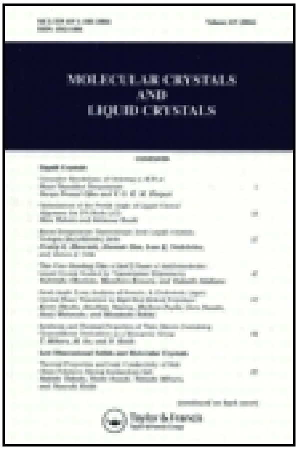

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Study of the Photoconductive and Optical Limiting Processes in Organic Nanostructures

V. A. Shulev [a b], S. V. Kascheev [a b], S. E. Putilin [c] & N. V. Kamanina [a b c]

[a] Vavilov State Optical Institute, Birzhevaya Line, St. Petersburg, Russia

[b] State Electrotechnical University, St. Petersburg, Russia

[c] State Institute of Fine Mechanics and Optics, St. Petersburg, Russia

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Study of the Photoconductive and Optical Limiting Processes in Organic Nanostructures

V. A. Shulev
S. V. Kascheev
Vavilov State Optical Institute, Birzhevaya Line, St. Petersburg, Russia and State Electrotechnical University, St. Petersburg, Russia

S. E. Putilin
State Institute of Fine Mechanics and Optics, St. Petersburg, Russia

N. V. Kamanina
Vavilov State Optical Institute, Birzhevaya Line, St. Petersburg, Russia; State Electrotechnical University, St. Petersburg, Russia; and State Institute of Fine Mechanics and Optics, St. Petersburg, Russia

Among other areas of application of materials doped with fullerenes or carbon nanotubes (CNTs), the special aspect is being made to investigate these nanostructures in the near and middle infrared. In the present paper, the infrared nonlinear transmission processes in fullerene- and nanotubes- containing organic systems based on polyimide, polyvinyl alcohol, prolinol, pyridine, and polyaniline have been considered. The thin films, gels, solution, and dispersed liquid crystal compounds have been studied at wavelengths of 805, 1047, 1080, 1315, and 2940 nm. Optical limiting properties and photoconductive peculiarities have been found. The possible limiting mechanisms have been discussed. It should be mentioned that the photoconductivity of nanostructure-doped systems varies in the range of 5–6 orders of magnitude. Additionally, the study with a microscope has been made. The quasi-photonic organic system has been obtained. Thus, the diffraction of a laser beam passing through this structure would be considered as one of the mechanisms to attenuate the laser beam.

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Address correspondence to N. V. Kamanina, Vavilov State Optical Institute, 12, Birzhevaya Line, St.-Petersburg 197376, Russia. E-mail: nvkamanina@hotmail.com

Keywords: fullerenes; laser-matter interaction; nanotubes; near and middle infrared spectral range; optical limiting; organic nanostructures; photoconductivity

1. INTRODUCTION

At the present time, the search for materials doped with fullerenes or nanotubes is a promising effective way to apply them in laser physics and information processing. Investigations of the nonlinear optical properties determined by the excitation of π electrons show evidence of the effective light absorption by charge-transfer complexes formed both between the donor part of an organic matrix molecule and fullerene (electron acceptor), as well as between the CNT odd electrons and organic media [1–7]. The affinity of fullerene in this complex exceeds that of the intramolecular organic acceptor. In the systems with CNTs, it is necessary to take into account the absorption of light by odd electrons as free charge carriers and the light-induced scattering. The appearance and enhancement of these processes lead to the following phenomena:

