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14. ABSTRACT

The project will focus on the implementation of nanoparticles in hybrid polymer-liquid crystal systems. In particular we will pursue the following tasks:
1. Preparing high optical quality suspensions of ferroelectric nanoparticles (LC DSFNP) in liquid crystals
2. Electro-optic response of LC DSFNP; measuring their dielectric and optical anisotropy
3. Two-beam coupling in LC DSFNP in cells combined with PVK:C60 layers
4. Analysis of the underlying mechanisms and interactions between nanoparticles, liquid crystals

The electro-optic response of cells with LC DSFNP will be investigated; measurements of how strongly the optical anisotropy and dielectric anisotropy can be increased by using suspensions will be determined, as compared with standard liquid crystals. In the next stage, we will explore in more detail the potential enhancement of reorientation via measuring two-beam coupling gain. For the observation of the photorefractive-like effects, the cells will be modified to include a photosensitive layer of PVK:C60. Two-beam coupling gain and coupling coefficient results will compared for cells with different nanosuspensions (Sn2P2S6 and BaTiO3) and liquid crystals, such as low refractive index and birefringence liquid crystal 6815 and high birefringence liquid crystal 1294.

The work proposed here will also be particularly relevant and important for gaining a better understanding of ferroelectric nanoparticles and liquid crystals interactions. We will carry out the analysis and modelling of experimental results, for example, in order to achieve a better understanding of the processes responsible for the interaction between nanoparticles and liquid crystal molecules

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ELECTRO-OPTIC AND PHOTOREFRACTIVE RESPONSE OF LIQUID CRYSTALS WITH INORGANIC FERROELECTRIC NANOPARTICLES

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Summary of the project

This project aimed to achieve the enhancement of photorefractive and electro-optical response of liquid crystals in hybrid configurations. By using ferroelectric nanocrystals as dopants and substrates with photosensitive surfaces, the improvement of dielectric anisotropy, birefringence and two-beam coupling gain was investigated.

The first part of the project concerned preparing cells, aligning and photoconductive layers. Furthermore, nanoparticles' suspension in liquid crystals LC 6815 and LC 1294 were prepared and their optical quality investigated. In this part, the dielectric and optical anisotropy were measured. The second part of the project was devoted to the measurement of two-beam coupling gain and investigations of another suspension: ferroelectric nanoparticles in LC TL205

All deliverables were successfully achieved and indeed the scope of the project went beyond the originally stated objectives and deliverables. First, not only the suspensions with $Sn_2P_2S_6$ (SPS) nanoparticles were prepared and analysed, but also $BaTiO_3$ nanoparticles. Secondly, we also investigated another low-refractive index liquid crystal LC 1550.

High optical quality, uniform alignment was accomplished after infilling of cells with nanoparticles-liquid crystals suspensions. Improved optical and dielectric anisotropy as well as two-beam coupling gain was also demonstrated for all the suspensions.

Introduction

The main thrust behind the proposed research is develop new nanomaterials, based on hybrid combination of liquid crystals and photorefractive nanocrystals, offering superior performance for controlling light beams' propagation and power. One of the main benefits of such nanomaterials is that they can be tailor-made and versatile. They respond to electric field and are photosensitive to specific regions of ultraviolet, visible or infrared light. The work on the project centred around two themes: first, on the materials preparation and their functionalisation, and the second, on their characterisation.

Methods, Assumptions, and Procedures

Ferroelectric particles of $Sn_2P_2S_6$ and $BaTiO_3$ ($\cong 1$ μm size), mixed with oleic acid in a weight ratio of 1:2, were milled to reduce their size to nanometers. The resulting nanoparticles, with the size between 10 and 100 nm, were then added to the nematic liquid crystals selected for this project, namely Merck 6815 and TL205; Lichem 1550 and 1294. They were added at a weight ratio 1:100 and ultrasonically mixed for five minutes, so their volume concentration was about 1 % in the liquid crystal matrix. Liquid crystals functionalized in this way were then used to infiltrate the cells.

The first type of cells was made from two glass substrates each covered by transparent ITO electrodes and by ~100 nm polyimide layers. To achieve a homogeneous planar alignment of liquid crystal, both polymer layers were unidirectionally rubbed with velvet. The cells' thickness, L, was 12 μm. The second type of cells was prepared for the two-beam coupling and diffraction experiments[1]. One of the cells' substrate, instead of a rubbed polyimide, was covered with a photoconductive type polymer. The polymer was polyvinyl carbazole doped with fullerene (PVK:C_{60}). The other substrate was covered with a layer of standard polyimide. The substrates were unidirectionally rubbed and uniform planar alignment was achieved. The cells were filled with either pure or functionalised liquid crystals.

