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Electric-field-induced reorientation of ferroelectric micro- and nano-platelets in the nematic liquid crystal

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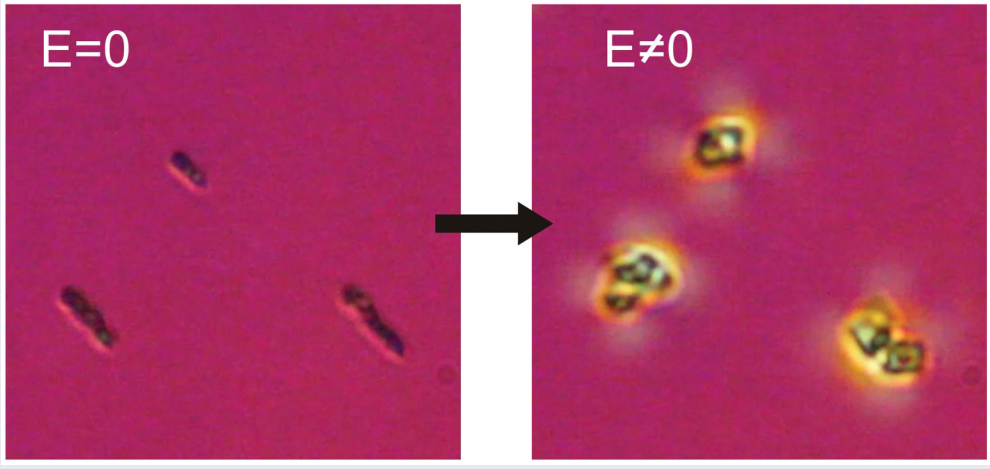
ABSTRACT

We demonstrate that ferroelectric layered perovskite $Bi_{3.8}Nd_{0.2}Ti_3O_{12}$ micro-platelets can be reoriented in the nematic liquid crystal by the linear coupling to an external electric field. The electric dipole moment of platelets is perpendicular to the plane of platelets and provides torque that rotates the platelets. The experiments were made in dispersions of ferroelectric platelets in a zero dielectric anisotropy nematic liquid crystal (LC), which excludes the reorientation of the dispersion via the dielectric coupling of a LC. Typical reorientation times for micrometre-size ferroelectric platelets are of the order of 100 ms for 0.5 V/μm applied electric field. The electric dipole moment in the absence of external field is very small and does not contribute to the force between the platelets. This could be either due to very narrow hysteresis loop of the ferroelectric material, or screening of dipolar electric field by ions in the LC. A stable and homogenous dispersion of ferroelectric nano-platelets could not be observed in any range of platelets' concentration. To create a ferroelectric LC the shape and thickness of the nano-platelets has to be controlled, and the electrostatic screening of dipolar field should be minimised.



KEYWORDS

Ferroelectric platelets; nematic liquid crystal; ferroelectric nematic; colloids

Introduction

Colloids suspended in thermotropic nematic liquid crystals (NLCs) are a hot topic of modern soft condensed matter research. These suspensions can be roughly divided into two classes depending on the size of particles: (i) nanoscale particles, which can improve or change the material properties of LC dispersions, and (ii) microscale particles, which can self-assemble in colloidal superstructures due to elastic deformation of the LC in their vicinity. The most fascinating example of nanoparticle-LC dispersions is ferromagnetic nematic LC [1,2], which is stable suspension of magnetic nano-platelets in a NLC. In a ferromagnetic NLC, the director can be reoriented by the external magnetic field due to the linear coupling between the collective magnetisation of the sample and the external magnetic field. The collective magnetisation is due to the collective coupling between the magnetic moments of platelets and nematic director [1,2]. The crucial element for the successful realisation of the ferromagnetic NLC are nano-platelets with very uniform thickness and magnetic moment of each platelet, which should be perpendicular to the platelet.

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There have been a number of studies of suspensions of ferroelectric nanoparticles in NLCs, with an aim to obtain ferroelectric nematic LC. It was demonstrated that nanoparticles can improve electro-optical characteristics of LC, featuring higher birefringence, shorter switching time, better contrast and lower threshold voltage [3]. Here the main challenge is the preparation of stable and aggregate-free dispersions of ferroelectric nanoparticles with well-defined shape [4,5]. The stability of nanoparticle dispersions in the NLC is a result of balance of electrostatic and elastically mediated forces between particles and interactions with surfaces [6,7]. However, recently two nematic compounds made of polar rod-like molecules were reported, with additional nematic phase. The nematic compounds exhibit strong dipolar molecular interactions, which results in 'ferroelectric-like' [8] and antiferroelectric ordering [9]. Very recently Boulder group demonstrated that one of this compounds exhibits truly ferroelectric nematic phase with strong polar order, extremely large spontaneous electric polarisation, large polar domains and fast switching at very low electric fields [10].

While ferroelectricity in nematic LCs using dispersion of ferroelectric particles could be realised only by dispersing very small nanoparticles with well-defined shape in the NLC, valuable information on the interparticle interactions could be gained from the studies of dispersions of much larger ferroelectric microparticles in the NLCs. In NLC dispersions of micro-particles, the elastic forces between particles usually prevail over the electrostatic forces, which are screened-out by the ions in the LCs. The elastic forces between microparticles are mainly due to overlapping of regions of elastically deformed nematic in the vicinity of particles due to the strong LC anchoring at the surface of particles. These elastic deformations cause strong forces between particles, which can stabilise 1D, 2D and 3D colloidal assemblies with a pair binding energy exceeding 1000s k_bT per micrometre diameter particle [11,12].

