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Impact of carbon nanotube geometrical volume on nonlinear absorption and scattering properties

Vijayakumar Sadasivan Nair [1], Aditya Pusala, Maryam Hatamimoslehabadi, Chandra S. Yelleswarapu*

Department of Physics, University of Massachusetts Boston, Boston, MA 02125, United States

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ABSTRACT

Nonlinear optical (NLO) properties of carbon nanostructures are of great interest due to their broadband spectral response. As carbon nanotubes (CNTs) can be synthesized with various lengths, thicknesses, and numbers of layers, their optical properties can also be different. We have performed side-by-side comparative studies of the relationship between the geometrical volume and NLO properties of CNTs. The real and imaginary components of the third order optical nonlinearity are obtained using well-known Z-scan technique. While the transmission and scattered light are detected using photodiodes, the generated photoacoustic signal is recorded simultaneously using an ultrasonic transducer. Results show an inverse relationship between the volume of CNTs and their NLO properties. This can be attributed to the availability of more nanoparticles within the laser beam profile and concurrent generation of scattering sites upon the absorption of incident radiation.

1. Introduction

Recent developments in the design and fabrication of nanoscale photonic devices have attracted significant attention to synthesis and characterization of a variety of nanomaterials such as graphene, carbon nanotubes, semiconductor nanoparticles, metal/dielectric nanocomposites, nanodiamonds, and organic nanostructures [1–6]. In particular, since their discovery by Iijima in 1991 [7], carbon nanotubes (CNTs) have been the subject of many experimental and theoretical studies [8–13]. CNTs are all-carbon nanomaterials with lengths ranging from several hundred nanometers to a few micrometers and diameters of less than 1 nm to tens of nanometers. Their high aspect ratio as well as their excellent mechanical, thermal, and electrical properties have been exploited for applications such as bio-chemical sensors [14], field emitters [15], solar cells [16], optical switches [17], broadband optical limiting, saturable absorbers in a mode-locking element [18–21], and molecular photoacoustic contrast agents for optical imaging [22–25]. Wu et al. reported the effect of aspect ratio on the network structure of CNT/polymer composites and their physical and mechanical properties [26]. Pötschke et al. [27] and Cipiriano et al. [28] observed that CNTs with large aspect ratios impart much higher storage moduli and viscosities compared to those with low aspect ratios. The aspect ratio of CNTs also effects the dielectric behaviour, electric percolation behaviour, and shielding effectiveness of the CNTs and CNT/Polymer composites [29,30].

Due to their wide-band absorption from π-plasmon excitation [31–33], CNTs are considered effective optical power limiting materials and have been extensively investigated both in suspensions and thin films [34–37]. Previous observation of carbon particle heating by laser irradiation lead to the conclusion that the NLO response is due to light scattering from a vapour shell generated around the particle [4,38–40]. Although past studies have demonstrated the influence of structural properties of CNTs such as shape, bundling effects, etc. on their nonlinear optical properties, a side-by-side comparison of CNT length, diameter, and volume with their NLO response is still a motivating topic. Such a systematic study can be extended to other types and shapes of nonlinear materials and may help in identifying practical material for power limiting applications.

We report the impact of dimension (length and diameter) of CNTs on their third order nonlinear optical properties. Optical and photoacoustic (PA) Z-scan techniques were used to study the nonlinear optical properties and photoacoustic response

* Corresponding author.
E-mail address: chandra.yelleswarapu@umb.edu (C.S. Yelleswarapu).
[1] Permanent address: Department of Physics, N. S. S. College Pandalam, Pathanamthitta, 689501, Kerala, India.

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respectively. While the transmitted optical signal was used to obtain the real and imaginary components of the third order optical nonlinearity, the photoacoustic signal informed of generation and transfer of thermal energy. In addition, simultaneous recording of scattered signal amplitude confirmed the nonlinear increase of scattering sites as laser fluence was increased. The results indicate that CNTs with small geometrical volume exhibit strong nonlinearity which can be attributed to the presence of more nanoparticles within the laser beam profile and concurrent generation of scattering sites upon absorption of incident radiation.

