Graphene oxide doped PDLC films for all optically controlled light valve structures

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ABSTRACT

We study the effect of graphene oxide (GrO) on the switching voltage of polymer dispersed liquid crystal (PDLC). The threshold voltage decreases with addition of GrO nanoparticles. Scanning electron microscopy (SEM) supported that the size of LC droplets in GrO-doped PDLC increase in comparison with non-doped one. PDLC:GrO layer was combined with $Bi_{12}SiO_{20}$ (BSO) inorganic substrate into a hybrid structure and based on the surface activated photorefractive phenomena typical for BSO, it allows the opaque-transparent states to be all optically controlled, operating faster and requiring less intensity due to the GrO addition in PDLC.

Keywords: polymer dispersed liquid crystals, graphene oxide, hybrid structure, inorganic crystals, space-charge field

1. INTRODUCTION

Polymer dispersed liquid crystals are well known compositions widely used as switchable windows, light-shutters, in display technology and as phase modulators [1-2]. Naturally, PDLC consists of submicron-size droplets of liquid crystal (LC) randomly distributed within a polymer matrix. Due to the refractive index mismatch between the polymer matrix (n_p) and the LC molecules, PDLC are opaque (scatter the light) at their initial state. In general, PDLC can be switched from the light-scattering to the transparent state by application of an electric field, which support the refractive indices match between the LC and the polymer. Usually, the switching voltages of PDLC are excessively high due to strong surface anchoring effects at the polymer matrix walls. In order to expand the applicability of PDLC, enormous effort has been made in lowering the switching voltage. Doping with nanoparticles (NPs) is one of the most efficient ways [3-5].

In general, the interactions between LC molecules and nanomaterials play fundamental role since the nanoparticles can significantly alter many LC properties that affect the practical applications. Among the nanoparticles frequently used are Au, Ag, ZnO, moreover quantum dots, carbon nanotubes and recently graphene and its derivatives: nanorods, graphene flakes, graphene oxide [4-9]. Due to the graphene superior benefits such as extraordinary electrical, optical, chemical and mechanical properties, the two-dimensional honeycomb structure of graphene shows remarkable interactions with the LC molecules therefore inspired huge fundamental and practical interest. For instance, multilayer graphene flakes can improve the electro-optic response in a nematic LC phase [7], the rod shapes of LC molecules tend to align along the alternate positions of the graphene hexagons, providing enhancement of nonlinear properties of PDLC [8]. Furthermore, the presence of carbon nanotubes has a favorable impact on LCs' electro-optical switching phenomena [9].

In more particular, graphene oxide –an oxidized form of graphene, laced with oxygen-containing groups, proved its advantage over the graphene as easy dispensability in water and other organic solvents due to the presence of the oxygen functionalities. This fact remains as a very important property when mixing with polymer or other organic matrixes in order to improve their electrical and mechanical properties. For example, it was reported that graphene oxide promotes vertical alignment of an LC without any surface treatment of the substrates [10].

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In this paper, we investigate the effect of GrO addition on electro-optical properties and structure of PDLC film and experimentally demonstrate that GrO doping increases the size of LC droplets and leads to decrease of the threshold voltage in comparison with non-doped PDLC. In addition, combination of GrO doped PDLC with BSO inorganic crystal into a hybrid structure is demonstrated. Based on photogenerated charge carriers in BSO substrate and high birefringence of PDLC layer, the hybrid structure allows the switching between opaque-transparent states to be all optically controlled. Moreover, GrO addition in PDLC improves the switching time and enhances the beam amplification value.

2. EXPERIMENT

2.1. **Graphene oxide addition in PDLC**

Graphene oxide (GO) was commercially obtained from Graphene Supermarket, Inc., with a specification of up to 10μm in diameter and 1 nm thickness. First, after drying the GrO powder in oven to evaporate any residual moisture, it was ball milled in a few drops of ethanol (wet milling) using Fritsch pulverisette machine. Figures 1(a,b) show the SEM image of GrO flakes before and transmission electron microscopy (TEM) image after the ball milling process.

