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Electric-Field-Induced Dispersion of Multiwalled Carbon Nanotubes in Nematic Liquid Crystal

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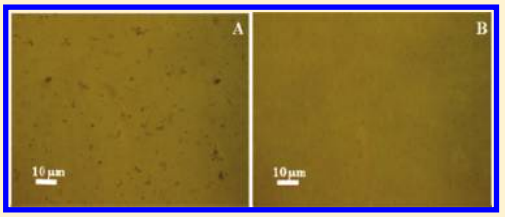
ABSTRACT: Effect of electric field and frequency on multiwalled carbon nanotubes (MWCNTs) dispersion in liquid crystal (LC) medium has been investigated. At zero field, large MWCNT aggregates are found due to insufficient dispersion throughout the cell under optical microscopy. As the vertical field strength increases gradually, the cluster sizes become smaller, and at above critical field strength, the clusters disappear and are dispersed finally into LC medium. The dispersion of CNT clusters remained stable even after the field is removed. Strong correlation of cluster sizes with field strength was also observed. The dispersion of clusters at above critical field was also confirmed by the light absorption. This robustness of field-induced dispersion of CNTs provides a new method of improving solubility of CNTs in LC medium, which can be advantageous in numerous CNT-LC optoelectronic devices.



1. INTRODUCTION

Unique anisotropic structure of carbon nanotubes (CNTs) with giant aspect ratio displays extreme anisotropic electric, magnetic, and optical properties along and across the tubes.[1] These properties are strongly dependent on the orientation of the CNTs, however, the high aspect ratio of the tubes along with their high flexibility leads to a high degree of physical entanglement, degrading anisotropy of CNTs. Therefore, it is essential to control orientation of CNTs on a macroscopic scale for applications to optoelectronic devices.

The CNTs interact via van der Waals forces, which are weak on the atomic scale, but the micrometer long CNTs accumulate the interaction energy of a few thousands electronvolts, resulting in the formation of agglomerations in the form of entangled ropes. These entangled ropes are very difficult to be dispersed with typical physical and chemical approaches.[2,3] Therefore, unidirectional alignment of CNTs in any media has not been accessible easily. Liquid crystal (LC) as an anisotropic, self-assembled long-range ordered molecular liquid facilitates large-scale alignment of the CNTs along their preferred direction called the director.[4] Furthermore, LCs are highly sensitive to external forces (electric, magnetic, mechanical) allowing for easy manipulation of the nanotubes orientation following the reorientation of the LC through elastic interaction via the director field. It has been experimentally observed that the LC director field cannot align large aggregates of CNTs particularly at high CNT concentration, as clearly visible under optical microscope.[5] Therefore, it is necessary to achieve better dispersion of CNTs, which leads to microscopic alignment of CNTs into the LC host.

Good dispersions of CNTs into LCs have received attention for their unique properties with potential applications in opto-electronics. Recent researches have focused on homogeneously dispersed CNTs into the host materials. A common way to do this is to directly mix SWCNTs or MWCNTs with nematic LC medium[4,6] or to first disperse CNTs in polar aprotic solvent such as dichloroethane (DCE)[7,8] and the polar protic compound, ethyl alcohol (EtOH), followed by mixing with nematic LC medium and vaporization of solvent.[9,10] Although ultrasonication process is generally used to prevent the aggregation of CNTs inside solution by counteracting van der Waals attraction of adjacent CNTs, the results are unsatisfactory. This approach is limited to small amounts of CNTs, which are prone to reaggregation during solvent evaporation. Another approach employs surface modification of CNTs for enhanced compatibility.[11] Such a modification is usually carried out by surfactant encapsulation or chemical functionalization through reactions onto the p-conjugated skeleton of CNTs.[12,13] Although chemical functionalization has been proposed to be a promising way to promote the disposability of CNTs, it should be noted that covalent surface modification can affect intrinsic mechanical, electrical, and optical properties of nanotubes.[14−16] Recently, the effect of strong electric field on the CNT clusters has been reported.[17,18] The CNT cluster could be stretched along the field direction above a critical field. With further increasing field, the CNT clusters could be ruptured and fragmented into small pieces. In this Article, we have investigated efficient dispersion of CNTs under external electric field in nematic LC host and furthermore the effect of electric field on the size of CNT aggregates. The dispersion of

