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Local deformation of liquid crystal director induced by translational motion of carbon nanotubes under in-plane field

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The translational motion of carbon nanotubes (CNTs) dispersed in a nematic liquid crystal (NLC) has been observed in the fabricated CNT-doped homogeneously aligned NLC cells by applying in-plane electric field. The long axis of CNTs was aligned along the LC director in the initial state. However, the CNTs above a critical ac electric field, due to their net charge, overcame the LC director field to generate translational motion and as a consequence distorted the local LC directors to have light leakage. We observed the motional textures in the form of vertical stripes in the local area between electrodes, which were explained by a translational motion of CNTs above critical ac fields. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2355535]

I. INTRODUCTION

Carbon nanotubes (CNTs) have been studied extensively due to their functional performances and technological importance. One of the bottleneck technologies is to align CNTs in a desired way. Recently, it was reported that the order in the CNT films using nematic liquid crystals (LCs) with a grooved surface or with an external field on a porous membrane substrate can be controlled, where the long axes of CNTs are known to align parallel to the nematic LC director **n**.[1] The conductivity measurements also demonstrated the existence of an electrically controlled reorientation of CNTs from the planar (homeotropic) to homeotropic (planar) in nematic LC using a vertical field.[2,3] It was also reported that the minute addition of CNTs dispersed in a twisted nematic LC affects the electro-optical properties of the cell when dc or ac voltage is applied.[4–10]

Besides the extensive studies on the effects of CNT on LC devices, there are few reports on the distortion of LC directors caused by the translational motion of CNTs. The CNTs at concentrations less than 0.01 wt % dispersed in LC medium were aligned parallel to the LC director in a LC film, either homogenously or homeotropically for cells with a cell gap of 60 μm, without disturbing the orientational ordering of the LC.[11,12] However, when a critical vertical ac field was applied, the CNTs experienced an electrical force and began to move, generating LC textures of white spots in a dark background with four-lobe shapes under a vertical ac electric field. In the homeotropic LC cell using a LC with positive dielectric anisotropy, the LC orientation is stabilized more by the vertical electric field and thus the cell should show a perfect dark state under crossed polarizers with increasing voltage if there is no source causing the deformation of the LC orientation. This suggests that the local deformation of the LC orientation can occur as a result of the existence of the CNTs.

This paper reports that the CNTs can undergo in-plane switching in a homogenously aligned nematic LC using an in-plane electric field. Moreover, when a critical in-plane ac field is applied, the CNTs begin translational motion between the electrodes and along the electrodes perturbing the LC director field.

II. CELL STRUCTURE AND SWITCHING PRINCIPLE OF THE CNT-DOPED IN-PLANE SWITCHING CELL

Figure 1 shows the cell structure of the CNT-doped LC cell, where the LC molecules are homogeneously aligned on the substrate. A small quantity of the single-walled CNTs (SWCNTs), 5×10^{-4} wt %, was doped in LC medium. The HiPCO SWCNTs (Carbon Nanotechnology Inc.) were used after nitric acid treatment to remove catalysts. The diameter of SWCNTs is less than 3 nm with a bundle size of a few tens of nanometer. Interdigitated opaque electrodes made from aluminum were placed on the bottom substrate only with an electrode width of 10 μm and a distance of 30 μm between electrodes, where both electrodes served as the

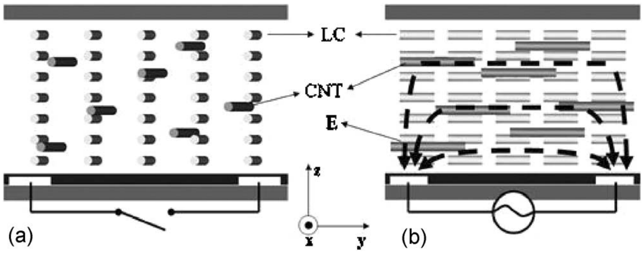

FIG. 1. Schematic diagram of the cell structure of the CNT-doped nematic LC cell in the off (a) and on (b) state.

