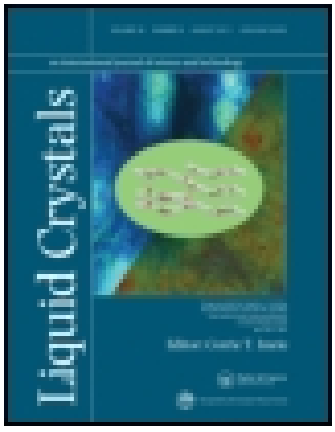

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Orientational and electro-optical properties of liquid crystal aligned with a directly spinnable carbon nanotube web

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Orientational and electro-optical properties of liquid crystal aligned with a directly spinnable carbon nanotube web

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We investigated the orientational and electro-optical properties of a nematic liquid crystal (LC) aligned with a directly spinnable carbon nanotube (CNT) web functioning both as an electrode and as an alignment layer. The LC molecules were uniformly oriented along the drawing direction of the CNT web and the spatially averaged birefringence was comparable to a rubbed polyimide sample. The CNT web sample also showed smaller residual DC and hysteresis compared to the polyimide sample.

Keywords: carbon nanotube web; birefringence; nematic liquid crystal; voltage holding ratio

1. Introduction

To obtain a uniform orientation of liquid crystal (LC) molecules in LC display devices, an alignment layer such as polyimide (PI) is coated onto an electrode and unidirectionally rubbed. The rubbing process forms grooves on the surface [1] and induces the alignment of the chains of PI.[2] The LC molecules align to the rubbing direction to minimise the interaction energy with the surface. However, the rubbing process generally leaves particulate impurities and electrostatic charges on the surface and this degrades the image quality of the LC devices. Various alignment methods to replace the rubbing process have been suggested such as ion beam irradiation [3] and photo-alignment methods [4–6] but with limited success.

More recently, nanoparticles have also been studied.[7–12] For instance, Kuo et al. reported a homeotropic orientation of LC using the polyhedral oligomeric silsesquioxane (POSS) nanoparticles.[7] Hwang et al. demonstrated a continuous control of the pretilt angle of LC using functionalised POSS.[8] Lee et al. showed that small amount of carbon nanotube (CNT) fibres dispersed in PI induced a uniform surface topography and a faster turn-off time.[9] Russell et al. showed that the films of aligned CNT bundles deposited on glass could align the LC molecules.[10] Moreover, Fu et al. [11] and Jian et al. [12] found that 10-cm-wide webs of aligned CNTs formed by drawing directly from specially grown 'forests' or arrays could function both as the alignment layer and electrode. However, in the previous literature,[11] the orientational ordering of LC and the temperature dependence of the LC ordering on the CNT web were not studied.

In this paper, we investigated the orientational and electro-optical properties of LC aligned with directly drawn CNT web. LC was applied to the pristine and rubbed CNT web and PI. We measured the spatially averaged birefringence Δn and $<(3/2)\cos^2\theta-1/2>$ value, where θ represents the local angular deviation of the molecular orientation from the average easy axis of the surface. The quantity in the bracket means the nematic order parameter S provided the easy axis of the surface is spatially uniform. We found the surface of the CNT web formed localised domains of tens or hundreds of nanometre scale. The temperature dependence of $<(3/2)\cos^2\theta-1/2>$ through the nematic phase was investigated. $<(3/2)\cos^2\theta-1/2>$ of LC between the unrubbed CNT web was lower than that of LC between the rubbed PI surface. However, $<(3/2)\cos^2\theta-1/2>$ of LC between rubbed CNT web is close to that of the rubbed PI sample. We also investigated the transmittance (TR)–voltage characteristics and residual DC of the CNT web samples. The CNT sample showed good modulation of TR by the electric field and less residual DC property.

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2. Experiments

Directly spinnable CNTs (dsCNTs) were grown as forests of parallel-aligned fibres on silicon wafers bearing 50 nm thermal SiO_2 and an iron catalyst layer of 2.5 nm deposited by e-beam evaporation. The wafers were first annealed in a 90-mm inner diameter quartz tube reactor at 680°C under helium (4000 sccm, 40 min). Acetylene (100 sccm) and hydrogen (100 sccm) were added to the flow and the reaction run for 20 min to give ~400-μm-long CNTs of 10 nm diameter. A web of dsCNTs was drawn from the front face of the dsCNT forest and laid onto a clean glass substrate.[13] The web was then wet with a little acetone to draw it firmly onto the glass surface and to densify it. The CNT web was then unidirectionally rubbed with a cotton cloth.

