Graphene oxide (GO) nanoparticles of two different sizes are dispersed in the nematic liquid crystal (LC) 5CB covering a wide concentration range. The dielectric properties, as well as the electrooptic behavior, including threshold voltage, elastic constant, and response times are investigated as a function of GO concentration. It is found that small graphene oxide flakes of mean size of 560 nm are better and easier dispersible than larger flakes of 2.8 µm mean size. The nematic–isotropic transition only increases slightly for the (GO+LC) hybrid systems. For increasing GO concentrations the threshold voltage and splay elastic constant dramatically increase, until saturation for a concentration of ≈1% by weight GO. The field driven switching-on time is practically independent of concentration, while the switching-off time, which is purely elastically driven, exhibits a strongly decreasing behavior. Dielectric spectroscopy reveals a noncollective relaxation which is absent in the neat liquid crystal. This may be attributed to a drastically slowed down molecular relaxation related to the rotation around the short axis of the liquid crystal molecules. When heating the thermotropic liquid crystal into its isotropic phase, the latter acts as a solvent for the GO particles, and a lyotropic nematic phase with largely reduced birefringence is formed.

1. Introduction

Nematic liquid crystals (NLCs) are essential materials for the scientific and industrial progress of the electrooptic display technology. The key characteristic that makes NLCs practical for the electrooptic devices is the long-range orientational order in combination with birefringence and dielectric anisotropy, i.e., the possibility to easily reorient the optic axis by application of electric fields.[1,2] The incorporation of various nanomaterials into liquid crystals (LCs), and the complexity of their interaction, have recently attracted much interest.[3–12] The addition of nanoparticles (NPs) to liquid crystals produces composite materials with additional functionality, and tunable optic, electric, magnetic, or electrooptic properties. Both molecular and macroscopic bulk properties are modified. Three main objectives have been proposed for producing LC-NP hybrid systems: (i) to change the properties of the liquid crystal, (ii) to modify the properties of NPs by exploiting the liquid crystal self-assembly, i.e., to produce self-assembled and ordered NPs, and (iii) to generate additional functionalities not obtainable by either materials on their own, for example in the use of sensor materials or photonic devices.

A similarity between NPs and the liquid crystal molecules is highly desirable for producing stable NP+LC mixtures. NPs with anisotropic shapes, such as carbon nanotubes, have formed a stable suspension in a liquid crystal material,[7] and their long axes follow the orientational order of the LC.[3,4,8–10] Recently, 1D nanoparticles, such as nanowires, were found to be effective for increasing the orientational order of liquid crystalline systems.[11] Rajh et al. compared the effects of nanowires, nanorods, and nanotubes; they concluded that, due to the small aspect ratio, the nanorods showed more compatibility than the other nanomaterials.[12] In addition, 2D graphene flakes doped in NLCs have improved electrooptic switching and dielectric anisotropy.[13,14]

An investigation, like the one presented in this paper, combining two modern functional materials, liquid crystals and graphene oxide (GO), is not only of fundamental interest but also of applicational relevance. The liquid crystal exerts its self-organization onto the anisotropic graphene oxide in order to provide alignment of the latter. This in turn opens promising possibilities for added functionality. For example, the originally insulating graphene oxide can be made conductive through reduction, for example at elevated temperatures.
It also exhibits an extremely large Kerr effect,[15] which could enhance the electrooptic properties of novel display types, such as blue phase LCDs. In electronics, reduced graphene oxide could act as transparent electrode materials for LEDs or solar cells, but especially also as a replacement for electrode material indium tin oxide (ITO) used for liquid crystal electrooptic cells and displays, orienting the GO at the substrate surfaces through a water based lyotropic liquid crystal. Further applications could be envisioned in biomedical applications, such as drug delivery systems, as cell membranes exhibit liquid crystalline order; or in the area of tunable sensor materials.

