AJP

ISSN : 0971-3093

Vol 30, No 12, December, 2021

ASIAN JOURNAL OF PHYSICS

An International Peer Reviewed Research Journal

Advisory Editors : W. Kiefer, FTS Yu & Maria J Yzuel

Special issue in honour of Prof D V G L Rao

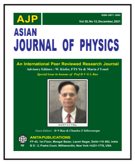
Prof D V G L N Rao

Guest Editors : **D N Rao** & ***Chandra S Yelleswarapu***

ANITA PUBLICATIONS

FF-43, 1st Floor, Mangal Bazar, Laxmi Nagar, Delhi-110 092, India

B O : 2, Pasha Court, Williamsville, New York-14221-1776, USA



Asian Journal of Physics
Vol. 30, No 12 (2021) 1647-1652
Available on: www.asianjournalofphysics.com

Nonlinear optical properties of carbon nanoparticles in sol-gel composites studied by optical and photoacoustic Zscan techniques

I M Kislyakov[1], I M Belousova[1], S K Evstrop'ev[1], T D Murav'eva[1], and C S Yelleswarapu[2]

[1]*S I Vavilov State Optical Institute, Kadetskaya line 5/2, St. Petersburg, 199034, Russia*

[2]*Department of Physics, University of Massachusetts Boston, 100 Morrissey Blvd, Boston, MA 02125, USA*

This article is dedicated to Prof DVGLN Rao

The paper presents optical and photoacoustic Z-scan studies of polymer composites containing fullerene and onion-like Astralen nanoparticles in comparison with their liquid suspensions. Effective nonlinear absorption coefficients obtained from the study manifest a change in nonlinear mechanisms resulting from the liquid-to-solid matrix transition, which give grounds to assert promising prospects of these materials as limiters of laser irradiation.

Keywords: Optical limiting, Z-scan, Photoacoustic Z-scan, Fullerene, Astralen, Polymer matrix, Nanocomposite.

1 Introduction

Carbon nanoparticles are broadly used in nonlinear optics as control elements of high-intensity irradiation. In many cases their nonlinear optical properties are predetermined by energy and kinetic peculiarities of the electronic structure of nanoparticles, which in their characteristics are similar to the structure of dye molecules commonly used in nonlinear optics. It mostly relates to small carbon particles, viz., fullerenes, single-wall carbon nanotubes, and possibly graphene, which have experimentally observable energy levels with pronounced characteristics [1-4]. At the same time some multi-layer nanoparticles with blurry electronic structure (onion-like and polygonal nanoparticles, multi-wall carbon nanotubes, and graphite particles) unexpectedly show conspicuous nonlinear optical properties [5]. The latter are determined by heat conversion properties of irradiation energy absorbance and its dissipation in the medium [6]. These types of materials possess advantages consisting of a broad spectral range of performance, high radiation, and photo-stability [7]. As for their disadvantages, one could point at the high influence of the matrix state on parameters of nonlinear optical effects. Namely, a dominant mechanism of nonlinear optical response, viz., light-induced scattering, is most effectively manifested in a fluid medium that is more or less viscous, while the goals of practical application of carbon nanoparticles in nonlinear optical elements in photonics require their incorporation in solid composites [8-10].

The present communication reports on two types of solid state composite optical materials on the platform of carbon nanoparticles: fullerene C_{60} and multi-layer polygonal onion-like nanoclasters (termed Astralen) [11], introduced in pores of a sol-gel. Optical and Photoacoustic Z-scan techniques were employed to obtain high-reliability complex data on nonlinear optical coefficients of absorption and scattering of solid composite materials in the visual spectral range (λ = 532 nm). We juxtapose results with those relating to analogous liquid compositions (toluene solution of fullerene C_{60} and aqueous suspension of Astralen).

