Photorefractive Properties of Some Nano- and Bio-Structured Organic Materials

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Abstract: Based on using the holographic recording technique the photorefractive parameters of some organic materials doped with nano- and bio-objects have been studied. Some spectral and structural features have been established. The area of application of the materials has been discussed in order to use them in the optoelectronics and biomedicine.

Keywords: Nano- and biostructures, laser-mater interaction, photorefractivity, liquid crystals, self-assembling, interface.

INTRODUCTION

Last two decade the structural, spectral, optical, and photorefractive features of the different types of the organic materials are studied under the nano- and biostructurization condition [1-5]. The main accent is given to show the perspective of the nano- and boiobjects to modify the structural and photorefractive properties. To analyze the photorefractive characteristics coincided with the nonlinear optical processes, one should take into account that when the electric field of the laser wave is less than the intra-atomic electric field correlated with the electron charge and with the Bohr radius, we should estimate the linear effect. But, when the electric field of the laser wave is larger than the intra-atomic electric field, we should draw the attention on the nonlinear optical features. Using this aspect, the values of optical susceptibilities play important role in nonlinear optical effect. Really, the most important optical characteristic of the all inorganic or organic materials with different symmetry is the induced dipole, whose can be expressed through dipole polarizabilities $\alpha^{(n)}$. These are in turn related by the proportional dependence to the nonlinear susceptibility $\chi^{(n)}$ and to the local volume υ of the materials (media). Thus, laser-matter interaction provokes the change in polarization of media and predicts the change in important properties, such as photorefractive, photoconductive and dynamic ones.

In the current paper some polymer and liquid crystal matrixes from cyanobiphenyl groups are chosen as the good models to optimize the photorefractive parameters *via* intermolecular charge transfer complex formation based on nano- and bio-objects using.

MATERIALS AND METHODS

The photorefractive properties have been investigated using the organic systems with initial charge-transfer complex (CTC) due to donor-acceptor interaction. They are: polyimide, pyridine (2-cyclooctylamine-5-nitropyridine – COANP) compounds as well as the nematic liquid crystals (NLC). As the effective intermolecular dopants both the nanostructured acceptors such as the fullerenes, quantum dots (QDs), dye WD-C4, as well as the bio-components, namely, red fish DNA have been used. The thin films of polyimides and COANP sensitized with fullerenes C_{60}, C_{70} and quantum dots (QDs) based on CdSe(ZnS) have been prepared with the thickness of 2-5 micrometers. Nanoobjects concentration was varied in the range of 0.003-5 wt.%. The fullerenes have been purchased from Alfa Aesar (Kurlsruhe, Germany), dye WD-C4 has been synthetized in the Laboratoire de Chimie - UMR CNRS 5182. The thickness of the LC cells with conducting electrodes deposited on the glass substrates were 10 micrometers. Water solution of DNA with concentration of 4.72 g/l has been used. The relation between the liquid crystal mesophase and this water solution was ~5:1.

The second harmonic of pulsed Nd-laser at wave length of 532 nm has been used. The laser energy

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density has been chosen in the range of 0.03×10^{-3}–0.6 J×cm^{-2}. The nanosecond laser regime with the pulse width of 10-30 ns has been applied. The amplitude-phase thin gratings have been recorded under Raman-Nath diffraction conditions at spatial frequency of 90-150 mm^{-1}. We have applied the holographic recording technique shown in Ref.7 to activate the grating at $\Lambda^{-1}\geq d$, where Λ is the spatial frequency, d is the thickness of the film.

RESULTS AND DISCUSSION

Laser-induced change in the refractive index Δn_i has been calculated using the mathematical approach from Ref. [6] and extended on the nanostructured organics in paper [8]. Thus, the diffraction efficiency response can be written using the equation:

$$\eta = \frac{I_1}{I_0} = \left(\frac{\pi \Delta n_i d}{2\lambda}\right)^2,$$

where Δni – induced change in the refractive index, I1 is the intensity in the first diffraction order, I0 is the input laser intensity, d is the thickness of the medium, λ is the wavelength of the light incident on the medium.

The basic results are shown in Table **1**. The visualization of the diffractive picture is shown in Figure **1**.

