A tunable carbon nanotube polarizer

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Abstract

The electro-optic response of a carbon nanotube (CNT) cluster has been investigated. The cluster absorbs incident light before stretching. In the presence of an electric field, the cluster starts stretching along the field direction and contracts back to its original stage when the applied voltage is removed. The stretched cluster absorbs and transmits incident light with its electric vector propagating parallel and perpendicular to the long axis of the stretched cluster, respectively. Utilizing this selective light absorption property of a CNT cluster, a tunable polarizer or non-emissive light modulator can be realized.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Tunable orientation of carbon nanotubes (CNTs), anisotropic nano-cylinders, under an electric field [1, 2] would allow CNTs to be used in dynamic polarizers or non-emissive light modulators due to their selective light absorption properties [3–6]. A static type of optical polarizer made of uniaxially aligned CNTs embedded in a polymer film with a degree of polarization of ~90% was demonstrated [6]. To maximize the polarizing efficiency of CNTs, macroscopic alignment of CNTs should be achieved. However, CNTs are easily agglomerated with each other due to strong van der Waals forces between them. In order to avoid this problem, research into the alignment of CNTs using a grooved surface and orientational ordering of liquid crystals was performed [7, 8] but the volume concentration in a host material was limited. Therefore, rather than trying to align individual CNTs, macroscopic alignment of the stretched CNT clusters under an electric field [9, 10] would give many benefits in applying CNTs as light modulators. We demonstrate the selective light absorption properties of a stretched CNT cluster and its application to dynamic polarizers as well as light modulators.

One of the key control parameters for the commercialization of a CNT-type field emissive display [11] is the alignment of individual CNTs. On the other hand, randomly orientated or uniformly dispersed CNTs in any transparent medium can absorb visible light by the $\pi-\pi^*$ transition of electrons and the normalized amount of light absorbed according to Beer–Lambert’s law is given by

$$\frac{I}{I_0} = \exp(-\varepsilon Cl)$$

where $\varepsilon$ is the extinction coefficient, $C$ is the concentration of CNTs and $l$ is the light path length [12]. Since the CNT has an uniaxial symmetry [6], $\varepsilon$ along the long axis of the CNT ($\varepsilon_\parallel$) is different from that perpendicular to the long axis ($\varepsilon_\perp$), leading to the anisotropic light absorption. Based on the above-mentioned concepts, we attempted to utilize CNT as a non-emissive light modulator and report experimental evidence of selective light absorption by the stretched CNTs, similar to the optical properties of a dichroic dye. The absorption level can be modulated by controlling concentration, size, and elongated length of CNT clusters upon applied electric field. With an optimized CNT cluster, it absorbs both electric field vector components of visible light, however, the stretched cluster selectively absorbs the incident light. We demonstrate that not only dynamic polarization control but also tunable light modulation can be performed with CNT clusters.

2. Experiment

The CNTs used in this experiment are thin multi-walled carbon nanotubes (t-MWCNTs) the outer diameter of which
range from 3 to 6 nm and typical lengths are dozens of micrometers. The t-MWCNT was synthesized by a catalytic chemical vapor deposition (CCVD) method using FeMoMgO catalysts prepared by a combustion method. The t-MWCNT powders of 100 mg were stirred in 1 M sucrose solution for an hour and the sucrose mediated t-MWCNT was ground in a mortar for an hour, in order to reduce the average length of the CNTs to 290 nm. 5 mg of the ground t-MWCNT was dispersed in 30 ml of ethanol by sonication for 15 min. A well-dispersed solution with a CNT concentration of 0.167 g ml$^{-1}$ was mixed with a nematic liquid crystal (LC) fabricated from Merck-Japan. Physical properties of the LC mixture were measured as birefringence $\Delta n = 0.077$ at $\lambda = 589$ nm, dielectric anisotropy $\Delta \varepsilon = -4$, and clearing temperature $75^\circ$C. Special care was taken to remove ethanol solvent using a solvent evaporator kept at 70$^\circ$C.

To fabricate an in-plane field cell, the opaque aluminum metal was deposited only on one-side of a glass substrate for the interdigitated electrodes. To generate in-plane fields with applied voltages, the bottom substrate had interdigitated electrodes with an electrode width of 10 $\mu$m and a distance of 40 $\mu$m between electrodes. The electrode-patterned bottom glass and the pristine top glass were additionally coated with homogeneous alignment layers of AL16139 (Japan Synthetic Rubber Co.) and subsequently rubbed in an antiparallel direction. The CNT-doped LC mixture was then filled into the fabricated in-plane cell with a cell gap of 60 $\mu$m through a capillary process at room temperature. To minimize the effect of the LC’s molecular reorientation during the CNT stretching, the rubbing direction was controlled to be perpendicular to the in-plane electric field. Thereby, the LC director was aligned initially perpendicular to the in-plane field so that the LC director between electrodes did not rotate at all, that is, the LC layer did not affect the polarization state of incident linearly polarized light. The main reason we used the LC as liquid is that it does not absorb the visible wavelength and also has a resistivity of $10^{13}$ $\Omega$ cm, so that a relatively high electric field can be tested in the cells without an electrical short. The electro-optical textures of the cell were observed by an optical microscope (OM, Nikon DXM1200) with a sinusoidal AC field at 60 Hz.

