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ABSTRACT

The first nonlinear-optical experiments with graphene date back over a decade, and a wide range of research breakthroughs has been reported since then, particularly on the third-order nonlinearities of the material. Graphene has been shown to exhibit extraordinary saturable absorption properties as well as extremely strong nonlinear refraction effects, both of which hold promise for practical use in nonlinear-optical devices. In this Perspective, after providing a very brief overview of the state of the art, I elaborate on the most relevant material parameters for future research and development activities in this domain, while also highlighting specific features of graphene's linear and nonlinear-optical properties that are sometimes overlooked in experiments. Finally, I present my view on what the opportunities and remaining challenges are in the practical exploitation of graphene for nonlinear-optical applications.

I. INTRODUCTION

Graphene is seen as one of the most revolutionary new materials of this century. The first successful isolation of a truly two-dimensional layer of carbon atoms in 2004 (Novoselov *et al.*, 2004) represented a full-fledged paradigm shift in material science and many other research disciplines, including optics and photonics (Bonaccorso *et al.*, 2010). Due to its unique linear energy band structure with zero bandgap and with charge carriers that behave as massless Dirac fermions, graphene exhibits extraordinary linear and nonlinear-optical properties (Yamashita, 2019; You *et al.*, 2019). The linear absorption of intrinsic, i.e., undoped, graphene for perpendicularly incident light equals 2.3%, a remarkably large value for a material just one atom thick. In addition, its third-order nonlinear-optical response—the lowest-order optical nonlinearity that is allowed in inversion symmetric materials, such as graphene—has also been shown to be very pronounced (Yamashita, 2019; You *et al.*, 2019).

This Perspective focuses on the third-order nonlinear optics of graphene, which comprises both absorptive and refractive processes. After providing a brief description of the state of the art in this research field, I take a closer look at the most relevant material parameters for future research and development activities in this domain. Finally, I present my view on the opportunities and remaining challenges in the practical exploitation of graphene for nonlinear-optical applications.

II. STATE-OF-THE-ART HIGHLIGHTS

Over the past decade, graphene's third-order nonlinear optics has been extensively investigated, and a wide range of new insights and breakthroughs has been reported. The goal of this brief state-of-the-art (s-o-t-a) section is to highlight those breakthroughs that underpin the perspective discussions in Secs. III and IV. A more detailed overview of the s-o-t-a can be found in several review papers published in recent years on this topic, such as Yamashita (2019) and You *et al.* (2019).

A. Absorptive nonlinear optics of graphene: s-o-t-a highlights

The main absorptive third-order nonlinear effects are two-photon absorption and saturable absorption. In particular, the latter has been extensively studied in graphene over the past decade. When photons are absorbed in graphene, free carriers are generated, and at sufficiently high irradiances, the free-carrier generation will experience Pauli blocking in the valence/conduction band. As such, the optical absorption will saturate. Inspired by earlier saturable absorption studies with carbon nanotubes (Hasan *et al.*, 2009; Sun *et al.*, 2010), the nonlinear-optics community turned its attention to graphene starting from 2009. In that year, Bao and coworkers measured the nonlinear transmission of quasi-undoped graphene samples at near-infrared telecom wavelengths and demonstrated saturable absorption with a low saturation carrier density {$N_{sat} \sim 10^{13}$ cm^{-2} for few-layer graphene [Fig. 1(a)]}, an ultrafast recovery time at (sub-)picosecond time scales, a wide operation bandwidth, and a modulation depth that could be varied by at least a factor of 10 by changing the number of graphene layers (Bao *et al.*, 2009). These pioneering experiments served as the starting point for several in-depth studies on the underlying physics [see, e.g., Xing *et al.* (2010), Vasko (2010), Marini *et al.* (2017), and Hafez *et al.* (2020)]. Moreover, different strategies were developed to further enhance graphene's saturable absorption behavior, e.g., by means of plasmonics (Wang *et al.*, 2015; Cox and García de Abajo, 2018; and Rafique *et al.*, 2021) or by moving to longer excitation wavelengths where the saturation threshold decreases (Yamashita, 2019). Note that in the THz domain almost full bleaching of graphene's absorption has been observed as a result of saturation (Mics *et al.*, 2015).

Graphene's unusual saturable absorption properties have attracted wide attention not only from a fundamental physics point of view but also for the purpose of practical applications. In 2009, Bao *et al.* reported on the successful implementation of graphene as a saturable absorber in a fiber laser to obtain modelocked operation with femtosecond laser pulses in the near-infrared telecom domain (Bao *et al.*, 2009). They deposited graphene on the output facet of a fiber pigtail in the laser cavity such that the laser beam propagated across the graphene sample in the perpendicular direction [Figs. 1(b) and 1(c)], like it would in a free-space excitation setup. Soon after, a graphene saturable absorber was demonstrated with the graphene sheet integrated *along* a side-polished fiber, a configuration where the 2D material was exposed to the evanescent fields of the fiber mode, resulting in guided-mode excitation along the plane of the graphene rather than across it [Figs. 2(a) and 2(b)] (Song *et al.*, 2010). Through this approach, the 2D material is able to withstand higher (kW range) peak powers in the modelocked laser cavity than when used in a perpendicular free-space excitation configuration, and at the same time, it can interact over a longer distance with the laser pulses (Song *et al.*, 2010). The pulse energies at which saturation kicks in can go below 1 nJ (Kuo and Hong, 2014). This guided-mode excitation approach became widely adopted over the years [see overviews in Martinez and Sun (2013), Zapata *et al.* (2016), Guo *et al.* (2019), and Peng and Yan (2021)], and the quality of such graphene-on-fiber saturable absorbers greatly improved along the way, thanks to the maturing graphene production techniques (e.g., chemical vapor deposition (CVD) growth, mechanical exfoliation, and liquid-phase exfoliation) and transfer techniques based on

