Features of the nanostructured materials for solar energy application:
Increased charge carrier mobility

N.V. Kamanina 1,2,3
1 Vavilov State Optical Institute, Kadetskaya Liniya V.O., 5-2, St.- Petersburg, 199053, Russia
2 Saint-Petersburg Electrotechnical University (“LETI”), St. Petersburg, Russia
3 Saint-Petersburg Technical University (“IFMO”), St. Petersburg, Russia
*corresponding author e-mail: nvkamanina@mail.ru

In this chapter the effect of both the fullerenes C_{60} and C_{70}, as well as the carbon nanotubes on the volt-ampere characteristics and on the mobility of charge carriers in conjugated organic systems based on polyimide, on 2-cyclooctylamino-5-nitropyridine, and on other nitro replaced aromatic compounds has been considered. It has been established that the carrier mobility in photoconductive nanoobjects-containing conjugated organic thin films exhibits a tenfold increase as compared to the nanoobjects-free organic films. Using the model polyimide matrix, the charge transfer complex formation between donor part of the organic matrix and carbon-based acceptor has been revealed as the main mechanism responsible for the increase of the charge carrier mobility.

Keywords: conjugated organic systems, nanoobjects, fullerenes, nanotubes, photoconductivity, mobility

1. Introduction

It is well known that the photosensitive media based on conjugated organic structures such as polyimide (PI), 2-cyclooctylamino-5-nitropyridine (COANP), N-(4-nitrophenyl)-(L)-prolinol (NPP), 2-(n-prolinol)-5-nitropyridine (PNP), and other nitro replaced aromatic compounds occupy an important place in a class of light-controlled systems used as the telecommunications components, as the solar energy elements, as the gas storage devises, as the recording systems based on PI, COANP, NPP, PNP by doping them preferably with the fullerenes or with the carbon nanotubes.

Unfortunately, these compounds are characterized by a low mobility of charge carriers, which is one of the factors limiting the broad area operation of the systems mentioned above. Some ways to sensitize these compounds with dyes have been previously proposed [6,9]. Really, for example, the structural formulas of the PIs and COANP compounds permit to postulate that triphenylamine fragment and NH-group is the donor part of these molecules which can provoke the development of the intermolecular charge transfer complex (CTC) via sensitization process. Moreover, the effect of the operating conditions and of the interface properties on the dynamic parameters improvement should be taken into account [7,8].

Based on the accumulated knowledge, the carbon nanobjects, such as fullere C_{60} and C_{70}, have been also used in order to modify the spectral and the dynamic properties of these composites [10-12]. These studies provoked the observation of the correlation effect between spectral, photorefractive and photoconductive features that has been shown in the latest publications [13-15]. Therefore, the study of the nanoobjects-doped materials and their intermolecular CTC formation process makes the possibility to find the appropriative way to increase the charge carrier mobility in such media. It is important both for the basic investigations of photoconductive and photorefractive optical features and for the practical applications, for example, in the nonlinear optical data processing systems [16] and in the solar energy devices [17], where an effective increase of one characteristic must be provided without significantly impairing other characteristics.

It should be mentioned that at present time the way to increase the sensitivity, resolution, dynamic parameters, etc. of organic compounds via the nanoobjects sensitization have been often applied. As the effective nanoobjects both the fullerenes C_{60} and C_{70}, as well as the carbon nanotubes (CNTs), carbon nanofibers, shungates, graphenes, quantum dots, etc. can be used in order to modify the volt-ampere features and increase the charge carrier mobility. It should be noticed that these nanoobjects have an outstanding combination of a unique energy levels, of the large values of the electron affinity energy, of the high mechanical hardness, of the good laser strength, and of the enhancing conductive peculiarities. Moreover, the coinciding between the photorefractive and the photoconductive parameters as well as between the spectral and the mechanical features has been observed as rule.

