Influence of the Nanostructures on the Surface and Bulk Physical Properties of Materials

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Fullerenes, nanotubes, quantum dots are considered as effective sensitizers to modify both the optical, nonlinear optical features, dynamic and polarization characteristics, as well as mechanical and spectral properties of the organic and inorganic materials. The correlation between photorefractivity and photoconductivity was supported and the relation between charge carrier mobility of pure conjugated structures and nanoobjects-doped ones has been revealed. An increase of transmission of nanostructured polarization films was observed. An extension of the nanocomposites applications area is considered.

PACS: 42.70.–a, 42.79.–e, 78.20.–e, 78.30.Na

1. Introduction

The properties of nanostructured materials and related phenomena were extensively studied during the last decade. Fullerenes, carbon nanotubes (CNTs), quantum dots (QDs, for example, such as CdSe(ZnS), etc.) were considered as new effective sensitizers. These investigations open new directions to study the bulk and surface properties for basic research and determine promising fields for practical applications of these systems [1, 2].

In studying the spectral, photorefractive, photoconductive properties of the organic materials and the mechanisms responsible for these phenomena, it was established that the main advantages of modifying the bulk properties by doping with fullerenes and quantum dots are the unique system of energy levels and a relatively high electron affinity, while the important properties of CNTs are their high conductivity and the variety of charge transfer mechanisms. Previously, we demonstrated [3–5] the formation of barrier-free charge transfer pathways, increased dipole moment, and increased specific (per unit volume) local polarizability in some organic matrices doped with fullerenes, carbon nanotubes and quantum dots, where the formation of intermolecular complexes predominates over the intramolecular donor–acceptor interaction. The possible schemes of charge transfer via different nanosensitizers and organic molecule donor fragment are shown schematically in Fig. 1.

Analyzing the data shown in Fig. 1, one can say that when emphasis is made on fullerene or quantum dots (for example, such as CdSe/ZnS) doping, it is neces-

sary to take into account the charge transfer between organic molecule donor fragment and nanosensitizers due to their high electron affinity energy (2.65–4.5 eV) that is more than the ones for intramolecular acceptor fragments. When the organics molecules are sensitized by CNTs, it is necessary to take into account the variety of charge transfer pathways, including those along and across a CNT, between CNTs, inside a multiwall CNT, between organic molecules and CNTs, and between the donor and acceptor moieties of an organic matrix molecules.
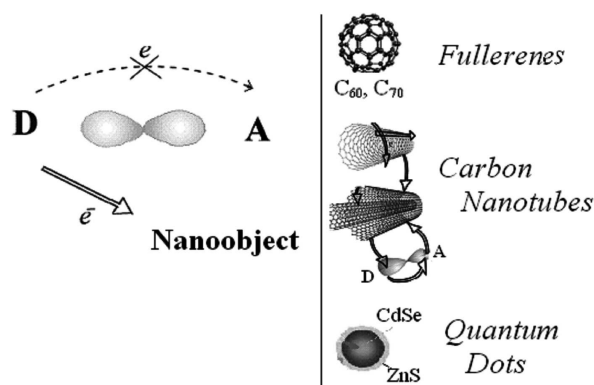

Fig. 1. Model consideration of the efficient charge transfer via nanoobjects doping.

In studying the surface and mechanical properties of the organic and inorganic materials the unique features of the carbon nanotubes, which modify the materials sur-

face with large advantage, should be taken into account
. Really, firstly, a little value of the refractive index of
the carbon nanotubes, $n \sim 1.1$, permits to develop the
effective intermediate layer between air and matrix materials. Secondly, the carbon nanotubes imaginary part
of the dielectric constant is close to zero in the near and
middle infrared spectral range that permits to save or
improve the spectral properties of the matrix materials
after nanoobjects placement on the surface. Thirdly, due
to large hardness of C–C bonds in carbon nanotubes, of
the order TeraPascal [6, 7], these nanoobjects improve
the surface and bulk hardness of matrix materials and
decrease the surface roughness.

