Flexible polymer dispersed liquid crystal film with graphene transparent electrodes

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ABSTRACT

A flexible polymer-dispersed liquid crystal (PDLC) film with graphene layers as transparent electrodes was fabricated by combining a UV curable polymer and a nematic liquid crystal. The PDLC film with a dimension of 5×10 cm^2 was flexible and operated normally with no damage when it was bent with a radius of 2 mm. Instead of using conventional transparent conducting film, the single-layer-graphene transferred on PET film was used as transparent electrodes. The thickness of the graphene-PDLC was about 210–220 μm. The single-layer-graphene grown by thermal chemical vapor deposition was transferred onto the PET film, and its sheet resistance was about 1.2 kΩ/□. The controllable transmission range between the on and off states was about 60% in the visible range. The response time for the turn-on and off processes were estimated to be 0.3 and 32 ms, respectively. This successful fabrication of graphene based PDLC is a crucial step toward paving the way for the commercialization of the emerging material, graphene.

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1. Background

Saving energy is an urgent and important issue with regard to mitigating global warming, and the so-called 'smart window' is predicted to be in widespread use in the near future. The smart window is a controllable window where transparent and opaque states can be switched by an electric field. The smart window has been expected to be a solution for buildings and transportation vehicles to save heating and cooling energy, as the radiation heat losses can be blocked by controlling the transparency of the windows. Among the various candidates of smart window materials, polymer-dispersed liquid crystal (PDLC) [1] [2] has come into wide use. Not only for use in windows, PDLC can be used also for screens, tunable optical modulators [3], and diffusers for transparent displays. Among the base materials for PDLC, the largest cost is incurred for transparent electrode materials like indium tin oxide (ITO). In fact, the price of ITO varies depending on the policy of major producing countries of indium, a rare earth element. As an alternative electrode for PDLC, conducting polymers [4] and silver nanowire [5] have been studied.

In this context, graphene has attracted great attention as a candidate of the transparent electrode to replace ITO [6]. A typical chemical-vapor-deposition (CVD) grown graphene film shows low sheet resistance of ~280 Ω/□, with ~80% optical transparency [7]. Not only for the purpose of ITO replacement, graphene also has a crucial advantage as the transparent electrode in terms of flexibility [8]. Due to its flexibility, some groups have attempted to use graphene for photonic device [9], flexible displays [10], touch panels [11], heating windows [12], solar cells [13], and smart windows [14–18]. Zhao et al. reported the polyaniline based electrochromic device (ECD) using graphene oxide in 2009 [14]. Aqueous dispersion of graphene oxide produced by the Hummers' method, were deposited as an electrode, and polyaniline film was spin-coated onto graphene oxide. However, polyaniline is a conducting, semi-flexible polymer, and graphene oxide is a well-known insulator, so strictly speaking, the graphene was not used as electrodes in their study. Ko et al., reported a Prussian Blue (PB) based ECD using graphene as transparent electrodes, where PB nanoparticles were electrodeposited on the graphene film directly [15]. However, the usage of graphene instead of ITO was not successful, as the response speed of graphene based ECD were about half as fast as ITO based ECD. The slow response was explained by a slow electron transfer from graphene [15]. As the electron transfer from graphene occurs mainly through a peripheral edge, the usage of graphene

electrode for a current-driving device like an ECD is not a good choice. However, the graphene has a large basal plane and can be a suitable electrode to apply the electric field. In the case of a voltage-driving device like a PDLC, the graphene can be used without loss of fast response, which was the motivation of this work.

2. Methods

The single-layer-graphene was grown on a copper (Cu) foil (25 μm thick, 99.8% purity, Alfa Aesar, item no. 13382) in a CVD chamber with mixed gas flow (H$_2$, 100 sccm and CH$_4$, 200 sccm) in 20 min at 1000 °C temperature. A PMMA (950 A4, MicroChem) film was coated on top of the Cu foil by spin coating (5 s, 500 rpm and 40 s, 4000 rpm). As the graphene layers were grown on both sides of the copper foil, unwanted back side graphene was removed by dissolving Cu foil partially, in iron (III) chloride (FeCl$_3$) solution, followed by a rinse with deionized (DI) water. For the complete Cu etching, the foil was floated in ammonium persulfate solution, ((NH$_4$)$_2$S$_2$O$_8$, 0.1 Mol) in 8 h. The PMMA film with graphene was rinsed three times in DI water. The film was attached to a commercial PET film with a 100 μm thickness, where the graphene side faced the PET film. The drying process to remove residual water was very critical, so as not to tear the graphene layer to pieces in the following process. The PMMA layer was removed by immersing the sample into acetone for an hour, and the sample was rinsed in isopropyl alcohol and DI water. The graphene layer was inspected by Raman spectrometer (inVia Raman microscope, Renishaw), scanning electron microscope (VEGA3, TESCAN), atomic force microscope (AFM, n-Tracer by Nano Focus Inc.), and an optical microscope. The AFM topographic image was measured in contact mode with a scan rate of 0.5 Hz, using cantilevers with 0.1 N/m spring constant. Sheet resistance was measured by the van der Pauw method with gold probes, where the current was 1 μA.