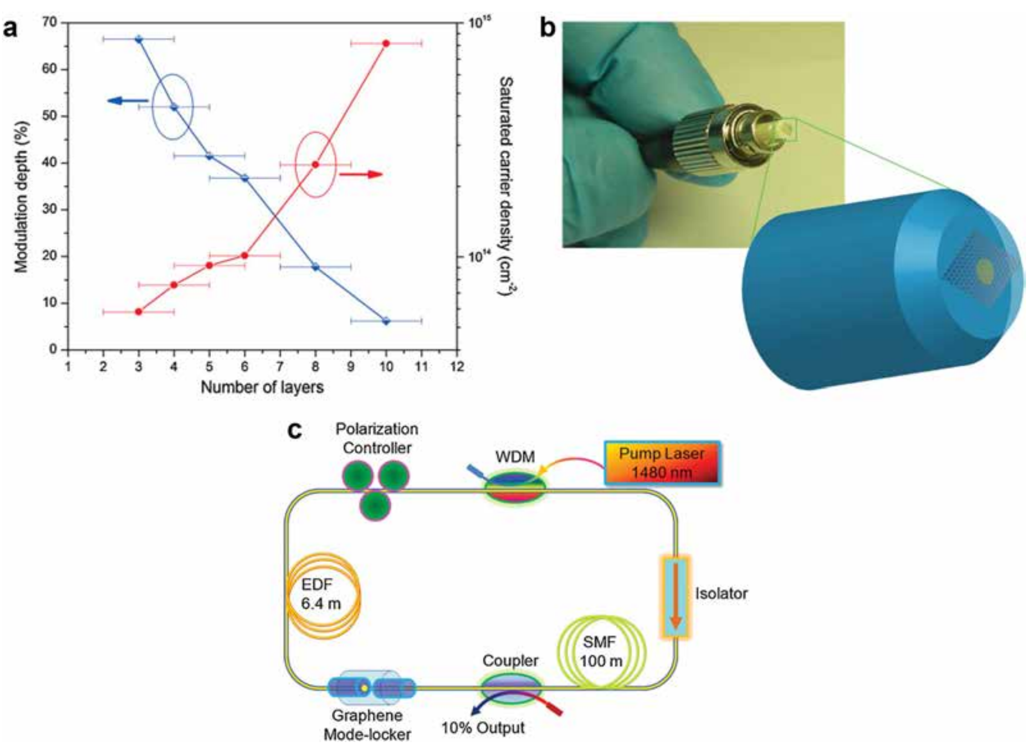

FIG. 1. (a) Saturation carrier density and modulation depth vs number of graphene layers, (b) photograph of a fiber pigtail coated with a graphene film and the corresponding schematic, and (c) fiber laser configuration with a graphene saturable absorber as the modelocking element. WDM: wavelength division multiplexer, EDF: erbium doped fiber amplifier, and SMF: single mode fiber. Reproduced with permission from Bao *et al.*, Adv. Funct. Mater. **19**, 3077–3083 (2009). Copyright 2009, John Wiley and Sons.

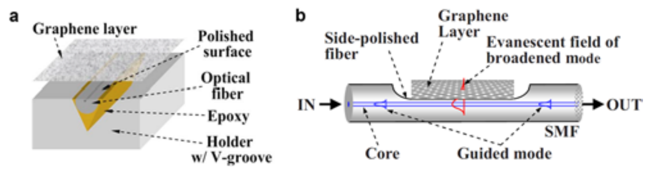

FIG. 2. (a) Schematic of a saturable absorber consisting of graphene deposited along a side-polished fiber. (b) Illustration of the evanescent field of the fiber mode interacting with the graphene layer. Reproduced with permission from Song *et al.*, Appl. Phys. Lett. **96**, 051122 (2010). Copyright 2010, AIP Publishing.

wet and dry chemical methods (Lee *et al.*, 2017; Chen *et al.*, 2021). Furthermore, the guided-mode excitation scheme did not remain limited to fibers only: starting from 2013, also on-chip waveguides made of silicon and silicon nitride were enriched with graphene placed along the waveguide surface to demonstrate saturable absorption within a laser cavity (Wong *et al.*, 2013; Kovacevic *et al.*, 2018; and Deng *et al.*, 2021). The advantage of graphene-on-waveguide saturable absorbers is that the waveguides' tiny modal area below 1 μm^2 can reduce the saturation pulse energy to less than 1 pJ (Deng *et al.*, 2021).

B. Refractive nonlinear optics of graphene: s-o-t-a highlights

Third-order nonlinear-optical refraction in graphene comprises, among others, third-harmonic generation, four-wave mixing, and phase modulation interactions, all of which rely on an irradiance-induced nonlinear change in the refractive index of the 2D material. In 2010, Hendry and co-workers carried out four-wave mixing experiments at visible and near-infrared wavelengths with graphene on a glass substrate in a free-space excitation setup [Figs. 3(a) and 3(b)]. By comparing the four-wave mixing conversion efficiency with that of gold [Fig. 3(c)], they extracted an extremely large magnitude of the third-order susceptibility $\left|\chi^{(3)}\right|$ ~ 10^{-7} esu ~10^{-15} m^2/V^2 for quasi-undoped monolayer graphene, a value that is about 5 orders of magnitude larger than that of silicon or 4 orders of magnitude larger than that of GaAs at 1550 nm wavelength (Hendry *et al.*, 2010). They also observed that the four-wave mixing response increased for multilayer graphene samples of up to six layers as a result of constructive interference of the radiated fields from the different layers (Hendry *et al.*, 2010). These seminal results would soon be followed by many more graphene characterization experiments in the free space, several of them using Z-scan(-like) measurements (Chen *et al.*, 2013; Demetriou *et al.*, 2016; Dremetsika *et al.*, 2016; and Thakur *et al.*, 2019), which allowed extracting not only the magnitude but also the sign of the nonlinearity. The sign turned out to be variable, as both positive and negative nonlinearities were measured. The former was reported for quasi-undoped graphene excited at relatively short wavelengths (e.g., 800 nm) (Chen *et al.*, 2013; Thakur *et al.*, 2019), while the latter was observed at longer wavelengths (e.g., 1550 nm) (Demetriou *et al.*, 2016; Dremetsika *et al.*, 2016). Graphene's nonlinear refraction was also found to become even more pronounced when combining the 2D material with, e.g., plasmonics (Calafell *et al.*, 2021) or quantum dots (Hong *et al.*, 2021) or when exciting it at THz wavelengths, yielding an enormously enhanced nonlinearity of $\left|\chi^{(3)}_{\mathrm{eff}}\right|$ ~ 10^{-9} m^2/V^2 (Hafez *et al.*, 2018).

While the nonlinear refraction measurements described above relied on free-space excitation of graphene, also guided-mode excitation of graphene deposited along fibers and on-chip waveguides was extensively explored for this purpose (Wu *et al.*, 2014; 2015; An *et al.*, 2020; Gu *et al.*, 2012; Vermeulen *et al.*, 2016; 2018; and Alexander *et al.*, 2017). Initially, four-wave mixing experiments were reported, and it was shown that depositing graphene on a silicon waveguide could result in a ten times larger nonlinearity magnitude than that of the bare waveguide [i.e., an effective nonlinear index $n_{2,\mathrm{eff}}$ with a magnitude of 4.8×10^{-17} m^2/W (0.44×10^{-17} m^2/W) for a graphene-covered (bare) silicon waveguide] (Gu *et al.*, 2012). After the initial four-wave mixing experiments, also phase modulation measurements were carried out (Vermeulen *et al.*, 2016; 2018). The latter entailed spectral broadening experiments with chirped laser pulses at telecom wavelengths in graphene-covered waveguides. For pulse peak powers of only a few Watts, a more than twofold broadening was obtained in a silicon nitride waveguide decorated with a mm-long section of quasi-undoped monolayer graphene (Vermeulen *et al.*, 2018) [Figs. 4(a)–4(c)]. The use of chirped input pulses in these broadening experiments also allowed extracting both the nonlinearity magnitude and sign of the graphene top layer. The nonlinearity sign turned out to be negative at telecom wavelengths (Vermeulen *et al.*, 2016) as it was also found in parallel in the free-space Z-scan(-like) experiments of Demetriou *et al.* (2016) and Dremetsika *et al.* (2016). Furthermore, the guided-mode excitation scheme employed in the study of Vermeulen *et al.* (2016; 2018) allowed investigating graphene's nonlinear refractive behavior as a function of interaction length. Unusual length dependences