Here we present our studies of ferroelectric layered perovskite $Bi_{3.8}Nd_{0.2}Ti_3O_{12}$ micro-platelets, dispersed in a NLC. The main purpose of our work was realisation of ferroelectric NLC, where the optical axis of a nematic could be switched linearly with an applied electric field, similar to switching of a ferromagnetic NLC [1,2]. To remove the effects of dielectric coupling, which is quadratic in the external electric field, we have used a mixture of positive and negative dielectric anisotropy NLCs, which resulted in zero dielectric anisotropy of the as prepared mixture ($\Delta\varepsilon = 0$). We describe the experiments where single ferroelectric micro-platelets were switched linearly with external field to analyse the time evolution of their re-orientation and compare it to director reorientation. Finally, we present experiments with LC dispersions of ferroelectric nano-platelets in our attempts to obtain ferroelectric nematic liquid crystal.

Materials and methods

Preparation of ferroelectric micro- and nano-platelets

We have used layered perovskite $Bi_{3.8}Nd_{0.2}Ti_3O_{12}$ micro-platelets, which were synthesised in the molten salt from Bi_2O_3, Nd_2O_3 and TiO_2 nanopowders using the similar procedure as for preparation of $Bi_4Ti_3O_{12}$ platelets [13]. The molar ratios of salts and target compound were: NaCl:KCl:$Bi_{3.8}Nd_{0.2}Ti_3O_{12}$ = 50:50:1. Two different temperatures, namely 900°C and 800°C, were selected in order to obtain micro-platelets of two different sizes (Figures 1(a,b)). After the reaction, the final product platelets were separated from the salt by washing with ultrapure water and dried at 60°C. This method was found to be inappropriate for the preparation of nano-platelets, since the shortening of the reaction time leads to the formation of highly aggregated particles. For this reason, the hydrothermal method was used for the synthesis of nano-platelets. Here the reagents $Bi(NO_3)_3 \times 5H_2O$ and $Nd(NO_3)_3 \times 6H_2O$ with molar ratio 3.8:0.2 were separately dissolved in methoxy-ethanol and in ultrapure water, respectively. Next, methoxy-ethanol solution of bismuth (III) nitrate was added dropwise

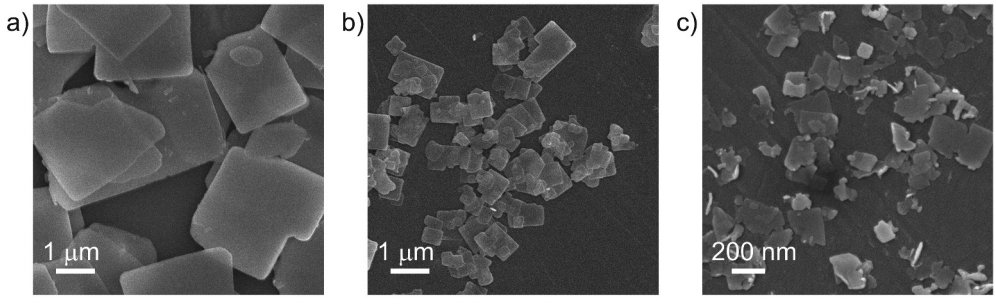

Figure 1. SEM images of $Bi_{3.8}Nd_{0.2}Ti_3O_{12}$ platelets with the three different average lateral sizes: (a) 3 μm, (b) 0.5 μm and (c) 200 nm.

into water solution of neodymium (III) nitrate. When 6 M NaOH solution was admixed into this clear solution, white precipitate appeared. After addition of TiO_2 nanopowder, the suspension was heated in the closed Teflon-lined autoclave at 200°C for 12 hours. After cooling to room temperature, the product powder was separated from the alkaline solution and washed with water till the neutral pH. Finally the nano-platelets were dispersed in ultrapure water. The shape and the size of all platelets were determined by using a field-emission scanning electron microscope (FE-SEM, JSM-7600 F, JEOL) and the thickness of platelets was determined by atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments) (Figure 1). All platelets are of rectangular shape, micro-platelets synthesised at 900°C are with the average lateral size of 3 μm and average thickness of 110 nm (Figure 1(a)), while micro-platelets synthesised at 800°C are with the lateral size of 0.5 μm and thickness of 40 nm (Figure 1(b)). Nano-platelets prepared by the hydrothermal method have average lateral size 200 nm and average thickness of 13 nm (Figure 1(c)).

Ferroelectric characteristics of the platelets were examined by the piezoresponse force microscopy (PFM) using AFM (Asylum Research, Molecular Force Probe 3D) [14]. Similar to the case of $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ plates [13,15], we have measured the amplitude and the phase of PFM signals of individual platelets in lateral and vertical direction. The measurements revealed that an individual $Bi_{3.8}Nd_{0.2}Ti_3O_{12}$ platelet shows ferroelectric polydomain structure with both out-of-plane and in-plane components of the polarisation. The exact values of local electric dipole moment could not be determined unambiguously.

