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Nonlinear absorption of laser radiation in the carbon nanotubes dispersions in ultraviolet and visible ranges

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Abstract. Carbon nanotubes have unique properties and applications in various fields such as nonlinear optics, flexible electronics, biocompatible composites for tissue repair, etc. The properties of carbon nanotubes can be tuned when exposed to laser radiation. The manifestation of nonlinear absorption properties can improve the methods of formation and processing of materials containing carbon nanotubes. In this work, the properties of nonlinear absorption in the ultraviolet (355 nm) and visible (532 nm) ranges depending on the type of carbon nanotubes and the type of solvent are investigated. The study was performed using the Z-scan method with pulsed exposure (pulse duration is 20 ns). It was shown that the homogeneity of the carbon nanotubes distribution in a liquid medium affects the nonlinear absorption of laser radiation. Single-walled carbon nanotubes in dimethylformamide showed the best nonlinear absorption coefficient and the lowest threshold fluence when the interaction of the medium with laser radiation becomes nonlinear. The demonstrated laser stability of nanotubes also makes them a promising material for laser radiation limiters and nonlinear optical switchers.

Keywords: laser radiation, nonlinear absorption, carbon nanotubes, UV range, visible range, nanosecond pulses, Z-scan

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Нелинейное поглощение лазерного излучения в дисперсии углеродных нанотрубок в ультрафиолетовом и видимом диапазонах

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Аннотация. Углеродные нанотрубки обладают уникальными свойствами и применением в различных областях. Проявление ими свойств нелинейного поглощения позволяет усовершенствовать методы формирования и обработки материалов, содержащих углеродные нанотрубки. В данной работе исследованы свойства нелинейного поглощения в ультрафиолетовом и видимом диапазонах в зависимости от типа углеродных нанотрубок и типа растворителя.

Ключевые слова: лазерное излучение, нелинейное поглощение, углеродные нанотрубки, ультрафиолетовый свет, видимый свет, наносекундные импульсы, Z-сканирование

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Introduction

Experimental study of nonlinear optical properties of nanodispersed media is an urgent task. It is known that optical parameters of condensed media such as absorption and scattering coefficients, as well as the refractive index are often not constant values. In addition to the linear component, they also have a nonlinear component, which depends on the intensity of the laser radiation incident on the medium [1].

Nonlinear optical properties of media affect the change in the parameters of laser radiation transmitted through the medium, such as the energy and power of laser radiation, the spatial shape of the laser beam, the direction of propagation of radiation, etc. In this regard, media with nonlinear optical properties are important for various applications such as optical limiting and switching, laser formation of three-dimensional materials, its processing, etc [2, 3]. The manifestation of nonlinear optical effects in various media depends on the parameters of laser radiation (continuous exposure or exposure to single pulses, duration of laser pulses, their energy, etc.), as well as the nonlinear optical properties of the medium [4]. One of the most promising objects are carbon nanotubes (CNTs), which have a uniform monotonic spectrum of linear optical transmission in the wavelength range from ultraviolet to near infrared radiation [5].

Laser radiation is a convenient tool for creating or precision modifying the surface of composites and nanosystems based on carbon nanotubes [6]. In turn, the increased absorption of laser radiation due to nonlinear processes such as reverse saturable absorption or multiphoton processes opens up new possibilities for laser 3D formation and patterning of CNT-based systems. In this paper, the nonlinear optical properties of dispersed media with single-walled and multi-walled carbon nanotubes were investigated under the influence of pulsed nanosecond laser radiation in the UV and visible ranges.

Materials and Methods

To study the nonlinear optical characteristics, liquid dispersions with CNTs were prepared. Two types of CNTs were used to create dispersions: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). Water and dimethylformamide (DMF) were used as solvents. The mass fraction of the complexes in the dispersion did not exceed 0.004 wt.%. This concentration was chosen so that the linear transmittance was greater than 60%. Ultrasonic treatment with a homogenizer was used to form homogeneous dispersed media. The power of ultrasonic treatment was 300 W and the duration of treatment was 1 h.