3. Experimental results

3.1. Observation of CNT stretching

A homogeneous mixture of superfluorinated nematic LC and multi-walled CNTs (0.1 wt% into LC) with a mean CNT length of 290 nm was filled into a homogeneously aligned LC cell. Utilizing optical microscopy (OM), it was realized that a homogeneous LC orientation could be successfully obtained by a rubbed alignment layer, and CNT clusters bigger than a micrometer were observed as dark spots in certain areas, as shown in figure 1. The size of the CNT cluster with an arbitrary shape in figure 1(a) is estimated to be $\sim 4.1 \mu$m in length. When an electric field larger than 2.0 $V_{rms}$ $\mu$m$^{-1}$ is applied, the CNT cluster starts to be elongated along the in-plane field direction and its elongated size increases up to 22.8 $\mu$m at 4.5 $V_{rms}$ $\mu$m$^{-1}$. Another CNT cluster with spherical-like shape and with a length of 1.7 $\mu$m was observed, as shown in figure 1(b). It also started stretching with increasing electric field and was found to stretch to 19.2 $\mu$m, which is over 1000% of its original length at a field strength of 3.5 $V_{rms}$ $\mu$m$^{-1}$. In order to study the dynamic stretching behaviors of CNT clusters observed in figure 1(a), time-dependent OM images of a CNT cluster were monitored by applying an in-plane field of 4.5 $V_{rms}$ $\mu$m$^{-1}$ and the results are summarized in

![Figure 1. OM images of CNT clusters with anisotropic shape (a) and spherical shape (b) in an LC medium depending on applied electric field.](image-url)
Figure 2. Time-resolved OM images of the CNT cluster in an LC medium during switching on and off at an applied electric field of 4.5 Vrms μm⁻¹.

Figure 3. OM images of the elongated CNT clusters in the LC medium at two different electric fields when the polarization direction of the incident light is perpendicular to the electrode direction: (a) 3.0 Vrms μm⁻¹ and (c) 4.5 Vrms μm⁻¹, respectively. Figures in (b) and (d) are OM images when the polarization direction of the incident light is perpendicular to the electrode direction. The arrow in the electrode indicates the transmission axis of the polarizer below the bottom substrate.

The CNT cluster is fully stretched along the in-plane electric field within a second. When the in-plane electric field is removed, the original spherical CNT cluster shape is completely recovered within a timescale similar to the turn-on process. The reversible shrinkage of the CNT cluster without an external electric field originates from the entropy increase, which is similar to the elastic behavior of polymeric materials.

3.2. Selective light absorption

Anisotropic selective light absorption properties of the CNT cluster in the visible wavelength range have been evaluated. The length of the CNT cluster increased from 4.1 μm to 13.7 μm, and 22.8 μm at 3.0 and 4.5 Vrms μm⁻¹, respectively, as shown in figures 3(a) and (c). Note that the polarizing direction of incident light is perpendicular to the electrode direction, which is parallel to the stretched axis of the CNT cluster. When the polarizing axis of the incident light was rotated to be parallel to the electrode direction, the CNT cluster image in figure 1(a) completely disappeared, as shown in figure 3(b). Additionally, it was observed that a highly stretched CNT cluster with a higher electric field was also barely observed, as shown in figure 3(d). Interestingly, selective light absorption takes place as soon as the CNT cluster starts to stretch. This result clearly indicates that the visible light with its electric vector (E∥) propagating along the long axis of the stretched CNT cluster is absorbed by the CNT cluster while the one (E⊥) propagating along the short axis of the stretched CNT cluster just passes through without absorption, because of anisotropic characteristics in ε. Nevertheless, the trace of the stretched CNT cluster in figure 3(d) was observed slightly, that is, it showed less perfect selective light absorption, although it is longer than that in figure 3(b). This is associated with the fact that the stretched cluster shows translational motion along the electrode direction mainly and partly perpendicular to the electrode direction under a strong electric field.

4. Discussion

Based on experimental OM results of the CNT clusters, it is realized that the unstretched clusters with spherical shape
Figure 4. Schematic diagram showing light absorption of incident light with $E_\parallel$ and $E_\perp$. The black sphere and the black cylinder indicate the cluster before and after elongation of the CNT cluster, respectively.

Figure 5. Schematic cell structures of a non-emissive transmissive display: (a) and (c) a dark state before applying an electric field and (b) and (d) a white state after applying an in-plane and vertical electric field, respectively. Here, the black sphere and the black cylinder indicate the cluster before and after the elongation of the CNT cluster, respectively.
applied to the cluster and the polarizer exists below the bottom substrate. Without a bias field, CNT clusters are not elongated and remain as isotropic objects blocking the incident polarized light so that the cell appears to be black, as represented in figure 5(a). When an in-plane electric field is applied as shown in figure 5(b), CNT clusters are stretched to be anisotropic, in which the long axis of the stretched CNT clusters is perpendicular to the polarizing axis of the incident polarized light. Then, the light penetrates the cell and appears to be white. When the in-plane electric field is removed, the stretched CNT clusters reversibly return back to the spherical isotropic CNT cluster owing to the elastic behavior of the CNT clusters. In the second case, vertical electric field is applied without a polarizer. Again, an incident light will be absorbed by the CNT clusters before applying an electric field, giving a dark state as shown in figure 5(c). When vertical electric field is applied, the CNT cluster will be stretched along the field direction perpendicular to the substrate, and then the incident light with two orthogonal electric vectors at the normal direction will propagate along the short axis of the CNT cluster, as illustrated in figure 5(d). Consequently, no light absorption occurs so that the modulator shows a white state. The contrast ratio of the modulator strongly depends on size, concentration of the cluster into transparent dielectric medium, and applied electric field strength.

5. Conclusion

In conclusion, we experimentally demonstrated that selective light absorption can be controlled by stretched CNT clusters under an applied electric field and the absorption level can be modulated by controlling the size, elongated length, and concentration of CNT clusters. Unlike an optical polarizer of CNTs embedded in a polymer film [6] in which the degree of polarization is fixed in space, the modulated shape of a CNT cluster clearly indicates that the selective light absorption can be tuned not only in space but also in time by external electric fields, possibly opening new avenues to control the polarization and light modulation of visible light.

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