After the synthesis, surface modification of platelets was accomplished by adding 1% of DMOAP silane into water suspension of platelets. It has been shown that this modification ensures strong perpendicular or homeotropic alignment of LC molecules at the surface of particles [11]. The platelets were then transferred from water to n-butanol and finally to the LC by keeping the sample at 60°C for substantial time, to evaporate the alcohol.

In all experiments we have used a LC mixture with zero dielectric anisotropy and for that purpose we have prepared a mixture of 5CB with positive dielectric anisotropy of Δε (26.2%) and CCN-47 with negative dielectric anisotropy of Δε (73.8%). Zero dielectric anisotropy of this mixture was measured in test cells with planar and homeotropic surface alignment, which were filled with this mixture. The response of this zero anisotropy mixture to electric field was tested under a polarising microscope. Upon the application of an electric field up to 6 V/μm the cells did not show any observable optical response. This means that we have successfully prepared a zero Δε LC, which still behaves as a true LC with elastic and optical properties of a nematic LC, but does not respond to an applied electric field. Having no response from the LC matrix, any observable electrooptic response of the LC should originate solely from the dispersed ferroelectric micro or nano-particles.

In the experiments we have used different concentrations of platelets in LC mixture, ranging from 0.02 wt% to 1.5 wt%. A suspension of platelets was inserted to different LC cells with planar or homeotropic LC orientation. Planar orientation at surfaces of the cells was achieved by using glass plates with a thin layer of rubbed polyimide (PI-2555, Nissan Chemicals), while homeotropic orientation was ensured by using glass plates coated with DMOAP silane (ABCR GmbH). We have used indium tin oxide (ITO) coated transparent glass plates of thickness 0.7 mm, which allowed for the application of a homogenous electric field. The gap between the two glass plates was kept with spacers of thickness 10–14 μm. The cells were filled with LC suspension in the isotropic phase using a capillary effect and quenched to the nematic phase to minimise the aggregation of platelets. We have used polarising optical microscope Nikon E600 with colour Canon EOS 500D camera and inverted polarising microscope Nikon TE2000 with a high-speed B/W camera (IDS, UI-3370CP), which was equipped with infrared laser tweezers system (Aresis Tweez 250Si) for manipulation of platelets.

Results and discussion

When ferroelectric micro-platelets with homeotropic surface anchoring of the LC are dispersed in a planar NLC cell, the orientation of platelets with respect to the far-field nematic director is dictated by the surface of platelets. Figure 2(a) shows an image of platelets in the NLC mixture taken between crossed polarisers, with the indicated director of rubbing, which is also the direction of NLC alignment. One can see that the platelets are perpendicular to the rubbing directions, which fits well with the perpendicular surface anchoring on the platelets. This is therefore the orientation with the minimum elastic distortion energy of the inserted platelet and there is no visible distortion of the director at the edges of the platelets, where one could expect a − 1/2 ring, running all around the periphery of the platelet.

We should point here that a platelet in a LC is in terms of topology equivalent to a sphere in the LC. It is well known that for homeotropic surface anchoring a sphere in a nematic is accompanied either by a point

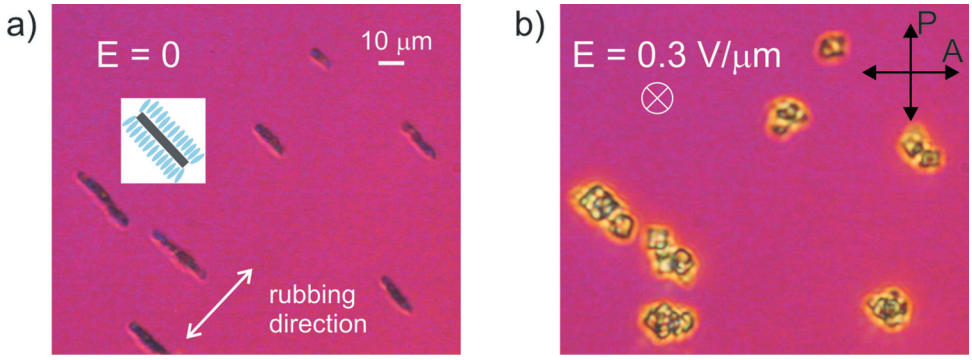

Figure 2. (Colour online) (a) Dispersion of ferroelectric micro-platelets with homeotropic surface anchoring in the nematic LC with $\Delta\varepsilon = 0$ in the planar cell with the thickness of 13 μm. No field is applied and the platelets are oriented with their plane perpendicular to the rubbing direction. The inset shows the schematic LC orientation around single platelet. (b) When the DC external electric field (U = 5 V) is applied, the platelets are rotated with their planes parallel to the surface of the cell. Both images were taken between crossed polarizers.

(hyperbolic hedgehog) defect or a closed loop (Saturn ring), encircling the sphere. When the sphere is transformed into a platelet (of finite thickness), one expects a Saturn ring encircling the platelet or an isolated point hedgehog centred at one of the platelet's surfaces if the surface anchoring is strong. In our case, we see no observable point defect, nor a ring encircling the platelet. This means that the surface anchoring is not very strong and the defects become 'virtual', i.e. depressed into the body of the particle. The director outside the particle then appears smooth, as is in our case.

