Research Article

Functional Smart Dispersed Liquid Crystals for Nano- and Biophotonic Applications: Nanoparticles-Assisted Optical Bioimaging

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Functional nematic liquid crystal structures doped with nano- and bioobjects have been investigated. The self-assembling features and the photorefractive parameters of the structured liquid crystals have been comparatively studied via microscopy and laser techniques. Fullerene, quantum dots, carbon nanotubes, DNA, and erythrocytes have been considered as the effective nano- and biosensitizers of the LC mesophase. The holographic recording technique based on four-wave mixing of the laser beams has been used to investigate the laser-induced change of the refractive index in the nano- and bioobjects-doped liquid crystal cells. The special accent has been given to novel nanostructured relief with vertically aligned carbon nanotubes at the interface: solid substrate-liquid crystal mesophase. It has been shown that this nanostructured relief influences the orienting ability of the liquid crystal molecules with good advantage. As a result, it provokes the orientation of the DNA. The modified functional liquid crystal materials have been proposed as the perspective systems for both the photonics and biology as well as the medical applications.

1. Introduction

It is well known that the nematic liquid crystals (NLC) as the suitable model systems for the nanoparticles including have been regularly investigated and successfully considered by the different scientific and technical groups. The reason is connected with the fact that this process permits predicting and optimizing the best conditions to make innovative physical models describing the photorefractive and photoconductive effects as well as the dynamic one. Unique optical, nonlinear-optical, electro-, acoustic-, magneto-, and thermoproperties of LCs are widely applied to laser physics, optical information processing, display technology, microscopy, biology, and surface defects identification, as well as medicine. An important feature of LC molecules is a high orienting capacity, which can be used to create novel sensitive composite materials. LC orients particles suspended in them and acts as the model molecular matrix easily controlled by an applied external field. Particles become sensitive to operating external field. As a result, the orientation of the LC matrix changes too with good advantage. Thus, the mutual influence of the LC matrix and particles introduced in them have been testified. Moreover, the influence of the interface between LC and solid substrate on the materials volumetric characteristics has been also under the consideration.

At present time, a study of organics systems, specially dispersed liquid crystals, when properties of mesophase can be reinforced by doping of the novel dyes, fullerenes, carbon nanotubes, gold nanoparticles, quantum dots, shungites, grapheme oxides, and so forth, holds the great promise
because they combine the properties of photosensitive components with their unique energetic levels and specific surface area and the electrooptical parameters of the LC mesophase too. Many types of the novel organic composites, the dispersed LC structures, and new nano- and biodopants have been realized and studied by complicated techniques [1–15].

In the present paper, the NLC systems structured with the 2-cyclooctylamino-5-nitropyridine (COANP)-C_{70} complex, quantum dots (QDs), DNA, and so forth have been comparatively studied as effective media for checking the laser-induced change of the refractive index and quasiisometric self-assembly features and to control the effect of the interface with carbon nanotubes (CNTs) on the volumetric LC parameters, for example, on the spectral parameters and on the refractive index too. To improve the refractive characteristics and change the order parameters of this structure, the role of the intermolecular charge transfer complex between the donor fragment of organic molecules and effective intermolecular electron acceptor has been revealed and confirmed. The results obtained have been compared with those typical for the pure LC cells. Moreover, the orientation and the visualization of the DNA in the NLC mesophase with novel interface relief have been shown. The extended area of the application, including the medicine area, has been predicted.

2. Materials and Experimental Conditions

Nematic liquid crystal (NLC) from the inertial classical cyanobiphenyl group has been chosen as the flexible matrix. Let us remember that, from one side, the NLC media permit orienting the nano- and bioparticles included in that with good advantage, and, from other side, the properties of the NLC can be easy modified via intermolecular doping. LC cells have been assembled in S-configuration with a gap width of 7–10 micrometers. LC films have been placed onto glass substrates covered with transparent conducting layers based on ITO contacts. The transparent conducting ITO has been modified via CNTs laser deposition technique with additional treatment with surface electromagnetic wave (SEW). The general view of the LC structure is shown in Figure 1. The arrow on the glass shows the direction of processing by SEWs. It should be remarked that the dimension of relief grooves shown in Figure 1(b) is connected with the wavelength of the CO_{2} laser of 10.6 micrometers.