- The new charge-transfer complex is characterized by the absorption cross section for an excited state of the organic molecule, which is significantly greater than that for the ground state. As a result, fullerene- or CNTs-doped nanomaterials exhibit the phenomenon of strong optical limiting (OL), in particular, in the infrared spectral range.
- An additional electric field gradient is formed when the charge transfer takes place. A change in the local and macroscopic polarization has been observed. As a result, the nanomaterial can reveal the high-frequency Kerr effect and exhibits high values of nonlinear refraction n_2 and nonlinear third-order susceptibility $\chi^{(3)}$.
- Fullerene- and nanotubes sensitization stimulates the self-arrangement of the nanomaterials. As a result, the order parameter of the organic nanomaterials increases. The self-organized nanomaterials are a good homogeneous structure that allows one to develop new organic quasi-photonic crystals.
- A significant (reaching several orders in magnitude) change in the dark conductivity and photoconductivity of the media with fullerenes or CNTs results in the drastic absorption of light by free charge carriers. Moreover, due to a special network development in these nanomaterials, they can be considered as promising structures to form organic solar elements.
- Fullerene- and nanotubes sensitization eliminates the free volume between large organic macromolecules. As a result, the organic

nanomaterials reveal good mechanical, temperature, and laser strengths. These modern nanomaterials have many covalent C–C bonds which are hard to break and can be compared with diamond in hardness. These materials can be used as promising structures to replace steel.

In the present article, the OL properties have been studied in the C_{60}-, C_{70}-, and CNTs-doped organic thin films, gels, dispersed liquid crystals, solutions based on polyimide, polyvinyl alcohol, prolinol, pyridine, and polyaniline structures under a laser irradiation at wavelengths of 805, 1047, 1080, 1315, and 2940 nm. It has been shown that the systems studied can be applied as laser power attenuators in the near and middle infrared spectral ranges.

2. EXPERIMENTAL

The experiments were performed with 3% solutions of photosensitive components in tetrachloroethane or benzene, which were sensitized by fullerenes (C_{60} and/or C_{70}) with content from 0.2 to 5 wt.% and by CNTs with content from 0.1 to 1.0 wt.%. CNTs were preliminarily treated for 5–30 s in gas-discharge plasma at a frequency of 0.44–40 MHz and a power density of 0.01–0.12 W/cm^3 in an inorganic gas or in a mixture of such gases at a pressure of 0.1–1.13 Torr. Thin films and dispersed liquid crystal cells had thicknesses within 5–10 μm, the solutions or gels were studied in an optical chamber with a thickness varied from 10 to 30 mm.

Pulsed Nd:$YLiF_4$- and Nd:$YAlO_3$- lasers with a pulse width of 8 and 10 ns were applied as the irradiation source to investigate OL at wavelengths of 1047 and 1080 nm, respectively. The femtosecond pulsed irradiation of a quasi-CW Ti-sapphire laser with a pulsewidth of 30 fs, a repetition frequency of 82 MHz, and a power of 150 mW was used to study OL at a wavelength of 805 nm. A photodissociative iodine laser and an Er^{3+}:YAG-laser with pulse widths of 50 ns and 500 microseconds, respectively, were applied to find OL features at wavelengths of 1315 and 2940 nm. Beam energies incident on and transmitted through the sample were measured. The OL scheme was analogous to that presented in paper [8].

3. RESULTS AND DISCUSSION

A general view of the films obtained based on the materials treated is presented in Figure 1 a and b. The homogeneity of the films was investigated with a scanning electron microscope (SEM) HU-11B at an

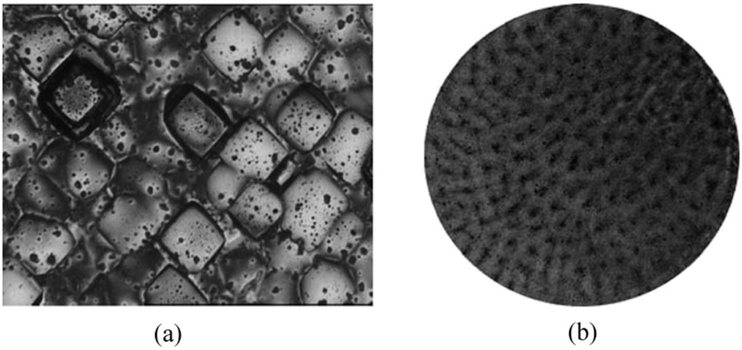

FIGURE 1 General view of the nanotubes-doped thin films on the Si-based (a) and glass (b) substrates.

