

Electroactive Superelongation of Carbon Nanotube Aggregates in Liquid Crystal Medium

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ABSTRACT

We report an effect of superelongation of carbon nanotube (CNT) aggregates driven by the electric field in a liquid crystal (LC) medium. The CNT aggregates started to elongate above a certain threshold field and sustained the elongation up to nearly 400% in the linear region with a large electroactive constant of $70 (\text{V}/\mu\text{m})^{-1}$. The original morphology of the CNT aggregates was restored upon removal of the field. The elongation was fully reversible below a certain breakdown field, irrespective of the nematic or isotropic phase of the LC medium. The overall process involved (i) the alignment of CNT aggregates to increase the dipole energy of aggregates in the presence of the bias voltage, (ii) stretching of the CNTs by sliding-out from the bundles, and (iii) the entropic elasticity that restores the randomly entangled CNT network of the original aggregates after suppression of the bias voltage.

Carbon nanotube (CNT) is a multifunctional nanomaterial that possesses excellent electrical, mechanical, thermal, and optical properties. Semiconducting CNTs have been utilized for the fabrication of nanotransistors and gas sensors with high selectivity.^{1,2} Because of CNT's peculiar geometry with unusually high aspect ratio and a nanometer scale diameter, it is possible to realize high emission current electron sources, which opens up several application areas in field emission displays and X-ray current sources.^{3–5} New concepts of nanobalance, nanotweezer, nanoactuator, and nanobearing/spring have been studied at laboratory levels.^{6–9} Recently, the CNT filters have been used for seawater desalination and petroleum and water filtration.^{10,11} These new findings provide potential opportunities for industrial applications.

In this Letter, we report a new phenomenon of superelongation of CNT aggregates under high electric field. This was realized by dispersing CNTs in a LC medium. Some of the CNTs that were not well dispersed were aggregated into clusters with sizes of a few micrometers or even greater. These clusters have been elongated along the direction of

the electric field when a bias above some threshold voltage was applied. The elongation reached up to 400% with fully reversible elongation and contraction. This procedure is similar to the elastomeric behavior of rubber. On the other hand, our CNT cluster gave rise to a large electroactive constant of $70 (\text{V}/\mu\text{m})^{-1}$, much larger than the typical value for electroactive polymer materials.

Thin multiwalled carbon nanotubes (t-MWCNTs) were synthesized by a catalytic chemical vapor deposition (CCVD) method using FeMoMgO catalysts prepared by a combustion method. The outer diameter of the pristine t-MWCNTs ranged from 3 to 6 nm with typical lengths of several μm . The metal content with MgO supporters of the pristine sample was extremely low, around 3.5 wt %, due to the high efficiency of the nanotube production method. This has been described in detail elsewhere.¹² Because the volume ratio of the metal content to the nanotube was much smaller than the corresponding mass ratio, this as-grown sample was directly used without further purification for this study. The t-MWCNT powders of 10 mg were dispersed in dichloroethane (DCE) of 100 mL by sonication for 24 h. The supernatant was decanted after centrifugation at 15 000 rpm for 30 min. The CNT lengths in the supernatant after

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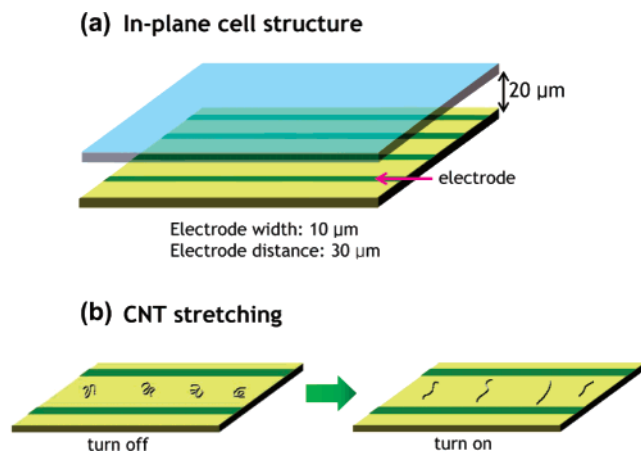


Figure 1. (a) Schematic structure of the in-plane liquid crystal cell. The electrodes (colored green) were laid on bottom substrate. (b) Schematic illustration of the stretching of the CNT aggregates by applied voltage.

centrifugation ranged from 0.1–1.5 μm and the most probable length was 250 nm.

