Chemistry: Bulgarian Journal of Science Education | *Volume 27 Number 5, 2018* | *Природните науки в образованието*

Education: Theory & Practice
Науката за образованието: теория и практика

Physics is an ever young science, Varna, October, 27 – 29, 2017
Физиката – вечно млада наука, Варна, 27 – 29 октомври 2017 г.

ELECTRICAL IMPEDANCE SPECTROSCOPY OF GRAPHENE-E7 LIQUID-CRYSTAL NANOCOMPOSITE

Todor Vlakhov, Yordan Marinov, Georgi. Hadjichristov, Alexander Petrov
Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences

Abstract. We have examined the electrical response of graphene-nanostructured liquid crystal E7. The nematic E7 was doped with graphene at concentration of 10^{-3} wt.%. Thin planar-oriented films with a thickness of 7 μm of this nanocomposite were studied by means of electrical impedance spectroscopy in the frequency range from 0.1 Hz to 1 MHz. Their electrical impedance at a room temperature was compared to that of identical films of pure liquid crystal E7 measured under the same experimental conditions. The doping with graphene leads to decrease in electrical conductivity of the studied nanostructured liquid-crystalline material and, thereby, to improvement of its electro-optical performance.

Keywords: electrical impedance spectroscopy, graphene-doped liquid crystals, nanocomposite materials

Introduction

One of the most widely known applications of the nematic liquid crystals (LCs), namelly in thin-film-transistor LC displays (in digital cameras, various monitors and large-screen high-definition television sets), has given evidence that the ions in these electro-optical materials impact the image quality due to the ionic shielding phenomenon. That is why, the development of novel LC-based composite materials is an exciting challenge for investigation in order to solve this problem. In recent years, important direction of the research work was the modification of the properties of LCs by doping with different nanoparticles (metallic, semiconducting, ferroelectric (Reznikov et al., 2003; Buchnev et al., 2005; Li et al., 2006; Qi & Hegmann, 2008; Shivakumar et al., 2011; Stamatoiu et al., 2012) in order to obtain improved electro-optical characteristics. It has been demonstrated that a very small amount of nanoparticles can strongly modify the dielectric, elastic and electro-optical properties of the host LC.

Among various nanoparticles, graphene is the carbon nanomaterial that is promising for improvement of the electrical properties of the nematics due to its electronic transport properties (Geim & Novoselov, 2007; Issi et al., 2014). In particular, Gökçen et al. (2012) have investigated the effect of graphene being doped in LC E7. The results showed that the dielectric and electrical behaviors of the LC E7 are strongly influenced by graphene. Also, it was found that the doping with graphene reduces the electrooptics-relevant threshold voltage of graphene-E7 nanocomposites (Gökçen et al., 2012). In the study presented here, we have examined the electrical response of E7 doped with very low amount of graphene (10^{-3} wt.%). To inspect the effect from graphene, our interest was concentrated on the frequency-dependent alternating-current (AC) electrical impedance of this nematic nanocomposite.

Experimental

We deal with the well known LC E7, commonly used. This LC was purchased from MERK. Catalogue data for E7 were as follows: E7 MERCK Art. 28658, 4-pentyl-4'-cyanobiphenyl plus 4-heptyl-4'-cyanobiphenyl. The commercial E7 substance is an eutectic nematic mixture with the nematic-to-isotropic transition temperature at ~ 58 °C. Due to the strong permanent dipole moment along the molecular axis arising from the high polarity of the constituent molecules, E7 has relatively large positive dielectric anisotropy, $\Delta\varepsilon_{\|} = 19$ and $\Delta\varepsilon_{\wedge} = 5.2$ at 20 °C and 1 kHz frequency (Drzaic & Muller, 1989).

