Dynamic electro-optic response of graphene/graphitic flakes in nematic liquid crystals

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Abstract: Electric field induced dynamic reorientation phenomenon of graphene/graphitic flakes in homogeneously aligned nematic liquid crystal (NLC) medium has been demonstrated by optical microscopy. The flakes reorient from parallel to perpendicular configuration with respect to boundary plates of confining cells for an applied field strength of as low as tens of millivolt per micrometer. After field removal the reoriented flakes recover to their initial state with the help of relaxation of NLC. Considering flake reorientation phenomenon both in positive and negative dielectric anisotropy NLCs, the reorientation process depends on interfacial Maxwell–Wagner polarization and NLC director reorientation. We propose a phenomenological model based on electric field induced potential energy of graphitic flakes and coupling contribution of positive NLC to generate the rotational kinetic energy for flake reorientation. The model successfully explains the dependence of flake reorientation time over flake shape anisotropy, electric-field strength, and flake area. Using present operating scheme it is possible to generate dark field-off state and bright field-on state, having application potential for electro-optic light modulation devices.

OCIS codes: (160.3710) Liquid crystals; (160.4236) Nanomaterials; (230.2090) Electro-optical devices; (250.6715) Switching; (110.0180) Microscopy.

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1. Introduction

Electric field induced reorientation of particles such as polymer cholesteric liquid crystal flakes (PCLC) due to their unique wavelength and polarization selective reflection properties has been widely studied for electro-optic devices and flexible, reflective display applications [1–5]. The switching or reorientation of PCLC flakes has particular interest in device applications, as they are well known for very low driving field (mV/μm) and hence the electro-optic devices made of PCLC flakes consume very low power. In addition, the PCLC flake display does not require polarizers and color filters, which satisfies cost effective bright display performances. However, PCLC flake switching technology still remains in early development stage, as uniformity of reorientation needs to be improved, and relaxation time needs to be shortened for further progress [4,5].

Graphene [6–9], an atom-thick carbon sheet, has its potential in diverse areas of electro-optic devices, especially for fabrication of flexible transparent electrodes due to the high elasticity and conductivity. Two-dimensional graphitic flakes [10–12] (layers of pi-stacked graphene sheets) are optically opaque, and possess anisotropic shape and electrical properties. Such unique combination of interesting physical properties instigates electric field induced switching behaviour investigation of graphitic flakes for future display application. On the other hand, nematic liquid crystal (NLC) [13,14] is one of the mesomorphic ordered states of

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organic molecules with anisotropic shape and has high resistivity of ~10^{13} Ω cm. The electric field induced uniform reorientation behaviour of NLC is well known to the scientific as well as display community and hence interesting to be the host fluid medium for investigating reorientation behavior of graphitic flakes. Recently, research based on laser tweezer has explored optical trapping induced realignment of anisotropic nonspherical particles in isotropic fluid (water) [15] and anisotropic liquid crystal phase [16,17], which have opened up the possibility of manipulating flake reorientation through external optic stimulus. However, this laser tweezer-realigning microrheological method leads to irreversible and arbitrary rotation and unexpected spinning dynamics during optical trapping process, which makes it hard for uniform flake rotation control as well as further display switching application. Therefore, for controllable flake switching display we firstly discover and demonstrate in the present paper the electric field induced dynamic reorientation phenomenon of suspended graphene/graphitic flakes in NLC medium and light modulation dependent on field induced reorientation. We rationally discuss the basic electric field induced reorientation mechanism of flakes in nematic liquid crystal medium and introduce the concept of comparison of this system with PCLC flakes for future display application. The relationship of the reorientation time of flakes with electric field strength, frequency, flakes size, and shape anisotropy is further discussed.

2. Experimental section

The functionalized graphene/graphitic flakes used for present investigation have been obtained from Sungkyunkwan University (Korean), which have been synthesized in two steps: room-temperature oxidation of precursor graphite to generate graphite oxide and low-temperature thermal exfoliation to obtain functionalized graphene, which consisted mostly of exfoliated graphene layer and some portion of stacked layer structures with an expanded interlayer spacing of 7.5 Å. Hence by the nomenclature viz. functionalized graphene; we have indicated the graphene synthesized in above mentioned procedure. Graphene generated in present synthesis scheme contains lesser defects over graphene sheets (relatively unbroken sp^2 hybridization carbon atom over graphene plane) and less oxygen content over graphene plane in comparison with commercial graphene oxide. The shape, uniformity and internal structure of the flakes have been characterized using optical microscopy (OM) and scanning electron microscopy (SEM). The synthesis and detailed physical characterization of the graphene flakes used in present investigation have been described elsewhere [18].

Commercially available positive dielectric anisotropic NLC mixture ($\Delta\varepsilon = + 5.3$) viz. ZLI-4792 and negative dielectric anisotropic NLC mixture ($\Delta\varepsilon = -5.2$) viz. MAT-04-284 purchased from Merck-Japan have been used for present investigation. The flake-NLC mixtures have been prepared by adding ~0.005 wt% of flake powders directly into mentioned NLC mixtures. In order to achieve homogeneity, the mixtures are ultrasonicated for an hour keeping temperature at 30 °C (frequency, 28 kHz; input power, 60 W).