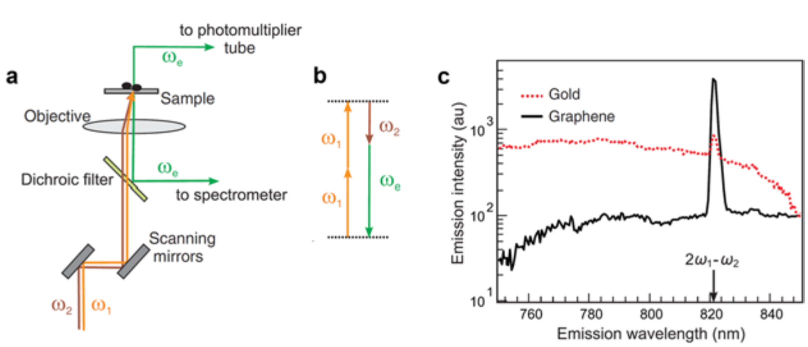

FIG. 3. (a) Schematic of the experimental layout for four-wave mixing experiments with graphene, using excitation beams with frequencies ω_1 and ω_2 generating emission at ω_e. (b) Diagram of energy conservation in the four-wave mixing process. (c) Four-wave mixing emission spectrum of a graphene monolayer excited with 969 nm/1179 nm pump wavelengths, compared to the emission of a 4 nm thick gold film under the same experimental conditions. Reproduced with permission from Hendry *et al.*, Phys. Rev. Lett **105**, 097401 (2010). Copyright 2010, American Physical Society.

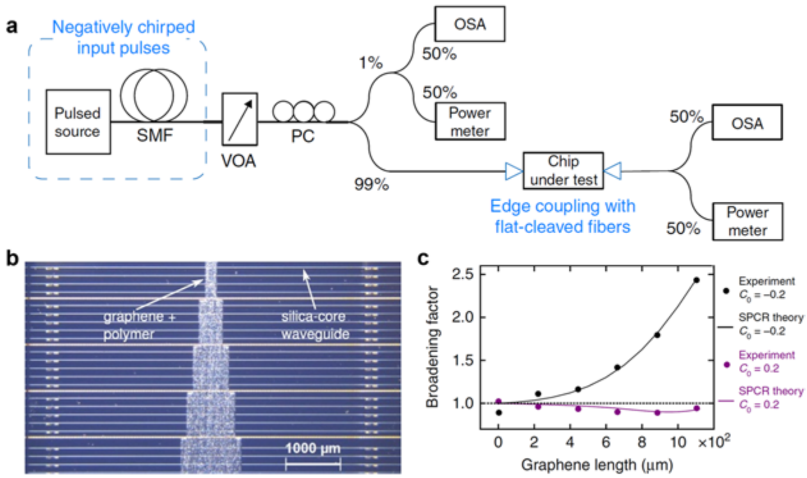

FIG. 4. (a) Setup for spectral broadening measurements of laser pulses in graphene-covered waveguides. SMF: single-mode fiber, VOA: variable optical attenuator, PC: polarization controller, and OSA: optical spectrum analyzer. (b) Microscope image of the waveguides covered with, respectively, 220, 440, 660, 880, and 1100 μm-long monolayer graphene sections. (c) Broadening factor vs graphene length for input pulses with 3 ps pulse duration, 2.7 W peak power, and 1563 nm wavelength and with either a positive or negative input chirp $C_0 = \pm 0.2$. The distinct curves for $C_0 = \pm 0.2$ point at a negative graphene nonlinearity. Both the experimental data points and the results from the SPCR theory are shown. Reproduced with permission from Vermeulen *et al.*, Nat. Commun. **9**, 2675 (2018). Copyright 2018, Springer Nature.

were observed, such as a quasi-exponential growth with distance of the pulse spectral broadening [see the curve for a negative input chirp in Fig. 4(c)] (Vermeulen *et al.*, 2018). This extraordinary behavior showed that nonlinear refraction effects in graphene are not necessarily due to a perturbative nonlinearity associated with bound-electron transitions, as it had been initially assumed. Instead, they are often better described as free-carrier refraction effects (Vermeulen *et al.*, 2018; Baudisch *et al.*, 2018) with essentially the same carrier dynamics as in the case of saturable absorption. Indeed, in many cases, graphene's nonlinear refraction mostly originates from photoexcited free carriers that experience Pauli blocking at sufficiently high irradiances. As such, one can speak of saturable photoexcited carrier refraction (SPCR) (Vermeulen *et al.*, 2018; Castelló-Lurbe *et al.*, 2020), with a saturation behavior similar as for saturable absorption (Demongodin *et al.*, 2019).

III. GRAPHENE CHARACTERIZATION IN THE FRAME OF NONLINEAR-OPTICAL EXPERIMENTS

Due to its single-atom thickness, graphene can be considered as a material that is "interface all over." As a result, its properties are heavily influenced by its production method, by the environments it is exposed to, and by the substrate material it is placed on—with fibers and on-chip waveguides also denoted here as "substrate." This also implies that different graphene samples could exhibit different nonlinear-optical characteristics. Hence, an in-depth characterization of the graphene sample used in nonlinear-optical experiments is extremely important both from fundamental science and practical application points of view.

In the scientific publications reporting on nonlinear-optical experiments with graphene, one generally finds information about the material production method, the number of graphene layers, and the substrate material, together with microscopic and/or spectroscopic characterization data. However, the doping level or Fermi level of the graphene sample is often not specified. The Fermi level is known to determine the linear optical properties of the 2D material, but it can also have a large impact on its nonlinear refraction efficiency (Alexander *et al.*, 2017; Jiang *et al.*, 2018; Soavi *et al.*, 2018; and An *et al.*, 2020) and its saturable absorber properties (Lee *et al.*, 2012; 2015). Several techniques have been developed to characterize graphene's Fermi level; most of them are based on electric field effect measurements (Novoselov *et al.*, 2004; Mitta *et al.*, 2021), Hall effect measurements (Mitta *et al.*, 2021), Raman spectroscopy (Bruna *et al.*, 2014), or infrared transmission

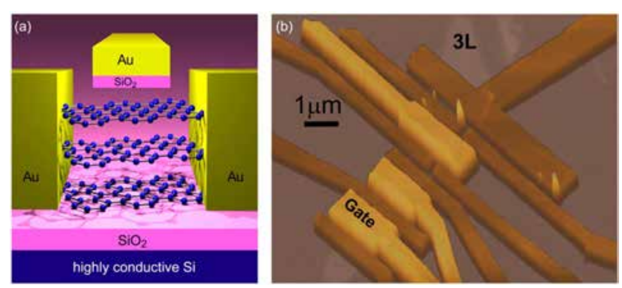

FIG. 5. (a) Schematic structure of double gated trilayer graphene on a flat substrate. The bottom gate is the Si substrate covered by SiO_2. The top gate is formed by SiO_2 and Au. The trilayer graphene is contacted by Au electrodes. (b) Atomic force microscopy image of graphene with top gates (light brown) and electrodes (dark brown). Reproduced with permission from Craciun *et al.*, Nano Today **6**, 42–60 (2011). Copyright 2011, Elsevier.