Corresponding author
e mail: iv.kis@mail.ru (Ivan Kislyakov)

2 Experimental details

2.1 Materials

The solid state composites were prepared using (1) solution of fullerene C_{60} (produced by "ILIP" JSC, St. Petersburg, the content of fullerene 99.9%) in toluene of spectroscopic purity, and (2) aqueous suspension of Astralen^{TM} ("Applied Nanotechnologies" JSC, St. Petersburg), stabilized by a surfactant. In addition, we used porous matrix of silicon dioxide, nanosized carbon particles, and organic polymer – poly(methyl methacrylate) (PMMA). Processing of composites included forming monolithic silicon dioxide matrix from a gel mixture (industrially produced silica sol, benchmarked K1; dimethylformamide and a solution of aluminum hydroxide). A volume fraction of organic compounds in the devised composites is 70%, an average pore size being about 10 nm. It was determined by particle sizes of the initial silica sol. Since the carbon nanoparticles had substantially different sizes (0.7 nm for C60 and ca 40 nm for Astralen), their introduction into silica-sol matrix was processed differently. Fullerenes were introduced into already formed solid porous structure of silica-sol from the solution by means of ultrasound processing. Astralen was added to a composite material in the course of its forming. Further, for getting optically transparent material, the porous structure of a xerogel with carbon nanoparticles, inserted into it, upon preliminary vacuum processing was filled with a monomer, MMA, with subsequent polymerization activation. Its layout is shown in Fig 1. Optical transmittance of the samples at a wavelength $\lambda = 532$ nm was 15% for a composite with C_{60} (3.5 mm layer thickness) and 19% for that with Astralen (12.1 mm layer thickness).

Fig 1. Photographs of composites containing C_{60} fullerene (left) and Astralen (middle and right)

2.2 Methods of nonlinear coefficients investigation

Coefficients of nonlinear absorption and scattering were investigated by the Z-scan technique with open and closed apertures, widely applied in nonlinear optics [12] when sample is moving along focused beam direction (Z-axis) with intensity dependence

$$I(Z) = E_p \lambda^{-1} \tau_p^{-1} Z_p^{-1} \left[1 + \left(\frac{z}{Z_0}\right)^2\right]^{-1} \tag{1}$$

where E_p and τ_p are the pulse energy and duration, respectively, and Z_0 is the Rayleigh length. Measurements in liquid media containing carbon nanoparticles were performed in optical cells with 2 mm optical path, which is less than the Rayleigh length, Z_0, of the focused laser beam ($Z_0 \approx 3$ mm). Since the solid samples are thicker than Z_0, we used photoacoustic Z-scan technique (PAZ-scan) for precise determination of their nonlinear coefficients [13,14]. PAZ-scan is based on the detection of the acoustic wave amplitude, the wave results from the relaxation of the absorbed light energy. The acoustic waves were registered using a 10 MHz, 1 inch focal length water immersion ultrasonic transducer (Olympus NDT U8517074). A custom-made sample cell housing unit was used wherein the quartz cell is placed and filled with water for acoustic signal transmission, Fig 2. The output of an pulse-periodic laser source Continuum Minilite II (frequency-doubled Nd:YAG): wavelength $\lambda = 532$ nm, pulse duration $\tau_p = 3$ ns, repetition frequency $f = 10$ Hz, was focused onto the sample using a lens of 18 cm focal length. The sample was mounted on an automated translation stage (Thorlabs NRT 150) and moved horizontally along the z direction through the focal point of the beam over 15 cm in steps of 5 mm. At each position the photoacoustic and optical signals were recorded by averaging the response of 20 laser pulses. Pulse energy was E_p = 35 μJ for all the samples except Astralen ones in optical scanning (E_p = 130 μJ). The beam waist at the focal plane was estimated to be 70 ± 5 mm.