Indium tin oxide (ITO)-coated transparent glass substrates are used for present investigation. To provide homogeneous alignment to the NLC molecules, the alignment layer viz. SE-6514 (Japan Synthetic Rubber Co.) is spin-coated on both substrates. The substrates are baked at 70 °C for 5 minutes and 200 °C for an hour. The baked alignment layers are uniformly rubbed by rubbing machine. The test cells are finally prepared by sandwiching a couple of anti-parallelly rubbed substrates preparing in above mention method, while 70 μm film spacer maintains uniform gap between substrates. The flake-NLC mixture is filled into test cells by capillary action at room temperature. Although most graphene layers are supposed to be single or few layers after exfoliation, some still remained as small flakes with a finite thickness to exhibit desired dark state. They can be identified by optical microscopy, which revealed significantly distinct thickness with several to hundred layers, opaque, and horizontally suspended flakes in NLCs with an area of 10-300 μm^2, and hence a volume of 10-450 μm^3. The sample textures are captured by Panasonic Digital 5100 camera with a time

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resolution of 100 ms attached with optical microscope (OM, Nikon DXM1200) while applying AC field (0 to 142 mV/μm) with a driving frequency (10 Hz to 5 kHz) through with arbitrary function generator (Tektronix AFG3022). The transmitted light intensity of the captured images has been analyzed with the help of IMT *i*-solution software (Image & Microscope Technology Co., USA).

3. Reorientation model

The tested functionalized graphene/graphitic flakes [18] in our work have been synthesized from natural graphite by chemical oxidation and subsequent low-temperature thermal exfoliation technique. The graphene/graphitic flake consists of exfoliated graphene layer and some portion of stacked layer structures with expanded interlayer distance of 7.5 Å, which still takes pi-stacked graphitic form while suspended in nematic liquid crystal medium because of the high π-stacking interaction between giant individual graphene sheets [19,20]. The flakes are insulating in nature due to their non-ignorable oxygen-containing functional groups attached to either sides or edges [21,22]. Moreover, the suspended graphene/graphitic flakes with distinct thickness through their opaqueness are observed in optical microscopic investigation.

The suspended graphene/graphitic flakes are anisotropic and have been investigated in anisotropic dielectric medium viz. nematic liquid crystal (NLC). Particularly, electrical polarizability for field parallel to symmetry axis of flakes as well as NLC molecule is different than that of field's perpendicular to the symmetry axis. Therefore, an external electric field E_0 induces an electric dipole with the moment p_G and p_{LC} that is not parallel to E_0 respectively over flake and NLC. Consequently, the electrostatic torques $p_G x E_0$ and $p_{LC} x E_0$ tend to rotate the suspended flake as well as NLC molecules to align parallel with the applied electric field. Note that graphene/graphitic flake reorientation does not depend on sign of the electric field but exists for time varying fields. Here we assume that the particle material has no permanent dipole moment and that the applied electric field is uniform over the flake dimensions. The electric field inside the particle E^+, to which the particle responds, varies with the rotation of the ellipsoid (assuming the suspended flakes as individual ellipsoids) and induces an effective polarization along each ellipsoidal axis *i* [23],

$$p_i = (\varepsilon_p - \varepsilon_h) E_i^+ \tag{1}$$

where,

$$E_i^+ = \frac{\varepsilon_h E_{0i}}{\varepsilon_h + A_i\left(\varepsilon_{ii} - \varepsilon_h\right)} \tag{2}$$

where ε_p and ε_h are the dielectric permittivity of the particle and host fluid, respectively, and E_{0i} is the applied electric field component along the particle axis *i*. Calculations for an electrically isotropic particle can be performed by considering $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33} = \varepsilon_p$. The ellipsoid is described by the axes lengths a_i, a_j and a_k and a depolarization factor A_i must be defined along each axis (where *i*, *j* and *k* are indices ordered according to the right handed coordinate system and *s* is the symbolic variable in the elliptical integral),

$$A_i = \frac{a_i a_j a_k}{2} \int_0^\infty \frac{ds}{\left(s + a_i^2\right)\sqrt{\left(s + a_i^2\right)\left(s + a_j^2\right)\left(s + a_k^2\right)}} \tag{3}$$

Hence, the effective induced dipole moment along each particle axis p_i is

$$p_i = \frac{4\pi}{3} a_i a_j a_k P_i = \frac{4\pi}{3} a_i a_j a_k \varepsilon_h K_i E_{0i} \tag{4}$$

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where we have defined the Clausius-Mosotti factor K_i along each ellipsoid axis as

$$K_i = \frac{\left(\varepsilon_p - \varepsilon_h\right)}{\left[\varepsilon_h + A_i\left(\varepsilon_p - \varepsilon_h\right)\right]} \tag{5}$$

The interaction energy density connected with reorientation of graphene/graphitic flakes in electric field is given by

$$V_1 = -\int_0^{E_{0i}} p_i \cdot dE = -\frac{2\pi}{3} a_i a_j a_k \varepsilon_h K_i E_{0i}^2 \tag{6}$$

