic LC cells [7, 13, 19, 20] thus giving rise to a shortened response time. Research into physical modification of LCs by added CNTs is still in its infancy. Nevertheless, the existing considerable potential for its implementation into LC devices is worth an eye on this exciting area. This paper demonstrates the exciting technology for opportunities in display applications.

2. LC/CNT suspensions

One fundamental consideration for the colloidal system of LC/CNT suspension is the relationship between the director orientation of the LC and the axial orientation of the CNTs. Experimental observations have shown that either single- or multi-walled (MW) CNTs dispersed in nematic LC solvents are orientationally ordered by the nematic matrix and are preferably parallel to the LC director in null external field [9, 10, 16, 21]. Density functional calculations within local density approximation have also suggested that the strong anchoring via inter-molecular hydrogen bonding induces a self-alignment of CNTs in the LC [18]. It is a pity that, in this analytical study, only one specific case, a (5, 5) armchair single-walled CNT, was considered and the other important types of nanotubes; i.e., zigzag and the most commonly encountered chiral type as well as MW analogues, were left untouched [18].

Distinctive nanomaterials behave very differently depending on their type, size and the environment in which they are dispersed. Nanoparticles shaped like filaments can circulate in a viscous solvent several times longer than their spherical counterparts [22]. Studies of percolation in rigid rod dispersions, both analytical [23] and numerical [24, 25], show that the critical volume fraction (CVF), corresponding to the percolation threshold, is inversely proportional to the

rod's aspect ratio. These known facts are of value of reference for researchers intending to rectify the physical properties of LCs used in photonic devices by the doping of nanomaterials such as a CNT. Because the effective utilization of CNTs in LC applications depends strongly on the ability to homogeneously disperse them throughout a LC hydrosol without destroying their integrity, CNTs are preferably pretreated to prevent physical entanglement or aggregation into bundles or fibrils and to promote the percolation limit [2].

3. Electro-optical performance

For the display application, superior EO performance, characterized by lower threshold and driving voltages [2–5, 14, 15], narrower hysteresis or lower residual dc [2–6, 8, 11, 14–17], shorter response times [7, 13, 19, 20] and weaker nematic flow [2, 14, 15], has been reported in LC cells doped with CNTs. The alterations of the first two features mentioned above are particularly pronounced for LCs (such as cyano-compounds) consisting of a high density of impurity ions. The effective formation of CT complexes in the LC/CNT dispersions in a field significantly depresses the ion effect, resulting in the observed suppression of the characteristic voltages as well as residual dc. While the reduction of either characteristic voltage is dramatic in the dc case, it is not as obvious in the ac [5]. This means that the advantage of CNT doping in TFT-grade LC cells addressed by ac will be somewhat limited in this regard [11].

The response times are one of the most prominent device characteristics in LCDs. Unfortunately in one of our earlier publications [3], data of optical transmission upon electrical switching off were incautiously acquired with an uncontrolled field-application duration, which prolonged the optical relaxation process (due to the image-sticking effect) and led to the incorrect statement that "a carbon-nanosolid additive slows down the relaxation process." A more careful and focused study of the dynamic response of homogeneously-aligned E7 cells incorporated with various CNT contents can be found in Ref. 7. It reveals that the rotational viscosity decreases with increasing CNT concentration (see Fig. 1) within the doping-level threshold determined by the percolation limit (~0.100 wt.% in our experiment). For the doping ratio of 0.050 wt.%, the rotational viscosity drops by 13% from 224.3 mPa·s of pristine E7 to 194.5 mPa·s in the suspension at 25 °C and by 23% from 33.6 mPa·s to 25.8 mPa·s at 55 °C as shown

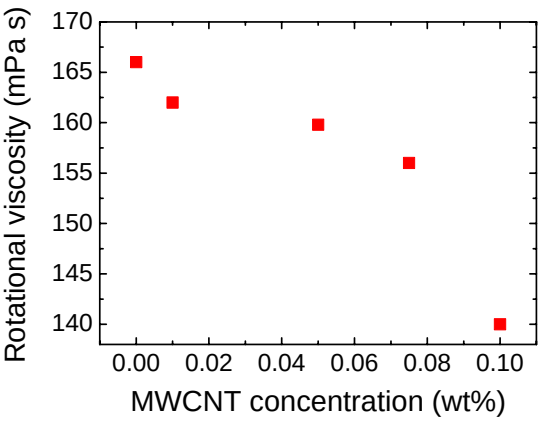

Fig. 1. Dopant-concentration dependence of E7's rotational viscosity at 30 °C.

