Graphene’s nonlinear-optical physics revealed through exponentially growing self-phase modulation

Nathalie Vermeulen1, David Castelló-Lurbe1,2, Mulham Khoder1, Iwona Pasternak3,4, Aleksandra Krajewska3, Tymoteusz Ciuk3, Włodek Strupinski4, JinLuo Cheng5, Hugo Thienpont1 & Jürgen Van Erps1

Graphene is considered a record-performance nonlinear-optical material on the basis of numerous experiments. The observed strong nonlinear response ascribed to the refractive part of graphene’s electronic third-order susceptibility $\chi^{(3)}$ cannot, however, be explained using the relatively modest $\chi^{(3)}$ value theoretically predicted for the 2D material. Here we solve this long-standing paradox and demonstrate that, rather than $\chi^{(3)}$-based refraction, a complex phenomenon which we call saturable photoexcited-carrier refraction is at the heart of nonlinear-optical interactions in graphene such as self-phase modulation. Saturable photoexcited-carrier refraction is found to enable self-phase modulation of picosecond optical pulses with exponential-like bandwidth growth along graphene-covered waveguides. Our theory allows explanation of these extraordinary experimental results both qualitatively and quantitatively. It also supports the graphene nonlinearities measured in previous self-phase modulation and self-(de)focusing (Z-scan) experiments. This work signifies a paradigm shift in the understanding of 2D-material nonlinearities and finally enables their full exploitation in next-generation nonlinear-optical devices.
Over the past several years numerous experiments have been carried out to study the response of graphene in parametric nonlinear-optical processes like four-wave mixing\textsuperscript{1–5}, third-harmonic generation\textsuperscript{6–9}, self-(de)focusing\textsuperscript{10–12}, and self-phase modulation (SPM)\textsuperscript{13–15}. These measurements mostly pointed at an extremely high effective third-order susceptibility $\chi^{(3)} \propto 10^{-7}$ esu in the 2D material, much higher than what theory predicts for graphene’s electronic third-order susceptibility $\chi^{(3)} \propto 10^{-9}$ esu\textsuperscript{16–19} in the density-matrix framework at the single-particle level\textsuperscript{20,21}. The origin of this large discrepancy between theory and experiments has so far remained unknown, hindering the full exploitation of graphene in nonlinear-optical applications. Several recent experiments also revealed that the sign of graphene’s effective $\chi^{(3)}$ is negative\textsuperscript{10,11,14}, but again without conclusive theoretical support. Hence, both the negative sign of the experimentally observed nonlinearity and its large quantitative discrepancy as compared to the theoretically predicted response have unclear origins at this point. This holds not only for graphene experiments with free-space optical excitation\textsuperscript{1,6–13} but also for the cases where graphene on a photonic chip is examined using waveguided excitation beams\textsuperscript{2–4,13,14}. The latter configuration is particularly interesting from a practical point-of-view as it allows exploring the potential of graphene for next-generation on-chip nonlinear-optical devices (e.g., record-performance on-chip frequency-comb and supercontinuum light sources) opening up new applications in optical telecommunication, biomedical imaging, absorption spectroscopy, and many other domains\textsuperscript{25–26).

To investigate graphene’s intrinsic nonlinear physics, one should ideally be working with a substrate free from any nonlinear-optical effects that could interact with those of the 2D material. In case of graphene-covered photonic chips, the core of the on-chip waveguides should preferably be made of SiO\textsubscript{2} for the larger part, since the nonlinearity of SiO\textsubscript{2} is orders of magnitude smaller than that of other materials typically employed for photonic chip fabrication (Si, InP, Si\textsubscript{3}N\textsubscript{4}, ...\textsuperscript{21,27}) and because its dielectric nature provides electrical isolation of the graphene.

![Figure 1](Image)

**Fig. 1** Illustration of the setup used for the experiments and its constituents. **a** Cross-section of the SiO\textsubscript{2}-core waveguides covered by graphene with poly (methyl methacrylate) (PMMA), and numerically simulated distribution of the electric (E) field intensity. **b** Top-view microscope image of the SiO\textsubscript{2}-core waveguides with regions 1–5 covered by, respectively, 220, 440, 660, 880, and 1100 µm-long graphene sections with PMMA (white areas in center). **c** Temporal power profile and phase profile of the negatively chirped input pulse measured with the frequency-resolved optical gating (FROG) technique (solid curves) and the corresponding fit assuming a quadratic phase profile with $C_0 = -0.2$ and $T_{FWHM,0} = 3$ ps (dashed curves). **d** Waveguide transmission as a function of graphene length as measured (dots) and the corresponding linear fit with slope $\alpha_{eff} = 4605$ m\textsuperscript{-1} (dashed curve). **e** Setup for the transmission and spectral broadening measurements. SMF single-mode fiber, VOA variable optical attenuator, PC polarization controller, OSA optical spectrum analyzer.
In this paper, we solve the long-standing theory-versus-experiments paradox in graphene nonlinear optics by investigating SPM of optical pulses in graphene-covered SiO$_2$-core waveguides. We observe an extraordinary spectral broadening behavior, and demonstrate through an in-depth theoretical and experimental analysis that the underlying nonlinear physics does not depend on refraction induced by graphene’s electronic $\chi^{(3)}$, but instead on a much more intricate phenomenon that we refer to as saturable photoexcited-carrier refraction (SPCR).

