## Ion charge in captivity in a nanotube-doped liquid-crystal cell (?)

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#### **Abstract**

Transient currents were measured in nematic liquid-crystal cells with and without doping of multiwalled carbon nanotubes. Comparative results suggest that the field-screening effect induced by the adsorbed charge is substantially suppressed by the carbon-nanotube dopant, leading to a reduction of the driving voltage and improved performance of display properties.

#### 1. Introduction

The field-screening effect in a liquid-crystal display, resulting from the (impurity) charges adsorbed on the interfaces between the alignment layers and liquidcrystal film, is the primary nuisance for it may cause a number of serious problems such as the image sticking, unreproducible gray levels, hysteresis of the transmission-voltage curve and the increased response time from the voltage decay over an activematrix-addressed pixel. Owing to the fact that electro-optical performance of a liquid-crystal device can be degraded by the accumulation of ion impurities on the alignment layers [1, 2], it is of great significance to understand how the transport of ionic charges in the liquid-crystal device induces the change in spatial distribution of the electric field or electric flux density and, in turn, influences the spacedependent orientation of the liquid-crystal director field under an externally applied voltage.

Previous experimental and theoretical endeavors at transient current have provided fundamental explanations for the nature of ion transport in cells composed of neat nematic liquid crystals [3-5]. Extended from our earlier study of transient currents, induced by the polarity reversal of a dc electric field applied across the cells consisting of two distinct (low-resistivity vs. thin-film transistor (TFT)-grade) pristine eutectic mixtures of nematogens [5], to a comparative investigation of transient-current behavior observed in planar-aligned cells of undoped and lightly-doped low-resistivity nematic liquid crystals, our continuing effort has demonstrated that a minute addition of multiwalled carbon nanotubes as a

dopant to an alkylcyano-based liquid crystal, currently still found its place in some simple twisted nematic display devices with direct addressing, gives rise to a remarkable reduction of the measured ion concentration, yielding improved electro-optical performance [6]. This finding is in good agreement with our previous report pertaining to the effects of carbon nanosolids on the electro-optical properties of a nematic liquid-crystal host [1, 2, 7, 8].

In this paper, we briefly present the experimental results as well as theoretical model of transient currents in undoped and multiwalled-carbon-nanotube-doped nematic cells of the nematic E7. We show how carbon nanotubes as a dopant in a nematic liquid-crystal cell invariably decrease the ion-charge concentration and, in turn, suppress the field-screening effect.

#### 2. Results

Transient currents in undoped and doped cells were measured by detecting the time-evolved voltage drop across a 1-M $\Omega$  load resistor in series by means of a digital oscilloscope at room temperature. The detailed experimental techniques can be found elsewhere [5]. To clarify how the nanoscale carbonaceous dopant, with a doping level of 0.05% by weight, affects the transport of ion impurities, the voltage-dependent charge densities, both deduced from the comparative data of polarity-reversed transient currents in undoped and doped cells, are displayed in Figure 1, which is adopted from Ref. 6. Clearly, the charge density, from a value called the residual charge density at null voltage, rises monotonically as a function of applied voltage and saturates to a constant, denoted by the saturation charge density  $Q_s$ . Comparison of  $Q_s$ between the lightly-doped cell and the undoped counterpart leads to the implication that carbon nanotubes as a dopant effectively reduce the saturated charge density to a half of the original value, namely, from 39 to 19 nC/cm<sup>2</sup>. This is presumably due to the formation of charge-transfer complexes, generating a nontrivial trapping-site density to permit the observed amount of moving charges to decrease as a result of

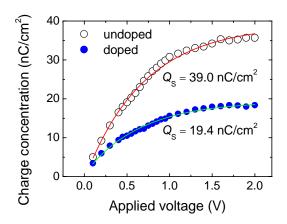


Figure 1. Voltage-dependent ion charge density.

rectification of interface properties as well as suppression of the double-layer effect. In other words, with the presence of the guest-carbon nanotubes as the electron acceptors—in the colloidal system, a substantial portion of the ion charge is trapped or in "captivity" in the liquid-crystal "cell." Certainly, it is easily understood that the higher the voltage applied, the higher the charge concentration measured and that this is true for both cells as illustrated in Figure 1. However, for the trapped ions in a nanotube-doped nematic cell, one can expect that the charge in captivity be liberated by elevated temperatures [9]. Indeed, we have observed the difference in measured charge concentration between an undoped cell and a doped one turning less pronounced at a higher ambient temperature because. By gaining thermal energy, the charge becomes more energetic to escape the trapping sites in the doped cell [9].

