06.1

The intermolecular interaction influence on non-linear optical properties in COANP–carbon nanoparticles system

© S.V. Likhomanova[1,2], N.V. Kamanina [1–3]

[1] JSC S.I. Vavilov State Optical Institute (SOI), St. Petersburg, Russia
[2] St. Petersburg Nuclear Physics Institute, National Research Center Kurchatov Institute, Gatchina, Russia
[3] St. Petersburg State Electrotechnical University „LETI", St. Petersburg, Russia
E-mail: lsv-87@bk.ru

Received August 11, 2021
Revised November 16, 2021
Accepted November 16, 2021

The main results of non-linear optical, spectral and current-voltage characteristics research of pyridine organic conjugated molecule-carbon nanoparticles combined system have been presented. The perspective of these materials further study in global trends of modern search of materials for optical limiting has been demonstrated also in the present paper.

Keywords: fullerenes, charge transfer complex, optical limiting, organic conjugated molecules

DOI: 10.21883/TPL.2022.02.52853.18990

In view of the ever-present need for protection of eyesight (e.g., for pilots of aircraft, etc.) and technical instruments from intense laser irradiation, the search for materials for optical limiting (OL) of laser radiation currently remains relevant. The topicality of this issue is reinforced by the constant expansion of the area of application of laser technology (medicine, education, science, residential use, urban environments). The development of materials engineering technologies for the production of new nanostructures and the modification of already known matrices of nonlinear optics and organic electronics also facilitates the search for new laser protection solutions.

Different organic and inorganic structures and their combinations are presently regarded as candidate media for OL of radiation [1–5]: phthalocyanines, poly(methyl methacrylate), polyimide, dyes, chromophores, biomolecules (exemplified by DNA molecules), and various nanoparticles (specifically, graphene (graphene oxide and reduced graphene oxide), fullerenes (C_{60}, C_{70}, and higher fullerenes), carbon nanotubes (single-walled and multiwalled), quantum dots, nanoparticles of metals and metal oxides, and semiconductor nanoparticles).

Two-photon absorption, scattering induced by the thermal reaction of a medium to laser radiation, free-carrier absorption, saturation backscattering, diffraction-grating scattering due to the photorefractive effect, and several other mechanisms may induce OL. The type of a mechanism manifested in a certain medium depends on the properties of incident laser radiation (its duration, power, operation mode (pulsed or continuous), wavelength) and the medium itself (carbon nanoparticles, metallic nanostructures, organic materials). For example, two-photon absorption [6], the induced photorefractive effect, and the Förster mechanism [7] are likely to be manifested in media irradiated with short (on the order of 100 fs) laser pulses; thermal scattering centers form in liquid media interacting with a long and high-power laser pulse; saturation backscattering is observed when carbon-containing matrices are irradiated with low-energy nanosecond laser pulses; and two-photon absorption manifests itself in such matrices irradiated with more intense laser pulses [8]. Free-carrier absorption is typical of media with metallic nanoparticles [9]. Note that natural media have several mechanisms competing with each other, and their combined action induces nonlinear optical limiting. In view of this, organic sensitized materials with intramolecular complexing are of interest.

Pyridine organic media (2-cyclooctylamino-5-nitropyridine, COANP) sensitized with carbon nanoparticles (fullerenes C_{60} and C_{70} and reduced graphene oxide) and polyimide materials with added C_{60} and C_{70} have been examined in several studies [10]. Continuing the research into the COANP–fullerene system in the present study, we examine solutions of COANP in tetrachloroethane with sensitizer C_{70} (42601, Fullerene powder 98% C_{70}, Alfa Aesar Company) concentrations ranging from 0.5 to 20 wt.% with respect to a dry COANP matrix. Figure 1 presents the values of limiting coefficient $k = W_{in}/W_{out}$ of laser radiation for different COANP concentrations at an incident energy density of $\sim 0.35\,J/cm^2$. The model diagram illustrating the principle of optical limiting is shown in the inset.