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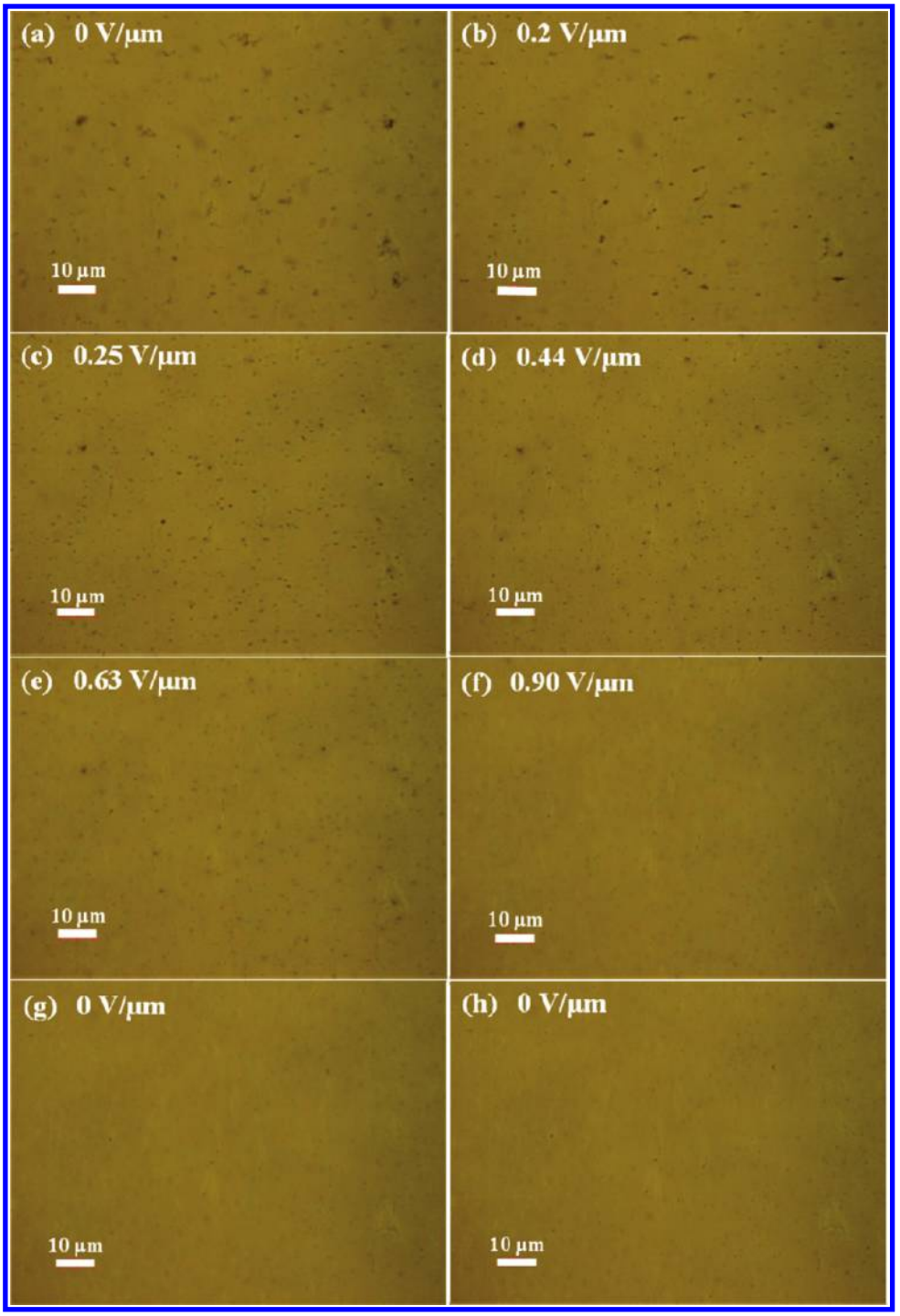

Figure 1. (a−h) Optical microphotographs of CNT-LC cell with respect to electric field (0, 0.20, 0.25, 0.44, 0.63, 0.90, and 0 V/μm) viewed through a linear polarizer, (g) optical image right after field is removed, and (h) optical image after field is removed and the cell is maintained for 48 h.