For the fabrication of the PI sample, a commercial polyimide SE7492 (Nissan) was coated onto an indium-tin-oxide (ITO)-coated glass substrate and baked at 200°C for 1 h. The cured substrates were rubbed with a cotton cloth and assembled in an antiparallel fashion. For the measurement of $<(3/2)\cos^2\theta-1/2>$, the cell gap d was fixed at 3.2 μm using bead spacers. Then, a commercial nematic LC mixture ZKC5071XX (JNC) was injected by a capillary action. For the measurement of TR vs. voltage, d of the PI and CNT web sample was maintained to be 40 μm, respectively, using a polypropylene film. The thicker d of the sample for the TR vs. voltage measurement is to avoid a contact and thermal heating effect of the CNT webs between both substrates. To measure the electro-optical properties of the samples, a He-Ne laser beam (λ = 632.8 nm) with a beam size of 1 mm was passed through a polariser, the cell, an analyser, a Soleil-Babinet compensator (Thorlabs, Newton, NJ, USA) and a detector. The birefringence Δn was measured by adjusting the Soleil-Babinet compensator. $<(3/2)\cos^2\theta-1/2>$ was measured by fitting Δn with the empirical equation $\Delta n = \delta n(1-T/T^*)^{\beta}$, where T is the absolute temperature, and T^*, δn and

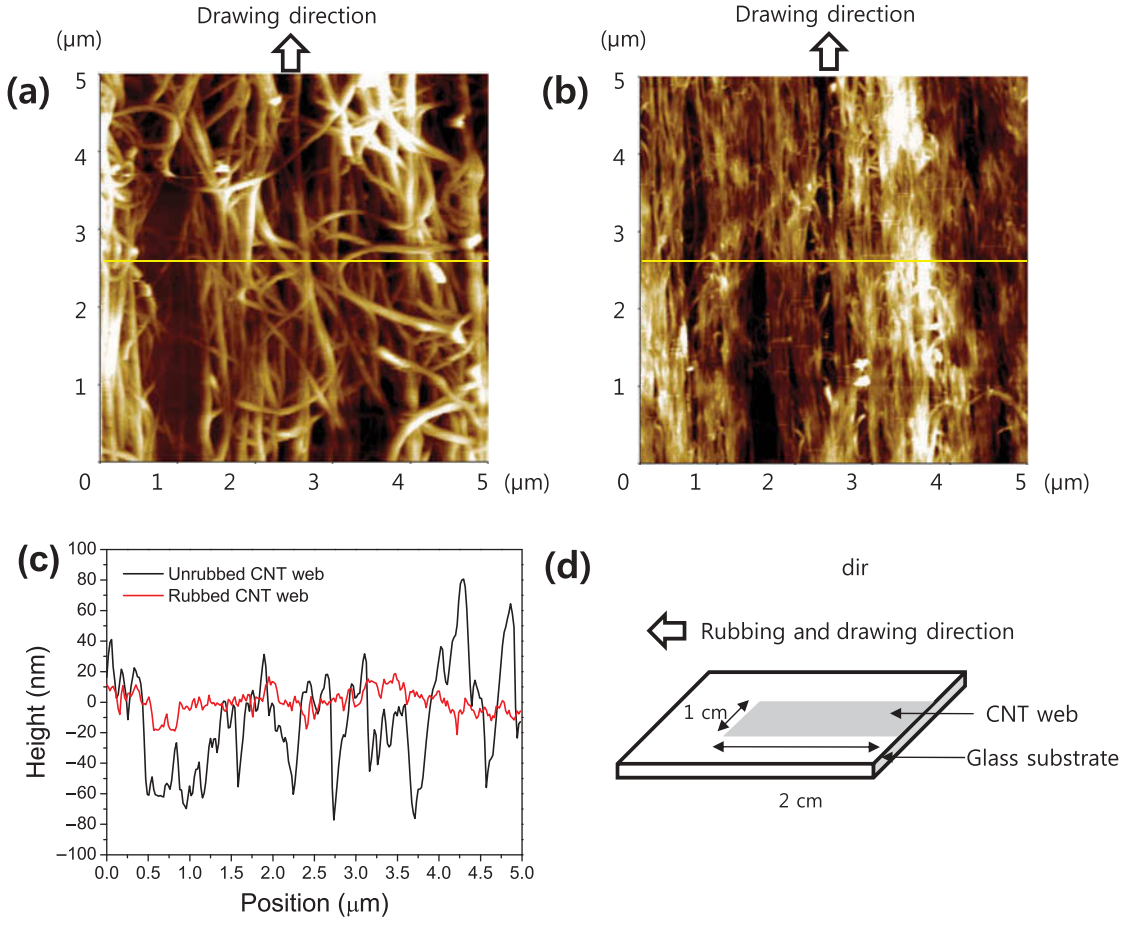

Figure 1. (colour online) AFM topographical image of (a) the unrubbed and (b) rubbed CNT web, (c) topographical height profile of a single transect in the CNT web along the horizontal lines in Figure 1(a) and (b). (d) Schematic illustration of the CNT web-attached substrate.