The E7 mixture has not been modified in any way before the nanocomposite preparation. To prepare graphene-E7 nanocomposite, graphene was added at the concentration of 10^{-3} wt.% to the LC E7. This mixture was centrifuged for 30 min at 4000 rpm; to make the constituents uniformly mixed, then heated above 60 °C to reach isotropic phase of the LC. The heated graphene-E7 dispersion was capillary filled into standard LC sandwich cells. Finally, the nematic phase of the E7 LC containing graphene was recovered. The LC cells were assembled with two 1 mm-thick 15 mm ´ 25 mm glass plates having their inner surfaces coated with conductive indium-tin oxide (ITO) and a polyimide alignment layer for planar orientation. The gap of the cells was $d = 7\ \mu$m. Besides the graphene-doped E7 layers with planar alignment, layers with the same dimensions were prepared by the same manner, but filled with E7 only (for reference measurements).

The characterization of the samples was performed by modular potentiostat/galvanostat SP-200 Bio-Logic (Bio-Logic Science Instruments). This compact and powerful computer-controlled instrument for impedance spectroscopy (Fig. 1) is well suited for precise measurements in the nanotechnology research. Hardware filtering allows removing unwanted electromagnetic noise which can affect the quality of the experimental data. The electrical impedance spectra were recorded in the frequency range $f = 10^{-1} – 10^{5}$ Hz. The AC electric field (in the sinusoidal waveform) was transversally applied to the film via the ITO electrodes. The electrically active area of the sample was $A = 1$ cm^2. The applied voltage was kept fixed at 10 mV (RMS). Thus, the corresponding electric field strength was much smaller than the Fréedericksz transition threshold of E7 (~ 0.85 V_{RMS}), thereby the electro-optical function of this LC was not activated. The experiments were carried out at ambient temperature.