The birefringence properties were investigated by illuminating the cells by a single beam with AC or DC field applied to their ITO electrodes and by putting a cell between crossed polarisers placed at 45^o with respect to the liquid crystal director.

The recording of the optical grating in LC cells was performed in standard two-beam scheme. Intensity gratings with a period $\Lambda \approx 2\text{-}10\,\mu$m, were recorded in a cell via interference of two *p*-polarized beams at 543 nm from He-Ne laser. The intensity of the incident beams in the plane of their intersection was $I_0 = 17$ mW/cm^2. The data acquisition system allowed us to monitor simultaneously the intensity of transmitted as well as diffracted beams. A set of electromagnetic relays controlled both the application of an electric field to the cell's electrodes as well as shutters that were used to switch-on/off the incident beams. A DC power supply and a wave form generator were used to apply either DC or AC electric fields.

The irradiation of the cells at the simultaneous application of the DC field resulted in the recording of a dynamic Raman-Nath diffraction grating and appearance of the self-diffraction of the recorded beams. The characteristics of the self-diffraction and the asymmetric energy exchange between the recording beams for the suspensions were qualitatively the same as for pure liquid crystals. The most efficient self-diffraction and beam coupling were observed when the cell was rotated away, so a normal of its incident surface did not coincide with the bisector of the angle between the recording beams. The optimum range of rotation angles was between 20-30^o, where the diffraction efficiency exceeded 20%.

The recording of the grating was accompanied by the intensity exchange between the recoding beams. To minimize the influence of linear diffraction, the incident beams had equal intensities. Beam coupling was observed as amplification of one of the recording beams at the expense of the depleting of the other one. To characterize the beam coupling, we measured the the ratio $G = I_{probe+pump}/I_{probe-pump}$, where $I_{probe+pump}$ is the intensity of the probe beam in the presence of the pump beam and $I_{probe-pump}$ is the intensity of the probe beam in the absence of the pump beam. To compare the performance of different cells we used the gain coefficient, Γ, defined as: $\Gamma = \frac{1}{L}\ln\frac{Gm}{m-G+1}$, m is the incident beams intensity ratio. The dependencies of the coefficient, Γ, on the DC field was measured for both pure liquid crystals and liquid crystal suspensions. Ferroelectric particles do not change the character of the dependence $G(V_{DC})$, but strongly enhance the energy exchange between the beams.

In the next stage of our investigation, we studied the dielectric anisotropy in the colloid and in the pure LC. The measurements were carried out by a standard bridge method at ν = 1 kHz in the cells with a planar alignment ($\varepsilon_{\perp}$) and homeotropic alignment (ε_{II}) of liquid crystals.

Results and Discussion

First part of the project: fabrication and initial characterisation

During the first part of the project, the following two tasks and three deliverables were completed. The results from this part of the project were already submitted in the mid-term report, but also included below.

Table 1 Tasks and deliverables for the first part of the project

Tasks	Deliverable	Status
T1: Preparing high optical quality suspensions of ferroelectric nanoparticles in liquid crystals and substrates with photosensitive layers.	D1. High quality substrates with PVK:C_{60} polymer and polyimide polymers on both substrates	completed
T2. Electro-optic response of suspensions: measurements of their dielectric and optical anisotropy.	D2. Suspensions of ferroelectric $Sn_2P_2S_6$ and $BaTiO_3$ in liquid crystals: LC 6815 and LC1294.	completed
	D3. Electro-optic response; dielectric and optical anisotropy measurements	completed

Task 1: Preparing high optical quality suspensions of ferroelectric nanoparticles in liquid crystals and substrates with photosensitive layers

The first task was devoted to the fabrication of cells and materials preparation. Initial components, standard ITO covered substrates, were covered with aligning layers. The aligning layers were made of rubbed polyimide or doped polyvinyl carbazole (PVK:C_{60}) to produce planar orientation of liquid crystals.

We developed a method of doping PVK with photosensitiser (C_{60}) and depositing it as a thin (100 – 300 nm) and uniform layer onto ITO covered glass substrates. C_{60} is soluble in organic solvents, but after testing several solvents, chlorobenzene was chosen. Chlorobenzene was also chosen for PVK to avoid dropping down C_{60} sediment. A saturated concentration of C_{60} solution was added to the PVK solution PVK and an estimated dopant concentration of C_{60} in the PVK (dry layer) was 14.9% by weight. Polymer films where deposited onto clean ITO covered glass substrates by spin coating and then the substrates were dried at 90^0 C for 30 minutes and at 180^0 C for 60 minutes.

The substrates were unidirectionally rubbed with velour cloth to achieve planar homogeneous alignment of liquid crystals.

