Direct observation of an irradiance dependent nonlinear refraction in CVD single layer graphene

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ABSTRACT

The nonlinear optical properties of single layer graphene are studied via Z-scan. The measurements are carried out at 1045 nm with a 360 femtosecond highly stable Yb doped mode-locked fiber laser. Under laser illumination single-layer graphene exhibits both a transmittance increase due to saturable absorption and a nonlinear phase-shift due to nonlinear refraction. The nonlinear refraction measurements were carried out from 0.5 to 8 GW/cm^2 revealing an expected irradiance-dependent nonlinear refraction. An effective nonlinear refractive index coefficient $\tilde{n}(I)$ is used to describe this and discriminate it from the conventional n_2 coefficient usually measured by Z-scan. The saturation level of the nonlinear phase-shift where the nonlinear response becomes irradiance dependent is deduced from the experimental data.

1. The manuscript

Graphene, a hexagonally symmetric two-dimensional single atomic layer of sp^2-bonded carbon atoms, possesses many exceptional optoelectronic properties which result from its unique band structure at the Dirac point where the valence band meets the conduction band [1–3]. Although it has been known as a theoretical concept for quite some time [4], a single layer has only recently been isolated from bulk graphite and transferred to a dielectric substrate [5]. This enabled the measurement of electrical and optical properties of single-layer graphene (SLG), the first truly two-dimensional atomic crystal, having a thickness of 0.35 ± 0.01 nm [6], and the fundamental unit for all graphitic allotropes.

Graphene presents broadband ultrafast saturable absorption [7,8] as a consequence of Pauli blocking in which carriers generated because of strong optical excitation lead to valence band depletion and conduction band filling, preventing additional absorption. This property led to the extensive use of graphene as a saturable absorption medium for laser mode-locking [9,10].

The gapless dispersion of graphene has led to the prediction of other strong nonlinear optical effects. Recently, broadband four-wave mixing in few-layer graphene has been reported [11]. This allowed the determination of the absolute value of the third-order susceptibility for a single graphene layer, namely $\left|\chi_{gr}^{(3)}\right| \simeq 1.5 \times 10^{-7}$ esu, which

corresponds to an equivalent n_2 of 1.5×10^{-9} cm^2 W^{-1}. This value for the third-order susceptibility is approximately 8 orders of magnitude larger than bulk dielectrics.

In addition, Z-scan measurements revealed a giant nonlinear refraction for few-layer graphene, in the orders of $\sim 10^{-9} - 10^{-7}$ cm^2 W^{-1} [12–15]. However, while most experimental reports demonstrate very high nonlinear refraction in graphene, they do not agree either on the order of magnitude or the sign of the nonlinearity. The reported values span a range of three orders of magnitude, with the sign of the nonlinearity differing between different researchers [12–15].

Recently, Dremetsika, et al. reported on the nonlinear refraction of single-layer graphene in an attempt to elucidate the issues regarding discrepancies in the order of magnitude and sign of the nonlinearity [16]. In the aforementioned work the authors investigate the nonlinear refraction of CVD-grown single-layer graphene via the indirect optical Kerr effect method and the Z-scan technique. They compare their experimental findings with the values found in the literature and they present a discussion on the existing theoretical works. The authors conclude that there is a considerable disagreement between them in terms of both the magnitude and sign of the nonlinearity. It is exactly these disagreements that create the need for additional experimental and theoretical investigations in order to fully resolve the issues of the sign and magnitude of the nonlinear refraction in single-layer graphene. It should be pointed out that the abovementioned work [16] was

limited to a narrow range of excitation irradiances, namely from 0.2 to 0.5 GW/cm^2.