The final dispersions were studied by dynamic light scattering (DLS). DLS was performed to determine the hydrodynamic radius of carbon nanotubes, as well as to determine the number of large agglomerates after preparation. The hydrodynamic radius corresponds to the size of the nano-object, based on the assumption of its spherical shape. Since carbon nanoparticles have a shape far from spherical, the values of the hydrodynamic radius for nanotubes only indirectly show the particle size. In this paper, the values of the hydrodynamic radius for nanotubes are used to assess the presence of individual “small” nanoparticles and “large” agglomerates of nanotubes in the dispersed medium. A large number of large agglomerates may indicate an increased contribution of scattering to the overall attenuation pattern, as well as reduced sedimentation stability of the dispersed medium. The obtained values of the hydrodynamic radii of the particles are presented in Table 1. The graph of the scattering intensity dependence on the hydrodynamic radius of nanoparticles for the carbon nanotubes dispersion has a bimodal distribution. The values of the hydrodynamic radius for peak number 1 correspond to individual separate nanoparticles. The values of the hydrodynamic radius for peak number 2 correspond to large agglomerates of carbon nanotubes. In general, it can be noted that SWCNTs show better sedimentation stability compared to MWCNTs. Nanodispersed media, the solvent of which was DMF, showed the smallest contribution of large agglomerates (less than 10%), which indicates the best stability of such dispersions.

Table 1

DLS results for prepared dispersions

Sample	Peak number	Hydrodynamic radius, nm	Contribution to the total scattering, %
SWCNT/water	1	250 ± 39	69
	2	13000 ± 4300	31
SWCNT/DMF	1	251 ± 43	91
	2	13000 ± 5400	9
MWCNT/water	1	312 ± 69	62
	2	21000 ± 5500	38
MWCNT/DMF	1	311 ± 66	78
	2	19000 ± 4200	22

Optical scheme of experimental setup is shown at Fig. 1. The nonlinear optical properties were evaluated by exposure to pulsed laser radiation with a pulse duration of 20 ns (laser LS-2147N-5, Lotis TII, Belarus). During the experiments using the Z-scanning method, the energy of the laser pulse acting on the nanodispersed medium was ≈ 350 μJ. The experiments were performed at wavelengths of 355 and 532 nm. Lenses with a focal length of 10 cm were used to focus the radiation, the radius of the beam at the lens focus was 35 μm. Optical transmission spectra were obtained using a Genesys 10 UV-Vis spectrophotometer (Thermo Fisher Scientific, US).

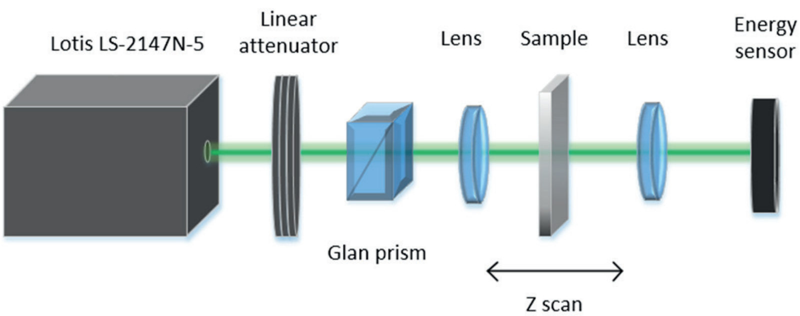

Fig. 1. Optical scheme of experimental setup

Results and Discussion

Experimental dependences of normalized transmittance on the position of the sample relative to the lens focus were obtained as a result of Z-scan experiments. Fig. 2 shows the experimental results for SWCNTs at a wavelength of 532 nm. For each sample studied, a decrease in normalized transmittance (T_{norm}) was obtained when approaching the lens focus. It is worth noting that the decrease in transmittance has a pronounced threshold character. The graphs clearly distinguish the areas of linear (when the normalized transmittance does not change) and nonlinear interaction.