Assuming θ to be instantaneous angle between flake surface normal and applied electric field where the field E_0 has been applied along z axis. Hence, Eq. (6) takes the form

$$V_1 = -\frac{2\pi}{3} a_i a_j a_k \varepsilon_h K_i E_0^2 \,\mathrm{Cos}^2\, \theta \tag{7}$$

Let us consider a slab of nematic liquid crystal of positive dielectric anisotropy in electric field along the layer normal (considered as z axis). The nematic director assumed to have a uniform planar orientation in the absence of electric field. We also assume that both the boundary substrates have identical homogeneous alignment and the nematic liquid crystal-graphitic flake mixture is perfectly insulating. It should be noted here that the angle 'θ' that the director makes with the substrate is identical to flake surface normal and applied electric field. Brochard and de Gennes calculated [24] the energy involved in considering wire like elongated inclusion within a nematic as a function of inclusion orientation, while all three elastic constants approximated to be equal; viz. $K_1 = K_2 = K_3 = K$. Exploiting the electrostatic analogy of an object at fixed potential they have computed the variation of energy with angle of orientation, while the anchoring at the surface was along the long axis of the wire. The graphene/graphitic flake can be considered as side by side assembly of elongated inclusion such as mentioned wire, and hence the elastic energy gained by the graphitic flake is estimated to differ from wire type inclusion by a constant scale factor. The graphene/ graphitic flake and the director field of nematic are initially aligned along same direction, while the applied electric field lies perpendicular to them. Introducing electric field, the graphene/ graphitic flake reorients along the applied field direction along with the nematic director, hence, experiences elastic torque by nematic director field [25]. As the graphitic flakes are freely suspended in positive dielectric anisotropic NLC medium while they are subjected to oscillating external electric field, hence we assume a proportionate propagation of electric field induced elastic distortion from host nematic liquid crystal medium to graphitic flakes. Considering a linear coupling between the electric field induced free energy gain of bulk liquid crystal to the suspended flakes, the energy gained by graphitic flakes by elastic coupling to NLC distortion is given by

$$V_2 = AK\theta^2 \tag{8}$$

where 'K' is the elastic constant of host liquid crystal under one elastic constant approximation, 'A' is multiplicative constant includes geometrical shape of the flake etc. Note that we have discussed details about the strong anchoring of nematic liquid crystal over graphene surface and hence, the angle 'θ' considered to be same between the normal to graphene surface and applied electric field as well as between nematic liquid crystal director anchored to graphene surface and boundary surfaces (Fig. 1).

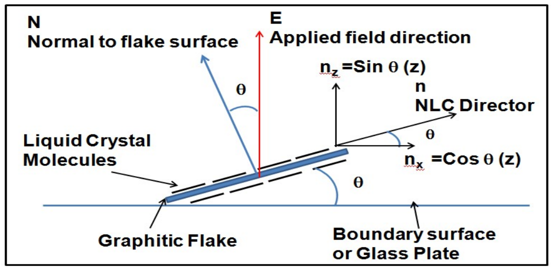

Fig. 1. Pictorial representation of the configuration of graphitic flake in nematic liquid crystals in order to realize reorientation.

Hence the reorientation of graphitic flakes in NLC medium can be described by the following Lagrangian

$$L = \frac{I_x\left(\dot{\theta}\right)^2}{2} + \frac{2\pi}{3} a_i a_j a_k K_i E_0^2 \cos^2\theta - AK\theta^2 \tag{9}$$

The power function P takes into account the energy dissipated in the process of graphene/ graphitic flake reorientation in liquid crystal medium due to viscosity of the nematic liquid crystal medium.

$$P = \frac{1}{2}\eta\dot{\theta}^2 \tag{10}$$

where 'η' represents rotational viscosity of the liquid crystal medium.

$$I_x = \rho I'_x = \rho a R_{gx}{}^2 \tag{11}$$

where I_x and I'_x represents the mass and area moment of inertia of the graphitic flakes with respect to x axis; R_{gx} is the radius of gyration with respect to x axis and 'a' is the flake area and 'ρ' is the mass per unit area of the flake. Hence the electric field induced reorientation of the graphitic flakes in positive dielectric anisotropic nematic liquid crystal medium can be represented by the following Eq. (12) under small angle approximation.

$$(\rho a R_{gx}{}^2)\ddot{\theta} + \eta\dot{\theta} + \left[\frac{4\pi}{3} a_i a_j a_k K_i E_0^2 + 2AK\right]\theta = 0 \tag{12}$$

Considering damping forces considerably smaller than electric field induced torque and elastic torque, the electric field induced rising time of graphene/ graphitic flake in nematic liquid crystal medium is given by

$$T = \frac{2\pi\sqrt{\rho a} R_{gx}}{\sqrt{\left(\frac{4\pi}{3} a_i a_j a_k K_i E_0^2 + 2AK\right) - \frac{\eta^2}{4\rho a R_{gx}{}^2}}} \tag{13}$$

It should be noted here that the dipolar interaction between induced liquid crystal dipoles with graphite dipole has been neglected in present model as their contributions are considered to be negligible for our present investigation.

