An active carbon-nanotube polarizer-embedded electrode and liquid-crystal alignment

A highly aligned CNT array sheet acts as a polarizer due to its anisotropic optical absorption. Polymer coating on the CNT sheet makes the CNT sheet flexible and bendable, while part of the CNT film is still exposed on the film surface. A grooved surface is formed associated with CNT array, rendering the alignment of liquid crystal (LC) molecules possible. Consequently, the polymer-embedded CNT sheet (P-ECS) film functions simultaneously as a polarizer, transparent electrode, and LC aligner. The LC cell device using P-ECS films shows a good bright-dark switching performance over any conventional LC components.

See Young Hee Lee, Seung Hee Lee et al., Nanoscale, 2020, 12, 17698.
We report a method for constructing an active optical polarizer using an aligned carbon nanotube (CNT) sheet that is flexible, bendable, transparent, conductive, and also serves to anchor liquid-crystal (LC) molecules. A horizontally aligned CNT sheet was obtained by mechanical stretching from a vertically grown CNT forest, which was then transferred onto a substrate. A liquid polymer was infiltrated into the CNT sheet followed by UV curing, while a part of the CNT sheet was still exposed on the film surface without polymer coating. The polymer-embedded CNT sheet (P-ECS) film with 10 layers of CNT sheets exhibited a good polarization efficiency of 87%, a sheet resistance of 340 $\Omega \cdot \text{sq}^{-1}$, and excellent ability to align LC molecules. The high stability of the P-ECS film was confirmed from the very low variation of sheet resistance (2%) and transmittance (10%) observed during a bending test of 1000 cycles. In addition, a twisted nematic LC device constructed using the P-ECS films shows a good bright−dark switching performance. The P-ECS film functions simultaneously as a transparent electrode, a film-type polarizer, and a LC alignment layer, demonstrating the multi-functionality of the active CNT film. This study thus highlights a wide range of possible applications for active polarizers and flexible displays.

Introduction

Carbon nanotubes (CNTs) could be viable alternatives to conventional materials used in electric devices owing to their mechanical resilience, high electrical conductivity, optical transparency, high aspect ratio, and the possibility to anchor liquid crystal (LC) molecules on their surface. In particular, the aligned CNT array along a preferred direction leads to anisotropic optical absorption, therefore it has been intensively investigated for its applications in optical polarizers. There are three ways to align CNTs: (i) Aligned CNTs can be directly synthesized by chemical vapor deposition (CVD) on quartz substrates, (ii) fabric CNTs can be woven from a CNT forest, and (iii) using an external shear force or electric/magnetic field to re-orientate CNTs dispersed in a liquid. However, the thickness and density of the aligned CNTs are limited in the direct synthesis method, and the degree of alignment from the reoriented CNTs in a liquid is very poor to meet the requirement of an optical polarizer. The aligned CNT sheets extracted from the CVD-grown CNT forest can function as flexible and active optical polarizers to offer comparable polarizer efficiency and the robust processing technique is suitable for industrial applications due to its scalability. However, the highly ordered CNT array is mechanically weak under external stresses such as bending, pressing, and strain. Therefore, the polymer-embedded CNT array has been intensively investigated to overcome this issue. The polymer effectively prevents the degradation of the aligned CNT array from the external stress. However, the CNT array is fully embedded within the polymer, limiting sheet conductance and more seriously prohibiting the LC anchoring effect on the CNT surface. In order to provide mechanical stability while retaining the inherent multi-functionality of the aligned CNT array, an exposure of CNTs on the polymer surface is a prerequisite condition for flexible LC display devices.

Herein, we report a method to fabricate a multi-functional optical polarizer using an aligned CNT sheet. The aligned CNT sheet was extracted by mechanically stretching it from a CNT forest and transferred onto a glass substrate, followed by polymer coating and UV curing with the partial exposure of CNTs. We were able to achieve high polarization efficiency, high conductance, and good LC alignment performance for...
the polymer-embedded CNT sheet (P-ECS) film. The film showed excellent stability during a bending test of 1000 cycles. Compared to previous single-7,10 or dual-functional CNT array films such as a LC aligner-electrode system18,19 we further demonstrated an active LC device using the multi-functional P-ECS film, which simultaneously acted as a transparent film-type polarizer, an electrode, and a LC alignment layer.