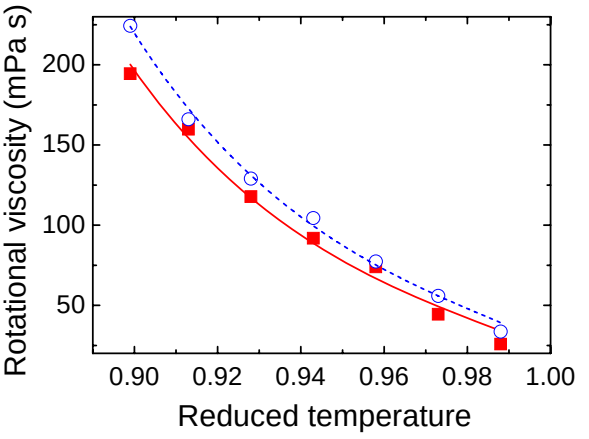

Fig. 2. Temperature dependence of rotational viscosities of neat E7 (○) and E7 doped with 0.050-wt.% CNTs (■) in the range of 25–55 °C.

in Fig. 2 [7]. It is clear that a similar report claiming the reduction of merely 5–10% is naturally restricted by the authors' lower doping threshold (~0.001 wt.%) [13]. If the extent of the reduction in rotational viscosity γ_1 surpasses the change in effective elastic constant K_{eff}, which is usually the case, it is no doubt that the shorter response times observed should be primarily attributed to the reduction of the rotational viscosity [7, 13, 19, 20].

A pioneering study of the effect of CNT doping on the device performance of a twisted-nematic (E7) LC cell suggests that a MWCNT additive restrains the backflow [2]. Although it is worth further rigorous studies for confirmation by others, interestingly, the allotrope carbon nanohorn has also been found to notably suppress the nematic backflow in a twisted-nematic (MLC-6292-100) host [26]. As a matter of

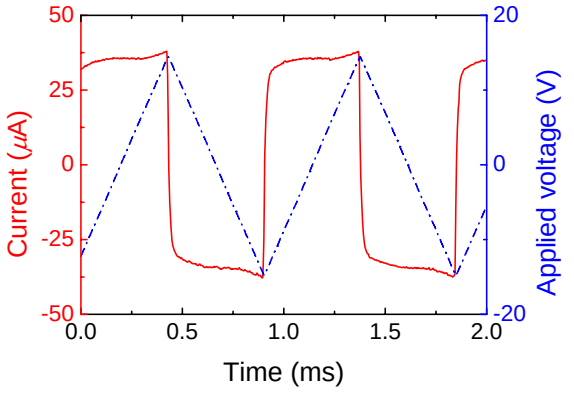

Fig. 3. Capacitance current due to the director reorientation induced by a triangular waveform at 1 kHz in an E7 cell at 25 °C.

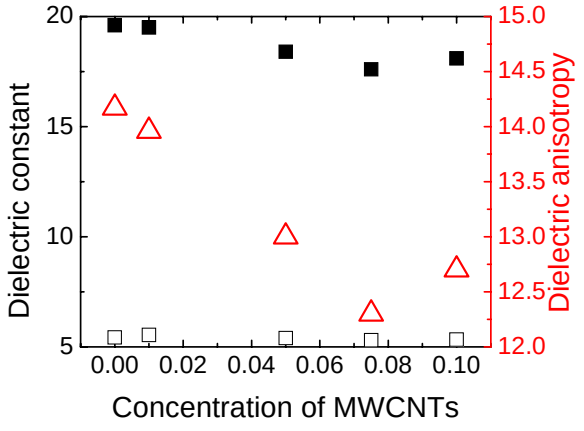

Fig. 4. Dopant-content dependence of dielectric constants (■: $\varepsilon_{\parallel}$; □: $\varepsilon_{\perp}$) and dielectric anisotropy (△: $\Delta\varepsilon$) obtained from the one-cell capacitance measurement on E7 cells at 25°C.

fact, the impact of a minute amount of MWCNTs doped in E7 on the both splay and bend elastic constants is quite minimal, whereas the twist elastic constant descends drastically by ~30% for the 0.100-wt.% suspension [27], as opposed to the increase by ~5% in a single-walled CNT suspension of a super-fluorinated LC mixture [13]. Accordingly, a twisted-nematic E7 cell may not respond faster by doping CNTs unless it takes advantage of other mechanisms.