CNTs with electric field was also identified by the measurement of transmitted light intensity.

2. EXPERIMENTAL SECTION

Thin multiwalled carbon nanotubes (t-MWCNT) with outer diameters ranging from 3 to 6 nm and typical lengths of dozens of micrometers were synthesized in this study by a catalytic chemical vapor deposition (CCVD) method using FeMoMgO catalysts prepared by combustion process.[3] The t-MWCNTs were dispersed in LC medium by stirring 100 mg t-MWCNT powders in 1 M sucrose solution for 1 h, followed by grinding in mortar for 1 h. A well-dispersed solution of 0.167 g/mL CNTs in ethanol was prepared by adding 5 mg of the grinded t-MWCNT in 30 mL of ethanol with a sonication for 15 min. The mixture was poured in a nematic LC, purchased from Merck-Japan, having the following physical properties: Δn = 0.077 at λ = 589 nm, dielectric anisotropy $\Delta\varepsilon = -4$, and clearing temperature = 75 °C.

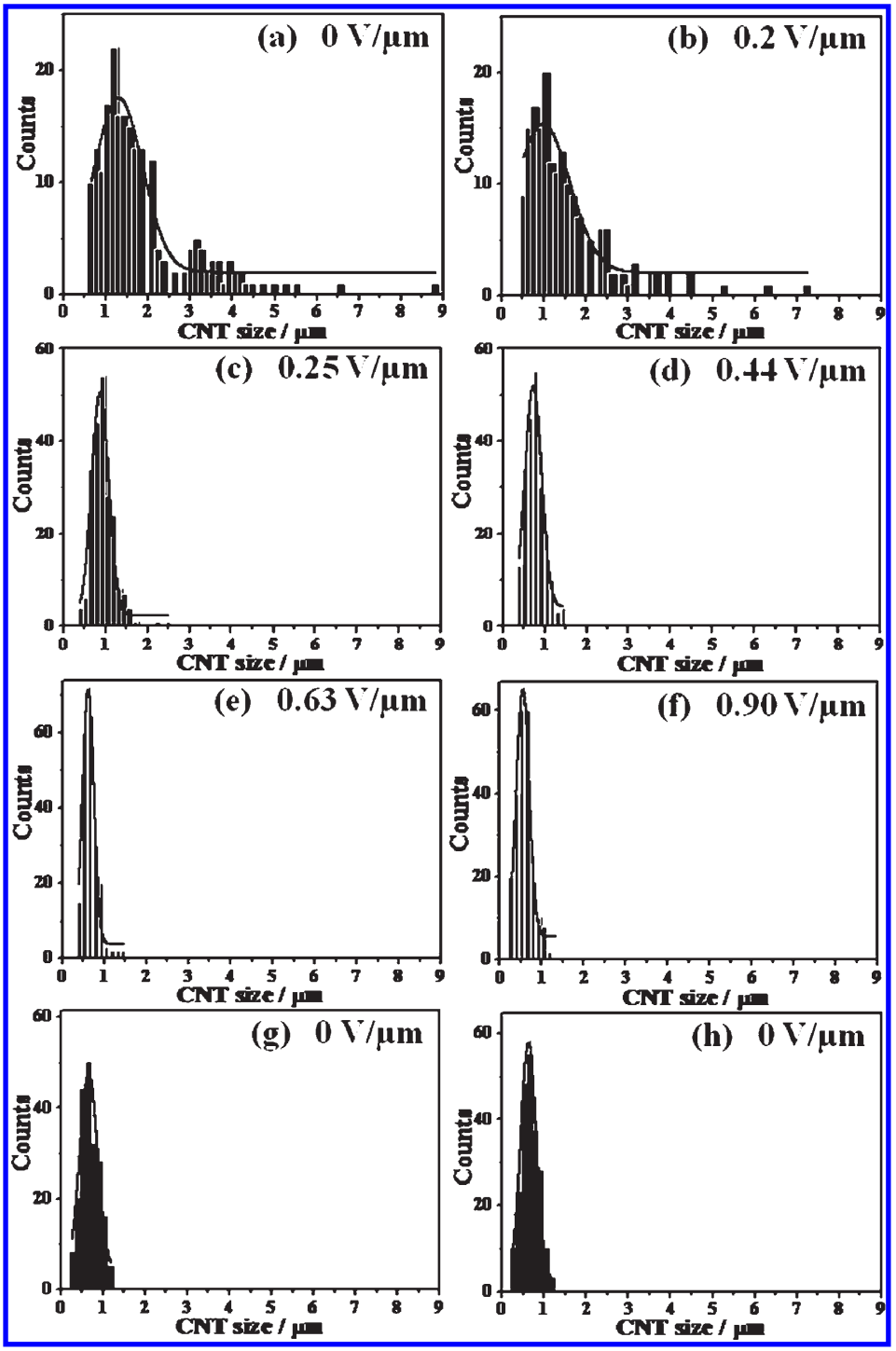

Figure 2. Size distributions of CNT clusters of CNT-LC cell that correspond to optical microphotographs of Figure 1.

The ethanol solvent was removed using a solvent evaporator kept at 70 °C.

The CNT−LC mixture with a CNT concentration of 0.1 wt % was further ultrasonicated at 40 kHz for 1 h to promote dispersion. This procedure helps to reduce the bundling of nanotubes and thus enhances CNT solubility. The CNT-LC mixture was then filled immediately into homogeneously aligned LC cell of 80 μm cell