Measurement of nonlinear optical parameters of graphene oxide by Z-scan

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Abstract. The behavior of the non-linear refraction index, the non-linear absorption coefficient and the complex value of the third-order electrical susceptibility of a concentrated graphene oxide solution at 50\% m/v and its corresponding dependence on the laser emission power by the Z-scan technique. The value of the non-linear refractive index $\eta_2$, non-linear absorption coefficient $\beta$ and the complex value of the electric susceptibility $\chi^{(3)}$ were obtained directly by quantifying the transmittance Normalized of the solution when exposed to the electromagnetic radiation of a Nd: YAG laser emitting at 532 nm in continuous wave mode. It was found that $\beta$ increases and $\eta_2$ decreases exponentially by increasing the emission power, respectively. In addition, it was observed that for powers greater than 30 mW, the phenomena of saturable absorption and non-linear refraction related to the effects of thermal induction and influence of the phenomenon of self-defocalization of the incident radiation, respectively, are manifested.

1. Introduction

Graphene is a center-symmetric material that is configured by a monolayer of carbon atoms spaced hexagonally on a two-dimensional network (2D) and is the basis of both (3D) graphite and (1D) carbon nanotubes [1]. This material has become a research center due to the potential applications it offers in the field of science and engineering. In materials physics, graphene presents superconductivity at relatively high temperatures at absolute zero. A graphene monolayer absorbs [2] around $\pi \alpha' \approx 2.3\%$ of the incident radiation on its surface, where $\alpha'$ is the absorption coefficient as a function of graphene oxide concentration ($\alpha' = 2.007 \text{ cm}^{-1}$ in this case). Graphene oxide has a fast band of saturable absorption [3] due to a change of the conduction band in the valence band, an adjustment of the thermal properties and the optimal properties and the spectroscopic phenomena of absorption and atomic emission [4]. In addition, this material has a high non-linearity, allows its application as thermal lens, optical limiter, laser mode locking [5] and frequency multiplication [6]. For graphene atoms, only three electrons form bonds $\sigma$ ($sp^2$ hybridization), these bonds are in a plane at 120$^\circ$ to each other, producing a flat structure, in addition, it is common that the fourth electron form weak links and makes graphene an excellent conductor [7].
2. Z-scan

Z-scan technique proposed by Sheik Bahae et al [8] is based on the study of the spatial distortion suffered by the profile of a Gaussian beam in the far-field region during the movement of the cell through the propagation axis +Z through the focus of a lens. The viability of the Z-scan technique to quantify the non-linear responses of a material focuses on the relative simplicity of its implementation and high sensitivity, the Figure 1 shows the experimental set up of the Z-scan system.

![Figure 1. Schematic of the experimental set-up for the Z-scan measurements with a closed-aperture.](image)

The measurement of the non-linear parameters is carried out with the following mathematical expressions [9]:

\[
\Delta T_{pv} = 0.406(1 - S)^{0.25}\Delta \Phi_0
\]

\[
|\Delta \Phi_0| \leq \pi
\]  \hspace{1cm} (1)

\[
\Delta \Phi_0 = \frac{2}{\pi \omega_0^2}k(\lambda)\eta_2L_{ef}P
\]  \hspace{1cm} (2)

where \(\Delta T_{pv}\) in Equation (1) represents the maximum and minimum normalized transmittance difference \(T_p - T_v\) and it depends on the position of the cell and is recorded in a photodetector, \(k(\lambda)\) and \(\omega_0\) are respectively the wave number as a function of wavelength and the beam waist radius of the laser, the latter is proportional to the power \(P\). Equation (2) quantifies the phase change \(\Delta \Phi_0\) of the incident beam, it’s proportional to the non-linear refractive index \(\eta_2\) and the effective length \(L_{ef}\) of the cell containing the solution. Since the intensity of the incident beam is Gaussian distributed over the cell, it is inferred that the non-linear refractive index \(\eta_2\) changes radially in the direction of the wavefront [10].

The complex value of third-order electrical susceptibility is determined by the expression \(\chi^{(3)}_{\beta,\eta_2} = \chi^{(3)}_R(\eta_2) + i\chi^{(3)}_I(\beta)\). Equation (3) provides the real part of \(\chi^{(3)}_{\beta,\eta_2}\), this parameter is responsible for self-focusing [11] or self-defocusing and is given by [8]:

\[
\chi^{(3)}_R = \frac{4}{3}\eta_0\epsilon_0c\eta_2
\]  \hspace{1cm} (3)

where \(\eta_0\) is the linear refractive index of the solution, the speed of light \(c\) and air dielectric constant \(\epsilon_0\). On the other hand, \(\chi^{(3)}_I\) is directly proportional to the non-linear absorption coefficient \(\beta\) and these parameters are related by the expressions [8]:

\[
\chi^{(3)}_I = \frac{\eta_0^2\epsilon_0c\lambda}{3\pi}\beta
\]  \hspace{1cm} (4)
\[
q_0 = \frac{P}{\pi \omega_0^2} \frac{\beta L_{ef}}{\sqrt{2}}
\]  

(5)

From Equation (4) and Equation (5) it is possible to build the electric susceptibility tensor \( \chi^{(3)}_{\beta,\eta_2} \), this physical quantity is characteristic of the material and defines the sensitivity of the material to external electromagnetic disturbances. Since the Z-scan technique is based on the perturbation of the incident beam in the far-field region, the transmittance must be normalized. Often the effects of non-linear absorption (if they exist) and refraction occur simultaneously, the value and sign of \( \Delta \Phi_0 \) are calculated by the theoretical curve for Z-scan configuration with a closed aperture and is defined by the function \([12]\):

\[
T_{\text{closed}}(x, \Delta \Phi_0) = \left( 1 + \frac{4x \Delta \Phi_0}{(x^2 + 1)(x^2 + 9)} \right) T_{\text{open}}(x, q_0)
\]

\[
\left| \frac{q_0}{x^2 + 1} \right| < 1
\]  

(6)

\[
T_{\text{open}}(x, q_0) = 1 - \frac{q_0}{x^2 + 1}
\]  

(7)

with \( x = Z/Z_R \), where \( Z_R \) is the Rayleigh distance. From Equation (6), it is possible to obtain symmetric and anti-symmetric transmittance curves, in general, this behavior is governed by the non-linear absorption, interaction quantified by the Equation (5), while the value and sign of \( q_0 \) are calculated by the theoretical curve of Equation (7).

