Faster in-plane switching and reduced rotational viscosity characteristics in a graphene-nematic suspension

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The in-plane switching (IPS) for a nematic liquid crystal (LC) was found to be considerably faster when the LC was doped with dilute concentrations of monolayer graphene flakes. Additional studies revealed that the presence of graphene reduced the rotational viscosity of the LC, allowing a reduction in the IPS response time and rotational viscosity in the LC. Above this optimal graphene concentration, the rotational viscosity was found to increase, and consequently, the LC no longer switched faster in IPS mode. The presence of graphene suspension was also found to decrease the LC’s pretilt angle significantly due to the π-π electron stacking between the LC molecules and graphene flakes. To understand the π-π stacking interaction, the anchoring mechanism of the LC on a CVD grown monolayer graphene film on copper substrate was studied by reflected crossed polarized microscopy. Optical microphotographs revealed that the LC alignment direction depended on monolayer graphene’s hexagonal crystal structure and its orientation. Published by AIP Publishing.

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I. INTRODUCTION

Graphene (GP) is a two-dimensional crystalline allotrope of carbon, where the carbon atoms are densely packed in a regular sp2-bonded atomic-scale hexagonal pattern. There is a modern theme of research direction, which examines how addition of two-dimensional graphene structure changes electrical, optical, thermal, and mechanical properties of graphene-nanocomposites.1–5 In another direction, liquid crystals (LCs) are widely used in optical display technology for their optical anisotropic properties. The two-dimensional honeycomb structure of graphene shows very interesting interactions with different phases of LCs. The hexagonal graphene nanostructure can be used to enhance the tilted smectic-C order.6 High-transmittance nematic LC displays can be produced from transparent graphene-conducting-layers.7,8 The vertical alignment of LC molecules can be achieved by graphene-oxide without any surface treatment of the substrate.9 Graphene-benzene composites can enhance the orientational order in a nematic phase.10 The strain chirality of graphene surface can propagate into the LC, exhibiting an electroclinic effect in the smectic-A phase and a macroscopic helical twist of the LC director in the nematic phase.11 And finally, monolayer graphene flakes can be rotated using a nematic platform.12 Moreover, there has been a huge research thrust over the past decade to understand the versatile interactions between LCs and various other nanomaterials. For example, the LC can transfer its orientational order onto various nanoparticles;12–20 ferroelectric nanoparticles can significantly enhance the LC’s orientational order parameter;21–25 and carbon nanotubes can modify the LC’s electro-optical properties.26–31 Therefore, understanding the nanomaterials driven modifications in the LC at the nanoscale interface and their subsequent effects on the bulk LC properties is an important and active area of research.

In this paper, we focus on the in-plane switching (IPS) characteristics of a nematic LC doped with several concentrations of monolayer graphene. The IPS is an optical display technology using nematic LC materials. The main goal for designing IPS technology was to solve the limitations, such as small viewing angle and low quality color reproduction for the twisted nematic (TN) LC displays.34,35 In-plane switching involves switching the orientation of LC molecules in the plane parallel to the glass substrate of the LC cell. This way almost the same optical retardation can be maintained over a wide angle of view for an IPS panel. However, one of the major disadvantages of the IPS technology is that its electro-optic switching time is slower than that of the TN displays.35 Therefore, studying the switching response of IPS cells to find ways to accelerate the response is an active research area in both fundamental and applied physics.36,37 In this paper, we experimentally demonstrate that the presence of dilute concentrations of graphene flakes in a nematic LC significantly accelerates the electric field driven IPS response time. Addition studies manifest that the presence of graphene reduces the rotational viscosity and the pretilt angle of the LC. The concentration dependent studies reveal the existence of an optimal graphene concentration for the faster electro-optic response in IPS mode. Above this optimal graphene concentration, the rotational viscosity increases, and as a result, the LC no longer responses faster.

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in IPS mode. To understand the LC–graphene interaction—which influences the reduction in pretilt angle, we have also studied the LC alignment mechanism on a graphene film grown on a copper substrate.

