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ABSTRACT
A thin layer of single-walled carbon nanotubes (SWCNTs) exhibiting optical anisotropy is prepared by electroactively elongating SWCNT agglomerates. SWCNTs are doped into a reactive mesogen (RM) solution, and the composite solution is spin-coated on an interdigitated-electrode substrate. The spherical shaped SWCNT agglomerates observed in the solution of thin layers are electroactively elongated and aligned along the direction of the external electric field. After elongating the SWCNT agglomerates, the transparency of RM-SWCNT thin composite layers increases by about 14%. In addition, the elongated SWCNT agglomerates present significant optical anisotropy such that an incident light with a polarization direction parallel and perpendicular to the elongated direction of SWCNTs is absorbed and transmitted, respectively. The electroactively elongating strategy adopted to realize the optical anisotropy of SWCNT agglomerates suggests a new way to fabricate an optically anisotropic SWCNT thin layer.

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Carbon nanotubes (CNTs) are nanometer-sized cylindrical tubes of graphite sheets, and because of their peculiar geometrical shape, CNTs can exhibit strong optical anisotropy.1–6 However, the exceptional anisotropy of isolated CNTs is hard to realize especially in relation to CNT composites.7–10 The dispersion of CNTs in the matrix essentially impedes the realization of isolated CNTs because of their aggregation. Among the alignment methods of CNTs commonly attempted, electroactively aligning CNTs present an attractive option.11,12 Electroactive elongation of CNTs has been performed in a lot of research studies, and the length and the functionalization of CNTs, the strength and frequency of the electric field, and the host medium of CNTs are critical in aligning CNTs.13–20 During the last decade, our research group has been focusing on the characterization of the anchoring effect of liquid crystal (LC) molecules on CNTs and the experimental investigation of electroactive elongation of CNT agglomerates in the LC medium. Due to a considerable amount of charge transfer from LC molecules to the CNTs, the anchoring of LC molecules on CNTs is further strengthened by electrostatic energy, and the charges are asymmetrically distributed on the CNTs induce a permanent dipole moment on the CNTs.21,22 When the isolated CNTs are doped in LC agglomerates and the LC-CNT composite medium is sandwiched between two indium tin oxide (ITO) flat electrodes, the CNT agglomerates can be electroactively elongated. Large-sized CNT agglomerates turn into small strips when the electric field increases gradually, and finally, CNT agglomerates are invisible in the LC medium. Dynamic
reorientation of CNTs is characterized when the LC-CNT composite medium has been observed by using a polarized optical microscope (POM), and the disappearance of electroactively elongated CNT agglomerates is attributed to the optical anisotropy of CNTs. The dynamic reorientation of CNTs in the LC medium may generate the short between top and bottom conductive substrates occasionally, which begets the disappearance of their continuous reorientation. The random size and occupation of CNT agglomerates increase the possible short between the electrodes; in addition, because of the fluid characteristics of the LC-CNT composite medium, the meticulous reoccupation of CNT agglomerates in the LC medium by adjusting the external electric field becomes impossible. How to prevent the short between the top and bottom electrodes becomes a challenging issue in electrically elongating and reorientating CNT agglomerates in the LC medium.

A simplified LC-CNT medium system with the LC-CNT medium coated only on the electrode substrate will effectively avoid the short between the top and bottom electrodes, but the fluid characteristics of the LC reduce the stability of the LC-CNT medium thin layer. Merck RM03-015 is an ideal alternative to liquid crystals as it could be spin-coated on substrates directly and will form a gel thin layer after a periodical baking and then become a solid thin layer after the UV curing process; therefore, we are trying to electroactively elongate CNT agglomerates in a one-dimensional RM03-015 gel thin layer and explore their orientation and the corresponding optical performances. In this manuscript, a thin composite layer consisting of the reactive mesogen (RM, RM03-015, \(n_0 = 1.525 \pm 0.005\), \(n_e = 1.667 \pm 0.005\), and \(\Delta n = 0.142 \pm 0.005\) obtained from Merck Co.) solution and single-walled carbon nanotubes (SWCNTs) is prepared by spin-coating the RM-SWCNT composite solution, and the optical anisotropy of SWCNTs is observed during electroactive elongation of SWCNT agglomerates. The spherical SWCNT agglomerates are stripped and aligned along the direction of the external electric field, and the transparency of RM-SWCNT thin composite layers increases by about 14%. The significant optical anisotropy of electroactively elongated SWCNT agglomerates along and perpendicular to the direction of the external electric field is observed by using a polarized optical microscope (POM), which intimates the potential application of thin composite layers of RM-SWCNTs for electro-optic devices. In the research studies related to the holographic display, it is possible for the electroactively elongated CNT agglomerates to realize the anisotropic absorption control on 3-D volume holographic gratings, based on the transverse surface plasmon resonance and longitudinal surface plasmon resonance.