2. Material and methods

Carbon nanotubes of various lengths (3 μm and 10 μm) and diameters (15 nm and 30 nm) were purchased from NanoLab Inc (Waltham, MA). The samples are abbreviated as S1 (15 nm, 3 μm), S2 (15 nm, 10 μm), S3 (30 nm, 3 μm) and S4 (30 nm, 10 μm) with structural volume varying as S1<S2<S3<S4. Aqueous suspensions of CNTs were prepared by dispersing the samples in double distilled water with 2 wt% sodium dodecylbenzenesulfonate (SDBS) using ultrasonication for 20 min. The linear optical transmissions of the samples were recorded using an Agilent 8452 spectrometer. In order to ensure a stable nanotube suspension, the linear transmissions of each sample were measured before and after the PAZ-scan experiment and found to be stable over long time periods. Additionally, the particles were uniformly dispersed and no precipitation was observed throughout the experiment. The NLO properties of these samples were characterized using an experimental arrangement as shown in Fig. 1 [41]. A frequency doubled Nd:YAG laser (Minilite II, Continuum) producing 532 nm wavelength pulses of 3 ns pulse width with 10 Hz repetition rate is focused with a 20 cm focal length lens. The sample is placed in a 2 mm quartz cuvette and mounted inside a custom made cell that contains water for ultrasound coupling. The sample cell is oriented at 45° with respect to the incident laser beam resulting in effective optical path length of 2.83 mm. The whole system is mounted on a XYZ translation stage (Thorlabs NRT 150) and translated such that the focal point of the beam is scanned by the sample along the beam direction (Z direction). During the scan, we simultaneously recorded transmitted and scattered optical signals as well as the generated photoacoustic signal [42]. Transmitted light amplitude is recorded by photodiode 1 while scattering light amplitude is recorded by photodiode 2. Concurrently, the absorbed energy is converted into heat. This produces pressure transients and thus wideband ultrasonic emission, which is recorded using a 10 MHz, 0.5 inch element diameter, 1 inch focal length focused water immersion transducer (NDT U8423240, Olympus NDT Inc.).

The thermal diffusion length for a pulsed laser beam is defined as $\mu_s \approx \sqrt{4D\tau_p}$ where D is the thermal diffusivity and τ_p is the pulse width [43]. For water, D is 0.143 × 10^{-6} m^2/s and the thermal diffusion length is calculated as μ_s = 40 nm, which is orders of magnitude smaller than the effective optical path length of the sample (2.83 mm) [44] meaning that for the present study, we are dealing with thermally "thick" samples. Basic equation of photoacoustic signal suggests that the observed PA signal only depends on the absorption and is independent of scattering process. However studies have shown that strong light scattering can change the "effective penetration depth" of the incident light resulting in changes to PA signal magnitude. In the case of thermally thick samples, where thermal diffusion length is less than the optical attenuation length, the heat deposited in the outer layer enhances the acoustic signal.

Assuming a spatial and temporal Gaussian profile for laser pulses, the open aperture (OA) normalized energy transmittance T(Z) is given by Refs. [45,46]

$$T(Z) = \sum_{m=0}^{m=\infty} \frac{\left(-\beta I(Z) L_{eff}\right)^m}{(m+1)^{3/2}}, \quad L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha} \tag{1}$$

where β is the nonlinear absorption coefficient, I(Z) is the laser intensity, L is the sample length and α is the linear absorption coefficient. Similarly, for closed by open curve, the normalized transmittance T(Z) is given by Refs. [45,46]

$$T(Z) = 1 - \frac{4\Delta\phi_0 x}{(x^2+1)(x^2+9)} \tag{2}$$

where $\Delta\phi_0$ is the on-axis nonlinear phase shift at the focus and $x = Z/Z_R$, where Z_R is the Raleigh length. By fitting the optical transmission curves to Equations (1) and (2), values for the third order nonlinear optical susceptibility $\chi^{(3)}$, nonlinear refractive index n_2, and β were estimated [45,46].

Photoacoustic data is fitted to the equation [38]

$$PA(Z) = 1 + \frac{\beta}{\alpha} \frac{E_p}{\tau_p \lambda Z_R \left(1 + \left(\frac{Z}{Z_R}\right)^2\right)} + \frac{\gamma}{\alpha} \left[\frac{E_p}{\tau_p \lambda Z_R \left(1 + \left(\frac{Z}{Z_R}\right)^2\right)}\right]^2 \tag{3}$$

where E_p is pulse energy and γ is the high third-order nonlinear coefficient. From this equation, it is clear that PA measurements can only detect pure light absorptive effects and are independent of the scattering process. However, in the case of thermally thick samples, if the thermal diffusion length is less than the optical attenuation length, the heat deposited in the outer layer enhances the acoustic signal. Hence, in the regime where nonlinear scattering meets this thermal diffusion condition, one can expect an enhanced acoustic signal.

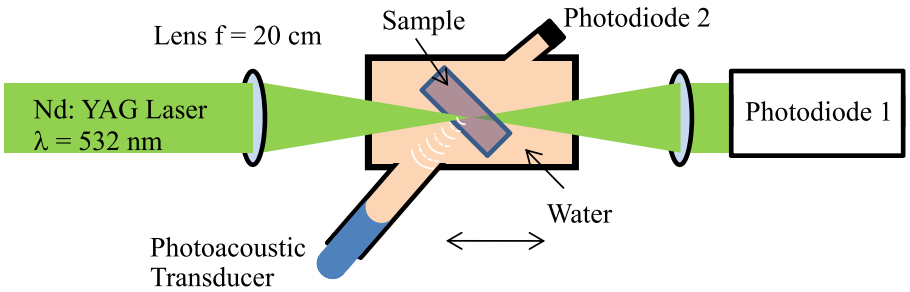

Fig. 1. Schematic of experimental setup used to obtain nonlinear optical transmission, scattering, and photoacoustic data.