The supernatant with a CNT concentration of 20.6 $\mu\text{g}/\text{mL}$ was poured into a nematic LC solution (superfluorinated LC mixtures used generally in thin-film transistor LC displays from Merck-Japan with the following physical properties: dielectric anisotropy $\Delta\epsilon = 7.4$, birefringence $\Delta n = 0.88$ at $\lambda = 589$ nm, clearing temperature of 87 $^{\circ}\text{C}$ with a nematic phase down to -40 $^{\circ}\text{C}$). After sonication of this mixture for 10 min, the DCE solvent was then removed using a rotary evaporator. The 0.01 wt % t-MWCNT/LC solutions were further sonicated for 10 min. This concentration was higher than that of the typical approaches.¹³ Thus, the aggregates of CNTs with different sizes were often observed. Because the carbon nanotubes were conductive, the conductivity of the LC cell can be increased slightly, especially at high CNT concentration.¹⁴ The effect of operation voltage and charge trapping by the CNT doping has been described elsewhere.^{13,15}

In-plane cells with homogeneous alignment, driven by in-plane electric field, were fabricated using alignment layers of AL16139 (Japan Synthetic Rubber Co.). For in-plane cells, the electrodes exist only at one substrate, with an electrode width of 10 μm , a distance of 30 μm between them, and a cell gap of 20 μm , as shown in Figure 1a. The in-plane cells were then filled with the CNT/LC mixture through a capillary process at room temperature. The electro-optical textures of the test cell were observed by the optical polarizing microscope (Nikon DXM1200) by applying either a sine wave or a direct current. The LC director was aligned initially parallel to the in-plane field, and thus the LC director between electrodes does not rotate under the field. Our interest is in the electrical response of nanotube aggregates. In the presence of an external field, the CNT aggregates are expected to be aligned and stretched, particularly at high field, as shown in Figure 1b.

At a high CNT concentration of 0.01 wt % in LC medium, the CNT aggregates were often observed with different size distribution. This was attributed to the CNTs that were not

well dispersed in LC medium in spite of our dispersion efforts described above. These aggregates were visible with the optical microscope even without a polarizer due to the different refractive index of CNTs from the host LC medium. Figure 2 shows photographs for the time evolution of one typical CNT aggregate observed with the optical microscope without a polarizer when a sine wave voltage of 145 V at 60 Hz was applied in a nematic phase between two consecutive electrodes. The CNT aggregate started to elongate along the field direction within a second. When the voltage was turned off, the morphology of the CNT aggregate was fully recovered to its original shape within a time scale similar to the turn-on process. The elongation of the CNT aggregates was observed above some threshold voltage. The threshold voltage varied with the size of the aggregate. A similar phenomenon was also observed in the isotropic LC phase. This implies that the elongation of the CNT aggregate is not associated with the alignment of the LC director. This phenomenon could be observed in any liquid medium. It should be emphasized that the effect of stretching of CNTs has not been reported so far, although CNTs could be aligned along the direction of the applied field by the induced dipole moment.¹⁶

Figure 3 presents the voltage dependence for the elongation of the CNT aggregate. Up to 110 V, an arbitrary shape of the CNT aggregate was retained without an appreciable stretching. Above this threshold voltage, the CNT aggregate kept extending. At 170 V, the CNT aggregate was elongated up to 400% of the original size, along the direction of the field in the linear region. On the other hand, the width of the CNT aggregate became narrower. It is noted that the CNT aggregate moved translationally in a random fashion under the sine wave voltage in addition to the elongation. This translational motion could be related to the charge trapping on the nanotubes such that the CNT aggregate could have a net charge.^{17–19} Additional evidence that the CNT aggregate was charged was a ballistic motion of the CNT aggregate along the field direction when the dc field was applied. It is also interesting to note that, above some breakdown voltage value, the CNT aggregate was fragmented into small pieces such that they were hardly visible through the optical microscope (Bear in mind that the resolution of the microscope is ~ 1 μm). This provides one way of dispersing CNT aggregates into small sizes by using a strong external field.

