Optoelectronics properties of broad-band reflectors improved by doping graphene modified with azobenzol group

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NH₂-terminated mesogenic group azobenzol was chemically grafted onto graphene (GOre) via amidation reaction. The resultant mesogenic group modified GO sheets (GOre-Az) were easily redispersed in common organic solvents or liquid crystals (LCs), facilitating the structure characterization and the device fabrication by solution processing. Broad-band reflectors could be obtained by doped different contents of GOre-Az nanosheets into chiral nematic liquid crystals (N*-LCs) media to a photo-polymerization. Experimental results showed that both the bandwidth of the reflection spectra and the location of reflection band of the GOre-Az doped composite films were better than the N*-LCs sample without GOre-Az. Effect of polymerization temperatures and doped contents of GOre-Az on the broad-band reflection of N*-LC composite films was investigated. The experimental results show that the doping nanomaterials can improve the performance of the LC medium. Our observations open up new possible applications for GO nanomaterials in intelligent optoelectronics industry, including reflective color displays, smart reflective windows.

1. Introduction

Liquid crystal (LC) is a state matter intermediate between the solid and liquid phases; it was first discovered by Reinitzer. The unique properties of LCs, such as optical anisotropy and response to electric field, made them popular materials for electronic displays. Dispersing nanoparticles (NPs) in liquid crystals (LCs) has long been studied in the LC display community for purposes such as lowering driving threshold voltage and improving response speed of the display devices [1-5]. Recently, effective media with NP inclusions in LC hosts have attracted much attention as a novel type of tunable optical properties. Moreover, LCs doped with nanomaterials would lead to many distinctive optical and electro-optical (E-O) characteristics including orientational control, low driving voltage, short response time, frequency modulation response, and memory effect [6-8].

Among currently available nanomaterials, graphene, classified as a two-dimensional (2-D) carbon allotrope, has attracted immense attention for potential applications in electronic devices and nanocomposites since its successful isolation in 2004 [9]. Electric field-dependent conductance studies reveal that the graphene flakes follow the nematic director that mechanically rotates on increasing an applied electric field [10-15]. Aromatic rings in LC molecules are oriented with hexagonal rings in graphene to have preferred orientation, providing a way to identify relative orientations of graphene domains and point defects [16].

As the interest in LC suspensions grows readily in current nanoscience, researchers have investigated the optical manipulation in a LC/graphene nanostructure [17] as well as applications of graphene in cholesteric [18] and polymer- dispersed [19] LCs recently.

To gain a deeper understanding of the photophysical porperties for an enhanced broad-band reflector, the azobenzol mesogenic unit (Az) have been chemically grafted onto surface of GOre sheet via amide reaction (GOre-Az). This paper will address the various issues associated with the practical broad-band reflector devices, which relies on a polymerization temperatures and doped contents of GOre-Az. The oriented influence by hexagonal rings in graphene and Az on the LCs was further investigated.

2. Experimental

2.1. Materials and Methods

Graphite powder (320 mesh) was purchased from Sinopharm Chemical Reagent. Co.,Ltd. Aminoazobenzol, isoamyl nitrite and hydrazine hydrate was purchased from Aladdin Reagent (Shanghai) Co., Ltd. 98% H_2SO_4, 30% H_2O_2, $KMnO_4$, $NaNO_3$, methanol and other reagent were purchased from Beijing Lan Yi Chemical Products Co., Ltd. GO was prepared using a modification of Hummers and Offeman's method.[20-22] In a typical reaction, 1 g

graphite, 1 g $NaNO_3$ and 50 mL H_2SO_4 were stirred together in an ice bath. $KMnO_4$ (6 g) was slowly added while stirring, and the rate of addition was controlled to prevent the mixture temperature from exceeding 20 °C. The mixture was then transferred to a 35 °C water bath and stirred for about 0.5 h, forming a thick paste. Subsequently, 50 mL deionized water was added gradually, causing an increase in temperature to 98 °C. After 15 min, the mixture was further treated with 150 mL de-ionized water and 10 mL 30% H_2O_2 solution. The warm solution was then filtered and washed with deionized water until the pH was 7 and dried at 65 °C under vacuum.
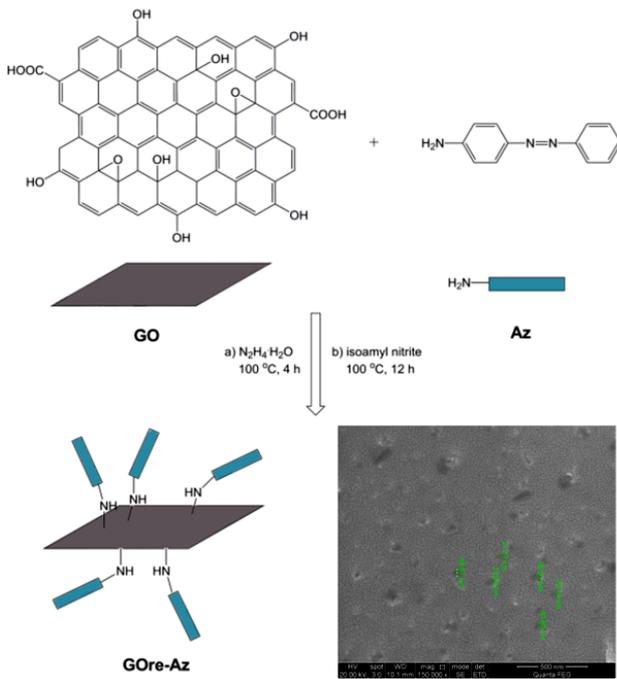