When an external electric field of sufficient strength ($E > 0.25$ V/μm) is instantaneously applied in the direction perpendicular to the cell, all platelets are gradually rotated for 90 degrees, as shown in Figure 2(b). The platelets are oriented perpendicular to the external electric field, which means that the net electric dipole moment of each platelet is pointing perpendicular to the platelet. One can also clearly see the region of deformed nematic LC in the intermediate vicinity of the platelet, which is evidenced by a local change of colour of birefringent LC from red to yellow. It should be stressed that we are using the LC mixture with zero dielectric anisotropy ($\Delta\varepsilon = 0$), which does not respond to the applied electric field. Any change of the orientation of the NLC in the vicinity of the rotated platelets is therefore caused by the rotation of platelets. Because of the orientational anchoring of the NLC molecules at the surface of the platelets, the director is forced to follow the rotation of platelet due to external electric field and this reorientation is also taking place in the very vicinity of the platelets, where the NLC gets distorted.

It is indicative from Figure 2(b) that the platelets are reoriented by the linear coupling of the electric field and spontaneous electric polarisation; when the direction of the field is reversed, the platelets rotate for 180°. There is an additional proof of this ferroelectric coupling: if there were no spontaneous electric polarisation, the only coupling mechanism would be dielectric coupling, which is quadratic in the field. Moreover, the shape anisotropy would force the platelets to orient along the lines of the electric field and not perpendicular to the field. This clearly indicates that reorientation in an applied electric field is due to the linear ferroelectric coupling.

We have also studied the dynamics of the platelet's rotation and accompanying LC reorientation, which is illustrated in Figure 3. First, less than 40 ms after the field is applied, the LC is clearly disturbed in the close vicinity of the platelet, even before the platelet starts to rotate. We think that this reorientation is caused by the liquid-crystal enabled electro-osmotic flow, and the application of the electric field induces the local motion of free charges due to the inhomogeneous LC orientation around platelets [16]. This also indicates increased concentration of ionic species in the very vicinity of the platelets, which is quite reasonable result. We have observed the same effect also in the vicinity of dispersed silica microspheres in the same LC.

The platelet is fully rotated 120 ms after the application of the field and it is indicative that the images taken are not sharp. This indicates a dynamic phenomenon is going on in the LC, which we think is the flow and backflow of the NLC. It is well known that fast reorientation of the nematic is accompanied by the transient flow of the material, and this makes the photographs not very sharp. This dynamic flow ceases within 240 *ms* and the images become sharp again (see panels 3, 4 and 5 in Figure 3.) Finally, after 0.5 *s* the reorientation of the platelet and the NLC is completed and the platelet finds its stable orientation with a minimum elastic

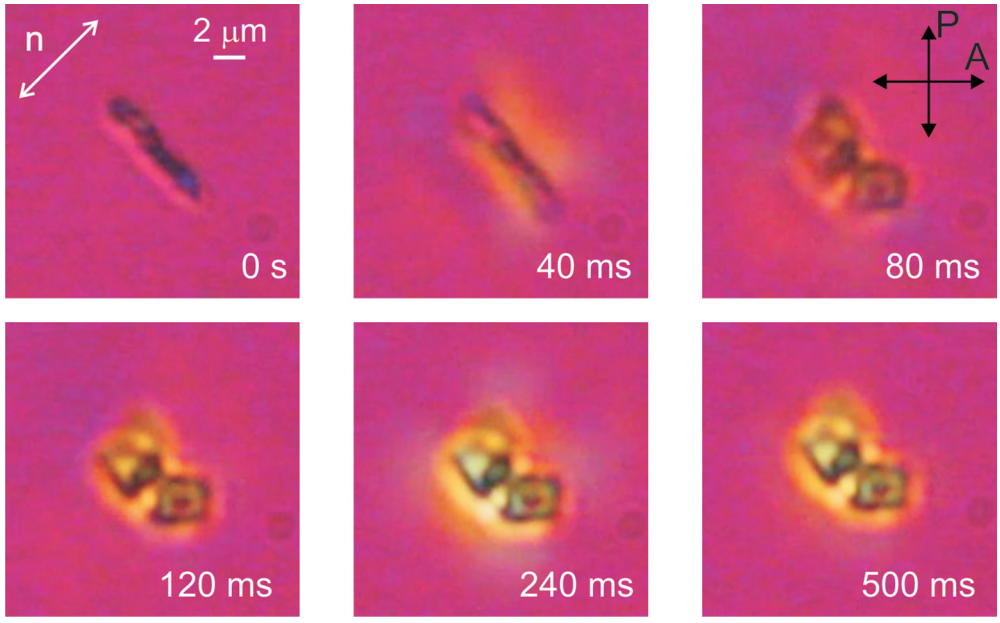

Figure 3. (Colour online) Snapshots of platelet reorientation during the application of the electric field after t = 0. The LC is first reoriented in the vicinity of the platelet at the time of 40 ms after the electric field is applied and before the platelet starts to rotate. After 80 ms the platelet is completely rotated into new stable orientation. A hydro-dynamical disturbance of the LC is visible around the edge of the platelet in panels 2 and 3, which is most likely due to the LC flow and backflow, making the photograph blurred. The image becomes clear at ~240 ms after the field application, which indicates the cease of the hydrodynamic flow.

energy. When the direction of the electric field is reversed, the platelet flips for 180° and attains its new stable position in the applied field.