The current study is devoted to detailed determining the possibility of increasing the charge carrier mobility in the systems based on PI, COANP, NPP, PNP by doping them preferably with the fullerenes or with the carbon nanotubes. The basic accent is given to the polyimide etalon materials.
2. Experimental conditions

The experiments were performed with thin films prepared from 3% solutions of the investigated compounds in tetrachloroethane or chloroform by the method of centrifugation. The films were modified by adding fullerenes C_{60} and/or C_{70} with the concentrations varied from 0.2 to 1 wt % and by adding carbon nanotubes with the content of 0.1 wt.% relative to the photosensitive component. The fullerenes have been purchased from Alfa Aesar (Kurlruhe, Germany). Single-walled CNTs have been received from Prof. A. Krestinin group (Chernogolovka, Moscow region, Russia), double-walled carbon nanotube powder XNM-HP-11050 has been received from XinNano Materials, Inc. (Taiwan), the mixture of the CNTs and carbon nanofibers has been done in the Vladimir State University (Vladimir, Russia) and in the Boreskov Institute of Catalysis (SB RAS, Novosibirsk, Russia).

It should be mentioned that both the matrix structures and the fullerenes as well are good soluble in tetrachloroethane solvent [18], which provided for the obtaining of sufficiently homogeneous films possessing high stability under the electric and the light treatment. It should be mentioned, that in order to make homogeneous COANP, NPP and PNP thin films some nonphotosensitive polyimides (without triphenylamine fragment) were used. It should be noticed that to prepare the homogeneous solutions with CNTs and carbon nanofibers an additional ultrasonic treatment was applied.

The thin films were deposited onto the glass or quartz substrates above preliminarily deposited transparent conducting layers based on the ITO (indium-tin-oxide contacts). The gold or alumina contacts were placed to the upper side of the thin organic films (see Fig.1, a). In order to increase the transparency of the ITO contacts the CNTs can be deposited on this contact too; than CNTs relief can be treated with surface electromagnetic wave (SEW) as has been previously shown in the paper [19]. It permits to measure the electric parameters with good advantage in the broad spectral range and at decreased level of the value of the bias voltage.

The bias voltage applied to the photosensitive layers was varied from 0.5 to 50 V. The current-voltage characteristics have been measured using voltmeter-electrometer B7-30 and Characteriscope-Z, type TR-4805. The current–voltage parameters were measured for the samples with various concentrations of fullerene and CNTs additive under the dark and under the variable illumination conditions. The spectral dependence of the photoconductivity was measured in a range of wavelengths from 200 nm up to the near IR region. The absorption spectra were measured on a SPEX Model 1403 spectrometer and using SF-26 instrument.

![Fig.1. The general view of the thin films with conductive contacts, a); and the change in the transparency of the ITO contacts in the visible spectral range under condition of the CNTs deposition, b).](image)

To find and to support the correlation between photoconductive and photorefractive features the thin holographic grating has been written at the thin film surface in the nanosecond pulse regime at the spatial frequencies placed in the range of 90-150 mm\(^{-1}\). The wavelength was in the visible spectral range; it was close to 532 nm. The laser-induced change in the refractive index has been estimated via four-wave mixing technique under the Raman-Nath diffraction regime analogous that shown in the paper [8].

3. Results and Discussion

The main experimental results are summarized in the Tables 1 and 2. Data in these tables represent the experimentally measured current–voltage characteristics of pure and nanoobjects-modified PI, COANP, NPP and PNP films under the condition of fullerene doping. One can see from the Table 1 and 2 that the increase in the current response can be observed after fullerene sensitization at the same level of the bias voltage. Approximately two orders of magnitude difference in the current has been observed. This fact is probably connected with the intermolecular CTC formation between the donor part of the organic molecule and the fullerene as well.
To support the CTC formation, the spectral dependence of the conductivity, the mass-spectrometry analysis, quantum-chemical calculations, and estimation of the absorption cross section changing have been previously made for some compounds [20,21]. For example, the mass spectroscopy data presented in the paper [20], point to the CTC formation between fullerene and triphenylamine and between fullerene and the HN group in the PI-C\textsubscript{70} and COANP-C\textsubscript{70} systems, respectively. For the COANP-C\textsubscript{70} film, curve contains two peaks. The first one is observed at 400 °C and corresponds to the release rate of the fragments with free fullerene masses. The second one is shifted to the temperature range of 520 °C and is associated with the decomposition temperature of the fullerene-HN group complex.

