Homeotropic liquid crystal device employing vertically aligned carbon nanotube arrays as the alignment agent

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Vertically aligned carbon nanotube (VA-CNT) arrays were grown on several chromium (Cr)-coated glass substrates using a plasma-enhanced chemical vapor deposition system. The CNTs were 2 μm long and had a site density of 2 × 10^9 cm⁻² on the surfaces. Two VA-CNT slides on Cr glass substrates were put together to design a homeotropic electro-optic liquid crystal (LC) device. A negative dielectric anisotropic LC was used in the device. The π-π stacking interaction between the LC and the VA-CNTs allows the LC material to align homeotropically in the cell. When an external electric field was applied using the transparent conducting Cr layers, the LC achieves a planar orientation above a threshold field. These results successfully demonstrate the optical, electro-optical operations, and the field-induced dynamic response of a homeotropic LC device employing the VA-CNT arrays as the homeotropic-alignment agent. This study significantly advances the range and understanding of nanostructured surfaces that provide vertical alignment of LCs.

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I. INTRODUCTION

In vertical-alignment (VA) liquid crystal (LC) cells (also called homeotropic LC cells), the LC material is initially aligned perpendicular to the substrates, and the application of an electric field perpendicular to the substrates can reorient the LC parallel to the substrate. This operation requires the LC material to be negative dielectric anisotropic so that it can align perpendicular to the electric field. These VA liquid crystal displays (LCDs) have many advantages compared to the traditional planar-nematic displays, such as a deeper black background, a higher on-axis contrast ratio, a rubbing-free process, a wider viewing angle, and simultaneous usability of both the background and the viewing area.

Conventionally, polyimide (PI) layers are used as the vertical-alignment agent in standard VA-LCDs [3], where the LC molecules align with the vertical part of the alkyl side chains of the PI layers. Consequently, the nematic phase achieves a homeotropic director profile inside the device [4]. However, these organic PI alignment layers have some disadvantages. For example, the PI layers are responsive to UV light and high temperature [5], and the alignment characteristics are affected when the PI-based LC devices are exposed to UV light and high temperature [5,6]. Thus, various inorganic alignment agents have been utilized recently in electro-optic LC devices. For example, planar alignment of LC was achieved using graphene [7–9], hexagonal boron nitride [10–12], and tungsten diselenide [13]; vertical alignment of LC was achieved using nanoporous anodic aluminum oxide films [14,15], ZnO nanorod and nanowire arrays [6,16,17], a pillarlike structure with 2–3-μm pitch [18], and SiO₂ films [19]. Photoaligning films are also very robust and possess excellent vertical-aligning properties [20]. Therefore, studying and understanding the alignment phenomena of the LC on different nanostructured substrates is an important avenue in fundamental research and may have potential applications in designing novel LC devices. In this work, we have studied the LC alignment on an inorganic nanostructured surface, vertically aligned carbon nanotube (VA-CNT) arrays, and used them as the alignment agent to design an electro-optic homeotropic LC device.

II. EXPERIMENTS, RESULTS, AND DISCUSSION

In this section, we present (A) the fabrication of the VA-CNT arrays-based homeotropic LC cell, (B) the electro-optical effect of the LC in the cell, and (C) the dynamic electro-optic switching response of the cell.

A. Fabrication of the homeotropic electro-optic LC cell employing the VA-CNT arrays

A plasma-enhanced chemical vapor deposition (PECVD) system at the facilities at NanoLab, Inc. [21] (Waltham, Massachusetts, USA) was commercially employed to grow VA-CNT arrays on chromium (Cr) coated glass substrates. For growing the VA-CNT arrays, the glass substrates were first coated with a Cr adhesion layer (2 nm) and then overcoated with nickel nanoparticles. In the PECVD system, the CNTs grow vertically from the substrate surface, and the CNTs are freestanding. The CNT length is related to the processing time, and the diameter depends primarily on the nickel particle size. The PECVD grown CNTs had multilayer graphitic sidewalls and a hollow core. Each CNT tip was capped with a nickel nanoparticle. The PECVD system was tuned to produce the VA-CNT arrays with a CNT site density of 2 × 10⁹ cm⁻², length 1.4–2 μm, and diameter...
energy associated with benzene rings on the CNT-honeycomb surface. The anchoring interaction is illustrated by matching the LC's interaction: anchoring of an LC molecule on the CNT surface due to \( \pi-\pi \) electron stacking. The yellow ellipsoid is a generic LC molecule, and the black cylindrical honeycomb structure is a CNT surface. A schematic representation of a homeotropic LC device employing VA-CNT arrays. Pictures of the VA-CNT arrays-based homeotropic LC cell sandwiched between two crossed polarizers with a backlight: (e) voltage off state, (f) voltage on \((V = 25\, \text{V})\) state.

In the present work, this \( \pi-\pi \) electron stacking interaction is the fundamental principle of our VA-CNT arrays-based homeotropic LC cell, where the VA-CNT arrays direct the LC alignment in the vertical direction in the cell.