A more detailed analysis of time evolution of platelet's reorientation was conducted by applying square-wave electric field, where the electric field is switched between two opposite directions, keeping the magnitude constant. Here, the platelets are following the field and are switching between two opposite directions, depending on the direction of the field, because the electric dipole moments of platelets are at all times linearly coupled to the external electric field. This is illustrated in Figure 4(a), where the snapshots of the platelet are taken for two opposite directions of the field and at zero field. This analysis was inspired by possible application of ferroelectric nematic dispersions for LC switching. To this aim we have measured the maximum angle of rotation of platelets as a function of frequency of the applied electric field, keeping the magnitude of the field at $E = 0.3\,\mathrm{V}/\mu\mathrm{m}$. Due to the high viscosity of LC, platelets need some time to rotate for 180° between two opposite orientations of the electric field. At higher frequency of the applied square waveform electric field, platelets are rotated only for some finite angle, which can be measured by the video-microscopy. As expected, the angle of rotation is proportional to the length of the electric field pulse, i.e. to the inverse frequency, which is presented in Figure 4(b). The maximum angle of rotation of a platelet is proportional to the inverse frequency of the applied electric field and is larger for smaller platelets, d is the lateral size of the particles. The cell thickness was 10 μm, the magnitude of the applied field was 0.3 V/μm. The measurements in Figure 4(b) are presented for three different sizes of the platelets, 1.5 μm, 2.3 μm and 6 μm. As expected, the rotation is faster for smaller platelets due to the lower hydrodynamic drag torque which is hindering the rotation. However it is clear that for frequencies above 10 Hz all observed platelets are not rotating at all – they are static and there is no switching. This is a similar to the switching of ferromagnetic LC, where ferromagnetic platelets are dispersed in the NLC and the fastest switching time is around 0.1 s or 10 Hz [17]. The dynamics of rotation of ferroelectric platelets in the NLC is also similar to the rotation of dielectric micro-platelets, where the time of the rotation of dielectric platelets is also around one second [18].

It is interesting to analyse the onset of switching of platelets when the magnitude of the applied electric field is increasing. Most of the individual platelets are gradually rotated with the increased electric field (Figure 5). Here the stable position of the platelet at certain voltage is determined by the minimisation of the elastic and electrostatic energy. The gradual rotation is also a sign that the platelet possesses permanent electric dipole moment already in the absence of electric field. Some

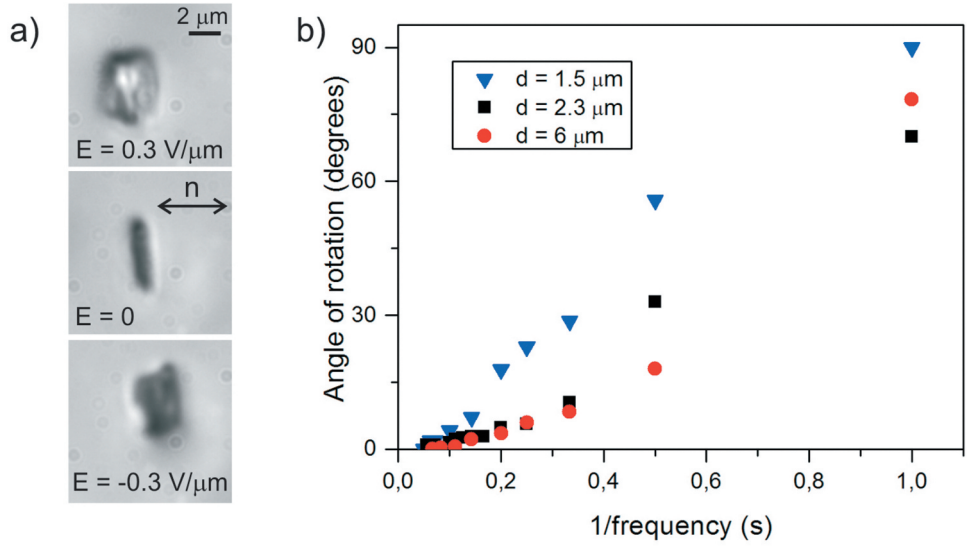

Figure 4. (Colour online) Time dependence of the rotation of a platelet in an AC electric field. a) The platelet is switched between two opposite directions, when the direction of the electric field is reversed. b) The maximum angle of the rotation of a platelet is proportional to the inverse frequency of the applied electric field and is larger for smaller platelets. The angle is measured from the zero field position, d is the size of the particles. The cell thickness was 10 μm, the magnitude of the applied voltage was 3 V.