2-Cyclooctylamino-5-nitropyridine (COANP) conjugated monomer that was studied carefully before in [16–20] has been used as a donor molecule to create the intermolecular charge transfer complex (CTC) with the fullerenes, CNTs, QDs, DNA, and so forth. It should be mentioned that the COANP system is a good model with an effective initial intramolecular charge transfer process between NH-donor group and NO_{2}-acceptor. This intramolecular interaction can be easily transferred to intermolecular one by modification via the nanoobjects sensitization [21,22]. The intermolecular CTC has been formed in this \( \pi \)-conjugated organic system doped with fullerene C_{60} and C_{70}–QDs, and so forth due to the large electron affinity energy of fullerene (it is close to 2.65 eV) or QDs (this value is placed in the range of 3.8–4.2 eV) that drastically exceeds the electron affinity energy of an intramolecular acceptor fragment of COANP because last value is close to 0.45 eV. The destructive and nondestructive control testing of the formation of the intermolecular CTC, namely, C_{70}–NO_{2}, has been supported by results of the nonlinear absorption study [23,24], Z-scanning technique [25,26], IR-spectral shift observation, mass-spectral and photorefractive experiments [22,24,26], order parameters changing [27], DSC analysis [28], quantum-chemical simulations [29], and so forth. For example, via DSC analysis, it has been shown that all transition temperature values have been shifted (such as a melting point, a point of crystallization, and a glass transition temperature) in the case of adding some amount of fullerene C_{70} in COANP. Moreover, recently, it has been shown by us that the same liquid crystal matrix photorefractive parameters have been changed not only via nanosensitization but via bioobjects doping too [30]. The intermolecular CTC have been supported by IR-spectral shift and order parameters increase as well.

The laser-induced change of the refractive index has been studied at the wave length of 532 nm under the Raman-Nath diffraction conditions [34–36]. Raman-Nath diffraction condition is realized in the case when the recorded grating period is larger than the thickness \( d \) of the treated sample. Beam energies incident on and transmitted through the sample in the first-order diffraction can be measured. Our experiments have been made in the nanosecond pulsed regime at the spatial frequency of 90–130 mm^{-1} and at the laser energy density ranged from 0.01 to 0.6 J cm^{-2}. The technical experimental scheme has been analogous to that explained before in detail in [37,38] and recently shown in [30] in the modified variant.

3. Results and Discussion

Let us briefly consider, for example, the effect of the nanostucturation of the LC media via the intermolecular CTC. We should consider a small local volume of the matrix model medium substantially smaller than the incident wavelength of the laser beams used to create the thin holographic grating. It is well known that, for a system with the dimensions smaller than the optical operating wavelength (\( \lambda = 532 \text{ nm} \) in our experiment; for comparison, LC molecules length is 15–100 angstroms, and fullerene molecules are 0.65–0.7 nm in size), the most important optical characteristic is the induced dipole, whose dependence on the applied local field can be expressed through dipole polarizabilities \( \alpha^{(n)} \). These are, in their turn, related to the nonlinear susceptibility \( \chi^{(n)} \) and are inversely proportional to the considered unit cell volume \( v \). It has been shown in [24,39,40] that third-order nonlinear susceptibility \( \chi^{(3)} \), which is responsible for the change in the local volume polarizability in COANP fullerene-based LC systems, is much larger than that one for the pure nonsensitized structures. This value (namely, cubic nonlinearity) can be evaluated for these materials via the four-wave mixing technique from the photoinduced change of the refractive index. The gained polarization provides...
Figure 1: Glass substrate with ITO conducting coatings and laser-deposited carbon nanotubes additionally treated with SEW ((a) photo of the substrate), ITO+CNTs relief+SEW ((b) ASM image), and general view of the nano- or biostructured LC cells ((c) photo of the real cell with the dimension of 20 × 22 mm).

