Effects of graphene on electro-optic switching and spontaneous polarization of a ferroelectric liquid crystal

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A small quantity of graphene flakes was doped in a ferroelectric liquid crystal (FLC), and the field-induced ferroelectric electro-optic switching was found to be significantly faster in the FLC + graphene hybrid than that of the pure FLC. Further studies revealed that the suspended graphene flakes enhanced the FLC’s spontaneous polarization by improving smectic-C* ordering resulting from the π–π electron stacking, and reduced rotation viscosity by trapping some of the free ions of the FLC media. These effects coherently impacted the FLC-switching phenomenon, enabling the FLC molecules to switch faster on reversing an external electric field. © 2014 AIP Publishing LLC.

Electro-optical switching phenomena of liquid crystals (LC) are a great deal of research interest for their extensive applications in optical display technology.1 Ferroelectric liquid crystals (FLC) are of particular interest in this area for their fast switching response in the chiral smectic-C* phase.2,3 In another direction, liquid crystalline platforms have been exploited very effectively over the past decade to transfer their long-range orientational order onto various nanoparticles.4–10 Interestingly, the interactions between the LCs and nanomaterials are versatile, as the nanoparticles can significantly alter many liquid crystalline properties that have practical applications. For examples, the presence of carbon nanotubes in an LC media has a favorable impact on LCs’ electro-optical switching phenomena,11,12 quantum dots modify the chiral pitch in cholesteric LCs,13 and ferroelectric nanoparticles significantly enhance the orientational order and induce nonvolatile electromechanical memory effect.10,14–16 Thus, understanding the interaction of nanoparticles with an LC and the principles governing the LC’s modified properties is an important area of fundamental and applied research.

Graphene is a crystalline allotrope of carbon with 2-dimensional properties. The carbon atoms in a graphene sheet are densely packed in a regular sp²-bonded atomic-scale hexagonal pattern. This 2-dimensional honeycomb structure of graphene makes it an interesting and important nanomaterial to study the LC—nanomaterial interactions along different directions. For examples, graphene oxide promotes vertical alignment of an LC without any surface treatment of the substrates;17 transparent graphene-conducting-layers can be used as electrodes to produce high-transmittance liquid crystal displays;18,19 and functionalized graphene can mutually self-assemble discotic liquid crystals.20 In this paper, we investigate the localized interactions at an FLC/graphene interface at the nanoscale and their macroscopic effects on the FLC. We experimentally demonstrate that when graphene flakes are dispersed in an FLC, the FLC + graphene system exhibits a faster ferroelectric switching compared to the pure FLC in the smectic-C* phase. It is also found that the flakes enhance the spontaneous polarization of the mixture due to a strong anchoring energy between the flakes and the FLC molecules. We finally show that this faster electro-optic response is a consequent effect of the increased spontaneous polarization and reduced rotational viscosity in the FLC + graphene hybrid.

Graphene flakes, obtained from Nanostructured and Amorphous Materials, Inc., contained both monolayers and multilayers of thickness ranging from 0.55 nm to 3.74 nm. The flakes were circular in shape and had an average diameter of 1.75 μm (minimum diameter = 0.5 μm and maximum diameter = 3.0 μm). The ferroelectric liquid crystal MX40636 (cooling phase sequence: Iso—97 °C—N*—82 °C—smectic-A*—76 °C—smectic-C*—10 °C crystal) was obtained from LC Vision, LLC. A small amount of graphene sample was first dispersed in toluene and mixed by a micro-homogenizer tip of 5 mm diameter at 35 000 rpm for 3 h, followed by sonication for 5 h. This process reduces the aggregation tendency of the flakes, creating a uniform mixture of toluene + graphene. The FLC was then added to the toluene + graphene mixture and shaken on a vortex mixer for 5 h at 2000 rpm followed by sonication for 5 h, allowing the FLC to dissolve completely into the solution. The toluene then was slowly evaporated at an elevated temperature, leaving a pure FLC + graphene mixture of 0.04 wt. %. Finally, the FLC + graphene sample was degassed under a vacuum for 2 h. For consistency, the pure FLC was also treated the same way, such as dissolving in toluene followed by a slow evaporation and degassing. Commercially manufactured planar LC cells (LC2–5.0) from Instec, Inc., with a 1.5° pre-tilt angle, 5 × 5 mm² indium tin oxide (ITO) coated area, and a d = 5 μm spacing were used for our experiments. Two cells were filled at temperature T > 100 °C in the isotropic phase by capillary action, one with FLC only and the other with the FLC + graphene mixture; from then on both cells always remained in the smectic-C* or higher temperature. Note that the small cell spacing tends to filter out any aggregates larger than d. Before performing any measurements, the graphene-doped FLC cell was examined using a polarizing optical microscope. The optical micrograph revealed a uniform smectic texture, like that of the pure FLC cell, indicating a...