In this paper, we investigate the dispersion of GO flakes into a standard thermotropic nematic material, 5CB. GO is made of monolayer graphene platelets that are surface and edge-oxygenated in the form of carboxyl, hydroxyl, or epoxy groups,[16,17] and have strong mechanical properties, chemical functionalization capability, and a large specific surface area. These oxygen functional groups allow high solubility of GO in water and other polar solvents. However, due to the anisotropic property of the medium, and the disturbance in the free energy and entropy, the dispersion of GO in an NLC is a major challenge.[18]

GO flake additive differs from graphene flake additives in many significant ways. Liquid-phase exfoliated graphene flakes, like the ones that have been previously added to NLCs, are comprised of small flakes of few-layer graphene; typically 500 nm laterally and 1–5 layers thick. More importantly, flake thickness and lateral size correlate, bigger flakes are also the thicker flakes. GO on the other hand provides us with 100% monolayer laterally and 1–5 layers thick. More importantly, flake thickness and lateral size correlate, bigger flakes are also the thicker flakes. GO on the other hand provides us with 100% monolayer flakes, with better control over flake size. Also, whereas graphene is a hydrophobic material, GO is a hydrophilic material, and this will result in a different interaction with liquid and liquid crystal solvents.

In this paper, the evolution of aggregates, along with the nematic properties of phase transition temperature and electrooptic parameters will be presented and discussed as a function of GO concentration. In addition, we study differently sized GO flakes, and in particular also the high concentration regimes, which was motivated by investigations of lyotropic systems.[16,17,19–21]

2. Results and Discussion

2.1. Characterization of the GO Flakes

The average size and polydispersity of GO flakes were characterized using scanning electron microscopy (SEM), with typical images for the small and the large flakes shown in Figure 1a,b. The GO flakes exhibit irregular polygonal shapes with relatively broad size distributions. The small flakes (GO-A) and the large flakes (GO-B) had a mean equivalent diameter of 0.56 ± 0.32 µm and 2.8 ± 1.6 µm, respectively. As shown in Figure 1c, the size distribution also contains smaller fragments, which are thought to be produced as a result of breaking down flakes during the exfoliation process.[14] Nevertheless, the two distributions are clearly separated, so that one can speak of two different GO sheet sizes.

2.2. Optical Polarizing Microscope Textures

The observation of the mixture (GO+LC) textures in sandwich cells by polarizing microscopy indicates the quality of alignment. As indicated in Figure 2, the orange texture inside the square is homogeneously aligned where GO flakes are well dispersed. The dark brown area inside the circle illustrates a GO aggregate, which disturbs the liquid crystal alignment. In addition, the aggregate sizes of the small flakes (Figure 2a) evolve slowly when compared to those of large flakes, Figure 2b. This implies that the small flakes are better dispersible than the large ones, as qualitatively expected. Interestingly, the aggregate sizes saturate at approximately 0.6 wt% of GO. Beyond this concentration, all of the director field appears strongly dominated by the dopant. Thus, the nematic liquid crystal loses its long range orientational order by doping GO flakes in excess of approximately 0.6 wt%. This will be discussed in further detail below when the electrooptic behavior is reported.

At very large concentrations of GO in 5CB, samples become extremely viscous, so that capillary filling of cells would not be possible anymore. Squeezing the sample to thin cell gaps appears to induce phase separation, which is more pronounced for the larger than the smaller flakes. This indicates that there is a stronger interaction between large GO flakes, leading to a stronger tendency for aggregation.

For various concentrations, the dispersions exhibited a change of state at the clearing temperature of 5CB. The
dispersion of GO in the now isotropic phase of the thermotropic liquid crystal, exhibits a possible lyotropic nematic phase with a clearly detectable, but small birefringence. The isotropic phase of 5CB could thus behave as a solvent for the dispersed graphene oxide (Figure 3a,b). This implies that the material exhibits orientational order, which can be attributed to one of two mechanisms, or a combination thereof. First, GO experiences the medium as an isotropic liquid to form a lyotropic nematic phase, which have recently been studied intensively with water as a solvent[16,17,20,21] (Figure 3c). Or second, due to the surface anchoring of 5CB molecules on the GO flakes, a large amount of mesogens are ordered at the aggregates, leading to very large and pronounced pretransitional effects, simulating a nematic phase.