In this work we address these issues of the sign and magnitude of the nonlinearity of graphene from an experimental point of view. Special emphasis is given to the magnitude of the nonlinearity and it is proposed that the discrepancies in the experimental values reported in the literature are affected by an irradiance dependence of the nonlinear refraction. We report on the experimental measurement of the nonlinear optical refraction of undoped CVD-grown single-layer graphene by employing the Z-scan technique over an excitation range from 0.1 to 8 GW/cm^2. We show that the SLG presents a negative irradiance-dependent nonlinear refraction. We distinguish between a low and a high irradiance regime. In the former, the conventional Kerr nonlinear refractive index coefficient n_2 can be deduced, whereas in the latter the nonlinear refraction coefficient becomes irradiance-dependent, which we refer to with the symbol $\tilde{n}(I)$. Although the irradiance-dependent nature of the nonlinear refraction in multilayer graphene has been previously pointed out [12], this is, to the best of our knowledge, the first time that such a saturable behavior of the nonlinear refraction is reported in single-layer graphene.

The irradiance dependence is attributed to the large values of high-order odd terms of the nonlinear susceptibility. More specifically, in a high irradiance regime and as the irradiance is increased after a certain threshold, aside from $\chi_{gr}^{(3)}$, higher order odd terms of the nonlinear susceptibility such as $\chi_{gr}^{(5)}$, $\chi_{gr}^{(7)}$ and so on become significant, leading to the irradiance dependence of the nonlinear refraction. This results in making the conventional n_2 coefficient unsuitable to describe the nonlinear refraction since it is usually related to the $\chi_{gr}^{(3)}$ term of the nonlinear susceptibility.

For experimental investigations of the nonlinear refraction property of graphene it is of great importance to take its irradiance dependence into account. It will have to be established in which regime the experimental values are obtained, namely: (i) at low irradiance before the nonlinear refraction saturates, therefore being described by the conventional n_2 coefficient, or (ii) at high irradiance where the nonlinear refraction saturates, therefore being described by an irradiance-dependent nonlinear refraction coefficient. The range of irradiances used in this work enabled the deduction, from the experimental data, of the saturation level of the nonlinear phase-shift where nonlinear response becomes irradiance dependent.

The CVD-grown graphene film investigated here was prepared by the chemical vapor deposition method [17,18], transferred onto a quartz substrate and characterized by optical microscopy, micro-Raman and absorption spectroscopy. More detailed results and analyses can be found elsewhere [19].

Here it should be noted that, theoretical studies showed that the nonlinear refractive index of doped graphene presents a dependence on the doping level as well [20]. In this work we did not dope our graphene sample, however some unintentional doping arising from the CVD fabrication process and the interaction of the graphene sample with the quartz substrate might be present. By examining the linear transmission spectra of our graphene sample from visible to near-Infrared wavelengths we did not observe any distinct absorption bands verifying that this unintentional doping, if present, is negligible and therefore in the specific work can be disregarded. The linear transmission spectra of our graphene sample from 250 to 2000 nm can be found in the supplementary information section. Additionally, more information on the linear absorption properties can be found in [19] where a detailed characterization of the graphene sample used in this work was performed.

The nonlinear properties of SLG were investigated via the Z-scan technique [21]. The SLG was subjected to femtosecond pulses emitted from a mode-locked Yb-doped fiber oscillator power amplifier system, IMRA$^\circledR$ FCPA μJewel D400 emitting 360 fs pulses at a central wavelength of 1045 nm and a pulse repetition rate of 500 kHz. The beam was focused using a 250 mm focal length BK7 Plano-Convex lens, with
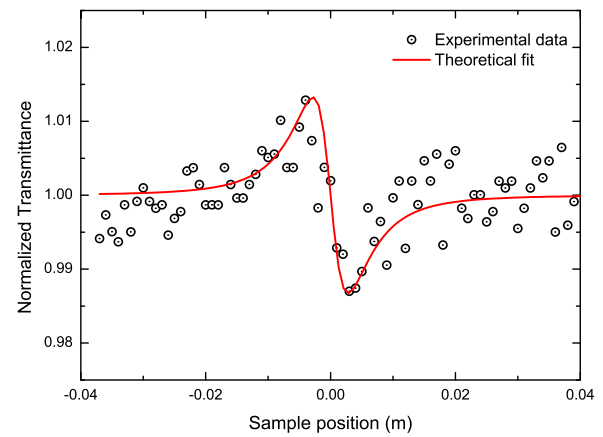

Fig. 1. Divided closed-aperture Z-scan trace for the SLG taken at a pulse energy of 100 nJ, corresponding to an irradiance of 8.14 GW cm^{-2}. The theoretical fit (red line) was calculated using a $\tilde{n}(I)$ coefficient of -6.8×10^{-9} cm^2 W^{-1}.