For some cells substrates polyimide (PI), instead of PVK, was needed as an alignment layer. Polyimide solution, dissolved additionally in acetone, was spin coated on substrates to produce a very thin, but uniform film. After prebaking and rubbing, it produced high quality and stable liquid crystal alignment.

The cells were assembled using either one PVK:C_{60} covered substrate and one PI covered substrate or two substrates with PI layers. Using 11 μm spacers, the cells were sealed by a UV glue on all, except one side. This side was then used to infiltrate the cells with liquid crystals and then sealed.

Deliverable 1	***Preparing high quality substrates with PVK:C_{60} polymer and polyimide polymers on both substrates***	***Status: achieved***

This part of the project also concerned the fabrication of nanoparticles. Sub-micron particles are produced by the process of fine milling of ferroelectric crystals. Micron size crystals are milled together with a surfactant for approximately 100 hours in a micro-mill. A typical surfactant used for this purpose is oleic acid. The finest, in size, particles are then dispersed in a liquid crystal host, kept at the isotropic phase. In this way nanoparticles of photorefractive, material thiohypodiphosphate $Sn_2P_2S_6$ (SPS) and barium titanate ($BaTiO_3$) were produced.

Suspensions of SPS and $BaTiO_3$ were made in liquid crystals in liquid crystals LC 6815 and in newly synthesised LC 1550. LC 1550 was made by our collaborators from Military University in Warsaw and they managed to reduce its ordinary refractive index below that of silica. Therefore, it is very promising for applications in waveguiding structures and devices. The suspensions were prepared with the concentration of 1% of nanoparticles in the nematic hosts.

The suspensions were used to infiltrate the cells prepared earlier and the inspection of their alignment showed high optical quality, providing uniform, planar alignment of the suspensions.

Finally, both SPS and $BaTiO_3$ nanoparticles were added to high birefringence liquid crystal LC 1294 using the same procedure as for the other liquid crystals. However, although the initial alignment was good, after a few days, it deteriorated and several domains could be observed via visual inspection. We are currently investigating this effect, but the most likely cause is the multi-component nature of LC 1294, which leads to the limited stability of the mixture

Deliverable 2	***Preparing suspensions of ferroelectric $Sn_2P_2S_6$ and $BaTiO_3$ in liquid crystals: LC 6815 and LC1294.***	***Status: achieved***

Task 2: Electro-optic response of suspensions – measurements of their dielectric and optical anisotropy

The optical parameters of functionalized with nanoparticles liquid crystals, namely birefringence, dielectric anisotropy and the phase transition temperatures were measured and then compared with those obtained in undoped liquid crystals.

The first set of electro-optic measurements concerned determining the magnitudes of electrically induced birefringence and the reorientation threshold. For these measurements, cells with both substrates covered with PI were used. The cells were illuminated by a single beam with AC field applied and put between crossed polarisers, placed at 45° with respect to the liquid crystal director. The transmitted light was collected on a photodiode placed behind the cell and the variation in intensity measured for increasing AC voltage. Figure 1 presents the comparison between results for: nominally pure LC6815, LC 6815+$BaTiO_3$ nanoparticles and LC 6815+SPS nanoparticles. Similar dependence was measured for the other liquid crystal investigated.