The basic idea and explanation, which we are using to explain the increase of the laser-induced refractive index (as well as the nonlinear refraction and the cubic nonlinearity) under nanostructurization process, have been early explained in the paper [9] and book [10]. It takes into account that the pathway of the charge transfer changes drastically *via* nanostructurization. The charge transfer reveals from the intramolecular donor fragment of organic conjugated molecules not to its acceptor fragment but to nanoobjects if the electron affinity energy of the nanoobjects is larger than the one for intramolecular acceptor fragment. As the results, from one side, we have obtained the dipole moment increase (optimization of the optical properties) and the charge carrier mobility improvement (optimization of the photoconductive parameters).

Regarding the structures with DNA it should be mentioned that it requires to make an additional experiments and to find an alternative method to test. However, the spectral characteristics reveal the IR shift for the DNA-doped LC with QDs, which permits to testify that the CTC formation process can be too involved to explain the refractive results. The spectra are shown in Figure **2**. It can be revealed that after 500 nm up to 1100 nm all doped LC cells with nano- and bio-objects have good transparency close to 60-85% when the transparency of the pure LC cell is limited by the level of 65-70%. Moreover, the self-assembling structures have been observed after nano- and biostructurization. Figure **3** shows this evidence.

Thus, just now one can say that the bio-objects can replace the nano-objects with good advantage due to the reason that they are the renewable source.

As an additional, we have observed interesting phenomena connected with the nanostructurization process influence on the interface modifications of the polyimide and COANP materials with the nano-objects. It has been established that the wetting angle increases before the saturation level (at which all nanoobjects make the complex with the organic

Table 1: Laser-Induced Change of the Refractive Index Δn_i of the Sensitized Organic Matrixes

Structure studied	Content of nano-objects, wt.%	Wave-length, nm	Energy density, J×cm^{-2}	Spatial frequency,mm^{-1}	Laser pulse width, ns	Δn_i
Pure polyimide	0	532	0.6	90	20	10^{-4}-10^{-5}
Polyimide +QDs CdSe(ZnS)	0.003	532	0.2-0.3	90-100	10	2.0×10^{-3}
Polyimide+C_{70}	0.2	532	0.6	90	10-20	4.68×10^{-3}
Polyimide+dye WD-C4	0.05-0.1	532	0.2	150	20	8-10.0×10^{-3}
COANP+C_{70}	5	532	0.9	90-100	10	6.89×10^{-3}
NLC+ Polyimide+C_{70}	0.2		0.1-0.3	90-100	10	1.2×10^{-3}
NLC+COANP+C_{70}	1	532	0.017-0.02	100	20	1.4×10^{-3}
NLC+DNA	0.1	532	0.1	120	30	1.39×10^{-3}
NLC+QDs CdSe(ZnS)+DNA	0.1	532	0.1	120	30	1.35×10^{-3}

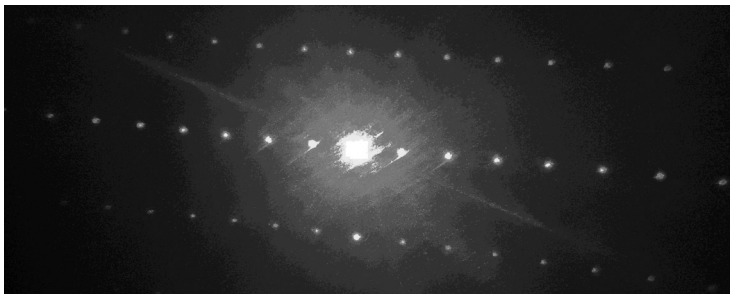


Figure 1: The diffractive grating generally recorded in the photorefractive media.