II. EXPERIMENTS AND RESULTS

The pristine graphene (GP) sample in ethanol solvent, obtained from Graphene Supermarket, Inc., contained more than 97% of monolayer flakes (with a small fraction of multilayer flakes) of an average thickness of 0.35 nm and an average lateral size of 550 nm. The ethanol + GP solution was first remixed by a micro-homogenizer tip of 5 mm diameter at 35 000 rpm for 15 min, followed by sonication for 4 h. The liquid crystal E7 (obtained from EMD Millipore Corporation, T\textsubscript{NI} = 60.5 °C) then was added to the ethanol + GP and sonicated for 5 h, allowing the LC to dissolve completely into the solution. The ethanol was evaporated slowly at an elevated temperature, leaving a pure LC + GP mixture. Finally, the LC + GP was degassed under vacuum for 1 h. The process was repeated to produce four known concentrations of graphene in the LC: E7 + GP 1 = 0.126 × 10\(^{-4}\), E7 + GP 2 = 0.939 × 10\(^{-4}\), E7 + GP 3 = 2.02 × 10\(^{-4}\), and E7 + GP 4 = 2.92 × 10\(^{-4}\) wt. %. For consistency, the pure LC was also treated the same way, such as dissolving in ethanol followed by a slow evaporation and degassing. Commercially manufactured planar IPS LC cells (IPS02A090uGVE, Instec, Inc.) were used for our experiments. The cell had the IPS indium tin oxide (ITO) pattern (IPS02A090uGVE, Instec, Inc.) were used for our experiments. The cell had the IPS indium tin oxide (ITO) pattern on the bottom substrate, while the top substrate was plain glass with the alignment layer and without ITO coating. The active area was approximately 100 mm\(^2\). The electrode width was 15 μm and the gap between electrodes was also 15 μm on the IPS pattern. The rubbing direction on the bottom substrate was parallel to the IPS electrodes. The rubbing direction on top substrate was antiparallel to that of the bottom substrate and the cell thickness was 8.8 μm. The cells were filled with the pure E7 or the E7 + GP mixtures at temperature T > 65 °C in the isotropic phase by capillary action and slowly cooled to room temperature.

The field-induced switching was studied from the electro-optic response of the IPS 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 IPS cell inside an Instec temperature controlled oven, an analyzer, and into a nanosecond Newport detector. The output of the detector was fed into a digital storage oscilloscope. The configuration of the optical set up is mentioned elsewhere.\(^{36}\) A DC electric field pulse of 2.4 V/μm (much higher than the threshold switching field) at a pulse interval of 20 Hz was applied to the cell, and the change in transmittance intensity as a function of time was detected by the oscilloscope. Transmittance responses were studied as a function of temperature for pure E7 and E7 + GP samples. The setup was computer controlled and data acquisition was performed using LabVIEW\(^{38}\) software.

Figure 1(a) represents the normalized transmittance intensity responses for the LC in IPS mode as a function of time as the field is turned on. Figure 1(a) depicts that when the applied field is turned on, the transmittance intensity increases as a function of time for E7, E7 + GP 1, and E7 + GP 2. It is clear from Fig. 1(a) that both E7 + GP 1 and E7 + GP 2 respond faster than pure E7. However, the electro-optic IPS response does not continue to get faster monotonically as the graphene concentration increases farther. The IPS response gets slower for E7 + GP 3 and E7 + GP 4 compared with that of the lower concentrations.

The time the transmittance intensity takes to rise from 10% to 90% of the maximum intensity, after the field is turned on, is defined as the optical switching time, \(\tau_{\text{on}}\). Figure 1(b) shows \(\tau_{\text{on}}\) as a function of temperature for E7 and all E7 + GP samples, listed in the legend. This figure manifests that \(\tau_{\text{on}}\) is significantly faster for E7 + GP 1 and E7 + GP 2 and then it gets slower for the higher concentrations. Finally, \(\tau_{\text{on}}\) for E7 + GP 4 does not show any significant change as compared with pure E7. This result depicts that there exists an optimal graphene concentration, which is E7 + GP 2 (0.939 × 10\(^{-4}\) wt. %), for the faster IPS response.