The GrO/ethanol suspension was steering in ultrasonic bath for 30 min and added into nematic LC (E7 Merck type) in concertation of 10^{-4} wt % relative to the total mass of the LC. The mixture was sonicated for 1 h, allowing the LC to dissolve completely into the solution. Next, the ethanol was evaporated at an elevated temperature of 80°C for 8 hrs.

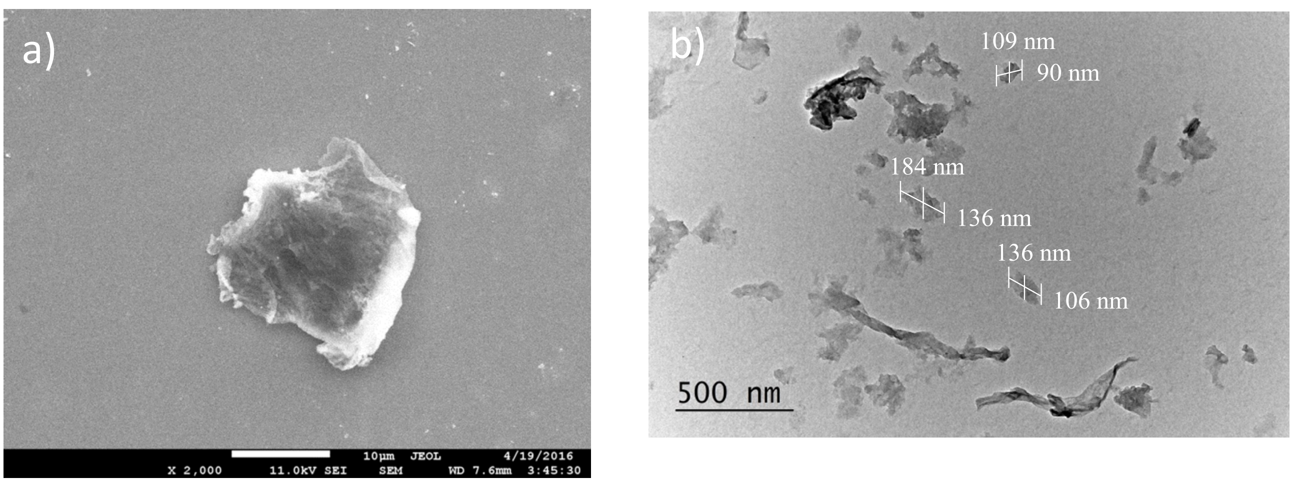

Fig.1 (a) SEM image of GrO before the ball milling and (b) TEM image of GrO particles at magnification 10 000x, after the ball milling.

2.2. GrO-doped PDLC samples preparation

PDLC samples were fabricated by phase separation method using PDLC solutions consisting of nematic LC, polymer matrix (NOA 65 UV glue) and GrO nanoparticles. The LC/GrO suspension was mixed with NOA 65 UV glue at 30:70 wt % ratio. The LC/GrO/monomer mixture was injected into an empty glass cell (commercially manufactured) with a gap of 8μm at the isotropic state at T = 90°C.

In addition, a reference PDLC cell (without GrO addition) was prepared using the same fabrication procedure and cell gap thickness. Finally, the ready cells were exposed with UV light (λ= 365 nm) with an intensity of 60 mW/cm^2 for 15 min at T = 20°C. The phase separation morphology was observed by SEM analysis using Philips 515 digitalized microscope (Fig. 2 (a,b)).

2.3. **Voltage-transmittance measurements**

For voltage - transmittance characteristics, each cell was placed between a 532 nm Verdi laser source and photodetector (Fig 3(a)). Since the polymer matrix determines the LC alignment, PDLC do not require need of polarizers. An alternating current (AC) voltage (r.m.s., frequency f = 1kHz) was applied to the electrodes across to the cell.

The threshold voltage (V_{th}) and the driving voltage (V_d) were measured when the transmittance reaches 10% and 90% of its maximum values T_{max}, i.e., at T_{10} and T_{90}. The contrast ratio was defined by the ratio T_{max}/T_{min}, *where* T_{max} and T_{min} are the maximum and minimum transmittance of the V-T curves.