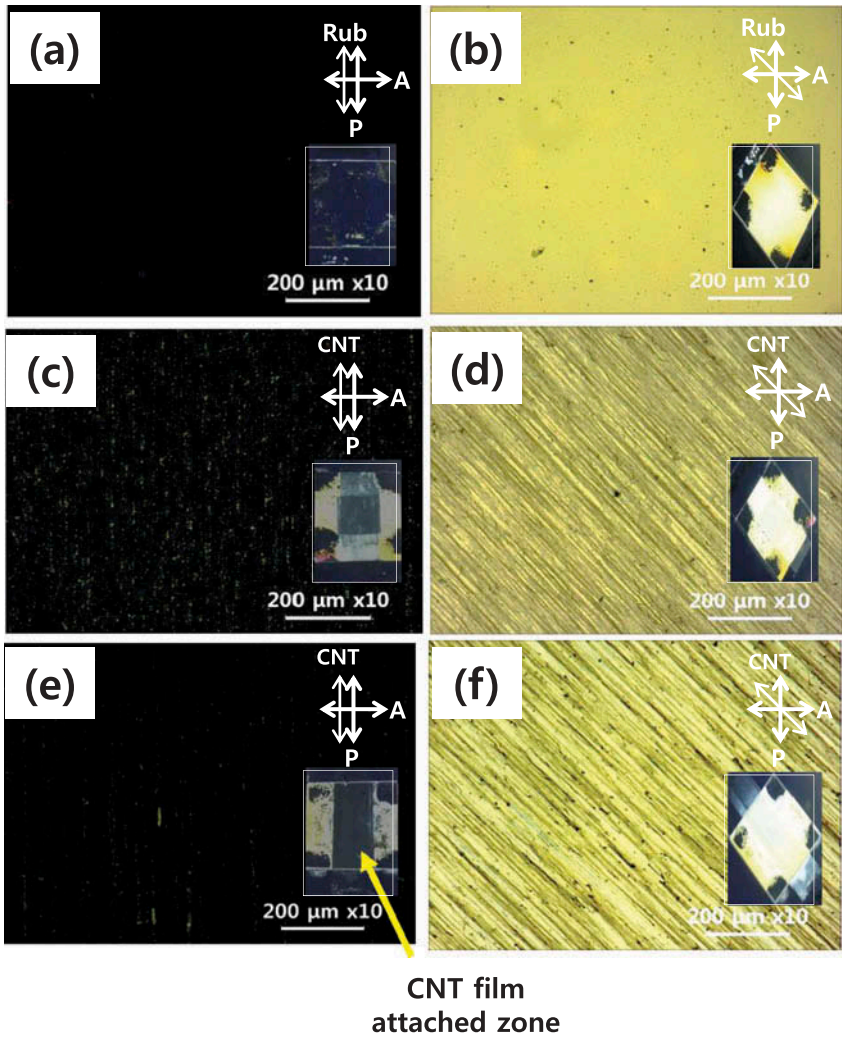

Figure 2. (colour online) POM image of the LC sample aligned with SE7492 (a) and (b), unrubbed CNT web (c) and (d), and rubbed CNT web (e) and (f). Rubbing direction and CNT direction were parallel to the polariser in Figure 2(a), (c) and (e), while those were at 45° to the polariser in Figure 2(b), (d) and (f). Insets show the fabricated samples.

β are fitting parameters.[9,14,15] Assuming $<(3/2)\cos^2\theta - 1/2 \geq 1$ at $T = 0$ K, $<(3/2)\cos^2\theta - 1/2>$ is given by $\Delta n(T)/\delta n$.