The RM solution (RMS03-015, \(n_0 = 1.525 \pm 0.005\), \(n_e = 1.667 \pm 0.005\), and \(\Delta n = 0.142 \pm 0.005\)) was obtained from Merck Co., and the SWCNTs were obtained from Hanwha Chemical Co., Ltd. The purification of SWCNTs was conducted according to the literature, and the purified SWCNTs are in a diameter of \(\sim 40\) nm and the length ranging from 400 nm to 1 \(\mu\)m. The RM-SWCNT composite solution was prepared by doping 0.02 wt. % SWCNTs. The composite solution was sonicated for 30 min at room temperature, then pre-spin-coated on an indium tin oxide (ITO) interdigitated electrode substrate (IPS) at 600 rpm for 30 s, and spin-coated at 3000 rpm for 2 min (the distance between each interdigitated electrode is 30 \(\mu\)m). Finally, the composite thin layer was baked at 80 \(^\circ\)C for 3 min. The thermal stability of RM-SWCNT thin composite layers was characterized by using a thermal gravimetric analyzer (NETZSCH, TG 209F3, Germany), and the transparency was evaluated by ultraviolet-visible transmission spectroscopy (UV-vis, UV-2101, Shimadzu, Japan). The electrical elongation of spherical SWCNT agglomerates was driven by an external voltage of 60 Hz, and the orientation and the optical anisotropy of electroactively elongated SWCNT strips were characterized by using an optical polarizing microscope (Nikon, DXM1200).

The SWCNT agglomerates and the electroactively elongated SWCNT agglomerates in RM-SWCNT thin composite layers are captured and characterized by using a POM, as shown in Fig. 1. Because SWCNTs are hard to be dispersed in RM, SWCNTs aggregate to spherical agglomerates, and the SWCNT agglomerates in...
an initially spin-coated RM-SWCNT thin composite layer are in various sizes. Spherical SWCNT agglomerates randomly orientate in the thin composite layer, as shown in Fig. 1; however, after applying a 60 Hz external voltage on IPS substrate, an inner electric field is generated and SWCNT agglomerates are elongated into strips along the direction of the electric field. The threshold voltage ($V_{th}$) of electroactively elongating SWCNT agglomerates is defined as the minimum voltage, generating SWCNT agglomerate morphology alternation along the direction of the external electric field, and in this case, the $V_{th}$ of SWCNT agglomerates in RM-SWCNT thin composite layers is characterized as 18 V. Finally, the electroactive elongation of SWCNT agglomerates terminates at an external voltage of 27 V. After a magnified observation, we find that these electroactively elongated SWCNT strips seem to be composed of small SWCNT rods. The formation of SWCNT dots is due to the broken equilibrium of interactions between isolated SWCNTs after removing the external electric field.

During the electroactively elongating process, each isolated SWCNT does not connect with one another in strips but maintain a suitable distance because of the equilibrium between electric forces and other forces. However, after removing the external electric field, the lack of electric forces results in the disequilibrium of forces, and thus, the surface tension generated from RM molecules dominates to form spherical dots in which the orientation of isolated SWCNTs intermingles. The electroactive response of SWCNTs to the external electric field could be well understood by modeling SWCNTs as cylinders, as shown in Fig. 2. In the external electric field, SWCNTs are polarized and the electric charges redistribute to each end, and the dipole movement is generated at the same time. In this case, the external electric field exerts the translational force to remove SWCNTs, and SWCNTs are forced to align along the direction of the electric field. However, because of the interfunction between isolated SWCNTs, partial SWCNTs get closer toward each other and thick macro strips gradually form, and the electroactively elongated SWCNT strips are observed. The net force working on SWCNT agglomerates generally is presented as