anti-reflective coating for 1050 nm. The SLG was translated through the focus along the beam path whilst simultaneously recording the far-field transmittance through both open- and closed-aperture detectors. A 3rd reference detector was used before the Z-scan setup to monitor the laser behavior, with the signal from all 3 detectors being directly fed to both a digital oscilloscope and a computer which recorded the reading of each detector for each sample position. All 3 detectors were Thorlabs photodiodes (PDA30G-EC). The waist of the beam along the beam path was measured using the knife-edge technique and was found to be 33 μm at focus. Moreover, the quartz substrate on which the graphene was deposited was translated through the focus along the beam path at the highest irradiances used in this work ($\sim$44 GW cm^{-2}) with no nonlinear absorption or refraction features observed on the open- and closed-aperture detectors, ensuring that the nonlinear response during our Z-scan measurements resulted only from the SLG.

Measurements were performed in two regimes. In an open-aperture regime wherein all the light transmitted through the sample is collected on a detector in the far field and in a closed-aperture regime where only an on-axis portion of the transmitted beam is collected by placing an iris in front of the far-field detector. The open-aperture Z-scan enables the characterization of nonlinear absorption, whereas the closed-aperture Z-scan enables the measurement of the nonlinear phase-shift and therefore the characterization of the nonlinear refraction. However, the effect of the absorptive nonlinearities is present in the closed-aperture trace too. In order to isolate the former from the latter, the closed-aperture trace is divided by the open-aperture trace as explained by Sheik-Bahae et al. in [21]. This yields a typical closed-aperture Z-scan trace, one that would be obtained in the absence of any absorptive nonlinearities. A closed-aperture Z-scan divided by the open-aperture Z-scan trace for the SLG following the above described method, with no averaging or normalization performed after it, is shown in Fig. 1. This trace was taken at a pulse energy of 100 nJ, corresponding to a peak irradiance of 8.14 GW cm^{-2}. The trace of Fig. 1 is characteristic of negative nonlinear refraction demonstrating the negative nature of the refractive nonlinearities in graphene as reported in [13,20,22]. The original open- and closed-aperture Z-scan traces used to obtain the divided Z-scan trace of Fig. 1 are presented in the supplementary information section.

Z-scan measurements under variable optical irradiances were performed. Open-aperture measurements show that the transmittance through the sample has an irradiance-dependent characteristic of saturable absorption. The irradiance versus normalized transmittance (at Z=0) for the SLG is plotted in Fig. 2. In addition, a selection of some of the open-aperture Z-scan traces used to construct Fig. 2 is presented in the supplementary information section. These traces are at increasing
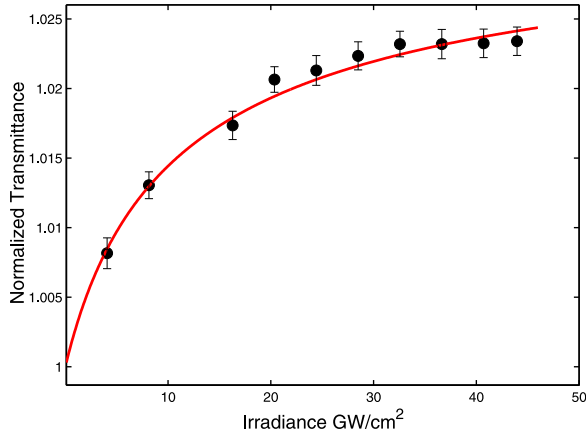
Fig. 2. Change in transmittance with input irradiance for the SLG. The black dots correspond to the experimental data, whereas the solid red line represents the theoretical fit.

Fig. 3. Change in nonlinear refraction with input irradiance for the SLG. The dots represent the experimental data acquired on three different spots on the graphene monolayer, whereas the solid line represents the theoretical fit using Eq. (2). The dashed black line represents the saturation irradiance I_{sat} for the nonlinear refraction.

irradiance levels illustrating the evolution of the saturable absorption in the graphene monolayer.