Fig. 1. Synthesis route of aminoazobenzol group grafted on graphene nanoplatelets, and FESEM images of GOre-Az

In a typical experiment, [23] 100 mg GO was loaded in a 500 mL round-bottom flask and 200 mL deionized water was then added. After stirring and ultrasonication for 1 h, 1 mL hydrazine hydrate was gradually added to the solution. Subsequently, the mixture was transferred to a 100 °C oil bath and stirred for 4 h, and the Gore was obtained. 1 g aminoazobenzol and 0.3 mL isoamyl nitrite were then added. The mixture was stirred vigorously at 100 °C for 12 h and then cooled to room temperature and filtered using a teflon filter (0.2 μm). The filter cake was washed with methanol until the filtrate was clear. The remaining black solid (GOre-Az) was dried under vacuum. All the characterizations of GOre-Az can be found in another submitting manuscript (Blue phaseliquid crystals effected by graphene oxide modified with aminoazobenzol group).

2.2. Preparation of Broad-band Reflectors

The cell's two inner surfaces with polyvinyl alcohol (PVA) layers were rubbed in perpendicular directions to provide a homogeneous orientation of LC molecules. The 25 μm thick polyethylene terephthalate (PET) films were used as a spacer of the cells. The N*-LCs used in this experiment were mixtured comprising nematic LCs (N*-LCs) with positive dielectric anisotropy SLC-1717, photo-initiator IRG-651, photo-polymerisable monomer (C6M) and chiral dopant (CD) were synthesized in our laboratory (See Fig. 2).

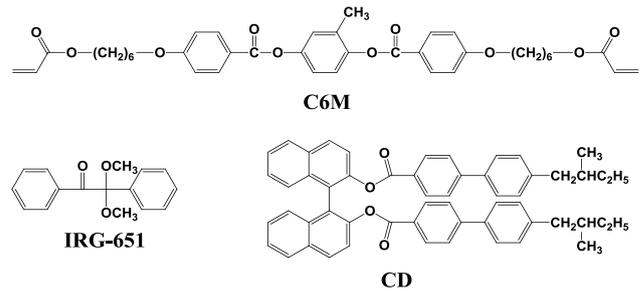**SLC-1717**: Mixture of LCs with positive dielectric anisotropy

Fig. 2. Chemical structures of compounds in the nematic LCs

These characterizations suggest that the azobenzol molecules have been successfully modified onto graphene oxide. Then the N*-LCs were doped with different contents of GOre-Az, separately. After ultrasonic dispersion and solvent evaporation, the blends were placed into planar treated cells by capillary action, and the cell gap was maintained at 25 μm by spacers. The compositions and the weight ratios of the four studied samples are listed in Table 1. Then the cells of samples 1-4 were irradiated with UV-light (2.0 mW/cm^{-2}, 365 nm) for 15 min at different temperatures, respectively. Thus, the N*-LC composite film with a permanent helical solid structure was prepared from the photo-polymerization of the molecules of C6M in the mixture. Finally, the cells were kept at room temperature.

The basic principle of Broad-Band Reflectors is Bragg reflection of chiral nematic liquid crystalline [24-27]. Here, SLC-1717 is the common nematic liquid crystalline, and the chiral nematic liquid crystalline can be obtained by doping chiral dopant CD. It is interesting that the pitch of chiral nematic liquid crystalline become temperature dependent because of doping CD. In the reference [27], it was proved that the content of CD can also affect the properties of reflected light.