$$ F_{E} = q \cdot \vec{E} + (\vec{p} \cdot \nabla) \cdot \vec{E}, $$

where $q$ are the generated electric charges, $\nabla$ is a del operator, and $\vec{p}$ is the equivalent generated dipole moment. $q \cdot \vec{E}$ indicates the columbic interaction between the generated charges over SWCNT agglomerates and the external field, and $(\vec{p} \cdot \nabla) \cdot \vec{E}$ reveals the interaction of the dielectric polarization component in SWCNT agglomerates by the electric field with spatially inhomogeneous field.

The size and the orientation of SWCNT agglomerates and the electroactively elongated SWCNT agglomerates are characterized and evaluated. The size of SWCNT agglomerates and electrically elongated SWCNT agglomerates is identified as the length of SWCNT agglomerates along the direction of the external electric field, and the exact size of SWCNT agglomerates is determined by referring to a scale bar. The elongation ratio of SWCNT agglomerates is defined as

$$ r = \frac{l}{l_0} \times 100\%, $$

where $l_0$ is the length of initial SWCNT agglomerates and $l$ is the length of elongated SWCNT agglomerates. As indicated in Table I and Fig. 3, the average length of elongated SWCNT agglomerates is about 27.91 $\mu$m, indicating that the SWCNT agglomerates are

| No. | $l_0$ ($\mu$m) | $l$ ($\mu$m) | $r$ (%) | $\theta$ (deg) | $S$  |
|-----|---------------|--------------|--------|---------------|------|
| 1   | 8.89          | 31.56        | 255.01 | -11           | 0.9454 |
| 2   | 14.22         | 33.33        | 134.39 | 13            | 0.9241 |
| 3   | 9.33          | 23.11        | 147.70 | 2             | 0.9982 |
| 4   | 18.22         | 28.44        | 56.09  | -2            | 0.9982 |
| 5   | 10.36         | 27.56        | 166.02 | -1            | 0.9995 |
| 6   | 11.11         | 31.56        | 184.07 | 8             | 0.9709 |
| 7   | ...           | 30.22        | ...    | -5            | 0.9886 |
| 8   | 9.78          | 28.00        | 186.30 | 5             | 0.9886 |
| 9   | 17.33         | 26.67        | 53.89  | 1             | 0.9995 |
| 10  | 8.89          | 30.67        | 244.99 | 16            | 0.8860 |
| 11  | 11.78         | 27.56        | 148.06 | -8            | 0.9709 |
| 12  | 11.11         | 27.56        | 184.07 | 8             | 0.9709 |
| 13  | 2.22          | 22.67        | 921.17 | -1            | 0.9995 |
| 14  | 4.44          | 21.78        | 390.54 | 1             | 0.9995 |
| 15  | 13.33         | 28.89        | 116.73 | -2            | 0.9982 |
superelongated to 122% compared with their initial average size (about 11.22 μm). The biggest elongation ratio of SWCNT agglomerates approaches to 921.17%, and the average elongation ratio is calculated as about 218.21%, which is smaller than that of CNT agglomerates in liquid crystals. The size of electroactively elongated SWCNT agglomerates (l) and the elongation ratio (r) of SWCNT aggregation are found to be restricted by the initial size of SWCNT agglomerates (l₀) and the distance (d) between two neighboring electrodes. When the electroactively elongated SWCNT agglomerates reach two neighboring electrodes, electrodes are shorted, and thus, the electric force working on elongating SWCNT agglomerates disappears and the electroactive elongation of SWCNT agglomerates terminates. In order to increase the elongation ratio (r) of SWCNT agglomerates, minimizing the initial size (l₀) of SWCNT agglomerates is an effective and efficient option.