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uniform director field. See the inset optical micrographs in Figure 1 (a) and (b) represent the textures for the pure FLC and the FLC + graphene mixture, respectively. Thus, at least on the length scales resolvable by visible light, the structure of graphene-aggregates must be small enough that they do not significantly perturb the director field due to their low concentration and uniform dispersion.

The field-induced ferroelectric switching was studied from the electro-optic response of the FLC 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 photo detector. The beam was polarized at an angle of $22.5^\circ$ with respect to the cells’ rubbing direction. The output of the detector was fed into a digital storage oscilloscope. A square wave at 0.5 Hz was applied across the cell and the change in transmittance intensity was detected as a function of time by the oscilloscope. Figure 1 represents the electro-optic response for the pure FLC and FLC + graphene cells in the smectic-C* phase for an applied peak-to-peak square wave voltage $V_{pp} = 10$ V.

Figure 1 clearly reveals that the FLC + graphene cell responses much faster than the pure FLC cell on reversing the applied voltage. Although we report the normalized intensity in Fig. 1, it is important to point out that the absolute transmittance intensity for the hybrid sample was reduced by 40% due to the graphene flakes’ optical absorption in the LC media. The time of the transmittance intensity takes to go from 10% to 90% of the maximum intensity is defined as the optical switching time, $\tau_{os}$. This electro-optic switching experiment was repeated applying different voltages, and the response time, $\tau_{os}$, is plotted as a function of $V_{pp}$ in Figure 2 for both the samples. The initial bump in the transmission curve in Fig. 1 is taken into account to extract $\tau_{os}$. It is clear from Fig. 2 that response time for the FLC + graphene mixture is faster than the pure one for all the applied fields.

The optical switching time, $\tau_{os}$ is proportional to the ferroelectric characteristic response time $\tau = \frac{Ps}{E}$, where $\gamma$ is the rotation viscosity, $P_s$ is the spontaneous polarization, and $E$ is the applied electric field. This equation suggests that an increase in $P_s$ and a decrease in $\gamma$ would give a faster response for a constant $E$. We therefore carried out experiments to determine $P_s$ and $\gamma$ for the pure FLC and FLC + graphene mixture.

A triangular wave at 10 Hz was applied across the cells by a commercial Automatic Liquid Crystal Tester (ALCTE, Instec, Inc.) to study $P_s$, $\gamma$, and free ion concentration, $n_i$, using the polarization reversal method. Figure 3 depicts the polarization, $P$, of the pure FLC and FLC + graphene samples as a function of applied triangular voltage $V_{pp}$. The polarization of an FLC initially increases with an increasing applied voltage, finally saturating above a threshold voltage. The saturated polarization is the spontaneous polarization, $P_s$. The inset of Fig. 3 shows the residual current bump...
Figure 3 shows that the FLC + graphene sample exhibit an enhanced $P_s$ compare to the pure FLC. Also, the polarization of the mixture saturates at a smaller voltage than that of the pure FLC. This result indicates a structural modification, especially in the order parameter, of the smectic-C* phase at the nanoscale due to the incorporation of graphene flakes. The higher value of $P_s$ manifests an improved order in the smectic-C* phase.