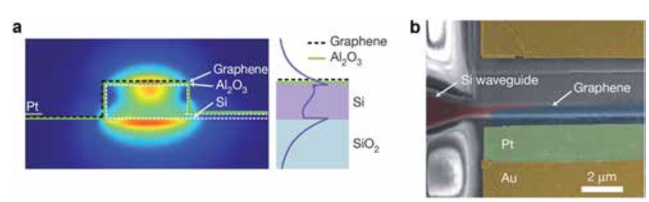

FIG. 6. (a) Left: Schematic structure of gated graphene on a waveguide, with an overlay of the waveguide mode plot. The graphene is contacted by a Pt electrode. The Si waveguide is covered by a thin layer of Al_2O_3 to form the gate. Right: Cross section through the center of the waveguide, with the purple curve showing the magnitude of the electric field. (b) Scanning electron microscopy image of the graphene gating structure. Reproduced with permission from Liu *et al.*, Nature **474**, 64–67 (2011). Copyright 2011, Springer Nature.

spectroscopy (Lee *et al.*, 2012). Besides characterizing the Fermi level, one can also actively tune it by applying gating to the graphene. Such gating has been successfully demonstrated for graphene on top of flat substrates, fibers, and on-chip waveguides (Figs. 5–7) [see, e.g., Craciun *et al.* (2011), Bruna *et al.* (2014), Jiang *et al.* (2018), Lee *et al.* (2015), An *et al.* (2020), Liu *et al.* (2011), and Alexander *et al.* (2017)], often over a wide Fermi energy range of the order of 1 eV. The pronounced impact that gating has on graphene's nonlinear-optical performance highlights the tunable nature of the 2D material. At the same time, it underlines how important it is to specify in all future publications at what Fermi level the reported measurements were taken. This recommendation also holds when neither gating nor (chemical) doping is applied to the graphene sample, as the 2D material often acquires unintentional doping already during the production phase (Ciuk *et al.*, 2013).

In the preparation of nonlinear-optical measurements, the first step should be to characterize the linear optical properties of the graphene sample and, in particular, its linear absorption α at low excitation powers. Such a linear optical characterization gives a straightforward "quality check" of the sample used (Bruna and Borini, 2009) and can also confirm the number of layers (Zhu *et al.*, 2014) and/or the doping level of the material

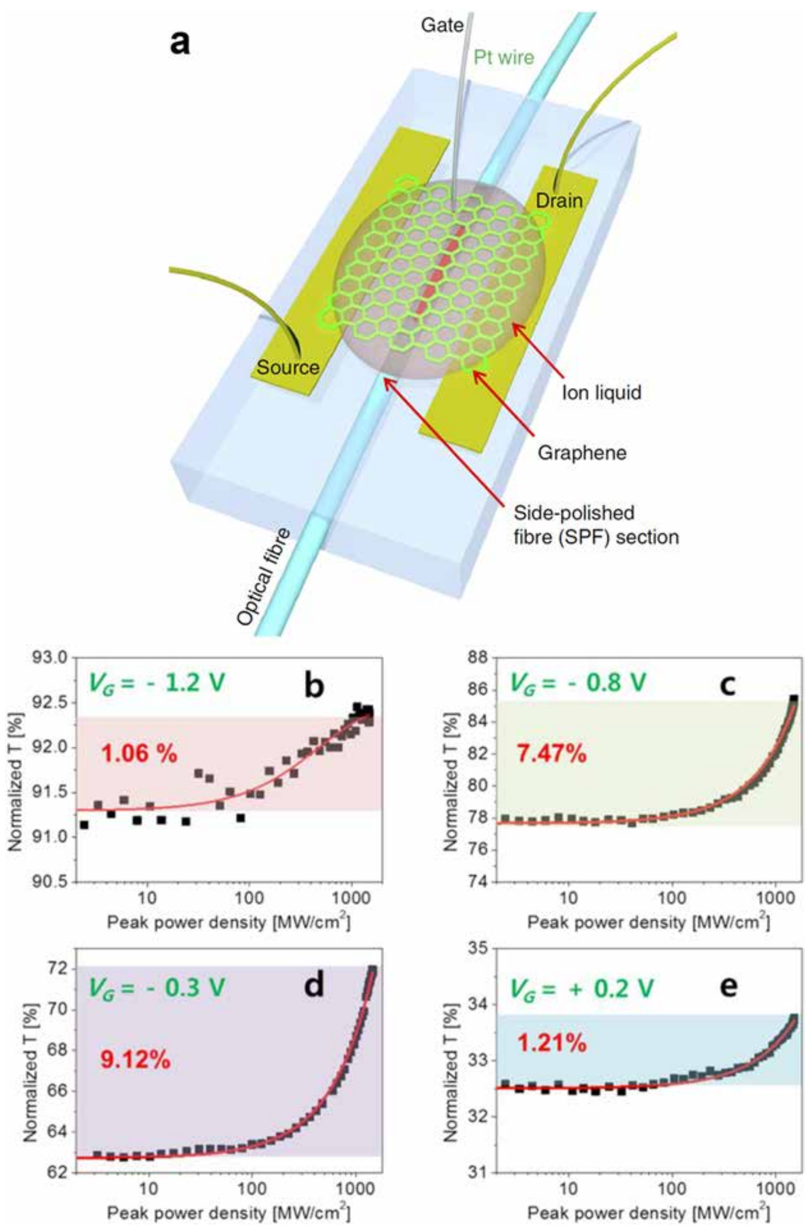

FIG. 7. (a) Schematic structure of gated graphene on a side-polished fiber. Normalized nonlinear transmission curves for bilayer graphene deposited on a side-polished fiber at applied gate voltages of (b) −1.2 V, (c) −0.8 V, (d) −0.3 V, and (e) +0.2 V. Reproduced with permission from Lee *et al.*, Nat. Commun. **6**, 6851 (2015). Copyright 2015, Springer Nature.

(Lee *et al.*, 2012). Care must be taken that the light polarization dependence of α is verified during the measurements (Zhang *et al.*, 2020) and that the loss contributions of the bare substrate material are factored out. α is also an essential parameter from an application point of view, as it strongly impacts the performance of practical graphene-based devices (see Sec. IV).

