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Spatial self-phase modulation of light in liquid dispersions based on conjugates of phthalocyanines and carbon nanotubes

P.N. Vasilevsky[1, 2] ✉, M.S. Savelyev[1], A.Yu. Tolbin[3],
D.I. Ryabkin[4], 1, A.Yu. Gerasimenko[1]

[1] National Research University of Electronic Technology, Moscow, Russia;

[2] Institute of Nanotechnology of Microelectronics of the RAS, Moscow, Russia;

[3] Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry RAS, Moscow, Russia;

[4] I.M. Sechenov First Moscow State Medical University, Moscow, Russia

✉ pavelvasilevs@yandex.ru

Abstract. The growth in the power of laser systems makes the problem of protecting photosensitive elements of optical systems and visual organs from high-intensity radiation an urgent issue. This work explores the possibility of optical limitation of quasi-continuous laser radiation using liquid dispersions of conjugates of phthalocyanines and carbon nanotubes. It has been found that the laser beam passes through the studied materials unchanged at low power (< 100 mW), and then begins to expand with the appearance of an interference pattern. The use of a limiting diaphragm makes it possible to block part of the laser radiation, which leads to the attenuation of the laser radiation passed through the "sample-diaphragm" system. This phenomenon can be used to protect light-sensitive elements in optical systems.

Keywords: laser radiation, carbon nanotubes, phthalocyanines, spatial self-phase modulation, optical limiting

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Пространственная фазовая самомодуляция света в жидких дисперсиях на основе конъюгатов фталоцианинов и углеродных нанотрубок

П.Н. Василевский[1, 2] ✉, М.С. Савельев[1], А.Ю. Толбин[3]
Д.И. Рябкин[4, 1], А.Ю. Герасименко[1]

[1] Национальный исследовательский университет «МИЭТ», Москва, Россия;

[2] Институт нанотехнологий микроэлектроники РАН, Москва, Россия;

[3] Федеральный исследовательский центр проблем химической
физики и медицинской химии РАН, Москва, Россия;

[4] Первый Московский государственный медицинский университет имени И.М. Сеченова, Москва, Россия

✉ pavelvasilevs@yandex.ru

Аннотация. Рост мощности лазерных систем делает актуальной проблему защиты светочувствительных элементов оптических систем и органов зрения от высокоинтенсивного излучения. В данной работе исследуется возможность оптического ограничения квазинепрерывного лазерного излучения с помощью жидких дисперсий конъюгатов фталоцианинов и углеродных нанотрубок. Установлено, что лазерный луч проходит через исследуемые материалы в неизменном виде при малой мощности (< 100 мВт), а затем начинает расширяться с появлением интерференционной картины. Использование ограничительной диафрагмы позволяет блокировать часть лазерного излучения, что приводит к ослаблению лазерного излучения, прошедшего через систему «образец-диафрагма». Это явление можно использовать для защиты светочувствительных элементов оптических систем.

Ключевые слова: лазерное излучение, углеродные нанотрубки, фталоцианины, пространственная самомодуляция фазы, оптическое ограничение

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Introduction

At present, sources of high-intensity laser radiation are widely used in optical systems for industrial [1], medical [2], and scientific [3] purposes. Laser scanning systems (LiDARs) [4], which generate high-intensity radiation and record a return signal, have recently been actively developed. The amplitude of the return echo signal depends on the distance to the scanned object [5]. Thus, if the distance between the lidar and the object is small, the detection system may be blinded or even damaged.

However, the problem of protecting the organs of vision and photosensitive sensors from exposure to high-intensity laser radiation arises [6]. A promising method of protection is the use of passive optical limiters, which are transparent at low intensity and begin to reduce their transmission only when the threshold value is reached.

