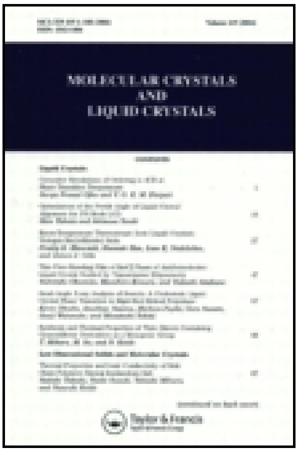

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Electrooptic Switching in Graphene-Based Liquid Crystal Cells

Markus Wahle [a], Olga Kasdorf [a], Heinz-S. Kitzerow [a], Yanyu Liang [b], Xinliang Feng [b] & Klaus Müllen [b]

[a] Department of Chemistry, Faculty of Science, University of Paderborn, Paderborn, Germany

[b] Max Planck Institute for Polymer Research, Ackermannweg, Mainz, Germany

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Electrooptic Switching in Graphene-Based Liquid Crystal Cells

MARKUS WAHLE,[1] OLGA KASDORF,[1]
HEINZ-S. KITZEROW,[1] YANYU LIANG,[2]
XINLIANG FENG,[2] AND KLAUS MÜLLEN[2]

[1]Department of Chemistry, Faculty of Science, University of Paderborn, Paderborn, Germany
[2]Max Planck Institute for Polymer Research, Ackermannweg, Mainz, Germany

Electrooptic cells containing two transparent graphene electrodes and a nematic liquid crystal are fabricated. Between crossed polarizers, the transmission of monochromatic light versus voltage shows the well-known maxima and minima that are characteristic of the Fréedericksz transition. The peaks appear approximately at the same voltage as those of conventional test cells equipped with indium tin oxide electrodes. This indicates that the conductivity of the graphene layers is sufficiently high to replace indium tin oxide. However, microscopic studies reveal that the alignment of the liquid crystal is not perfect, yet. Means of improving the alignment are suggested.

Keywords Fréedericksz effect; graphene; nematic liquid crystals; transparent electrodes

1. Introduction

Graphene, the two-dimensional analog of graphite, is a very promising nanomaterial for electronic, optoelectronic and electrooptic applications, owing to its high electric conductivity, reasonable transparency and unexpectedly high mechanical and thermodynamic stability. In spite of the theoretical prediction that monoatomic layers of graphene are instable, very thin layers of graphene flakes and few-layer graphene turned out to be manufacturable [1] and easy to handle for practical purposes. Graphene behaves like a zero-gap semiconductor due to the unusual dispersion relation of its electronic structure. Local gating allows electric field control of the carrier type and density [1–6]. The electric conductivity of graphene is very high owing to charge carrier mobilities up to $15{,}000\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. Appropriate doping enables the fabrication of field-effect transistors that operate at room temperature [14]. Because of the promising perspectives of carbon-based electronics, various

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Address correspondence to Heinz-S. Kitzerow, Department of Chemistry, Faculty of Science, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany. Tel.: +49-5251 605764; Fax: +49-5251 604208; E-mail: Heinz.kitzerow@upb.de

fabrication methods have been developed. For example, graphene layers can be prepared by mechanical exfoliation [1], by synthesis from organic molecules [7], by exfoliation of graphite via chemical oxidation followed by chemical reduction [8,9], or the growth on metal substrates by chemical vapor deposition [10].

The experiments described in the present paper are performed in order to explore the applicability of graphene layers as transparent electrode materials for liquid crystal displays. In a previous paper, graphene layers were demonstrated to serve very well as transparent electrodes in organic solar cells, owing to their very high conductivity and optical transparency [9,11]. Graphene layers were also tested as electrode materials for liquid crystal displays [12,13]. An electric field-induced Fréedericksz transition [14] was observed when a liquid crystal was sandwiched either between a small graphene sheet ($\approx 30\,\mu m$ in diameter) and a glass substrate coated with indium tin oxide (ITO) [12] or between a larger ($8 \times 8\,mm^2$) graphene layer and an ITO electrode [13], respectively. Here, we report our first efforts to address a liquid crystal layer by means of two graphene electrodes, thereby allowing one to replace ITO electrodes completely.