One of the drawbacks in these investigations of the GO flakes is opacity; with increasing the concentration the cell needed more backlight to capture the texture, as can be seen from the transmitted light intensity as a function of concentration (Figure 3d).

2.3. Fractal Analysis of the GO Aggregates

The aggregates of graphene oxide in 5CB exhibit a complicated, irregular structure, which suggests a further investigation by fractal methods. The images with a resolution of 2048 × 1088 pixels were analyzed as a function of GO concentration, with the box dimension method, using the fractal analysis software (Benoit 1.3). The textures were carefully thresholded and converted to a binary image, as exemplary demonstrated in Figure 4a,b. The fractal dimension $D_b$ is calculated from the proportionality[22]
where $N$ is the number of boxes of length $d$ being occupied by the aggregate.

Figure 4c depicts the fractal box dimension as a function of graphene oxide concentration. It is found that this saturates at a value of approximately $D_b = 1.9$ at 0.2 wt% of large GO flakes, and 0.4 wt% for the smaller GO flakes. It should be noted that $D_b = 1.9$ is exactly the dimension one would expect for 2D percolation clusters at the percolation threshold, $p_c$. And indeed, at approximately these concentrations, the GO aggregates form a cluster that spans the whole sample, as expected.

2.4. Nematic–Isotropic Transition ($T_{N-I}$)

The nematic to isotropic transition of 5CB, being a single-component room-temperature nematic, occurs within ±0.1 °C at 35.4 °C. The suspension of GO flakes into 5CB is not strictly a molecular doping process, so one would not expect a resulting behavior described by the thermodynamics of mixtures. Nevertheless, it is a colloidal suspension process where GO flakes disperse in the LC matrix. Thus, an effect on the system is to be expected, even if different than that from molecular mixtures. Even more so, if the nanoparticles possess a certain functionality, such as ferroelectric or ferromagnetic properties. For instance, Kurochkin et al. have shown that ferroelectric nanoparticles behave as a dopant, changing the order parameter of the nematic phase and enhancing the clearing temperature,[23] whereas multiwall carbon nanotubes resulted in a decrease.[8]

By determining the change of transmitted light intensity between crossed polarizers and simultaneously measuring the cell capacitance, the nematic to isotropic transition can be determined accurately. The two different GO flake sizes exhibited a similar qualitative trend on the phase diagram, with the larger flakes leading to slightly higher transition temperatures than those observed for the smaller GO flakes (Figure 5). This may be caused by a difference in mesogen anchoring on the flakes.

2.5. Dielectric Properties

The resulting parameters of the dielectric measurements, $\varepsilon'$, $\varepsilon''$, and $\Delta\varepsilon'$, as a function of GO concentration in 5CB are shown in Figure 6a,b. The dielectric anisotropy decreases for both the small and the large GO flakes until a constant value is reached at ~0.6%–1% by weight. It is interesting to note that the dielectric constants parallel and perpendicular...
to the director exhibit a different behavior for the small and
large flakes above this concentration, with the former one
increasing, while the values for latter stay constant. The overall
dielectric behavior may be attributed to liquid crystal molecules
being anchored at the surface of the graphene oxide sheets. As
the concentration increases, more liquid crystal is influenced
by the GO and the dielectric response decreases. \( \varepsilon'_1 \) decreases,
as more molecules are anchored in planar conditions, while \( \varepsilon'_\perp \) increases. This would indicate, that the graphene oxide sheets
remain parallel to the cell boundaries (Figure 6c), as can be
expected.

2.6. Fréedericksz Transition

The re-orientation of the director under an electric field \( E \) is
referred to as a Fréedericksz transition. For a nematic liquid
crystal, the director experience a torque proportional to \( \Delta\varepsilon' E^2 \), \([24]\)
where \( \Delta\varepsilon' \) is the dielectric anisotropy, \( \Delta' = \varepsilon'_1 - \varepsilon'_\perp \). Due to
anchoring conditions, a threshold voltage \( V_{th} \) is observed,
which is of importance for the application of liquid crystals in
display devices

\[
V_{th} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta\varepsilon'}}
\]

where \( K_{11} \) is the splay elastic constant.