The characteristic rise time for IPS mode\(^{37}\) can be described as

\[
\tau_{\text{on}} = \frac{10}{100 - \frac{\tau_{\text{on}}}{100}}
\]
\[
\tau_{\text{rise}} = \frac{\gamma_1}{\varepsilon_0 |\Delta \varepsilon| E^2 - K_{22} \frac{\pi^2}{d^2}},
\]

where \(\gamma_1\) is the rotational viscosity, \(d\) is the cell thickness, \(\Delta \varepsilon\) is the dielectric anisotropy, \(\varepsilon_0\) the is the free space permittivity, \(K_{22}\) is the twist elastic constant, and \(E\) is the applied electric field. Note that \(\tau_{\text{rise}}\) is not equal to the electro-optic response \(\tau_{\text{eo}}\). \(\tau_{\text{rise}}\) is the time the nematic director takes to rotate in IPS mode from parallel to perpendicular with respect to the IPS electrodes, as the field is turned on. However, the electro-optic response is mainly due to the director’s rotation after the field is turned on. Therefore, neglecting the backflow in the cell, one can write \(\tau_{\text{rise}} \propto \tau_{\text{eo}}\). From Eq. (1), for a constant \(d\) and \(E\), the IPS response would be faster for a reduced \(\gamma_1\) and an enhanced \(\Delta \varepsilon\).

We therefore performed experiments to study \(\gamma_1\) and \(\Delta \varepsilon\) for the LC samples. The rotational viscosity for the nematic samples was obtained by measuring the transient current induced by a DC field across a planar-aligned capacitive type cell configuration.\(^{38-40}\) When a DC field (much higher than the threshold field) is applied across a planar LC cell, the induced current \(I(t)\) through the cell shows a time response as the nematic director goes through the dynamic rotation. The current response is given by

\[I(t) = \frac{A (\Delta \varepsilon \varepsilon_0)^2 E^3}{\gamma_1 \sin^2[2\theta(t)]},\]

where \(A\) is the area of the cell, \(E\) is the electric field, and \(\theta\) is the angle the director makes with the electrodes at a given time. At \(\theta = 45^\circ\), \(I(t)\) reaches its peak, \(I_p = \frac{A (\Delta \varepsilon \varepsilon_0)^2 E^3}{\gamma_1}\) at the peak time

\[t_p = \left| \frac{\gamma_1 (-\ln(\tan \theta_o))}{\Delta \varepsilon \varepsilon_0} \right| \frac{1}{E^2},\]

where \(\theta_o\) is the pretilt angle. A DC field pulse of 1 V/\(\mu\)m with a pulse interval of 1 Hz was applied across the cell to generate \(I(t)\). Then, \(I(t)\) in the cell was detected as a function of time through a load resistor in series by a digital storage oscilloscope. The inset in Fig. 2(a) shows \(I(t)\) as a function of time for two different samples E7 and E7 + GP 2 at \(T = 30^\circ\)C. The peak current, \(I_p\), was detected from the \(I(t)\) vs. time graph to extract \(\gamma_1\) from the known values of \(E\), \(\Delta \varepsilon\), and \(A\). The measurement of \(\Delta \varepsilon\) is discussed in the next paragraph. Figure 2(a) represents \(\gamma_1\) as a function of temperature for pure E7 and all E7 + GP hybrids, listed in the legend. Clearly, E7 + GP 1 and E7 + GP 2 exhibit a significant decrease in \(\gamma_1\). Interestingly, E7 + GP 3 and E7 + GP 4 do not show any further decrease in \(\gamma_1\), verifying the existence of the optimal concentration at E7 + GP 2. Figure 2(b) shows \(\gamma_1\) (right Y axis) and \(\tau_{\text{eo}}\) (left Y axis) as a function of graphene concentration at \(T = 30^\circ\)C. Clearly, \(\Delta \varepsilon\) increases monotonically for E7 + GP 1 and E7 + GP 2, and then it starts to decrease for E7 + GP 3 and E7 + GP 4. The result shown in the bottom inset in Fig. 3 also independently exhibits the presence of the optimal concentration, E7 + GP 2, for the enhancement in \(\Delta \varepsilon\).