**Table 1** Current-voltage parameters of the pure and of the fullerene-doped PIs and COANP thin films.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>PI+0.2 wt.% C\textsubscript{70}</th>
<th>Pure COANP</th>
<th>COANP+1.0 wt.% C\textsubscript{70}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Light</td>
<td>Dark</td>
<td>Light</td>
</tr>
<tr>
<td>0</td>
<td>5.0\times10^{-14}</td>
<td>2.77\times10^{-12}</td>
<td>2.5\times10^{-13}</td>
<td>4.3\times10^{-12}</td>
</tr>
<tr>
<td>5</td>
<td>2.4\times10^{-11}</td>
<td>2.98\times10^{-11}</td>
<td>1.80\times10^{-12}</td>
<td>5.0\times10^{-11}</td>
</tr>
<tr>
<td>10</td>
<td>3.97\times10^{-13}</td>
<td>6.96\times10^{-11}</td>
<td>7.65\times10^{-12}</td>
<td>1.1\times10^{-10}</td>
</tr>
<tr>
<td>15</td>
<td>5.05\times10^{-13}</td>
<td>1.01\times10^{-10}</td>
<td>1.7\times10^{-11}</td>
<td>2.3\times10^{-10}</td>
</tr>
<tr>
<td>20</td>
<td>6.65\times10^{-13}</td>
<td>1.44\times10^{-10}</td>
<td>2.5\times10^{-11}</td>
<td>3.7\times10^{-10}</td>
</tr>
<tr>
<td>30</td>
<td>9.72\times10^{-13}</td>
<td>2.5\times10^{-10}</td>
<td>5.3\times10^{-11}</td>
<td>8.0\times10^{-10}</td>
</tr>
<tr>
<td>40</td>
<td>1.19\times10^{-12}</td>
<td>3.8\times10^{-10}</td>
<td>9.0\times10^{-11}</td>
<td>1.4\times10^{-9}</td>
</tr>
<tr>
<td>50</td>
<td>1.53\times10^{-12}</td>
<td>5.7\times10^{-10}</td>
<td>1.5\times10^{-10}</td>
<td>2.4\times10^{-9}</td>
</tr>
</tbody>
</table>

**Table 2** Current-voltage parameters of the pure and of the fullerene-doped NPP and PNP thin films.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>NPP+1.0 wt.% C\textsubscript{60}</th>
<th>Pure PNP</th>
<th>PNP+1.0 wt.% C\textsubscript{60}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Light</td>
<td>Dark</td>
<td>Light</td>
</tr>
<tr>
<td>0</td>
<td>~10^{-14}</td>
<td>0.12\times10^{-11}</td>
<td>~10^{-14}</td>
<td>0.2\times10^{-11}</td>
</tr>
<tr>
<td>5</td>
<td>0.65\times10^{-12}</td>
<td>0.14\times10^{-11}</td>
<td>~10^{-9}</td>
<td>0.4\times10^{-9}</td>
</tr>
<tr>
<td>10</td>
<td>0.38\times10^{-11}</td>
<td>0.54\times10^{-11}</td>
<td>~10^{-9}</td>
<td>0.17\times10^{-8}</td>
</tr>
<tr>
<td>15</td>
<td>0.4\times10^{-11}</td>
<td>0.57\times10^{-11}</td>
<td>~10^{-9}</td>
<td>0.25\times10^{-8}</td>
</tr>
<tr>
<td>20</td>
<td>0.45\times10^{-11}</td>
<td>0.6\times10^{-11}</td>
<td>~10^{-9}</td>
<td>0.3\times10^{-8}</td>
</tr>
<tr>
<td>30</td>
<td>0.52\times10^{-11}</td>
<td>0.8\times10^{-11}</td>
<td>~10^{-9}</td>
<td>0.37\times10^{-8}</td>
</tr>
<tr>
<td>40</td>
<td>0.12\times10^{-10}</td>
<td>0.2\times10^{-10}</td>
<td>~10^{-9}</td>
<td>0.48\times10^{-8}</td>
</tr>
<tr>
<td>50</td>
<td>0.15\times10^{-10}</td>
<td>0.35\times10^{-10}</td>
<td>~10^{-9}</td>
<td>0.7\times10^{-8}</td>
</tr>
</tbody>
</table>
For the PI-C$_{70}$ film, curve contains three peaks. The first one is observed also close to 400 °C. The second peak is located at 560 °C and associated with the decomposition of the fullerene-triphenylamine complex. It should be noticed that the melting temperature of these PIs is 700-1000 °C, thus, the third peak at the temperature higher 700 °C corresponds to the total decomposition of PI matrix. Moreover, it should be mentioned that the electron affinity of the fullerenes is close to 2.65 eV, that is twice as large as that of an intramolecular acceptor fragment of polyimide, and forth-fifth times larger than that for COANP acceptor fragment. It can support the intermolecular CTC rather than the intramolecular one.