2. Experimental Methods

The electrooptic characteristics of the Fréedericksz transition are studied for two nematic liquid crystal mixtures in test cells equipped with two transparent graphene electrodes (Fig. 1). The graphene electrodes are fabricated as follows: graphene oxide sheets were deposited from an aqueous dispersion (0.25 mg/ml) by spin coating onto quartz substrates that were pretreated by exposure to oxygen plasma to make them hydrophilic. The films were then reduced thermally under Ar flow, as described previously [11] to produce graphene electrodes. The latter step of the process was executed at two different temperatures, 1000°C and 600°C, respectively. At high temperature, the reduction is more complete and results in highly conducting layers. At the lower temperature, the conducting layer contains a reasonable content of oxygen, which reduces the conductivity but leads to a more hydrophilic surface, thereby improving the wetting conditions for aqueous solutions. The graphene-coated substrates are cut, cleaned, and equipped with an alignment layer. For the latter purpose, poly(vinyl alcohol), PVA, was deposited by spin coating from an aqueous solution (1% by weight) at 400–3000 rpm. Subsequently, the surface of the PVA is rubbed with a poplin cloth in order to promote parallel alignment of the liquid crystal director. Finally, two substrates separated by Mylar sheets are assembled to give an electrooptic test cell with an active area of approximately $1\,cm^2$ and a cell gap between 5 and $15\,\mu m$.

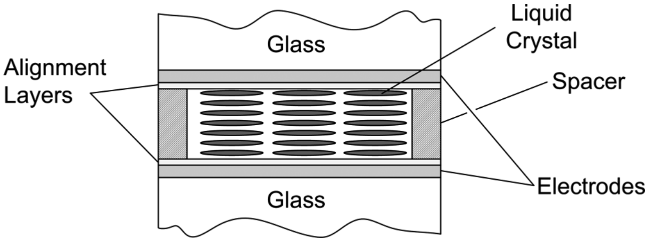

Figure 1. Schematic set-up of the samples.

Table 1. Prepared samples, their substrates, the sample thickness d [values obtained from the electrooptic I(V) characteristics] and critical voltages. [Abbreviations: ITO: indium-tin-oxide, PVA: poly(vinyl alcohol), PI: poly imide.]

Tag	Liquid crystal	Substrates	Thickness *d* (μm)	Critical voltage (V)
A	E7	Graphene	7.51	1.2
B	E7	ITO, PVA	7.07	0.9
C	E7	Graphene	12.05	1.3
D	E7	ITO, PI (KRSO-10)	10.38	0.9
E	MLC 6815	Graphene	4.63	2.3
F	MLC 6815	ITO, PI (KRSO-6)	7.00	2.0
G	MLC 6815	Graphene	7.53	2.9
H	MLC 6815	ITO, PI (KRSO-6)	7.40	2.1

Two different liquid crystal mixtures, E7 and MLC 6815 (both from Merck, Darmstadt, Germany), are investigated. The wide temperature range nematic mixture E7 consists of 51% 4-cyano-4′-pentylbiphenyl (5CB), 25% 4-cyano-4′-heptylbiphenyl (7CB), 16% 4-cyano-4′-octyloxybiphenyl (8OCB), and 8% 4-cyano-4′-pentylterphenyl (5CT). It has a rather large birefringence ($n_e = 1{,}7366$, $n_o = 1{,}5213$, $\Delta n = 0{,}2153$ at $\lambda = 589\,\text{nm}$ and $T = 298\,\text{K}$) and results in an optical retarder, where the phase shift between the ordinary and the extraordinary beam is very large and can be measured accurately. In contrast, the liquid crystal MLC 6815 contains saturated organic compounds and exhibits a small birefringence ($n_e = 1{,}519$, $n_o = 1{,}467$, $\Delta n = 0{,}052$ at $\lambda = 589\,\text{nm}$ and $T = 298\,\text{K}$). Thus, it can be employed for direct electrooptic switching from a bright to a dark state without dispensable modulations of the intensity. After filling, the alignment of the liquid crystal cells was inspected in a polarizing microscope. For electrooptic measurements, the respective cell was placed between crossed polarizers and adjusted with its rubbing direction at 45° with respect to the plane of polarization of the incident light. The intensity of transmitted monochromatic light from a sodium lamp ($\lambda = 589\,\text{nm}$) was measured as a function of the mean square value of an a.c. voltage ($f = 1\,\text{kHz}$). The results are compared to conventional Fréedericksz cells equipped with ITO electrodes. The latter cells were assembled from commercial glass substrates (Optrex Europe) coated with indium tin oxide. Also commercially available test cells (type KRSO-6 and KRSO-10 from E. H. C. Corp., Japan) were filled with the respective liquid crystals for comparison. The investigated samples can be found in Table 1.

3. Results and Discussion

Unfortunately, the graphene layers annealed at 600°C turned out to lack mechanical stability: During the process of rubbing, they are removed from the substrates. Thus, the following results correspond to graphene substrates that were annealed at 1000°C. The latter graphene layers exhibit a thickness of $\delta = \sim 6\,\text{nm}$ and a conductivity of $\sigma = 500\text{–}550\,\text{S/cm}$, which results in a sheet resistance $R = (\sigma \cdot \delta)^{-1} < 2\,\text{k}\Omega$.