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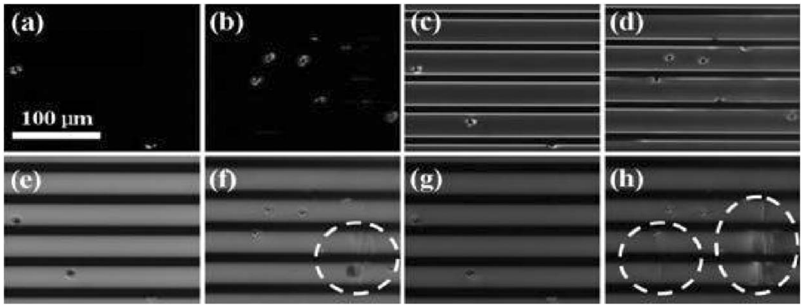

FIG. 2. Optical microphotographs of the cells with the LC only and SWCNT-doped LC cell, when the applied voltages were 0 V_{rms} [(a) and (b)], 10 V_{rms} [(c) and (d)], 60 V_{rms} [(e) and (f)], and 120 V_{rms} [(g) and (h)], respectively.

source and common electrodes. For a cell fabrication, a homogenous alignment layer (AL-16139 from Japan Synthetic Rubber Co.) was first spin coated to a thickness of 800 Å on an electrode-patterned glass substrate. A rubbing process was then performed on the substrate to align the nematic LC. The same alignment layer was coated on another glass substrate without an electrode, and the similar rubbing process was then performed. The cell was assembled to give a cell gap (d) of 9 μm, where the plastic balls were used to maintain the cell gap. Finally, the superfluorinated LC mixtures purchased from Merck Co. (dielectric anisotropy $\Delta\varepsilon = +7.4$ at 1 kHz, birefringence $\Delta n = 0.088$ at $\lambda = 589$ nm, flow viscosity $\eta = 18$ mm^2/s, at 20 °C) was filled at room temperature by the capillary action. A LC cell without the SWCNTs was also fabricated with a cell gap of 8.8 μm. When a bias voltage is applied, a horizontal field (E_y) was generated mainly between electrodes due to the electrode structure. Therefore, if the LC directors make some angle with respect to the horizontal field, the LC molecules will experience some twist deformation, as indicated in Fig. 1.

A polarizer and analyzer crossed with each other were attached to one of the transmission axes coincident with the LC director. Considering the light transmittance in this cell, the normalized transmittance is described as follows:[13]

$$T/T_o = \sin^2 2\psi(V) \sin^2(\pi d \Delta n_{\text{eff}}(V)/\lambda),$$

where ψ is a voltage-dependent angle between the LC director and the crossed polarizer axes, and $d\Delta n_{\text{eff}}$ is also a voltage-dependent effective cell retardation value.

III. OBSERVATION OF LC TEXTURES UNDER IN-PLANE ELECTRIC FIELD

The fabricated test cells were observed using optical polarizing microscopy (Nikon DXM1200) by applying a dc and sine wave voltage of 60 Hz. The voltage-dependent textures of the cell with and without SWCNTs were compared. Figure 2 shows optical microphotographs as a function of the applied voltage for both cells. In the cell, the LC director was aligned to maintain 80° with respect to E_y. Without a bias voltage the optic axis of the LC director coincided with one of the crossed polarizers ($\psi = 0°$). Therefore, the cells appeared black. However, several spots appeared in the dark state, which originated from the deformation of the LC director around the spacers [see Figs. 2(a) and 2(b)]. Other than these spots related to the spacers, the cell maintained a complete dark state without light leakage even in the presence of SWCNTs. This suggests that the long axis of SWCNTs was aligned parallel to the LC director **n**, which is in good agreement with the previous reports.[1–3,10,11] By increasing ac voltage up to 10 V_{rms}, the LC director was rotated in plane with increasing ψ due to a dielectric torque between the LC and field. Hence, transmittance began to occur, continuously. The twist deformation mainly occurred with the most twisted angle in the midlayer, because the LCs at both surfaces of electrodes were strongly anchored. Interestingly, there was no difference in transmittance between the pure LC and the SWCNT-doped LC cells, as shown in Figs. 2(c) and 2(d). This confirms that the SWCNTs may also rotate along with the LC directors. Otherwise, there should be a difference in luminance between the areas in the SWCNT-doped LC cell because the unrotated SWCNTs generate the deformation of LC directors. Previous studies have reported that for fields larger than about 1.8 V/μm, the SWCNTs are oriented parallel to the field, thereby overcoming the orientational influence of the grooved surface.[1] This suggests that the orientation of the SWCNTs in the plane can be controlled at a much lower critical field with the assistance of the twist deformation of the LC layers. The critical field that initiates CNT motion may depend on the net charge and length of the SWCNTs and the viscosity of the LC medium.