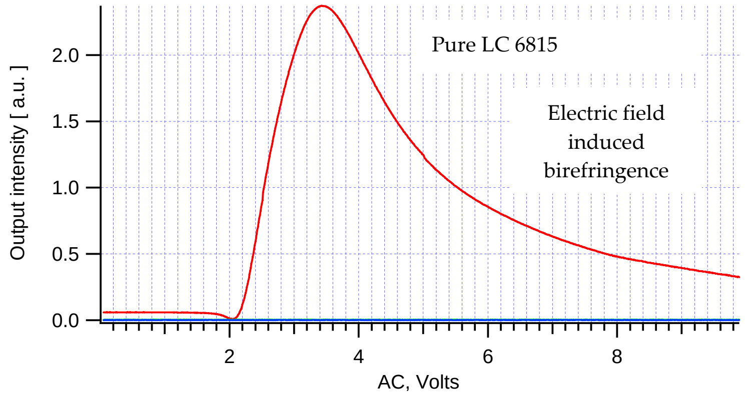

Figure 1a

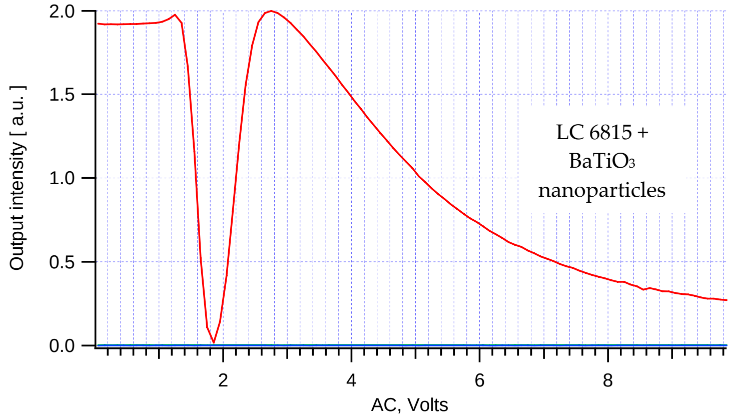

Figure 1b

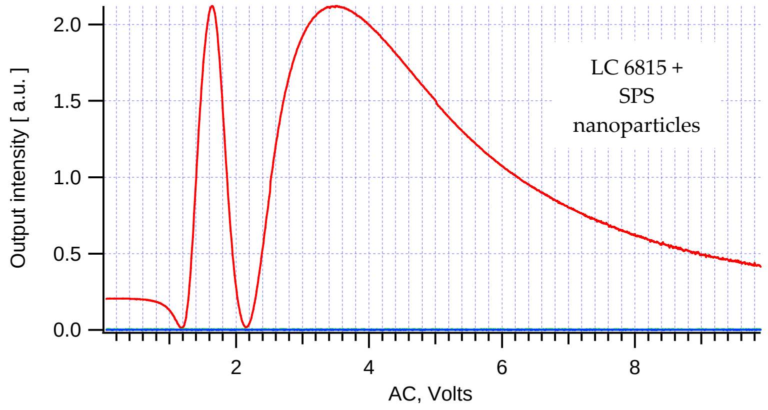

Figure 1c

Figure 1 Induced birefringence of pure liquid crystal LC 6815 (a), suspension of $BaTiO_3$ nanoparticles in LC 6815 and suspension of SPS nanoparticles in LC6815 (c).

Figures 1a, b and c demonstrate the increased birefringence of suspensions with ferroelectric SPS particles in liquid crystals by inducing larger phase retardation as compared with either pure liquid crystal or with $BaTiO_3$ suspensions in liquid crystals. The results of birefringence calculations[2] are shown in the table below and confirm our previous qualitative observations.

Investigating the dielectric properties, the impedance of the cell was measured to estimate the dielectric permittivity of the samples, $\varepsilon = \varepsilon^{'} + \varepsilon^{''}$ using standard auto balancing bridge method and using at the frequency of 10^3 Hz. This frequency was chosen based on earlier experiments on the frequency dependencies of $\varepsilon^{'}, \varepsilon^{''}$ of nematic ferroelectric suspension. The experimental set-up was calibrated by the prior measurements of the empty cells.

For completeness, the phase transition temperatures were measured. Furthermore, as in some hybrid organic-photorefractive systems pretilt angles can increase, we inspected our cells for any possible changes[3] in the value of that parameter. No change in pretilt angles was observed, as compared with pure liquid crystals, but increase in nematic to isotropic phase transition temperature was measured. Using a controllable hot stage and a polarizing microscope, changes in liquid crystal structure could be detected. The samples' temperature was controlled with the precision of 0.05°C.

The table below summarises the optical and dielectric anisotropy results as well as phase transition temperatures for liquid crystals 6815, 1550 and another low refractive index liquid crystal LC 18523.

Table 2 Comparison of dielectric and optical anisotropy and phase transition parameters for pure and ferroelectric suspension in low refractive index liquid crystals.

	Δε	**Δn**	**T, °C**
LC 18523	2.1	0.05	57
LC 18523+ $BaTiO_3$	4.8	0.09	68
LC 18523+SPS	6.2	0.10	69
LC 1550	2.38	0.05	79
LC1550+$BaTiO_3$	3.36	0.071	84
LC1550+SPS	4.46	0.09	86
LC 6815	2.14	0.05	65.5
LC6815+$BaTiO_3$	3.76	0.07	71.4
LC6815+SPS	4.39	0.09	72.5

First, this table confirms systematic and consistent improvement in increased birefringence and dielectric anisotropy for liquid crystals with nanoparticles. Secondly, it demonstrates that SPS nanoparticles, with their larger size and more wide distribution, give rise to stronger enhancement in the electro-optic parameters, as compared with $BaTiO_3$. Dielectric anisotropy increased by up 230% for the case of $BaTiO_3$ nanoparticles and as much as much as up to 300% for the case of SPS nanoparticles. Similarly, the induced birefringence increased by up to 180% for liquid crystals with $BaTiO_3$ nanoparticles and up to 200% for liquid crystals with SPS nanoparticles. Finally, increase in phase transition temperatures was observed that ranged from 5 to 12°C between pure liquid crystals and those with ferroelectric nanoparticles. For phase transition temperatures, the difference between the SPS and $BaTiO_3$ nanoparticles appeared to be less critical.

