MECHANISMS OF THE OPTICAL LIMITING IN THE COANP-FULLERENES AND RELATED SYSTEM

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Abstract.
The mechanisms of the optical limiting (OL) in the two-component medium consisting of the π-conjugated organic molecule 2-cyclooctylamino-5-nitropiridine (COANP) and the carbon nanoparticles (fullerenes, graphene oxide) have been considered in the current work. The influence of an intermolecule charge transfer complex (CTC) on the nonlinear optical parameters increase has been shown as well.

1. Introduction

The π-conjugated organic molecules have unique nonlinear optical properties that make them as the effective applied media for optoelectronic devices. The new synthesis method and the transformation of known organic molecules expand a possibility of using these materials (1,2). Another attractive group for the nonlinear optics (NLO) is the carbon nanomaterials: the carbon allotropes such as fullerenes, carbon nanotubes, graphene/graphene oxide, nanodiamonds, shungite (3,4). A compound of these two molecules groups is of interest for detailed investigation. COANP (2-cyclooctylamino-5-nitropyridine) π-conjugated organic molecule has been considered as a main media in our research (Fig.1).

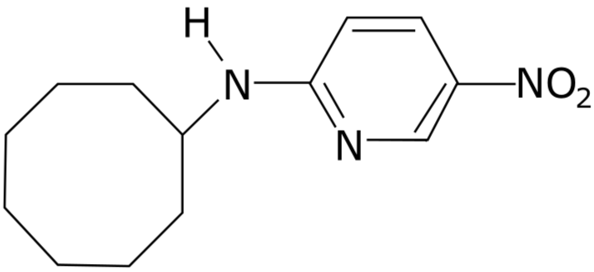


Figure 1. COANP-molecule

The first study of the COANP linearity and nonlinearity properties has been conducted in the work (5). Our scientific group is studying the nonlinear properties the COANP sensitized with the carbon nanoparticles extensively (6-10). We have obtained (7) the laser radiation limiting in the COANP-fullerene C_{70} solution in the tetrachloroethane up to 6-18 times with input energy density from 0.1 J/cm^2 up to 0.6 J/cm^2. These results have been measured up for the solution with 0.5-20 wt.% of C_{70} and with the energy density of 0.35 J/cm^2. The optimal sensitizer concentration has been determinated at the level of 10 wt.%. Another investigated applicable system was liquid crystal (LC) sensitized with the COANP+C_{70} complex. The calculated nonlinear parameters, such as: n_2 *u* $\chi^{(3)}$ were 0,77 × 10^{-10} cm^2/W and 2.4 × 10^{-9}

cm^3/erg (8), respectively. The next step in our investigations was modified not only the volume of the LC cell but the cell substrate surface with the oriented carbon nanotubes (CNT). It has been shown (9) that the transmittance increases up to 10% in the visible and near IR-spectral range. The possibility of the application this system for bio-investigations has been shown in works (10).

2. Experimental condition

To continue and to expand the investigations of the refractivity changes in the organic media sensitized with the carbon nanostructure the graphene oxide has been considered as a sensitizer for COANP. The thin film with the thickness of 3-4 μm of the COANP-graphene oxide material was coated on a glass substrate and the diffraction grating was recorded under the Raman-Nath diffraction conditions at the spatial frequency of 90-100 mm^{-1} on the ones surface using laser radiation with the wavelength of λ = 532 nm and the energy density of 0.2-0.6 J/cm^2 (Fig.2).

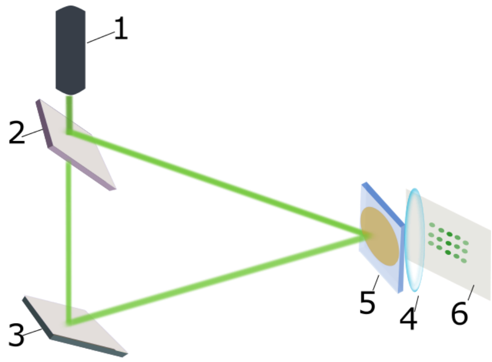


Figure 2. The experimental equipment for diffraction grating record: 1- Nd:YAG-laser, 2 – beamsplitter plate, 3 – mirror, 4 – lens, 5 – sample, 6 – screen

The nonlinear parameters were calculated using well known Akhmanov theory extended on the nanostructured materials in the papers (6,11):