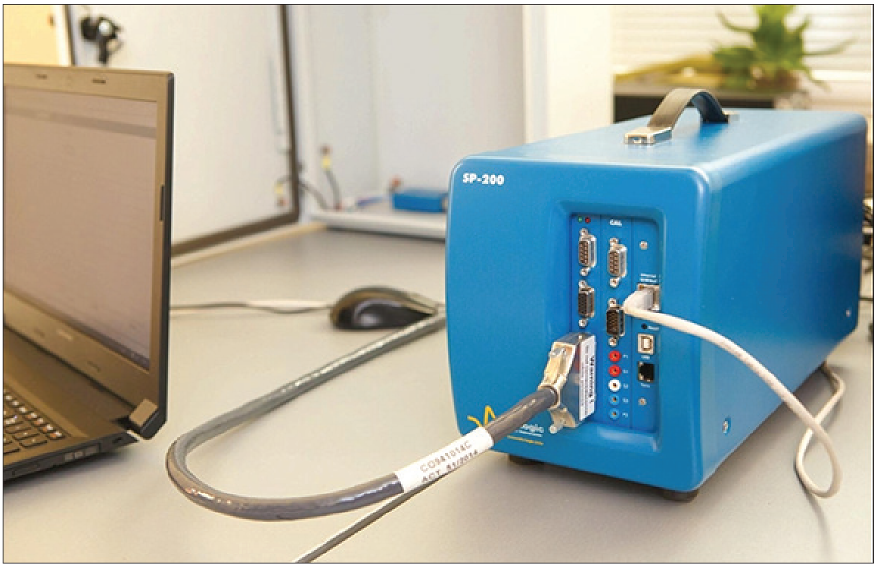

Figure 1. Bio-Logic SP-200 instrument

Results and discussion

Experimental data in the present study were obtained by Complex Electrical Impedance Spectroscopy. By this experimental technique (Barsoukov & Macdonald, 2005), both real Re(*Z*) and imaginary Im(*Z*) parts of the complex electrical impedance (*Z**) can be simultaneously measured as a function of the frequency *f* of the AC electric field applied on the sample. It should be mentioned that the results obtained by impedance spectroscopy strongly depend on the temperature of the studied material, and reasonably, on the phase of the LC. In our case, the LC E7 in the examined samples is in the nematic phase, a state that is highly anisotropic. Actually, the nematic is the simplest of the LC phases and the one with the highest symmetry. In this state of LC matter, the LC molecules possess long-range orientational order, but no positional order of their centres of mass, with the long axis of the LC molecules aligning roughly along an average direction, called the nematic director. In this phase, the optical, electro-optical, electrical and dielectric properties of E7 LC were well established (Amundson, 1996; Jian et al., 2011). By the electric-field induced Fréedericksz transition that is the basic principle of electro-optic operation of the nematic LCs, a collective reorientation of the LC director takes place along the direction of an electric field applied to LC material having positive dielectric anisotropy, i.e. the LC medium is reoriented from planar to homeotropic orientation (director parallel to perpendicular to the electrode plane) (De Gennes & Prost, 1993). The value of Fréedericksz transition threshold of the LC E7 is V_{th} = (0.85 ± 11 %) V_{RMS} measured at 20°C (Amundson, 1996). Since the applied voltage (10 mV_{RMS}) in the present experiment is bellow V_{th} , during our experiment the films under study remain in predominantly planar orientation, as initially imposed by the alignment layers of the films (Fig. 2).

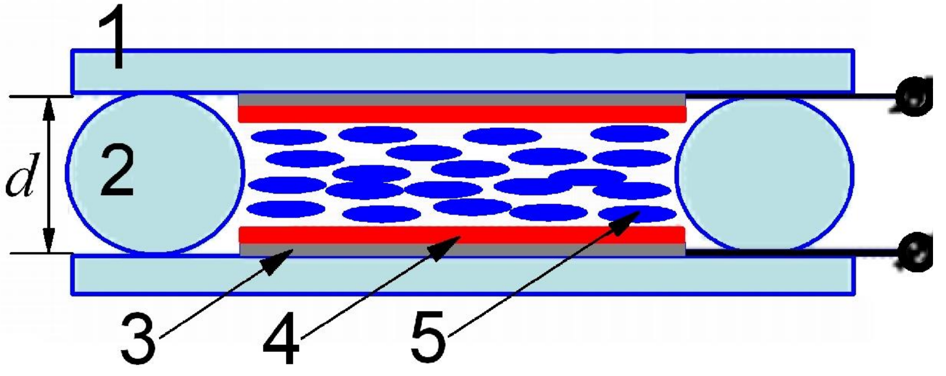

Figure 2. Schematic of planarly-aligned LC cell: 1 – the plane glass/ITO substrate, 2 – spacer, 3 – plane electrode (of ITO), 4 – alignment layer, 5 – elongated rod-like LC molecule (E7)

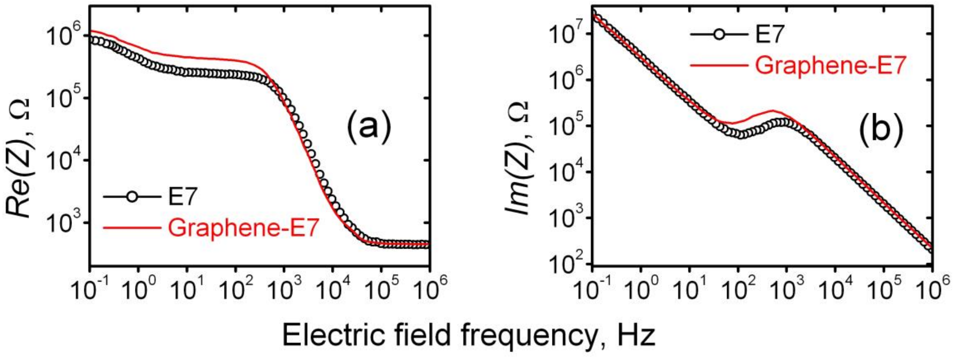

Figure 3. Data obtained by impedance spectroscopy: (a) real and (b) imaginary parts of complex electrical impedance measured for the samples with: E7 (open circles); graphene-doped E7 (solid lines). The temperature of the films was 26° C

