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Study of nonlinear optical properties of Carbon nanotubes synthesized by Nickel and Nickel-Cobalt catalysts using Z-scan technique

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ABSTRACT

The nonlinear optical properties of carbon nanotubes (CNTs) have been studied by using the Z-scan technique. Experiments are performed by CW second harmonic of Nd-YAG laser at 532 nm wavelength with a power of 40 mW. The samples are synthesized by the chemical vapor deposition (CVD) method in the presence of Nickel and Nickel-Cobalt catalysts. In this work, for the first time, effect of the type of catalyst has been investigated with CNTs being a set of series single-walled and multi-walled nanotubes with different diameters. Nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) were measured by a closed and open aperture experimental configuration of Z-scan. The experimental results show that the two-photon absorption effect is the dominant nonlinear process in the samples. The results approve the capability of the samples to be used as an optical limiter device. The nonlinear optical refractive index and nonlinear absorption coefficient of samples are in the order of 10^{-6} cm^2/W and 10^{-1} cm/W, respectively. The sign of nonlinear refractive index of the samples is negative which indicates that the sample has acted as a divergent lens.

1 Introduction

Since the discovery of CNTs by the Japanese scientist, Sumio Iijima in 1991[1], they have attracted a huge attention because of their distinctive physical properties and great potential applications. Therefore numerous researchers have encouraged studying their unique properties. CNTs have been introduced as multifunctional transporters in biomedical applications, especially in the field of cancer therapy and diagnosis [2].

The results of several experiments show that CNTs possess very high nonlinear optical susceptibilities. CNTs have notable and ultrafast second and third order nonlinearities and saturation absorption in the near infrared (NIR) and visible regions [3, 4]. Large nonlinear absorption and refraction coefficients of CNTs estimated from femtosecond z-scan measurements [5].

One of the most important properties of nonlinear materials is optical limiting that corresponds to the third-order susceptibility coefficient. Nowadays, protection of the human eye and instruments like sensors, detectors, and other optical components against intense laser beam has attracted great attention. Optical limiting effects in single-wall and multi-wall

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CNTs have been investigated in the infrared and visible spectral regions with nanosecond laser pulses [6 -11].

In this research, we present an experimental study on measuring the nonlinear refractive index and nonlinear absorption coefficient of CNTs samples, which are synthesized by the CVD method in the presence of Nickel and Nickel-Cobalt catalysts by closed and open aperture z-scan arrangement. The z-scan method is a well-known and simple technique for examination of nonlinear properties of matter introduced for the first time in 1989 by M. Sheik-Bahae and his coworkers [12,13].

We have organized our work as follows. After introduction, in Section 2, basic formula of the Z-scan method is explained briefly. In Section 3, the sample preparation and details of the experiments are described as experimental results are discussed. A brief conclusion is given in Section 4.

2 Basic Formula

2.1 Nonlinear refractive index

The Z-scan method is a sensitive and simple method for measuring the nonlinear absorption coefficient and refraction index of nonlinear materials, which are dependent on the intensity of incident light. Schematic of Z-scan experimental setup is shown in Figure 1. As depicted in Figure 1, a lens focuses the Gaussian laser beam and the transmittance of a nonlinear sample is measured through a finite aperture placed in front of the detector D2 while the sample is moving from –z towards the +z or vice versa. Around the focal point, the intensity of transmitted light by the sample on the aperture varies based on the self-focusing or defocusing of optical beam. The transmittance of the nonlinear medium is measured in the far field, as a function of sample position (z) with respect to the focal plane. In Figure 1, a beam splitter (BS) is applied to divide the intensity of the laser beam into two parts. The optical power reflected by the beam splitter measured by detector D1 is taken as the reference beam. The transmittance of the nonlinear sample is normalized by the reference quantity.

In the situation of third order nonlinearity, the refraction index of material is expressed in terms of light intensity [13]:

$$n = n_0 + n_2 I \ , \tag{1}$$

where n_0 is the linear refractive index, I is the light intensity in the material and n_2 is the nonlinear refractive index. In the MKS system of units, I and n_2 are expressed in W/m^2 and m^2/W, respectively.