$$\eta = \left(\frac{\pi \Delta n d}{2\lambda}\right)^2$$

$$\Delta n = n_2 I$$

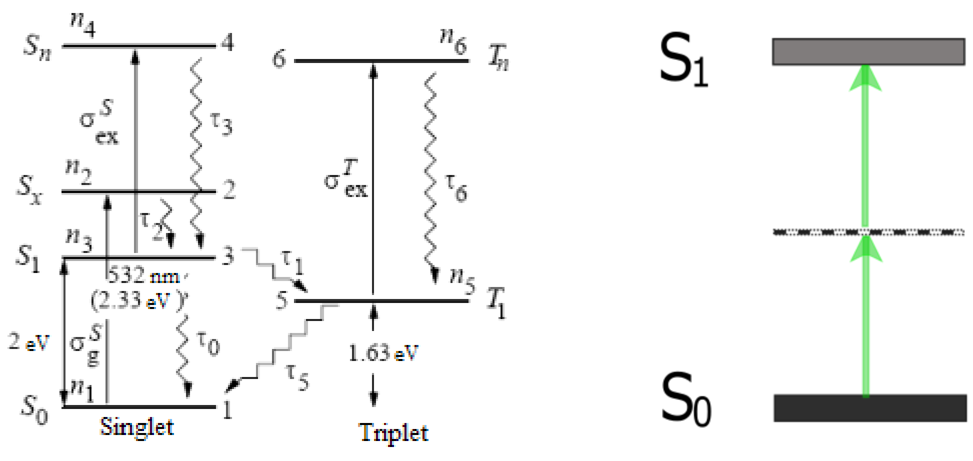
$$\chi^{(3)} = \frac{n_2 n_0 c}{16\pi^2},$$

where η – the diffraction efficiency, Δn – the light induced nonlinear refractive index, n_2 – the nonlinear refractive coefficient, $\chi^{(3)}$ – the third order nonlinear susceptibility, I – the intensity of the laser beam, n_0 – the linear refractive index, c – the light velocity.

3. Results and discussion

The nonlinear optical parameters for thin film of the COANP-graphene oxide are: Δn=0,95$\times 10^{-2}$, n_2=4,84$\times 10^{-10}$ cm^2/W, $\chi^{(3)}$=1,6$\times 10^{-8}$ cm^3/erg. These parameters could be compared with the same parameters for the COANP+fullerenes (n_2=10^{-10}-10^{-9} cm^2/W, $\chi^{(3)}$=10^{-8} – 10^{-9} cm^3/erg) (11) and over the analogous value for the

polyimide sensitized by different carbon nanostructures (n_2=10^{-11}- 10^{-10} cm^2/W, $\chi^{(3)}$=10^{-10} – 10^{-9} cm^3/erg) (12).
Let us to draw the attention on the several mechanisms to explain the nonlinear properties for the π – conjugated organic molecules and carbon nanoparticles.
The thermally induced nonlinear scattering (NLS) based on a Mie scattering theory consists of two possible way. One of them is formation of vapor bubbles and the second NLS way is formation carbon microplasmas. The both way could be realized in carbon nanotubes, nanowires and nanorods solvent due to the intensive input laser beam (13).
For investigated carbon systems (fullerenes and graphene oxide) the mechanism of the reverse saturable absorption (RSA) could be applied as the main OL mechanism. RSA is described with the five energy level (Fig. 3 (a)) and based on a difference in cross sections for the excited and the unexcited fullerene molecule (7). The cross section of the singlet-triplet excited state (σ^S_{ex}, σ^T_{ex}) in the fullerene is larger than the one of the unexcited molecule (σ^S_g). The population of excitation levels increases with the laser energy increase, so the absorption increases.



(a) (b)

Figure 3. (a) The fullerene energy level, (b) The energy level for TPA mechanism

The π-conjugated materials (COANP) posses the two photon absorption mechanism to describe NLO effects. The including a virtual energy level in a molecules energy system explains the possibility of simultaneous two photon absorption (Fig.3 (b)) (14).
To calculate the nonlinear optical parameters by the recording diffraction grating is possible due to high frequency photorefractive Kerr effect. This effect is appeared in the materials that posses the third order nonlinear susceptibility $\chi^{(3)}$. Such materials include COANP-molecule (15) and graphene oxide (16). For OL the recorded lattice diffraction patterns would play the role of the scattering centers.
But the most interesting mechanism for OL is appeared in a combination of two types molecule, namely: COANP and carbon nanoparticles. The π-conjugated organic material COANP is formed by donor-acceptor mechanism: the acceptor fragment of COANP-molecule is NO_2-group that has the electron affinity energy of 0.45 eV. The same parameter for the fullerene C_{60} is 2.67 eV and for C_{70} is 2.68 eV. So the process of the electron transfer from the organic molecule donor-part to the stronger carbon-acceptor is possible and leads to intermolecular charge transfer complex formation (6,17). The intermolecular CTC has the larger distance for the barrier free electron

pathway that provokes the large dipole moment formation and as a result it has revealed the increased absorption cross section, large polarization and enlarged nonlinear optical susceptibilities as well. The increased absorption cross section influences on the efficiency growth of RSA mechanism as one of the main mechanism for optical limiting for the fullerenes. The increased nonlinear susceptibilities lead to amplification of the nonlinear optical properties, such as the two-photon absorption and the photorefractive Kerr effect. The formation of the intermolecular CTC has been supported by the results in previous work (7,9).

For case COANP-graphene oxide we should mentioned that the graphene and graphene oxide are well known carbon allotropes in sp^2 – orbital hybridization and their chemical and physical properties are determinated by extended π- system. We assume that the interaction between π-conjugated molecule and graphene oxide leads to formation a new system with increased NLO processes.

4. Conclusion

To summarize the results, it can be concluded that there is a combination of several mechanisms for OL in the investigated materials: RSA, Kerr effect, TPA, but sensitization the π-conjugated organic molecule COANP by carbon nanoparticles: fullerenes and graphene oxide leads to increase all of these mechanisms due to formation a new intermolecular system.

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