gap by the capillary action at room temperature. The cell for present investigation consists of transparent indium-tin-oxide (ITO)-coated glass substrates. As an insulator, a thin homogeneous polymer alignment layer viz. SE-6514 (Japan Synthetic Rubber) was spin-coated onto the ITO-coated glass substrates, followed by soft baking at 70 °C for 5 min and hard baking 200 °C for 1 h. The electro-optical textures of the cell were observed by an optical microscope (OM, Nikon DXM1200) while applying sinusoidal ac field (60 Hz) to the test cell. The size distribution of the CNT clusters was determined from 200 sampling in the area of 118 × 95 μm^2. The intensity of transmitted light has been recorded with the help of IMT *i*-solution software (Image & Microscope Technology, Princeton, NJ).

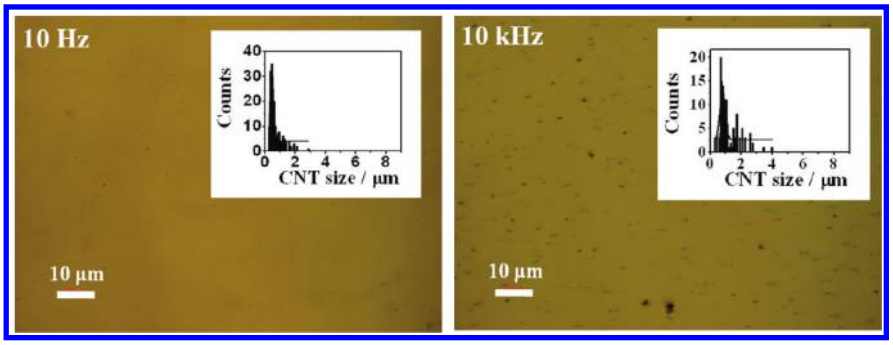

Figure 3. Optical microphotographs of CNT-LC mixture in the field off state after application of 2.1 V/μm field with driving frequency 10 Hz (a) and 10 kHz (b), respectively. The insets of corresponding Figures show the histogram analysis of the MWCNTs cluster sizes; least-squares fitted with Gaussian distribution function.

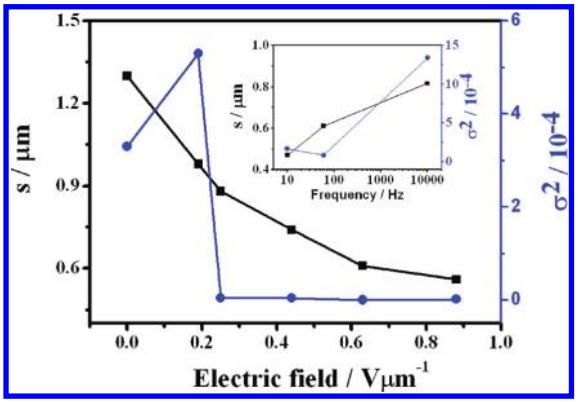

Figure 4. Variation of the mean size and distribution width of CNT clusters as a function of electric field strength. The inset shows the mean size and distribution width as a function of frequency of applied AC field after high field treatment in the field off state.