2. Experimental conditions

To reveal a modification of bulk properties, the organic
thin films based on π-conjugated polyimide (PI) sensitized with fullerenes, nanotubes or quantum dots have
been chosen for the study. In addition, a nematic liquid crystal (NLC) was also used as an organic matrix.
The concentration of fullerenes and quantum dots was
varied in the range of 0.003–1.0 wt.%, the ones of carbon nanotubes was in the range of 0.01–0.1 wt.%, The
films were obtained by using the centrifuge deposition.
The thickness of the films was 2–5 micrometers. The LC
cell thickness was 5–10 micrometers. The nanostructured
LC films were placed onto glass substrates covered with
transparent conducting layers based on ITO contacts.
The nanostructured monomer or polymer films were deposited on the substrate with ITO contact. For the electric measurements, gold contact was put to the polymer
upper side. The bias voltage applied to the photosensitive polymer layers has been varied from 0 to 50 V. The
current–voltage characteristics were measured under the
illumination conditions from dark to light illumination.
Voltmeter-electrometer B7—30 and Characteriscope—Z,
type TR-4805 was used for these photoconductive experiments. The photorefractive characteristics have been
studied using four-wave mixing technique analogous to
paper Ref. [8]. The second harmonic of pulsed Nd-laser
at wave length of 532 nm has been used. The laser energy
density has been chosen in the range of 0.1–0.5 J cm^{-2}.
The nanosecond laser regime (the pulse width was 10–
20 ns) was applied. The amplitude-phase thin gratings
were recorded under Raman–Nath diffraction conditions
at spatial frequency of 90–150 mm^{-1}.

To reveal the surface properties modification of the materials via carbon nanotubes placement, CNTs were laser
deposited onto the surface of optical materials or polarization films in vacuum using p-polarized radiation of a
quasi CW CO$_2$ laser. During the deposition, the CNTs
were oriented by applying an electric field with strength
of 50–200 V/cm. The optical transmission measurements
were performed using an SF-26 spectrophotometer operating at 200–1200 nm wavelength range and using Perkin
Elmer Lambda 9 spectral device for UV and IR study.
The results of spectral measurements were checked using calibrated optical filters. The error in transmission
measurements did not exceed 0.2%.

3. Results and discussion

3.1. Bulk properties

Table I represents the current-voltage characteristics
of some pure and nanosensitized compounds. The basic
accent was given on conjugared PIs. It should be mentioned that the current–voltage characteristics of pure
and nanoobjects-doped PIs were measured for the samples with various concentrations of fullerene C$_{70}$ or C$_{60}$
additives, nanotubes and quantum dots under the conditions of dark and light illumination. Table I presents the
current–voltage characteristics data under light irradiation.

One can see from the Table I that the increase in the
current response can be observed after fullerene sensitization. This fact is connected with the charge transfer
complex (CTC) formation between donor part of the organic molecule and fullerene. To support the CTC formation, the mass-spectrometry analysis has been made.
The mass spectroscopy data point to the CTC formation
between fullerene and triphenylamine in the C$_{70}$-PI systems [9]. Photoconductive measuring shows that an increase in photoconductivity by at least two orders of magnitude is observed for all fullerene-doped films. Therefore, photoconductivity and mass spectrometry data confirm the complex formation in the studied structures.
Regarding the nanotubes-sensitized PI compounds, it
should be mentioned, that the fact of dramatical increase
in photocurrent can be explained by the additional complex mechanisms responsible for the electron moving in
the conjugated organics with nanotubes. The additional
odd electron from the core of the nanotubes should be
taken into consideration. More than six orders of magnitude difference in the current were observed at the same
value of bias voltage. These data are in good coinciding
with the data obtained in the paper Ref. [10]. Increase of
current response has been found in PI doped with little
content of QDs based on the system of CdSe/ZnS.

Some procedure to estimate the charge currier mobility
for the pure, fullerene-, nanotubes-, and quantum dots-
doped PI has been made. It should be noticed that for PI
conjugated systems we have drown the attention mostly
on the role of charge carrier mobility rather than on their
concentration. This is explained by the fact that in this
type of organics the conductivity activation energy coincides with the mobility activation energy, plotted in the
double logarithmic scale, the values of conductivity and
mobility (measured at equal temperatures and electric
field strengths) fit to the same straight line inclined at
45° relative to the coordinate axes. The charge carrier
mobility was estimated via the Child–Langmuir current–
voltage relationship by the method proposed in paper
Refs. [11, 12]. The charge carrier mobility of pure and
nanoobjects-doped samples were estimated at the same
density of the current, bias voltage, thickness of the films,
and dielectric permittivity. The following relationship
was found:

$$\mu_{\text{pure}} < \mu_{\text{fullerenes}} < \mu_{\text{NT,QD}}. \tag{1}$$

Photocurrent of polyimides with different nanoobjects.