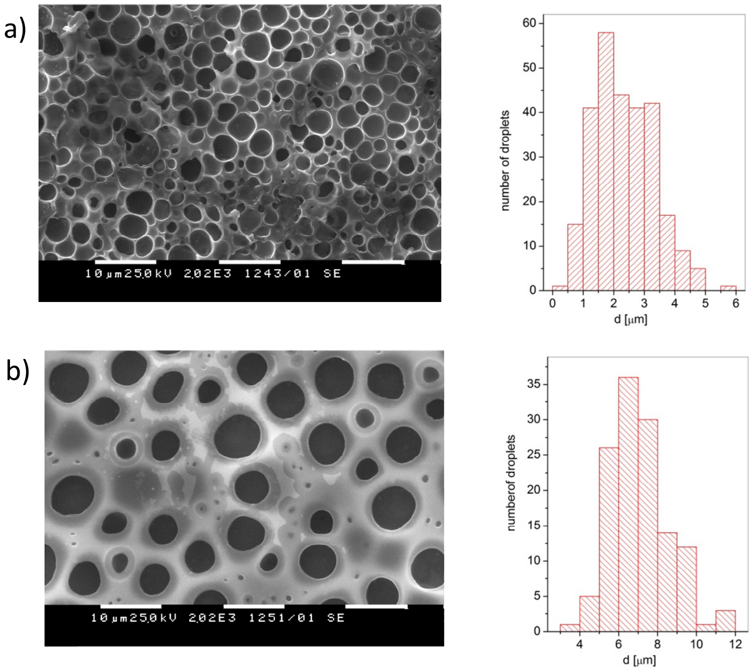

Fig.2 SEM images: (a) PDLC reference sample (mean diameter of the droplets d=2358 nm, standard deviation SD = 967 nm) and (b) PDLC doped with Gr oxide (concentration 10^{-4} wt %) (mean diameter of the droplets: d=7070 nm, standard deviation SD=1512 nm).

2.4. **Fabrication of hybrid structure and two-beam coupling experiments**

Based on the reduced driving voltage of GrO-doped PDLC, it was combined together with the BSO inorganic crystal, well known as one of the fastest photoconductive and photorefractive materials [11, 12]. BSO crystal plate was cut from the bulk crystal grown by the Czochralski method [13] and optically polished with a thickness of 0.3 mm. An empty cell composed of BSO crystal and a glass substrate has been assembled. The LC/GrO/monomer mixture was injected by capillary method and ready cell was exposed with UV light following the same fabrication procedure discussed in 2.2.

Reference sample made with the same thickness of BSO crystal plate and non-doped PDLC has been prepared for comparison.

The two-beam coupling set-up was arranged using 532 nm laser, split to two linearly polarized beams. First, the laser beam was divided on two-beams with the same intensities 1:1 ratio. Next, the ratio between two beams has been experimentally optimized to $I_{signal}/I_{pump} = 1/70$, where the full angle 2θ between the two interacting beams was 37° .

3. RESULTS AND DISCUSSIONS

3.1. **Voltage - transmittance characteristics**

Without application of an electric field, the effective index of LC droplet is $(2n_0+n_e)/3$ where n_0 and n_e are the ordinary and extraordinary index of LC, respectively. Because of the index mismatch between the LC and surrounding polymer matrix (n_p) the PDLC scatter the light and appears opaque at its original state. The application of electric filed to the PDLC film caused transparency once the index of electrically aligned LC molecules (n_0) matches the index of polymer. Figure 3 shows the V-T curve behavior for GrO-doped PDLC and reference PDLC sample. Obviously the GrO addition decrease the driving voltage in comparison with the reference PDLC sample. These results are supported by SEM analysis, shown at Fig. 2(a,b) verifying that GrO addition increases the size of LC droplets which are inversely proportional to the threshold voltage [14].