Between crossed polarizers, all investigated cells, ITO or graphene based, show characteristic oscillations of the transmitted light intensity as function of the applied

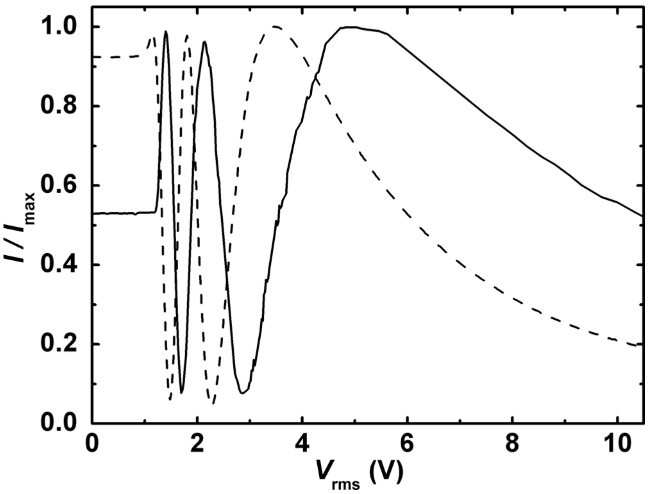

Figure 2. Transmitted intensity versus applied voltage (f = 1 kHz) for the liquid crystal E7 (samples A and B). The respective cell was placed between crossed polarizers and adjusted with its rubbing direction at 45° with respect to the plane of polarization of the incident light. The solid line shows the transmittance of the graphene-based cell A, the dashed line the transmittance of the ITO-based cell B.

voltage (Fig. 2). This is the result of the reorientation of the liquid crystal under the influence of the applied electrical field. For light propagation along the field, the difference $\Delta n_{eff} = n_{e,eff} - n_o$ between the effective extraordinary refractive index $n_{\mathrm{e,eff}}$ and the ordinary refractive index n_{o} of the liquid crystal decreases continuously with increasing voltage and approaches zero in the limit of infinitely high voltage. When the azimuthal angle φ between the director and the plane of polarization of the indent light is adjusted at $\varphi = 45°$, the intensity I of the transmitted light is given by [15]

$$I = \frac{1}{2} I_o \sin^2\left(\pi \Delta n_{eff} \frac{d}{\lambda}\right), \tag{1}$$

where I_{o} is the lamp intensity, d is the cell thickness and λ is the wavelength of the incident light. According to Eq. (1), the intensity I shows maxima and minima if the quantity $(2\Delta n_{eff} d/\lambda)$ is equal to an odd or an even integer, respectively. Equation (1) was used to calculate the cell thickness from the intensity and the known birefringence at zero voltage. For this purpose, the minimum and maximum values of the transmitted intensity were calibrated by placing the cell at high applied voltage between perpendicular and parallel polarizers, respectively. After determination of the sample thickness, Eq. (1) was used to determine the values of the effective birefringence for the voltages corresponding to the extreme values of the transmitted intensity.

The electrooptic characteristics of two samples of E7 filled cells are shown in Figure 2. The contrast ratio between the last maximum and the last minimum of graphene cell (sample A) is about 13.0, while the ITO cell (sample B) shows a higher contrast, about 21.9. The graphene samples A and C have a critical voltage of

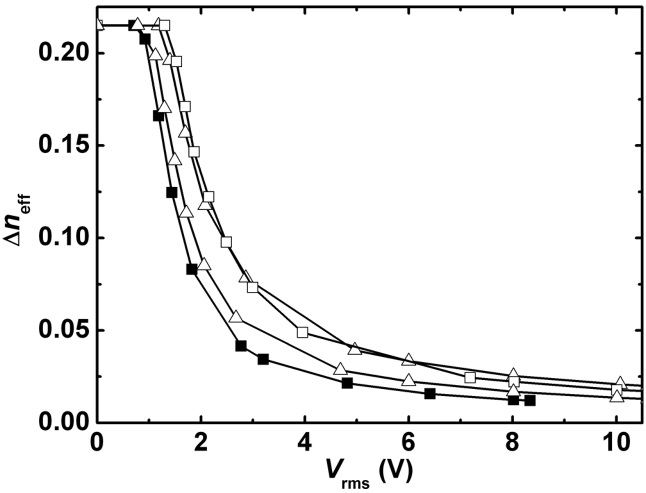

Figure 3. Effective birefringence Δn_{eff} versus voltage for light ($\lambda = 589\,\text{nm}$) propagating perpendicular to the cell plane: (■) sample A, (▲) sample B, (□) sample C, (Δ) sample D.

1.2 V and 1.3 V. This is slightly higher than the reference cells B and D, which both show a critical voltage of 0.9 V. In order to give a better comparison between cells of different layer thickness, Figure 3 shows the effective birefringence Δn_{eff} versus the applied voltage. The samples show almost identically characteristics. Figure 3 indicates that the graphene cells need a slightly higher voltage in order to achieve the same effective birefringence Δn_{eff} as the ITO based cells.