Bias voltage	Current, A, under light irradiation			
V	Pure PI	PI+0.2 wt.% C70	PI+0.1 wt.% CNT	PI+0.003 wt.% QD
0	2.77×10^{-12}	4.33×10^{-12}		
1			Close to 10^{-4} - 10^{-3}	
5	2.98×10^{-11}	5.0×10^{-11}		
10	6.96×10^{-11}	1.1×10^{-10}		
15	1.01×10^{-10}	2.3×10^{-10}		
20	1.44×10^{-10}	3.7×10^{-10}		
30	2.5×10^{-10}	8.0×10^{-10}		Close to 10^{-9} - 10^{-8}
40	3.8×10^{-10}	1.4×10^{-9}		
50	5.7×10^{-10}	2.4×10^{-9}		

Laser-induced change of the refractive index.

Structure	Nanoobjects content, wt%	Energy density J cm^{-2}	Λ mm^{-1}	Δn	Ref.
Pure PI	0	0.6	90	$10^{-4} \div 10^{-5}$	[13]
PI +quantum dots based on CdSe(ZnS)	0.003	0.2–0.3	100	2.0×10^{-3}	current
PI+C70	0.2	0.5–0.6	90	4.68×10^{-3}	[13]
PI +nanotubes	0.1	0.3–0.5	100-150	5.5–5.7×10^{-3}	[13]
Polymer-dispersed LC based on PI–C70 complex	0.2	0.1–0.3	90–100	1.2×10^{-3}	current

The results of these calculations show that the introduction of fullerenes leads to a tenfold increase in the mobility, but introduction of nanotubes or quantum dots reveals increase of mobility by two or more orders of magnitude. Thus, charge carrier mobility of pure PI films placed in the interval from 10^{-7} to 10^{-5} cm^{2}V^{-1}s^{-1} can be increased to 10^{-4}–10^{-3} cm^{2}V^{-1}s^{-1}.

This fact correlates with increase of dynamic properties of the nanostructures-doped conjugated films and liquid crystal cells [3]. It should be noticed that at smaller quantum dots concentration than nanotubes concentration, the charge carrier mobility has been found a little bit larger for QD-doped structures in comparison with nanotubes-doped ones and at smaller nanoobjects concentration, the charge carrier mobility has been found a little bit larger for nanotube-doped structures in comparison with fullerene-doped ones.

It should be noticed that the photoconductive parameters coincide with the photorefractive ones. Really, for polyimide matrixes the basic results regarded to the laser-induced change of refractive index, Δn, under condition of different nanoobjects sensitization and at varied spatial frequency, Λ, are shown in Table II.

It should be taken into account that for fullerene-doped PI irradiating laser energy density W_{in} of 0.5–0.6 J cm^{-2} corresponds to 350–400 kcal mol^{-1} at molecular mass of PI units of 750. The rotation threshold is 100–700 kcal mol^{-1} [14]. This effect is likely to result in a better arrangement of PI donor fragment (triphenylamine) and fullerene planes, and hence in efficient CT between them [15].

From the laser-induced changes of the refractive index, the nonlinear refraction n_2 and the third order susceptibility $\chi^{(3)}$ were determined via procedure shown in the paper. [13]. They were, respectively: $\sim 10^{-7}$ cm^{2}kW^{-1} and $\sim 10^{-9}$ esu for thin conjugated films of the nanoobjects-doped organic structures, $\sim 10^{-6}$ cm^{2}kW^{-1} and $\sim 10^8$ esu for thin films of the nanoobjects-doped polymer-dispersed liquid crystals. The model explaining improving of nonlinear optical and of dynamicń features of the nanoobjects-doped organic structures via increase in dipole moment and local volume polarizability were firstly early presented in the paper Ref. 3. It has been postulated that the same evidences have been found for the structures based on 2-cyclooctylamino-5-nitropyridine (COANP), N-(4-nitrophenyl)-(L)-prolinol (NPP), polyanilyne (PANI) doped with nanoobjects.

It should be mentioned that nonlinear optical parameters of nanoobjects-doped structures are larger than those obtained for traditional nonlinear inorganic systems and for pure organics. Moreover, the data testify that nonlinear characteristics of the materials studied are close to those for Si-based structures and larger than the ones for classical inorganic widely used crystal of LiNbO$_3$,

that provoke the organics structures with nanoobjects to be used in extended area of optical and non-linear optical applications.

3.2. Surface properties

Unique influence of the nanoobjects placement on surface mechanical hardness and roughness of the soft materials of UV an IR range has been shown in paper Ref. 16. As new aspect of this study the nanoobjects structurization of inorganic systems has been found for polyvinyl alcohol (PVA) iodine films used as polarizators in display and telecommunications schemes.

We have studied polarizers, such as iodinated PVA films with a thickness of 60–80 μm, which were coated on both sides by ~ 0.05 μm thick layers of single walled CNTs.