In case of saturable absorption experiments, the parameters to be determined are the saturation carrier density N_{sat}, the relative modulation depth, and the effective carrier relaxation time τ_{eff} in case the measurement setup allows for time-resolved pump-probe transmission measurements (Bao *et al.*, 2009). The saturation carrier density N_{sat} is a very important material property of the graphene sample (Bao *et al.*, 2009), but it is not always explicitly specified in the literature since excitation-related quantities, such as saturation irradiance, power, energy, or fluence, are more commonly used. The relative modulation depth is another material parameter that is defined as the ratio between graphene's saturable loss and total linear loss α, i.e., $\alpha_s/\alpha = \alpha_s/(\alpha_s + \alpha_{ns})$, with α_s and α_{ns} representing the saturable and non-saturable loss, respectively (Bao *et al.*, 2009). The third material property, τ_{eff}, is a function of both a fast and slow decay time related to carrier–carrier and carrier–phonon intraband and interband scattering processes in graphene (Dawlaty *et al.*, 2008). The combination of N_{sat}, the modulation depth, and τ_{eff} measured for a given graphene sample determines its performance as a saturable absorber and hence also governs the pulsed laser performance that can be obtained with it.

Turning now to the characterization of graphene's nonlinear refraction, many works in the literature report on the conversion efficiency of wave mixing processes, such as four-wave mixing and third-harmonic generation. While conversion efficiencies are very relevant for practical applications, quantifying the actual nonlinearity of the graphene sample provides even more valuable information. Here, special care must be taken to properly separate the refractive nonlinearity contributions of the substrate material and the graphene on top (Vermeulen *et al.*, 2016). The refractive nonlinear coefficients that are commonly reported for graphene are the third-order susceptibility $\chi^{(3)}$ [or equivalently the third-order conductivity $\sigma^{(3)}$ (Cheng *et al.*, 2014)], the effective nonlinear index $n_{2,eff}$, and also the free-carrier refraction coefficient σ_{FCR} (Vermeulen *et al.*, 2018; Demongodin *et al.*, 2019). Using $\chi^{(3)}$ is, in principle, only allowed for a purely perturbative nonlinearity induced by bound-electron transitions, while graphene often produces non-perturbative nonlinear refraction induced by free carriers (Vermeulen *et al.*, 2018; Baudisch *et al.*, 2018). In the latter case, it is more appropriate to use σ_{FCR} rather than $\chi^{(3)}$, and in addition, a proper quantification of the carrier relaxation time τ_{eff} and the saturation carrier density N_{sat} becomes as relevant here as it is for saturable absorption (Vermeulen *et al.*, 2018; Demongodin *et al.*, 2019; and Castelló-Lurbe *et al.*, 2020).

As mentioned in Sec. II B, besides measuring the magnitude of graphene's refractive nonlinearity, it is also important to determine its sign using, for example, Z-scan(-like) characterization in a free space configuration or chirped-pulse-pumped spectral broadening measurements in a waveguide configuration. The refractive nonlinearity of graphene can be either positive or negative (Castelló-Lurbe *et al.*, 2020) and hence can interact in different ways with that of the substrate. In case both the 2D material and the substrate feature equal nonlinearity signs, there will be mutual enhancement of the nonlinear responses, while opposite signs will lead to counteracting nonlinear behaviors (Vermeulen *et al.*, 2016). While the latter is undesirable for many applications, such a counteraction can also open up innovative applications that were not considered previously (see Sec. IV B).

IV. EXPLOITING GRAPHENE'S NONLINEAR OPTICS: OPPORTUNITIES AND REMAINING CHALLENGES

A. Absorptive nonlinear optics of graphene: Opportunities and challenges

Graphene performs very well as a fast saturable absorber and has already been embedded in various fiber laser setups to obtain pulsed operation, either in the modelocked or Q-switched regime (Guo *et al.*, 2019; Peng and Yan, 2021). As pointed out in Sec. II A, when integrated along an optical fiber, it can interact with the evanescent fields of the fiber mode so that no damage can occur in the 2D material at kW laser powers and the interaction length can be tailored for optimal performance (Song *et al.*, 2010). Various graphene-on-fiber transfer techniques were developed over the years (Chen *et al.*, 2021), but to enable commercialization of such saturable absorbers, additional standardization and upscaling of the techniques will be required. An ideal solution would be to have high-quality CVD growth of graphene directly on the fiber surface. Direct CVD growth of graphene on dielectric surfaces with a low surface energy is usually challenging, but the progress recently made in this area looks promising (Kahn *et al.*, 2018).

An alternative platform for guided-mode excitation of graphene is on-chip waveguides. These feature a smaller modal area than fibers, and as such, the combination of graphene with on-chip waveguides allows reducing the saturation pulse energies down to sub-pJ values (Deng *et al.*, 2021). However, placing a saturable absorber based on a photonic chip rather than a fiber within a fiber laser cavity results in higher insertion losses because of the inefficient fiber-to-chip coupling used so far, with typically at least 5 dB loss per interface (Wong *et al.*, 2013; Kovacevic *et al.*, 2018; and Deng *et al.*, 2021). Recent advances in optical interconnect manufacturing, such as two-photon polymerization-fabricated fiber-to-chip coupling structures with reduced coupling losses around 1.5 dB (Vanmol *et al.*, 2020), could provide a solution for this issue. Note also that transferring graphene on planar photonic chips is considered more straightforward than on fibers, but in both cases, direct graphene growth on the waveguiding media would be beneficial from the point of view of standardization and upscaling (Kahn *et al.*, 2018).

There are also interesting opportunities in the tunability of graphene's saturable absorption properties, regardless of the type of substrate material it is placed upon. Changing its Fermi level leads to a change in modulation depth (Lee *et al.*, 2012; 2015). As such, graphene's saturable absorption behavior can be varied in real time by means of gating (Lee *et al.*, 2015) [Figs. 7(a)–7(e)]. In fact, this real-time tunability represents a very important advantage of graphene as compared to other 2D materials considered for saturable absorption. To reduce the saturation carrier density N_{sat}, one can increase the number of graphene layers, although this will also affect the modulation depth (Bao *et al.*, 2009). Indeed, when replacing few-layer graphene by 10-layer graphene, the relative modulation depth can decrease by an order of magnitude due to the increased non-saturable loss caused by enhanced scattering in graphene multilayers (Bao *et al.*, 2009). An alternative approach to lower N_{sat} is to move to longer operation wavelengths, as pointed out earlier. Finally, both the effective relaxation time τ_{eff} and N_{sat} can be reduced by combining graphene with plasmonic structures (Wang *et al.*, 2015; Rafique *et al.*, 2021) or by exploiting the plasmonic response in graphene nanoribbons (Cox and García de Abajo, 2018). However, it is not clear yet what modulation depths such configurations could yield and how they can be realized for graphene on a fiber or waveguide.