The liquid crystal MLC 8615 with low birefringence was used to test the more practical case when direct switching from a bright to a dark state – without additional extrema – is requested. The respective light intensities as a function of

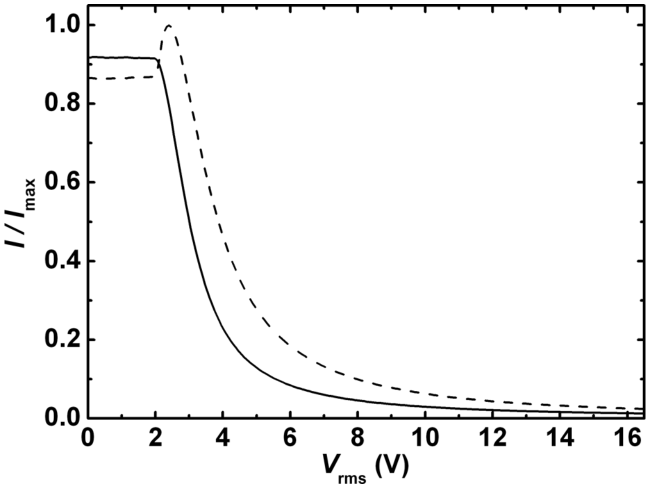

Figure 4. Transmitted intensity versus applied voltage (f = 1 kHz) for the liquid crystal MLC 6815 (samples E and F) between crossed polarizers. The solid line shows the transmittance of the graphene-based cell E, the dashed line the transmittance of the ITO-based cell F.

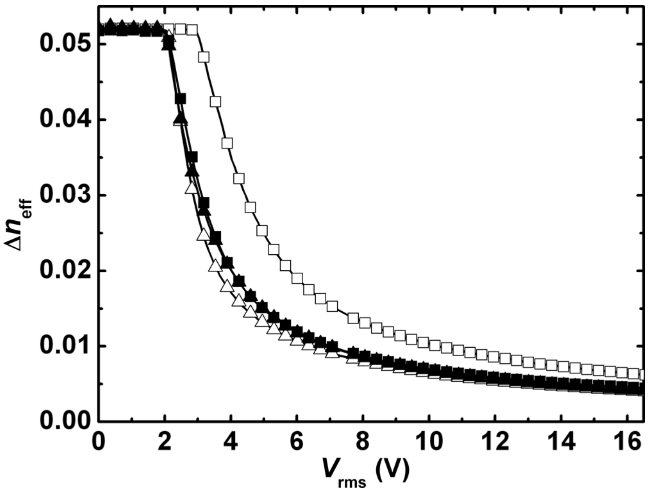

Figure 5. Effective birefringence Δn_{eff} versus voltage for light ($\lambda = 589\,\mathrm{nm}$) propagating perpendicular to the cell plane: (■) sample E, (▲) sample F, (□) sample G, (Δ) sample H.

the applied voltage for sample E and F are shown in Figure 4. As expected, sample E shows no local extremum, because the phase retardation is smaller than π. Analysis of the intensities reveals a cell thickness of 4.63 µm. In contrast to sample E, the corresponding ITO reference cell, sample F, shows an initial increase of the intensity with increasing voltage before the intensity decreases (Fig. 4). This can be attributed to the relatively large cell thickness of sample F, which was determined to be 7.00 µm. Again the critical voltage of the graphene sample is slightly higher (2.3 V) compared to the commercial sample b (2.0 V). The effective birefringence Δn_{eff} of samples E – H as a function of the applied voltage can be found in Figure 5. Again, the characteristics of the liquid crystal MLC 8615 obtained for different substrates are similar, but the graphene cells need a slightly higher voltage to reach the same effective birefringence.

4. Conclusions and Perspectives

In conclusion, our results indicate that nematic cells addressed exclusively by two graphene electrodes can be fabricated. Beyond previous achievements [12,13], our samples show a reasonable active area and require no counter-electrode made of a material other than graphene. The voltages required for electrooptic switching are only slightly higher than those observed in samples with conventional ITO substrates. However, the proper choice of alignment layers is an issue that needs further attention. Unfortunately, our preliminary attempt to improve the wetting conditions for an aqueous PVA solution failed, since the more hydrophilic graphene layers obtained by annealing at only 600°C turned out to be less stable than the substrates annealed at 1000°C. Nevertheless, the latter substrates show reasonable results for PVA alignment layers. In order to improve the alignment further, we suggest to compromise by varying the annealing temperature between 600 and 1000°C or to use other alignment layers, which may be fabricated – for example – by oblique evaporation of silica, by the deposition and rubbing of non-polar polymers, or by polarized light-induced physical or chemical alignment [16,17].

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