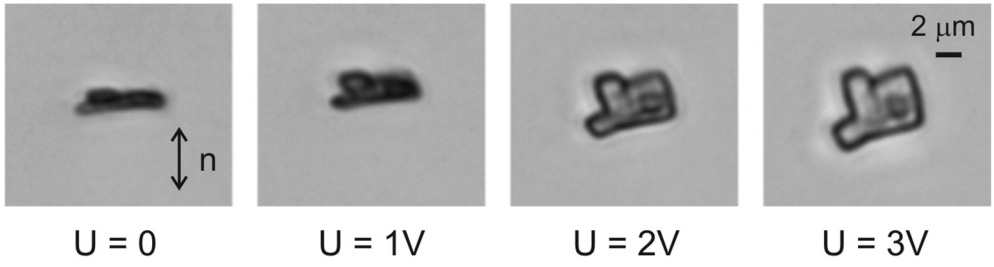

Figure 5. The ferroelectric microplatelet is gradually rotated with the increase of the applied external field. The cell thickness was 12 μm.

of the platelets are rotated abruptly for 90 degrees at certain voltage, what is a sign that in these platelets the electric dipole moment can be enhanced by the external electric field via the reorientation of domains.

When the magnitude of the applied electric field is increased to very high values ($E > 0.5 - 0.8\,\mathrm{V}/\mu\mathrm{m}$, depending on the concentration of ions), parallel rolls (Williams domains) are observed in all field of view. The rolls are perpendicular to the nematic director and they appear due to the electro-convection effect and movement of free charges in the NLC under the electric force of the applied field [19,20]. These rolls also appear in the pure LC sample without platelets but at much higher field ($E > 1.5\,\mathrm{V}/\mu\mathrm{m}$). This indicates that the density of free charges in the pure sample is lower and the conductivity of the NLC is increased by the addition of ferroelectric platelets and accompanying ionic species. The electric-field induced rolls completely prevail over the LC reorientation caused by the rotation of platelets, and the experiment cannot be controlled any more. This imposes a limit on the maximum electric field that can be used in the experiments with ferroelectric-doped nematic below $E < 0.5\,V/\mu\mathrm{m}$. When we increase the frequency of the applied electric field to $f = 1kHz$, we observed electrophoretic motion of the platelets, with the velocity of the platelets proportional to E^2, as it has been already observed and explained by Lavrentovich et al. [21].

The observed rotation of platelet in the external electric field in principle allows for the estimation of the magnitude of spontaneous electric dipole moment p of platelet. By measuring the threshold electric field E_{th}, which is required for the rotation of the platelet for 90 degrees, we can estimate the electric dipole moment of the platelet. The key for this estimate is the change of the elastic energy between the zero-field and field-rotated states of the platelet. Obviously, the elastic energy of the field-rotated state is higher than the zero field state and the increase of the energy can be calculated using the Landau-de Gennes free energy minimisation approach [22]. The elastic energy

difference between these two states is calculated to $\Delta W_{ela} = 4 \cdot 10^{-16} J/m^2$ for the square platelet with dimensions 4 μm × 4 μm × 0.3 μm. This increase of the elastic energy needs to be compensated by the decrease of the electric energy of the electric dipole of the platelet in an external electric field $W_{ele} = -\vec{p} \cdot \vec{E_{th}}$, where E_{th} is the threshold electric field for platelet reorientation. The threshold electric field is determined by the threshold voltage $U_{th} = 3V$, cell thickness $d = 12\ \mu m$ and the average dielectric constant of the LC mixture $\varepsilon_{av} = 8$; $E_{th} = U_{th}/\varepsilon_{av} d \approx 0.03\,\mathrm{V}/\mu\mathrm{m}$. Finally we get an estimate for the electric dipole moment of the platelet $p \approx 10^{-20}\mathrm{Asm}$. It should be noted here that the elastic energy was calculated for perfect square-form platelets and in the limit of very strong surface anchoring. In reality particles are not perfect cubes, they have round corners and defects, surface anchoring can be substantially weaker and consequently the elastic energy could be lower than estimated. This means that also the actual dipole moment could be actually much smaller than estimated.

If the platelets have an electric dipole moment, an electrostatic force between two platelets should exist, provided it is not screened by ions. In the case of platelets with parallel electric dipole moments this force should be in the pN range for separation of $r = 10\ \mu$m between the centres of platelets:

$$F_{dip} = \frac{3p^2}{4\pi\varepsilon_{av}\varepsilon_0 r^4} \cong 30pN. \qquad (1)$$

This is relatively strong force for micro-objects, which should readily be observed in liquid crystals. However we have not observed any such strong interaction between platelets in any of the experiments.

We have performed many pair interactions experiments using the laser tweezers and video-microscopy to measure the separation dependent force between the two platelets. In the nematic phase we have observed very weak attractive force in the range of $0{,}1pN$, which is a typical elastic force between micro-objects in NLCs [11]. When the sample was heated to the isotropic phase, we have not observed any measurable interactions between the platelets. There are two possible reasons for this apparent absence of the electrostatic force between platelets: (i) Spontaneous dipole moment of platelets is negligible and the observed rotation of platelets in the external electric field is caused by the field induced dipole moment or (ii) the electric field of the dipolar moments of individual platelets is screened by ionic impurities in the LC.

We have performed additional pair interaction experiments in the external electric field, where platelets should have an induced dipole moment. In this set of experiments we have used homeotropic cells, where the platelets are oriented with their surfaces parallel to the substrate already in the absence of external electric field. When the DC electric field is applied, the interaction between platelets was observed. In most of the cases the interaction is repulsive (Figure 6), two platelets were moving away from each other, which is a clear sign that dipole moments in both platelets are induced in the same direction.