4. Result and discussion

The dynamic reorientation of graphene/graphitic flakes under AC electric field has been investigated in positive and negative dielectric anisotropic NLC medium. As mentioned earlier, the large plane surface of the flakes induces very high adsorption of nematic liquid crystal molecules over the flake surface. Here, considering the structural similarity between graphene layer and typical NLC molecule (calamitic NLCs consist of few covalently bonded benzene rings followed by functional groups at ends), strong London interaction is anticipated. Consequently the anisotropic flakes possess planar alignment so as the NLC [17]. As discussed previously, the difference in dielectric permittivity of graphene/graphitic flakes and nematic liquid crystal host will lead to the large charge accumulation located at the flake-NLC fluid interface due to Maxwell-Wagner (interfacial) polarization [23]. The applied external electric field acts on dipole induced by interfacial charge accumulation and causes the flake to reorient to energetically stable configuration. This is interesting to mention here that electric field induced reorientation has been observed for graphene/graphitic flakes in both positive and negative dielectric anisotropy NLC medium. Figure 2 schematically represents the side-view of electric field induced reorientation process occurring in graphitic flake display with and without external electric field while suspended in positive and negative NLC medium. In positive NLC medium, the flake suspends parallel to NLC director in field off state [Fig. 2(a)] and regularly reorients in the field direction by applied electric field [Fig. 2(b)]. The blue arrow points the electric field induced turn on direction of graphene/graphitic flake; while the flakes relaxes to initial state with help of NLC reorientation after removing field as shown in red arrow direction. On the other hands, when negative NLC medium is used, representative flake is also found to be suspended parallel to the NLC director [Fig. 2(c)] and exhibits field induced reorientation along field direction at field on state as shown in blue arrow direction [Fig. 2(d)]; however, the complete relaxation process is not realized in the absence of an electric field pointed out through the red arrow because this flake reorients by 90°and equilibrates in the minimum-energy orientation. Moreover, surface anchoring induced physical deformation of NLC in the vicinity of graphene plane due to the strong π-stacking between graphene plane and LC molecules in on state is minimal unlike that in the positive NLC. This restoring force of the physical deformation between the planar surface state and LC director is not strong enough to induce mechanical torque the flake back into the original orientation. The observation is reminiscent with CNT + NLC hybrid system [26], in which the surface anchoring formed local anisotropic nematic LC domain around CNT. The distorted LC director in the close vicinity of the suspended CNT in isotropic phase of NLC does not help the relaxation process of CNTs and thus cannot relax back to original orientation after turning the electric field off in the isotropic state of NLC. Therefore, the reorientation of NLC director has been considered to play an important role for reorientation and relaxation of graphene/graphitic flakes in NLC medium. Hence, most of the following experimental investigations are reported for graphene/graphitic flake reorientation in positive NLC medium. However, considering our tested flake with different thickness, the effect of distinct stacked layers of flake onto the reorientation has also been tested (Fig. 3). Figures 3(a)-3(d) show optical microphotographs of different reorientation process of almost transparent few layered graphene flake [Figs. 3(a),3(b)] and micrometer-thick graphitic flakes [Fig. 3(c),3(d)] with and without field of 85 mV/μm. The relationship of response time of the abovementioned flakes as a function of different applied field has been exhibited in Fig. 3(e). Comparison of the rising and relaxing process of two representative graphene/graphitic flakes with different stacked-layers indicates only the few layered almost transparent graphene flake (case 1) possesses slightly faster electric field induced rising time [Figs. 3(a),3(c)] and relaxation time [Figs. 3(b),3(d)] compared to that using micrometer-thick graphitic flakes (case 2). Therefore, the experimental realization of electric field controlled reorientation process of opaque graphitic flake in NLC matrix has future application potential in light modulating devices. Hence we have analyzed such process in light of phenomenological theoretical model considering dual contribution of electric field induced free energy of graphitic flakes and reorientation of NLC medium having positive dielectric anisotropy for opaque graphitic flake but not transparent graphene flake.

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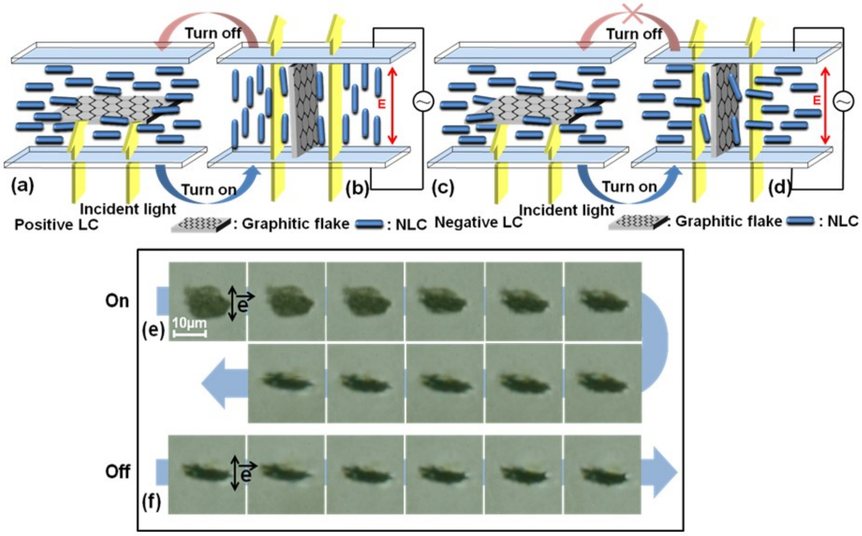

