

Effect of carbon nanotubes on the field-induced nematic switching

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A small quantity of carbon nanotubes (CNT) was doped in a nematic liquid crystal (LC), and the LC + CNT hybrid was found to exhibit a faster field-induced nematic switching compared to that of the pure LC. The field-induced switching time was probed by means of the electro-optic response of the samples. The hybrid system also revealed a reduced rotational viscosity and an enhanced dielectric anisotropy. The results suggest that the hybrid system undergoes a faster field-induced switching, as the CNTs favorably alter the rotational viscosity and the dielectric anisotropy of the nematic matrix. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4846676>]

Nematic liquid crystals (LC) have gained great research interests in recent years for transferring their long-range orientational order onto dispersed nanomaterials.^{1–8} Experiments have shown that a low concentration of carbon nanotubes (CNT) sample can be organized in a nematic matrix over macroscopic dimensions by dispersing them in LCs.^{1,2} This is a two-way street—the CNTs in an LC matrix also share their inherent properties with the adjacent LC molecules, giving rise to remarkable physical phenomena, such as an electromechanical memory effect,^{9,10} an essence of chirality transmission,¹¹ an induction of macroscopic helical twist,¹² and an effect of super-elongation of CNT-clusters in the nematic matrix.¹³ Thus, a dilute suspension of CNTs in an LC platform is a unique assemblage of an anisotropic dispersion in an anisotropic media, which makes it an important and active area of research for realizing the LC-CNT interactions and the principles governing CNT-assembly through a nematic mediated platform.

The nematic phase of an LC shows dielectric anisotropy due to the anisotropic nature of the molecules where ϵ_{\parallel} and ϵ_{\perp} are the components parallel and perpendicular to the molecular long axis, respectively. For a positive dielectric anisotropic LC, $\epsilon_{\parallel} > \epsilon_{\perp}$, and so, the *director field* (average direction of LC molecules) reorients parallel to an applied electric field. In a uniform homogeneously aligned parallel-plate cell configuration, the nematic director is initially aligned perpendicular to the applied electric field due to the LC-substrate surface anchoring; but the director can reorient parallel to the applied field if the field magnitude is above a critical threshold. This is the essence of a Fréedericksz transition. When the applied voltage across the cell is much higher than the threshold voltage (V_{th}), the nematic director undergoes a dynamic response to rotate along the applied field. We found that when a small amount multiwall carbon nanotubes (MWCNT) was doped in 4-cyano-4'-pentylbiphenyl (5CB) LC, the director's response to the external field was significantly faster compared to that of the pure LC. We also found that an increase in dielectric anisotropy and a decrease in rotational viscosity in the LC + CNT system played important roles in this faster field-induced nematic switching.

The MWCNTs were obtained from Nanostructured & Amorphous Materials, Inc. and had an outer diameter in the range of 8–12 nm, inner diameter 3–5 nm, and length 500–2000 nm. A small amount of MWCNT sample was first dispersed in acetone and shaken on a vortex mixer for 5 h, followed by sonication for 5 h. This process reduces the bundling tendency of the MWCNTs. The liquid crystal 5CB then was added to the acetone + CNT mixture and sonicated for 5 h, allowing the LC to dissolve completely into the solution. Finally, the acetone was evaporated at an elevated temperature, leaving a pure LC + CNT mixture with approximately 0.005 wt. % MWCNTs in the LC. Commercially manufactured LC cells (SA100A200uG180, planar rubbed from Instec Research Instrumentation Technology) with a 1° pre-tilt angle, 1 cm² semitransparent indium tin oxide (ITO) coated area, and a $d = 20 \mu\text{m}$ spacing were used for our experiments. Two such cells were filled at temperature $T > 40^{\circ}\text{C}$ in the isotropic phase by capillary action, one with the LC only and the other with the LC + CNT hybrid. The cells then were very slowly brought down to the room temperature at 25 °C and from then on they always remained in the room temperature. Note that the small cell spacing tends to filter out any nanotube aggregates larger than d . Before performing any measurements, the CNT doped LC cell was examined using a polarizing optical microscope. The optical micrographs revealed uniform nematic textures, like that of the pure LC cell, indicating a uniform director field, shown in Fig. 1. There was no indication of phase separation or agglomerates at any temperature. Thus, at least on the length scales resolvable by visible light, the structure of CNT-aggregates (if any) must be small enough that they do not perturb the director field due to their low concentration and uniform dispersion.