A photocurable adhesive (NOA65, Norland) with a refractive index n$_p$ = 1.524 was used as a polymer matrix, and a commercial nematic liquid crystal (LC, C7, Qingdao Intermodal Trading Ltd.) with n$_o$ = 1.528 and n$_e$ = 1.732 was adopted. NOA65 and LC were mixed with a 50:50 weight ratio, and the mixture was spin-coated with 500–1000 rpm, on top of the graphene coated PET film. The coated film thickness was in the range of 10–20 μm. This thickness can be controlled by the spinning speed, which affects the electro-optical properties of PDLC [19]. The sample was irradiated with UV light to polymerize NOA65, and liquid crystal (LC) was segregated from polymer forming micro-sized droplets. A Hg lamp with 1 kW power, at a 23 cm distance was used as a UV light source, and the irradiation time was about 15 s. After the irradiation, the coated layer on the graphene became hazy, and another graphene-coated PET film was placed on top of it. Fig. 1 shows the schematics of the graphene based PDLC device and the electrical wiring with the silver paste. The transmission spectrum of the PDLC with different voltages applied was measured by a UV/Vis spectrometer (Cary 5000, Varian). Parallel transmission as a function of the driving voltage was measured with a laser diode (λ = 635 nm) and a photodiode.

3. Results and discussion

The scalability is a crucial issue for the purpose of commercialization, and the CVD growth of the graphene on Cu foil is a suitable method up to date, as a roll-to-roll process is possible with CVD [6]. Adjusting growth time was a difficult process to produce a complete covering layer without consuming unnecessary time. As shown in Fig. 2(a), a long time was spent for heating and annealing, and the growth time was about 20 min. When the growth time was not enough, the nucleation of the graphene grain was observed as
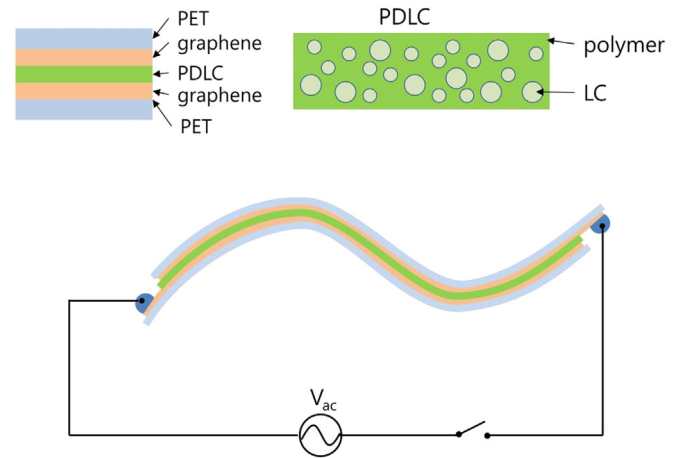

Fig. 1. A schematic shows the graphene based PDLC device and electrical wiring with silver paste. This device was stretchable, as well as flexible.

shown in Fig. 2(b), SEM image, and (c), AFM image. These images were taken after the graphene layer was transferred onto Si wafer, and the PMMA layer was dissolved completely. The graphene grains were observed to be dispersed evenly in a rough way, but in a large scale, a stripe pattern was found, which must originate from the morphology of the Cu foil. The commercial Cu foil has a stripe pattern with ~100 nm roughness formed in the rolling process. Thus, it can be said that the location of the nucleation was affected by the surface morphology of the Cu foil. When the growth time was equal or longer than 20 min, the grains were interconnected, and the sheet resistance decreased in the order of 1 kΩ or less.

In the transfer process, the PMMA layer thickness was estimated as a few hundred nanometers and its surface morphology has the same track originating from the Cu foil as shown in Fig. 3(a). This optical microscopic image was taken after the PMMA film with the graphene layer was attached on the PET film. The graphene layer was not visible in this image as it was extremely thin. Before dissolving the PMMA film, extreme caution was required to avoid possible damage on the graphene layer. As the surface of the PMMA film was not flat, moisture or gas (air) could have remained between the graphene layer and the PET film. Inspection under an optical microscope was not able to distinguish the existence of either moisture or gas. However, serious damage on the graphene layer was found after dissolving PMMA, as shown in Fig. 3(b). The shape of the torn graphene layer also has a footprint of the stripe pattern, which was the suggestive evidence that the problem came from gaps between PMMA and PET films.

In order to remove the air and water at the gaps, some extra treatments like heating or vacuuming were attempted, but the results were not successful. To avoid the air trapping, air bubbles observed below the PMMA film in the liquid after etching the Cu foil were pushed out, using a bent plastic bar. The best way to remove the water was hanging the sample out for more than an hour to let the water flow down. With these treatments, the graphene layer was transferred successfully onto PET film with no damage as shown in Fig. 3(c) and the adhesion force was strong enough for the graphene layer to survive in the next chemical processes. Raman spectroscopy was performed on the graphene layer as shown in Fig. 3(d). 2D-band peak (2700 cm^{-1}) with single Lorentzian shape was about 3 times higher than G-band peak (1580 cm^{-1}), and D-band peaks (1360 cm^{-1}) was much lower than the other peaks, confirming that the high quality single-layer-graphene was indeed grown [20].

Concerning the PDLC structure, optical microscopic inspection