Fig. 2. An electro-optic response of graphitic flake display: In positive NLC, flake lies parallel to the cell substrate before applying an electric field, blocking the incident light (a) and the flake is oriented nearly perpendicular to the cell substrate after applying vertical electric field and allows optical transmission, respectively (b). Note that the applied electric field is normal to the cell plane. In negative NLC, a flake aligns parallel to the cell substrate before applying an electric field, blocking the incident light (c) and in field on state, the flake reorients along the field direction (d). However, the LC deformation is minimal since the NLC with negative dielectric anisotropy prefers orientation perpendicular to the field direction. Hence, once the flake is orientated along the field direction, the flake does not completely relax to the initial state because there is no triggering force to rotate the flake to the original state. (e,f) Optical microphotographs exhibiting reorientation of a representative graphitic flake as a function of applied electric field in negative dielectric anisotropy liquid crystal. (e) Switching field on: Following the arrow from left to right: 0 mV/μm, 14.0 mV/μm, 28.0 mV/μm, 42.0 mV/μm, 57.0 mV/μm, 71.0 mV/μm, 85.0 mV/μm, 100.0 mV/μm, 114.0 mV/μm, 128.0 mV/μm, 142.0 mV/μm; (f) Switching field off: Following the arrow from left to right: field off 1 sec, field off 2 sec, field off 3 sec, field off 4 sec, field off 5 sec, field off 6 sec, respectively. (The labelled black arrow in the images indicates the easy axis of flake).

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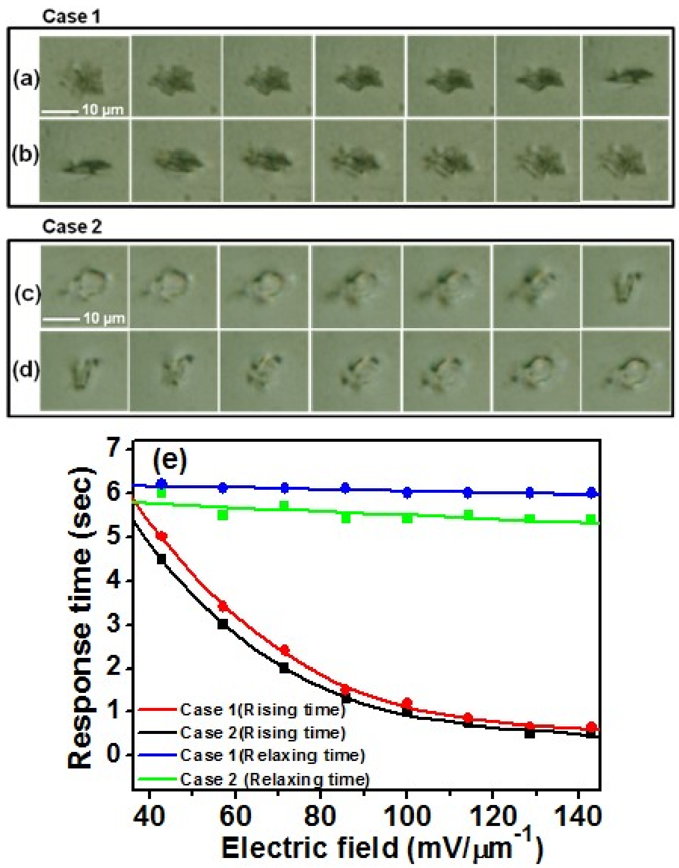

Fig. 3. Optical microphotographs of response time of two representative graphene/graphitic flakes with different stacked-layers with and without field of 85 mV/µm in positive dielectric anisotropy nematic liquid crystal medium. (a,b) Rising and relaxing process of flake (case 1): (a) Rising process: According to the arrow from left to right: field on 0 sec, field on 0.5 sec, field on 0.7 sec, field on 0.9 sec, field on 1.1 sec, field on 1.3 sec, field on 1.5 sec, respectively. (b) Relaxing process: According to the arrow from left to right: field off 0 sec, field off 1 sec, field off 2 sec, field off 3 sec, 4 sec, 5 sec, 6 sec, respectively. (c,d) Rising and relaxing process of flake (case 2): (c) Rising process: According to the arrow from left to right: field on 0 sec, field on 0.3 sec, field on 0.5 sec, field on 0.7 sec, field on 0.9 sec, field on 1.1 sec, field on 1.3 sec, respectively. (d) Relaxing process: According to the arrow from left to right: field off 0 sec, field off 1 sec, field off 2 sec, field off 3 sec, 4 sec, 5 sec, 5.5 sec, respectively. (e) The relationship of the response time of the abovementioned flakes as a function of applied field. (Case 1: Aspect ratio: 1: 1, Flake area: 85 µm^2; Case 2: Aspect ratio: 2: 1, Flake area: 75 µm^2).