The field-induced nematic switching was studied from the electro-optic response of the LC cells. The optical setup consisted of a beam from a 5-mW He-Ne laser at wavelength 633 nm that passed through a polarizer, the cell, a crossed analyzer, and into a nanosecond Newport detector. The beam was polarized at an angle of 45° with respect to the cells' rubbing direction. The output of the detector was fed into a digital storage oscilloscope. A dc voltage pulse with a pulse interval of 25 Hz was applied across the cell and the change in transmittance as a function of time (when the voltage was on) was detected by the oscilloscope. The response time was

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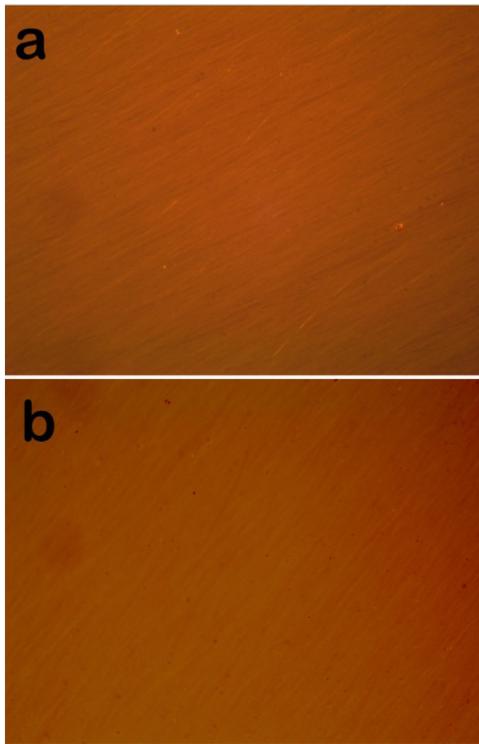


FIG. 1. Optical micrographs under a crossed polarized microscope at 25 °C for (a) 5CB and (b) 5CB + CNT.

studied for several different voltages much higher than the threshold switching voltage. The setup was computer controlled and data acquisition was performed using LabVIEW® software.

Figure 2 shows the field-induced switching response for both pure LC and LC + CNT hybrid cells for two different voltages. These optical responses clearly depict that the hybrid cell responds faster when the field is turned on. The rise time τ_{rise} for each applied voltage is obtained from the time the cell takes to reach 10% of its maximum transmittance intensity. τ_{rise} for both the cells is then plotted as a function of applied voltage in Fig. 3.

Now the question we ask: why does the presence of CNTs significantly reduce the field-induced nematic switching time? For a planar aligned LC cell, the director's response to an external field is given by¹⁴

$$\tau_{\text{on}} = \frac{\gamma_1 d^2}{\Delta\epsilon\epsilon_0 V^2 - K_{11}\pi^2}, \quad (1)$$

where γ_1 is the rotational viscosity, d is the cell thickness, $\Delta\epsilon$ is the dielectric anisotropy, ϵ_0 is the free space permittivity, K_{11} is the splay elastic constant, and V is the applied voltage. Note that τ_{on} is not directly the optical response. It is the time the director takes to rotate from planar to homeotropic configuration without any backflow in the cell. However, since the optical response is mainly due to the director's rotation when the field is on, one can write $\tau_{\text{rise}} \propto \tau_{\text{on}}$, neglecting the backflow in the cell. Thus, from Eq. (1), for a constant d and V , the response would be faster for a reduced γ_1 , an enhanced $\Delta\epsilon$, and a reduced K_{11} . It has been shown before that a small amount of CNTs does not appreciably alter K_{11} .⁸ Therefore, separate experiments were performed to find γ_1 and $\Delta\epsilon$ for the pure LC and hybrid system.