We have also measured the time dependence of the separation between platelets during repulsion and we have calculated the electrostatic force, assuming that it is equal to the viscous force exerted on the platelet. However, the calculated force does not follow the power law dependence predicted by Equation (1) and we were not able to determine the electric dipole moment p of platelets. Nevertheless, a number of experiments confirm that the electric dipole moment of the platelet is increased in the direction perpendicular to the plane by the external electric field.

In a truly ferroelectric nematic liquid crystal, the size of platelets should be much smaller than the wavelength of visible light. For example, ferromagnetic platelets in ferromagnetic nematic LC are typically 100 nm square platelets with a thickness of only few nanometres. In the following we were therefore gradually reducing the size of platelets and increasing their concentration to obtain the hypothetical ferroelectric LC mixture. First we have studied dispersion of micro-platelets with the average lateral size 0.5 μm and the thickness of 40 nm (Figure 1(b)). When we applied the AC electric field with the voltage $U = 4V$and frequency 1 Hz we have observed again rotation of platelets like in the case of much larger platelets (Figure 7). Also in this case the platelets are linearly coupled to the external field and are rotated for 180° degrees, when the field is reversed. However, the collective reorientation of LC is faint and the optical contrast between images during the switching is mostly due to the different absorption of light on the platelets.

In order to increase the contrast between the two states under opposite electric field, we increased the concentration of platelets, but unfortunately we could not obtain a homogenous dispersion of platelets. By increasing the concentration many agglomerates appear due to the elastic attractive forces between the platelets. Clearly, the repulsive electric force between adjacent electric dipole is not strong-enough to compensate for the elastic attraction. Several aggregates have adhered to the surface and the rotation of particles was strongly hindered at high platelet concentrations.

When the platelet size was further decreased to 200 nm and average thickness 13 nm (Figure 1(c)), the particles are too small to be observed under optical

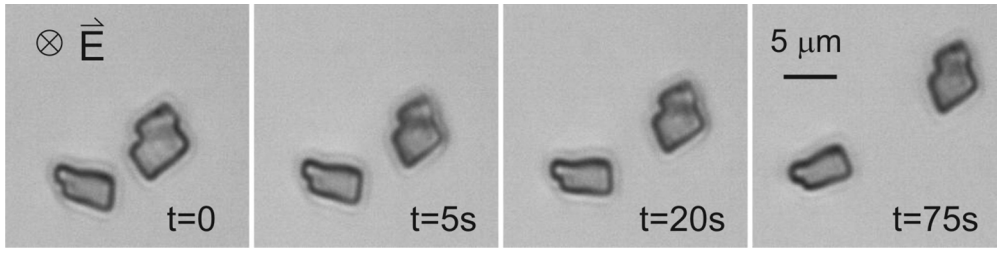

Figure 6. The repulsive electrostatic interaction is observed between two platelets in the homeotropic NLC when the DC field is applied. Dipole moments of both platelets are induced in the direction of the field.

microscope. Only small aggregates of particles could be resolved, since they induce deformation of director field, which can be clearly seen under polarising microscope (Figure 8). When the electric field was reversed ($E = 0.4\mathrm{V}/\mu\mathrm{m}, f = 1Hz$), rotation of small aggregates was observed, but no macroscopic collective LC reorientation took place (Figure 8(a,b)). When even stronger field was applied, the ionic motion became observable and the reorientation of LC occurred due to electro-convection rolls (Figure 8(c,d)). This was also observed in the case of micro-platelets and even pure nematic at somewhat larger fields.

When we further increased the concentration of nano-platelets, we have experienced the same problem of platelet aggregation, as in the case of micro-platelets. Many small aggregates appeared, which mainly adhered to the substrates after the electric field was applied. We have used several different volume concentrations of platelets, ranging from 0.02% to 1.5%, as well as different preparation procedures to prevent the aggregation of particles, but we could not obtain homogenous dispersion free of aggregates. We should note that this problem of particle aggregation is also crucial for preparing ferromagnetic LC dispersions [1,2]. In that case uniform hexagonal particles with magnetic dipole moment perpendicular to the plane and with uniform thickness of 5 nm were used. It has been shown that the platelet shape and magnetic moments perpendicular to the plane of platelets are crucial for the realisation of ferromagnetic phase, which was accomplished also in the isotropic solvent of butanol [23].

Ferroelectric platelets in our experiments possess some dipole moment perpendicular to the plane, but the detailed AFM analysis have shown that nano-platelets are of irregular shape with the average thickness of 13 nm with the standard deviation of 6 nm, which is probably the main reason that we could not obtain homogenous LC dispersion of nano-platelets. Furthermore, the experiments indicate that the net spontaneous electric polarisation of platelets is low. This could be either due to very narrow hysteresis loop of the ferroelectric material in thin platelets or the electric dipole is screened by the ionic species, which are evidently present in our NLC. We conjecture that the depolarisation field in ferroelectrics, which is the reason for screening of ferroelectric polarisation by the free charge carriers in the ferroelectric platelet (internal screening) and/or by the adsorbed charged species from the surrounding NLC (external screening) [24] could be the main reason that the establishing of ferroelectric NLC is more difficult than ferromagnetic NLC, where there is no screening of ferromagnetic polarisation. On the other hand, the platelets do show induced electric polarisation, which is evidenced by their reorientation in an external electric field.