Fig. 3 reports raw data for the complex electrical impedance Z^* measured for considered films of either E7 or graphene-doped E7 as a function of frequency f of the external electric field (in our case, applied perpendicular to the film plane). Due to the same geometrical dimensions of both samples (thickness and electrically-active surface area), it can be made not only qualitative, but also quantitative comparison. As seen, there is some frequency range, namely bellow 1 kHz, in which the impedance of the sample with graphene-doped E7 is higher than that of the sample with pure E7. Notice, the low-frequency measurements give information on electrical conductivity and ionic contributions. The trend of lowering of the ionic conductivity can be seen in the research on nematic E7 doped with graphene at concentration of 0.05 wt.% (Gökçen et al., 2012), as well as for nematic LC 4-cyano-4'-pentylbiphenyl (5CB) doped with graphene at concentration of 0.005 wt.% (Basu et al., 2015). Note that in our case the graphene concentration is even less (0.001). Generally, the impedance spectra in Fig. 3 can be further analyzed and both AC and direct-current (DC) conductance may be exactly calculated by applying suitable theoretical model, e.g., through the corresponding frequency spectra of the complex dielectric permittivity and their fits. But the main result for the effect from graphene nanodopants is visible even from the data for electrical impedance.

The effect of graphene nanoparticles can be clearly seen in the Nyquist plots (the imaginary part versus the real part of the impedance) of our LC samples (with or in the absence of graphene). Fig. 4 shows the corresponding impedentiometric response of both samples to be compared. The Nyquist plot consists of a part of semicircle towards higher frequency side, followed by a steep line at lower frequency side. The semicircle represents the bulk material (such shape is relevant to equivalent circuit of capacitance and resistance connected in parallel). The value of the bulk resistance (R_b) of the material can be determined from the point of intersection of the high-frequency end of the semicircle with the Re(*Z*) axis (Barsoukov & Macdonald, 2005). It is seen from Fig. 4 that compared to the reference cell made with pure E7, the graphene-doped E7 exhibits higher R_b . According to the simplified expression $\sigma = d/(R_b A)$, where *d* and *A* are the thickness and effective electrically-active area of the examined LC films, respectively (Barsoukov & Macdonald, 2005), from the data in Fig. 4 one can roughly estimate that the conductivity σ for our sample with graphene-doped E7 is nearly twice lower than the one of the reference E7 sample.

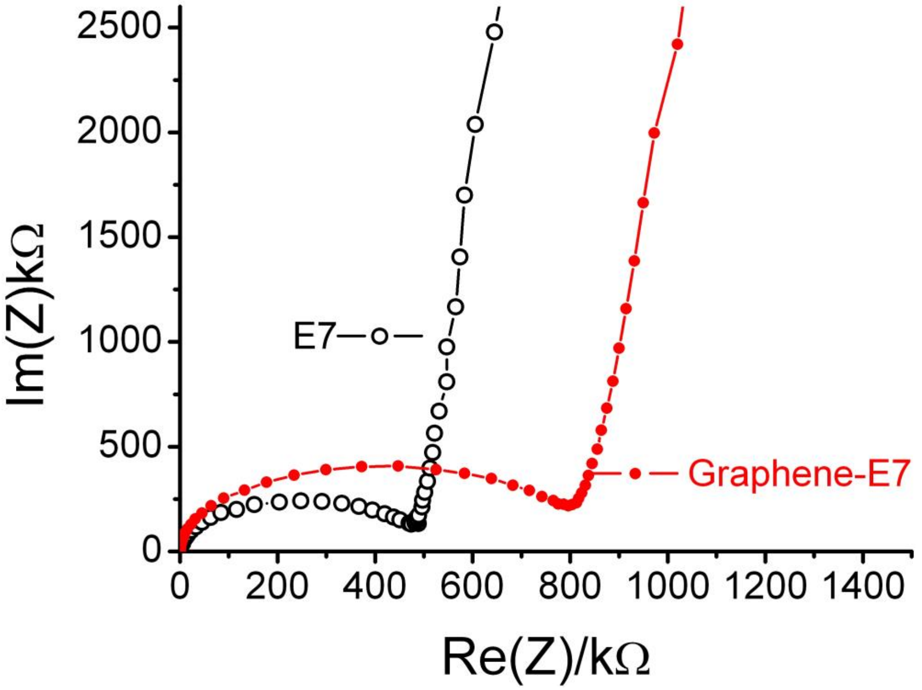

Figure 4. Nyquist complex impedance plots for the samples under study (relevant to data given in Fig. 3).