Figures 4(a) and 4(b) show the optical microscopic images of arbitrary shaped graphitic flake in positive NLC with gradually increasing AC electric field (frequency 60 Hz, strength varied from 0 mV/µm to 142.0 mV/µm) and switching of field off for 6 second duration. The corresponding figures clearly depict continuous flake reorientation consequently companying with variation of dark state in accordance with applied field. The flake consistently reorients almost 90° about its long axis parallel to the applied field direction with gradually increasing AC electric field from 0 mV/µm to 142.0 mV/µm [Fig. 4(a)]. Once the driving field is removed, the flake returns to their initial state in planar alignment in the range of field off time of 6 sec [Fig. 4(b)]. This reorientation behavior is reliable and reproducible for hundreds of times. The optical transmittance has been measured locally on regions surrounding the graphene flake in ~20 µm × 20 µm area from optical microscopic images using *i* solution image analysis software. Figure 4(c,d) depicts the field dependent variation of transmitted light intensity surrounding graphitic flake. Initially, transmission intensity is low as most of the transmission is blocked by considerably large effectively exposed area of the opaque flake in the direction of propagation of light. As the flake reorients with the increasing applied field, the transmission gradually increases [Fig. 4(c)]. On the other hand the flake gradually recovers to its initial state and hence corresponding transmittance decreases and reaches almost to its initial state after field removal [Fig. 4(d)]. The mentioned observation confirms electric field controlled reorientation of two-dimensional graphitic flake with varying electric field according to optical images of Figs. 4(a),4(b). Hence the light transmission modulation is evidently controlled by graphitic flake reorientation and relaxation. Thus electric field controlled uniform reorientation and relaxation of graphitic flake and subsequent modulation of transmission intensity provides us a promising method for making new polarizer free electro-optic flake device. This is necessary to mention here that graphitic flakes in positive NLC medium requires few seconds to return back to initial planar alignment after oscillatory electric field induced ~90° rotation, and during negative NLC medium the flake can only reorient but not relax completely without help of NLC relax for device application. Note that PCLC flakes in liquid medium, which does not have reorientation ability of NLC director, requires even 2 days for returning back to their initial state, which is a serious drawback for applications [2–4].

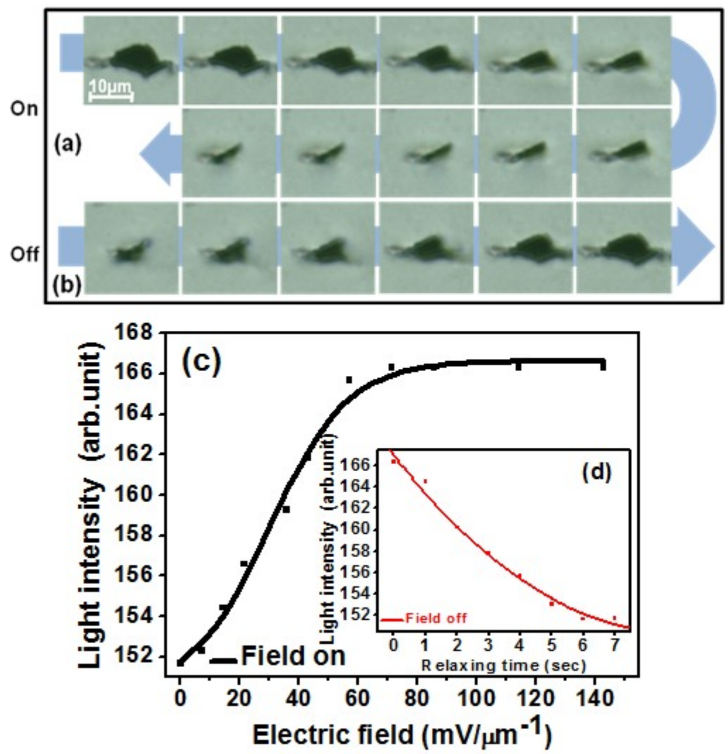

Fig. 4. Optical microphotographs (a, b) of reorientation of a representative graphitic flake with respect to electric field in positive dielectric anisotropic nematic liquid crystal medium. (a) Switching field on: According to the arrow from left to right, the applied field is 0 mV/μm, 7.0 mV/μm, 14.0 mV/μm, 21.0 mV/μm, 35.0 mV/μm, 42.0 mV/μm, 57.0 mV/μm, 71.0 mV/μm, 85.0 mV/μm, 114.0 mV/μm, 142.0 mV/μm. respectively; (b) Switching field on: According to the arrow from left to right: field off 1 sec, field off 2 sec, field off 3 sec, field off 4 sec, field off 5 sec, field off 6 sec, respectively. (c,d) Transmitted light intensity of flake reorientation which corresponds to optical microphotographs of Figs. 4(a),4(b).