The nematic phase shows dielectric anisotropy, \(\Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp}\), where \(\varepsilon_{||}\) and \(\varepsilon_{\perp}\) are the dielectric components parallel and perpendicular to the nematic director, respectively. An Automatic Liquid Crystal Tester (Instec, Inc.) was used to measure the dielectric constant \(\varepsilon\) as a function of electric field at 1000 Hz for E7 and E7 + GP samples using planar-aligned capacitive type cells. Figure 3 shows a typical Fréederickz transition where \(\varepsilon\) increases as a function of electric field for E7 and E7 + GP 2 in the deep nematic phase at \(T = 30^\circ\)C (the other graphene concentrations are not shown to keep the figure less crowded). The top inset in Fig. 3 demonstrates the temperature dependence of \(\Delta \varepsilon\) for E7 and E7 + GP 2. The bottom inset in Fig. 3 shows \(\Delta \varepsilon\) as a function of graphene concentration at \(T = 30^\circ\)C. Clearly, \(\Delta \varepsilon\) increases monotonically for E7 + GP 1 and E7 + GP 2, and then it starts to decrease for E7 + GP 3 and E7 + GP 4. The result shown in the bottom inset in Fig. 3 also independently exhibits the presence of the optimal concentration, E7 + GP 2, for the enhancement in \(\Delta \varepsilon\).

Pretilt angle is the initial slant angle of the liquid crystals from the aligning substrate. For IPS LC displays, the viewing angle characteristics strongly depend on the pretilt angle, \(\theta_p\).\(^{41}\) It has been theoretically predicted and experimentally observed that the smaller the pretilt angle of the liquid crystal, the wider the viewing angle characteristics for the IPS panel.\(^{41}\) There is a research direction to optimize the pretilt angle to improve the viewing angle further for the IPS panel.\(^{42-44}\) Therefore, we have studied the effect of graphene on the pretilt angle of E7. It has been shown that one of the

![FIG. 2. (a) Rotational viscosity, \(\gamma_1\), as a function of temperature for E7 and all the E7 + GP hybrids, listed in the legend. Inset: Transient current, \(I(t)\) as a function of time for E7 and E7 + GP 2 at \(T = 30^\circ\)C. (b) \(\gamma_1\) (right Y axis) and \(\tau_{\text{eo}}\) (left Y axis) as a function of graphene concentration at \(T = 30^\circ\)C. Dotted lines are guide to the eye. Typical error bars are shown.](https://i.imgur.com/3xY.png)
most accurate methods to measure $\theta_o$ is the transient current $I(t)$ method, which has been employed to measure $\gamma_1$ in this paper. After extracting $\gamma_1$ from the peak transient current, one can use Eq. (3) to find $\theta_o$ from the peak time (see the inset in Fig. 2(a)) for E7 and all E7 + GP samples. Figure 4 depicts $\theta_o$ as a function of temperature for all the samples listed in the legend. Evidently, E7 + GP 1 and E7 + GP 2 exhibit almost a 50% decrease in $\theta_o$ in the room temperature regime. Also note that above the optimal concentration (E7 + GP 2) $\theta_o$ does not decrease anymore.