Table 1. Chemical compositions of samples 1-4

Samples	GOre-Az wt%	CD wt%	C6M wt%	N-LCs/ wt%
1	0.0	3.0	10	87.0
2	0.3	3.0	10	87.0
3	0.5	3.0	10	87.0
4	0.8	3.0	10	87.0

3. Results and discussion

The transmission spectra versus applied field of these samples were collected by a UV/visible spectrophotometer (JASCO V-570). Fig. 3 shows that the transmission spectra of samples 1-4 before polymerization, and the differences of curves are little. Fig. 4a shows the transmission spectrum of sample 1 without any dopants after polymerization, and Fig. 4b-4d show the transmission spectra of samples 2-4 after polymerization. The work presented here focuses on the quite surprising observation that samples 2-4 doped with GOre-Az exhibited a larger broadening of reaction bandwidth than sample 1 which without dopants. As the polymerization temperature increases, the reflected centre wavelengths were red shifted obviously.
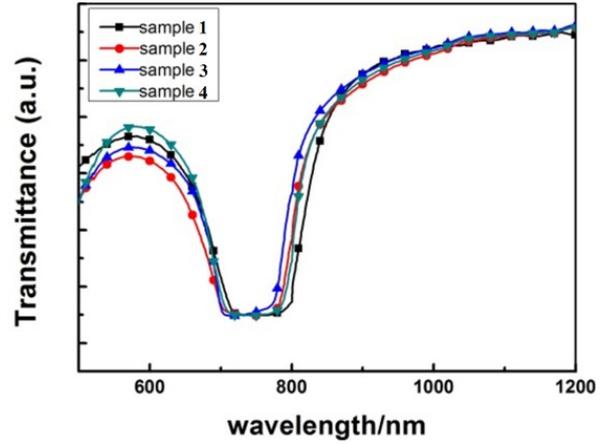

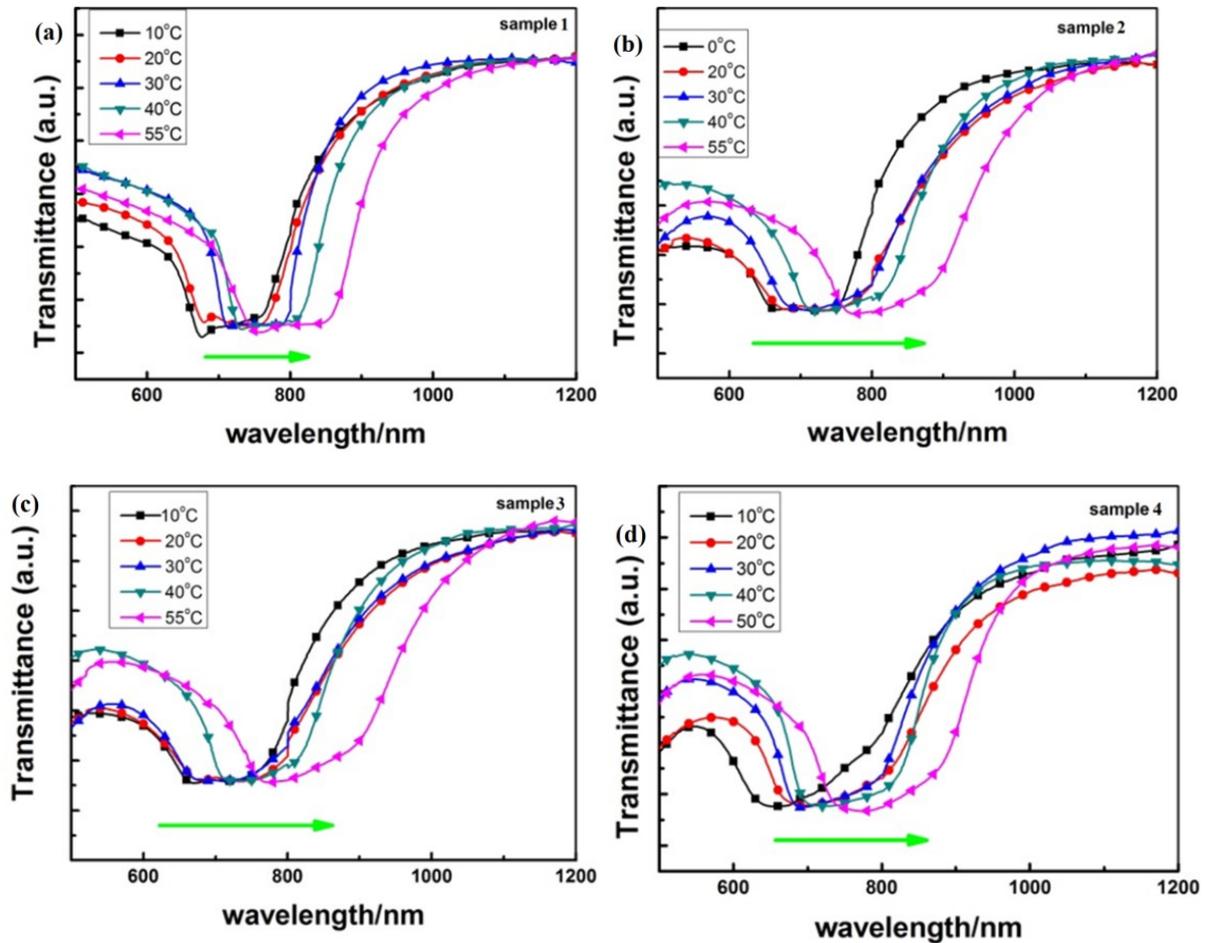Fig. 3. The transmission spectra of samples 1-4 before polymerization

