Anomalous Electrokinetic Dispersion of Carbon Nanotube Clusters in Liquid Crystal Under Electric Field

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An anomalous electrokinetic dispersion after contraction of carbon nanotube (CNT) cluster suspended in a vertically aligned nematic liquid crystal (LC) cell is demonstrated. CNT aggregates were firstly aligned toward the field line by dielectrophoretic (DEP) torque and secondly they were elongated above a certain threshold field due to interaction between the induced dipole moment of CNTs and external ac electric field. Below a certain breakdown field, the original morphology of the CNT aggregates was restored after the removal of the field where the elongation was fully reversible. Above breakdown electric field, CNT aggregates were ruptured and fragmented into small pieces and consequently CNTs were well dispersed in LC medium.

Keywords: Carbon Nanotube, Stretching, Dispersion, Liquid Crystal.

1. INTRODUCTION

The unique structural identity and outstanding electrical and mechanical properties of carbon nanotubes (CNTs) make these systems promising candidates for next generation nano devices. Indeed, many prototype CNT-based devices such as field-effect transistors, room temperature rectifiers, memory devices, electron field emitters, sensitive gas detectors, and nanoscale rotational actuators and motors have already been demonstrated. Although tremendous progress has been made towards understanding the properties of individual CNTs, investigating the bulk anisotropic properties and utilizing them for practical applications have been hindered by the lack of materials with controllable degree of alignment. A uniform alignment is often essential, and in general the ability of aligning nanotubes in a predetermined direction is of great importance. In spite of several approaches that have been developed for aligning CNTs during growth and post growth, the post-growth manipulation is still a fundamental issue. Though some of the post growth manipulation methods available today provide a good way to control both alignment and orientation of CNTs, manipulation of the whole agglomerated CNTs for nano/micro actuator applications is still a Herculean task.

In our earlier work, we have reported super elongation of CNT clusters suspended in nematic LC mixture in the field direction. Not only manipulation of individual CNTs and clusters, but a complete dispersion of CNTs in liquids is also vital for many applications in particular for composites and nanoscale molecular devices. In spite of our extreme efforts to completely disperse the CNTs in LC to study the electro optic properties of CNT doped LC cell, a few agglomerates of CNTs were seen in the LC especially when the doping amount of CNTs exceeds the critical weight percent. In the present work, we demonstrate an unusual initial contraction of CNT aggregates and subsequent dispersion at higher applied fields.

2. EXPERIMENTAL DETAILS

The superfluorinated nematic LC mixture employed in this study was purchased from Merck and used as received. Its physical properties are listed as follows: dielectric anisotropy $\Delta e = 7.4$, birefringence $\Delta n = 0.088$ at the incident light wavelength $\lambda = 589$ nm, and nematic phase between $-40$ and $87 ^\circ$C. The LC cell consists of two...
glass substrates of which the inner surfaces are coated with a thin and transparent indium-tin-oxide (ITO) electrode. To achieve a vertical alignment, a thin polyimide layer (AL-60101 from Japan Synthetic Rubber Co.) was coated on the ITO-glass substrates.

The thin multi-walled CNTs (t-MWCNTs) were synthesized by the catalytic chemical vapor deposition using FeMoMgO catalyst. The t-MWCNT had a number of tube walls of 2~6 with the corresponding diameters of 3~6 nm, an inner diameter of 0.7~2.6 nm. The t-MWCNT sample was shortened by chemical cutting using H₂SO₄/HNO₃ (3:1). Through filtering with deionized water (pore size = 0.45 μm) and centrifuging in dichloroethane (DCE) solvent (at 8000 rpm for 30 min), the processed t-MWCNT had an average length of 250 nm. Figure 1 shows the length distribution of the processed t-MWCNTs obtained by the dynamic light scattering (Photal ELS-8000, Otsuka Elect.). The maximum peak was located near 250 nm with rather wide distribution up to nearly 1 μm. Some long t-MWCNTs were still retained even with strong acid treatment by H₂SO₄/HNO₃. This was removed by centrifugation. The dispersion stability was significantly improved with negligible precipitates. Nevertheless, some aggregates of t-MWCNTs were still formed after evaporation of solvent in the cell.

The t-MWCNTs in a powder type were not dispersed instantly in LC medium. In order to disperse t-MWCNTs in LC medium, 10⁻² wt% of t-MWCNTs was dissolved into DCE solvent, followed by mixing with nematic LC. The amount of weight percentage of t-MWCNTs was determined by measuring the remaining CNTs on the filter and very nominal amount of CNTs was found to be altered after centrifugation. If the proper conditions such as sonicating time and power were not satisfied, t-MWCNTs would aggregate themselves during the dispersion process. After the solvent evaporation, we measured the clearing point of LC mixture to confirm the solvent evaporated perfectly. This gave rise to the same clearing temperature as the pure LC. The t-MWCNT-dispersed LC mixture was thoroughly sonicated for an hour and filled into the LC cell by capillary action at room temperature. Without further treatments, the vertical LC alignment was achieved in the cell with a 60 μm cell gap in most of parts but some areas do not show vertical alignment due to CNT clusters.