Influence of CNTs as an additive on the dielectric anisotropy $\Delta\varepsilon$ of E7 is studied by means of two distinct experimental techniques. Here, the dielectric constants in a pristine cell and a cell doped with MWCNTs of various concentrations are measured by the one-cell (namely, parallel-cell) and two-cell (i.e., parallel-and-perpendicular-cell) capacitance measurements. A typical current signal induced by the change in capacitance (or dielectric constant) in the triangular waveform at 1 kHz is shown in Fig. 3. The results show that, for a prefect alignment of the LC and CNTs, the two-cell capacitance measurement yields no obvious difference in $\Delta\varepsilon$ between the pure and doped cells. In contrast, interesting results from dynamic electric responses are revealed in the one-cell capacitance measurement. It indicates that, in the colloidal system, the parallel dielectric constant is slightly reduced, which can be explained by the lower order parameter after applying the high voltage [28]. This result, obtained from the one-cell measurement, is contrary to the results reported by Huang's group [15], who claims that $\Delta\varepsilon$ increases from ~14 to ~20 in an E7 cell doped with 0.01-wt.% CNTs.

Neat E7 possesses very large $\Delta\varepsilon$, indeed, which may obscure the contribution by the high-aspect-ratio CNTs. Close examination on similar effects in ZLI-4792 (Merck) using the one-cell measurement method shows that four important physical properties associated with the device characteristics are all lowered by doping MWCNTs with a concentration of 0.071 wt.%. Note that, in comparison with E7, ZLI-4792 has much lower concentration of impurity ions, indicating that the measurements of the physical properties displayed in Table 1 are carried out with relative ease and the data are quite reliable. It is almost recognized that, in the absence of a field, a dilute CNT colloidal dispersion in a LC exhibits higher order than the undoped mesomaterial. These results imply that the likely trend of the effects of CNT doping is a lowered order parameter in a field, presumably owing to the nonunisonant orientation between LC molecules and the CNTs.

It has been observed that the clearing temperature T_c of E7 is greatly enhanced from ~60 to ~100 °C by the incorporation of ~0.1–0.2% MWCNT content [1]. Such a promotion of the nematic–isotropic transition of E7 by a CNT additive has not been reported by a second group. Indeed, our study shows that T_c, birefringence and pretilt angle [29] remain the same within the experimental error for an E7 suspension dispersed with 0.050-wt.% CNTs.

TABLE 1. Physical properties measured in 4-μm-thick pristine and CNT-doped ZLI-4792 cell at 24 °C.

Sample	γ_1 (mPa·s)	$\Delta\varepsilon$	K_{11} (pN)	K_{33} (pN)
pristine	127	5.11	11.1	23.0
doped	114	4.95	10.7	21.1

4. Concluding remarks

Clearly for the effects of CNT doping on the physical properties of LCs and their device characteristics, there are still numerous mysteries awaiting exploration especially because of various, and some controvertible, results obtained by different research groups. One should keep in mind that some seemingly contradictory results may actually originate from the difference in LC materials, CNT types and combinations used in the studies. Besides, the observations are undoubtedly subject to change due to uncontrolled material purity, CNT aspect ratio, and sampling of CNTs and even different measuring techniques, just to name a few.

It is for sure that, to this stage, further and thorough investigations are much desired. Research along this line should clearly specify the type of CNTs, aspect ratio, size distribution and concentration accuracy. It should preferably include a careful inspection on the consistent and persistent EO performance. Although it is now still too early to consider its adoption into current LCD technologies, the existing potential is conceivably significant for the display community, as new, technically advanced dispersion methods and high-quality functionalized CNTs tailored to possess excellent dispersability in LCs are realized.

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6. References

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