Deliverable 3	***D3 Electro-optic response; dielectric and optical anisotropy measurements***	***Status: achieved***

Second part of the project: electro-optic characterisation and two-beam coupling

Task 3: Electro-optic response of suspensions of ferroelectric nanoparticles in LC TL205

Our experiments so far focussed on low refractive index liquid crystals (LC 18523, 6815 and 1550), where consistent enhancement of dielectric and optical anisotropy was observed. In the third task of this project we investigated liquid crystal TL205 – both pure and doped with SPS and $BaTiO_3$. US AF research labs in Ohio used this liquid crystal, doped with $BaTiO_3$ nanoparticles, in cells with solid-state photorefractive windows and high two-beam coupling gain was achieved. In our case, TL205 with $BaTiO_3$ nanoparticles will be used the cells with PVK:C_{60} layers, for comparison with the other type of hybrid cells.

As for the other liquid crystals considered, TL205 dielectric and optical anisotropy were measured both with and without $BaTiO_3$ nanoparticles. Additionally, for the pure version of this is material we could compare the data with the Merck catalogue sheet. Table 3 summarises the main results.

Table 3 Dielectric and optical anisotropy for pure and $BaTiO_3$ suspension in LC TL205

	TL 205	**TL 205 (data sheet)**	**TL 205+ $BaTiO_3$**
ε_{II}	3.6	4.1	4.5
$\varepsilon_{\perp}$	7.6	9.1	10.6
Δε	4.2	5.0	6.1
Δn	0.2	0.21	0.25

The values of anisotropies for undoped LC TL205 from our measurements were approximately 15% lower than those provided in its data sheet. It is likely that the presence of additional aligning layers contributed to this difference and we will investigate this effect.

An important conclusion could be drawn for TL 205, namely that both its dielectric and optical anisotropies increased, as in case of low refractive liquid crystals, when ferroelectric nanoparticles were added. However, this increase, in particular Δn, was only approximately 25%.

Deliverable 4	***D4 Electro-optic response; dielectric and optical anisotropy measurements in LC TL205***	***Status: achieved***

Task 4: Two-beam coupling gain in suspensions of ferroelectric nanoparticles in cells with PVK:C_{60} layers

The suspensions developed in the previous stages of the project were used to test the efficiency of energy exchange in two-beam coupling process. The irradiation of the cells at the simultaneous application of the DC field resulted in the recording of a dynamic Raman-Nath diffraction grating and appearance of the self-diffraction of the recorded beams.

Given the lack of long-term stability of LC 1294, in this task we concentrated on the other liquid crystals of interest: LC 6815, TL205 and LC 1550 – the liquid crystal that we used instead of LC 1294.

Figure 2 presents the two-beam coupling results measured, first for pure LC 6815 and then its functionalised versions: either with $BaTiO_3$ or SPS nanoparticles.

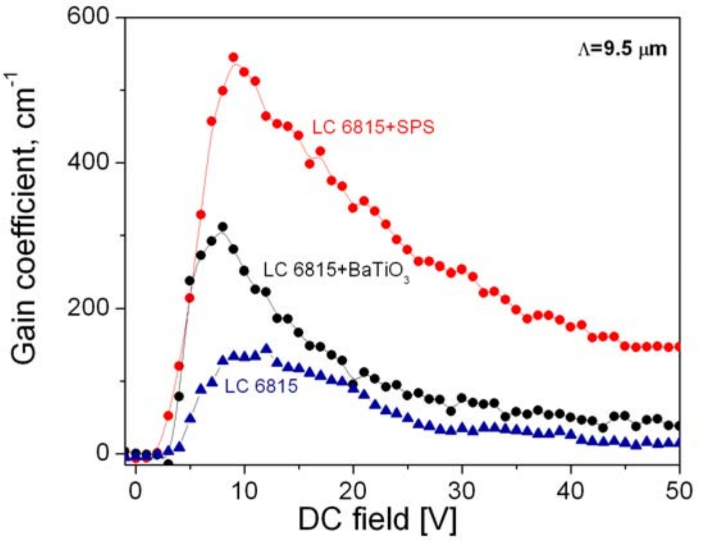

Figure 2 Two-beam coupling in LC 6815: pure and with ferroelectric suspensions for Λ=9.5 μm

Similarly as in case of previously reported LC 18523, an increase of factor of 5 of the coupling coefficient was measured. In the next part of the experiment we reduced the grating spacing by approximately a half (4 μm) and measured two-beam coupling gain again. The enhancement of gain by approximately a factor 5 was again measured, but the overall value of coupling coefficients was lower than for the case of 9.5 μm grating spacing **(**Figure 3**).**