In our experiment, we put together two VA-CNT slides to make a cell with an average cell gap, \( d = 9\, \mu m \). The cell was filled with a negative anisotropic LC material BYVA-01 (Instec, Inc.), which has a transition temperature \( T_{\text{NI}} = 92\, ^\circ\text{C} \), dielectric anisotropy \( \Delta \varepsilon = -4.9 \), and birefringence \( \Delta n = 0.092 \). The nematic LC director aligns vertically along the CNT-long axis at the two VA-CNT slides due to the \( \pi-\pi \) stacking interaction, and then the entire cell achieves homeotropic alignment due to the nematic correlation from one slide to the other, as schematically shown in Fig. 1(d).

It was shown that thin Cr films \((2–10\, \text{nm})\) are highly transparent over the full wavelength range, still maintaining high electrical conductivity [35]. Therefore, Cr films \((2–10\, \text{nm})\) can function as high-quality transparent electrodes [35]. In our PECVD method, a 2-nm Cr adhesion layer on each glass slide was used for the growth of the VA-CNT arrays. These Cr layers were employed as the transparent electrodes in the VA-CNT arrays-based homeotropic LC cell, and therefore, no additional indium tin oxide (ITO) electrodes were needed.

To realize the electro-optical functionality of this cell, it was first sandwiched between two crossed polarizers with a backlight, and the picture of the entire cell is shown in Fig. 1(e). The black region in the dotted rectangle shows the homeotropic alignment of the LC inside the cell. Some regions outside the dotted rectangle show bright texture—these are the areas where Mylar spacer sheets were used to maintain an average cell gap, \( d = 9\, \mu m \). An AC voltage \( V = 25\, \text{V} \) \((f = 1000\, \text{Hz})\) was then applied using the transparent Cr electrodes, and the region in the dotted rectangle was

[FIG. 1. (a) An SEM image of a top view of VA-CNT arrays. (b) An SEM image of a side view of VA-CNT arrays. The dashed line shows the vertical direction, and the solid line shows the average deviation of the CNTs from the vertical. (c) Schematic illustrations of LC-CNT interaction: anchoring of an LC molecule on the CNT surface due to \( \pi-\pi \) electron stacking. The yellow ellipsoid is a generic LC molecule, and the black cylindrical honeycomb structure is a CNT surface. A schematic representation of a homeotropic LC device employing VA-CNT arrays. Pictures of the VA-CNT arrays-based homeotropic LC cell sandwiched between two crossed polarizers with a backlight: (e) voltage off state, (f) voltage on \((V = 25\, \text{V})\) state.]
found to turn bright, as shown in Fig. 1(f), which indicates the reorientation mechanism of the LC from homeotropic to planar state on the application of the voltage. A little variation in brightness and color in the dotted rectangle in Fig. 1(f) indicates a slight variation in the cell gap.

B. Electro-optical effect of LC in the VA-CNT arrays-based homeotropic LC cell

Now that we have established that the VA-CNT arrays-based homeotropic LC cell exhibits the required electro-optical effect, we have carried out the voltage-dependent transmittance experiment [1]. This experiment was conducted using an optical setup where the cell was mounted on a rotational stage between two crossed polarizers. A 5-mW He-Ne laser beam of wavelength 633 nm was sent through the polarizer, the VA-CNT arrays-based homeotropic LC cell, the crossed analyzer, and into a photodetector, which was fed into a DC voltmeter to measure the transmitted intensity.

An AC voltage $V = 40 \text{ V}$ ($f = 1000 \text{ Hz}$) was first applied across the cell to change the LC to planar orientation, and then the cell was rotated using the rotational stage to receive the maximum transmitted intensity at the DC voltmeter. This was done to ensure that when the LC achieved planar orientation on the application of the voltage, the nematic director $\hat{n}$ in the cell was oriented at $45^\circ$ with respect to the crossed polarizers. Then the AC voltage was turned off. Next, the applied AC voltage ($f = 1000 \text{ Hz}$) across the cell was gradually ramped up from 0 to 40 V, and the change in the transmitted intensity was recorded from the DC voltmeter. The same experiment was also carried out under the crossed polarized microscope with a white light source, and several micrographs of the VA-CNT arrays-based homeotropic LC cell at different applied voltages were taken. When the applied voltage across the cell exceeds the Fréedericksz threshold value, the director $\hat{n}$ rotates from the initial homeotropic orientation to planar orientation, and the LC’s effective birefringence, $\langle \Delta n \rangle$ changes as a function of the applied voltage. In our optical setup, the director $\hat{n}$ was oriented at $45^\circ$ with the crossed polarizers at high voltage. Therefore, if $I_0$ is the intensity of the plane-polarized light incident on the VA-CNT arrays-based homeotropic cell, then the transmitted optical intensity $I$ at the exit of the analyzer shows an oscillatory behavior according to the equation [1,36]

$$I = I_0 \sin^2 \left( \frac{\pi d \langle \Delta n \rangle}{\lambda} \right),$$

where $\lambda$ is the wavelength of the laser beam and $d$ is the cell gap.