At a glance, the lower conductivity we have observed for graphene-doped E7 as compared to undoped E7 contradicts the good conductivity and high electron mobility of graphene (Geim & Novoselov, 2007; Issi et al., 2014). Indeed, such effect is in contrast with the cases of inclusion of graphene in other materials, for instance - polymers, in which the conductivity is increased by the insertion of graphene (Alzari et al., 2016). In the present case for LC E7, graphene nanodopats are in a LC medium with a moderate (up to low) conductivity. This LC is known to have high impurity ion concentration. Moreover, the high concentration of ions in the bulk of the nematic LCs in cells having alignment layers is well known and has been demonstrated by means of impedance and dielectric spectroscopy in the low-frequency range, e.g., from 0.5 Hz to 200 kHz (Murakami & Naito, 1997). The concentration of impurity ions and diffusion behavior of the ion charge in nematic LCs have been thoroughly investigated by the same experimental techniques in the low-frequency range (Murakami et al., 1996; Nakanowatari & Ono, 1996; Murakami & Naito, 1997; Sawada et al., 1999; Costa et al., 2001).

In the LC displays, the presence of excess ions causes several problems, such as slow responses, long-term image sticking effects, and short-term flicker effects (Yang, 1990; Takahashi, 1991; De Vleeschouwer et al., 1999; 2001a; 2001b; Sasaki, 2001). Obviously, the presence of graphene leads to neutralization of part of these free charge carriers in the nanocomposite studied here. Most likely, this occurs by ion-trapping processes (the corresponding physical mechanism is complex and needs further investigation and detailed treatment that is out of the scope of the present study). In consequence, the ionic shielding should also be reduced at the corresponding frequency values. Being in graphene-LC mixture, graphene decreases the ion transport and this does result in a reduction of rotation viscosity of the graphene-LC mixture. Thus, the above result is of importance because it implies that the studied nanostructured LC material should exhibit an improved electro-optical performance, similarly to other LC nanocomposite materials in which the doping with graphene (or graphene derivative) makes better their electro-optic properties (relevant to the applications of such materials in devices), e.g., as reported in (Kumar et al., 2014; Basu et al., 2015; Al-Zangana et al., 2016; Lapanik et al., 2016). Such positive effect is also known for carbon nanotubes-doped nematic LCs: slight amounts of these nanodopants reduce the ion concentration and, thus, depress the unwanted ion-charge effects in the nematic LCs (Baik et al., 2005; Chen & Lee, 2006; Rahman & Lee, 2009; Jian et al., 2010).

Conclusion

Employing electrical impedance spectroscopy in the frequency range from 0.1 Hz to 1 MHz at room temperature, we have examined the change in the electrical response of the nematic LC E7 due to doping with graphene at concentration of 10^{-3} wt.%. It was demonstrated that even at this very low concentration the graphene nanodopants reduce the ionic conductivity of the studied nanostructured LC material. This fact confirms the results reported previously from other researchers and suggests a better electro-optic performance of thin films made of the studied graphene-E7 LC nanocomposite than those of the E7 oneself. The observed important modification applies to a certain frequency range, in our case mostly apparent in the low-frequency range, bellow 1 kHz.

The effect discussed in this work for nematic LC films containing graphene would certainly be useful in materials science and in modern nanotechnology, e.g., for development of novel LC-based nanocomposite materials for room-temperature electro-optic devices. Surely, the incorporation with other functional materials from carbon nanostructure family should improve other physical and operation parameters, electro-optic properties and technological applications of the nematic LC nanomaterials (such further characterizations are in progress).