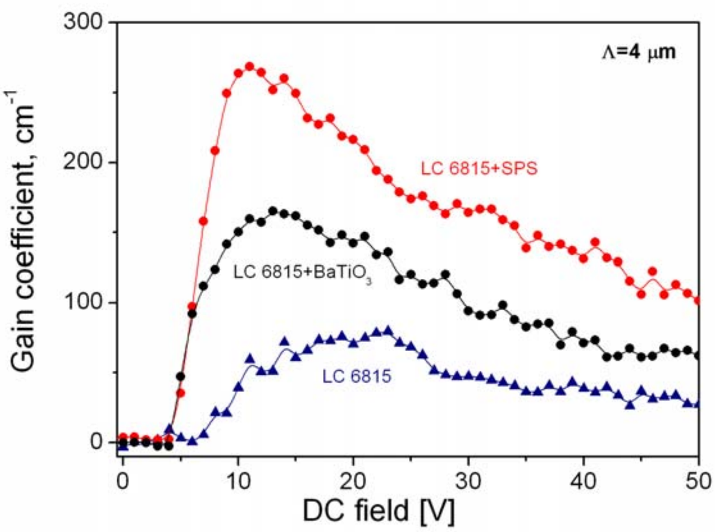

Figure 3 Two-beam coupling in LC 6815: pure and with ferroelectric suspensions for Λ=4 μm

The lower gain observed for smaller grating spacings is consistent with the expected penetration of the electric field into the liquid crystals bulk. This penetration depth is of the order of the grating spacing and that determines the thickness of the grating/"gain" medium. For 4 μm grating spacing, Raman-Nath diffraction was still observed.

It is worth noting also that for both cases of grating spacings, SPS nanoparticles gave stronger gain enhancement than $BaTiO_3$ nanoparticles.

Similar dependence was measured for LC 1550 with either SPS or $BaTiO_3$ nanoparticles. Figure 4 compares the two-beam coupling data for LC 1550+SPS nanoparticles for different grating spacings – from 9.5 μm to 2.5 μm – namely starting from the Raman-Nath to approaching the Bragg regime. However, at 2.5 μm, the Raman-Nath diffraction was still present. As for the case of LC 6815, two-beam coupling gain was reduced for higher resolution gratings.

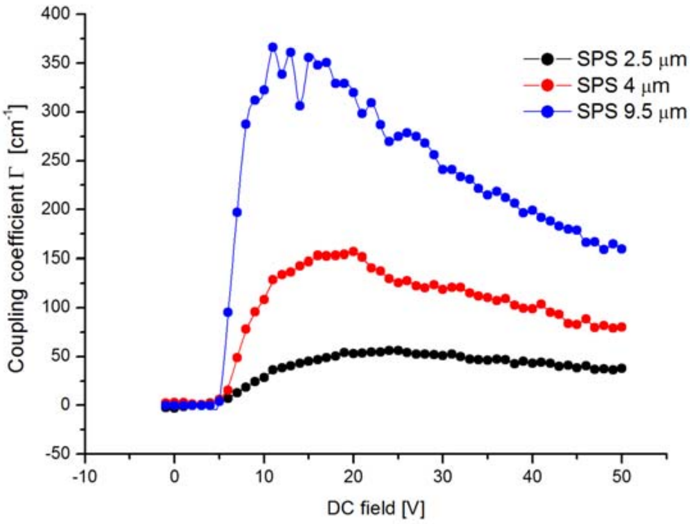

Figure 4 Two-beam coupling gain for LC 1550 with SPS nanoparticles versus DC field for different values of grating spacings

The dependence of two-beam coupling gain on the applied DC field for increasing resolution of gratings was also checked for LC 1550 with $BaTiO_3$ nanoparticles. Figure 5 presents the main results.

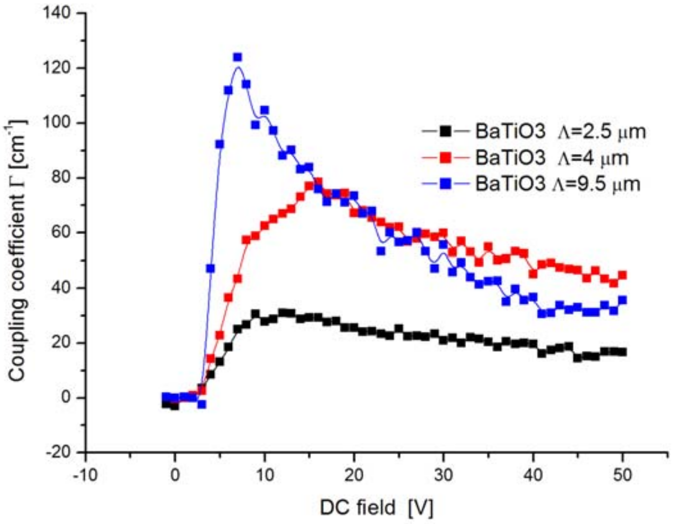

Figure 5 Two-beam coupling gain dependence on DC field for LC 1550 with $BaTiO_3$ nanoparticles for different values of grating spacings

The net value of gain was smaller than for the case of SPS nanoparticles, but again the gain was lower gain for smaller grating spacings.