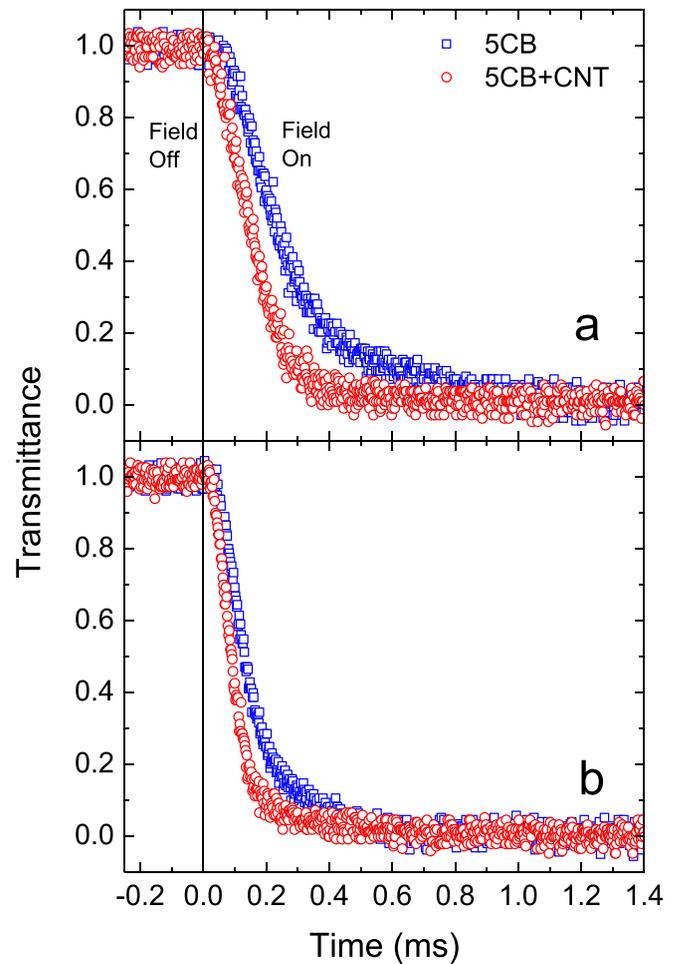


FIG. 2. Dynamic response of the normalized transmittance for 5CB and 5CB + CNT at 25 °C when the voltage is turned on for two different voltages, (a) 30 V and (b) 42 V.

An ac capacitance bridge technique¹⁵ was employed to measure the dielectric constants of the samples. Fig. 4 shows the capacitance of the pure LC cell and the hybrid cell as a function of the applied voltage at 1 kHz. The dielectric constants parallel to the director ϵ_{\parallel} and perpendicular to the director ϵ_{\perp} were extracted from the capacitance vs. voltage graph, and then dielectric anisotropy was obtained from the

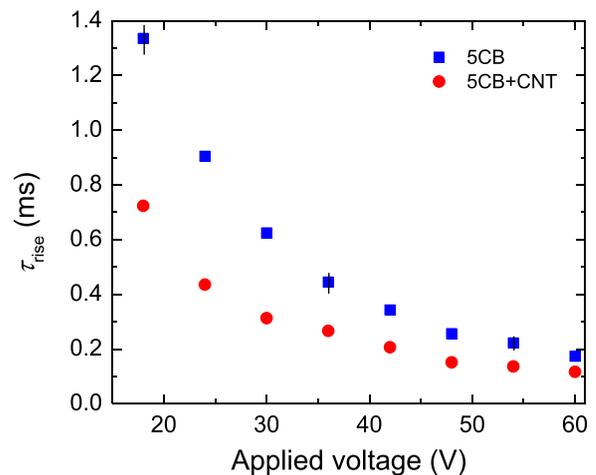


FIG. 3. Rise time τ_{rise} as a function of applied voltage for 5CB and 5CB + CNT. Typical error bars are shown.