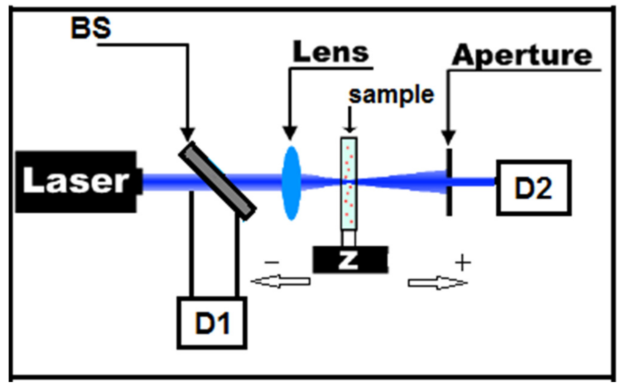

Figure 1. Schematic diagram of Z-scan experimental setup for measuring the nonlinear refractive index of a sample.

The nonlinear refractive index (n_2) may be negative or positive. If $n_2<0$, the sample has a negative lensing effect that leads to more collimation of beam as the sample is moved towards focal point of the lens, thus the transmittance of aperture is increased. As the sample is on the +z side of the focus and moves away from the focal point, the negative lensing effect causes the beam to diverge, which reduces the aperture transmittance. For large $|z|>>0$ the irradiance is reduced and the transmittance returns to the original linear value. This design of z-scan is known as the closed aperture z-scan. The normalized transmittance, T, as a function of z is given by [13]:

$$T(z) = 1 - (4x \ / (x^2 + 9)(x^2 + 1))\Delta\phi_0 \, , \tag{2}$$

with

$$\Delta\phi_0 = k_0 n_2 I_0 L_{eff} \ , \tag{3}$$

where $k_0=2\pi/\lambda_0$ is the wave vector, λ_0 is the wavelength of laser in the free space, I_0 is the intensity of laser at the focal point, $x=z/z_0$ and $z_0=\pi(w_0)^2/\lambda_0$ is the diffraction length of the laser beam, w_0 is the radius of the beam waist at the focus, $L_{eff} = [1-\exp(-\alpha_0 L)]/\alpha_0$, is effective thickness, L is the thickness of sample, and α_0 is the linear absorption coefficient which can be obtained by the following equation which results from the Beer-Lambert law [14]:

$$\alpha_0 = -\frac{1}{L} Ln \frac{I}{I_0}$$

The difference between the normalized peak and valley transmittance in the closed aperture setup, $\Delta T_{p\text{-}v}$, is obtained by [13]:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} \left|\Delta\phi_0\right| \ \ for\ \Delta\phi_0 \le \pi , \qquad (4)$$

where S is the ratio of optical power passing through the aperture. Equation (3) gives the nonlinear refractive index (n_2) values as follows:

$$n_2 = \frac{\lambda_0 \Delta T_{p-v}}{2\pi L_{eff} I_0 [0.406\,(1-s)^{0.25}]}.$$

2.2 Nonlinear absorption

The z-scan method can be applied to measure both the nonlinear refractive index and the nonlinear absorption coefficient of materials [13]. The z-scan setup without aperture (S=1), which is known as the open aperture (OA) setup, is used to study the nonlinear absorption. The absorption in nonlinear materials is related to the saturation absorption or multi-photon absorption or free carrier absorption effects. The dependence of the absorption coefficient of nonlinear materials on the light intensity is as follows:

$$\alpha = \alpha_0 + \beta I , \qquad (5)$$

where β is the nonlinear absorption coefficient. The normalized transmittance as a function of z, for an OA z-scan arrangement is fitted by [13]:

$$T(z, S=1) = \sum_{m=0}^{\infty} \left[-q_0(z)\right]^m / (m+1)^{3/2} \ ,$$

for $|q_0(0)| < 1$, (6)

$$q_0(z) = \beta I_0 L_{eff} / (1 + z^2 / z_0^2) . \qquad (7)$$

3 Experiment

3.1 Preparation of samples

We synthesized CNTs by the CVD method by using two different Nickel and Nickle-Cobalt catalysts. These CNTs have the diameters about 13-100 nm and 27-120 nm, which have been prepared by Nickel and Nickle-Cobalt catalysts, respectively [15, 16]. We mixed 1 mg of CNT with 1 ml of ethanol, and put the mixture in ultrasonic for 30 minutes, to achieve a uniform solution. A quartz cell with 1 mm thickness filled the solution. The cell was holding on an optical rail and moved along the direction of laser beam by an electrical engine.

3.2. Z-scan experiments

The z-scan experiment is performed with a continuous wave Gaussian beam at 532 nm wavelength by using second harmonic of Nd-YAG laser with power of 40 mW. The laser beam is focused to a beam waist of w_0=34 µm with a lens of 5 cm focal length. The transmission for the samples is measured with and without aperture in the far-field of the lens, as the sample moves through the focal point. In the closed aperture configuration, an aperture of 60% transmittance is placed in front of the detector.