Figure 4 presents the change of the length and width of the CNT cluster with applied voltage. The voltage was limited below the breakdown value. Because the total volume of the CNT aggregate is presumably constant, its length increases while its width decreases with changing field due to the conservation of volume. When the width was reduced to 1 μm or less, the changes between voltages were indistinguishable due to the limit of resolution in optical microscope. The measured ratio of the length strain to the width strain was -6.26 in the linear region. With a simple cylindrical model for the CNT aggregate ($V = \pi r^2 l$), where V is the cylinder volume of the CNT aggregate, and r and l are the radius and length of the CNT aggregate, respectively, and the theoretical value for the strain ratio $(\Delta l/l)/(\Delta r/r)$ is

In-plane field 145 V (AC, 60 Hz)

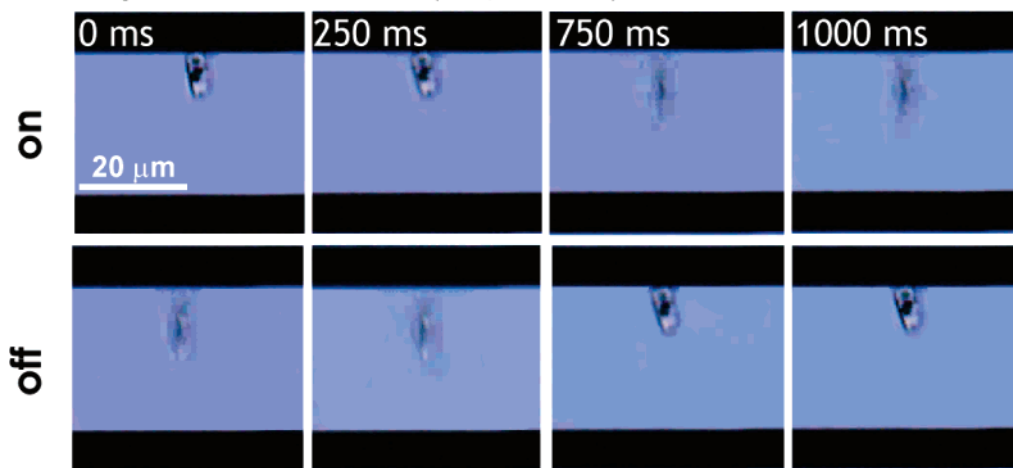


Figure 2. Time-evolution of one CNT aggregate in LC cell within 1 s during (a) turn-on and (b) turn-off voltages with the optical microscope. The CNT aggregate was positioned between two electrodes. It exhibits an elongation along the field direction and an elastic recovery of an original shape.

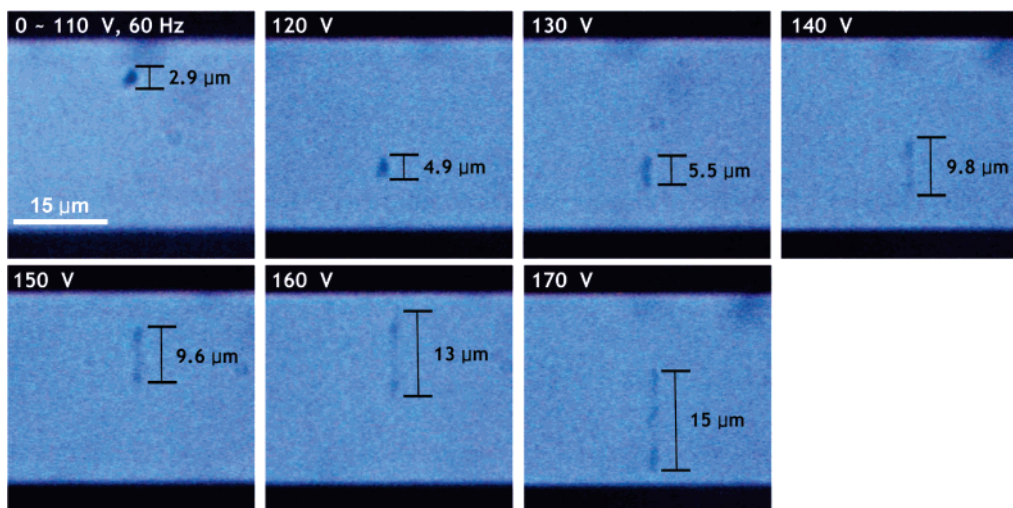


Figure 3. Still cut images of one CNT aggregate depending on the applied voltage. The measuring rods depict the length of CNT aggregate.