Let us to draw the attention namely on the model polyimide matrix. It should be postulate that when the etalon polyimide compound has been doped with CNTs, the increase of current response extends the values of ~10$^{-4}$-10$^{-3}$ A. These data are in good coinciding with the data obtained in the paper [22]. Perhaps, this dramatic increase in current can be explained by the influence of the additional odd electron from the core of the nanotubes that should be taken into consideration. Thus, more than six orders of magnitude difference in the current has been observed at the same value of the bias voltage for the PIs doped with the CNTs in comparison with that doped with fullerenes.

Based on these experimental results, the charge carrier mobility can be estimated using the Child–Langmuir current–voltage relationship via equation (1) proposed in the book [23]:

$$\mu = 10^{13} \frac{I_d^3}{eV^2}.$$  \hspace{1cm} (1)

Here the parameters are following: $I$ is the current density, $d$ is the thin film thickness, $\varepsilon$ is the dielectric constant, $V$ is the value of bias voltage. It should be taken into account that the area of upper electrode contact should be considered in order to estimate the current density.

The results of these calculations show that the introduction of fullerenes leads to a tenfold increase of the mobility in comparison with the charge carrier mobility value of the pure PI materials but introduction of the CNTs predicts more than two-three orders of magnitude enhancement of this parameter. It should be mentioned that traditionally pure polyimides shows the value of the charge carrier mobility placed in the range from 10$^{-7}$ up to 0.5×10$^{-5}$ cm$^2$×(V-1×s-1) [1]. It should be remarks that the conductivity activation energy of some conjugated organic systems, including polyimide ones [1], coincides with the mobility activation energy due to the fact that plotted in the double logarithmic scale, the values of conductivity and mobility (measured at equal temperatures, electric field strengths) fit the same straight line inclined at 45 ° relative to the coordinate axes. It can predict some simple suggesting that a change in the conductivity $\sigma$ with the temperature and field strength is completely determined by changes of the carrier mobility $\mu$ rather than by their concentration as a function of these parameters. Thus, the nanoobjects sensitization provokes to obtain the drastic increase of the charge carrier mobility and explains the modern efforts to use conjugated polymer systems in the solar energy area.

Let us to support the consideration of the increase of the charge carrier mobility via the consideration proposed in the papers [24,25]. The main idea to improve the photorefractivity, switching and photoconductivity of the nanoobjact-doped organic media, including liquid crystal ones, is based on the dramatically changing of the local volume polarizability correlated with the dipole polarizability due to the effective intermolecular CTC in the nanoobjact-doped organic systems. When external fields (electric of light one) apply to such sensitized organic conjugated systems, the pathway of the charge carrier transfer is changed. The electrons are directed not to the intra-molecular acceptor fragment but to the nanoobjects if the electron affinity energy of the nanoobjects is higher than that for intra-molecular acceptor fragment. For example, electron affinity energy of intra-molecular acceptor fragment of polyimide (dimide) is close to 1.1–1.4 eV, the same one for fullerenes is ~2.65 eV. Thus, the electron affinity energy of the intermolecular acceptor fragment is two times higher. Moreover, the fullerenes as good acceptor can occupy up to six electrons [17]. Therefore, the incorporated nanoobjects are stronger sensitizers and they can dominate the acceptor fragments of the intra-molecular complexes. In this case the field gradients are formed and the enhanced additional dipole moment is observed. Moreover, the donor fragment (triphenylamine) of the polyimide molecule undergoes a conformational transformation from the neutral tetrahedral form to the ionized planar one under external fields [26,27]. This effect, along with less dimensions of the triphenylamine fragment (0.5 nm) than those of the fullerene molecule (~0.7 nm), causes aligning their molecular planes in parallel and supports the efficient intermolecular CTC too.