To optimally engineer N_{sat}, the modulation depth, and τ_{eff} all simultaneously, further investigations will be needed (Hussain, 2019), both from theoretical and experimental points of view. The latest theoretical frameworks [e.g., Marini *et al.* (2017) and Hafez *et al.* (2020)] account for several effects, such as doping, carrier temperature, and carrier–carrier interactions, and they clarify many of graphene's experimental saturable absorption properties. However, there still exist discrepancies regarding, e.g., the relaxation time values (Marini *et al.*, 2017). Further insights from both modeling and experiments could address these and at the same time provide new routes for graphene-based saturable absorption "at its best" with customized tailoring to meet the targeted specifications.

B. Refractive nonlinear optics of graphene: Opportunities and challenges

Graphene has been shown to exhibit strong third-order nonlinear refraction, and when integrated along an optical fiber or on top of an on-chip waveguide, the interaction length can be chosen such that optimal performance is obtained. Both four-wave mixing and phase modulation experiments were carried out with graphene-covered fibers and waveguides (Wu *et al.*, 2014; 2015; An *et al.*, 2020; Gu *et al.*, 2012; Vermeulen *et al.*, 2016; 2018; and Alexander *et al.*, 2017), and the observed effects were very pronounced, even at sub-Watt excitation powers and sub-mm-scale interaction lengths (Vermeulen *et al.*, 2018). The third-harmonic generation response of graphene has mostly been studied using free-space excitation rather than guided-mode excitation (Kumar *et al.*, 2013; Hong *et al.*, 2013; 2021; Baudisch *et al.*, 2018; Jiang *et al.*, 2018; Soavi *et al.*, 2018; and Calafell *et al.*, 2021), since for this nonlinear process the longer interaction length available in waveguiding media can only be efficiently exploited if the widely spaced fundamental and third-harmonic wavelengths are phase matched. Advanced dispersion engineering and intermodal phase matching [see, e.g., Efimov *et al.* (2003) and Surya *et al.* (2018)] have already enabled phase-matched third-harmonic generation in waveguiding media without graphene (Fig. 8), so it would be interesting to investigate the change in conversion efficiency when adding graphene to these bare waveguiding structures.

From an application perspective, graphene's nonlinear refraction, although pronounced, is further away from practical usage as compared to its saturable absorption functionality. The manufacturability of refractive and absorptive graphene devices is essentially the same (see Sec. IV A), but the lossy nature of graphene has a different impact on their respective application fields. When graphene on a fiber or on-chip waveguide is used as a saturable absorber in a laser cavity, its unwanted absorption loss (i.e., the non-saturable loss α_{ns}) can be compensated for by the gain that the laser amplifier

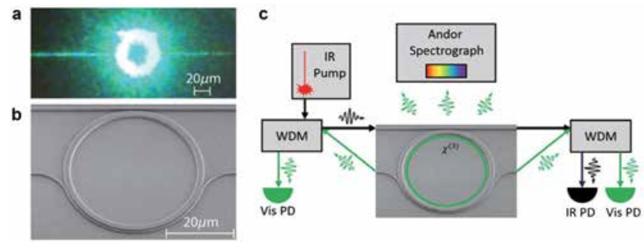

FIG. 8. (a) Spectrograph image of third-harmonic light scattered from a bare ring waveguide device designed for third-harmonic generation with intermodal phase matching. (b) Scanning electron microscopy image of the ring device. (c) Schematic of the experimental setup. An infrared (IR) pump beam is coupled into the ring through a wavelength division multiplexer (WDM). Two visible photodetectors (Vis PDs) and one IR photodetector (IR PD) were used to monitor the third-harmonic output and the IR transmission, respectively. Reproduced with permission from Surya *et al.*, Otpica **5**, 103–108 (2018). Copyright 2018, Optica Publishing Group.

provides. In contrast, nonlinear refraction devices, such as all-optical wavelength converters, broadband light sources, or nonlinear pulse compressors, usually do not contain amplifying media, and the implementation of graphene in such devices tends to result in a significant reduction of the overall output power as compared to the input power. A possible solution could be to further enhance the material's refraction efficiency such that the required graphene length on the fiber or waveguide can be shortened and the losses reduced. As pointed out in Sec. II B, orders-of-magnitude refraction enhancements have been obtained by adding plasmonics or quantum dots or by applying THz excitation to graphene samples in the free space (Calafell *et al.*, 2021; Hong *et al.*, 2021; and Hafez *et al.*, 2018). However, it remains to be seen how these enhancement approaches should be implemented for graphene on a fiber or waveguide and what the overall refraction-versus-loss balance would be in that case. Alternatively, one can focus on reducing the unwanted graphene losses. Electrical gating as illustrated in Figs. 6 and 7 can indeed reduce the losses in graphene, but it also influences the nonlinear refraction efficiency of the 2D material. Hence, to enable practical nonlinear refraction devices based on gated graphene-covered fibers and waveguides, one needs to determine the gating conditions where sufficiently low absorption for real-life applications is combined with high-performance device operation.

It is clear that further investigations, both theoretical and experimental, will be required to find the optimal refraction-versus-loss balance for all of the approaches described in this section. A wide variety of theories on graphene's nonlinear refraction have been presented over the past decade [see, e.g., Zhang and Voss (2011), Cheng *et al.* (2014; 2015), Mikhailov (2016), Baudisch *et al.* (2018), and Castelló-Lurbe *et al.* (2020)], but the importance of free-carrier refraction effects requiring non-perturbative treatment has become more apparent over the past few years (Vermeulen *et al.*, 2018; Baudisch *et al.*, 2018; and Castelló-Lurbe *et al.*, 2020). The theoretical frameworks of Baudisch *et al.* (2018) and Castelló-Lurbe *et al.* (2020) describe free-carrier-induced nonlinear refraction in graphene starting from its fundamental material properties. Both the Fermi level and carrier temperature were shown to have an important impact on the refractive behavior, and the calculation results were also validated with experimental data. In one of the frameworks (Castelló-Lurbe *et al.*, 2020), the so-called population recipe (Butcher and Cotter, 1990) was adopted to obtain a closed-form expression containing σ_{FCR}, for the nonlinear response, an expression that can be readily embedded in the pulse propagation equations used for waveguiding media. This approach is beneficial for practical device design as it allows predicting graphene's nonlinear refractive behavior in both free-space and guided-mode configurations (Castelló-Lurbe *et al.*, 2020; Linale *et al.*, 2022). At the same time, the population recipe it relies on only holds for excitation pulses of at least 100 fs. Very recently, another model was introduced that, although not as easily accessible as the framework in Castelló-Lurbe *et al.* (2020), allows dealing with excitation pulses shorter than 100 fs in graphene-covered waveguides (Sahoo *et al.*, 2021).