3. RESULT AND DISCUSSION

Figure 1 shows the optical microscopic images of MWCNT-doped LC medium with gradually increasing ac electric field strength. The corresponding figures clearly depict the homogeneous distribution of CNT agglomerates and also the cluster size appears to be reduced with increasing field. Figure 1g,h shows the textures of the same location of the sample right after the field and after 48 h with the field-off, respectively. No appreciable difference was observed between two states, indicating that the clusters are permanently deformed with field. Interestingly, the sizes of CNT clusters shown in Figure 1g,h are much smaller than those of the initial CNT−LC mixture.

The optical microscopic textures have been analyzed, and the corresponding cluster's size distribution up to the least detectable length scale under optical microscopic (0.2 μm) is depicted in the histogram in Figure 2. The illustrated histograms have been analyzed by statistical probabilistic approach. Gaussian distribution has been used in our case as a first approximation, which tends to cluster around a single mean value. The Gaussian distribution function is expressed as follows

$$y = y_0 + \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-(x-s)^2/2\sigma^2\right) \quad (1)$$

where y_0 is a scale factor and s is the mean (location of the peak) and σ^2 is the variance (the measure of the distribution width). The continuous line over respective histograms shown in Figure 2a−h depicts the best-fit curves in accordance with eq 1. The pristine sample without field shows the CNT mean cluster size of ∼1.3 μm. However, the size distribution of CNT clusters appears to vary noticeably as the field strength increases. The mean value of the cluster size was found to be decreased with increasing field strength. The mean size of CNT clusters after application of 2.1 V/μm field is reduced to ∼0.6 μm. More importantly, when turning off the voltage after high electric field treatment of ∼2.1 V/μm, the dispersed CNTs (Figure 1g) do not show reaggregating tendency even after sufficiently long time of 48 h (Figure 1h). Corresponding histogram analysis results are shown in Figure 2g,h. The mean size of CNT aggregates remains unchanged at ∼0.6 μm. Note that the concentration of the modified t-MWCNT in LC for the present investigation is significantly larger than the usual percolation limit of CNTs in nematic CNT−LC mixture.[19] This resulted in the formation CNT clusters in our cell. It has been known that nematic LC molecules interact strongly with CNT surface via $\pi-\pi$ stacking.[20] When the entangled CNT clusters are outstretched by the strong electric field, the exposed CNT surface enhances to anchor LC molecules, thus preventing CNTs from being reaggregated to form clusters back. These results are remarkable because the percolation limit of CNTs in LC medium can be overcome to increase CNT concentration.

Figure 3 shows the optical microscopic images of MWCNT-doped LC medium subjected to noticeably low ∼10 Hz (Figure 3a), and significantly high ∼10 kHz (Figure 3b) AC frequency in the field off state after application of 2.1 V/μm field, respectively. The homogeneous distribution of CNT agglomerates along with variation in cluster size as a function of frequency is evident. Corresponding distribution of MWCNT cluster sizes has been depicted as insets of respective figures with least-squares fitting following eq 1. The average cluster sizes of MWCNTs are found to be at ∼0.5 and 0.6 μm, respectively, for 10 and 60 Hz driving frequency; however, it increases to ∼0.8 μm for 10 kHz driving frequency. We have also investigated the textures of the same locations of the samples right after application of electric field and after 48 h with the field-off states, similar to previous investigations and confirmed the dispersion stability (figure not shown).