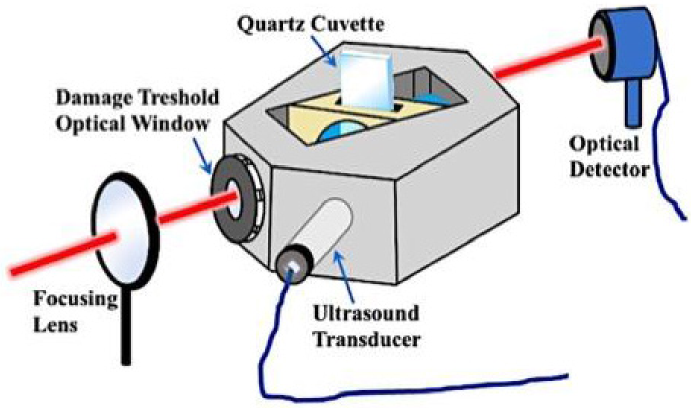


Fig 2. Schematic of the photoacoustic Z-scan setup

3 Result and Discussion

The solution of C_{60} exhibits salient properties of nonlinearity of the refractive index, manifested in closed aperture measurements, while in the Astralen suspension the refractive index nonlinearity was not observed. Moreover, reduction of the aperture area S down to the utmost small values (0.03 S) during Z-scan of the Astralen suspension did not cause any noticeable change of optical limiting parameters. The latter casts in favor of a nonlinear absorption mechanism. In the present work, we did not study nonlinear refractive index of fullerene, which is fairly well studied elsewhere [15]. We focused on analysis and juxtaposition of nonlinear absorption coefficients of fullerene and Astralen in liquid and solid media. They are represented by the open-aperture Z-scan curves (Fig 3). The results have been fitted by theoretical Z-dependent functions of the normalized optical transmittance within assumption of Gaussian distribution of the focused beam intensity [12],

$$T_{norm}(Z) = \sum_{m=1}^{\infty} \frac{-\beta I(Z) L_{eff}}{(m+1)^{3/2}}, \quad L_{eff} = \frac{1-e^{-\alpha L}}{\alpha} \tag{2}$$

for the first nonlinear absorption coefficient, β and

$$T_{norm}(Z) = \sum_{m=1}^{\infty} \frac{(-2\gamma I^2(Z) L'_{eff})^{m-1}}{(2m-1)!\sqrt{(2m-1)}}, \quad L'_{eff} = \frac{1-e^{-2\alpha L}}{2\alpha} \tag{3}$$

for the second nonlinear absorption coefficient, γ. Here, α is the linear absorption coefficient, and L is the sample thickness. Usually, four first terms in the sums in Eqs (2) and (3) are enough to fit the results within the experimental spread.

Photoacoustic Z-scan results are shown in Fig 4. The dependence of photoacoustic signal on Z complies to an expression [13]:

$$T_{norm}(Z) = 1 + \frac{\beta}{\alpha} I(Z) + \frac{\gamma}{\alpha} I^2(Z). \tag{4}$$

Fitting of experimental data in accord with Eqs (2- 4) permitted to estimate nonlinear absorption coefficients.

Their values are given in Table 1.

Table 1. Nonlinear absorption coefficients of the samples

Sample	α, cm^{-1}	β, cm/W	γ, cm^3/W^2
Optical Z-scan results			
C_{60} solution	8.06	$1.21\cdot10^{-7}$	0
C_{60} solution diluted	2.75	$4.6\cdot10^{-8}$	0
C_{60}-doped sol-gel	5.41	$8.2\cdot10^{-9}$	$4.1\cdot10^{-15}$
Astralen suspension	1.0	$6.1\cdot10^{-9}$	$1.3\cdot10^{-17}$
Astralen-doped sol-gel	1.38	$0.7\cdot10^{-9}$	$2.3\cdot10^{-17}$
Photoacoustic Z-scan results			
C_{60}-doped sol-gel	5.41	$5.5\cdot10^{-9}$	$1.2\cdot10^{-16}$
Astralen-doped sol-gel	1.38	$1.7\cdot10^{-9}$	$2.4\cdot10^{-17}$

Nonlinear optical limiting in solutions of C_{60} shows mainly quadratic dependence of transmittance against I_0, determined by coefficient β, which is caused by the reverse saturable absorption (RSA) effect [2]. The proportionality of the coefficient β to the fullerene C_{60} concentration (or α) is demonstrated, which confirms the reliability of the obtained results. Also obtained β values agree with the literature data [1].