-2α , where α is an anisotropic expansion factor. The estimated $\alpha = 3.13$ implies the presence of large anisotropic response to the external electric field. The elongation involves the alignment of the CNT aggregate first. At high field, the CNT bundles can be stretched further to make them thinner. Because the CNTs form bundles by van der Waals forces, some CNTs can slide out of the bundles by a similar “sword-in-sheath” effect as in multiwalled carbon nanotubes and contracted by the restoring van der Waals interaction energy upon removal of the external field.⁹ The elongation and contraction of the CNT aggregate with changing field were repeatable from numerous aggregates, although it was rather difficult to record them due to the random translational motion. Nonetheless, all the CNT aggregates repeated the similar elongation and contraction as described above more than 100 times. The maximum length of elongation relied on the size of the original CNT aggregates.

The observed phenomenon of the reversible elongation of the CNT aggregate is intriguing in several aspects. This is different from the superplastic elongation of a single-walled

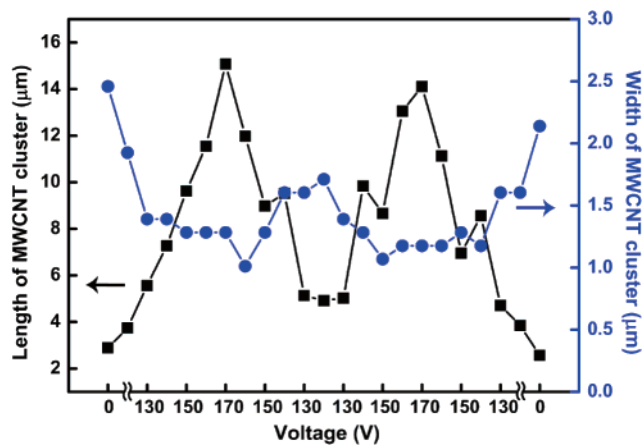


Figure 4. Voltage-dependent width and length of a CNT cluster.

carbon nanotube induced by the mechanical stress that involved the reduction of the diameter.²⁰ The CNT aggregate is composed of randomly entangled individual nanotubes decorated by the LC molecules. Our t-MWCNTs have

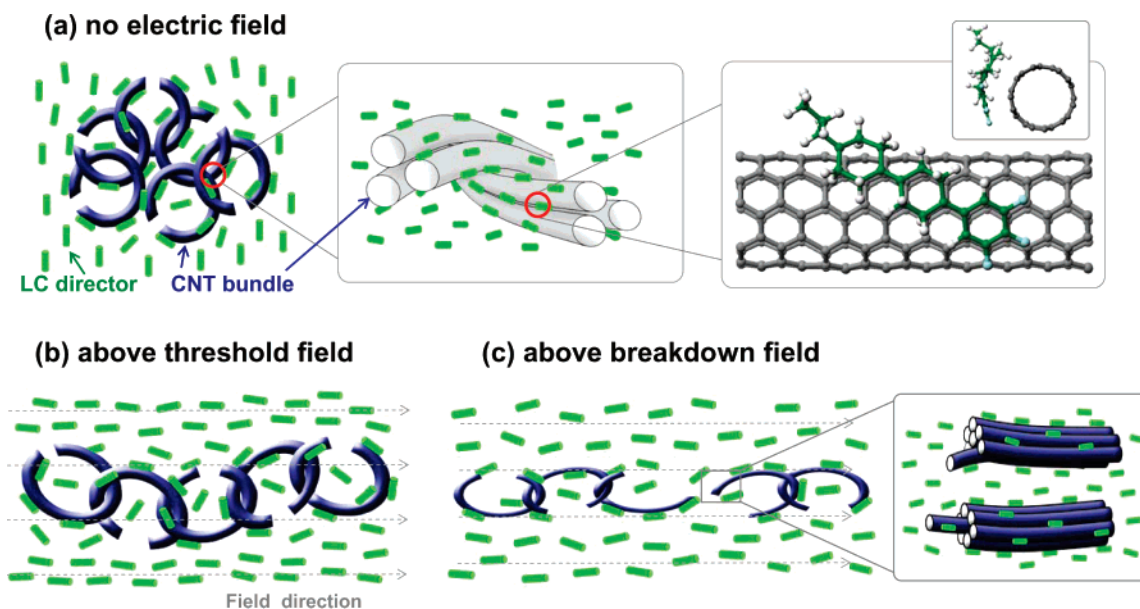


Figure 5. Schematic illustrations of the CNT clusters in the LC cell under (a) no electric field, (b) above threshold field, and (c) above breakdown field. The extrusion of individual nanotubes or small-size bundled CNTs by the strong external field is also demonstrated in the inset.