**Results**

Spectral broadening in graphene-covered SiO$_2$-core waveguides. The graphene-covered SiO$_2$-core waveguides employed in our experiments, here also referred to as hybrid waveguides, feature a cross-section as illustrated in Fig. 1a. The graphene top layer grown by means of chemical vapor deposition features a carrier density of $6.5 \times 10^{12}$ cm$^{-2}$ as a result of unintentional doping$^{28}$, and is patterned with plasma etching$^{29}$ to create sections with variable length $L$ between 220 and 1100 µm on the waveguides as shown in Fig. 1b. More detailed information on the geometrical properties of the waveguides and the material characteristics of the graphene top layer can be found in Methods, Supplementary Notes 1–2 and Supplementary Figures 1–3. The waveguides’ fundamental quasi-transverse electric (TE) mode is excited with picosecond (ps)-duration input pulses at $\lambda = 1563$ nm in the telecom band (see also Methods). The input can be described by a pulse amplitude $A(0,t) = [A(0,0)|\exp[i\phi(0,t)] = \sqrt{P_0}U(0,t)|\exp[-i\alpha t^2/T_0^2]$ featuring a modest incoupled peak power $P_0$ up to 2.7 W, a temporal shape $U(0,t) = \text{sech}(t/T_0)$, a full-width-at-half-maximum pulse duration $T_{FWHM}$ = 1.76 T0 = 3 ps (Fig. 1c) and a quasi-linear input chirp $\partial_t \phi(0,t) = -(\sim 2\alpha_0 t)/T_0^2$ with a negative chirp parameter $\alpha_0 = -0.2$ (Fig. 1c). We work with negatively chirped input pulses as these allow the graphene to induce the strongest spectral broadening of the pulses in the low-power regime$^{34}$. The resulting broadening factor is defined as the square of the pulses’ rms spectral width$^{30}$ at the waveguide output facet ($z = z_{out}$) divided by the corresponding value at the input ($z = 0$), i.e., $\mu^2 = \mu^2_{\text{out}}/\mu^2_{\text{in}}$ with $\mu_0(z) = (\int_{-\infty}^{\infty} |A|^2 dz)/(\int_{-\infty}^{\infty} |A_0|^2 dz)$. Prior to the broadening experiments, we measure the transmission of the pulses in the hybrid waveguides to characterize the graphene-induced optical absorption as a function of graphene length $L$. We observe a linearly increasing effective loss along graphene length with a slope $\alpha_{\text{eff}} = 4605$ m$^{-1}$ (Fig. 1d). The general experimental setup used for both the transmission and spectral broadening measurements is illustrated in Fig. 1e.

When carrying out the spectral broadening experiments, we observe, as shown in Fig. 2a–c, an extraordinary exponential-like growth of the graphene-induced broadening as a function of its length up to at least $L = 1100$ µm, while its dependence on input power is very weak. In the next sections, we analyze this remarkable behavior to reveal the nonlinear physics taking place in the 2D material.

**Comparison with conventional SPM.** It is widely accepted that spectral broadening of optical pulses in a nonlinear material typically originates from SPM$^{31}$ based on the material’s electronic third-order susceptibility $\chi^{(3)}$. This process relies on the $\chi^{(3)}$-induced nonlinear part of the refractive index $\Delta n_{\text{eff}}(z,t) \propto \chi^{(3)}[A(z,t)]^2$, which impacts the pulse chirp (and hence the spectral width) through the chirp-index relation $\partial_t \phi(z,t) \propto \int_{-\infty}^{\infty} \Delta n(z,t) \partial_z A(z,t) dz$. As such, the chirp induced by conventional $\chi^{(3)}$-based SPM obeys the well-established expression$^{34}$ (after introducing $\tau = t/T_0$ and $|\tilde{U}(\tau)|^2 = |U(0,t)|^2$):

$$\partial_t \phi(z,t) = K P_0 \partial_t |\tilde{U}|^2 [\Theta_1 e^{-\alpha_{\text{eff}} z} \alpha_{\text{eff}}]^0 \quad (1)$$

with the proportionality constant $K = y = \hat{\chi}^{(3)}[\mu_0]$ being the medium’s nonlinear parameter $y$ function of $\chi^{(3)}$ (ref.$^{31,32}$) or function of weighted $\chi^{(3)}$ contributions in case of hybrid waveguides$^{33}$ with $[\Theta_1 e^{-\alpha_{\text{eff}} z} \alpha_{\text{eff}}]^0$ representing the effective length, and with $\Theta_1 = 1$ (the latter function is introduced to facilitate comparison with other chirp formulas further on). The resulting spectral width thus varies linearly with input power $P_0$ and with effective length$^{31}$, leveling off starting from $z > \alpha_{\text{eff}}^{-1}$.