The graphical variation of mean and variance as a function of applied electric field strength and frequency of AC field is shown in Figure 4. The mean of cluster size is electric field strength-dependent and is reduced rapidly after some threshold field, in this case, 0.25 V/μm. The variance gradually decreases as the field strength increases. This implies that large-size clusters have

a tendency to be disrupted by the field. The observed phenomenon can be explained by taking into account the large induced dipole moment in CNT clusters due to their high aspect ratio[21] and dielectrophoretic properties.[6,18] The individual CNTs in aggregates are aligned along the field direction to minimize the dipolar energy. Clusters are stretched by the field against van der Waals forces between individual CNTs. When the external field exceeds van der Waals interaction of CNTs, the cluster starts to slide out of the large-size bundles and dissociate into small sizes above a critical field. Hence the net force applied to CNT bundles is represented by

$$\vec{F}_{\text{elec}} = q\vec{E} + (\vec{p}\cdot\vec{\nabla})\vec{E} \quad (2)$$

where q represents the induced charge, ∇ is a del operator, and $\vec{p}$ is the equivalent induced dipole moment. The first term $q\vec{E}$ describes the columbic interaction between the induced charges over CNT clusters and applied external field. The additional force term $(\vec{p}\cdot\vec{\nabla})\vec{E}$ arises from interaction of dielectric polarization component induced in the particle by electric field with spatially inhomogeneous field.[18] According to the effective dipole method, the dielectrophoretic force on a particle can be approximated as the dot product of the equivalent dipole induced on the particle $\vec{p}$ with the gradient of the applied electric field, $\nabla\vec{E}$. The importance of dielectrophoretic force over the cluster size distribution becomes noticeable through the frequency-dependent investigations. The MWCNTs clusters undergo

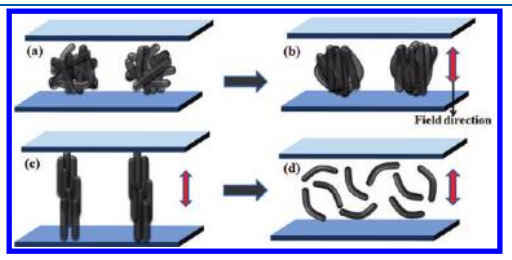

Figure 5. Schematic diagram showing dispersing behavior of CNT cluster in the cell in the presence of applied ac field. (a) Field off state, (b) CNT was reoriented with field direction, (c) individual CNTs could be extracted out from bundle or CNT cluster, and (d) dispersion of the CNT cluster.