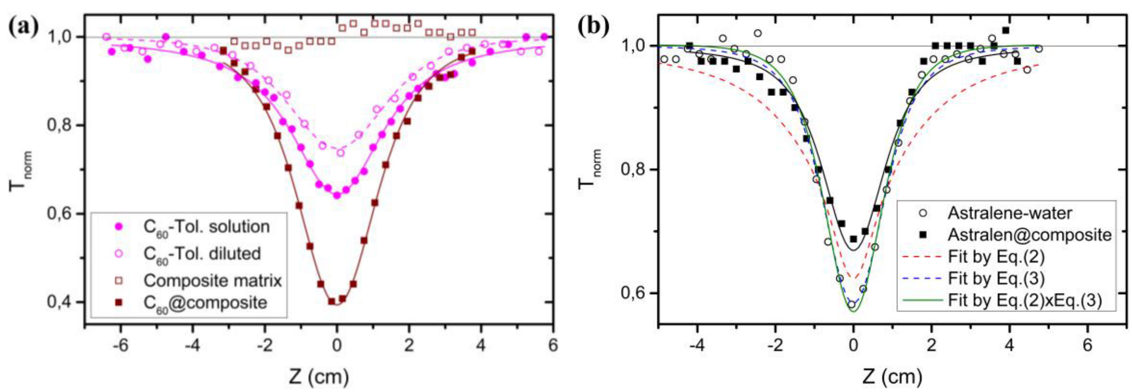


Fig 3. Open-aperture optical Z-scan curves for the systems containing (a) C_{60} fullerene and (b) Astralen.

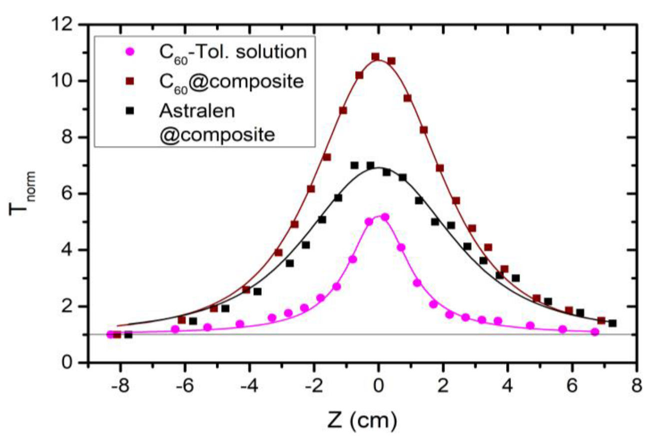


Fig 4. Photoacoustic Z-scan curves for the systems under study.

Samples with a large contribution of nonlinear scattering in the nonlinear Z-scan curves show a better agreement with the theoretical dependence (Eq (3)) described by the second nonlinear coefficient γ. So, using the example of Astralen suspension in Fig 3 (b), we compare approximations by Eq (2), Eq (3) and by both together. It can be seen that the latter option demonstrates a slightly better description of the curve than only by Eq (3), whereas Eq (2) does not correspond to the shape of the curve at all. The same effect we observed earlier in the studies of carbon black suspensions whose nonlinear optical response is determined solely by nonlinear scattering [16].

The β value of C_{60} in solid matrix dramatically falls while the value of the next-order absorption coefficient γ is growing up. This testifies a change in the nature of the nonlinear process. Indeed, RSA conditions are disturbed due to an aggregation-induced perturbation of fullerene triplet levels, so the nonlinearity of the sample is the result of nonlinear scattering, whose Z-scan appearance is better described with the addition of the cubic intensity term.

Optical Z-scan of solid polymer samples gives rather incorrect values of the nonlinear coefficient as a consequence of an error caused by a big sample thickness. Results of the photoacoustic signal processing are not sensitive to the sample thickness and, therefore, allow to obtain adequate values, which for Astralen turn out to be similar to the values in liquid media. The results for Astralen suspensions also reveal a remarkable contribution of the γ-nonlinearity, which implies again the prevalence of the nonlinear scattering under the selected experimental conditions. The nonlinear scattering coefficients are smaller than in C_{60}-composite because of the smaller linear absorption coefficient.

4 Conclusion

We have worked out nonlinear optical composites including nanoparticles of fullerenes and Astralens (multi-layer polygonal onion-like carbon clusters). A study into their nonlinear optical characteristics by methods of optical and photoacoustic Z-scan provided information on effective first and second nonlinear absorption coefficients. We have shown that C_{60} change its nonlinear manifestation from RSA to nonlinear scattering upon aggregation. Nonlinear scattering samples are better described with the addition of a cubic intensity term (the second nonlinear coefficient γ). Values of these coefficients give reason to assert promising prospects of these materials as limiters of laser irradiation.

Acknowledgements

Nonlinear optical measurements have been carried out in the laboratory of Professor DVGLN Rao at UMass under his active support. The authors are grateful to him for his collaboration and guidance over the years. This work was also supported by the Russian Foundation of Basic Research (Grant Nos. #11-03-01106-a, and #13-03-01111-a) and Ministry of Education and Science of Russian Federation (GOSK No. #14.513.12.0003).