Such dependences on power and length, however, are totally different from those seen in our experiments: indeed, as shown by the dash-dot lines in Figs. 2a, b, conventional-SPM theory cannot provide a qualitative nor quantitative description for the observed exponential-like growth of the broadening all the way to $L = 1100$ µm (i.e., far beyond $z = \alpha_{\text{eff}}^{-1} = 217$ µm), and likewise it cannot provide an adequate description for the measured broadening as a function of power (note that a zoom-in of the conventional-SPM modeling curves is provided in Supplementary Figure 4 and discussed in Supplementary Note 3).

**Confirmation of chirping-based nature.** As the observed spectral broadening in the graphene-covered waveguides cannot be explained quantitatively nor qualitatively by conventional $\chi^{(3)}$, dependent SPM, we have to reconsider the very basics of the process at work and verify whether it is effectively based on chirping or rather on absorption-induced pulse shaping.

If absorption-induced pulse shaping governed the spectral broadening in the graphene-covered waveguides, then the phase $\phi(z,t)$ of the pulse envelope would not change along the propagation path, and when injecting different pulses that share the same input amplitude $|A(0,t)|$, the evolution in $|A(z,t)|$ along the propagation path would be the same as well for these pulses. In that case, when performing broadening experiments for two different input pulses $p_1$ and $p_2$ with opposite input chirp parameters $\mu_{p_1}^0 \approx -\mu_{p_2}^0$ but with the same input amplitude $|A(0,t)|$ (and hence the same $P_0$ and $T_{FWHM}$), the resulting spectral widths $\mu_{p_1}^2(p_1)/\mu_{p_2}^2(p_2)$ along the waveguides would obey the following relation:

$$\mu_{p_1}^2(z) - \mu_{p_2}^2(z) = 4 \left( \left( C_{p_1}^0 \right)^2 - \left( C_{p_2}^0 \right)^2 \right) \int_{-\infty}^{\infty} \left( \frac{t^2}{T_0^2} \right) |A(p_1)(z,t)|^2 dt \approx 0 \quad (2)$$

for all values of $z$. Dividing Eq. (2) by the input spectral width $\mu_{p_1}^2(p_1) \approx \mu_{p_2}^2(p_2) \equiv \mu_{\text{in}}^2$ yields the following relation between the broadening factors $\mu_{p_1}^2(p_1)/\mu_{\text{in}}^2$ for input pulses $p_1$ and $p_2$:

$$\mu_{p_1}^2(z)/\mu_{\text{in}}^2 \approx \mu_{p_2}^2(z)/\mu_{\text{in}}^2 \quad (3)$$

for all values of $z$. Logic tells us then that if in reality the relation of Eq. (3) is not fulfilled for all values of $z$, then the underlying broadening mechanism cannot rely on absorption-induced pulse shaping and instead has to be based on chirping.

With this theory in mind, and taking the input pulse used for Fig. 2a as pulse $p_1$ with $P_0 = 2.7$ W, $T_{FWHM} = 3$ ps, and $C_{p_1}^0 = -0.2$, we subsequently generate a second input pulse $p_2$ with the same peak power and pulse duration and with...
Fig. 2 Results of the broadening experiments. a Broadening factor as a function of graphene length for an incoupled peak power of 2.7 W. b Broadening factor as a function of incoupled peak power indicated in blue, magenta, and green for graphene lengths of 220, 660, and 1100 μm, respectively. Both graphs show the experimental data points (with a measurement error below 5%), the results from our saturable photoexcited-carrier refraction (SPCR) theory (numerical solution from Eqs. (4) and (5), and analytical solution from Eq. (6)), and the results from the theory for conventional self-phase modulation (SPM) using graphene’s strong effective χ(3) = −10−7 esu as extracted from earlier experiments. c Normalized experimental input spectrum and output spectra for graphene lengths of 660 and 1100 μm excited with an incoupled peak power of 2.7 W. The spectra are normalized to their respective peak power values