Despite the challenging refraction-versus-loss equilibrium as pointed out above, graphene might find applications well beyond the well-established nonlinear device functionalities, such as all-optical wavelength conversion and nonlinear pulse compression. For example, as pointed out in Sec. II B, when moving from telecom excitation wavelengths around 1550 nm to short-wave near-infrared wavelengths around 800 nm, the refractive nonlinearity of quasi-undoped graphene can switch sign from negative to positive (Chen *et al.*, 2013; Vermeulen *et al.*, 2016; Demetriou *et al.*, 2016; Dremetsika *et al.*, 2016; and Thakur *et al.*, 2019). As such, one could conceptualize a graphene device that spectrally broadens pulses in one spectral domain, while inducing spectral narrowing in another. In addition, when considering operation at a fixed wavelength, graphene could be exploited as a material that cancels out unwanted nonlinear effects from other materials with opposite nonlinearity sign. Along the same lines, it could even extend the scope of the "periodic poling" method, often used for second-harmonic generation, toward third-order processes, such as four-wave mixing (Vermeulen *et al.*, 2016). To give an example, while bare silicon waveguides exhibit a positive nonlinearity at telecom wavelengths, a negative value was measured after coverage with quasi-undoped graphene (Vermeulen *et al.*, 2016). As such, periodic poling could be obtained by alternating silicon waveguide sections with and without graphene coverage. An important question remains: Could the graphene nonlinearity switch sign simply by tuning its Fermi level with gating? Recent experimental results, indeed, imply real-time tunability of graphene's nonlinear refraction both in magnitude and sign by means of gating (Alexander *et al.*, 2018). This makes graphene, probably, the most versatile nonlinear refractive material known to date, and the possibilities it enables for future graphene-on-fiber/waveguide devices are just beginning to reveal themselves.

V. CONCLUSION

The past decade has brought major progress in the research on graphene's saturable absorption and nonlinear refraction behavior. Recent studies have shown that the latter often originates from free carrier effects, just like saturable absorption. Both nonlinear phenomena also strongly depend on the fundamental material properties of the graphene sample under study and particularly on its Fermi level, so it is of crucial importance to consistently provide this information in future works.

Integrating graphene along fibers and on-chip waveguides allows tailoring the interaction length to optimize the nonlinear performance and at the same time represents an important step forward toward practical graphene-based nonlinear-optical devices. Graphene-on-fiber/waveguide saturable absorbers have already been successfully embedded in fiber laser cavities to obtain modelocked laser operation with ultrashort femtosecond pulses. Graphene's nonlinear refraction, however, is further away from practical usage as compared to its saturable absorption functionality, as the material's lossy nature has a different impact on the respective application fields. Nevertheless, the nonlinearity enhancement approaches demonstrated recently and the tunability of graphene's optical properties by means of gating enable several optimization strategies to ensure that the material's practical applicability will be determined by its advantageous nonlinear properties rather than its losses. Furthermore, the versatile nonlinearity sign of graphene might open up functionalities not considered before, such as "periodic poling" for four-wave mixing. Further theoretical and experimental study, combined with advanced device manufacturing, will pave the way to the optimal exploitation of graphene's unique nonlinear-optical properties in real-life applications.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

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

Alexander, K., Savostianova, N. A., Mikhailov, S. A., Van Thourhout, D., and Kuyken, B., "Gate-tunable nonlinear refraction and absorption in graphene-covered silicon nitride waveguides," ACS Photonics **5**, 4944–4950 (2018).

An, N., Tan, T., Peng, Z., Qin, C., Yuan, Z., Bi, L., Liao, C., Wang, Y., Rao, Y., Soavi, G., and Yao, B., "Electrically tunable four-wave-mixing in graphene heterogeneous fiber for individual gas molecule detection," Nano Lett. **20**, 6473–6480 (2020).

Bao, Q., Zhang, H., Wang, Y., Ni, Z., Yan, Y., Shen, Z. X., Loh, K. P., and Tang, D. Y., "Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers," Adv. Funct. Mater. **19**, 3077–3083 (2009).

Baudisch, M., Marini, A., Cox, J. D., Zhu, T., Silva, F., Teichmann, S., Massicotte, M., Koppens, F., Levitov, L. S., García de Abajo, F. J., and Biegert, J., "Ultrafast nonlinear optical response of Dirac fermions in graphene," Nat. Commun. **9**, 1018 (2018).

Bonaccorso, F., Sun, Z., Hasan, T., and Ferrari, A. C., "Graphene photonics and optoelectronics," Nat. Photonics **4**, 611–622 (2010).

Bruna, M. and Borini, S., "Assessment of graphene quality by quantitative optical contrast analysis," J. Phys. D: Appl. Phys. **42**, 175307 (2009).

Bruna, M., Ott, A. K., Ijäs, M., Yoon, D., Sassi, U., and Ferrari, A. C., "Doping dependence of the Raman spectrum of defected graphene," ACS Nano **8**, 7432–7441 (2014).

Butcher, P. and Cotter, D., *The Elements of Nonlinear Optics* (Cambridge University Press, Cambridge, 1990).

Calafell, I. A., Rozema, L. A., Iranzo, D. A., Trenti, A., Jenke, P. K., Cox, J. D., Kumar, A., Bieliaiev, H., Nanot, S., Peng, C., Efetov, D. K., Hong, J.-Y., Kong, J., Englund, D. R., García de Abajo, F. J., Koppens, F. H. L., and Walther, P., "Giant enhancement of third-harmonic generation in graphene-metal heterostructures," Nat. Nanotechnol. **16**, 318–324 (2021).

Castelló-Lurbe, D., Thienpont, H., and Vermeulen, N., "Predicting graphene's nonlinear-optical refractive response for propagating pulses," Laser Photonics Rev. **14**, 1900402 (2020).

Chen, J.-h., Xiong, Y.-f., Xu, F., and Lu, Y.-q., "Silica optical fiber integrated with two-dimensional materials: Towards opto-electro-mechanical technology," Light: Sci. Appl. **10**, 78 (2021).

Chen, W., Wang, G., Qin, S., Wang, C., Fang, J., Qi, J., Zhang, X., Wang, L., Jia, H., and Chang, S., "The nonlinear optical properties of coupling and decoupling graphene layers," AIP Adv. **3**, 042123 (2013).

Cheng, J. L., Vermeulen, N., and Sipe, J. E., "Third order optical nonlinearity of graphene," New J. Phys. **16**, 053014 (2014).

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

Ciuk, T., Pasternak, I., Krajewska, A., Sobieski, J., Caban, P., Szmidt, J., and Strupinski, W., "Properties of chemical vapor deposition graphene transferred by high-speed electrochemical delamination," J. Phys. Chem. C **117**, 20833–20837 (2013).

Cox, J. D. and García de Abajo, F. J., "Transient nonlinear plasmonics in nanostructured graphene," Optica **5**, 429–433 (2018).

Craciun, M. F., Russo, S., Yamamoto, M., and Tarucha, S., "Tuneable electronic properties in graphene," Nano Today **6**, 42–60 (2011).

Dawlaty, J. M., Shivaraman, S., Chandrashekhar, M., Rana, F., and Spencer, M. G., "Measurement of ultrafast carrier dynamics in epitaxial graphene," Appl. Phys. Lett. **92**, 042116 (2008).