References

1. Couris S, Koudoumas E, Rutht A A, Leach S, Concentration and wavelength dependence of the effective third-order susceptibility and optical limiting of C_{60} in toluene solution, *J Phys B: At Mol Opt Phys*, 28(1995)4537–4554.
2. Rao S V, Rao D N, Akkara J A, DeCristofano B S, Rao D V G L N, Dispersion studies of nonlinear absorption in C_{60} using Z-scan, *Chem Phys Lett*, 297(1998)491–498.
3. Chen Y, Bai T, Dong N, Fan F, Zhang S, Zhuang X, Sun J, Zhang B, Zhang X, Wang J, Blau W J, Graphene and its derivatives for laser protection, *Prog Mater Sci*, 84(2016)118–157.
4. Yamashita S, Nonlinear optics in carbon nanotube, graphene, and related 2D materials, *APL Photonics*, 4(2019) 034301; doi.org/10.1063/1.5051796.

5. Kislyakov I M, Arutyunyan N R, Obraztsova E D, Sheiko I S, Povarov S A, Venediktova A V, Yelleswarapu C S, Nonlinear optical studies of SWCNT+ coproporphyrin III hybrid systems. In Advanced Materials Research, (Trans Tech Publications Ltd), 818(2013)132–136.
6. Vivien L, Lancon P, Riehl D, Hache F, Anglaret E, Carbon nanotubes for optical limiting. *Carbon*, 40(2002) 1789–1797.
7. Venediktova A V, Vlasov A Y, Obraztsova E D, Videnichev D A, Kislyakov I M, Sokolova E P, Stability and optical limiting properties of a single wall carbon nanotubes dispersion in a binary water-glycerol solvent, *Appl Phys Lett*, 100(2012)251903; doi.org/10.1063/1.4729790.
8. Zidan M D, Allaf A W, Allahham A, Al-Zier A, Investigation of optical nonlinearity of C-60 doped acetylenedicarboxylic acid polymer, *Opt Laser Technol*, 68(2015)60–66.
9. Nikolaeva A L, Vlasov A Y, Kislyakov I M, Elokhovskiy V Y, Zorin I M, Povarov S A, Nano-carbon in a hydrogel matrix for nonlinear optical applications, *Opt Mater*, 66(2017)338–343.
10. Hussain S A, Comparison of graphene and carbon nanotube saturable absorbers for wavelength and pulse duration tunability, *Sci Rep*, 9(2019)17282; doi.org/10.1038/s41598-019-53686-1.
11. Shames A I, Katz E A, Panich A M, Mogilyansky D, Mogilko E, Grinblat J, Belousov V P, Belousova I M, Ponomarev A N, Structural and magnetic resonance study of astralen nanoparticles, *Diamond Relat Mater*, 18(2009)505–510.
12. Van Stryland E W, Sheik-Bahae M, Z-Scan,/ Characterization Techniques and Tabulations for Organic Nonlinear Materials, (eds) Kuzyk M G, Dirk C W, (Marcel Dekker Inc.),1998, 655–692.
13. Yelleswarapu C S, Kothapalli S-R, Nonlinear photoacoustics for measuring the nonlinear optical absorption coefficient, *Opt Express*, 18(2010) 9020–9025.
14. Yelleswarapu C S, Kothapalli S R, Rao D V, Photoacoustic Z-scan for the measurement of third-order nonlinear absorption coefficient, In Nonlinear Frequency Generation and Conversion: Materials, Devices, and Applications X 2011, (Vol. 7917, p. 79171I), International Society for Optics and Photonics.
15. Ganeev R A, Ryasnyansky A I, Redkorechev V I, Fostiropoulos K, Priebed G, Usmanov T, Variations of nonlinear optical characteristics of C60 thin films at 532 nm, *Opt Commun*, 225(2003)131–139.
16. Kislyakov I M, Yelleswarapu C S, Nonlinear scattering studies of carbon black suspensions using photoacoustic Z-scan technique, *Appl Phys Lett*, 103(2013)151104; doi.org/10.1063/1.4824448

[*Received*: 01.10.2021; *revised recd*: 01.12.2021; *accepted*: 03.12.2021]