The orientation of elongated SWCNT agglomerates (θ) is defined as their orientation deviation from the external electric field direction, and similar to the orientational order parameter of liquid crystals, the orientation order parameter of electroactively elongated SWCNT agglomerates is defined as

$$S = \frac{1}{2} (3 \cos^2 \theta - 1),$$

where θ is the angle between their orientation deviation from the external electric field direction. For zero deviation, S = 1, and for 90° deviation, S = 0. As shown in Table I and Fig. 4, after a rough characterization, we find that electroactively elongated SWCNT agglomerates mostly orientate within ±5° and S concentrates between 0.8860 and 0.9995. However, a small amount of electroactively elongated SWCNT agglomerates deviate orientation more than ±10°. The orientation difference of electroactively elongated SWCNT agglomerates here is due to the different interfunction between isolated SWCNTs. In the pristine SWCNT agglomerates, each isolated SWCNT orientates randomly. However, during the electroactively elongating process, the isolated SWCNT is polarized and forced to orientate along the direction of the external electric field. Due to the initially random distribution and orientation of isolated SWCNTs, the electrical charge distribution in SWCNT agglomerates is...
nonuniform, which, in turn, generates the uneven electric forces to rotate isolated SWCNTs in agglomerates. Thus, the intermingled isolated SWCNTs lead to the deviated orientation of SWCNT agglomerates. As indicated in Fig. 4(b), most of the elongated SWCNT agglomerates orient with the S approaching to 1.

The optical anisotropy of CNTs has been investigated for a long period, and the orientation of CNTs determines the optical anisotropy of CNTs. Our research group has been engaged in exploring the optical anisotropy of CNT agglomerates since 2007, and we realize that electroactively elongated CNT agglomerates are optically anisotropic due to the uniform orientation of isolated CNTs. The optical anisotropy of electroactively elongated SWCNT agglomerates in an RM-SWCNT thin composite layer is characterized by using a POM, as shown in Fig. 5. By rotating the analyzer by 90°, the visible SWCNT strips disappear even though some SWCNT dots are still seen, which reveals that electroactive elongation of SWCNT agglomerates in RM-SWCNT thin composite layers is an effective and efficient way to fabricate an optical anisotropic SWCNT thin composite layer.

The thermal stability of the RM-SWCNT composite is characterized by using a thermal gravimetric analyzer, as shown in Fig. 6(a). RM-SWCNT thin composite layers are highly thermal resistive, and the thermal decomposition temperature of RM-SWCNT thin composite layers reaches at about 360°C. However, the slight decomposition of the RM-SWCNT composite starts at about 100°C similar to the original RM. The spin-coated RM-SWCNT thin composite layer is transparent, but its transmittance is slightly above 70% only in the visible region, as shown in Fig. 6(b). The block effect generated from SWCNT agglomerates is the main cause responding to the low transparency of RM-SWCNT thin composite layers. By electroactively elongating SWCNT agglomerates, the transparency of RM-SWCNT thin composite layers increases and the highest transmittance in the visible region rises over 80%. According to the synopsis, RMS03-015 is photo-crosslinkable and the hard homeotropic RMS03-015 thin layer could be obtained only after being exposed to UV light ($\lambda_{\text{max}} = 365 \pm 10$ nm, $I = 70 \pm 10 = \text{mW/cm}^2$) for about 10 s. Therefore, the increased transparency of RM-SWCNT thin composite layers is due to the generated optical anisotropy of isolated SWCNTs along the direction of the external electric field.

In conclusion, an optical anisotropic SWCNT thin layer is prepared by electroactively elongating SWCNT agglomerates in a RM-SWCNT thin composite layer, which is prepared by directly doping SWCNTs in the RM solution. By electroactively elongating SWCNT agglomerates, the spherical SWCNT agglomerates turn into strips and align along the direction of the external electric field. The average elongating rate of SWCNT agglomerates reaches about 400%; however, the elongating rate of SWCNT bundles is restricted by the initial size of SWCNT agglomerates. Most of the elongated SWCNT bundles orient in the direction along the direction of the external electric field, and some SWCNT agglomerates intermingle because of the nonuniform charge distribution. RM-SWCNT thin composite layers are thermally stable and highly transparent, and by electroactively elongating SWCNT agglomerates, the transparency of RM-SWCNT thin composite layers is further increased by 14%. The proposed electrical elongation of SWCNT agglomerates in RM-SWCNT thin composite layers reveals a new method to prepare optical anisotropic SWCNT thin layers.

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