3. Results and discussion

Figure 1(a) shows the atomic force microscopy (AFM) topographical image of the CNT web before rubbing. The CNT web was drawn in the direction depicted with an arrow. Although the morphology was not completely uniform, the overall orientation of the CNT fibrils was elongated in the drawing direction. Figure 1(b) is the AFM image of the CNT web after rubbing. The CNT fibrils were more uniformly aligned to the rubbing direction. Figure 1(c) shows the topographical height of the single transect of the unrubbed and rubbed CNT webs perpendicular to the drawing direction as shown by the yellow lines in Figure 1(a) and (b), respectively. The peak-to-peak height of the unrubbed CNT grooves was 40–120 nm and the typical separation between the neighbouring grooves was about 200–400 nm. On the other hand, the peak-to-peak height of the rubbed CNT grooves was less than 20 nm and the separation was reduced compared to the unrubbed surface. Thus, the surface uniformity and the anisotropy of the CNT fibrils were improved by the rubbing process.

Figure 2 shows the polarising optical microscopy (POM) images of the LC sample aligned with SE7492 (Figure 2(a) and (b)), unrubbed CNT web (Figure 2(c) and (d)) and rubbed CNT web (Figure 2(e) and (f)). The rubbing direction and the CNT direction were parallel to the polariser in Figure 2(a), (c) and (e), while those were at 45° to the

polariser in Figure 2(b), (d) and (f). With the CNT direction parallel to the polariser, the unrubbed CNT sample showed significant light leakage (Figure 2(c)). The rubbed CNT sample showed a uniform dark state (Figure 2(e)) and, at 45° to the polariser, a bright state (Figure 2(d)) comparable to the SE7492 sample (Figure 2(a) and (b), respectively). The insets show the fabricated sample images. The samples showed a clear change of brightness when the sample was rotated between the crossed polarisers, indicating a homogeneous alignment of LC.

Figure 3(a) shows the spatially averaged Δn of the samples as a function of $T–T_{NI}$. Note that the bare CNT web has an intrinsic retardation of about 5 nm. We measured the retardation of the CNT web vs. temperature and subtracted the background from the retardation of the LC-filled sample. Although the unrubbed CNT web sample showed significant decrease of Δn, the rubbed CNT web sample was very close to the SE7492 sample. Then, we fitted the Δn data using empirical equation as described in the experimental section. We used the T_{NI} value for T^* and selected the initial β value as 0.2 based on literature values of a general nematic LC.[15,16] The lines in Figure 3(a) correspond to the fitted curve and the data was well approximated to the empirical equation. The $<(3/2)\cos^2\theta–1/2>$ data deduced from Δn (Figure 3(b)) also show the rubbed CNT web sample is close to the SE7492 sample, whereas the unrubbed CNT sample is lower. At T = 25°C, S of the SE7492 sample was 0.61, while S of the rubbed CNT web was 0.58. In addition, both samples showed similar temperature dependence. Thus, the alignment of the LC sample between the rubbed CNT web was comparable to the one between the rubbed PI surface through the nematic phase. Probably, the LC molecules between the CNT web with anisotropic grooves adapt parallel orientation to the CNT fibrils to minimise free energy.[1] In addition, the π–π interaction between the CNT web and the LC molecules might contribute to the uniform LC orientation.[9] A question can be raised why the POM image of the rubbed CNT cell in Figure 2(f) is darker than the pure SE7492 sample in spite of the similar Δn. This is due to the light absorption of the CNT web. The CNT web absorbs about 47% of unpolarised light.