accelerating voltage of 75 kV. The dependence of the output energy E_{out} on the input one E_{in} for the polyimide thin films with and without initial donor-acceptor interaction is shown in Figure 2. The dependence of the nonlinear attenuation level on the input energy density for nanotube-doped gels based on polyvinyl alcohol is presented in Figure 3. Analyzing the data of Figure 2, one can found that a more pronounced attenuation of the incident beam is related to the absorption of light by charge-transfer complexes in the photosensitive

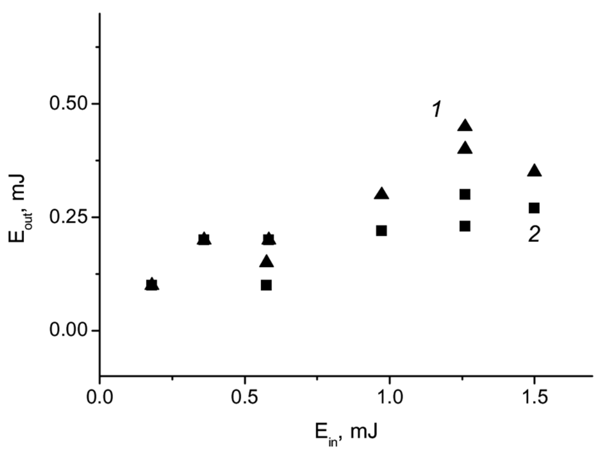

FIGURE 2 Dependence of the output energy (E_{out}) on the input one (E_{in}) for films: (*1*) nonphotosensitive and (*2*) photosensitive polyimide doped with CNTs. The wavelength was 1080 nm, and the laser pulse duration was 10 ns. The laser sport diameter was 1 mm.

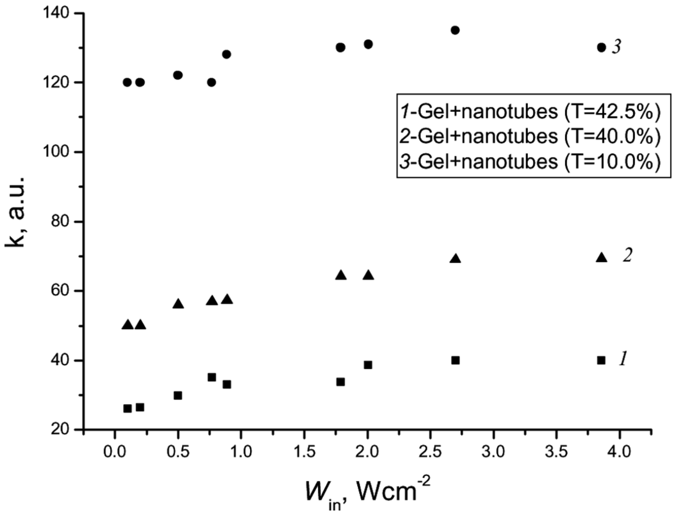

FIGURE 3 Level of nonlinear attenuation on the input energy density for the CNT-doped gel based on polyvinyl alcohol with different initial transmissions. The wavelength was 805 nm, and laser pulse duration was 30 fs. The laser sport diameter was 2 mm.

polyimide matrix. However, the determining contribution to the nonlinear absorption is due to CNTs, which is confirmed by the results of photoconductivity measurements. Indeed, it was established that the current changes from 10^{-13} A in pure matrices to 10^{-6}–10^{-3} A in the CNT-doped matrices at the same bias voltage of 10 V. It should be noted that the enhanced generation of charge in CNTs implies the operation of mechanisms such as the radiation absorption by free charge carriers and the charge transfer between the organic matrix and CNTs, which does not contradict the data in Figure 2. Moreover, a quasi-photonic crystal based on the polyimide-CNT system has been created (see Fig. 1), which requires to discuss an additional laser attenuation mechanism due to the energy losses via diffraction. Really, it has been established in our previous investigations [7,9–11] for the materials doped with nanoobjects that the light-induced change in the refractive index $\Delta n_{laser\text{-}induced} \sim 10^{-3}$ is significantly greater than the thermal component $\Delta n_{therm} \sim 10^{-4} - 10^{-5}$. As a result, the nonlinear third-order susceptibility $\chi^{(3)}$ calculated from the nonlinear laser-induced change in the refractive index has been revealed in the range 10^{-10}–10^{-8} esu for fullerene- or nanotubes-doped organic materials. It has been known that $\chi^{(3)}$ is proportional to the local polarizability and inversely proportional to the considered unit cell volume [12]. Thus,