The linear absorption coefficient of samples (α_0) are determined by measuring the transmitted power of samples for different and small values of incident power (linear regime) when the sample is placed at the focal point of the lens. To reduce the intensity of the incident beam, different neutral optical filters are used. The sample thickness (L) was 1mm.

4 Results and discussion

Variations of the output power versus the input power of the samples synthesized with Nickel and Nickel-Cobalt catalysts in the weak incident situation are shown in Figures 2a and 2b, respectively. The linear absorption coefficient for the samples synthesized by Nickel and Nickel-Cobalt catalysts were obtained from the slope of the graphs are equal to 0.373 mm^{-1} and 0.089 mm^{-1}, respectively. To obtain the nonlinear absorption coefficient, we used the open aperture z–scan setup. In this arrangement, the aperture will be removed. Thus, the entire transmitted beam from the sample reaches the detector. It is obvious that measurements carried out by the open aperture z-scan method are not sensitive to the nonlinear refractive index. Using the data obtained from the OA z-scan experiment the nonlinear absorption coefficient is obtained as [17]

$$\beta = \left(2\sqrt{2}(1 - T(z) / I_0 L_{eff}\right) \times (1 + \left(z / z_0\right)^2), \qquad (8)$$

where β is the nonlinear absorption coefficient, I_0 (t) is the laser beam intensity at the focus, and z=0. We note that L_{eff} is the effective length of the sample, z_0 is the diffraction length of the Gaussian beam: $z_0=\pi(w_0)^2/\lambda_0$, and T(z) is the normalized transmittance intensity [17]. The radius of beam waist at the focus is $w_0 = (2P/\pi I_0)^{1/2}$, where P is input power of the laser light.

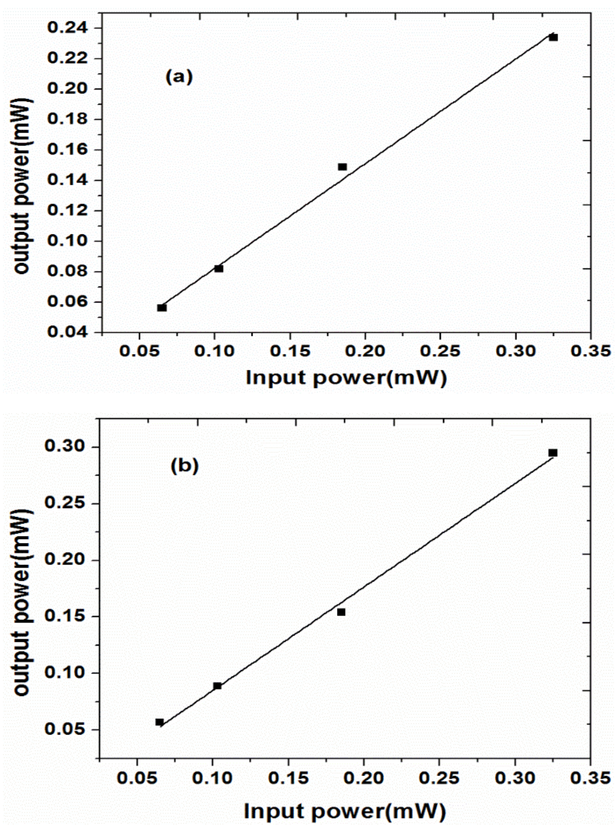

Figure 2. Variations of the output power versus the input power of the samples synthesized by (a) Nickel and (b) Nickel-Cobalt catalysts in the weak incident situation.

Figure 3 shows the experimental data obtained from the OA z-scan for the two samples. The deep in transmission when the sample passes through the focus is the characteristic of two-photon absorption. The nonlinear absorption coefficient of the samples are obtained by Eq. (8) as the values are given in Table 1. We found that, the nonlinear absorption coefficient of the sample synthesized by the Nickel catalyst is almost 6 times greater than the sample synthesized by the Nickel- Cobalt catalyst.

Figure 4 shows the experimental data obtained from CA z-scan for the two samples. The difference between the normalized peak and valley transmittance curve in the closed aperture setup is $\Delta T_{p\text{-}v}$. We determined $\Delta T_{p\text{-}v}$ and obtained the nonlinear refractive index of the samples using Eqs. (3) and (4), as the values are given in Table 1. From the measured closed aperture z-scan data, for both samples, the nonlinear refractive index was obtained as order of 10^{-6} cm^2/W.