Regarding the nanotubes doping, we should take into account approximately 7 ways for the charge carrier moving: 1 – inside the organic molecules, when the donor-acceptor interaction has been presented, 2 and 3 – between the organic conjugated molecules and CNTs under the conditions of different relation of electron affinity energy of the organic molecules and CNTs, 4 – across the CNTs, if they are the multiwall ones, 5 – between the CNTs, 6 – along the nanotubes, 7 – inside the CNTs. This complicated process can be illustrated as can be shown in Fig.2,a. Moreover, it is natural to suggest that variations in the angle of the nanoobject orientation relative to the intramolecular donor can significantly change the pathway of charge carrier transfer [25], which will lead to changes of the electric field gradient, of the dipole moment (proportional to the product of charge and distance), and of the mobility of charge carriers. Some scheme to show this situation is presented in Fig.2,b. The picture shows the intermolecular electron moving between...
Thus, the system studied may feature a transition from intramolecular charge transfer between donor (triphenylamine) and acceptor (diimide) fragments to the intermolecular charge transfer, which can provoke the bathochromic shift in the absorption spectrum. This shift has been previously observed in the fullerene-sensitized polyimide [20] and can be supported via simple equation (2) as well [28]:

$$h\nu_{CTC} = I_D - E_A - \Delta W.$$  (2)

Here $h\nu_{CTC}$ is the energy of an exciting photon, $I_D$ is the donor ionization potential, $E_A$ is the acceptor electron affinity energy, $\Delta W$ is the energy of the bond polarization. For example, for the studied polyimide–C$_{70}$ system we have $I_D = 6.5$ eV (for triphenylamine), $E_A = 2.65$ eV (for fullerene), $\Delta W = 1.5$ eV, and $h\nu_{CTC} = 2.35$ eV, which is corresponded to the wavelength of 532 nm in comparison with 380-420 nm for the pure PI matrix.

Regarding the comparative influence of the fullerenes and the CNTs on the photorefractive features one can see the data presented in the Table 3 [29-32].

Table 3. Laser-induced change of the refractive index of the refractive index of the sensitized polyimides.