The maximum transmittance difference for the SLG is $\Delta T \simeq 0.023$ indicating complete saturation of the absorption. The theoretical fit of Fig. 2 was obtained by numerically solving the propagation equation $dI/dz = -\alpha(I) \times I$ for a beam passing through a thin medium which presents both saturable absorption and two-photon absorption (2PA) following the method reported by Wang et al. [23], with the total nonlinear absorption coefficient $\alpha(I)$ at a given incident irradiance I given by: [23,24]

$$a(I) = \frac{a_0}{1 + \frac{I}{I_{sat}}} + \beta I \qquad (1)$$

where α_0 is the linear absorption coefficient, I_{sat} is the saturation irradiance and β is the 2PA coefficient. At the highest irradiances used here, ~44 GW cm^{-2}, no evidence of 2PA was observed, in agreement with Yang et al. [24] who reported negligible 2PA in single-layer graphene. Therefore, the 2PA coefficient in Eq. (1) is zero and the above simulation becomes a simple saturation modeling. The fit yielded a saturation irradiance, $I_{sat} = 5.2$ GW cm^{-2}, in very good agreement with the values reported in [24] for single- and bilayer graphene.

Closed-aperture measurements performed under variable optical irradiances reveal the irradiance dependence of nonlinear refraction. In this high-irradiance regime, the exact modeling would require us to take into account $\chi_{gr}^{(3)}$ and higher order odd terms of the nonlinear susceptibility, such as $\chi_{gr}^{(5)}$ and so on. However, from the experimental data an effective irradiance-dependent nonlinear refractive index $\tilde{n}(I)$ can be derived by fitting each of the closed-aperture Z-scan traces with the simplified closed-aperture fitting formula from Sheik-Bahae et al. [21]; this fitting is shown in Fig. 1. The irradiance-dependent nonlinear refractive index coefficients, $\tilde{n}(I)$, obtained from the fits are plotted against irradiance in Fig. 3.

To ensure the validity of the extracted $\tilde{n}(I)$ coefficients the closed-aperture Z-scans were, for each irradiance level, repeated at least three times both for the same position and also for different positions on the sample. The fitting curve for each closed-aperture trace was then manually adjusted to capture the full magnitude of the nonlinearity. The extracted nonlinear coefficient values from each fit were compared to verify that all fits of traces taken at the same irradiance level give the same nonlinear coefficient value. The $\tilde{n}(I)$ coefficients obtained from closed-aperture Z-scans on different positions on the sample are denoted as sets 1 to 3 and represented with different colors in Fig. 3. The observed nonlinear refraction for the SLG was negative for the
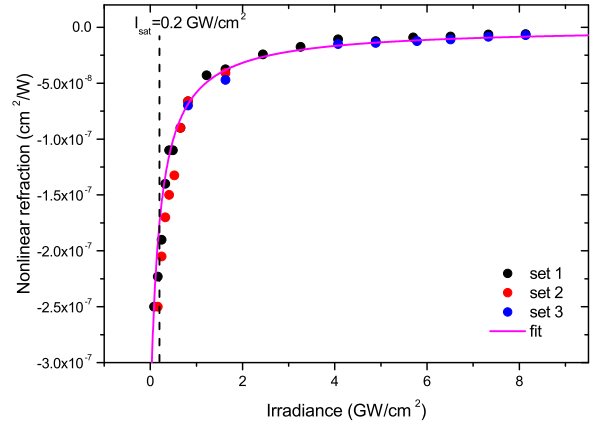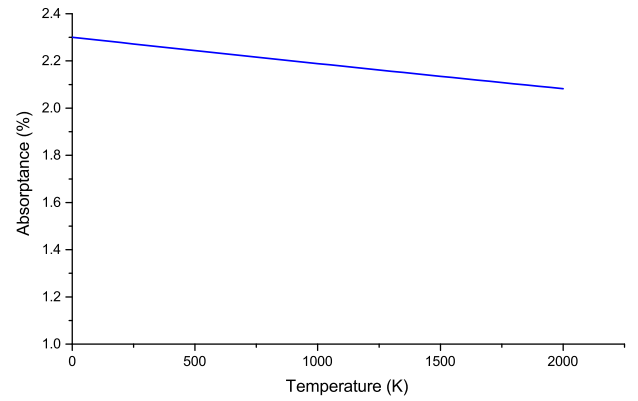

Fig. 4. Change in linear absorption as a function of temperature for single-layer graphene.

whole range of irradiances used in this investigation. One can see that $\tilde{n}(I)$ increases with increasing irradiance or decreases if it is considered in absolute values, until it reaches a constant value of $\tilde{n}(I) \approx -0.9 \times 10^{-8}$ cm^2 W^{-1} for irradiances $I > 5$ GW cm^{-2}.