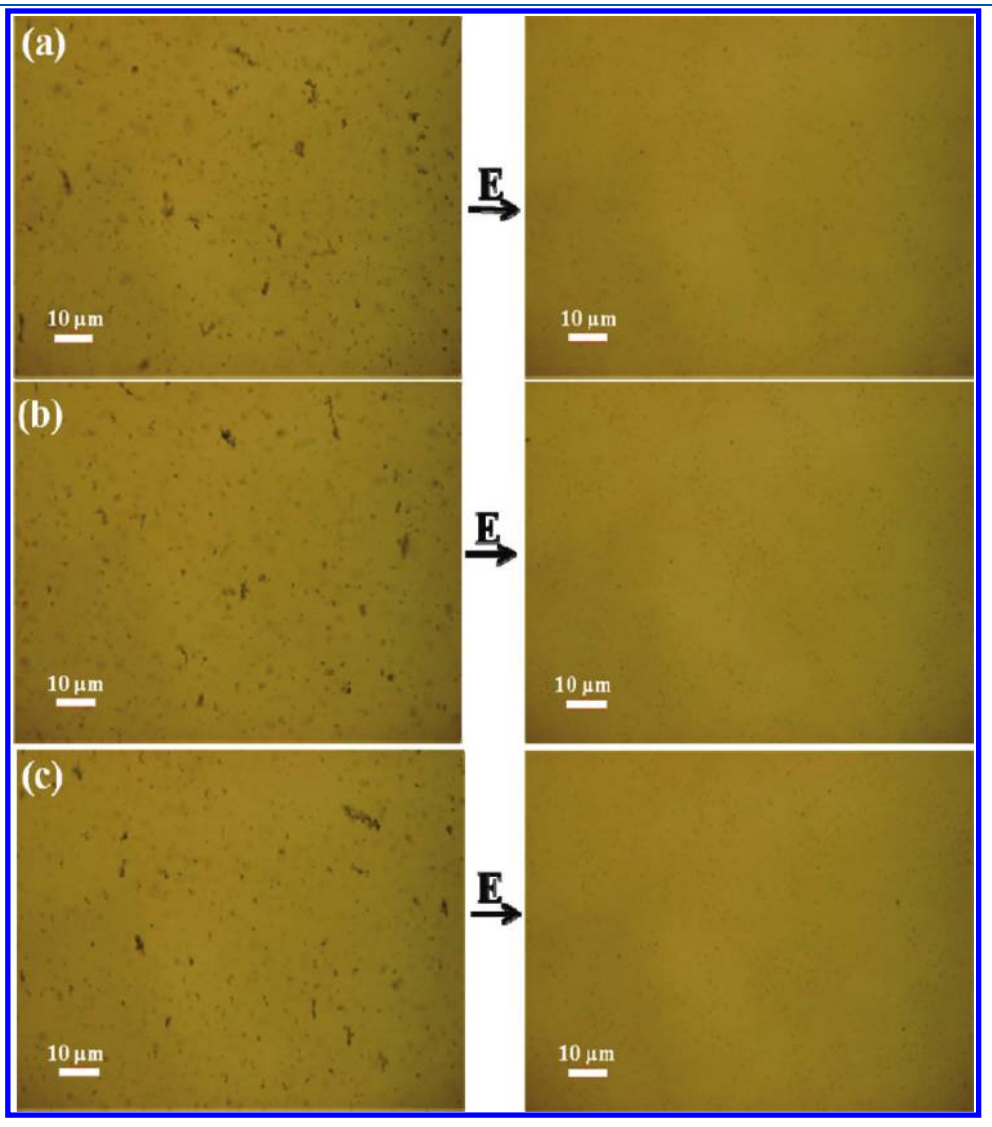

Figure 6. Optical microphotographs of CNT-LC cell in different areas (a−c) before and after electric field.

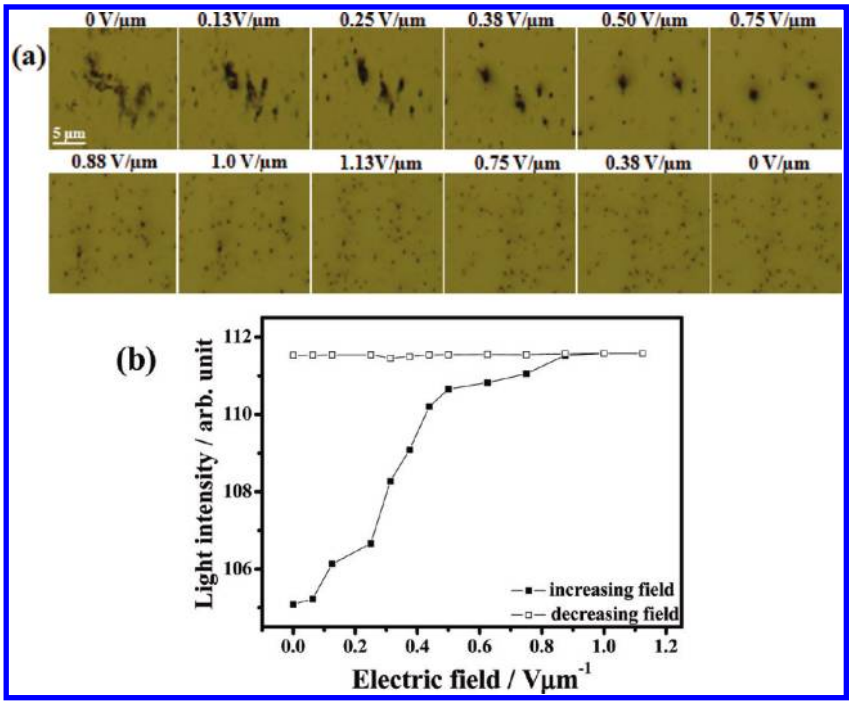

Figure 7. Optical microphotographs (a) and transmitted light intensity (b) of CNT clusters in LC medium with respect to applied electric field.

dielectrophoretic force-driven movement in between the top and bottom substrates of the test cells while subjected to low frequency and sufficiently high electric field.[6] However, when the frequency is sufficiently high, dielectrophoretic force driven movement of MWCNT clusters almost vanishes. Considering $\pi-\pi$ stacking between head part of LC molecule and CNT wall, the MWCNT clusters do not have to undergo repeated medium (LC)-induced frictional effect in higher frequency, which is quite obvious in lower frequency. Hence, lower frequency driving was found to be more effective in the process of dispersion of MWCNTs clusters in LC medium.