C_{0}^{(p2)} = +0.2 (Fig. 3a). Hereto, we make use of our pulse-chirp control method which is explained in Methods. Using this newly generated input pulse p2, we again perform spectral broadening measurements with the graphene-covered waveguides, yielding the broadening factors shown in purple in Fig. 3b. There is a very large difference between the broadening data for input pulse p1 shown in black (cf. Fig. 2a) and those for input pulse p2: whereas the former exhibit strong spectral broadening, the latter show spectral narrowing (i.e., broadening factors smaller than 1). In other words, Eq. (3) clearly is not fulfilled, so the dominant broadening process in the graphene-covered waveguides cannot rely on absorption-induced pulse shaping and instead must be based on chirping. In addition, this observation of spectral narrowing for a positively chirped input pulse points at a self-defocusing nonlinearity being at play here. In what follows, we investigate if the underlying physics can be explained by chirping effects induced by photoexcited free carriers in the graphene.

Analysis based on SPCR. While the optical pulses are traveling through the graphene-covered waveguides, they experience graphene-induced optical absorption and as such give rise to photoexcited free carriers with a density \( N_{c}(z, t) \), altering the refractive index \( n_{\text{carriers}} \propto N_{c}(z, t) \) and yielding pulse chirping

\[
\partial_{t} \varphi(z, t) \propto \int_{0}^{t} n_{\text{carriers}}(z', t') \, \text{d}t' \propto \int_{0}^{t} N_{c}(z', t') \, \text{d}t'.
\]

This phenomenon is generally known as free-carrier-refraction (FCR)-induced chirping and has already been studied in waveguides made of 3D-semiconductor materials. Yet, in the specific case of graphene-covered waveguides, FCR-induced chirping turns out to be much more complex than in the 3D-semiconductor-based waveguides where it has been examined so far. The reason is that here the time evolution of \( N_{c} \) along the pulse propagation path strongly depends on the possible occurrence of saturation (i.e., \( N_{c} \sim N_{\text{sat}} \)) in the graphene due to Pauli blocking and therefore we refer to the resulting chirping as ‘saturable photoexcited-carrier refraction (SPCR)’-induced chirping. To model this new phenomenon, we employ the following phenomenological equations for the propagation of the optical pulses in the hybrid waveguides and for the time evolution of the free-carrier density:

\[
\partial_{t} A(z, t) = -\frac{\alpha_{\text{eff}}}{2} A(z, t) - i\sigma_{\text{FCR}} N_{c}^{(\text{SPC})}(z, t)A(z, t) \tag{4}
\]

\[
\partial_{t} N_{c}^{(\text{FCR})}(z, t) = \eta_{\text{IPA}} \frac{\omega}{h} \left[ 1 - \frac{N_{c}^{(\text{FCR})}(z, t)}{N_{\text{sat}}} \right] |A(z, t)|^{2} - \frac{N_{c}^{(\text{FCR})}(z, t)}{\tau_{c}} \tag{5}
\]

In Eq. (4), \( \sigma_{\text{FCR}} \) represents the graphene-induced FCR coefficient, and \( N_{c}^{(\text{SPC})} \) the photoexcited free-carrier density in graphene. We note that there is no explicit free-carrier-induced defocusing nature as phenomenologically observed above, and we have also verified from a physics point of view that for graphene and the free-carrier densities present here the nonlinearity sign is indeed negative.

In the cross-section of the electrically isolating SiO2-core waveguides covered with graphene, the photoexcited carriers can only exist in the graphene top layer. Hence, \( N_{c}^{(\text{FCR})} \) becomes \( N_{c}^{(\text{SPC})} \) as used in Eq. (4), and \( \eta_{\text{IPA}} = \alpha_{\text{eff}} \). We can readily quantify the different parameter values in Eqs. (4) and (5) since they have been measured either in the experiments presented here or in previous works (Table 1). Particularly important is the value of \( \tau_{c} \), which is known to be around 1 ps for photoexcited carriers in graphene on top of a dielectric and thus close to \( T_{0} \).
For comparison we also plot again the broadening factors for input pulse p1 with graphene length (in purple). Both the experimental data points and the results from our saturable photoexcited-carrier refraction (SPCR) theory are shown. As opposed to the chirp for conventional SPM featuring only a fixed-shaped chirp profile,

\[ \partial_z \varphi(z, \tau) = \left[ -\sigma_{\text{FCR}} \frac{a_{\text{eff}} T_c}{\hbar \omega} \right] P_0 \partial_z \left[ U_z^2 \left( \Theta \partial_z e^{-a_{\text{eff}} z} \right) \right] \]

