Electrical-field effect on carbon nanotubes in a twisted nematic liquid crystal cell

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We have fabricated twisted nematic cells doped by carbon nanotubes (CNTs). The CNTs with a minute amount of doping did not perturb the liquid crystal orientation in the off and on state. The hysteresis studies of voltage-dependent transmittance and capacitance under ac and dc electric field showed that the residual dc, which is related to an image sticking problem in liquid crystal displays, was greatly reduced due to the ion trapping by CNTs. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2158509]

Recently, effects of carbon nanotubes (CNTs) on liquid crystal (LC) cell have been studied in several ways. It has been proved that the long axis of CNTs is aligned parallel to the LC director[1] and, with a bias voltage, CNTs also try to orient along the LC director.[2–4] Effects of a minute addition of carbon nanosolids, such as C_{60} and multiwalled CNTs (MWNTs) in a twisted nematic (TN) LC cell have also been reported.[5] However, in their work, the LC material, 5CB that has a high dielectric anisotropy ($\Delta\varepsilon$) of 20, was used and moreover only the dc effect has been reported. The dc-dependent transmittance curves showed a large hysteresis, irrespective of doping nanosolids or not. They claimed that the hysteresis was reduced slightly with an addition of CNTs but the origin of the reduced hysteresis has not been clarified.

In thin-film transistor (TFT)-liquid crystal displays (LCDs), the LC cell should be driven by ac voltage. Otherwise the ion charges will be trapped at an interface between the alignment layer and LC layer, forming a net dc component (called a residual dc). This will nullify the applied voltage so that the image cannot be generated according to the input signal voltage, resulting in an image sticking problem.[6] Besides, the LC cell should have high resistivity such that an applied signal can be held without a leakage current. Otherwise, the flickering of images appears. Therefore, in TFT-LCDs, the low residual dc and high voltage holding ratio are the key requirements to exhibit a high image quality. At present, the super-fluorinated LC mixtures show a high resistivity larger than $10^{13}\ \Omega\,\mathrm{cm}$.[7] Nevertheless, in real TFT-LCDs, the excess ions which may come from the original cell materials or cell manufacturing process are present in the cell. Thus it is common to observe the image sticking mainly due to the residual dc associated with ion trapping at interface between the LC layer and the alignment layer.[6] In our works, we have fabricated the single walled CNT (SWNT) and MWNT-doped TN cells and studied effects of the CNTs on electrical and electro-optical properties of the TN cell, when the dc or ac voltage is applied. We found that the residual dc was significantly reduced in the presence of a small amount of CNT doping. This was attributed to the large electron affinity of CNTs that induces strong charge transfer from the adjacent LC molecules and consequently ion trapping.

For cell fabrications, the super-fluorinated LC mixtures from Merck-Japan with physical properties ($\Delta\varepsilon=7.4$, birefringence $\Delta n=0.088$ at $\lambda=589$ nm, clearing temperature 80 °C with a nematic phase down to −40 °C) were used. As an alignment layer, the polyimide SE-7492 (Nissan Chemicals, Japan) was coated on indium tin oxide patterned glass. The rubbing was then performed on two substrates with rubbing directions perpendicular to each other. The dispersed SWNTs and MWNTs in dichloroethane solvent with 5×10^{-4} and 10^{-3} wt% were doped in the LC, respectively, and after evaporating the solvent, the mixture was filled into the cell by capillary action at room temperature. The cell gaps for the pure LC, SWNT- and MWNT-doped cells were 4.5, 4.5, and 4.6 μm, respectively. We attached the crossed polarizers to the TN cell in a normally white mode so that the cell shows a white state before applying voltage.

We first observed the pure LC and CNT-doped cells macroscopically by a naked eye and microscopically under polarizing optical microscope by applying voltage up to 10 V. We could not find any difference between them, indicating that a small amount of MWNTs does not disturb the LC orientation and may follow the LC orientation with bias voltage. However, we could observe the worm-like white lines in the MWNT-doped TN cell at a high field intensity of 26 V/μm [see Fig. 1(c)], which originates from the birefringence generated by distorting the LC director, similar to the previous observations.[3] Since this was not observed at all in

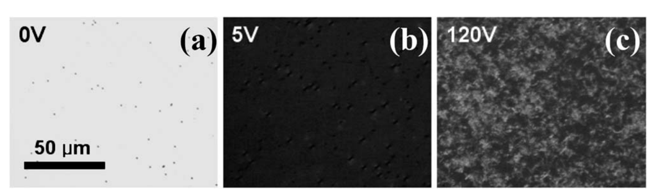

FIG. 1. Microphotographs of a MWNT-doped TN cell in the on state with field intensities of (a) 0 V/μm, (b) 1 V/μm and (c) 26 V/μm. The spots at 0 V are due to ball spacers.