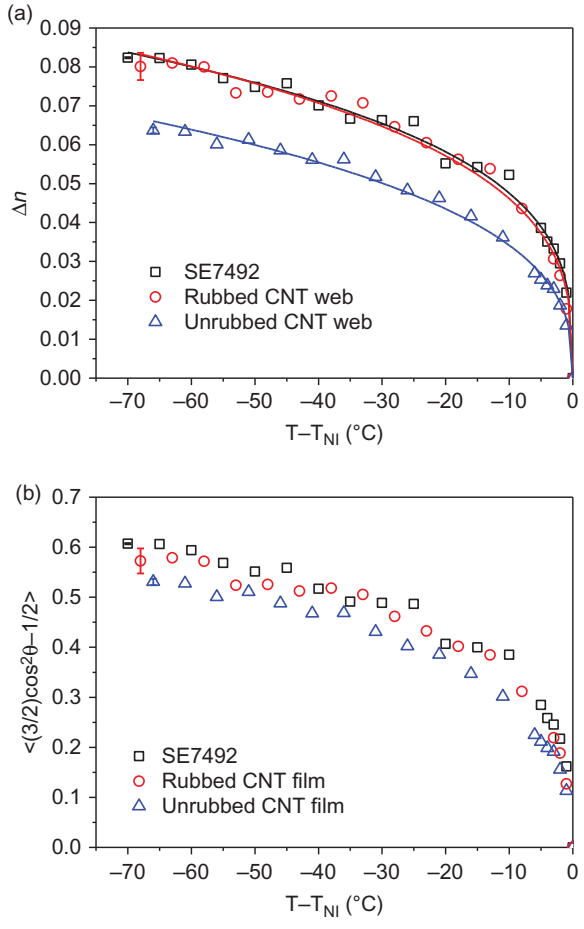

Figure 3. (colour online) (a) Spatially averaged Δn of the LC sample aligned with SE7492 and CNT web vs. $T–T_{NI}$. Lines are the fitted curve according to the Haller's equation. (b) Spatially averaged $<(3/2)\cos^2\theta–1/2>$ value of the corresponding samples vs. $T–T_{NI}$. Error bar represents standard deviation obtained from three different points of the sample.

We measured TR of the samples vs. applied voltage (Figure 4). To minimise resistive heating of the sample, the cell gap of the SE7492 and the CNT samples was maintained at 40 μm, as described in the experimental section. The operation voltage of the rubbed CNT sample was slightly larger than the SE7492 sample and this is probably due to the lower density of the CNT web than the ITO. About 80% of the surface was covered with CNT fibrils in Figure 1 (b) and the switching voltage is expected to be

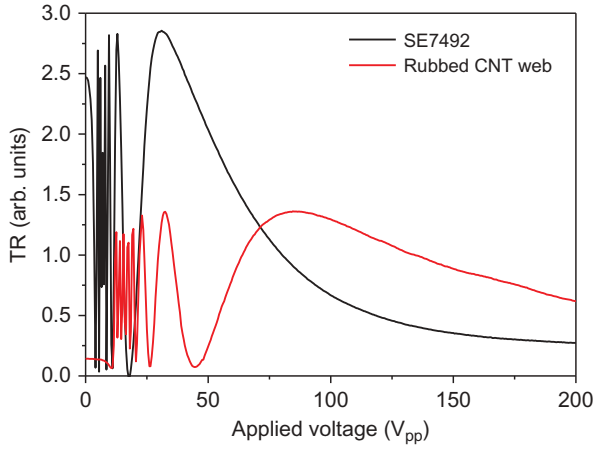

Figure 4. (colour online) TR of the samples aligned with rubbed SE7492 and CNT web vs. applied voltage.

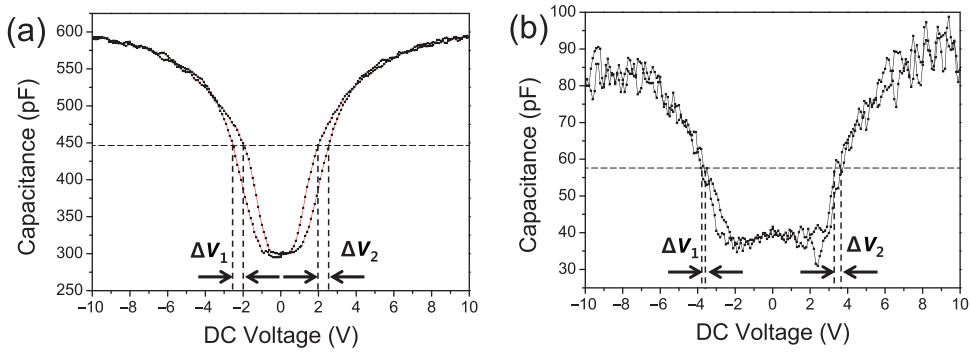

Figure 5. (colour online) Capacitance vs. applied DC voltage of the (a) SE7492 and (b) rubbed CNT samples. The residual DC is defined as $(\Delta V_1 + \Delta V_2)/2$.

reduced provided the whole area is covered with the CNT fibrils. The total phase retardation of the samples were similar between 14π and 15π, but the maximum TR of the CNT web sample was smaller than the SE7492 sample due to the absorption of light by the CNT web as described earlier. For larger TR, a normally white LC mode such as the twisted nematic (TN) would be better in the viewpoint of the display application where the CNT web is used as a polariser.[11,12]

Figure 5 shows the residual DC properties of the SE7492 and rubbed CNT samples. The residual DC was defined as $(\Delta V_1 + \Delta V_2)/2$, where ΔV_1 and ΔV_2 are the voltage difference showing the half of the maximum capacitance in the course of increasing and decreasing the voltage. Because the CNT sample has no insulating layer between the electrode and LC, the sample showed smaller capacitance and less residual DC. This less hysteretic response can simplify the driving scheme in the display application.