with \( \Theta = 1/(1 + x) \), where \( x = \left( \eta_{1PA} T_c e^{-a_{\text{eff}} z} P_0 \right) / (\hbar \omega N_{\text{sat}}) \). As opposed to the chirp for conventional SPM, the chirp of Eq. (6) does not simply scale linearly with \( P_0 \) in the numerator, but instead exhibits a reduced dependence on the power due to the presence of \( P_0 \) in the denominator of \( \Theta \). This weak power dependence implies that strong broadening with an exponential-like growth over distance can be obtained even at very low input powers, and at the same time shows that the experimental results presented here cannot be ascribed to modulational-instability-induced spectral changes with power-dependent gain. It should be noted that, whereas the relative powers in the spectral sidebands of Fig. 2c increase when going from short to long graphene lengths, their absolute powers decrease because of the strong graphene-induced one-photon absorption which occurs at all wavelengths in the spectra. Still, there will be potential for actually creating new wavelengths at weak pump powers when further optimizing the balance between the one-photon absorption efficiency and the SPCR efficiency, so that the spectral sidebands could grow also in absolute power.

Possible approaches for optimizing this balance are, e.g., by varying graphene’s doping level or by changing the pump wavelength.

Finally, comparing Eq. (6) with Eq. (1) also shows that the quantity \(-\sigma_{\text{FCR}} a_{\text{eff}} T_c / (\hbar \omega)\) takes up the role of proportionality constant \( K \). The most striking features of this quantity are its negative sign and its dependence on graphene’s FCR efficiency rather than on the electronic \( \chi^{(3)} \).

Table 1 Values of the parameters in Eqs. (4–6) for graphene-covered SiO2-core waveguides

| Parameter | Value | Reference |
|-----------|-------|-----------|
| \( \alpha_{\text{eff}} \) (m\(^{-1}\)) | 4605 | Transmission exp. |
| \( \tau_c \) (ps) | 1 | 39 |
| \( N_{\text{sat}} \) (m\(^{-1}\)) | \( \sqrt{10^{37}} \) | 39 |
| \( \sigma_{\text{FCR}} \) | \( 1 \times 10^{-5} \) | Broadening exp.\(^b\) |

\(^a\)The uncertainty interval on the FCR coefficient is extracted from the data measured at different power levels.

\(^b\)The values of \( \alpha_{\text{eff}}, \tau_c, N_{\text{sat}} \) are 1D graphene carrier densities within the waveguide cross-section.
that seen here for graphene-on-SiO₂: it exhibits a linear effective-length dependence in line with the conventional-SPM model of Eq. (1) characterized by \( K = Y_{gr-on-Si} = -1.7 \times 10^3 \text{ W}^{-1} \text{ m}^{-1} \), yielding \( \chi^{(3)}_{eff} = -10^{-7} \text{ esu} \) for the graphene top layer. Furthermore, the broadening measured there in graphene-on-Si is of the order of a few percent, which is small compared to the broadening well in excess of 200% observed here in graphene-on-SiO₂ (Fig. 2a, b).

Although the broadening in graphene-on-Si is in line with the conventional-SPM model, the actual physical process taking place in the graphene is again SPCR and can be described by the model of Eqs. (4) and (5). It should be noted that here the graphene-generated free carriers can also exist in the underlying Si semiconductor waveguide, turning \( N_{gr}^{FF} \) in Eq. (5) into the average carrier density defined over the entire cross-section of the hybrid waveguide and \( \eta_{IPA} = \alpha_{eff} D \) with \( D \) the waveguide thickness (220 nm in this case). The use of spatially averaged carrier densities stems from the often employed semiconductor-based waveguide description as outlined in ref.32, and also implies implementing an average decay time value incorporating the decay times of the different constituents and mechanisms in the waveguide cross-section. Due to the nanosecond-scale carrier lifetime in the underlying Si waveguide32,42, we here have a much larger decay time \( \tau_c \) than when the carriers remain confined to the graphene (see above where a decay time for only the graphene top layer and not for the electrically isolating SiO₂-core waveguides could be defined). As shown in the Supplementary Table 1, we can readily quantify the other parameter values for graphene-on-Si in concert with our previous results. When implementing these in Eqs. (4) and (5) to model SPCR in the graphene top layer, we find an excellent qualitative and quantitative agreement with the experimental data for graphene-on-Si, as depicted in Fig. 5. The agreement is in fact significantly better than that obtained for the conventional-SPM model, which confirms that also in our previously reported measurements with graphene-on-Si, SPCR is at the heart of the observed spectral broadening.

By deriving from Eqs. (4) and (5) an approximated analytical solution for the chirp induced in graphene-on-Si with \( \tau_c \gg T_0 \) (Supplementary Equation 1), we find that here the quantity \(-\alpha_{FCR} \sqrt{\eta_{IPA} T_0} / (\hbar \omega P_0) \) acts as proportionality constant \( K \). This quantity produces both the negative sign and the order of magnitude for the extracted effective \( Y_{gr-on-Si} \). At the same time, it is one order of magnitude smaller than the quantity \( K = -\alpha_{eff} \tau_c / (\hbar \omega) \) for the graphene-covered SiO₂ waveguides (Eq. (6)). This explains why the spectral broadening we observed in the hybrid Si waveguides as shown in Fig. 5 is considerably smaller than that of their SiO₂ counterparts discussed above. Further information on the SPCR modeling results for the hybrid Si waveguides can be found in Supplementary Note 4 and Supplementary Figure 5.