In this regard, an important task is the search for new nonlinear optical materials, the transmission of which depends on the intensity of the incident laser radiation. Carbon nanotubes (CNTs) and phthalocyanines (Pcs) have unique properties that make them promising for optical limiting [7, 8]. For example, carbon nanotubes and their conjugates have excellent transmission in the UV–Vis region, which indicates the possibility of their broadband application for protection against radiation with different wavelengths [9]. In this work, liquid dispersions of conjugates of metal-free phthalocyanines and single-walled carbon nanotubes (SWCNT+PcHH) were studied under the influence of quasicontinuous femtosecond laser radiation. Pcs molecules can be attached to CNTs through covalent interaction [10, 11] as well as π-π stacking method [12]. However, in the above works, studies of nonlinear optical attenuation based on the effects of nonlinear absorption and scattering were carried out. In this work, for the first time we present results on the study of nonlinear refraction in dispersion based on SWCNT+PcHH conjugates and the possibility of using such effect to attenuate laser radiation.

Materials and Methods

Irradiation was carried out in a quasi-continuous mode. To generate laser radiation, a Coherent Chameleon Ultra titanium-sapphire pulsed femtosecond laser was used. The pulse repetition frequency was 80 MHz, the pulse duration was 140 fs, and the wavelength was 800 nm. The optical path length in the nanodispersed medium was 2 mm. During irradiation, the cuvette was positioned horizontally. To limit the laser radiation, a diaphragm with a diameter of 0.15 cm was installed. The size of the diaphragm was chosen so that the radiation completely passed through it in the absence of a sample.

SWCNT+PcHH were mixed in distilled water and dimethylformamide (DMF). The concentration of nanoparticles in the dispersion was 0.025 mg/mL. To create a homogeneous liquid dispersion, processing was carried out in an ultrasonic homogenizer for 1 hour.

Nonlinear refractive index n_2 and theoretical limiting curves (dependence of output power on input power) were calculated using the Fresnel-Kirchhoff diffraction integral. In general terms the intensity I at the observation point r' placed in the near zone of diffraction (Fresnel zone) can be calculated as:

$$I(r') = \frac{1}{\lambda}\int_{-\infty}^{+\infty} I_0 \exp\left(-\frac{2r^2}{w_0^2}\right) * \exp\left[i\left(-k\frac{(r-r')^2}{2R} + \varphi(r)\right)\right] dr, \tag{1}$$

where λ is the wavelength, w_0 is the radius of the laser beam at the point of exposure, R is the radius of curvature of the wavefront, $\varphi(r)$ is the phase shift. The phase shift in the general case is of the following form:

$$\varphi(r) = \frac{2\pi}{\lambda}\left(\int n dz - \int n_0 dz\right), \tag{2}$$

where $n = n_0 + n_2 I$ is the total refractive index, n_0 is the linear refractive index. The main task is to determine the shape of the phase inhomogeneity during irradiation. When irradiating a thin medium (thickness d is much smaller than the Rayleigh length) using a laser beam with a Gaussian spatial profile (Fig. 1), one can neglect the small beam divergence near the focus inside the medium and consider the phase inhomogeneity in the form of a cylinder. Then $\varphi(r)$ will be defined as:

$$\varphi(r) = \frac{2\pi}{\lambda} n_2 I_0 d \exp\left(-\frac{2r^2}{w_0^2}\right), \tag{3}$$

where I_0 is the total laser beam intensity.

Then, by substituting (3) into (1) and passing from intensity to power, we obtain the final expression for the interference pattern arising from spatial phase self-modulation:

$$I(r') = \frac{1}{\lambda}\frac{2P_0}{w_0^2\pi}\int_{0}^{+\infty} \exp\left(-\frac{2r^2}{w_0^2}\right) * \exp\left[ik\left(-\frac{(r-r')^2}{2R}\right) + n_2\frac{2P_0}{w_0^2\pi} d \exp\left(-\frac{2r^2}{w_0^2}\right)\right] dr. \tag{4}$$