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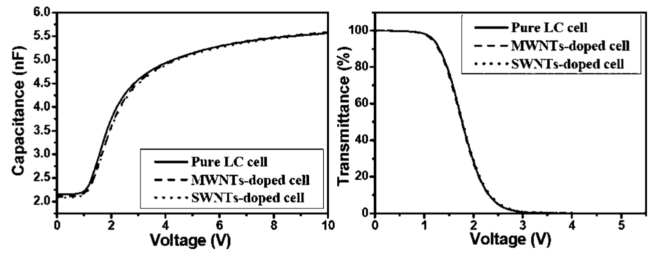

FIG. 2. Measured voltage-dependent (a) capacitance and (b) transmittance curves by applying ac voltage.

the pure LC cell, we could conclude that these textures are related to the motion of the MWNTs generated by interaction between net charge of the MWNTs and ac field, and in addition, the MWNTs are uniformly distributed throughout the cell. Similar textures are observed even in the SWNT-doped cell.

We next measured electrical and electro-optic characteristics of the cell. Figure 2(a) shows the voltage-dependent capacitance (V-C), when ac square wave voltage is applied with 1 kHz. The capacitance of the CNT-doped cell was slightly lower than that of the pure LC cell up to an applied voltage of 5 V. With further increasing voltage to 10 V, both cells reached the same value and then the turnover of the capacitance amplitude was observed, although the difference between them was small. The voltage-dependent transmittance (V-T) characteristics were also investigated as shown in Fig. 2(b). As clearly indicated, the effect of CNTs on V-T curves was not much differentiated such that all the cells show almost the same Fredericks transition voltage, implying that the existence of CNTs in LC does not affect appreciably physical parameters of the LC layer such as dielectric anisotropy and elastic constants (K), since in the TN cell, the threshold voltage V_{th} is proportional to $\pi(K/\varepsilon_0\Delta\varepsilon)^{1/2}$. Another measurement of a voltage holding ratio to compare electrical characteristics was performed with an applied signal of square wave 5 V with 60 Hz. All the cells showed a high voltage holding ratio of 98% at room temperature, again supporting the behavior of V-C curves so that the MWNT-doped cell does not form a current pathway.

We then measured the residual dc by the voltage-dependent capacitance and transmittance hysteresis curves. The dc voltage was swept from 0 to +10 V, and then changed from +10 to −10 V, and finally from −10 to 0 V, with each step of 0.1 V. Amplitudes of the residual dc at positive and negative cycles, which are defined as the voltage difference between rise and fall at half of the maximum capacitance, were 0.248 and 0.252 V in the pure LC cell, respectively, while they were 0.005 and 0.004 V in the MWNT-doped cell, as appeared in Fig. 3(a). This is a somewhat surprising result that the amount of residual dc was greatly reduced in the CNT-doped cell. Since the existence of residual dc affects the transmittance, we also measured the V-T hysteresis, as shown in Fig. 3(b). This reveals that in the pure LC cell, the amplitudes of hysteresis at V_{10}, V_{50}, and V_{90} (here, the subscript indicates a relative transmittance with respect to the maximum transmittance) were about 0.13, 0.16, and 0.19 V at both positive and negative cycles, respectively, while they were all less than 0.003 V in the MWNT-doped cells, in excellent agreements with the V-C results. The SWNT-doped TN cell also shows similar results compared to those in the MWNT-doped cell. These results imply that the CNTs do trap ions.

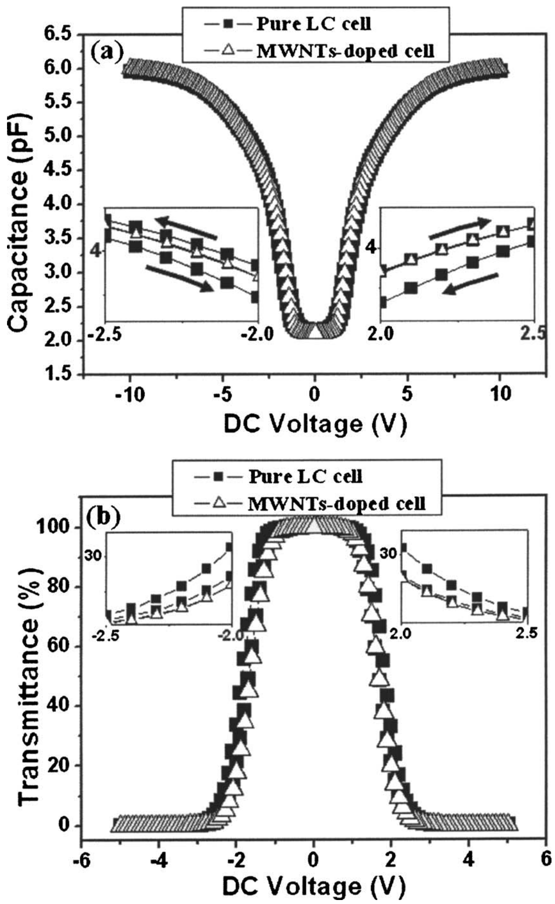

FIG. 3. Measured hysterisis curves in voltage-dependent (a) capacitance and (b) transmittance by applying dc voltage.