Further increases in the ac voltage to 60 V_{rms} and then to 120 V_{rms} resulted in more LC layers trying to orient parallel to the horizontal electric field, i.e., perpendicular to the electrode direction. In the LC cell, the transmittance changes only in relation to the variation in $\sin^2 2\psi(V) \sin^2(\pi d \Delta n_{\text{eff}}/\lambda)$, which is time independent, as shown in Figs. 2(e) and 2(g). However, in the SWCNT-doped LC cell, the transmittance between the electrodes in local areas began changing at 60 V_{rms} in the form of vertical stripes (see circles). Furthermore, the width and size of vertical stripes were not uniform and fluctuated with time and at higher voltage, the number of stripes are increasing in a direction parallel to the horizontal field, as shown in Fig. 2(h), and in some cases, the vertical stripes moved to and fro between the electrodes. This strongly suggests that the motion of stripes appearing in the SWCNT-doped LC cell is related to the presence of the CNTs. The nonuniformity in stripe width might have originated from the various length distributions of the SWCNTs.

In order to understand the motion of SWCNTs along a horizontal ac field, particularly without an accompanying twist deformation of LC layers, cells were fabricated, where the rubbing direction was perpendicular to the electrode direction ($\mathbf{E}_y \| \mathbf{n}$). In the pure LC cell, the LC layers did not

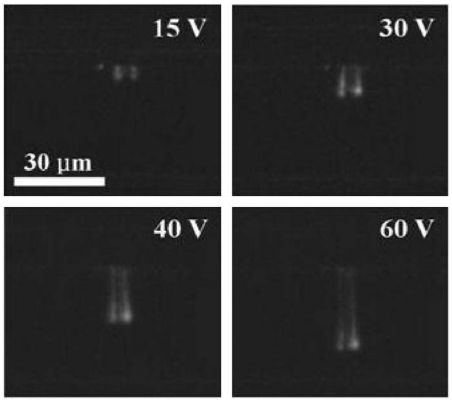

FIG. 3. Optical microphotographs of the SWCNT-doped LC cell describing the generation of two vertical stripes with increasing voltage.

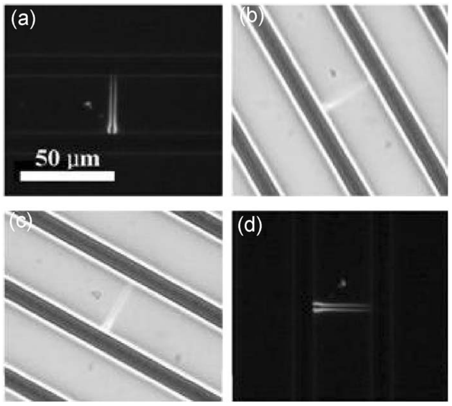

FIG. 4. Optical microphotographs of the SWCNT-doped LC cell at 120 V_{rms} showing that the upper texture translates along the electrode direction between the electrodes while the lower texture jumps over the electrode as a function of time: (a) 0 ms, (b) 33 ms, (c) 132 ms, and (d) 396 ms.

experience twist deformation with the bias voltage, i.e., $\psi = 0$ such that the cell remained dark up to an applied voltage of 120 V_{rms}, as was expected. The CNT-doped cell also showed a clear dark state at the initial state. On the other hand, when the applied voltage was 15 V_{rms} (0.5 V/μm near $z=0$), the light transmittance began to occur in patterns of two short vertical stripes with a dark line between them, as shown in Fig. 3. Interestingly, one end of the stripes was initially anchored near the electrodes. The height of the vertical stripes then increased with increasing applied voltage. The height of the stripe was saturated at approximately 60 V_{rms} (2 V/μm near $z=0$), outreaching the size of the electrode distance. Another cell with an electrode distance of 10 μm was tested. Again the height of the stripe was extended to 10 μm. The height of the stripes was attributed to a distance of their motion and is not related to the length of the CNTs, which is much shorter than the electrode distances of 10 and 30 μm. Once the stripe reached a certain size, a fast translational motion occurred along the field direction between electrodes.