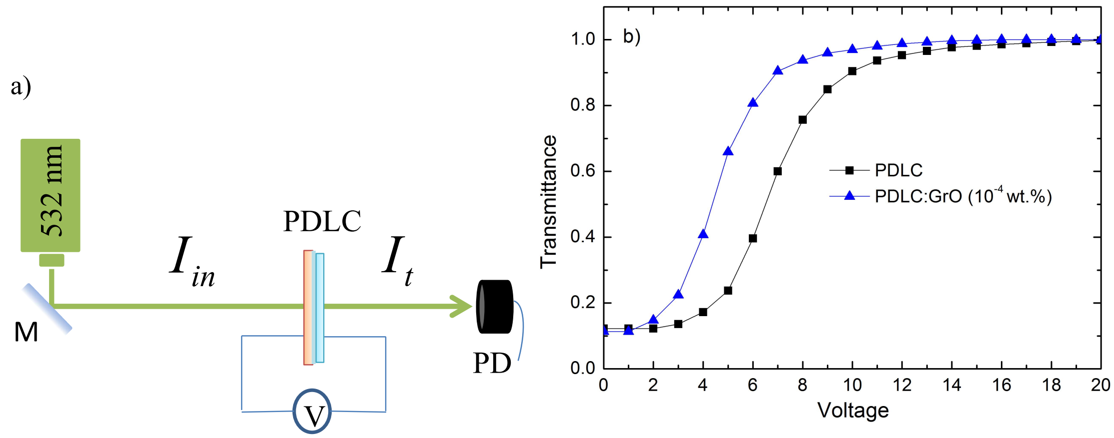

Fig.3 Voltage-Transmittance set-up and experimentally measured V-T values for GrO (10^{-4} wt %) doped-PDLC and PDLC reference sample.

Generally, the switching characteristics of PDLC depend on the LC type, the size of LC droplets and anchoring properties of the LC boundaries. Usually, the switching voltage is inversely proportional to the PDLC thickness and given by [14]:

$$E_{sw} = \frac{V_{sw}}{d} \approx \frac{1}{3R}\left(\frac{\varepsilon_{(LC)}}{\varepsilon_{(P)}} + 2\right)\left(\frac{K(l^2-1)}{\varepsilon_0 \Delta\varepsilon}\right)^2 \qquad (1)$$

where d-is the thickness of PDLC layer, R - characteristic radius of LC droplets, $\varepsilon_{(P)}$ and $\varepsilon_{(LC)}$ - real part of the dielectric constant of the polymer matrix and LC, K - Frank elastic constant, l - aspect ratio of the droplets, $\varepsilon_0 = 8.854\times10^{-12}$ Fm^{-1} - permittivity under vacuum, $\Delta\varepsilon$ - dielectric anisotropy of the LCs.

3.2. Light-induced transparency and beam-coupling effect

First, both BSO/PDLC:GrO and BSO/PDLC hybrid structures were illuminated with 532 nm Gaussian laser beam (1 mm waist) and transmitted light intensity changes have been detected by photodetector (inset set-up in Fig.4)). Figure 4 shows the time dependent transmitted beam intensity trough the samples. As it seen, at the beginning both structures scatter the incident light because of the mismatch between the refractive indices of the LCs and the polymer binder. After few ms, transmitted light intensity starts to increase indicating that the structure starts to respond to light. Although both structures turns out to highly transparent state, for BSO/PDLC:GrO it takes faster time, suggesting that LC molecules in a droplets surrounded with GrO particles tend to re-align easier (requiring less driving voltage). The same test have been performed on Glass/PDLC/Glass reference sample, made with the same thickness. No noticeable changes of the transmittance with the time have been detected on it, as it seen from Fig. 4 .

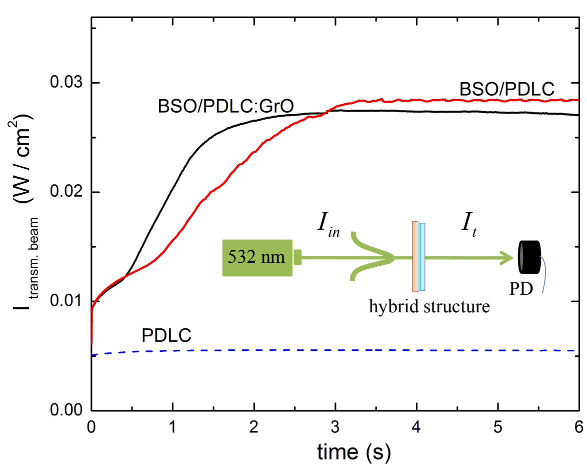

Fig.4 Transmitted light intensity as a function of time for BSO/PDLC:GrO and BSO/PDLC samples. Dash line stands for PDLC reference cell.