The experimental data of Fig. 3 show that the nonlinear refraction follows a clear saturation law given by: [25,26]

$$\tilde{n}(I) = \frac{n_2}{1 + \frac{I}{I_{sat}}} \qquad (2)$$

where n_2 is the conventional nonlinear refractive index coefficient, I is the field irradiance and I_{sat} is the saturation irradiance for the nonlinear refraction. The line of best fit yields $n_2 = -3.5 \times 10^{-11}$ m^{2}W^{-1} and $I_{sat} = 0.2$ GW cm^{-2}. When the irradiance is increased, starting from $I > I_{sat} \approx 0.2$ GW cm^{-2} the nonlinear phase-shift saturates and therefore the nonlinear response becomes irradiance dependent. The saturation irradiance for the nonlinear refraction is shown in Fig. 3 with the vertical dashed line.

As the irradiance levels used in this work were very high, a detailed thermal analysis was performed to ensure there is no contribution of thermal effects to the nonlinear measurements. We have investigated the change in the linear absorption of the SLG as a function of the temperature rise. The result is shown in Fig. 4.

As it can be seen the change in absorption is very small even in the case of very high temperatures suggesting that there is no manifestation of thermal effects. More specifically for 0 K the absorption is at 2.3%,

equal to the universal absorption of a single graphene layer, whereas for a temperature rise in the orders of 2000 K the absorption slightly reduces to about 2.08%. Fig. 4 was obtained using the expression we derived from our thermal analysis, namely:

$$A(\omega, T) = A_0 \left(1 + \frac{1}{2\pi} \arctan \frac{2TT_\omega}{T^2 - T_\gamma^2 - T_\omega^2} \right) \tag{3}$$

where T_ω and T_γ are short-hand notation characteristic temperatures given by $T_\omega \equiv \frac{\hbar\omega}{2k_B}$ and $T_\gamma \equiv \frac{\hbar\gamma_2}{2k_B}$ with k_B being the Boltzmann constant and γ_2 being the inverse relaxation time of graphene [27]. The wavelength was chosen to be 1045 nm to match the experimental wavelength, yielding $T_\omega = 6530$ K, whereas the value for the inverse relaxation time was taken to be $\gamma_2 = \frac{1}{20fs} = 5 \times 10^{13}$ s^{-1} [13] yielding $T_\gamma = 188$ K. The analytical derivation of Eq. (3) is included in the supplementary information section.

In summary, we have directly studied the nonlinear phase-shift of CVD single layer graphene via closed-aperture Z-scan measurements under variable irradiances. These revealed a negative irradiance-dependent nonlinear refraction, which follows a clear saturation law. Two irradiance regimes are identified: (i) a low-irradiance regime before the nonlinear refraction saturates, therefore being described by the conventional Kerr nonlinear refractive index coefficient n_2, and (ii) a high-irradiance regime where the nonlinear refraction saturates, therefore being described by an effective irradiance-dependent nonlinear refraction coefficient, $\tilde{n}(I)$. The saturation level of the nonlinear refraction was calculated by using the $\tilde{n}(I)$ coefficient deduced from the experimental data. However, for an accurate measurement of the nonlinear refraction coefficient, at any given irradiance the Z-scan technique should be extended to fully capture the higher order odd terms of the nonlinearity. Additionally, in order to fully resolve the issues of the sign and magnitude of the nonlinear refraction, we believe there is a need for additional investigations in its relation with the chemical potential of graphene, which is also shown to have an effect on both the sign and magnitude of the nonlinear refraction [20].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.optcom.2020.126535.

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