<table>
<thead>
<tr>
<th>Structure studied</th>
<th>Nano-objects content wt.%</th>
<th>Energy density, $J_{\text{scm}}^2$</th>
<th>Spatial frequency, $\text{mm}^{-1}$</th>
<th>Laser-induced change in the refractive index, $\Delta n_i$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure polyimide</td>
<td>0</td>
<td>0.6</td>
<td>90</td>
<td>$10^{-2}$-$10^{-3}$</td>
<td>[29]</td>
</tr>
<tr>
<td>Polyimide+C$_{60}$</td>
<td>0.2</td>
<td>0.5-0.6</td>
<td>90</td>
<td>$4.2\times10^{-3}$</td>
<td>[30]</td>
</tr>
<tr>
<td>Polyimide+C$_{70}$</td>
<td>0.2</td>
<td>0.6</td>
<td>90</td>
<td>$4.68\times10^{-3}$</td>
<td>[30]</td>
</tr>
<tr>
<td>Polyimide+nanotubes</td>
<td>0.1</td>
<td>0.5-0.8</td>
<td>90</td>
<td>$5.7\times10^{-3}$</td>
<td>[13]</td>
</tr>
<tr>
<td>Polyimide+double-walled carbon nanotube powder</td>
<td>0.1</td>
<td>0.063-0.1</td>
<td>100</td>
<td>$9.4\times10^{-3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>Polyimide+double-walled carbon nanotube powder</td>
<td>0.1</td>
<td>0.063-0.1</td>
<td>150</td>
<td>$7.0\times10^{-3}$</td>
<td>[31]</td>
</tr>
<tr>
<td>Polyimide+carbon nanofibers (type MIG)</td>
<td>0.1</td>
<td>0.6</td>
<td>90-100</td>
<td>$11.7\times10^{-3}$</td>
<td>[32]</td>
</tr>
<tr>
<td>Polyimide+carbon nanofibers (type 65BR)</td>
<td>0.1</td>
<td>0.1-0.3</td>
<td>90-100</td>
<td>$12.0\times10^{-3}$</td>
<td>[32]</td>
</tr>
</tbody>
</table>
The calculation of the refractive index change has been made via procedure proposed and applied in the publications [13,30,33] from experimentally found values of the diffraction efficiency. It can be clear observed that intermolecular CTC effectively influences the refractive parameters via the fact that the charge drift process has been dominated at the smaller values of spatial frequencies (at large grating period written by laser beams and bigger distance for pathway of charge). However, the diffusion process has been dominated at larger value of spatial frequencies (at smaller grating period). It should be emphasized that in our laser recording experiment charge drift process can be activated by electrical part of high intensity of laser wave without direct electric filed (bias voltage) application. Based on the laser induced change of the refractive index it can be postulated that CNTs doping effects more drastically influence the photorefractive parameters than the fullerene doping one. This fact can be additionally explained by increased surface energy of CNTs and nanofibers and their large number of odd electron from the core of nanotubes. Analyzing the photorefractive characteristics change depended on the type of nanoobjects, one can find the correlation between the photorefractive and photoconductive parameters as well.

4. Conclusion

Thus, to summarize the results, one can conclude the following. As the feature of the nanostructured materials the increase in the charge carrier mobility should be found which can be explained by efficient intermolecular charge transfer process. Moreover, as the results of the effective intermolecular CTC formation, the following evidences should be mentioned:

- The field gradient is formed as the charge transfer pathway changes (the charge goes not to the intramolecular acceptor fragment but to the intermolecular carbon acceptor).
- The increased pathway for the electron under the condition of the intermolecular CTC formation predicts the increase of the dipole moment and increased mobility. That is why the new potentials to apply nanoobjects-doped structures to develop the organic solar energy elements and the gas storage schemes can be realized.
- This complex is of a higher excited state absorption cross section than the ground state one. Using the quadratic dependence between absorption cross section and dipole moment it can provoke the appropriate change in the charge carrier mobility.
- Nanooobjects sensitization and complex formation provokes new spectral and energy range for the treated conjugated structures. The bathochromic shift is observed and new absorption band in the IR spectra range appears in the nanoobjects-doped materials.
- The effective photorefractive effect realized in these structures is generally correlated with the photocoherent ones.

Acknowledgements The author would like to thank Dr.V.E.Vaganov (Vladimir State University, Vladimir, Russia), Dr. I. V. Mishakov (Bioresk Institute of Catalysis SB RAS, Novosibirsk, Russia), Prof. A. V. Krestinon (Chernogolovka, Moscow region, Russia), Prof. V. I. Berendyaev (Karpov Research Institute, Moscow, Russia), Prof. N. M. Shmidt (Ioffe Physico-Technical Institute, Saint-Petersburg, Russia), Dr. V. I. Studeonov, Dr. P. Ya.Vasilev, and Dr. S. V. Serov (Vavilov State Optical Institute, Saint-Petersburg, Russia) for their help at different steps. The author would like to acknowledge her foreign colleagues Prof. I. Kityk, Prof. F. Kajzar and Prof. D. Uskokovic for their helpful discussion at different international scientific conferences. The present study was partially supported by the RFBR grants ##10-03-00916 (2010-2012), 13-03-00044 (2013-2015) and by the Project “BIOMOLEC” (via FP7 Program, Marie Curie action, 2011-2014).

References