The graphitic flake reorientation phenomenon in positive NLC has been investigated as a function of driving frequency, applied AC field strength as well as shape anisotropy and area of flakes. The frequency dependent rising time of flakes for different applied AC field strength and for different aspect ratio (length to bredth ratio) of flakes for approximately constant flake area (140-150 μm^2) is exhibited in Figs. 5(a) and 5(b), respectively. A amplitude modulated square wave form has been generated with arbitrary function generator (Tektronix AFG3022) for above investigation. The reorientation of various graphitic flakes has been observed within the wide frequency bandwidth (10 Hz to 5 kHz). Figure 5(a) shows the rising time of the graphene flakes (exemplary aspect ratio 2:1) as a function of frequency for different applied electric field strengths. Consistent reduction of flake rising time as a function of increasing applied electric field is evident. Remarkably, the rising time of graphitic flake does not vary as a function of frequency hence can be considered frequency independent above 60 Hz. This is important to mention here that previous investigation over alternating electric field driven reorientation of PCLC flakes in isotropic medium exhibits frequency dependence over reorientation time in very wide band of 10 Hz to 1 kHz. Also, the flakes do not reorient at all below and above mentioned frequency range [2,4]. Such frequency dependence over flake movement imposes serious restriction over industrial application of PCLC flakes. Figure 5(b) shows the frequency dependence of rising time for exemplary flakes having different aspect ratio viz. (1.4:1, 1.8:1, 2.5:1) however, approximately constant flake area of ~(140-150) μm^2. The rising time is found to decrease with increasing aspect ratio maintaining the flake area constant over entire investigated frequency range. This observation can be explained following Eq. (13), where it has been shown that the rising time is directly proportional to the radius of gyration of the flake, where the viscosity term in the denominator appears to be negligible. For approximately two dimensional graphene flakes with invariant surface area however increase in anisotropy indicates subsequent increment of flake length at the cost of reduction of flake breadth. The radius of gyration of a rigid body physically implies the radius of a uniform thin hoop (or ring), having the same moment of inertia (about an axis passing through its geometric center), as the given body about the specified axis. Hence, with increasing shape anisotropy of any arbitrary shaped approximately two dimensional object viz. graphitic flake, however maintaining constant surface area the radius of gyration should decrease due to significant reduction of short axis length in comparison with long axis. Actually, maintaining constant surface area of flakes between calculated area of 140-150 μm^2 moment of inertia of the flakes having different aspect ratio viz. (1.4:1, 1.8:1, 2.5:1) along the long (reorientation) axis are 160, 140 and 95 μm^4, respectively. Thus the experimental observations about rising time viz. (2.7, 2.5 and 2.1 Sec) agree well with the square root of moment of inertia of the flakes in Eq. (13), which are in compliance with previously described model.

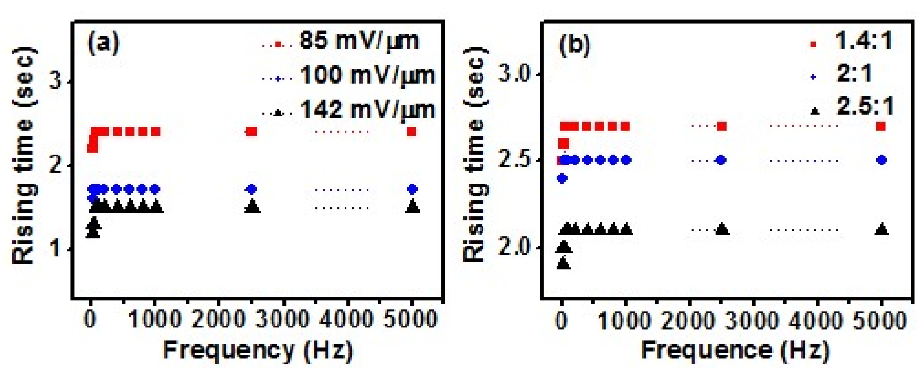

Fig. 5. The relationship of reorientation time of a representative flake with aspect ratio of 2: 1 as function of frequency (a) and the reorientation time of various flakes with different aspect

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ratio as function of frequency at specified electric field for flake area fixed between 140 - 150 μm^2 (b).

Figure 6(a) shows the 60 Hz AC electric field dependent rising and relaxation time of graphitic flakes in positive NLC medium. The reorientation of flakes is observed at field strength as low as 10 mV/μm. However, the reorientation process remains incomplete until the applied field strength reaches 60 mV/μm. The rising time clearly shows decreasing trend with increasing applied electric field. On the other hand the relaxation time (the time required for the flakes to return to initial planar configuration) of graphitic flakes in NLC medium is found to be independent of applied field strength. Interestingly, both rising time and relaxation time are of the order of few seconds. The model derived electric field dependent rising time [Eq. (13)] is least square fitted with experimentally determined electric field dependent rising time of graphitic flakes in NLC medium for different flake sizes in Fig. 6(b). This is interesting to notice here that the electric field dependent rising time profile is similar for significantly different flake area and aspect ratio, which indicates the dominance of dielectric torque over the flake system. The least square dependence on electric field has been clearly detected during the measurement of the flake reorientation time as function of field. From Eq. (13), the averaged reorientation (rising) time of several graphitic flakes shows satisfactory agreement between the theoretical model and experimental curves by successive least square fitting above 50 mV/μm applied field strength as depicted in Fig. 6(b). In addition, the relaxation time of several flakes has also been measured under the same condition of reorientation test. The approximately similar response time has been shown on second time scale after removing different certain applied field strength. The difference of reorientation and relaxation time further supports the coupling contribution of flakes/NLC host for theoretical model analysis.