Polarized optical microscope (POM, Nikon L-UEPI, Japan) with a digital camera (Nikon DMX1200, Japan) was utilized to observe the change in CNT cluster shape responding to the applied electric voltage of the sinusoidal waves with 60 Hz.

3. RESULTS AND DISCUSSION

Most of the CNTs introduced in the cell are dispersed by the dispersion processes discussed in the experimental section and are found to align in the LC director direction due to the self aligning property of the LC molecules even when the cell is not subjected to an applied field. However, a few undispersed CNT clusters were present in the LC medium due to its pronounced agglomeration tendency which is a major drawback in the utilization of CNTs as a bulk material, especially when the CNT is doped into the nematic LC mixture more than 10⁻² wt%. The CNTs in these clusters can not be easily manipulated due to the intermolecular van der Waals forces between the CNTs.

When the cell was subjected to applied ac field, the CNT clusters were found to be undisturbed until a threshold voltage of 30 V is reached. Beyond this voltage, an interesting phenomenon of contraction in width of CNT clusters was observed in homeotropically aligned cell, as shown in Figure 2. The cross sectional area of the cluster measured from its mean length and width at 100 V showed that the cluster area decreased to 82% of its original size. On gradual decrease of field below 100 V, the contracted CNT cluster was found to recover its original size. The field-dependent contraction is attributed to an aligning and stretching of the CNT cluster in the field direction. In our earlier experiment with a homogeneously aligned cell driven by in-plane field we have demonstrated the electroactive elongation of the CNT cluster which supports our logic that the observed contraction is due to stretching of cluster in the direction of applied field in a vertically aligned nematic cell. To measure the extent of contraction, the percentage of compression strain was calculated using the relation Strain% = (Δa/a) x 100, where Δa is the difference in the cluster area before and after application of field and a is an original cluster area. The increase of strain percentage as a function of applied voltage is shown in Figure 3. The CNT cluster was found to lose its contracting behavior beyond 100 V and dispersed completely when a high voltage of 140 V was applied.

Having now confirmed that the observed contraction and expansion of the CNT clusters is due to the stretching of CNT clusters in tune with the applied field in the
LC medium, it is of interest to understand the observed results within the context of a simple mechanism which may enable the design of improved nano- and micro-electromechanical systems. In the present investigation, the overall contraction which is viewed as stretching of CNTs in the field direction is explained using dielectrophoresis. Dielectrophoresis is a non contact manipulation technique with a high spatial resolution, becoming increasingly popular because of the high degree of controllability and the low equipment costs involved. The observed contraction of the CNT cluster might be understood as follows.

Firstly the polarizable CNT cluster in the vertically aligned LC cell is aligned and translated along the field direction by dielectrophoretic torque and force, respectively. Secondly the CNTs moved in the field direction are chained by inter CNT (dipole–dipole) interactions. To understand CNT alignment with electric fields, we consider an effective dipole moment \( (P) \) of a CNT induced by an applied field \( E \),

\[
P = \alpha E
\]

where \( \alpha \) is the polarizability\(^{35} \)

\[
\alpha = \frac{V(\epsilon_2 - \epsilon_1)}{1 + \left[ (\epsilon_2 - \epsilon_1) / \epsilon_1 \right]} L
\]

where \( V = \pi r^2 l \) is the volume of the CNT and \( L = (4\pi r^2 l^2) [\ln(l/r) - 1] \) is the depolarization factor along the tube axis, \( \epsilon_2 \) and \( \epsilon_1 \) are permittivities of the CNT and LC medium, respectively, and \( l \) and \( r \) are the length and radius of the CNTs, respectively. Substituting Eq. (2) into (1), we get

\[
P = \frac{V(\epsilon_2 - \epsilon_1)E}{1 + \left[ (\epsilon_2 - \epsilon_1) / \epsilon_1 \right]} L
\]

For a nanotube oriented at an angle \( \theta \) with respect to \( E \) (see Fig. 4), unless \( \theta \) is close to 90°, the induced dipole moment along the long axis of CNTs can be written as

\[
P = \frac{V(\epsilon_2 - \epsilon_1)E \cos \theta}{1 + \left[ (\epsilon_2 - \epsilon_1) / \epsilon_1 \right]} L
\]

The torque on the dipole moment is given by\(^{35} \)

\[
\tau = |P \times E| = F_t \times l = \frac{V(\epsilon_2 - \epsilon_1)E^2 \sin 2\theta}{2[1 + \left( (\epsilon_2 - \epsilon_1) / \epsilon_1 \right)] L} \]

where \( F_t \) is the force applied on the CNT dipole to rotate and align the tubes along the field direction. The torque exerted on CNTs in the cluster oriented at different angles from 90° showed that the maximum torque is exerted on CNTs oriented at 45°.
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After being aligned in the field direction, the CNTs in the host medium, they experience the force $F_{\text{elec}}$ to the field direction,

$$F_{\text{elec}} = -qE + p\nabla E$$

(6)