In the absence of electric field, the CNTs are entangled in the form of bundles due to strong van der Walls interaction, as shown in Figure 5a. Applied electric field induces fast reversing equal and opposite charges in the terminal of CNTs. Therefore, above a certain field, columbic interaction $(q\vec{E})$ overcomes van der Waals forces, and the clusters are oriented to the direction of the field to increase dipole energy (Figure 5b). With further increase in field, the CNTs are likely to be charged because of charge transfer that takes place between CNT and LC molecules.[20] The charge transfer is more severe for those CNTs outside the cluster that interact heavily with the adjacent LC molecules. These CNTs will be forced to stretch out by the external field and will be separated if the Coulombic force $(q\vec{E})$ overcomes van der Waals force between CNTs (Figure 5c). Applying a certain high electric field (breakdown field), the columbic interaction $(q\vec{E})$ crushes the chain between CNTs by overcoming the van der Walls interaction, and hence CNT aggregates are fragmented into small pieces, as shown in Figure 5d. Consequently, CNT aggregates were effectively dispersed because of the application of strong electric field.

To investigate the homogeneity of dispersion as the effect of high electric field over CNTs aggregates, we have captured a series of images under optical microscope from different areas of the cell, as shown in Figure 6a−c. The sizes of the CNT aggregates of different areas shown in the left optical microscopic images are large enough to be seen in the field-off state. However, the sizes shown in the right optical microscopic images become significantly smaller (<1 μm) after high electric field treatment, The mean cluster size is found around 1.1 μm initially, which is downshifted to 0.6 μm despite the presence of CNTs in the mixture in excess of previously reported percolation limit.[19]

Figure 7a shows the electric-field-induced variation in optical microscopic images of one area of the cell with significantly large CNT cluster that strongly absorbs an incident light. With increasing applied electric field, the decrease in darkened area is clearly visible. This further confirms the phenomenon, as discussed in the above section. The optical transmittance has been measured locally on regions surrounding CNTs clusters in $\sim$12 μm $\times$ 12 μm area from optical microscopic images using *i* solution image analysis software. Figure 7b depicts the electric field dependence of transmitted light intensity surrounding CNT agglomerate for the CNT−LC mixture. Initially, transmission intensity is low because most of the transmission is blocked by a significantly large area covered by CNT cluster. As the area covered by CNTs cluster decreases with the increasing applied field, the transmission gradually increases, indicating reduction in size of CNT cluster with increasing electric field. Note that the contribution of the LC to the overall light intensity is negligible because homogeneously aligned NLC with negative dielectric anisotropy used for this investigation, which does not reorient under applied electric field. More importantly, the change in transmission was found to be irreversible as a consequence of occurrence of irreversible changes in CNT cluster morphology. Hence, the present investigation supports the dispersion capability of applied electric field as per our previous demand. Consequently, this change of light intensity under electric field also provides us a promising method for making new dynamic light modulator.

4. CONCLUSIONS

We have demonstrated strong AC electric field and frequency-dependent dispersion phenomenon of MWCNT clusters in LC medium. The amount of dispersed nanotubes is higher than previously reported percolation limits in LC mixture. The dispersion process is found to be stable even after a sufficiently long time interval of electric field treatment such that the CNTs do not show reaggregating tendency in LC matrix. A competitive interplay of intra CNT van der Waals interaction and electric-field-induced outstretching Coulomb force allows us to stretch CNT clusters in the applied electric field direction. Hence, whereas the entangled CNT clusters are outstretched by the strong electric field, the exposed CNT surface enhances anchoring of LC molecules due to $\pi-\pi$ stacking, preventing CNTs reaggregation and assuring dispersion stability. The importance of dielectrophoretic force over MWCNTs dispersion in LC medium has also been explored. Highlighting a comparatively darker area in the cell with high MWCNT cluster density, we have furthermore depicted the improvement in transmitted light intensity as a function of applied electric field, and the change is found to be irreversible as a signature of electric-field-induced dispersion of MWCNT in nematic LC host.

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