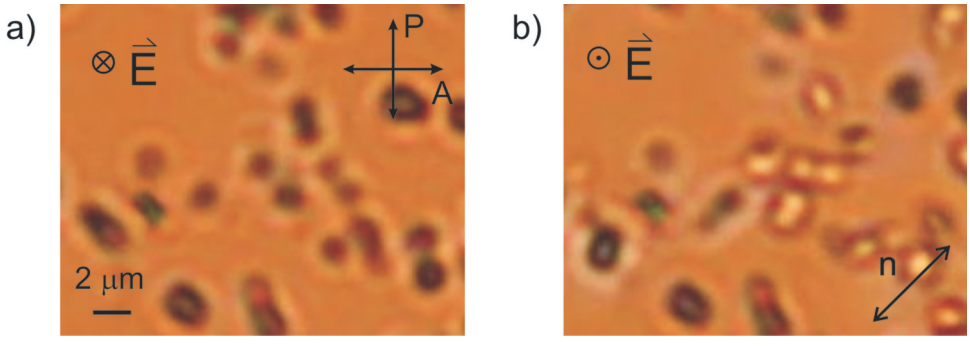

Figure 7. (Colour online) Ferroelectric micro-platelets with average lateral size 0.5 μm dispersed in the NLC are rotated for 180° degrees, when the electric field is reversed (U = 4 V, d = 10 μm).

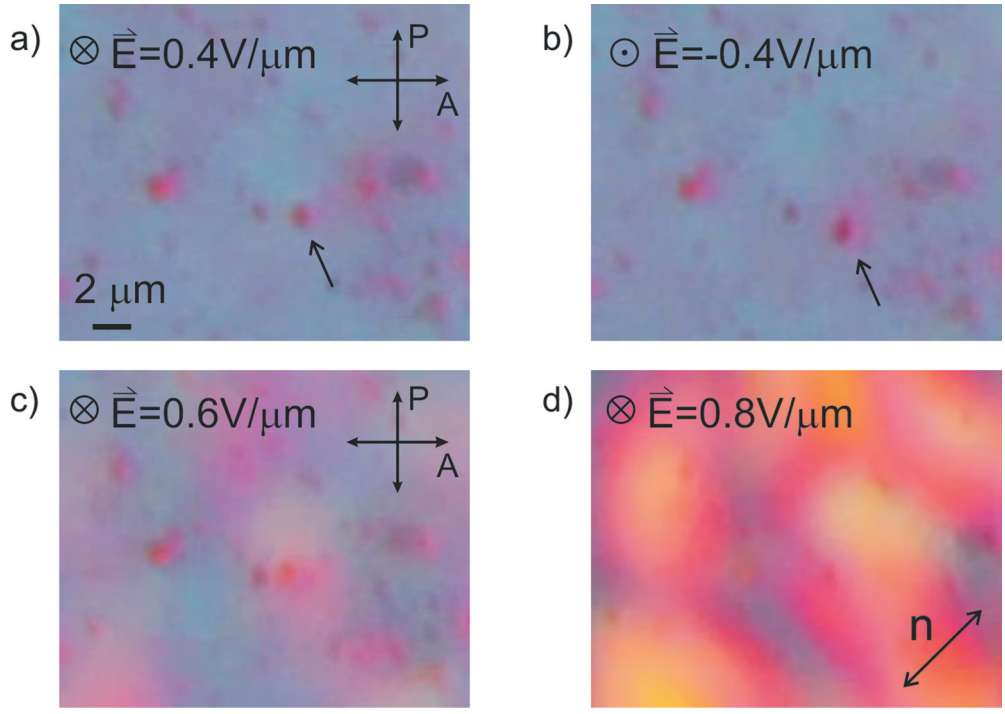

Figure 8. (Colour online) Ferroelectric nanoplatelets dispersed in the NLC. (a,b) When the weak reversed electric field is applied (E = 0.4 V/μm) only few aggregates are rotating (one is marked with an arrow). (c,d) LC is reoriented due to the appearance of electro-convection rolls when the stronger electric field is applied (E > 0.5 V/μm).

Conclusions

We have shown that ferroelectric platelets can be rotated in the nematic liquid crystal by the external electric field. The electric dipole moment of platelets is perpendicular to their plane and it is linearly coupled to the external electric field. The rotation of platelets is accompanied with the LC reorientation in the vicinity of platelets due to the strong LC anchoring at the surface of platelets, which can be used as a new method for indirect LC switching. However the switching of LC platelets with external electric field is relatively slow, with a cut-off frequency of 10 Hz, due to the high LC viscous drag. All attempts to obtain homogeneous dispersion of ferroelectric nano-platelets failed. The main problems are clusters of nano-platelets and their attraction to the surfaces. We conjecture that the irregular shape of nano-platelets, their inhomogeneous thickness and ionic screening prevent the formation of the homogenous LC polar dispersion, which could be switched by the rotation of nano-platelets. The preparation of stable ferroelectric nematic dispersion is a major material engineering problem, which involves the synthesis of very uniform, thin and polarised platelets and significant decrease of ionic concentration in the LC.

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Disclosure statement

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