Similar to the first cell, the number of textures increased with increasing voltage over the whole area. This is similar to the behavior observed in the CNT-doped twisted nematic cell where the wormlike LC textures were generated uniformly over the whole area by the CNT at high field.[10] In Fig. 4, the time evolution of these textures showed that the stripes moved to and fro between the electrodes and along the electrode direction (their moving speed increased with increasing voltage) and a few of them jumped over the electrodes. These motions were not observed under the dc field. Furthermore, we noticed that the widths of the white lines had various distributions, which may be related to the various bundle sizes of the SWCNTs. These patterns are different from those generated in an electrolytic mode.[14]

Some studies have reported that SWCNTs were attracted to the microelectrode array by an induced dipole moment under ac electric field[15] and nanowires in suspension[16] can be driven to align parallel to the electric field but accelerate along the field gradient using ac electric field at 1 MHz. In their studies, the nanorods were suspended in an isotropic solvent so that the textures generated in this report were not observed. Furthermore, the translational motion between the electrodes was not observed, which might be due to the high frequency (megahertz) ac field applied compared with the frequency (60 Hz) used in these experiments.

In order to feature the LC molecular orientation in the stripes, the cell under the crossed polarizers was rotated up to 90° azimuthally. Figure 5(a) shows one typical stripe at 120 V_{rms} at an azimuthal angle of 0°. As clearly indicated, in the SWCNT-doped cell, two white lines appeared with the dark line in between them.[17] The observed textures in the region showed a difference in transmittance with the other areas at every angle, and the white lines never became dark textures, as shown in Figs. 5(b)–5(d). If the LC directors in the white lines orient in one direction, e.g., 45° with respect to the electrode direction, the white lines should show a dark texture when the cell is rotated by 45°. Yet, this dark line generated by the coincident LC directors with one of the transmission axes of the crossed polarizer became obscured by the time-averaged transmittance, because the transmittance is proportional to $\sin^2(2\psi)$ and ψ is a function of time.

In order to understand the generation of such textures, 15 V_{rms} with 1 Hz was applied. The results show that the texture was generated at one electrode and reached another electrode in a positive cycle. The texture then moved back to

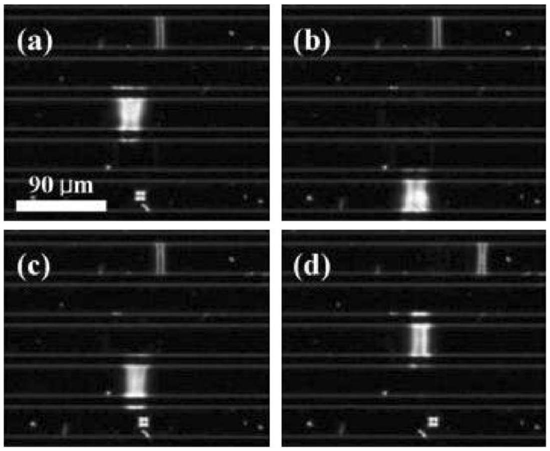

FIG. 5. Optical microphotographs of the SWCNT-doped LC cell at 120 V_{rms} as a function of the angles between the crossed polarizers and the rubbing direction parallel to the in-plane field direction: (a) 0°, (b) 30°, (c) 60°, and (d) 90°.

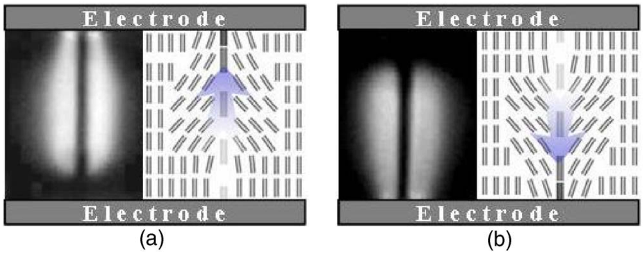

FIG. 6. Optical microphotographs and LC orientation of the SWCNT-doped LC cell at 15 V_{rms} with 1 Hz during (a) positive and (b) negative cycles.