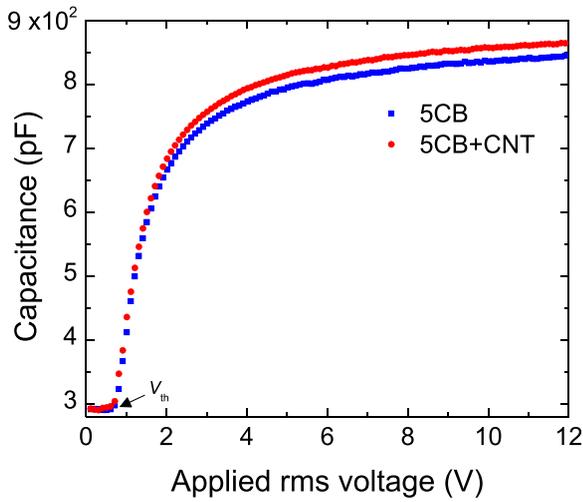


FIG. 4. Voltage (1 kHz) dependent capacitance for 5CB and 5CB + CNT cells at 25 °C. $V_{th} = 0.7$ V for both the cells.

equation, $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$. The results show that at 25 °C, $\Delta\epsilon_{LC} = 13.1$ and $\Delta\epsilon_{LC+CNT} = 13.9$. It has been shown before¹⁰ that the surface anchoring energy, through π - π electron stacking,¹⁶ between the CNT-wall and the LC, induces local short-range orientation order of LC molecules surrounding the CNT, having the average short-range director along the CNT axis. Thus, the suspended CNTs in the nematic media act as local anchoring fields, along the global nematic director, that collectively amplify the orientational order parameter in the matrix. This enhancement in orientational order results in an increased dielectric anisotropy for the hybrid system. In addition, CNTs also exhibit a high dielectric anisotropy due to their structural aspect ratio,¹⁷ and therefore, they contribute to the overall increase in $\Delta\epsilon$ as well. This enhanced $\Delta\epsilon$ for the LC + CNT system is consistent with the finding that the hybrid responses faster to the external electric field.

Rotational viscosity, γ_1 of an aligned liquid crystal represents an internal friction among LC directors during the rotation process. The magnitude of γ_1 depends on the detailed molecular constituents, structure, intermolecular association, and temperature. Rotational viscosity is an important parameter for many electro-optical applications employing liquid crystals, because the response times of the LC devices are linearly proportional to this parameter. The rotational viscosity for 5CB and 5CB + CNT was obtained by measuring the transient current induced by a dc voltage across a planar-aligned configuration.^{18,19} When a dc voltage (much higher than the threshold voltage) is applied across a planar LC cell, the induced current $I(t)$ through the cell shows a time response as the director goes through the dynamic rotation. The current response is given by

$$I(t) = \frac{A(\Delta\epsilon\epsilon_o)^2 V^3}{\gamma_1 d^3} \sin^2[2\varphi(t)], \quad (2)$$

where A is the area of the cell and φ is the angle the director makes with the electrodes/substrate at a given time. At $\varphi = 45^\circ$, $I(t)$ reaches its peak $I_p = \frac{A(\Delta\epsilon\epsilon_o)^2 V^3}{\gamma_1 d^3}$ at the peak time