Results and discussion

The free-standing CNT sheet was extracted from a vertically grown multiwalled CNT (MWCNT) forest. One edge of the CNT forest was pulled mechanically in the form of a sheet and attached to a U-shaped guide (Fig. 1a). Free-standing CNT sheets were rotated using a mechanical motor for an increase in the number of CNT layers (n). The CNT sheets were then transferred onto the glass substrate (Fig. 1b). The transferred CNTs were preferentially aligned along the pulling direction, although slight deviations were present, as seen in the field-emission-scanning electron microscopy (FE-SEM) image (Fig. 1b). The polarization-angle dependent Raman spectra show a high degree of alignment of CNTs (inset of Fig. 1b and Fig. S1a in the ESI†). When the angle between the aligned axis of CNTs and the polarized axis of input light approaches from 0° to 90°, the normalized G-band (near 1575 cm\(^{-1}\)) intensity measured using a Raman microscope, and (c) polymer-coating: the SEM image of the P-ECS film. (e) 3D image, (f) 2D height morphology, and (g) line profile corresponding to the red line in (f).

Fig. 1 Fabrication of a polymer-embedded CNT sheet (P-ECS) film. (a) Mechanical pulling for the alignment of CNTs, (b) a free-standing CNT sheet transferred on a substrate along with SEM image with the inset for polarization angle-dependent G-band (1575 cm\(^{-1}\)) intensity measured using a Raman microscope, and (c) polymer-coating: the SEM image of the back side showing CNTs without the polymer with the inset showing the polarization angle-dependent transmittance of the CNT sheet and P-ECS film at a wavelength of 550 nm. (d) AFM image of the surface of the P-ECS film: (e) 3D image, (f) 2D height morphology, and (g) line profile corresponding to the red line in (f).

The orientation ordering of CNTs in the P-ECS film was largely retained after UV curing. The CNTs were partially exposed at the bottom surface of the P-ECS film because of their direct, intimate contact with the glass substrate (Fig. 1c). This exposure of CNTs on the surface is the key to realizing an active CNT electrode with LC alignment. Only a few CNTs were partially exposed on the film surface, and hence the G-band Raman signal was negligible (Fig. S1c, ESI†). The polarization-angle dependent transmittance was measured to evaluate the degree of alignment of CNTs after polymer coating (Fig. S1d and e, ESI†). The transmittance (wavelength, \(\lambda = 550\) nm, \(n = 10\)) both before (black symbols) and after polymer coating (red symbols) is reduced with an increased misorientation angle (\(\theta\), a polarized axis of the light from the aligned axis of CNTs). Although the transmittance was slightly decreased after polymer coating from 7.7% to 7.3% (\(\lambda = 550\) nm, \(\theta = 0^\circ\)), no appreciable change was found (inset of Fig. 1c). By tilting the crossed polarizer-analyzer from 0° to 90°, the normalized brightness of the P-ECS film before and after the coating showed similar tendencies (Fig. S2, ESI†), which was confirmed by polarized optical microscopy (POM) measurements. The thickness of the CNT sheet was 3.6 \(\mu\)m with 8 CNT layers (Fig. S3, ESI†). As seen in the atomic force microscopy (AFM) images (Fig. 1e-g), the surface of the P-ECS film was grooved with a typical valley of 30–70 nm and a width of 2–3 \(\mu\)m, and the fine wrinkles were generated on the grooved surface by the individually exposed CNTs, irrespective of the number of CNT layers (Fig. S4, ESI†).

We measured the transmittance at \(\lambda = 550\) nm (7% @550 nm) and sheet resistance (\(R_s\)) of the P-ECS films with a different number of CNT layers (Fig. 2a). Both 7% @550 nm (Fig. S5, ESI†) and \(R_s\) decrease as the number of CNT layers increases. The transmittance reaches ~42% for 3 CNT layers, and \(R_s\) is as low as 340 \(\Omega\) \(\square^{-1}\) for the sample with 10 layers. The variation in transmittance during the 1000 bending test is found to be very low (±10%) regardless of the number of layers in the range of 3–10 layers (Fig. 2b). The \(R_s\) value changes within ±2% (Fig. 2c). Since the \(R_s\) value is relatively high compared to those of previous studies (70–200 \(\Omega\) \(\square^{-1}\)),22 the \(R_s\) value can be further reduced by replacing MWCNTs with extremely high-conductive single-walled CNTs.