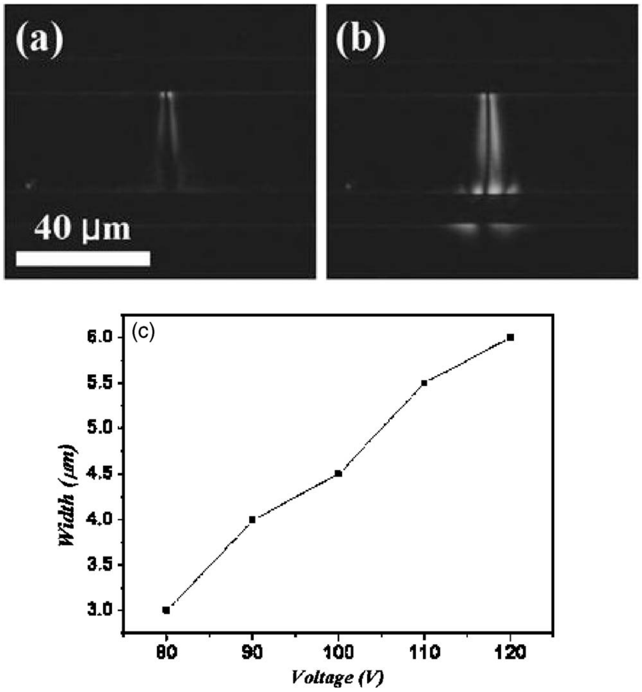

FIG. 7. Optical microphotographs of the SWCNT-doped LC cell showing an increase in the linewidth of the vertical strips at different voltages [(a) 60 V_{rms} and (b) 120 V_{rms}]. (c) Line width of the vertical strips as a function of the applied voltage.

the original position in negative cycle, as shown in Fig. 6. During the positive cycle, the SWCNT moved from bottom electrode to the top electrode, and thus the deformation of the LC directors was generated along the moving direction symmetrically at both sides. During the negative cycle, the SWCNT moved back to the original position, deforming the LC orientation in a reverse way. This clearly shows that at a sufficiently high electric field at 60 Hz, SWCNTs moved back and forth between electrodes, deforming the orientation of the LC directors at the same frequency as the applied one. Consequently, ψ becomes a function of time, which means that there was no condition at which the two white lines showed a dark state. As will be discussed later, the CNTs can hold a net charge from a permanent dipole moment of CNTs, and thus, translational motion is generated above critical ac field by overcoming the LC director field locally. This is in good contrast with LC molecules with induced dipole moment under field. If the medium has only induced dipole moment, only orientational motion along the field direction occurs instead of translational motion under ac electric field.

It was also observed that the width of a vertical stripe increased with increasing applied voltage, after the stripe height reaches the electrode distance, as shown in Fig. 7. The linewidth is strongly correlated to the deformation of LC directors, increasing almost linearly from 3 to 6 μm with voltages from 60 to 120 V_{rms}. This indicates that once the CNTs translate to and fro between electrodes, the amplitude along electrode direction (x) could be increased with increasing voltage due to inhomogeneous electrical force originated from field gradient so that the deformation region of the LC directors increases along electrode direction. Finally, the textures were observed as a function of the SWCNT concentrations and temperature. It was found that the number of stripe textures appearing at the same field intensity increased with increasing concentration, as shown in Fig. 8, and these textures were not observed at temperatures above the clearing point of the nematic LC. This confirms that the textures could be observed only under the distortion of the birefringent medium.

A schematic modeling was developed to explain the origin of the translational motion of the SWCNTs dispersed in a LC medium. In this simplified model, it was assumed that the CNT is a rigid rod with a charge interacting with the LC molecule. This rod was placed in an inhomogeneous external field in an in-plane switching device, i.e., $\mathbf{E}_{\text{ext}}(y,z)=(E_y\mathbf{j}+E_z\mathbf{k})\sin\omega t$ in Fig. 1. In our dc experiment, CNTs moved to one electrode instantaneously without revealing the persistent dynamical motion of patterns, unlike the one in ac field. If the CNT has an induced dipole moment but no permanent dipole moment under an electric field, only the reorientation of the CNT would occur along the field direction, similar to LC molecule, as commented above. Therefore, this translational motion under an ac field is possible due to alternating electrical force F $(=qE_{\text{ext}}=qE_o\sin\omega t)$ only when the CNT rod possesses a net excess charge q.