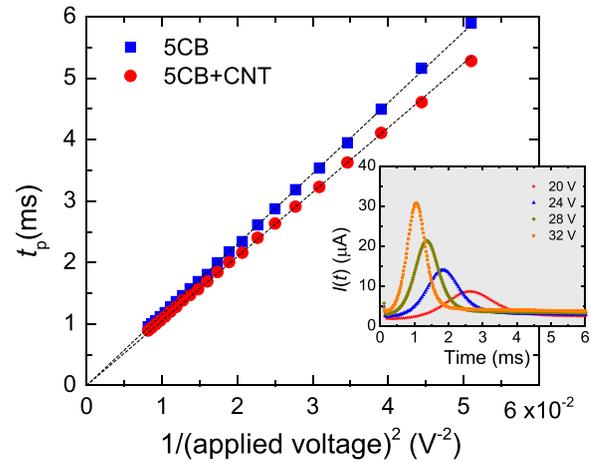


FIG. 5. Transient current peak time, t_p as a function of $(\text{applied voltage})^{-2}$ for 5CB and 5CB + CNT at 25 °C. Linear fits are shown. Inset: Transient current $I(t)$ as a function of time for 5CB + CNT for four different applied voltages listed in the legend.

$$t_p = \left[\frac{\gamma_1 d^2 (-\ln(\tan \varphi_o))}{\Delta\epsilon\epsilon_o} \right] \frac{1}{V^2}, \quad (3)$$

where φ_o is the pre-tilt angle. Note, $\varphi_o = 1^\circ$ for the cells used in this experiment; so $-\ln(\tan \varphi_o)$ is a positive number, and t_p vs. $\frac{1}{V^2}$ shows a positive slope. Several dc voltage pulses, one at a time, with a pulse interval of 1 Hz were applied across the cell to generate $I(t)$. Then, $I(t)$, induced by the applied voltage, in 5CB and 5CB + CNT cells were detected through a load resistor in series by a digital storage oscilloscope. Fig. 5 shows t_p as a function of $\frac{1}{V^2}$ for 5CB and 5CB + CNT cells. The inset represents $I(t)$ as a function of time for the 5CB + CNT cell for four different applied voltages. γ_1 for the respective samples were extracted from the respective slopes of t_p vs. $\frac{1}{V^2}$ graph with the known parameters; see Eq. (3). It is found that at 25 °C, γ_1 for 5CB and 5CB + CNT are 96 mPa s and 84 mPa s, respectively. This dramatic decrease in γ_1 for the LC + CNT system is consistent with the finding that the hybrid system undergoes a faster switching on application of an electric field. We attribute this phenomenon to the ion trapping process of the MWCNTs. It has been shown²⁰ that the MWCNT's ion trapping coefficient is around 0.4—which is higher than that of the other carbon allotropes. The presence of ions would result in an increase in rotational viscosity, slowing down the director's response to an external field. MWCNTs, being suspended in the system, lower the free ion concentration, decreasing the rotational viscosity for the overall system. Thus, the hybrid system shows an accelerated response when the field is turned on.

It has been recently shown that a high electric field across a CNT can cause a resistance blow-up effect,^{21–23} significantly changing the RC time constant in a capacitive circuit. However, in our experiment, the CNTs ($< 2 \mu\text{m}$) are much smaller than the cell gap ($20 \mu\text{m}$), and therefore, at given concentration (0.005 wt. %), they do not short out the electrodes in the homeotropic configuration. Thus, the field across the CNTs is not strong enough to cause any resistance blow-up effect. Since, there is no anomalous dielectric behavior observed at any voltage applied, we believe that the

electro-optic switching time is not affected by the resistance blow-up effect.

In conclusion, we have observed that a dilute suspension of CNTs in a nematic LC results in a significantly faster nematic switching effect on application of an electric field. Additional experiments have revealed that the presence of the CNTs exhibit an enhanced dielectric anisotropy and a reduced rotational viscosity for the composite system. These changes act favorably to reduce the field-induced switching time. The future direction involves a CNT-concentration dependent study to investigate the threshold limit of the concentration above which the system no longer switches faster.

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