Fig. 4. The transmission spectra of samples 1-4 were irradiated with UV-light (2.0 mW/cm^{-2}, 365 nm) for 15 min at different temperatures, respectively

Moreover, it is interesting to find that the reflected bandwidth is affected by doping the GOre-Az nanosheets. It can be seen from Fig. 5 that all the samples 2-4 which contain GOre-Az nanosheetes with different contents exhibit an increase of Δλ as the temperature increases. The max Δλ at the highest polymerization temperature was about 200 nm for LC doped GOre-Az, and Δλ was widened about 30 nm comparing that without GOre-Az.

For samples 2-4, the differences of Δλ at the same polymerization temperatures and different contents of the GOre-Az are little, and it is suggested that the contents have little effect on the results. In addition, the centre wavelengths are not appreciably affected by doping GOre-Az. The experimental results confirm that the nanomaterials are pivotal for enhancing the performance of the N*-LC media.
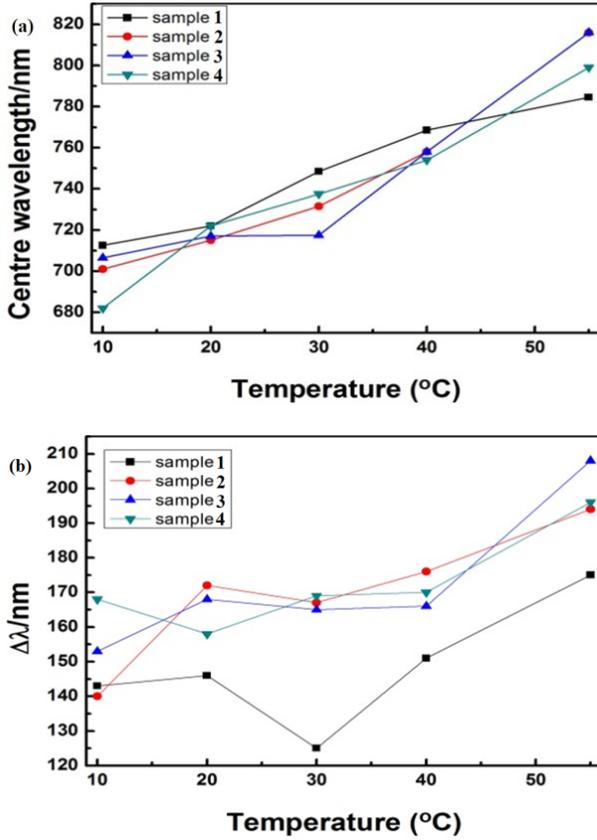
Fig. 5. (a) The reflection bandwidth dependence of the temperature for samples 1-4; (b) The centre wavelength dependence of the temperature for samples 1-4