Acknowledgments. Work supported by research project DFNI-TO2/18 "Nanostructured liquid crystals for tunable photonic devices" – National Science Fund of Bulgaria.

REFERENCES

Al-Zangana, S., Iliut, M., Turner, M., Vijayaraghavan, A. & Dierking, I. (2016). Properties of thermotropic nematic liquid crystal doped with graphene oxide. *Adv. Opt. Mater.*, *4*, 1541 – 1548.

Alzari, V., Nuvoli, D., Sanna, V., Caruso, T., Marino, S., Scaramuzza, N. & Caruso, T. (2016). Study of polymeric nanocomposites prepared by inserting graphene and/or Ag, Au and ZnO nanoparticles in a TEGDA polymer matrix, by means of the use of dielectric spectroscopy. *AIP Adv.*, *6*, art. no. 035005.

Amundson, K. (1996). Electro-optic properties of a polymer-dispersed liquid-crystal film: temperature dependence and phase behavior. *Phys. Rev. E*, *53*, 2412 – 2422.

Baik, I.-S., Jeon, S.Y. & Lee, S.H. (2005). Electrical-field effect on carbon nanotubes in a twisted nematic liquid crystal cell. *Appl. Phys. Lett.*, *87*, art. no. 263110.

Barsoukov, E. & Macdonald, J.R. (2005). *Impedance spectroscopy: theory, experiment, and applications.* Hoboken: John Wiley & Sons.

Basu, R., Garvey, A. & Kinnamon, D. (2015). Effects of graphene on electro-optic response and ion-transport in a nematic liquid crystal. *J. Appl. Phys.*, *117*, art. no. 074301.

Buchnev, O., Cheon, C.I., Glushchenko. A., Reznikov, Y. & West, J.L. (2005). New non-synthetic method to modify properties of liquid crystals using micro- and nano-particles. *J. Soc. Inf. Display*, *13*, 749 – 754.

Chen, H.-Y & Lee, W. (2006). Suppression of field screening in nematic liquid crystals by carbon nanotubes. *Appl. Phys. Lett.*, *88*, art. no. 222105.

Costa, M.R., Altafim, R.A.C. & Mammana, A.P. (2001). Ionic impurities in nematic liquid crystal displays. *Liq. Cryst.*, *28*, 1779 – 1783.
De Gennes, P.G. & Prost, J. (1993). *The physics of liquid crystals*. Oxford: Clarendon Press.
De Vleeschouwer, H., Verweire, B., D'Have, K. & Zhang, H. (1999). Electrical and optical measurements of the image sticking effect in nematic LCD's. *Mol. Cryst. Liq. Cryst.*, *331*, 567 – 574.
De Vleeschouwer, H., Bougrioua, F. & Pauwels, H. (2001a). Importance of ion transport in industrial LCD applications. *Mol. Cryst. Liq. Cryst.*, *360*, 29 – 39.
De Vleeschouwer, H.; Verschueren, A.; Bougrioua, F.; Van Asselt, R.; Alexander, E.; Vermael, S.; Neyts, K.; Pauwels, H. (2001b). Long term ion transport in nematic liquid crystal displays. *Jpn. J. Appl. Phys.*, *40*, *Part 1*, 3272 – 3276.
Drzaic, P.S. & Muller, A. (1989). Droplet shape and reorientation fields in nematic droplet/polymer films. *Liq. Cryst.*, *5*, 1467 – 1475.
Geim, A.K. & Novoselov, K.S. (2007). The rise of graphene. *Nature Mat.,* *6*, 183–191.
Gökçen, M., Yıldırım, M. & Köysal, O. (2012). Dielectric and AC electrical conductivity characteristics of liquid crystal doped with graphene. *Eur. Phys. J. Appl. Phys*., *60*, art. no. 30104.
Issi, J.-P., Araujo, P.T. & Dresselhaus, M.S. (2014). Electron and phonon transport in gaphene in and out of the bulk (pp. 65 – 112). In: Aoki, H. & Dresselhaus, M.S. (Eds.). *Physics of graphene.* Heidelberg: Springer.
Jian, B.-R., Tang, C.-Y. & Lee, W. (2011). Temperature-dependent electrical properties of dilute suspensions of carbon nanotubes in nematic liquid crystals. *Carbon*, *49*, 910 – 914.
Kumar, V., Kumar, A., Biradar, A.M., Reddy, G.B., Sachdev D. & Pasricha, R. (2014). Enhancement of electro-optical response of ferroelectric liquid crystal: the role of graphene quantum dots. *Liq. Cryst.*, *41*, 1719 – 1725.
Lapanik, V., Timofeev, S. & Haase, W. (2016). Electro-optic properties of nematic and ferroelectric liquid crystalline nanocolloids doped with partially reduced graphene oxide. *Phase Trans.*, *89*, 133 – 143.
Li, F., West, J., Glushchenko, A., Cheon, C.I. & Reznikov, Y. (2006). Ferroelectric nanoparticle/liquid-crystal colloids for display applications. *J. Soc. Inf. Display*, *14*, 523 – 527.
Murakami, S. & Naito, H. (1997). Electrode and interface polarizations in nematic liquid crystal cells. *Japanese J. Appl. Phys.*, *36*, 2222 – 2225.
Murakami, S., Iga, H. & Naito H. (1996). Dielectric properties of nematic liquid crystals in the ultralow frequency regime. *J. Appl. Phys.*, *80*, 6396 – 6400.