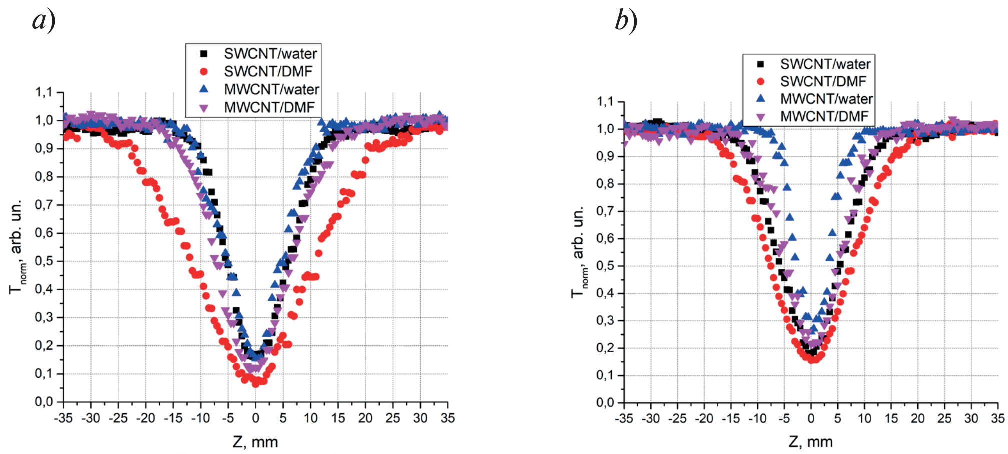

Fig. 2. Dependences of normalized transmittance on Z-axis coordinate for samples at a wavelength of: 532 nm (*a*), 355 nm (*b*)

This phenomenon can be described as follows: the leading edge of the nanosecond pulse acts as an exciter of the medium, itself interacting with the medium linearly. When the medium goes into an excited state, the trailing edge begins to be absorbed much more strongly, which leads to a decrease in the transmittance of the medium.

Based on the experimental dependences obtained, such optical parameters of the studied media as linear absorption, nonlinear absorption, and threshold fluence were calculated. To determine these parameters, the threshold model based on the radiative transfer equation was used [7]. The results are presented in Table 2.

CNTs in DMF showed a larger nonlinear absorption coefficient compared to aqueous dispersions. This is explained by the lower value of surface tension for DMFA. In this way a homogeneous distribution of nanoparticles in the material is achieved, while large agglomerates in aqueous dispersion are slower to enter the excited state.

Table 2

Calculated values of optical coefficients for liquid dispersed media with CNTs

Sample	Wavelength, nm	Linear absorption coefficient, 1/cm	Nonlinear absorption coefficient, cm/GW	Threshold fluence, J/cm^2
SWCNT/water	532	1.54 ± 0.03	70 ± 5	0.2 ± 0.02
	355	1.68 ± 0.03	76 ± 5	0.18 ± 0.02
SWCNT/DMF	532	1.57 ± 0.03	133 ± 7	0.16 ± 0.02
	355	1.68 ± 0.03	108 ± 6	0.15 ± 0.02
MWCNT/water	532	1.57 ± 0.03	68 ± 5	0.21 ± 0.02
	355	1.74 ± 0.03	35 ± 3	0.22 ± 0.03
MWCNT/DMF	532	1.50 ±0.03	95 ± 5	0.19 ± 0.02
	355	1.72 ± 0.03	40 ± 3	0.1 ± 0.02

The studied media demonstrated high laser stability during the experiments. Optical transmission spectra were obtained before and after the Z-scan experiments (Fig. 3). The graphs show no changes in linear transmission (T_0) after laser exposure, which is especially important for optical applications such as nonlinear optical limiters and switches. This also indirectly indicates the prevalence of nonlinear absorption of light over scattering. Nonlinear scattering of light occurs at scattering centers such as laser-induced solvent bubbles [8] or other inhomogeneities that arise under the action of laser radiation, which lead to a change in the linear absorption of the material [9]. In addition, inhomogeneities can lead to a change in the concentration of CNT in the area of influence, which also negatively affects the nonlinear optical properties of dispersion.