The first term $qE$ describes the columbic interaction between the charges of particles and external field. The additional force term $p\nabla E$ arises from interaction of dielectric polarization component induced in the particle by electric field with spatially inhomogeneous field.36 Up to a voltage of 30 V (threshold voltage), the CNT aggregates are in the form of bundles due to strong van der Waals interaction energy, as shown in Figure 5(a). The contraction in the width of CNT aggregate takes place above the threshold voltage. Above threshold voltage, the DEP force overcomes van der Waals force and some of the CNTs slide toward the electric field direction by overcoming van der Waals interaction between CNTs in the aggregate. If the field is removed, the CNTs slide back to their original morphology due to strong van der Waals interaction energy, which is similar to the ‘sword in sheath’ phenomenon.37 The CNTs are contracted only up to certain breakdown voltage (100 V). Because of the induced dipole of CNTs, one end of the CNT along the field direction will have positive charges, while the other end will have negative charges. Therefore after sliding, the positive and negative induced charges come closer to each other. Hence they are interconnected with each other due to electrostatic Coulomb force, whereas DEP at this stage stretches the CNTs in the field direction (Fig. 5(b)). With further increase of the field, some of CNTs again slide from its aggregate due to DEP force and interconnection between them takes place. This leads to the formation of series of chains of CNTs along the field axis and hence the width of the CNT aggregate is contracted (Fig. 5(c)). In the voltage range of 100–140 V, the DEP force competes with electrostatic Coulomb force between charges in CNTs and CNTs finally get ruptured. Above 140 V, the DEP force crushes the chain between CNTs by overcoming the Coulomb force and hence CNT aggregates are fragmented into small pieces. Consequently, CNTs are dispersed into the LC medium as shown in Figure 5(d). Different forces dominate in three different voltage ranges. From 0–30 V range, van der Waals force is dominated to form cluster. Above 30 V, the DEP force overcomes van der Waals force and the width of the CNTs starts contracted. In voltage range of 30–100 V, electrostatic Coulomb force and DEP force are effective to cause the chaining and stretching of CNT cluster in the field direction. In the voltage range of 100–140 V, the DEP force competes with Coulomb force. Above 140 V, the DEP force breaks the CNT cluster into small pieces. Consequently CNTs are dispersed in the host LC medium.

Furthermore, the strength of the dipolar intermolecular particles, i.e., intermolecular CNT attraction relative to thermal agitation may be characterized by the unitless chaining parameter39

$$\lambda = \frac{\pi}{2} \varepsilon_0 \varepsilon_1 a^3 (\beta E)^2 / k_0 T$$

(7)

where $a$ is the particle radius, $\varepsilon_0$ is the permittivity of free space, $k_0$ is the Boltzmann’s constant and $T$ is the absolute temperature. In general, dielectric permittivity of CNT ($\varepsilon_1$) is far greater than the permittivity of the nematic LC ($\varepsilon_2$), therefore $\beta = (\varepsilon_1 - \varepsilon_2)/(\varepsilon_2 + 2\varepsilon_1)$, which is the particle dipole coefficient can be approximated to be $\sim 1$. For the present system, since the inclusion is a cylindrical nanotube, the effective radius of the inclusion $a$ may be
replaced by the radius of gyration ($r_g$) of the nanotube. Considering the most probable length of the nanotube ($l$), if 250 nm and the radius ($r$) of the nanotube is about 3 nm in the present case and assuming that the nanotube is a rigid cylinder, the radius of gyration of the nanotube is given by.

$$a = r_g = \left(\frac{r^2}{2} + \frac{l^2}{12}\right)^{1/2} \approx \frac{l^2}{12} \approx 72.17 \text{ nm}$$

To achieve chaining and stretching, the parameter $\lambda$, which is the ratio of polarization energy to thermal energy, must be greater than one. To gain insight into the interaction that enables the growth of these CNT interconnects, we estimated $\lambda$. Typically, for a field range of 0.5 V/μm to 1.66 V/μm, which is exerted on the CNT and keeping the other values as $T = 290$ K, $r_g = 72$ nm, $\beta = 1$, and the average relative dielectric permittivity $\varepsilon_r = 5.86$ for the LC medium, we find that the value of $\lambda$ is greater than one (1.9 to 20.81) throughout the experimental field range. A significantly high $\lambda$ value (more than ten) for higher fields demonstrates the chaining of CNTs and hence stretching of CNT cluster is highly feasible in the present setup.

4. CONCLUSIONS

In conclusion, we have demonstrated the contraction of CNT clusters in a vertically aligned nematic LC cell in the presence of applied ac field. The CNT cluster undergoes: (1) the alignment of CNTs in the field direction due to DEP torque, (2) translation of CNTs in the field direction due to DEP force, (3) chaining and stretching of CNTs by intermolecular CNT interactions due to induced dipole moment and DEP force, respectively, and (4) CNT cluster is ruptured and subsequently dispersed into the LC medium due to DEP force. The chaining parameter which measures the magnitude of stretching of CNT cluster was found to be more than ten for higher applied fields, indicating that the CNT cluster can be stretched continuously as the field increases up 1.66 V/μm. Our present work highlights the activator-like behavior of CNTs at low fields and a peculiar field-induced dispersion of CNTs in LC at higher fields.

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References and Notes

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