It is well known that for a single-pitch N*-LC, $\Delta\lambda$ is given by $\Delta\lambda = \Delta n \times P$, and non-uniform pitch N*-LC, $\Delta\lambda$ is given by $\Delta\lambda = \Delta n \ (P_1+P_2+P_3+\ldots\ldots+P_n)$. Here, Δn is the intrinsic birefringence, and P is the pitch length of the N*-LC.[28] In case of the GOre-Az–N* -LC composites, it is found that the inherent Δn is irrespective of the temperature in our experiment. Thus, we presume that it is the variational P that results in the broadening of reflected bandwidth. To broaden the bandwidth, Broer et al. obtained a pitch gradient distribution in polymer stabilized N*-LC gels by using the differences in reactivity and diffusion rate of the monomers during the photo-polymerization [29]. Bian et al. got a non-uniform pitch distribution in N*-LC gels by mixing the particles with different pitches of the N* phase together followed by making LC monomer molecules crosslink in photo-polymerization.[30] Herein, we infer that a non-uniform pitch distribution could be generated by doping GOre-Az nanomaterials into N*-LCs under the photo-polymerization. From Fig. 5, as the temperature increases, the reflected centre wavelength was red shifted obviously. This is due to the fact that the helical twist power (HTP) of the chiral dopant (CD) decreases as the temperature increases. According to the formulas: $P=1/(xc\cdot HTP)$, the helical pitch increases as the temperature increases. Just as Fig. 5 shows, the centre wavelengths of samples 1-4 shift to longer wavelength

with the increase of temperature.

In order to better understand how the GOre-Az nanosheets influence the orientation of LC molecules and form a non-uniform pitch distribution, a presumed mechanism is proposed as shown in Fig. 6. In some regions, the alignment of the LC molecules which are the nearest to the UV-curing polymer network is well stabilized and the rearrangement of LC molecules with the change of temperature is difficult. Because the HTP of the chiral dopant decreases with the increase of temperature, the pitch length of the blend has tendency to increase as the temperature rise, consequently resulting in a non-uniform pitch distribution (P_0, P_1, P_2). The pitch distribution in the composites is statically uniform (P_0) before polymerization [Fig. 6 (a) and (c)]. The GOre-Az nanosheets and azobenzol mesogenic unit will align along the orientation of LC molecules due to a large alignment energy caused by the enhanced anchoring force through sample surface area in nanomaterials [31].
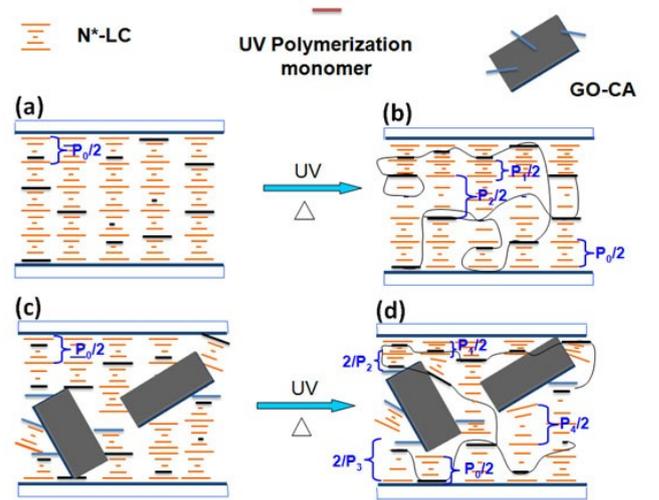

Fig. 6. Schematic representation of the mechanism for the composites, (a) cell without GOre-AZ before polymerization; (b) cell without GOre-AZ after polymerization; (c) cell with GOre-AZ before polymerization; (d) cell with GOre-AZ after polymerization

Because of the photo-polymerization, the GOre-AZ nanosheets would mechanically move, which in turn distorts the neighbour LC molecules owing to the strong adhering force from the surface of GOre-Az nanosheets, consequently resulting in a non-uniform pitch distribution (P_0, P_1, P_2, P_3, P_4) combine with the influence of temperature as shown in Fig. 6 (d). After the formation of the polymer network, the longer pitch of the samples in the specified regions surrounded by the polymer network is frozen. Because the effect of every nanosheets is almost the same, so that the new pitch originated from the introduction of nanosheets is almost similar. With increasing the content of GOre-AZ nanosheets, no more new pitch would be automatic generated, then the $\Delta\lambda$s were not affected by the content.

4. Conclusions

In conclusion, we have successfully synthesized the effective functionalization of graphene oxide sheets with NH_2-terminated mesogenic groups. Broad-band reflectors were achieved by introducing GOre-Az nanosheets with different contents into chiral nematic liquid crystals with photo-polymerization. It was found that the reflection bandwidth depends on the polymerization temperature obviously, and the doped GOre-Az nonaomaterials also broaden the reflection bandwidth. However, the contents of the GOre-Az nonaomaterials barely affect the reflection bandwidth. All the results can prove that (1) the polymerization temperatures exhibit red shift effect for the reflection centre wavelength due to HTP; (2) the introduction of GOre-Az nonaomaterials can broaden $\Delta\lambda$ due to interaction between LCs and GOre-Az; (3) increasing the content of GOre-AZ nanosheets is useless for broadening reflection bandwidth.

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