The polarizers contained polarization films with either parallel or mutually perpendicular (crossed) orientations, depending on the need to obtain the initial bright or dark field. It was found that the modification (nanostructuring) of the surface of polarization films by CNTs led to some increase in the optical transmission for the parallel component of incident light (see curves 1 and 2 in the Fig. 2), while retaining minimum transmission for the orthogonal component (see curves 3 and 4 in Fig. 2).
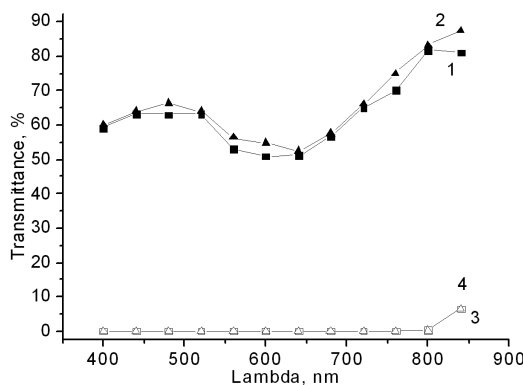

Fig. 2. Transmittance for the parallel (1,2) and orthogonal (3,4) part of light before (1,3) and after (2,4) nanotreatment procedure of the polarizer film.

4. Conclusions

The influence of nanoobjects, based on fullerenes, carbon nanotubes and quantum dots, on bulk and surface physical properties of optical materials was studied and the observed results are discussed here. The correlation between photorefractivity and photoconductivity has been considered as the feature of nanoobjects-sensitized organics. The relation between charge carrier mobility of pure conjugated structures and nanoobjects-doped ones has been revealed. The nonlinear optical parameters, such as nonlinear refraction and cubic nonlinearity, for nanoobjects-doped systems were calculated and the place of them among nonlinear characteristics of traditional nonlinear materials was postulated. Moreover, as new vision, the surface modification of polar-

ization films via nanostructurisation procedure was revealed. The nanostructuring of the surface of polarization films by CNTs led to a 2–5% increase in the optical transmission in the visible spectral range for the parallel component of incident light, while retaining minimum transmission for the orthogonal component. As the results of investigations, the potential area of applications of the materials is in optoelectronics and laser optic. Examples of possible applications are: telecommunication systems, gas storage and solar energy accumulation, as well as in the field of nonlinear optics and in search for 3D-media and new display elements.

Acknowledgments

References

[1] S. Couris, E. Koudoumas, A.A. Ruth, S. Leach, *J. Phys. B: At. Mol. Opt. Phys.* **8**, 4537 (1995).

[2] J. Robertson, *Mater. Today* **7,** 46 (2004).

[3] N.V. Kamanina, *Physics-Uspekhi* **48**, 419 (2005).

[4] N.V. Kamanina, S.V. Serov, V.P. Savinov, *Tech. Phys. Lett.* 36, 40 (2010).

[5] N.A. Shurpo, M.S. Vakshtein, N.V. Kamanina, *Tech. Phys. Lett.* **36**, 319 (2010).

[6] S. Namilae, N. Chandra, C. Shet, *Chem. Phys. Lett.* **387**, 247 (2004).

[7] M.M.J. Treacy, T.M. Ebbessen, J.M. Gibson, *Nature* 381, 678 (1996).

[8] N.V. Kamanina, N.A. Vasilenko, *Opt. Quantum Electron.* **29**, 1 (1997).

[9] N.V. Kamanina, A.I. Plekhanov, *Optics and Spectroscopy* **93**, 408 (2002).

[10] Xiaowen Jiang, Yuezhen Bin, Masaru Matsuo, *Journal Polymer* **46**, 7418 (2005).

[11] F. Gutman, L.E. Lyons, *Organic Semiconductors*, Wiley, New York 1967.

[12] M.M. Mikhailova, M.M. Kosyreva, N.V. Kamanina, *Technical Physics Letters*, **28**, 450 (2002).

[13] N.V. Kamanina, S.V. Serov, V.P. Savinov, D.P. Uskoković, *Int. J. Mod. Phys. B)*, **24,** 695 (2010).

[14] V. Bershtein, V. Egorov, *DSC in Physical Chemistry of Polymers*, Chemistry, Leningrad 1990.

[15] Y.A. Cherkasov, N.V. Kamanina, E.L. Alexandrova, V.I. Berendyaev, N.A. Vasilenko, B.V. Kotov, *Proceed. SPIE* **3471**, 254 (1998).

[16] N.V. Kamanina, P.Ya. Vasilyev, S.V. Serov, V.P. Savinov, K.Yu. Bogdanov, D.P. Uskokovic, *Acta Phys. Pol. A*, **117**, 786 (2010).