**Pertinence to free-space Z-scan measurements.** The impact of our SPCR analysis goes beyond the process of spectral broadening in graphene-covered waveguides: it actually shows that graphene’s nonlinear phase modulation ability measured in any kind of free-
space or waveguide-based experiment depends on its free-carrier generation and refraction efficiencies, rather than on its electronic $\chi^{(3)}$. Sophisticated free-space Z-scan techniques were developed over the years for distinguishing the electronic $\chi^{(3)}$ contribution from two-photon-absorption-generated free-carrier contributions in 3D semiconductors $^{34,43-45}$; their application to graphene with one-photon-absorption-induced carriers is yet to be explored.

The currently available standard Z-scan measurement results (or Z-scan-like phase modulation results) for graphene on dielectric substrates and excited with ~100 fs pulses can be fitted using the macroscopic formula $\Delta n \propto \chi^{(3)}(3)|A|^2$ along the conventional-SPM notation$^{8-12}$. In these experiments $\tau_c(\text{exps}) < T_0$, and as shown above, the underlying SPCR physics indeed produces conventional-SPM-like behavior for this lifetime/pulse-length ratio. The $\chi^{(3)}$ extracted from these Z-scan experiments consistently is of the order of $10^{-7}$ esu$^{9-12}$.

In contrast, Z-scan results obtained with longer, ps-scale pulse lengths $T_0 \approx \tau_c$ yield a $\chi^{(3)}$ that is about one order of magnitude larger ($10^{-6}$ esu)$^{8,11}$, but no conclusive physical explanation for the difference in Z-scan nonlinearities measured in the two lifetime/pulse-length scenarios was given in those works. Yet, when looking at our results for the ps-pumped graphene-covered SiO$_2$ waveguides featuring $T_0 \approx \tau_c$, an effective graphene nonlinearity $\chi^{(3)} \propto 10^{-6}$ esu would be needed to account for the observed strong broadening factors. This value is also one order of magnitude larger than the $\chi^{(3)}$ extracted in our previous work from Y$_{GR}$-on-Si where $\tau_c > T_0$ applied. We point out that, in addition to nonlinearity magnitudes, our experiments have also revealed the nonlinearity behavior as a function of propagation distance in the hybrid waveguides, clearly indicating the occurrence of SPCR instead of conventional SPM. Such measurements as a function of interaction length are less straightforward to implement in Z-scan experiments with free-space light beams propagating across atomically thin graphene sheets. Finally, it is interesting to note that for Z-scan measurements with fs-scale pulse excitation graphene’s nonlinearity is expected to increase with increasing pulse length $T_0$, as can be derived from our graphene-on-Si results with $K = -\sigma_{\text{FCSR}} \sqrt{(\eta_{\text{IPA}} T_0)/(h\omega P_0)}$ for $\tau_c > T_0$.

**Discussion**

In conclusion, we have revealed the origin of the long-standing quantitative discrepancy between the theoretical $\chi^{(3)}$-based predictions and the experimental observations for graphene’s nonlinear phase-modulation ability in SPM and Z-scan investigations. Rather than relying on graphene’s electronic $\chi^{(3)}$, the measured phase modulation effects arise from a more complex phenomenon we refer to as saturable photoexcited-carrier refraction. Depending on the ratio between the carrier lifetime and the pulse length used, the SPCR-induced physics can either mimic the tendencies of conventional $\chi^{(3)}$-based phase modulation, or produce a totally different behavior. A striking example of the latter is the exponentially growing spectral broadening we have seen for ps pulses propagating in graphene-covered SiO$_2$-core waveguides. This behavior relies on both up-chirping and down-chirping along variable chirp profiles and is totally different from the earlier studied FCR-induced spectral broadening in 3D-semiconductor waveguides. The determining factors for this exceptional behavior are the short $\tau_c$ for photoexcited carriers in graphene and the saturability of the 2D material. This exponential broadening growth opens up new routes to exploiting graphene for on-chip spectral broadening of laser signals and, in case of an optimized balance between the one-photon absorption efficiency and the SPCR efficiency, for actually creating new wavelengths in on-chip frequency-comb and supercontinuum light sources. Furthermore, as the optical pulse power turns out to have a limited impact on the broadening efficiency, one could even envisage frequency-comb and supercontinuum generation at record-low input power levels. In other words, our findings thoroughly change how nonlinear-optical devices could be operated when enhanced with graphene. The SPCR model presented here provides a qualitative and quantitative description for both the cases where such extraordinary broadening behavior is produced and the cases where conventional $\chi^{(3)}$-based broadening is mimicked. It also reveals the physical origin of the negative sign of graphene’s effective $\chi^{(3)} = -10^{-7}$ esu as extracted from our previous on-chip broadening experiments and from Z-scan experiments where mimicked $\chi^{(3)}$-based behavior was produced in the regime of $\tau_c > T_0$. Although the focus in our work has been on graphene-based nonlinear phase modulation, it is interesting to note that also for other nonlinear processes such as four-wave mixing and third-harmonic generation effective nonlinearities of a similarly large magnitude have been measured. This calls for investigating also these other nonlinear processes in graphene$^{7}$ and 2D materials in general$^{46-48}$ through the use of free-carrier dynamics modeling as we used here. We note that for some of those experiments (e.g., the third-harmonic-generation measurements reported in ref. 7) nonlinearity magnitudes below $10^{-7}$ esu were reported, but also for those measurements the insights we have obtained here regarding, e.g., the impact of the pulse duration on the nonlinearity strength in Z-scan experiments can be relevant. A more in-depth understanding of the fundamental 2D-material nonlinearities will finally allow the full exploitation of their great potential in next-generation (on-chip) nonlinear-optical devices.