It has been shown that liquid crystal molecules can stabilize themselves on the honeycomb pattern of carbon nanotubes or graphene due to a strong anchoring of $\pi-\pi$ electron stacking with a binding energy of $-2\,\text{eV}$. Figure 4(a) schematically represents a natural smectic-C phase. Figure 4(b) schematically shows that a graphene surface can enhance smectic-C ordering by stabilizing both the positional order and the tilted orientational order of the FLC molecules, relying on the $\pi-\pi$ electron stacking between the LC’s benzene rings and the graphene-honeycomb structure. (Note that we use a generic molecular structure (in red) of a liquid crystal to show a smectic-C ordering on a graphene flake; the actual molecular structure of FLC MX40636 is not used in Fig. 4(b).) From this strong interaction, the FLC layers at the graphene/LC interface can form an enhanced smectic-C domain (ESD). The ESDs can be formed on both sides of a graphene flake. One can visualize the suspended graphene flakes in the FLC media as local anchoring fields that form the ESDs which collectively amplify the positional order and the tilted orientational order in the matrix. This enhancement in smectic-C ordering can increase the overall spontaneous polarization in the FLC + graphene mixture, as reflected in Fig. 3. For simplicity, if we assume that volume fraction of the FLC that exhibits the enhancement in spontaneous polarization is $(P_s^{\text{FLC}+\text{graphene}} - P_s^{\text{FLC}})/P_s^{\text{FLC}}$ then the average characteristic extrapolation length, $\xi$, would be $\sim 50\,\text{nm}$—the distance over which the graphene surface transmits the enhanced order into the bulk LC. Figure 4(c) schematically represents the graphene induced ESDs and their propagation into the LC media. The actual size and shape of the ESDs would depend on the diameter and the number of layers of the graphene flakes.

Figure 5 represents $P_s$ for the pure FLC and FLC + graphene hybrid as a function of reduced temperature $\Delta T_{AC}$ ($\Delta T_{AC} = T - T_{AC}$, where $T_{AC}$ is the smectic-C to smectic-A transition temperature). This critical behavior also indicates that the spontaneous polarization increases when graphene flakes are incorporated into the FLC media. It is important to mention here that $T_{AC}$ for the FLC + graphene mixture is 1.5°C more than that of the pure FLC—which, perhaps, is another indication of smectic-C-stabilization in the hybrid system.

Rotational viscosity, $\gamma$ depends on the detailed molecular constituents, structure, intermolecular association, temperature, and the presence of free ions in the media. We
obtained $\gamma$ using the equation, $\gamma = \frac{APV_m}{\Delta T_{AC}}$, where $I_m$ is the peak value of the residual current bump and $V_m$ is the applied voltage where $I_m$ occurs. Both these parameters are obtained from the inset of Fig. 3. Figure 6 represents $\gamma$ as a function of $\Delta T_{AC}$ for the pure FLC and FLC + graphene samples. The result depicts a dramatic decrease in $\gamma$ for the FLC + graphene mixture. To explain this behavior of the hybrid system, we obtained the free ion concentration, $n_i$, for both the samples and plotted them in the inset of Fig. 6. We determined the free ion concentration from the ion-bump occurred after the polarization reversal bump, as shown in the inset of Fig. 3 (note that ion-transport is a slower process than polarization reversal process). Interestingly and coherently, the result indicates a significant reduction of free ions in the hybrid sample. Note that all measurements were carried out with the same type of commercially available cells from Instec, Inc. Therefore, if there are any ions generated from the cell’s polymer alignment layers or/and the surrounding glue, they must be consistent in both the cells, and thus, the observed change in $n_i$ is only due to the presence of the graphene flakes. We attribute the phenomenon of reduction of free ions to the ion-trapping process by the dispersed graphene sheets. It has been recently shown that for a finite graphene sheet (diameter < 1 μm) there is a nonzero electrostatic field near the surface. The electrostatic field decays only slowly with increasing size and is always non-negligible near edges. In our experiments, the diameter of the graphene flakes has a range from 0.5 μm to 3.0 μm. Therefore, the electrostatic fields from these finite graphene sheets (mainly from those are <1 μm) can capture some of the mobile ions in the LC media. The larger sheets can also trap some free ions on their edges due to the presence of the graphene flakes. These findings are important for nanoscale manipulation of nanomaterials via LCs and orientation control of LC molecules using their interactions with nanomaterials.

To summarize, we have experimentally demonstrated that when a small quantity of graphene flakes is dispersed in an FLC, the flakes facilitate a faster ferroelectric switching response by enhancing the spontaneous polarization and reducing the rotational viscosity. The increase in spontaneous polarization is attributed to the π-π electron stacking between the LCs’ benzene rings and graphene-honeycomb structure, as this interaction can enhance smectic-C ordering. The decrease in rotational viscosity is ascribed to the reduction of free ions in the hybrid media as a result of the ion-trapping process by the flakes. These findings are important for nanoscale manipulation of nanomaterials via LCs and orientation control of LC molecules using their interactions with nanomaterials.

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