III. DISCUSSIONS

The results clearly indicate that the presence of graphene, especially at the optimal concentration (E7 + GP 2), reduces the rotational viscosity, enabling the LC to respond faster in IPS mode. One of the possible reasons for the reduction in $\gamma_1$ is that doping graphene in the LC modifies the order parameter and, in succession, alters the rotational viscosity26 of the LC + GP samples. The modification in order parameter can be explained from the dielectric data, shown in Fig. 3. An LC’s $\Delta \varepsilon$ is proportional to the scalar nematic order parameter,45 and therefore, a change in $\Delta \varepsilon$ indicates a modification in the net orientational order in the LC. In this experiment, the change in $\Delta \varepsilon$ indicates that the presence of graphene flakes changes the average orientational order parameter in the LC, and as a result, $\gamma_1$ is altered. The nematic to isotropic transition temperature for E7 + GP 2 sample was found to be 1.2 °C lower than that of pure E7—which which also indicates the change in $\gamma_1$ in the hybrid system. The other possible reason for the change in $\gamma_1$ of the hybrid samples is related to the difference of rotational velocity between the nematic LC and the dopant in a dilute suspension form.26 When an electric field, much higher that the Fréedericksz threshold field, is applied across the LC + GP hybrid, the LC molecules experience a torque, and being embedded in the nematic matrix the graphene flakes also experience a torque, rotating with the nematic director.12 This torque is related to their individual dielectric anisotropies. Their individual dielectric anisotropies with the structural aspect ratios give rise to a change in rotational viscosity of the LC + GP hybrids. In another direction, graphene flakes have been found to trap free ions in the LC.46 The presence of excess free ions can enhance $\gamma_1$ in an LC.25 Therefore, it is also possible that $\gamma_1$ is altered due to the redistribution of free ions in the LC because of graphene’s ion trapping process.

To explain the reduction in the pretilt angle for the E7 + GP hybrids, we first need to understand the anchoring mechanism of the LC molecules on graphene. It has been shown that liquid crystal molecules can stabilize themselves on the honeycomb pattern of graphene47,48 or carbon nanotubes,16 employing the $\pi-\pi$ electron stacking with a binding energy of ~2 eV. However, it is very difficult to visualize the effect of this strong interaction in a LC + GP colloidal system. We therefore obtained CVD grown monolayer graphene film on a copper foil from Graphene Supermarket, Inc. The graphene film was continuous, with irregular holes and cracks. In addition, the graphene film was polycrystalline (i.e., the presence of grains with different crystallographic orientation). A thin layer of LC was coated on top of the graphene film. The alignment of the LC on graphene film was then studied by reflected crossed polarized microscopy and the results are presented in Fig. 5. It is known that between two crossed polarizes, if the nematic director $\hat{n}$ is parallel to the polarizer (or the crossed analyzer), a dark state is achieved. A bright state with the maximum intensity appears when $\hat{n}$ is at 45° with the polarizer (or with the crossed analyzer). It is worth mentioning that the bare monolayer graphene film on copper foil appears completely dark under the reflected crossed polarized microscope. After coating a thin LC layer on the graphene film, different crystallographic graphene domains with grain boundaries are clearly visible in the microphotographs in Figs. 5(a)–5(c). Two domains, 1 and 2, are labeled in Figs. 5(a)–5(c) and their

FIG. 3. Dielectric constant, $\varepsilon$, as a function of electric field at $T = 30^\circ$C for E7 and E7 + GP 2. Top inset: dielectric anisotropy, $\Delta \varepsilon$, as a function of temperature for E7 and E7 + GP 2, listed in the legend in the main figure. Bottom inset: dielectric anisotropy, $\Delta \varepsilon$, as a function of graphene concentration at $T = 30^\circ$C. Typical error bars are shown.

FIG. 4. Pretilt angle, $\theta_o$, as a function of temperature for E7 and E7 + GP hybrids, listed in the legend. Dotted lines are guide to the eye. Typical error bars are shown.
molecules can assume three different orientations separated by 60°. Note schematically illustrated in Fig.5(e) by matching the LC’s benzene rings on the graphene-honeycomb structure. Three possible LC domains on graphene grains with different crystallographic orientation are illustrated. Graphene grain boundaries are also shown with black lines. The dark or bright states of these LC domains are demonstrated by showing the nematic director (^n, n^) orientation with respect to the polarizer and analyzer.