4. Conclusion

To summarise, we studied the orientation of LC aligned with the CNT web working both as the electrode and as the alignment layer. We found that *S* of the rubbed CNT web sample was comparable to the rubbed polyimide sample. The rubbed CNT web sample showed similar retardation with less residual DC compared to the polyimide sample. Because the alignment layer is absent in the CNT sample, the CNT web is expected to simplify the fabrication process reducing the production cost. As a next step, we are planning to improve the anisotropy of the CNT web and increase the surface density of the CNT fibrils for greater electro-optical properties.

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References

[1] Berreman DW. Solid surface shape and the alignment of an adjacent nematic liquid crystal. Phys Rev Lett. 1972;28:1683–1686. doi:10.1103/PhysRevLett.28.1683.
[2] Geary JM, Goodby JW, Kmetz AR, Patel JS. The mechanism of polymer alignment of liquid-crystal materials. J Appl Phys. 1987;62:4100. doi:10.1063/1.339124.
[3] Chaudhari P, Lacey JA, Lien SCA, Speidell JL. Atomic beam alignment of liquid crystals. Jpn J Appl Phys. 1998;37:L55–L56. doi:10.1143/JJAP.37.L55.
[4] Shannon PJ, Gibbons WM, Sun ST. Patterned optical properties in photopolymerized surface-aligned liquid-crystal films. Nature. 1994;368:532–533. doi:10.1038/368532a0.
[5] Usami K, Sakamoto K, Tamura N, Sugimura A. Improvement in photo-alignment efficiency of azobenzene-containing polyimide films. Thin Solid Films. 2009;518:729–734. doi:10.1016/j.tsf.2009.07.079.
[6] Chrzanowski MM, Zieliński J, Olifierczuk M, Kędzierski M, Nowinowski-Kruszelnicki E. Photoalignment – an alternative aligning technique for liquid crystal displays. JAMME. 2011;48:7–13.
[7] Kuo CW, Jeng SC, Wang HL, Liao CC. Application of nanoparticle-induced vertical alignment in hybrid-aligned nematic liquid crystal cell. Appl Phys Lett. 2007;91:141103. doi:10.1063/1.2794007.
[8] Hwang SJ, Jeong SC, Hsieh IM. Nanoparticle-doped polyimide for controlling the pretilt angle of liquid crystals devices. Opt Express. 2010;18:16507. doi:10.1364/OE.18.016507.
[9] Lee H, Yang S, Lee JH, Park YS. Improvement of the relaxation time and the order parameter of nematic liquid crystal using a hybrid alignment mixture of carbon nanotube and polyimide. Appl Phys Lett. 2014;104:191601. doi:10.1063/1.4875615.
[10] Russell JM, Oh SJ, LaRue I, Zhou O, Samulski ET. Alignment of nematic liquid crystals using carbon

nanotube films. Thin Solid Films. 2006;509:53–57. doi:10.1016/j.tsf.2005.09.099.
[11] Fu W, Liu L, Jiang K, Li Q, Fan S. Super-aligned carbon nanotube films as aligning layers and transparent electrodes for liquid crystal displays. Carbon. 2010;48:1876–1879. doi:10.1016/j.carbon.2010.01.026.
[12] Jiang K, Wang J, Li Q, Liu L, Liu C, Fan S. Superaligned carbon nanotube arrays, films, and yarns: a road to applications. Adv Mater. 2011;23:1154–1161. doi:10.1002/adma.201003989.
[13] Huynh CP, Hawkins SC. Understanding the synthesis of directly spinnable carbon nanotube forests. Carbon. 2010;48:1105–1115. doi:10.1016/j.carbon.2009.11.032.
[14] Haller I. Thermodynamic and static properties of liquid crystals. Prog Solid State Chem. 1975;10:103–118. doi:10.1016/0079-6786(75)90008-4.
[15] Rao L, Gauza S, Wu ST. Low temperature effects on the response time of liquid crystal displays. Appl Phys. 2009;94:071112.
[16] Lee H, Kim H, Yang S, Hwang J, Lee JH, Choi J. Electro-optical properties of a nematic liquid crystal aligned with a mixture of nanofibres and polyimide. J Phys D Appl Phys. 2014;47:345303. doi:10.1088/0022-3727/47/34/345303.