For both the small and the large GO flakes, the threshold
voltage and the determined splay elastic constant are depicted
in Figure 7a,b, respectively. For increasing GO concentration
an increase of threshold and elastic constant are observed, until
saturation is reached for both at a concentration of about 1% by
weight. The effect is much more pronounced for the small
GO flakes than the larger ones, and leads to threshold voltages
which are approximately one order of magnitude larger than
those of the neat liquid crystal. Also the elastic splay constant
dramatically increases (note the logarithmic scale in Figure 7b by
about two orders of magnitude).

It is again likely that both the drastic increase in threshold
voltage, as also that of the splay elastic constant, are due to a
strong planar anchoring of the liquid crystal molecules on
the surface of the GO sheets, which remain parallel to the
substrate plane as an electric field is applied. Increasing flake
concentration leads to an increase in threshold voltage and
elastic constant, until all of the liquid crystal is dominated by
the dispersed graphene oxide. At this concentration, saturation
behavior is observed. Note, that the GO saturation concentra-
tion of \( \approx 1\% \) by weight is observed for dielectric, threshold and
elastic parameters, and corresponds quite well to the concentra-
tion where the fractal dimension of aggregates saturated and a
cluster of GO spans the whole sample.

2.7. Electrooptical Response Time

The two typical response times of the director for the field-off
and field-on state are \([23,26]\)

\[
\tau_{\text{decay}} = \frac{\gamma_1 d^2}{\pi^2 K_{11}} \quad \text{and} \quad \tau_{\text{rise}} = \frac{\gamma_1 d^2}{\Delta\varepsilon' \varepsilon_0 V^2 - \pi^2 K_{11}}
\]

where \( \gamma_1 \) is the rotational viscosity, \( d \) the cell gap, \( \Delta\varepsilon' \) the dielec-
tric anisotropy, \( K_{11} \) the splay elastic constant, and \( V \) the applied

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**Figure 4.** Exemplary demonstration of a) image thresholding to a b) binary picture of the GO aggregates (white). c) Results of a fractal analysis of images as a function of GO concentration, according to Equation (1). The saturation fractal box dimension at large concentrations approaches \( D_b = 1.9 \), the dimension expected from a percolation cluster at the perco-
lation threshold. The solid lines are a guide to the eye.

**Figure 5.** Nematic to isotropic phase transition \( T_{NI} \) as a function of gra-
phene oxide concentration for small and large GO flakes. The arrows
show the two phase thermotropic regions. The solid lines are a guide
to the eye.
Figure 8 depicts both times as a function of GO concentration for both the small and the large flake sizes. The on-time represents the electric field driven switching process, and is found to be rather independent of dopant concentration, within the limits of error. This is the case for both flake sizes, which display the same switching-on times (Figure 8a). These results imply, that with increasing concentration the GO-liquid crystal dispersions becomes drastically more viscous, a behavior which is indeed qualitatively observed simply by shearing or steering the samples. In Figure 8b the off-time is depicted as a function of GO concentration. This process is purely elastically driven and shows a decreasing switching time for increasing GO concentration. The behavior is more pronounced for the large flakes than for the small ones.