When some graphene flakes are preferentially attached to the substrate, they promote planar anchoring, as shown in Fig. 5, and presumably pulls the LC molecules close to the substrate due to $\pi-\pi$ stacking, reducing the average pretilt angle. We have also used a simple approach to check the presence of graphene flakes, spontaneously deposited from the LC+GP hybrid, lying face-on the substrates of the cell. We first disassembled the cell which initially contained the E7+GP 2 sample. We then blew away the E7+GP 2 sample using a dust blaster. Then we reassembled the cell and filled it with pure E7. This reassembled cell with pure E7 shows a pretilt angle of 2.2° at 30°C—which is smaller than that of the pure E7 cell (4°) and slightly higher than that of the original E7+GP 2 cell (1.8°) at 30°C. Even though the pretilt angle in the reassembled cell with pure E7 is little higher than the original cell with the suspension, the results indicate the presence of the adsorbed graphene layers on the substrates, since both the pretilt values are significantly smaller than that of the pure E7 cell.

Finally, the presence of the optimal graphene concentration may be explained from the graphene aggregation point of view. Pure E7 and E7+GP hybrids were examined under a transmitted crossed polarized microscope. E7, E7+GP 1, and E7+GP 2 revealed uniform nematic textures, with no indication of phase separation or agglomerates of graphene at any temperature. When the graphene concentration increases above 0.939 × 10⁻⁴ wt. % (i.e., above the optimal concentration E7+GP 2) in the LC, the flakes start to aggregate. Figures 6(a) and 6(b) show the microphotographs of E7+GP 2 and E7+GP 4 samples, respectively, inside 5 μm thick planar cells. Only 5 μm spacer particles are visible in

FIG. 5. (a)–(c) Microphotographs of a thin layer of LC on a CVD grown graphene film on copper foil under a crossed polarized reflected microscope at three different rotational angles, 0°, 45° and 90°, respectively. Two domains, 1 and 2 are labeled to see how their intensities change through rotation. (d) Normalized intensity as a function of angle of rotation for domains 1 and 2. (e) Schematic representation of the alignment of nematic LC molecules on graphene due to $\pi-\pi$ electron stacking. The blue ellipsoids are LCs and the black honeycomb structure is graphene surface. The LC molecules are shown in red in the ellipsoid due to electron stacking.
Fig. 6(a) for E7 + GP 2 sample. Figure 6(b) clearly shows several dark spots in addition to the 5 μm spacer particles for E7 + GP 4 sample. These dark spots are much smaller than the 5 μm spacer particles. We identify these dark spots as graphene aggregates. Three of such dark spots are highlighted using dashed circles in Fig. 6(b). Aggregated graphene flakes would not effectively interact with LC molecules through π−π stacking. Also, being embedded in the LC, the graphene flakes act as external additives, and can increase the internal friction when they are aggregated. We therefore believe that γ₁ starts to increase due to graphene aggregation above the optimal concentration, and subsequently, τon increases. For similar reasons, the changes in Δε and θ₀ are noticed above the optimal concentration.

IV. CONCLUSION

We have experimentally demonstrated that when a small quantity of monolayer graphene flakes is dispersed in E7 LC, the electro-optical IPS response gets faster. Our results indicate that there exists an optimal graphene concentration, above which the LC no longer switches faster in IPS mode. The faster IPS response is attributed to the reduction in rotational viscosity in the LC due to the presence of graphene flakes. The enhancement in dielectric anisotropy for the hybrid systems indicates an increase in the orientational order parameter. Our results indicate that the presence of graphene flakes changes the way the LC interacts with the substrates, exhibiting a significantly smaller pretilt angle. The reduction in pretilt angle is attributed to the LC–graphene interaction which promotes planar LC alignment. The reduction in rotational viscosity and pretilt angle of the LC may have technological applications in IPS mode for faster electro-optic switching and improving the viewing angle, respectively.

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