Table 1: Laser-induced change of the refractive index $\Delta n_i$ in the structured LC cells treated at $\lambda = 532$ nm.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Dopants content, wt.%</th>
<th>Energy density, $\text{J/cm}^{-2}$ at 514.5 nm</th>
<th>Spatial frequency, $\text{mm}^{-1}$</th>
<th>Pulse duration, ns</th>
<th>$\Delta n_i$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure LC</td>
<td>0</td>
<td>0.2 $\text{W/cm}^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>LC based on COANP–C$_{70}$</td>
<td>5</td>
<td>$17.5 \times 10^{-3}$</td>
<td>100</td>
<td>20</td>
<td>$1.4 \times 10^{-3}$</td>
<td>[24]</td>
</tr>
<tr>
<td>LC based on COANP–C$_{70}$</td>
<td>1</td>
<td>$30 \times 10^{-3}$</td>
<td>90</td>
<td>10</td>
<td>$1.45 \times 10^{-3}$</td>
<td>Now</td>
</tr>
<tr>
<td>LC based on COANP–C$_{70}$</td>
<td>1</td>
<td>$30 \times 10^{-3}$</td>
<td>130</td>
<td>10</td>
<td>$1.1 \times 10^{-3}$</td>
<td>Now</td>
</tr>
<tr>
<td>LC based on COANP–CNTs</td>
<td>0.5</td>
<td>$18.0 \times 10^{-3}$</td>
<td>90–100</td>
<td>10–20</td>
<td>$3.2 \times 10^{-3}$</td>
<td>[32]</td>
</tr>
<tr>
<td>LC based on COANP–C$_{70}$</td>
<td>0.5</td>
<td>$30 \times 10^{-3}$</td>
<td>100</td>
<td>10</td>
<td>$1.2 \times 10^{-3}$</td>
<td>[33]</td>
</tr>
<tr>
<td>LC based on COANP–CNTs</td>
<td>0.1</td>
<td>$30 \times 10^{-3}$</td>
<td>100</td>
<td>10</td>
<td>$2.8 \times 10^{-3}$</td>
<td>[33]</td>
</tr>
<tr>
<td>LC based on DNA*</td>
<td>0.1</td>
<td>0.1</td>
<td>90–120</td>
<td></td>
<td>$1.39 \times 10^{-3}$</td>
<td>[30]</td>
</tr>
<tr>
<td>LC based on QDs CdSe(ZnS)+DNA</td>
<td>0.1</td>
<td>0.1</td>
<td>90–120</td>
<td></td>
<td>$1.35 \times 10^{-3}$</td>
<td>[30]</td>
</tr>
<tr>
<td>LC based on QDs CdSe(ZnS)+DNA</td>
<td>0.1</td>
<td>0.1</td>
<td>130</td>
<td></td>
<td>$1.0 \times 10^{-3}$</td>
<td>Now</td>
</tr>
</tbody>
</table>

*Content of DNA (salmon fish) in the water solution was $\sim 4.72 \text{ g/L}^{-1}$, and the relation between LC and DNA was 5 : 1.

a strong interaction between new domains with activation of the intermolecular CTC. This mechanism provokes the self-assembly features and increases of the refractivity and conductivity when NLC has been doped with nano- or bioobjects.

The basic photorefractive results have been shown in Table 1 including the comparative data obtained in the previously made studies; see [24, 30–33].

For better understanding, the data are presented in Table 1; the nature of the included particles, variation of their concentration, value of the energy density, and range of the spatial frequency are shown. The induced birefringence $\Delta n_i$ clearly demonstrates the creation of the CTC via possible changes in the charge transfer electron pathway and the amount of charge. It will lead to changes in the electric field gradient, dipole moment (proportional to the product of charge and distance), and mobility of charge carriers. This process permits proposing the method to make the LC systems with the increased activated birefringence.