**Methods**

**Fabrication of graphene-covered SiO$_2$-core waveguides.** Photonic waveguides with spot-size converters at the end facets were fabricated in a multi-project wafer run of the LionX foundry (https://www.lionx-international.com). The spot-size converters allow edge coupling with flat-cleaved fibers placed at the waveguides’ input and output facets, yielding a fiber-chip-fiber coupling efficiency around $-10$ dB. The cross-sectional waveguide geometry consists of a SiO$_2$ core region (thickness around 500 nm) with above and below a stripe of SiNx (stripe thickness around 170 nm). The foundry also provided a top oxide layer above the upper SiNx stripe (see Supplementary Note 1 and Supplementary Figure 1). The photonic chips delivered by the foundry were 8 mm wide, and featured a top oxide thickness of around 300 nm above the waveguides while above the spot-size converter regions the oxide thickness was several μm. The 300 nm-thick oxide above the waveguides was then almost completely removed using h-BF etching prior to the graphene transfer, so that the remaining top oxide thickness was below 50 nm. The waveguides used in the broadening experiments all feature a stripe width of 1300 nm, yielding single-mode quasi-TE operation in the telecom band around 1550 nm.

Monolayer graphene was grown on a high-purity 35 μm-thick polycrystalline copper foil using chemical vapor deposition (CVD) of methane in a commercially available Black Magic Pro system. The time and flow rate settings were optimized such that monolayer graphene growth was ensured. Afterwards a 200 nm-thick layer of poly(methyl methacrylate) (PMMA) was spincoated on top of the graphene. After electrochemical delamination of the CVD-grown graphene film in a 1 M aqueous solution of potassium chloride, it was deposited on top of the photonic chip along the wet-transfer method$^{28}$ and annealed at 120 °C for 12 h. To create graphene sections of varying length on the waveguides, the graphene with the PMMA on top was patterned using O$_2$ plasma etching and a mechanical mask laser-cut in a 200 μm-thick steel plate to define the openings to be etched$^{28}$. The PMMA was not removed after the etching step, so that the refractive index in the region above the graphene remained sufficiently high for having a strong optical field in the monolayer. By experimentally comparing spectral broadening with and without PMMA, we have verified that the PMMA has no influence on the observed broadening behavior. We have also checked through on-chip Hall-effect measurements that the graphene exhibits a usual level of unintentional doping (see Supplementary Note 2 and Supplementary Figure 3).

**Optical experiments.** The pulsed laser source used to excite the graphene-covered waveguides is an optical parametric oscillator OPO (APE Levante IR) generating picosecond pulses at a repetition rate of 80 MHz. To create input pulses with
either a positive or negative chirp, we made use of the chirp modification that the OPO pulses experience when injected in sufficiently long fiber sections. To determine the appropriate fiber length for achieving a given chirp modification, one can make use of our pulse-chirp control method based on the generalization-length formalism. The chirped pulses were then coupled into and out of the hybrid waveguides by means of flat-cleaved fiber probes positioned horizontally at the waveguides' end facets, and their peak power was varied using a variable optical attenuator. A 99:1 coupler was inserted in front of the incoupling fiber probe to split off 1% of the input pulse power towards a power meter (Newport 2832-C with 818-SL detector head) and an optical spectrum analyzer (Yokogawa AQ6370D) for monitoring both the input power and spectrum. Along the same approach the output power and spectrum were measured just behind the outcoupling fiber probe using a second power meter and optical spectrum analyzer. Prior to the optical measurements, the input pulse duration and phase/chirp profile were characterized by means of a frequency-resolved optical gating (FROG) instrument (Coherent Solutions HR150).