diameters of about 3–6 nm and are floppy, just like single-walled carbon nanotubes. Therefore, they form aggregates of entangled random networks to some degree. When t-MWCNTs are dispersed in the LC medium, CNTs start to interact with LC molecules. It is known that the LC molecules can be strongly anchored on the CNT wall via electrostatic interaction in addition to π -stacking of hexagonal rings.¹⁷ Therefore, the interaction energy between CNTs becomes weaker due to the decorating LC molecules on the CNT surface. At high CNT concentration, the dispersion of particularly long CNTs becomes poor, often forming CNT aggregates, as illustrated in the schematic of Figure 5a. Such a CNT aggregate can be elongated by the electric field or by the external mechanical stress. In our case, the elongation is driven by the electric field. The individual CNTs in the aggregate are aligned along the field direction to maximize the dipole energy, as shown in Figure 5b. Furthermore, some CNTs could be extracted out from the large-size bundles, as illustrated in Figure 5c.

When the field is turned off, the change of the Helmholtz free energy (ΔF) during elongation is governed by the entropic term ($-T\Delta S$) rather than the internal energy (ΔU), where T and S are the temperature and entropy of the system, respectively. ΔU between CNTs can be neglected due to the presence of the decorating LC molecules. This system then emulates the elastomeric polymer, where the original shape is recovered by the entropic elasticity, when the field is turned off. This similarity is further rationalized by the large strain of up to 400% in the linear region that is again similar to that of an elastomer. However, in CNT aggregates, no specific cross-links exist among CNTs except weak van der Waals interactions. The recovery is perhaps related to the high elastic modulus of the CNT cluster or to the entropy maximization. Some CNTs can be disentangled into small pieces above a certain breakdown field value, which then renders the overall process irreversible as observed in our

Table 1. Electroactive Constants along the Field Direction for Various Materials

material types	actuation electric field ($V/\mu\text{m}$)	actuation strain (%)	piezoelectric constant ^a ($V/\mu\text{m}$) ⁻¹
CNT aggregates	5.67	~400	~70
ferroelectric	> 10	2	~0.2
(piezoelectric) polymers ²⁷			
dielectric	> 50	< 200	~4
electroactive polymer ³⁰			

^a Piezoelectric constant = (actuation strain)/(actuation electric field).

experiment. Therefore, the hook model as illustrated in the figure is more reasonable than the cross-link model. This model also resembles the previous simulation results of two hooks released by the external stress.²¹ The strong external electric field exceeds that of van der Waals interaction between CNTs in this case. Because the elongation of the CNT aggregate is driven by an electric field, such a CNT aggregate can be regarded as an electroactive material. The piezoelectric constant (strain per field) was evaluated from the slope of Figure 4. This value was $70 \text{ (V}/\mu\text{m})^{-1}$ along the field direction, much larger than $0.2 \text{ (V}/\mu\text{m})^{-1}$ of the typical electronic electroactive polymers (EAPs).^{22–29} In Table 1, we compared our results with typical electronic EAP materials. The CNT aggregate with repeatable elongation and contraction could be ideal material for an efficient actuator and smart shape memory devices.

In summary, we have reported a new phenomenon of the superelectroactive elongation of the CNT aggregate in a LC medium. The elongation reached up to 400%, independent of the nematic or isotropic phase of the LC medium. The original shape was recovered in the absence of field. The elongation and contraction were repeatable with voltage variation below threshold voltage. While the piezoelectric constant was $70 \text{ (V}/\mu\text{m})^{-1}$, i.e., extremely large compared

to a conventional piezoelectric material, the CNT aggregate resembled an elastomer material with high expansion coefficient.

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