In addition, the barrier-free charge transfer will be influenced by competition between the diffusion and drift of carriers during the creation of diffraction patterns with
various periods and, hence, differing charge localization at the grating nodes and antinodes. Indeed, in the case of nanocomposites irradiated at small spatial frequencies (large periods of recorded grating), a drift mechanism of the carrier spreading in the electric field of an intense radiation field will most probably predominate, while, at large spatial frequencies (short periods of recorded grating), the dominating process is diffusion. The general view of the experimental holographic scheme and the grating recorded on the studied media is shown in Figure 2. It should be noticed that so many orders of the diffraction can be observed which corresponded not to the Bragg diffraction regime but, namely, to the Raman-Nath one. It should be mentioned that the classical ellipsometry method has been used as an additional one in order to support the increase of the refractive parameters. Really, the data shown in Figure 3 support this fact. The experiments have been performed using Horiba Jobin Yvon Uvisel device with the PSA-scheme.

One can see from Figure 3 that an introduction of the nano- and bioparticles provokes the increase of the refractive index in comparison with the same value in regard to pure LC. In the current experiments, the intermolecular CTC based on the COANP-C70 has been used and the DNA molecules have been applied. The nano- and biostructuration process leads to activate the self-assembly mechanism and permits observing the new large oriented numerous domains in the doped LC media. Finally, the structured LC composites with the new domains that have other orientation and order parameters have been testified before for the pure nematic LC media.

The new domains activated in the LC via intermolecular CTC formation are shown in Figure 4. One can observe the pictures with 2D or 3D local area which indicate the quasimectic transition from inertial nematic pure LC mesophase to polarized structured LC composites. The same effect has been shown in the previously reported paper [27] with checking the change of the transition temperature from the nematic phase (61 degrees) to quasissmectic one (48 degrees) and via increase of the order parameters supported by NMR-analysis too. For comparison, the pure LC, LC+COANP-C70 CTC, LC with DNA, and LC with DNA and QDs are shown. The scale under Figures 4(a) and 4(b) is equal to 10 microns. The scale for Figures 4(c) and 4(d) is equal to 500 microns. One can see the appearance of the domains under the nano- and biostructuring.

It should be mentioned that the use of the luminescent QDs permits visualizing the DNA molecules in the LC media at the relief with CNTs. The basic views of the novel relief which has been used for the identification of the DNA and testing its form are shown in Figure 5. Different optical methods based on the optical spectroscopy and based on the AFM-analysis have been applied in order to support these results. Moreover, it should be noticed that both approaches indicate the coinciding profile of the made relief with the wavelength of the IR-laser operated at the wavelength of 10.6 micrometers.

It should be noticed that CNTs structured relief made on the ITO-coatings has been developed in vacuum using p-polarized radiation of the IR quasi-CW CO2 laser operating at the wavelength of 10.6 μm and at the power of 30 W. As an addition, relief has been modified by a surface electromagnetic wave (SEW) in order to have the orienting LC ability with good advantage. The detailed 2D and 3D AFM-images of the relief are shown in Figure 6.

During the deposition, the CNTs were oriented in the vertical position by applying the electric field with the strength of 100–600 V/cm. This procedure permits obtaining the significantly modified ITO-coatings characteristics due to the fact that CNTs have been covalent bonded with the ITO-layers that influences the transmission spectrum and the mechanical and laser strength of the material surface, as well as decreases the roughness [41–43]. For example, the application of CNTs leads to the formation of an effective layer at the substrate-CNT interface, since the nanotubes (with a refractive index of n = 1.1) significantly reduce the Fresnel reflection losses by a factor of about 20. To support the change of the refractive interface parameters, the ellipsometry method has been used once again. Figure 7 presents the data in regard to decrease of the refractive index.
of the ITO-coatings when CNTs have been laser deposited at the interface and oriented via applying the electric field with the strength of 100 V/cm.