Nakanowatari, J. & Ono, K. (1996). Effect of the thickness of alignment layer on the low-frequency dielectric dispersion of a nematic liquid crystal. *Japanese J. Appl. Phys.*, *35*, L111 – L113.

Qi, H. & Hegmann, T. (2008). Impact of nanoscale particles and carbon nanotubes on current and future generations of liquid crystal displays. *J. Mater. Chem.*,*18*, 3288 – 3294.

Rahman, M. & Lee, W. (2009). Scientific duo of carbon nanotubes and nematic liquid crystals. *J. Phys. D: Appl. Phys.*, *42*, art. no. 063001.

Reznikov, Y., Buchnev, O. & Tereshchenko, O. Reshetnyak, V., Glushchenko, A. & West, J. (2003). Ferroelectric nematic suspension. *Appl. Phys. Lett.*, *82*, 1917 – 1919.

Sasaki, N. (2001). A new measurement method for ion density in TFT-LCDs. *Mol. Cryst. & Liq. Cryst. Sci. & Tech.*, *367*, 671 – 679.

Sawada, A., Tarumi, K. & Naemura, S. (1999). Effects of electric double layer and space charge polarization by plural kinds of ions on complex dielectric constant of liquid crystal materials. *Japanese J. Appl. Phys.*, *38*, 1418 – 1422.

Shivakumar, U., Mirzaei, J., Feng, X., Sharma, A., Moreira, P. & Hegmann, T. (2011). Nanoparticles: complex and multifaceted additives for liquid crystals. *Liq. Cryst.*, *38*, 1495 – 1514.

Stamatoiu, O., Mirzaei, J., Feng, X. & Hegmann , T. (2012). Nanoparticles in liquid crystals and liquid crystalline nanoparticles (pp. 331 – 394). In: Tschierske, C. (Ed.). *Liquid crystals: materials design and self-assemby.* Heidelberg: Springer.

Takahashi, S. (1991). The investigation of a dc induced transient optical 30-Hz element in twisted nematic liquid-crystal displays. *J. Appl. Phys.*, *70*, 5346 – 5350.

Yang, K.H. (1990). Charge retention of twisted nematic liquid-crystal displays. *J. Appl. Phys.*, *67*, 36 – 39.

✉ **Dr. Georgi Hadjichristov (corresponding author)**
Georgi Nadjakov Institute of Solid State Physics
Bulgarian Academy of Sciences
72, Tzarigradsko Chaussee Blvd.
Sofia, BG-1784, Bulgaria
E-mail: georgibh@issp.bas.bg