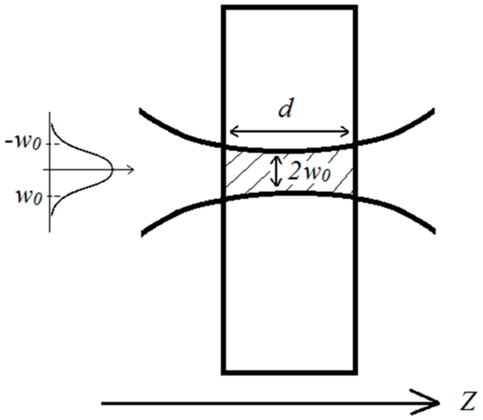

Fig. 1. Irradiation of a thin medium with a focused laser beam

Results and Discussion

To study the limiting power and calculate the nonlinear refractive index using the Fresnel-Kirchhoff diffraction integral, the dependences of the power transmitted through the "sample-diaphragm" system on the incident power as well as spatial profiles were obtained (Fig. 2). Green line in Fig. 2, *a* shows a radius of the diaphragm. It is found that the transmitted power increase linearly at low incident power. However, a sharp decrease in transmission is observed when the incident power reaches ~ 130 mW and ~ 100 mW for dispersion in water and DMF, respectively. This is due to the fact that at these powers the laser beam begins to expand significantly. A further increase in power leads to a further expansion of the beam with the formation of an annular structure. The appearance of such an interference pattern is a consequence of spatial self-phase modulation. In this case, due to the Gaussian shape of the incident beam, the change in the refractive index will be different at different points of the medium, forming a refractive index gradient, which leads to the self-defocusing effect.

At the same time, the phase of the laser radiation changes in the medium, which leads to the appearance of an interference pattern on the screen. The dark areas correspond to radiation that is in antiphase, and the light areas correspond to interference maxima. Fig. 2, *c* shows the wavelike shape of the curve. This is also due to the hitting of the interference maxima and minima. Based on the results of calculations, the values of the nonlinear refractive index of 0.19 and 0.29 cm^2/MW were obtained for SWCNT+PcHH in water and DMF, respectively.

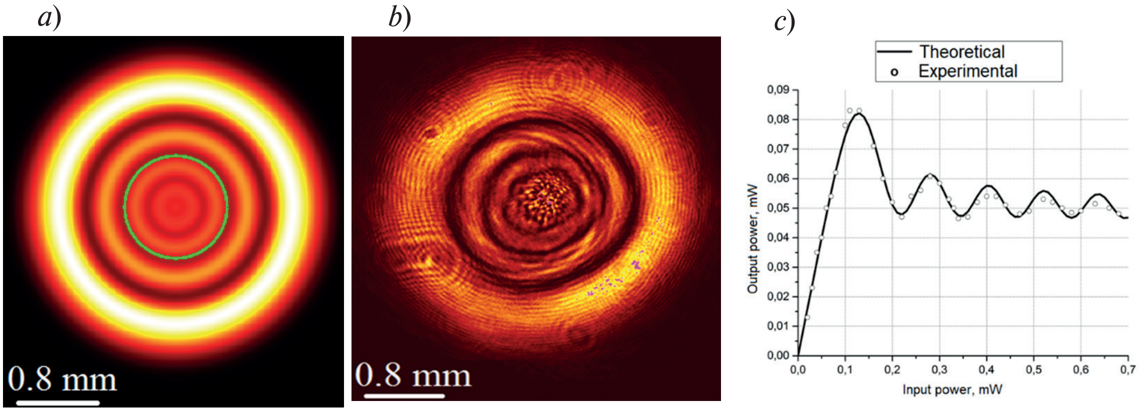

Fig. 2. Theoretical (*a*) and experimental (*b*) shape of the beam passed through the SWCNT+PcHH dispersion in DMF at an incident radiation power of 300 mW and dependence of the transmitted power on the incident power (*c*)

Conclusion

It was shown that the laser beam changes spatial beam profile when a threshold value of the incident power is reached. The appearance of an interference pattern is a consequence of spatial self-phase modulation. The beam expansion can be used to limit the intensity of laser radiation. Thus, SWCNT+PcHH dispersions can be used as an optical limiters for the protection of optical systems sensors and visual organs.

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THE AUTHORS

VASILEVSKY Pavel N.
pavelvasilevs@yandex.ru
ORCID: 0000-0002-5733-8497

SAVELYEV Mikhail S.
nanonlin@yandex.ru
ORCID: 0000-0003-1255-0686

TOLBIN Alexander Yu.
tolbin@inbox.ru
ORCID: 0000-0002-5541-5401

RYABKIN Dmitrii I.
ryabkin@bms.zone
ORCID: 0000-0002-1327-5690

GERASIMENKO Alexander Yu.
gerasimenko@bms.zone
ORCID: 0000-0001-6514-2411

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