In the following, we describe the procedure to align LC molecules on the CNT surface. Due to \(\pi-\pi\) stacking, the
anchoring of the aromatic hexagonal rings of the LC molecule on the CNT surface is energetically favored. In a typical LC molecule with 2–4 hexagonal rings, several orientations of the LC molecules are possible when anchored on the surface of CNTs (Fig. 3a). In neighboring LC molecules, they energetically prefer to align their long axes parallel to each other owing to steric hindrance. When the LC suspension is added dropwise onto the grooved P-ECS film, LC molecules flow along the groove direction and pile up on the aligned CNT surface. Consequently, at high LC density, the LC molecules are aligned preferentially along the long axis of the CNT surface (Fig. 3b).

The alignment of LC molecules was confirmed by POM for the LC-coated P-ECS film \((n = 8)\). The incident light was linearly polarized using a polarizer located under the P-ECS film. The polarizer and the alignment direction of CNTs, as well as the LCs, are parallel to each other, resulting in a bright state (Fig. 3c). When the analyzer on top of the P-ECS film is \(\pi\)-stacking between aromatic hexagonal rings in LC molecules (orange ellipsoid) and the hexagonal C–C network of the CNT. (b) Horizontally aligned LC molecules along the long axis of CNTs. Polarized optical microscopy measurement to evaluate LC alignment: LC-coated P-ECS film with (c) one polarizer (parallel direction, bright state), (d) crossed polarizer–analyzer (dark state), and (e) 45° tilted polarizer–analyzer (medium bright state). UV-Vis transmittance and absorbance spectra of two overlapped P-ECS films with various numbers of CNT layers: parallel and perpendicular (f) transmittance and (g) absorbance, and (h) polarization efficiency and dichroic ratio at 550 nm; \(n\) is the number of CNT layers.

The intensity was normalized using the relationship \((T_\parallel/T_\perp)(T_\parallel + T_\perp)\times100\) (1)

Thus, PE is improved by increasing the number of CNT layers and it reaches 87% \((\lambda = 550 \text{ nm, } n = 1)\) (Fig. 3h) while remaining almost constant in the entire visible range (Fig. S8, ESI†). The polarization performance can be evaluated by the degree of polarization (DOP) as well as the dichroic ratio. The DOP defined using \((T_\parallel - T_\perp)/(T_\parallel + T_\perp)\) shows a similar dependence on the number of CNT layers to the PE result reaching \(~0.72\) at \(\lambda = 550 \text{ nm, } n = 10\) (Fig. S8f, ESI†). The dichroic ratio \((R)\) is calculated by the ratio of parallel to perpendicular absorption coefficient \((A_\parallel/A_\perp)\). The dichroic ratio \((\lambda = 550 \text{ nm})\) increases gradually with an increasing number of CNT layers from 1.05 \((n = 1)\) to 1.42 \((n = 10)\) (Fig. 3h). These simply indicate that the polarization performance is improved with an increasing number of CNT layers, which is a trade-off to the transmittance.

Finally, we fabricated a twisted-nematic LC cell device using P-ECS films to simultaneously function as the electrode, polarizer, and LC alignment layer. LC molecules were placed in a gap with the help of spacer tape of 5 \(\mu\text{m}\) thickness, between two orthogonally stacked P-ECS films. Under these conditions, the molecules of the LC are twisted by 90° (left schematic of Fig. 4a). The light illuminated into the LC cell is transmitted through the cell via the twisted LC molecules, giving rise to a bright state (Fig. 4b). When voltage is applied between the top and bottom P-ECS films, the LC molecules are aligned vertically along the electric field owing to the positive dielectric anisotropy of the LC molecules. Here, P-ECS films act as an active medium. Thus, the LC cell \((n = 8)\) shows the dark state at an applied voltage of 15 V (Fig. 4c).