Deliverable 5	***D5 Enhanced two-beam coupling gain in suspension of ferroelectric nanoparticles in low refractive index liquid crystals***	***Status: achieved***

Finally, we investigated LC TL205 with $BaTiO_3$ nanoparticles. This liquid crystal has higher birefringence and refractive indices (see Table 3), but the change in dielectric and optical anisotropy observed earlier suggested that this liquid crystal could be suitable as efficient material for two-beam coupling. Indeed, as presented in Figure 6, significant increase – approximately a factor of 4 – in coupling coefficient was achieved. The case presented in Figure 6 is for Λ=9.5 μm.

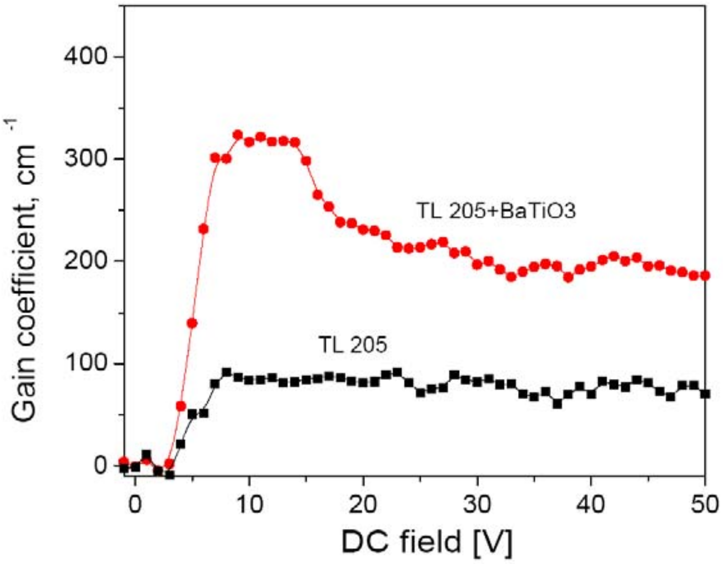

Figure 6 Enhanced two-beam coupling gain for LC TL205 with $BaTiO_3$ nanoparticles versus applied DC field

Further investigation of LC TL205 with SPS nanoparticles will be carried out, including the measurements in the Bragg regime, so the results can be more directly compared with those obtained in hybrid cells with photorefractive solid-state windows.

Deliverable 6	***D6***	***Enhanced two-beam coupling gain in suspension of ferroelectric nanoparticles in LC TL205***	***Status: achieved***

Task 5: Exploring the method of increasing the liquid crystals pretilt angle

In the final task of the project, we explored new ideas and developments in surface alignment to increase the initial liquid crystal pretilt angle. The additional challenge is for these aligning layers to be easily removed, so the underlying substrate can be re-used and is not damaged.

Over the past several years different methods were proposed to achieve a high pretilt angle, ideally being between 30 to 60°. Examples of such techniques include: SiO_2 evaporation[4]; blending polymers and then exposing them to UV light[5,6] or using azo-dye doped polymer films[7]. Unfortunately, while high pretilt angles were demonstrated, these methods suffer either from the lack of stability with time or are not practical for producing a large number of cells at the same time.

One new method that was proposed recently can partly answer one of the challenges. In the work by Yeung and co-workers[8] an adjustable pretilt angle was demonstrated. By mixing two types of polymide – one that promotes planar alignment with another which imposes a vertical alignment, a pretilt angle could be changed from 0 to 90°. The anchoring energy remained fairly constant for all the pretilt angles. One drawback of that technique is that it still relies on polymide that is not easily removed from substrates.

Achieving a high pretilt angle could be of significant benefit for two-beam coupling process, especially in thin liquid crystal cells, where the whole cell has to be tilted to observe gain. However, the methods and techniques to achieve that would need to be covered by a separate project. First of all, the Yeung method could be investigated in detail. For example, by reducing the baking time of the mixed polyimide, its adhesion to the substrate could be minimised to for more easy removal. Secondly, the photoalignment method could be explored on soft polymers, such as cinnamate copolymers. While such technique may not be practical for large scale industrial devices or for large volume of commercial cells, it may work on a lab scale for demonstrator type devices. Such investigation could be beneficial not only for optoelectronic, but also for display applications.