Now, a question arises as to why the existence of MWNTs dispersed in a nematic LC medium significantly reduces the residual dc. We performed density functional calculations within local density approximation.[8,9] Figure 4 shows the anchoring of LC molecule on CNTs. The binding was greatly enhanced by maximizing an aromatic ring interaction, as shown in top view of Fig. 4. The interaction energy is close to −2 eV, independent of the presence of the functional groups at the edge of CNTs. This strong binding energy is attributed to a charge transfer (0.45 and 0.23 e for open and H-functionalized CNTs, respectively) from LC molecule to CNT due to strong electron affinity of CNTs. The shortest bond length is 2.2 Å for H at LC molecule and carbon atom at CNT. The binding nature is therefore a hydrogen bonding rather than a simple van der Waals interaction. This strong anchoring in fact induces a self-alignment of CNT molecules in LC medium, as observed in our experiments. Furthermore, this excess charge induces a permanent dipole moment in the CNT which originates from the asymmetric LC molecular anchoring on CNT axis, although the value relies on the position of LC molecule, the presence of functional group of CNT, and CNT length.[10] The existence of a permanent dipole moment can easily capture the ionic impurities in the cell, and thus we can expect the reduction of residual dc. The ion trapping will be more prominent at higher field by generating stronger induced dipole moment. This is why we observed slightly larger capacitance at high

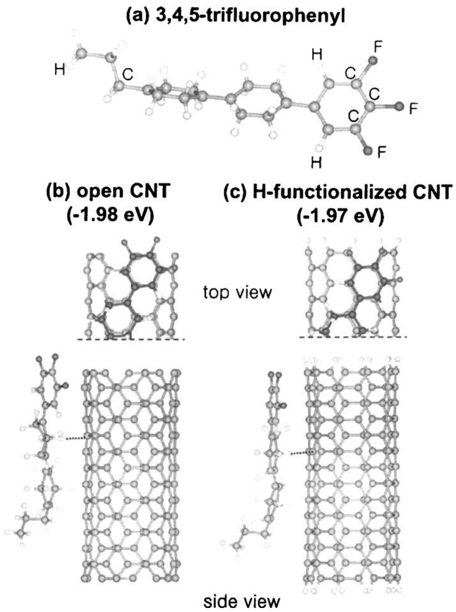

FIG. 4. The optimized geometries of (a) 3,4,5-trifluorophenyl LC molecule, and those interacting with (b) open CNT and (c) H-functionalized CNT. The dashed lines in (b) and (c) are the shortest bond lengths of hydrogen atom at LC molecule and carbon atom at CNT.

voltage region in the MWNT-doped cell than in the pure LC cell in Fig. 2.

In order to demonstrate experimentally that the CNTs do have a net charge, a vertically aligned MWNT-doped LC cell with 60 μm cell gap was evaluated. As presented in Fig. 5(a), the cell showed a dark state under the crossed polarizers at 0 V. As the applied ac voltage increased, the LC oriented more perfectly parallel to a vertical electric field, giving rise to a darker state. However, at a high ac voltage of 120 V, the spots with four-lobe textures appeared, which are associated with a motion of CNTs, as shown in Fig. 5(b).[3] We note that no rotational but translational motion of these textures was observed under ac field at low frequency, indicating the presence of a net charge and a permanent dipole moment. As the voltage was reduced to zero, the white spots still appeared,

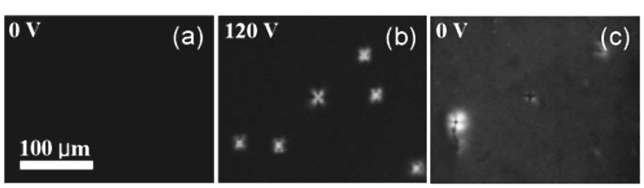

FIG. 5. Microphotographs of a MWNT-doped vertically aligned LC cell at (a) 0 V, (b) 120 V, and (c) 0 V released just after applying 120 V.

instead of going back right away to a clear dark state [see Fig. 5(c)]. However, after 10 s, all these spots disappeared and the cell recovered a clear dark state. Those white spots generated from the distortion of LC directors originate from CNTs with the accumulated ions and/or charge transfer that are shown from our theoretical calculations. In addition, since these spots exhibited a translational motion, the CNTs were not trapped at the interface and thus the residual dc was significantly reduced.

In summary, we have investigated effects of CNTs on a nematic liquid crystal medium by fabricating twisted nematic cells. The electrical measurements of voltage-dependent capacitance and voltage holding ratio exhibited that the existence of a minute amount of CNTs did not affect the cell capacitance and voltage holding characteristics, and yet the amplitude of the residual dc was greatly reduced due to the ion trapping by CNTs that have a permanent dipole moment. The electro-optic measurements of voltage-dependent transmittance also confirmed that the residual dc was reduced. We believe that this work will have a great impact in reducing the residual dc which is a long standing problem in the conventional TFT-LCDs and also suggest that the residual dc in an active area can be indeed reduced by introducing ion-trapping sites such as CNTs in a nonactive area of the LCDs.

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