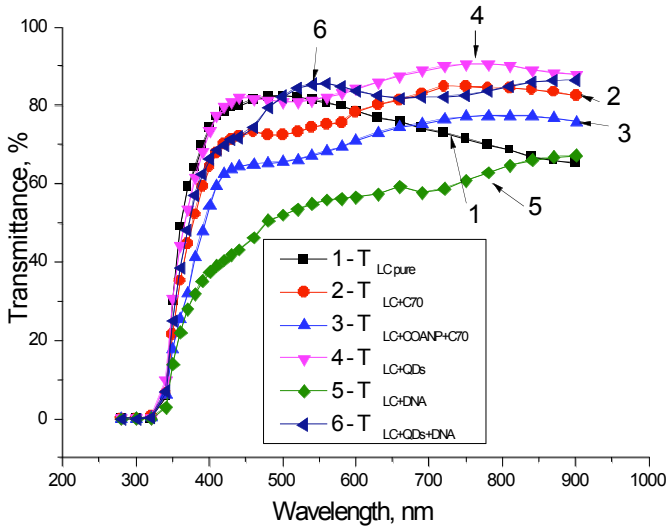
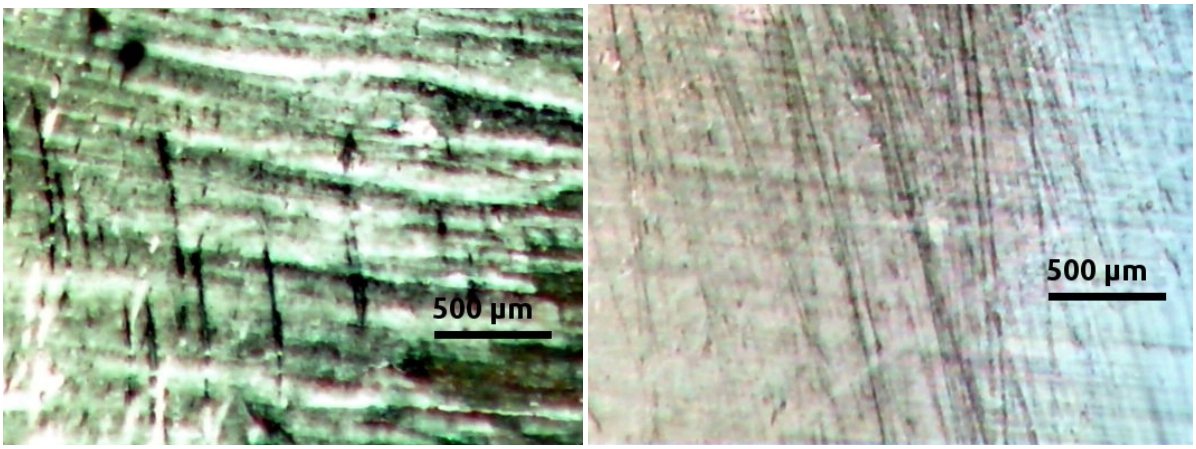


Figure 2: Spectral parameters of the LC with nano- and bio-objects.



(**a**) (**b**)

Figure 3: The networks inside the LC media doped with nano- and bio-objects: LC+C_{70} (**a**) and LC+DNA (**b**).

molecule donor fragment) and decreases, if the concentration of the nanoobjects extends the saturation level. These results are in the good coinciding with the Figure **3a** and **b** and can be supported and slightly correlated with the previous one when we have studied the formation of the fullerene network, namely the fullerene skeleton forming chains of quasi-pentagonal and hexagonal shapes and then used for the formation of the thin film structure [11].

CONCLUSION

It has been expected and supported that the affective nanoobjects can be efficiently used at present time. Doping with these nanoobjects, namely with

fullerenes and quantum dots, significantly influences the photorefractive properties of nanobjects-doped organic matrices. An increase in the electron affinity and specific area implies a dominant role of the intermolecular processes leading to an increase in the dipole moment, local polarizability (per unit volume) of medium, and mobility of charge carriers. Special role of the dipole moment as a macroscopic parameter of a medium accounts for a relationship between the photorefraction and the photoconductivity characteristics. Thus, the photorefractive parameters change can be considered as the indicator of following dynamic and photoconductive characteristics change. It has been supported that the new network inside the organic nanostructured matrixes changes the wetting phenomena and microhardness of the materials. The database of the nonlinear features of the polyimide and the liquid crystal materials with different sensitizers, including DNA, has been extended. This study can be useful in order to collect the new knowledge in the nano-and bio-materials science and to extend the area of the application of the structured organic systems *via* replacement of the nano-objects by renewable bio-objects.

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