The data presented in Figure 7 are correlated with the fact that transparency of the ITO-layer under the conditions with different treatment methods can be changed dramatically. This fact is shown in Figure 8. CNTs have been oriented with different electric field placed in the range from 100 to 600 V/cm. It permits obtaining the promising LC cell with this optimizes relief in order to improve the visualization and orientation of the CTC based on the nano- and bioobjects doping.

It should be drawn to attention that the relief mentioned above has been nontoxic and can provoke the orientation of the DNA molecules successfully. This relief can be proposed to orient other bioobjects, for example, erythrocytes, stomatocyte, and poikilocytes, in order to check their form and configuration as the express approach.

Let us remember that we have the practice to orient the bioobjects in the LC media. Really, the orientation of other bioobjects, such as the erythrocytes, has been made by us and reported early in [44–46]. The results of these studies showed that the structurization of an NLC mesophase can be induced not only by the introduction of dyes or fullerene-containing CTC complexes but also by adding of the nonelectrically neutral biological components such as human blood erythrocytes. Good prospect has been opened by the investigations in this direction using the methods of dynamic holography for the observation of diffraction on the ordered biaxial structures and the NMR for the monitoring of changes in the NLC order parameter in the presence of erythrocytes. These investigations have been also useful for medicine by providing the means of monitoring changes in the shape of human blood cells using NLC mesophase.

Thus, in the current study, the same affect has been revealed and supported for the DNA by applying the different techniques. It has provoked the modified improved properties of the LC systems by both the nano- and the bioobjects structuration of the body of the LC and by the nanostructuration of the interface. These evidences are supported via four-wave mixing technique and via self-assembling microscopy observation as well as via some innovative theoretical idea about the dipole increase in the polarized composites, which have been explained in detail in the previously published papers [38–40]. Moreover, some relief modification influences on the refractive and spectral
properties of the LC mesophase are shown now and previously have been presented in [47] when LCs have been doped with the different types of the lanthanides nanoparticles.

4. Conclusions

To summarize the results, one can testify the following basic conclusions:

(i) Nano- and biostructuration of the nematic LC-mesophase body provokes the efficient self-assembly effect that connects with the increase of the order parameters and reveals the 2D and 3D LC systems instead of the 1D ones.

(ii) Nano- and biostructuration of the nematic LC-mesophase body leads to increase of the birefringence that can be checked via holographic recording technique.

(iii) Nanostructuration of the interface between LC mesophase and solid substrate directly influences on the decrease of the refractive index of the ITO-coatings due to the effective covalent bonding of the CNTs with the smaller refractive parameters.

(iv) Additional treatment of the nanostructured interface between LC mesophase and solid substrate with surface electromagnetic wave provokes the development of the novel orienting nontoxic relief responsible for the promising orientation of the DNA molecules, which can be visualize at these conditions with good advantage.

(v) Structuration processes mentioned above of the LC body and of the interface between LC mesophase and solid substrate extend drastically the area of the application of the nematic LC not only for the technical optoelectronics and theoretical nanophotonic applications but for the biology and medical use.
too due to express analysis use to test the form or configuration of the bioobjects.

Indeed, it should be remarked that, for future experimental evidences of the intermolecular charge transfer complex formation in the nematic LC doped with both the nanoobjects and the bioobjects, the scanning electron microscopy supporting should be used.

**Disclosure**

Some parts of the results presented in the current paper have been discussed at the scientific seminar, Czestochowa University (December 12, 2012, Poland), at the Nanotechnology Session in the framework of the MMT-2014 Conference (July 28–August 1, 2014, Ariel, Israel), at and the 3rd International Workshop on Nano and Bio-Photonics (6–11 December 2015, Cabourg, France).

**Competing Interests**

The authors declare that they have no competing interests.

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Figure 7: Dependence of the refractive index on wavelength of the pure ITO-coatings at the glass substrate and of the ITO-layer structured with CNTs deposited under the condition when electric field has been used.

Figure 8: IR-transmittance spectra of the ITO-layers with laser-field has been used.

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