3. Synthesis and experimental setup

The Figure 2 shows the chemical structure of graphene oxide. This compound was prepared through the modified Hummers method. Briefly, 2 g of graphite powder grade SP-1 (Union Carbide Corporation) were added an Erlenmeyer and followed for slowly addition of 100 mL of sulphuric acid 95-97%. The mixture was subjected to constant stirring at 1000 rpm and 60°C. Then, 9 g of potassium permanganate were added slowly in rates of 0.5 g/min, keeping the temperature at 60 °C. This conditions were maintained during 24 hours. After of this, hydrogen peroxide 30% was added drop by drop for stop the oxidation. Then, we added 500 mL of distillate water and it let to decant during 24 hours at 27 °C. Finally, we eliminate residual acids in graphene oxide by washing and centrifugation up to obtain a pH of 5 and a wish concentration of graphene oxide. Using a continuous wavelength Nd:YAG laser (532 nm) with TEM\(_{00}\), \( \omega_0 = 40 \) μm, \( Z_R = 9.45 \) mm, \( L_{ef} = 0.091 \) mm, \( \eta_0 = 1.333 \) and using variable power, we studied the evolution of non-linear properties in diluted graphene oxide using the Z-scan technique, see set up in Figure 1. The laser radiation was focused by a 100 mm focal lens, while the cell traveled 70 mm starting from -35 mm in reference to the focal point. The laser power was calibrated with a 3A-P-V1 Head RHS sensor and NOVA II power meter. The transmittance of the solution was monitored from a computer and recorded with a Newport LBP-1-USB CCD camera. The graphene oxide absorption spectrum is shown in Figure 3, its was obtained with a UV-VIS EVOLUTION 60S Thermo Scientific spectrophotometer, this allowed us to determine the linear absorption coefficient \( \alpha' \) and infer about the efficiency and effects of the wavelength used in our work. the linear refractive index \( \eta_0 \) was obtained with an Abbe refractometer calibrated with distilled water and room temperature of 26 °C.
4. Experimental results

The normalized transmittance spectra for closed and open aperture Z-scan measurements are shown in Figure 4, it’s observed a quantifiable non-linear refraction responses from 10 mW of laser power, while for powers greater than 30 mW manifest simultaneously with the non-linear absorption due to the thermal induction effect produced by the laser power on the behavior of \( \eta_2 \). It can be seen that graphene oxide has a non-linear refractive index with a negative sign like \( \chi^{(3)} \), which it supposes a domain of the self-defocusing phenomenon as a product of the divergent behavior of the solution by the induced Kerr optical effect. The maximum of transmittance because of \( \beta \) indicates that the absorption type is saturable [13] and the range of powers in which there is greater contribution of the phenomenon is observed. The Table
1 shows the value of the non-linear optical parameters for the solution and the behavior between the non-linear refraction index and the non-linear absorption coefficient follow a characteristic pattern that is not affected with respect to the growth of the power, a pattern that adjusts to an exponential growth and decay in $\beta$ and $\eta_2$, respectively.

![Normalized transmittance for closed and open aperture Z-scan measurements as a function of solution position and $\lambda = 532$ nm in continuous mode. (a) Closed aperture and (b) Open aperture.](image)

**Figure 4.** Normalized transmittance for closed and open aperture Z-scan measurements as a function of solution position and $\lambda = 532$ nm in continuous mode. (a) Closed aperture and (b) Open aperture.

**Table 1.** Non-linear refraction index, non-linear absorption coefficient, real and imaginary susceptibility as a function of power.

| Solution at 50% m/v | $\eta_2$ | $\beta$ | $\chi_R^{(3)}$ | $\chi_I^{(3)}$ |
|---------------------|---------|---------|----------------|----------------|
| Power (mW)          | $(-10^{-9}$ cm$^2$/W) | $(-10^{-5}$ cm/W) | (-10$^{-23}$ esu) | (-10$^{-25}$ esu) |
| 10                  | 8.622   | $q_0 = 0$ | 7.591          | $\beta = 0$    |
| 20                  | 9.268   | $q_0 = 0$ | 8.160          | $\beta = 0$    |
| 30                  | 9.683   | 20.690  | 8.525          | 75.814         |
| 40                  | 10.640  | 13.809  | 9.367          | 50.600         |
| 50                  | 12.540  | 4.360   | 11.041         | 15.976         |

5. Conclusions
The nonlinear parameters were characterized by Z-scan technique for $\lambda = 532$ nm in continuous mode, the normalized curve of transmittance for the nonlinear refractive index and nonlinear absorption coefficient manifested a negative sign. $\chi_R^{(3)}$ and $\chi_I^{(3)}$ was obtained in graphene oxide solution, which decreased the measure of transmittance in the vicinity of the focus, this as a consequence of self-defocusing of the incident beam. In our closed and open aperture Z scan experiments, for powers greater than 30 mW saturable absorption was manifested despite maintaining a constant transmission of 1% ($S = 0.01$).
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