Deliverable 7	***D7 Reporting on new methods for achieving high pretilt angle***	***Status: achieved***

Table 4 Tasks and deliverables for the second part of the project

Tasks	Deliverable	Status
T3. Electro-optic response of suspensions of ferroelectric nanoparticles in LC TL205	D4. Electro-optic response; dielectric and optical anisotropy measurements in LC TL205	completed
T4. Two-beam coupling gain in suspensions of ferroelectric nanoparticles in cells with PVK:C_{60} layers	D5 Enhanced two-beam coupling gain in suspension of ferroelectric nanoparticles in low refractive index liquid crystals	completed
	D6 Enhanced two-beam coupling gain in suspension of ferroelectric nanoparticles in LC TL205	completed
T5. Exploring the method of increasing the liquid crystals pretilt angle	D7. Reporting on new methods for achieving high pretilt angle	completed

Conclusions

In conclusion, we successfully demonstrated the improvement of electro-optic and photorefractive response in suspensions of ferroelectric nanoparticles in liquid crystals.

First, cells with the suspensions with SPS and $BaTiO_3$ nanoparticles were fabricated and their high optical quality as well as long term stability demonstrated. The only exception was LC 1294, but this material even in its pure form had stability problems with domains forming with time.

Secondly, for all low refractive index and low birefringence liquid crystals investigated, enhanced optical and dielectric anisotropies were confirmed. This effect is not unique to that class of materials as similar trend was measured in LC TL205, which has "standard" refractive indices (1.52 and 1.74) as well as relatively high anisotropy (0.21). However, the increase in anisotropies following the addition of nanoparticles was much smaller for TL 205 than for low refractive index liquid crystals. It is likely therefore that nanoparticles do not induce any significant change in the alignment of liquid crystals as otherwise the liquid crystals with high Δn would be affected more. All the liquid crystals investigated were mixtures rather than single components.

Thirdly, enhanced two-beam coupling gain was consistently measured in all the suspensions investigated. The coupling coefficient could be increased by as much as a factor of 5 with the values reaching 600 cm^{-1}. However, these optimum values were measured in the Raman-Nath regime with a typical grating spacing of 9.5 μm. Two-beam coupling for higher resolution gratings spacings was also investigated and the reduction in the gain observed. Indeed, the Bragg regime was not reached even at 2.5 μm, as Raman-Nath diffraction was still observed. This reduction of gain is expected as the penetration of electric field into the liquid crystal bulk is of the order of the grating spacing, which means that for smaller grating spacing, the effective grating/medium thickness is also smaller. The gain enhancement measured in TL205 is particularly interesting as in our earlier work no change was observed for liquid crystal E7.

Fourthly, we observed that the enhancement of both the anisotropies and gain was higher for the case of suspensions with SPS nanoparticles then for $BaTiO_3$ nanoparticles. It is indeed intriguing given that SPS nanoparticles are less symmetrical than $BaTiO_3$, they aggregate more easily and have a wider distribution in size, as our earlier work demonstrated.

Finally, we explored new routes to create high pretilt angles. Having aligning layers with adjustable pretilt angles of $30\text{-}50^{o}$, could enable us to depart from experimental geometry constrains and have light beams incident normally on the surface of the cells. It would certainly be an interesting idea to pursue, but our research suggest that more effort would have to be devoted to optimise the two techniques that are the most promising – photoalignment on soft polymers and experimenting on the mixtures of polyimides and their baking.

The results obtained in this project should aid better understanding of hybrid liquid crystal-ferroelectric nanoparticles materials, but they also indicate that more work should be devoted to the measurement of their basic parameters, such as refractive indices, elastic constants, order parameter as well as inspecting the distribution of nanoparticles in liquid crystals by for example X-ray diffraction.

References

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[1] F. Kajzar, S. Bartkiewicz, A. Miniewicz, Appl. Phys. Lett., **74**, 2924 (1999).

[2] S. -T. Wu, U. Efron, L. D. Hess, Appl. Opt. **23**, 3911 (1984)

[3] G. Cook, J. L. Carns, M. A. Saleh, D. R. Evans, Mol. Cryst. Liq. Cryst. **453**, 141 (2006).

[4] B. Jerome, P. Pieranski, M. Boix, Europhys. Lett. **5**, 693 (1988).

[5] J. Y. Hwang, D. S. Seo, Jap. J. Appl. Phys**. 40**, 4160 (2001)

[6] M. Schadt, K. Schmitt, V. Kozinkov, V. Chigrinov, Jpn. J. Appl.Phys., Part 1 **31**, 2155 (1992).

[7] S. Furumi , K. Ichimura, Adv. Func. Mat. **14**, 247 (2004)

[8] F. S. Yeung, J. Y. Ho, Y. W. Li, F. C. Xie et al, , Appl. Phys. Lett, **88**, 051910 (2006)