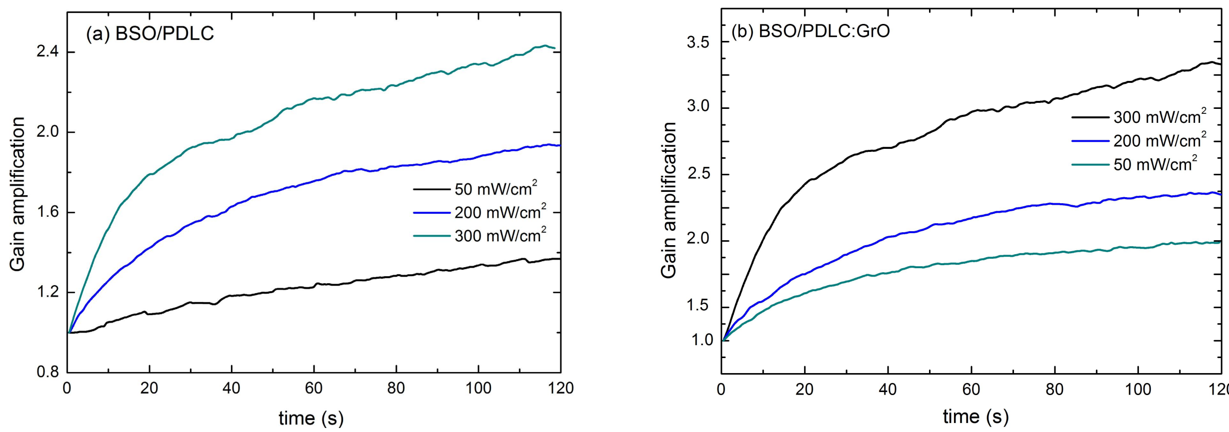

Fig.5 Gain amplification behavior during the two-beam coupling experiments for (a) BSO/PDLC and (b) BSO/PDLC:GrO samples.

We suppose that detected reverse switching from initial opaque state to the transparent state comes from BSO crystal substrate. Due to its high absorption and photoconductivity, the laser beam illumination caused charge carrier's generation, which migrate by diffusion to form an inhomogeneous distribution and resultant space charge field (E_{sc}). This photo-induced field, generated inside the BSO , can rise strong enough to spread out into the PDLC layer, realigning the LCs molecules inside the droplets and thus to change the LCs director, consequently the refractive index and transparency of the structures [15]. Hence, the main operation principle of the proposed structure is based on the photorefractive phenomena

Owing to the above demonstrated ability of space-charge field to realign the LCs molecules, the two-beam coupling experiments

have been performed. The ratio between the pump and signal beam has been experimentally optimized to $I_s/I_p = 1/70$, where the full angle 2θ between the two interacting beams was 37°. The gain ration G depends on the refractive index modulation and the phase shift between the space-charge field and the optical interference pattern by :

$$\Gamma = \frac{1}{d}\log_e(G) \tag{2}$$

where G is the gain ratio and d is the penetration depth of space charge field into the LC layer [11].
Figure 5 (a,b) show the amplified behavior of the signal beam passing throughout the structures, depending on the light intensity. As it seen, the GrO addition in PDLC enhances the beam amplification value during the two-beam coupling experiment. Further optimization of the proposed hybrid structure by different concentration of GrO addition, effect on the threshold voltage and droplets size is in progress.

4. CONCLUSIONS

In conclusion, we study the effect of Graphene oxide addition in PDLC layers and experimentally demonstrate that GrO doping increases the size of LC droplets and leads to decrease of the threshold voltage in comparison with non-doped PDLC. In addition, GrO doped PDLC layer was combined with BSO inorganic crystal into a hybrid structure. Due to the photo-generated charge carriers and created space charge field in BSO substrate, the hybrid structure allows opaque-transparent states to be all optically controlled. Moreover, GrO addition in PDLC improves the switching time and enhances the beam amplification value during the two-beam coupling experiment.

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