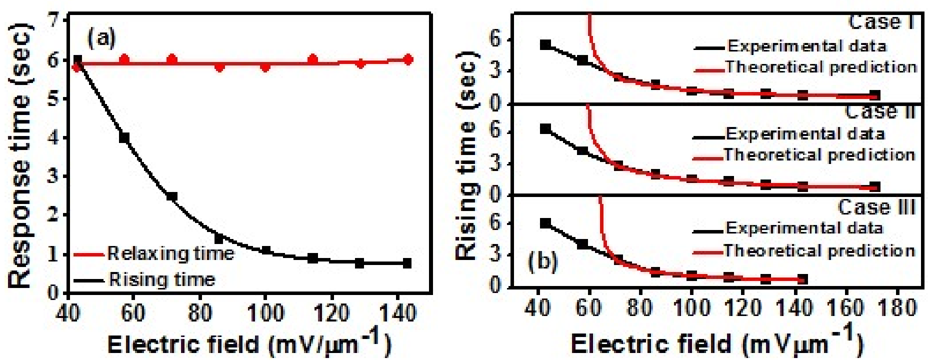

Fig. 6. The relationship of the averaged reorientation time of several graphitic flakes as a function of applied field. (Case I: Aspect ratio: 2.6: 1, Flake area: 85 μm^2; Case II: Aspect ratio: 2: 1, Flake area: 65 μm^2; Case III: Aspect ratio: 3.6: 1, Flake area: 20 μm^2).

Figure 7 shows the rising time as a function of flake areas for 85 mV/μm field at 60 Hz. The rising time is found to exhibit increasing trend with increasing flake area. Typical microscopic flake images have been replicated in the diagram in order to emphasize their shape anisotropy. The length to breadth anisotropy ratio expressed in arabic numerals has also been included in the image. The experimentally determined rising time for several similar area flakes with different aspect ratio has been clubbed together for comparison by dotted circles. Hence increase in shape anisotropy is evidently reducing rising time of graphitic flakes and the observation is in compliance with the phenomenological model as described earlier. Moreover, solid line encircled similar aspect ratio flakes with increasing area shows increase in rising time. The experimental observation can be anticipated from phenomenological model derived Eq. (13) since the rising time is directly proportional to the square root of flake area. Hence the flake with the bigger area with comparable aspect ratio possesses slower response time in comparison with smaller area flakes with similar aspect ratio while the effect of rotational viscosity of liquid crystal medium does not appear to play predominant role.

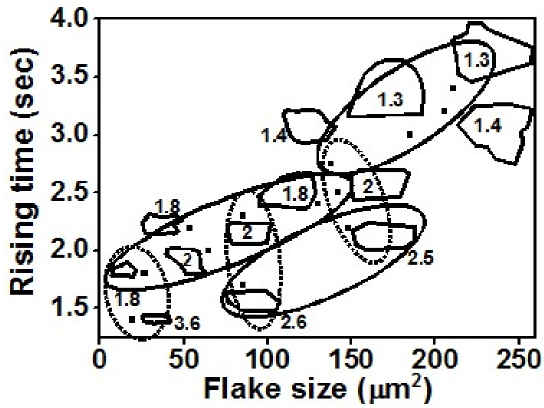

Fig. 7. The relationship of reorientation time of flakes as function of graphitic flake area. (The labelled arabic numerals in the picture indicate aspect ratio).

5. Conclusion

The electric field induced reorientation process of opaque ~1 μm thick, 20-200 μm^2 area, and irregular shaped graphitic flakes in nematic liquid crystal medium has been demonstrated. Construction mechanism of such flake in nematic liquid crystal medium has been proposed based on intuitive arguments. The electric field induced flake reorientation process consisting of rising and relaxation steps both are of few seconds duration and the processes are highly reproducible hence regular in positive dielectric anisotropic nematic liquid crystal medium. The rising process of graphitic flakes in nematic positive liquid crystal is found to depend on applied electric field strength, flake area and flake aspect ratio. A phenomenological model has been proposed which successfully illustrates the dependence of flake rising time over its aspect ratio, surface area and electric field strength. The mentioned reorientation or switching process of graphitic flakes provides a new way to control transmission properties of optical properties of the device with an electric field. Electro-optic devices based on switching graphitic flakes are useful in areas such as optics and photonics, switchable ‘smart window’ or information displays such as ‘electronic paper’.

Acknowledgments

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