The voltage-dependent transmittance \((V-T)\) was measured for devices with a different number of CNT layers (Fig. 4d). The intensity was normalized using the relationship \(\{T/\%_{\text{min}}\} / \{T/\%_{\text{max}}\}\), where \(T/\%_{\text{min}}\) and \(T/\%_{\text{max}}\) are the minimum and maximum transmittance values in the \(V-T\) curve.
Performance of the twisted-nematic LC cell device using P-ECS films: (a) Schematic illustration of an LC cell with and without applied voltage. Optical microscopy images of the LC cell device with 8 layers in (b) voltage-off and (c) -on states (15 Vrms). (d) Voltage-dependent normalized transmittance curves for devices with a different number of CNT sheets. (e) Threshold voltage (Vth) and the minimum transmittance (T%min) under an applied voltage of 15 V.

Experimental section

Fabrication of the P-ECS film

One edge of a CNT forest (A-Tech System Co., Korea) was drawn as a sheet form using a U-shaped guide. The free-standing CNT sheet (15 mm × 70 mm) was transferred onto the hydrophobically treated glass substrate (25 mm × 70 mm). The CNT-transferred substrate was covered by another glass substrate (top) with spacer tape of 100 μm thickness. The UV-curable monomer (NOA 63, np = 1.56, Norland Products Inc.) was dropped at the gap entrance and then exposed to UV irradiation (Hamamatsu, LC8 L9588) of an intensity of 15 mW cm⁻² for 5 min. Finally, the P-ECS film was peeled off from the glass substrates.

Fabrication of the LC cell device (Fig. S12, ESI†)

The P-ECS film was supported by flat substrates (glass) to prevent bending. A metal wire was bound to the CNT-exposed face of the P-ECS film using silver paste. The LC molecular suspension (ZLI-4792, Δn = 0.0969, at 589 nm and 20 °C, Δε = 5.3, Tni = 92 °C, Merck Advanced Technology) was added dropwise onto the film surface. Spacer tape of 5 μm-thickness was pasted on both the edge sides of the film along the longitudinal CNT direction. Another LC-coated P-ECS film was orthogonally laminated on the spacer (one drop filling method).

The degree of CNT alignment and the surface morphology were observed by FE-SEM (Hitachi SU-70) and AFM (Bruker, Multimode-8). The normal and polarized transmittances and Raman spectra were measured by UV-Vis spectroscopy (Scinco S-3100) in the 350–800 nm wavelength range and using a Raman microscope (NTEGRA Spectra, NT-MDT) with a wavelength of 532 nm, respectively. The sheet resistance was determined by non-contact eddy current probe measurements (Napson, EC-80P). The stability of the transmittance and the sheet resistance values of the P-ECS film were tested using an in-house bending test system. The bending radius was 2 mm, and the repeating step was 200 cycles. The alignment of LC molecules on the P-ECS film was confirmed by POM (Nikon, Eclipse E600 W POL). The voltage dependent-transmittance of the LC cell device was measured using a LC measurement system (Sesim Photonics Technology, LCMS-200). The voltage-
dependent transmittance of the standard cell was simulated using a TechWiz LCD 2D tool (Sanayi System Co., Ltd). The polar anchoring energy was measured using a LCD physical properties measurement system (RDMS-200 and LCR meter, Agilent 4248A).

Conclusions

An active CNT polarizer film that is flexible, bendable, and transparent with good polarization efficiency was fabricated. The exposed CNTs rendered the surface conductive and brought about the alignment of LC molecules. Bending tests of 1000 cycles confirmed the excellent stability of transmittance and sheet resistance. Moreover, the bright transmittance and sheet resistance. Furthermore, the multi-functional P-ECS film can lead to cost reduction by merging and replacing several components into one component.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Basic Science Research Program of the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education (2016R1D1A1B01007189), the National Research Foundation of Korea (NRF) grant funded the Korea government (MSIT) (No. 2019R1A5A8080326), and the Institute for Basic Science of Korea (IBS-R011-D1).

Notes and references