Graphene oxide (Graphene oxides Ref.GO.Z.10-1.23, Nanoinnova Technologies) was investigated with the purpose of expanding the range of carbon nanomaterials that could be used as efficient sensitizers for organic molecules. Graphene features unique physical (high carrier mobility, durability, thermal conductivity) and linear and nonlinear optical properties that make it a viable material for nonlinear optics. The COANP–graphene system was examined in our experiments in the form of thin films (3–4 μm). The following photorefractive parameters of the medium were calculated: light-induced refraction coefficient Δn, nonlinear refraction n_2, and nonlinear third-order susceptibility $\chi^{(3)}$ (based on the measurement of the first-order diffraction efficiency). Recording was performed at a spatial frequency of 90–100 mm^{-1}. The following values were determined as a result: $\Delta n = 0.95 \cdot 10^{-2}$, $n_2 = 4.84 \cdot 10^{-10}$ cm^2/W, and $\chi^{(3)} = 1.6 \cdot 10^{-8}$ cm^3/erg.

The presence of third-order nonlinear parameters in media affects self-action processes (self-focusing, defocusing, etc.) and photorefraction, which is understood as the formation of an amplitude-phase diffraction grating shifted in space relative to the interference bands of incident laser radiation. The latter effect may be used to record diffraction gratings, fabricate memory elements, and establish optical limiting, since incident radiation is scattered additionally at diffraction orders.

The formation of an intermolecular charge–transfer complex (CTC) needs to be considered when the mechanisms of optical limiting for systems based on organic molecules sensitized with carbon nanoparticles are analyzed. A COANP molecule consists of donor (NH) and acceptor (NO_2) groups and is an intramolecular CTC. The electron affinity energy for NO_2 is 0.45 eV. Fullerene has an electron affinity energy of 2.67–2.68 eV, which allows it to accumulate the charge from the donor part of a donor–acceptor COANP molecule interacting with it and form an intermolecular CTC. The theoretical possibility of CTC formation in the COANP–fullerene system was analyzed in [11]. The Hartree–Fock method was used to demonstrate the CTC formation in systems with both C_{60} and C_{70}. The CTC formation was verified experimentally in [12,13] through the use of spectrometric and DSC analysis. The obtained spectra demonstrated a bathochromic shift and deepening of color of the studied media. This is attributable to an

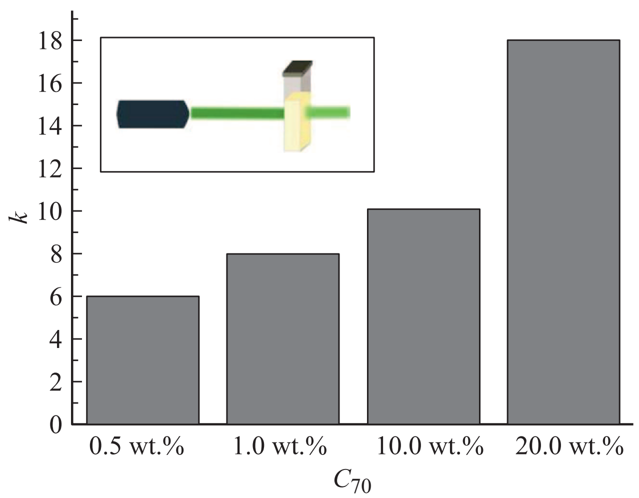

Figure 1. Limiting coefficient k in a 1% COANP solution in tetrachloroethane with concentrations of 0.5, 1.0, 10.0, and 20.0 wt.% of added fullerene C_{70}. The model diagram illustrating the reduction in intensity of visible laser radiation propagating through the studied solution is shown in the inset.

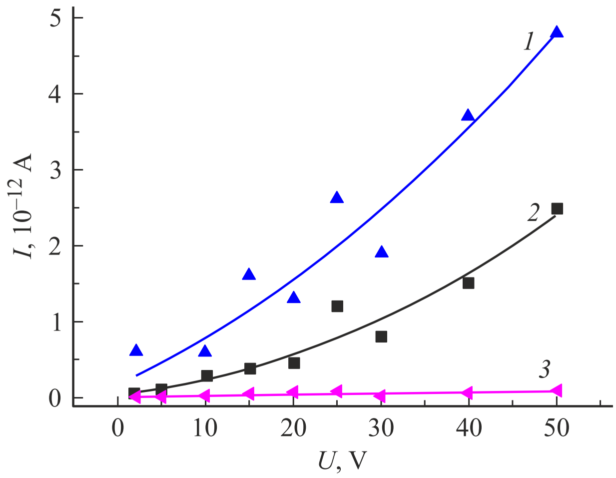

Figure 2. Current–voltage characteristics: *1* — COANP + 5 wt.% C_{70} under irradiation; *2* — COANP + 5 wt.% C_{70}, dark regime; *3* — clean COANP matrix.