Table 1. The calculated nonlinear refractive index and nonlinear absorption coefficient using the Z-scan method.

sample	ΔT_{p-v}	n_2 (cm^2 / W)	β(cm / W)	Ref.
CNT film (Ni)	0.59	9.44×10^{-6}	1.80×10^{-1}	This work
CNT film (Ni/Co)	0.56	7.90×10^{-6}	6.90×10^{-2}	This work
SWCNT/1,2-dichlorobenze suspension	1.95	1.83×10^{-6}	1.94×10^{-3}	[21]
MWCNT/1,2-dichlorobenze suspension	2.80	3.19×10^{-7}	6.93×10^{-4}	[21]

Due to the peak-valley curves, the sign of the nonlinear refractive index of the nanotubes is negative which indicates that the sample has acted as a divergent lens. The results show that the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) of the sample synthesized by the Nickel catalyst (with smaller diameter) are greater than the sample synthesized by the Nickel-Cobalt catalyst (with larger diameter) which are in good agreement with the results of Riggs et al. [18] and Jin et al. [19].

This result is consistent with the nonlinear scattering model as well as formation of micro sized plasmas [19]. The obtained values of nonlinear absorption coefficient and nonlinear refractive index for the samples in our research are more than the calculated nonlinear optical parameters n_2 and β for carbon nanotubes in 1,2-dichlorobenzene [20].

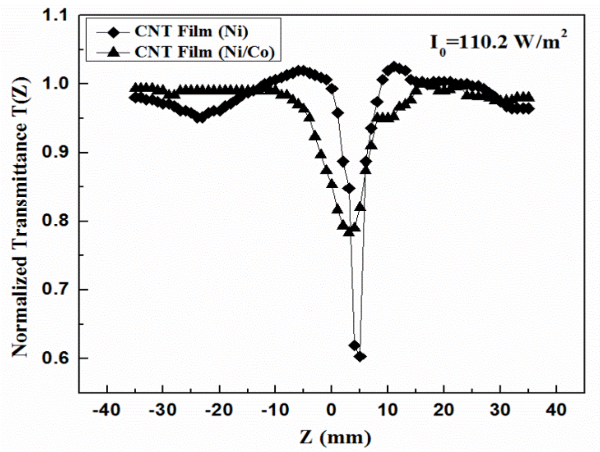

Figure 3. Open-aperture Z-scan curve to measure the nonlinear absorption coefficient of CNTs thin films synthesized by Nickel and Nickel-Cobalt catalysts.

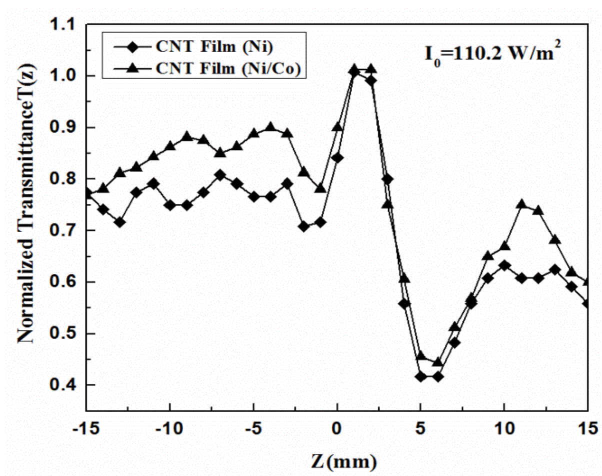

Figure 4. Closed- aperture Z-scan curve to measure the nonlinear refractive index of CNTs thin films synthesized by Nickel and Nickel-Cobalt catalysts.

There are many experimental parameters that are effective on the values of nonlinear refractive index n_2 and nonlinear absorption coefficient β, such as the pulse wavelength and duration of the incident laser, the solvent effect and nanotubes structures, size and length [19, 21-23]. According to the results of this study, we can conclude that CNTs are useful for applications in optical limiting.

5 Conclusions

In this study, the nonlinear refractive index and nonlinear absorption coefficient of the CNTs synthesized with Nickel and Nickel -Cobalt catalysts were determined. For this purpose, we used the z- scan technique, by applying the second harmonic of Nd: YAG laser at the wavelength of 532 nm and an output power of 40 mW. Measurements show that the synthesized CNTs have negative refractive index, which can acted as a divergent lens. In addition, the results indicate that the obtained nonlinear refractive index and nonlinear absorption coefficient of the synthesized sample with Nickel catalyst are greater than the sample synthesized with Nickel and Cobalt catalyst. Since by the particle size reduction, the ratio of surface to volume increases more atoms are involved in the interaction with photons, hence we can concluded that nanotubes with smaller diameters have more nonlinear refractive index and nonlinear absorption coefficient and also have stronger limiting effect.

Acknowledgments

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