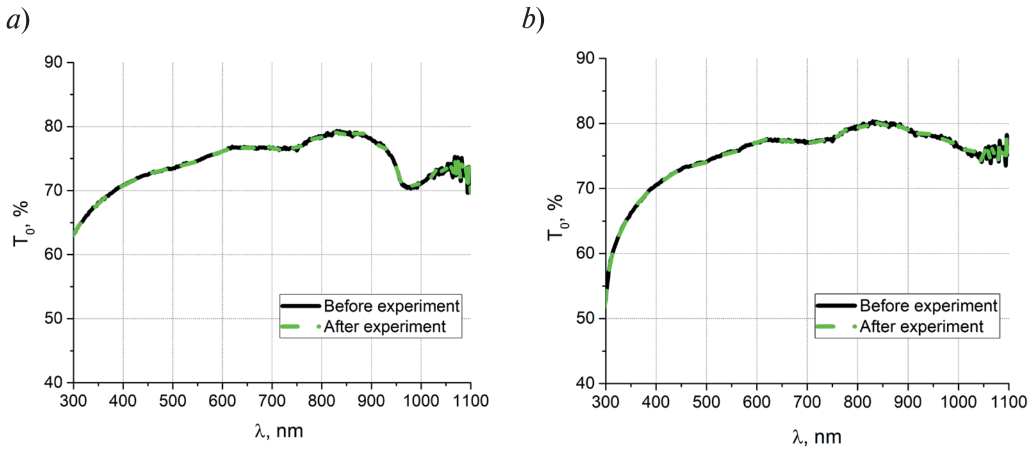

Fig. 3. Optical transmission spectra of dispersed media before and after the experiment: SWCNT/water (*a*), SWCNT/DMF (*b*)

Conclusion

It is shown that SWCNTs in the liquid dispersion medium have better nonlinear absorption properties in comparison with MWCNTs. The choice of solvent is also an important factor that influences the aggregability of nanoparticles in the dispersion. Thus, SWCNTs in solvents with lower surface tension have a greater potential for nonlinear absorption applications. Exposure of the prepared samples to laser radiation does not cause changes in the linear transmission of dispersions.

REFERENCES

1. **Ganeev R.A., Usmanov T.,** Nonlinear-optical parameters of various media, Quantum Electronics. 37 (7) (2007) 605.
2. **Vivien L., Lancon P., Riehl D., Hache F., Anglaret E.,** Carbon nanotubes for optical limiting, Carbon. 10 (40) 2002 1789–1797.
3. **Nair V.S., Pusala A., Hatamimoslehabadi M., Yelleswarapu C.,** Impact of carbon nanotube geometrical volume on nonlinear absorption and scattering properties, Optical Materials. 73 (2017) 306–311.
4. **Sorokina I.T.,** Cr_2^+-doped II–VI materials for lasers and nonlinear optics, Optical Materials. 26 (4) (2004) 395–412.
5. **Kuang Y., Liu J., Sun X.,** Ultrashort single-walled carbon nanotubes: density gradient separation, optical property, and mathematical modeling study, The Journal of Physical Chemistry C. 116 (46) (2012) 24770–24776.
6. **Zhao Y., Han Q., Cheng Z., Jiang L., Qu L.,** Integrated graphene systems by laser irradiation for advanced devices, Nano Today. 12 (2017) 14–30.
7. **Tereshchenko S.A., Savelyev M.S., Podgaetsky V.M., Gerasimenko A.Y., Selishchev S.V.,** Nonlinear threshold effect in the Z-scan method of characterizing limiters for high-intensity laser light, Journal of applied physics. 9 (120) (2016) 093109.
8. **Mansour K., Soileau M.J., Van Stryland E.W.,** Nonlinear optical properties of carbon-black suspensions (ink), Journal of the Optical Society of America B. 9 (7) (1992) 1100–1109.
9. **Côa F., de Souza Delite F., Strauss M., Martinez D.S.T.,** Toxicity mitigation and biodistribution of albumin corona coated graphene oxide and carbon nanotubes in Caenorhabditis elegans, NanoImpact. 27 (2022) 100413.

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