electron-density shift induced by the CTC formation. The results of DSC analysis reveal shifts of phase transitions toward higher temperatures occurring when the concentration of C_{70} molecules increases. The measured current–voltage characteristics for COANP and COANP–C_{70} also provide indirect evidence of the CTC formation. The current–voltage characteristics after sensitization with fullerene are nonlinear (curves *1*, *2* in Fig. 2). The obtained results suggest that the carrier mobility and the conductivity increase; this increase is accompanied by effective transition of electrons from the generation region to the unirradiated region with subsequent carrier trapping in the dark region.

Intermolecular CTCs form not only in COANP–fullerene systems, but also in other organic conjugated matrices sensitized with nanostructures with higher electron affinity energies than those corresponding to the case of an intramolecular CTC [14].

Having analyzed the results of recent studies performed around the world for the purpose of discovery of new OL materials, one may conclude that the examined systems are relevant and promising candidates. π-Conjugated organic molecules (COANP) sensitized with carbon nanoparticles (fullerenes, carbon nanotubes, reduced graphene oxide) may be considered as potential materials for nonlinear optics.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A. Kumar Singh, T.-Ch. Jen, Micro and Nanosystems, **13** (1), 74 (2021). DOI: 10.2174/1876402912999200805164359

[2] B.S. Ragunath, K. Sangeetha, R.R. Babu, Cryst. Res. Technol., **55** (4), 1900190 (2020). DOI: 10.1002/crat.201900190

[3] Y.-J. Liu, Q.-H. Li, D.-J. Li, X.-Zh. Zhang, W.-H. Fang, J. Zhang, Angew Chem Int. Ed., **60** (9), 4849 (2021). DOI: 10.1002/anie.202012919
[4] S.J. Varma, J. Kumar, Y. Liu, K. Layne, J. Wu, C. Liang, Y. Nakanishi, A. Aliyan, W. Yang, P.M. Ajayan, J. Thomas, Adv. Opt. Mater., **5** (24), 1700713 (2017). DOI: 10.1002/adom.201700713
[5] C.S. Hege, O. Muller, L. Merlat, J. Appl. Polymer Sci., **136** (10), 47150 (2019). DOI: 10.1002/app.47150
[6] S. Perumbilavil, A. López-Ortega, G. Kumar Tiwari, J. Nogues, T. Endo, R. Philip, Small, **14** (6), 1701001 (2018). DOI: 10.1002/smll.201701001
[7] N.V. Kamanina, S. Putilin, D. Stasel'ko, Synth. Met., **127** (1-3), 129 (2002). DOI: 10.1016/S0379-6779(01)00602-6
[8] R. Kumar, A. Kumar, N. Verma, V. Khopkar, R. Philip, B. Sahoo, Appl. Nano Mater., **3** (9), 8618 (2020). DOI: 10.1021/acsanm.0c01284
[9] P. Nancy, J. Jose, N. Joy, S. Valluvadasan, R. Philip, R. Antoine, S. Thomas, N. Kalarikkal, Nanomaterials, **11** (4), 880 (2021). DOI: 10.3390/nano11040880
[10] N.V. Kamanina, S.V. Serov, N.A. Shurpo, S.V. Likhomanova, J. Mater. Sci.: Mater. Electron., **23** (8), 1538 (2012). DOI: 10.1007/s10854-012-0625-9
[11] N.V. Kamanina, E.F. Sheka, Opt. Spectrosc., **96** (4), 599 (2004). DOI: 10.1134/1.1719152.
[12] S.V. Likhomanova, N.V. Kamanina, J. Opt. Technol., **83** (6), 369 (2016). DOI: 10.1364/JOT.83.000369.
[13] S.V. Likhomanova, N.V. Kamanina, J. Phys.: Conf. Ser., **741** (1), 012146 (2016). DOI: 10.1088/1742-6596/741/1/012146 2016
[14] G. Zhao, G. Wei, W. Zhu, F. Ke, S. Guang, F. Zhang, H. Xu, J. Appl. Polymer Sci., **135** (18), 46100 (2018). DOI: 10.1002/app.46100