3. Conclusion

Graphene oxide—thermotropic nematic dispersions were investigated for two different sizes of GO flakes and as a function of concentration. It is found that the transition from the nematic to the isotropic state of the thermotropic liquid crystal only slightly increases with graphene oxide concentration, and that smaller graphene flakes are easier to disperse than larger ones, which was to be expected. Electrooptic properties which are relevant for applications of such dispersions in devices, such as threshold voltages, response times, and elastic constants, were investigated for increasing concentration of two differently sized GO flakes. It is demonstrated that...
threshold voltage and elastic splay constant strongly increase with increasing concentration, until saturation at a GO concentration of ≈0.6%–1% by weight. While the switching-on times are practically unaffected, the off-times strongly decrease for increasing GO concentration, more so for the large flakes than the smaller ones. The results imply that the viscosity of the dispersions strongly increases for increasing GO concentration, a behavior which is also observed qualitatively, and which can be expected. Dielectric spectroscopy reveals a relaxation, which is absent in the neat liquid crystal material. This is attributed to strongly anchored liquid crystal molecules on the surface of the GO flakes, thus drastically hindering the molecular rotation around the short axis, and decreasing the relaxation frequency dramatically. The latter scenario also accounts for the saturation in threshold voltage, dielectric anisotropy, and elastic constant at ≈1% GO in 5CB, as discussed above. It is interesting to note that when the thermotropic liquid crystal is heated above its clearing temperature, it acts like a crystal is heated above its clearing temperature, it acts like a liquid.

4. Experimental Section

First, stable dispersions of GO-water were prepared by a modified Hummers method,[27] and then transferred by solvent exchange into isopropanol making Solution A of a known concentration. Mixtures of different weight percentage (wt%) of GO flakes were prepared by adding the definite amount of Solution A to (70 mg) of 5CB (SYNTHON Chemicals GmbH & Co. KG, Germany), making Solution B. To achieve a stable suspension; the solutions were sonicated for 1 h. To prevent the GO from chemical reduction, the solvents were evaporated at 45 °C for 24 h. After cooling below the clearing temperature, the remaining GO in 5CB dispersion was sheared and mixed with a spatula for better dispersion. For consistency, the pure 5CB was treated the same way by dissolving in isopropanol followed by the evaporation to provide the same preparation conditions needed for later experiments.

ITO coated glasses from VisionTek Systems Ltd. of thickness 1.1 mm, and ITO resistance 10 Ω cm⁻¹, were cut into 1.5 cm x 2 cm sized substrates. The glasses were washed in different solvents and sonicated for 30 min. The ITO was then etched to leave the central parts of the glass with 0.5 cm width of ITO. Etching was carried out by using polyimide Kapton tape as a protective layer and immersion in hydrochloric acid (30%) for 7 min. The glasses were again washed for the final time, dried and plasma cleaned for 2.5 min to remove any organic residues. At last, the substrates were spin coated with a solution of polyvinyl alcohol in water (0.5 mg mL⁻¹) and unidirectionally and antiparallel rubbed with a velvet cloth. Instead of filling the pre-made cells by the usual capillary action method, the mixture of GO+5CB was sandwiched between the ITO glasses and then sealed with UV glue (Norland N68). The cell thickness was controlled by a Mylar spacer (13 µm). This process was found to produce more reliable results, because size exclusion due to capillary filling is avoided. The cell assembly process is summarized schematically in Figure 9. Finally, the quality of the cells was tested by polarizing microscopy.

Dielectric spectroscopy investigations were performed using an Agilent Precision LCR Meter E4980A, which was operated in the parallel equivalent circuit mode in a frequency range of 20 Hz to 2 MHz with an applied voltage, \( V_{ac} \), of 0.05–20 V. The perpendicular component of the dielectric permittivity \( \varepsilon_\| \) was measured below the Fréedericksz threshold \( V_{th} \) while the parallel component of the dielectric permittivity \( \varepsilon_\perp \) that can be measured as the electric field was increased to well above the Fréedericksz transition.

All of the electrooptic experiments were made using a microscope based system with an optical bandpass filter (Thorlab) of 632 nm wavelength for monochromatic light. For the threshold voltage measurements, the voltage sweep of the LCR meter was synchronized with the transmitted light intensity recorded by a photodiode through a digital meter (Agilent 34401A). The electrooptic response time was measured with a carrier signal of 5 kHz and 20 V amplitude, modulated with a 50 mHz square wave, using a signal generator (Agilent 33220A). The transmitted light intensity was recorded on a digital oscilloscope (Tektronix TDS 2024C) and averaged to reduce statistical noise. Apparatus operation and data acquisitions were carried out using LabView.

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