**Numerical simulations.** The quasi-TE mode in the graphene-covered waveguide as shown in Fig. 1a was calculated using Lumerical MODE Solutions software. The pulse propagation formula Eq. (4) was solved by means of an Adams method, and the free-carrier rate Eq. (5) was solved along the same approach used for the free-carrier rate equation in silicon waveguides.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: 22 February 2018 Accepted: 15 June 2018
Published online: 11 July 2018

**References**

1. Hendry, E., Hale, P. J., Moger, J., Savchenko, A. K. & Mikhailov, S. A. Coherent nonlinear optical response of graphene. *Phys. Rev. Lett.* 105, 097401 (2010).

2. Gu, T. et al. Regenerative oscillation and four-wave mixing in graphene optoelectronics. *Nat. Photon.* 6, 554–559 (2012).

3. Ji, M. et al. Enhanced parametric frequency conversion in a compact silicon-graphene microring resonator. *Opt. Express* 23, 18679–18685 (2015).

4. Alexander, K., Savostianova, N. A., Mikhailov, S. A., Kuyken, B. & Van Thourhout, D. Electrically tunable optical nonlinearities in graphene-covered SiN waveguides characterized by four-wave mixing. *ACS Photonics* 4, 3039–3044 (2017).

5. Wu, Y. et al. Generation of cascaded four-wave mixing with graphene-coated waveguide disperser. *Photon. Res.* 3, A64–A68 (2015).

6. Kumar, N. et al. Third harmonic generation in graphene and few-layer graphene microring resonator. *Opt. Express* 24, 13033–13043 (2016).

7. Dremetsika, E. et al. Measuring the nonlinear refractive index of graphene using the optical Kerr effect method. *Opt. Lett.* 41, 3281–3284 (2016).

8. Dremetsika, E. & Kockaert, P. Enhanced optical Kerr effect method for a detailed characterization of the third-order nonlinearity of two-dimensional materials applied to graphene. *Phys. Rev. B* 96, 235422 (2017).

9. Ishizawa, A. et al. Optical nonlinearity enhancement with graphene-decorated silicon waveguides. *Sci. Rep.* 7, 45520 (2017).

10. Vermeulen, N. et al. Negative Kerr nonlinearity of graphene as seen via chirped-pulse-pumped self-phase modulation. *Phys. Rev. Appl.* 6, 044006 (2016).

11. Wu, R. et al. Purely coherent nonlinear optical response in solution dispersions of graphene sheets. *Nano. Lett.* 11, 5159–5164 (2011).

12. Cheng, J. L., Vermeulen, N. & Sipe, J. E. Third-order nonlinearity of graphene: effects of phenomenological relaxation and finite temperature. *Phys. Rev. B* 91, 235320 (2015).

13. Cheng, J. L., Vermeulen, N. & Sipe, J. E. Numerical study of the optical nonlinearity of doped and gapped graphene: from weak to strong field excitation. *Phys. Rev. B* 92, 235307 (2015).

14. Mikhailov, S. A. Quantum theory of the third-order nonlinear electrodynamic effects of graphene. *Phys. Rev. B* 93, 085403 (2016).
stichting grant UABR/007/09, the Research Foundation Flanders (FWO) under Grants GA00213N and G0F6218N (EOS-convention 30467715), the VUB-OZR, BELSPO-IAP, and Methusalem. The LioniX foundry and Cathleen De Tandt from VUB-ETRO are acknowledged for the photonic chip fabrication and postprocessing, respectively. The nonlinear-optical experiments were performed in the Photonics Innovation Center at Vrije Universiteit Brussel (VUB Photonics Campus—Vollezelestraat 46, 1755 Gooik, Belgium).

D.C.-L. is grateful for funding from Subprograma Atracció de Talent—Contractes Postdoctorals de la Universitat de València.

**Author contributions**

N.V., D.C.-L., and J.V.E. proposed and devised the experiments. J.V.E. built the setup. N.V. devised the photonic chip design. I.P., A.K., and T.C. carried out the graphene growth, transfer, and patterning, respectively. J.V.E., M.K., and N.V. performed the experiments. D.C.-L. analyzed the experimental data and developed the theory underpinning the experiments. J.C., W.S., and H.T. contributed to discussing the nonlinearity calculations, the free-carrier physics, and the nonlinear-optical physics, respectively. N.V. wrote the manuscript with input from all authors.

**Additional information**

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-05081-z.

**Competing interests:** The authors declare no competing interests.

**Reprints and permission** information is available online at http://npg.nature.com/reprintsandpermissions/

**Publisher’s note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2018