TABLE 1 Comparative Data on Infrared Optical Limiting

Systems	Initial transmission, %	Wavelength, nm	Pulse duration, ns	OL threshold, $J \cdot cm^{-2}$	Destruction level, $J \cdot cm^{-2}$	Ref.
Composites with Ag nanoparticles		3800–4200	250	0.005–0.025		[14]
2-(n-prolinol)-5-nitropyridine–C_{60}	65–70	2940	500 μs	0.9–1	$\geq$1.5	[15]
Polyimide–C_{70}	~80	1315	50	0.6–0.7	~2	[16]
Polyimide–C_{70}	~80	1315	50	0.08–0.1 (keeping in mind the Xe-lamp irradiation which pumps an iodine laser)	~2	[17]
Liquid crystal–polyaniline–C_{60}	70	1080	10	0.1–0.3	$\geq$0.5	[18]
Stabilized gels based on PVA–CNTs	10–70	1080	10	0.07	>5	Present work
CNTs solution in tetrachloroethane	50–70	1080	10	0.9–2	>5	Present work
Suspension of carbon nanoparticles in water and CS_2	~80	1064	10	0.12–0.7		[19]
Zn-phthalocyanine–C_{60}	75–80	1064	Some ns			[20]
Suspension of carbon nanotubes in water and chloroform	$\geq$90	1064	6	0.15–0.35		[21]
Polyimide–C_{70}	~79–85	1047	8	0.6–0.7	~2.5–3	[22]
Mg-phthalocyanine–C_{60}	70	1047	8	1.5	>3	[23]
Liquid crystal–2-cyclooctylamino-5-nitropyridine–C_{70}	65	805	70 fs		>0.5	[24]
Liquid crystal–polyaniline–C_{60}	67.5–89	805	30 fs	0.09–0.25	>0.5	Present work
Solution of C_{60}	84	710–740	10	2		[25]

due to an increase in the local and general polarizabilities of nanoobjects-doped organic materials, an additional mechanism of the infrared OL can be related to the photorefraction. It is in a good agreement with the data obtained in [13] for $\chi^{(3)}$ of the nanotubes and nanotubes-doped organic systems, where $\chi^{(3)} = 8.5 \times 10^{-8}$ esu has been determined.

Thus, the attenuation of laser radiation by a factor of at least 5 to 10 was achieved in thin-film systems with nanoobjects (for example, with CNTs) in the IR range, and the more than 100-fold decrease in the radiation intensity was observed in the CNT-containing gels at wavelengths of 1080 and 805 nm. A summary of the data obtained in these experiments on the IR OL at other wavelengths is presented in Table 1 in comparison to the results published by other researchers. The manifestations of mechanisms such as the plasmon resonance, laser-induced heating, light-induced complex formation and scattering, multiphoton absorption, absorption by free carriers, and others are considered as the main factors determining the OL in the near- and in the middle-IR spectral range.

4. CONCLUSION

The near and middle infrared optical limiting properties of the fullerene- and nanotubes-doped conjugated organic structures based on polyimide, polyvinyl alcohol, prolinol, pyridine, polyaniline, and polymer-dispersed liquid crystals have been studied to apply these materials as effective nonlinear absorbers in order to protect the human eyes and technical devices from high-intensity laser irradiation. The OL threshold and the level of destruction of different nanomaterials have been found. The basic mechanism responsible for the infrared optical limiting has been discussed. The place of the materials studied among other nonlinear optical systems attenuating the high-energy irradiation in the near and the middle infrared spectral range has been shown.

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