According to the previous reports[10,18,19] on density functional calculations within local density approximation, the binding nature between the LC and CNT is a hydrogen-bonding rather than a simple van der Waals interaction due to the charge transfer from LC molecule to the CNT. As a result, the CNT has a net charge and the presence of net charges in the CNT can also trap ions that are present in LC cells. This strong anchoring induces a self-alignment of the CNT molecules in a LC medium. This also generates a permanent dipole moment in the CNT which originates from the asymmetric LC molecular anchoring on the CNT surface.

From experimental observations and modeling, it was realized that the CNT had a net charge. Further questions remain on the motion of the CNTs such as (i) why one end of the two stripes started at any electrode after applying a criti-

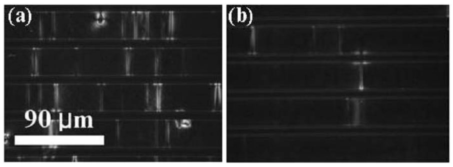

FIG. 8. The number of stripes at two different concentrations: (a) 5×10^{-4} wt % and (b) 5×10^{-5} wt %.

cal ac field and (ii) why some CNTs moved along the electrode direction and some jumped over the electrodes, after the height of stripes reached the electrode interval. When the field was applied, the CNTs were attracted to the nearby electrodes by electrical force as observed previously.[15] If the applied voltage has low frequency such as 1 Hz, the CNTs will experience repulsive and attractive interactions alternatively as a result of the electrodes. Hence, they will be driven from one electrode to another electrode. However, with increasing frequency such as 60 Hz, the repulsive and attractive forces affecting CNTs from electrodes are not the same as each other and further change so quickly that the translational motion of the CNTs starts at one electrode but cannot reach the opposite electrode just after applying a critical field $\mathbf{E}_c$ at which the motion of the SWCNTs is generated. Nonetheless, with increasing voltage, the CNTs experience a stronger force so that translational motion becomes larger, finally reaching the opposite electrode. Besides, we find that the intensity of $\mathbf{E}_c$ decreases with decreasing frequency of the applied voltage.[20] The $\mathbf{E}_c$ depends on the charge to mass ratio of the CNTs because the acceleration of the CNT is proportional to $E_{\text{ext}}q/m$, which explains clearly why all the CNTs do not exhibit the same $\mathbf{E}_c$.

Now, an explanation of the second question is as follows. This is because, in our device, the field is not uniform along the vertical distance of the cell since the electrodes exist only on the bottom substrate and some CNTs may not be in a straight form. Therefore, a repulsive force exists once the CNT reaches the opposite electrode as a result of an attractive interaction. However, this repulsive force cannot be precisely in the horizontal field (y) direction, i.e., an electrical force can exist along the x direction, resulting in some of the CNTs moving along the electrodes. Besides, some can be accelerated enough to jump over the electrode depending on the ratio of q/m at strong enough electric field, because the CNTs are driven from one electrode to another electrode. Nevertheless, an exact calculation of $\mathbf{E}_c$ and the field intensity for the CNTs to jump over the electrodes need to be clarified further.

IV. SUMMARY

In this study, a CNT-doped nematic LC cell driven by an in-plane field was fabricated. The CNTs were well aligned with the LC director at the early stage. When a critical ac field was applied, the CNTs began translational motion between the electrodes as a result of electrophoretic motion and with further increases in voltage, some CNTs experience a translational motion along the electrodes and jumped over the electrodes. The motion of the CNTs caused the deformation of the LC director field near the CNTs, which created the LC textures observed under optical polarizing microscopy. This study demonstrates that the orientation of the CNTs dispersed in a nematic LC medium can be controlled in the plane, as well as in three dimensions, and further local disturbances of the LC cell retardation are possible as a result of the motion of the CNTs. More detailed works on frequency-dependent CNT motion and the correlation between the LC textures and CNT size are currently underway.

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