Figure 2 represents the electro-optical effect of the VA-CNT arrays-based homeotropic LC cell. Figure 2(a) exhibits the normalized transmittance (i.e., normalized $I/I_0$) of negative anisotropic LC-BYVA01 and positive anisotropic LC E7 in the VA-CNT arrays-based homeotropic cell as a function of the applied AC voltage. Note that LC-BYVA01, being negative anisotropic, exhibits the oscillatory response in the homeotropic cell, according to Eq. (1), as it undergoes homeotropic to planar orientation. One the other hand, the positive anisotropic LC E7 shows a featureless behavior as it is already parallel to the external field in the homeotropic cell.

The number of oscillations (i.e., the number of maxima during a complete reorientation of the director) in the transmittance vs voltage curve in Fig. 2(a) is given by $(d/\Delta n/\lambda)$ [35]. Using $\Delta n = 0.092$ for LC-BYVA01, $\lambda = 633 \text{ nm}$ for the He-Ne laser, and the LC cell gap, $d = 9 \mu\text{m}$, we obtain...
of anchoring strength as the alignment agent in the cell. Therefore, a strong interaction strengthens the polar anchoring energy in the cell. As stated before, the LC-CNT interaction energy is given by two characteristic times, \( \tau_{\text{on}} \) (voltage on) and \( \tau_{\text{off}} \) (voltage off) \([38,39]\)—which are defined as

\[
\tau_{\text{on}} \propto \frac{\gamma_1 d^2}{\Delta \varepsilon |\varepsilon_0 V^2 - K_{33} \pi^2|}, \quad \tau_{\text{off}} \propto \frac{\gamma_1 d^2}{K_{33} \pi^2},
\]

where \( d \) is the cell gap, \( \gamma_1 \) is the rotational viscosity, \( \Delta \varepsilon \) is the dielectric anisotropy, \( V \) is the applied voltage, \( \varepsilon_0 \) is the free space permittivity, and \( K_{33} \) is the bend elastic constant. These switching times for the LC-BYVA01 in the V A-CNT arrays-based homeotropic cell were studied using the optical setup similar to the voltage-dependent transmittance experiment. In this case, the output of the detector was fed into a digital storage oscilloscope to detect the change in transmitted intensity as a function of time when a 25-V square-wave voltage of 25 Hz was applied across the cell. The field-induced dynamic response is shown in Fig. 4.

For a homeotropic cell, the optical switching on, \( \tau_{\text{on}} \), is defined by the time span needed by the transmitted intensity to go from 0.2 to 0.8 [0, 1]—which is the time span needed for the transmitted intensity to reach its saturation value.

For a homeotropic cell, the optical switching on, \( \tau_{\text{on}} \), is defined by the time span needed by the transmitted intensity to increase from 0.2 to 0.8. This good uniformity of planar alignment under applied voltage was obtained due to the slightly tilted CNTs that give an azimuthal (in-plane) anisotropy to the LC molecules.
to rise from 10% to 90% of its maximum value when $V$ is turned on. After $V$ is turned off, the transmitted intensity through the test cell decreases, and the optical switching off, $\tau_{\text{off}}$, is defined by the time needed by the transmitted intensity to drop from 90% to 10% of its maximum value. For the LC-BYVA01 in the VA-CNT arrays-based homeotropic cell, we found that $t_{\text{on}} = 2.3$ ms and $t_{\text{off}} = 10$ ms from Fig. 4. For a proper comparison, this experiment was carried out for the commercial PI-based VA cell ($d = 9 \mu$m), and we found that $t_{\text{on}} = 2.0$ ms and $t_{\text{off}} = 11.3$ ms. We ran this dynamic electro-optic switching experiment for the VA-CNT arrays-based homeotropic device in a cyclic manner and kept it running for more than 24 hrs, and we have not seen any changes in response.

III. CONCLUSION

To summarize, we have experimentally demonstrated that the VA-CNT arrays can function as the homeotropic-alignment agent in an LC cell due to the $\pi$-$\pi$ electron stacking interaction between the LC and the CNT surface. No additional ITO electrodes were needed in this cell as the Cr adhesion layers for the growth of the VA-CNT arrays successfully functioned as the transparent electrodes. This cell showed a typical Fréedericksz transition with the standard electro-optical effect when an electric field was applied across the cell. The field-induced dynamic response exhibited the two characteristic times $t_{\text{on}}$ and $t_{\text{off}}$. These response times are within the comparable range of the traditional PI-based VA cells. Thus, the inorganic VA-CNT arrays can be an excellent alternative to the traditional organic PI layers for a homeotropic-alignment agent when a substitute is required. Studying various LC-substrate interactions and then developing alternate LC alignment methods is an important direction for both fundamental and applied research. This study advances the conceptions about, and methodology toward, nanoscale manipulation of LCs and LC-orientation control using their interactions with VA-CNT arrays. Our future studies involve optimizing the length and the site density of CNTs, and measurements of polar anchoring energy, voltage holding ratio, residual DC charge, contrast ratio, thermal stability, and UV stability of this VA-CNT arrays-based homeotropic cell.

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