The transient current in a nematic liquid crystal submitted to a polarity-reversed field is affected by the spatial distribution of the electric flux density, also known as the electric displacement, as well as the change in effective dielectric constant as a function of the orientation of the nematic director field. simulate the spatial distribution of the director orientation, expressed by the tilt angle, before and after the polarity reversal of the externally applied electric field, the boundary-layer model [3] is used in this study for simplicity. The orientation of the liquid-crystal director can be described by an exponential decay function [3]. Here, the cell thickness is divided into 1000 divisions calculation. Using the refined transient current equation [10] modified from that given by Sugimura et al. [3] and adopting the boundary-layer model with

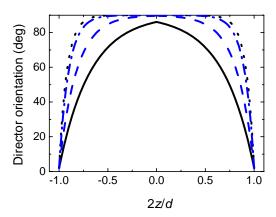


Figure 2. Simulation of nematic director orientation before (solid line: E7 cell; dashed line: E7/MWCNT cell) and after (doted line: E7 cell; dot-dashed line: E7/MWCNT cell) field polarity reversal.

the physical parameters of E7 and the nanotube dispersion, the steady-state, one-dimensional spatial distribution of the director orientation is obtained and illustrated in Figure 2. Note that in this figure the abscissa spans from z = -d/2 to z = +d/2. comparison with the change in director orientation in the undoped cell, it is obvious from Figure 2 that the action of polarity reversal itself is not as significant for the nanotube-doped one. This suggests that the liquid-crystal molecules in the doped cell would experience almost same effective field prior to and after the polarity reversal because the field-screening effect induced by the adsorbed ion charges is suppressed by doping nanotubes into the nematic liquid crystal. It is reminded here that, beyond the threshold voltage, the director orientation or the angular displacement of the nematic director is sensitive to the effective voltage. As a whole, it can be expressed as

$$V_{LC} = V_{appl} - V_{EDL} [1 - \exp(-t/\tau)],$$
 (1)

where  $V_{\rm LC}$ ,  $V_{\rm appl}$ , and  $V_{\rm EDL}$  are the effective applied voltage to the liquid crystal, the externally applied voltage, and the voltage drop in the electrical double-layer, respectively, and  $\tau$  is the relaxation time. Note that the voltage drop in the electrical double-layer is proportional to the maximal possible voltage drop  $V_{\rm d}$  and is also a function of the applied voltage expressed as

$$V_{\text{EDL}} = V_{\text{d}} \left\{ 1 - \exp[-(V_{\text{appl}} - V_{\text{th}})] \right\},$$
 (2)

where  $V_{\rm th}$  is the threshold voltage of the liquid crystal. Based on our experimental study reported recently, the experimentally data, deduced from the adsorbed charge densities and the diffusion lengths, show that  $V_{\rm d}$  is 0.55 V for the E7 cell and 0.35 V for the nanotube-doped counterpart, confirming that doping carbon nanotubes into nematic liquid crystals suppresses the field-screening effect [6]. It is also clear now that the adsorbed ion charges are reduced and the counteracting internal electric field is weakened in the doped cell, one can expect that the dc driving voltage would be lower in the cell doped with carbon nanotubes, which is in consistence with the electro-optical phenomena of carbon-nanotube-doped nematic cells observed in our previous study [2].

Even for the fluorinated nematic liquid-crystal mixtures that possess a high resistivity and are currently employed in the TFT industry, excess ions originating from the mesogenic materials intrinsically or from cell manufacturing process are present more or less in the cell. As mentioned briefly in the beginning of this section, the mechanisms explaining the trapping of the charge in dilute colloidal solutions of carbon nanotubes dispersed in liquid crystals are involved with the formation of charge-transfer complexes in the blended system. By means of spectroscopy, evidence of existence of a third matter through intermolecular interaction in the solution is provided by the fact that neither the absorption spectrum nor the fluorescence spectrum of the solution is equal to the sum of that of liquid crystal and of multiwalled carbon nanotubes [11]. We have found that the central wavelengths of the new bands, depending on the concentration of the solutes (liquid crystal or carbon nanotubes), shift in the spectra. Furthermore, from the experimental and theoretical data the smallest proportion of liquid crystal to nanotubes is found to be about 100:1 in a chargetransfer complex [11]. Recently, density functional calculations within local-density approximation performed by a group led by Lee and Lee [12] have revealed that the charge transferred from a liquid crystal molecule to a neighboring open carbon nanotube is calculated to be 0.45 e and that to a Hfunctionalized nanotube to be 0.23 e. Moreover, the permanent dipole moment in the carbon nanotube induced by the excess charge is efficiently capable of capturing the ion impurities [12]. These findings and arguments certainly convey that ion charge can be trapped by the dopant, leading to the suppression of the field screening.

#### 3. Conclusions

A theoretical model of transient current induced by a polarity-reversed field proposed by Sugimura *et al.* [3] has been modified. Using the refined model, we can explain how carbon nanotubes as a dopant in a nematic liquid-crystal cell rectify the electro-optical properties. This study shows that the charge density of the doped cell is lower than that of the undoped one. Because the double-layers become thinner in the cell doped with carbon nanotubes, the undesired field-screening effect is suppressed. This finding is significant for liquid-crystal display performance and may suggest promising alternatives to conventional nematic materials for LCDs.

Detailed description of the one-dimensional theoretical analysis in the model that takes into account the transport mechanisms of the immobilized and mobilized charges in the liquid-crystal bulk will be reported in a full-length journal paper [10]. The effects of the induced change in director orientation as well as the variation of the effective dielectric constant have been obtained within this model, which is in qualitative consistence with the literature reported previously by Lee and co-workers [1, 2, 6–9].

### 4. Acknowledgements

This work was supported by the National Science Council of the Republic of China (Taiwan). The corresponding author also gratefully acknowledges financial support from the Ministry of Economic Affairs, Taiwan, under Technology Development for Academia Project No. 94-EC-17-A-07-S1-046.

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