Demetriou, G., Bookey, H. T., Biancalana, F., Abraham, E., Wang, Y., Ji, W., and Kar, A. K., "Nonlinear optical properties of multilayer graphene in the infrared," Opt. Express **24**, 13033–13043 (2016).

Demongodin, P., El Dirani, H., Lhuillier, J., Crochemore, R., Kemiche, M., Wood, T., Callard, S., Rojo-Romeo, P., Sciancalepore, C., Grillet, C., and Monat, C., "Ultrafast saturable absorption dynamics in hybrid graphene/Si_3N_4 waveguides," APL Photonics **4**, 076102 (2019).

Deng, M., Liao, Z., Chen, Y., Yang, N., Yan, X., Zhang, C., Dai, N., and Wang, Y., "On-chip ultrafast pulse generation based on graphene-silicon hybrid waveguides," Photonics Res. **9**, 1660–1666 (2021).

Dremetsika, E., Dlubak, B., Gorza, S.-P., Ciret, C., Martin, M.-B., Hofmann, S., Seneor, P., Dolfi, D., Massar, S., Emplit, P., and Kockaert, P., "Measuring the nonlinear refractive index of graphene using the optical Kerr effect method," Opt. Lett. **41**, 3281–3284 (2016).

Efimov, A., Taylor, A., Omenetto, F., Knight, J., Wadsworth, W., and Russell, P. St. J., "Phase-matched third harmonic generation in microstructured fibers," Opt. Express **11**, 2567–2576 (2003).

Gu, T., Petrone, N., McMillan, J. F., van der Zande, A., Yu, M., Lo, G. Q., Kwong, D. L., Hone, J., and Wong, C. W., "Regenerative oscillation and four-wave mixing in graphene optoelectronics," Nat. Photonics **6**, 554–559 (2012).

Guo, B., Q. l. Xiao, Wang, S. h., and Zhang, H., "2D layered materials: Synthesis, nonlinear optical properties, and device applications," Laser Photonics Rev. **13**, 1800327 (2019).

Hafez, H. A., Kovalev, S., Deinert, J.-C., Mics, Z., Green, B., Awari, N., Chen, M., Germanskiy, S., Lehnert, U., Teichert, J., Wang, Z., Tielrooij, K.-J., Liu, Z., Chen, Z., Narita, A., Müllen, K., Bonn, M., Gensch, M., and Turchinovich, D., "Extremely efficient terahertz high-harmonic generation in graphene by hot Dirac fermions," Nature **561**, 507–511 (2018).

Hafez, H. A., Kovalev, S., Tielrooij, K. J., Bonn, M., Gensch, M., and Turchinovich, D., "Terahertz nonlinear optics of graphene: From saturable absorption to high-harmonics generation," Adv. Opt. Mater. **8**, 1900771 (2020).

Hasan, T., Sun, Z., Wang, F., Bonaccorso, F., Tan, P. H., Rozhin, A. G., and Ferrari, A. C., "Nanotube–polymer composites for ultrafast photonics," Adv. Mater. **21**, 3874–3899 (2009).

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

Hong, H., Wu, C., Zhao, Z., Zuo, Y., Wang, J., Liu, C., Zhang, J., Wang, F., Feng, J., Shen, H., Yin, J., Wu, Y., Zhao, Y., Liu, K., Gao, P., Meng, S., Wu, S., Sun, Z., Liu, K., and Xiong, J., "Giant enhancement of optical nonlinearity in two-dimensional materials by multiphoton-excitation resonance energy transfer from quantum dots," Nat. Photonics **15**, 510–515 (2021).

Hong, S.-Y., Dadap, J. I., Petrone, N., Yeh, P.-C., Hone, J., and Osgood, R. M., "Optical third-harmonic generation in graphene," Phys. Rev. X **3**, 021014 (2013).

Hussain, S. A., "Comparison of graphene and carbon nanotube saturable absorbers for wavelength and pulse duration tunability," Sci. Rep. **9**, 17282 (2019).

Jiang, T., Huang, D., Cheng, J. L., Fan, X., Zhang, Z., Shan, Y., Yi, Y., Dai, Y., Shi, L., Liu, K., Zeng, C., Zi, J., Sipe, J. E., Shen, Y.-R., Liu, W.-T., and Wu, S., "Gate-tunable third-order nonlinear optical response of massless Dirac fermions in graphene," Nat. Photonics **12**, 430–436 (2018).

Khan, A., Islam, S. M., Ahmed, S., Kumar, R. R., Habib, M. R., Huang, K., Hu, M., Yu, X., and Yang, D., "Direct CVD growth of graphene on technologically important dielectric and semiconducting substrates," Adv. Sci. **5**, 1800050 (2018).

Kovacevic, G., Shirahata, T., Wu, B., Yuan, P., Xiao, T.-H., Jin, L., Inoue, T., Maruyama, S., Cheng, Z., Set, S. Y., and Yamashita, S., "Patterned graphene on SiN waveguides for mode locking of fiber lasers," Jpn. J. Appl. Phys., Part 1 **57**, 102701 (2018).

Kumar, N., Kumar, J., Gerstenkorn, C., Wang, R., Chiu, H.-Y., Smirl, A. L., and Zhao, H., "Third harmonic generation in graphene and few-layer graphite films," Phys. Rev. B **87**, 121406(R) (2013).

Kuo, H.-H. and Hong, S.-F., "Nanographene-based saturable absorbers for ultrafast fiber lasers," J. Nanomater. **2014**, 631928.

Lee, C.-C., Miller, J. M., and Schibli, T. R., "Doping-induced changes in the saturable absorption of monolayer graphene," Appl. Phys. B **108**, 129–135 (2012).

Lee, E. J., Choi, S. Y., Jeong, H., Park, N. H., Yim, W., Kim, M. H., Park, J.-K., Son, S., Bae, S., Kim, S. J., Lee, K., Ahn, Y. H., Ahn, K. J., Hong, B. H., Park, J.-Y., Rotermund, F., and Yeom, D.-I., "Active control of all-fibre graphene devices with electrical gating," Nat. Commun. **6**, 6851 (2015).

Lee, H. C., Liu, W.-W., Chai, S.-P., Mohamed, A. R., Aziz, A., Khe, C.-S., Hidayah, N. M. S., and Hashim, U., "Review of the synthesis, transfer, characterization and growth mechanisms of single and multilayer graphene," RSC Adv. **7**, 015644 (2017).

Linale, N., Fierens, P. I., Vermeulen, N., and Grosz, D. F., "A generic model for the study of supercontinuum generation in graphene-covered nanowires," J. Phys.: Photonics **4**, 015001 (2022).

Liu, M., Yin, X., Ulin-Avila, E., Geng, B., Zentgraf, T., Ju, L., Wang, F., and Zhang, X., "A graphene-based broadband optical modulator," Nature **474**, 64–67 (2011).

Marini, A., Cox, J. D., and García de Abajo, F. J., "Theory of graphene saturable absorption," Phys. Rev. B **95**, 125408 (2017).

Martinez, A. and Sun, Z., "Nanotube and graphene saturable absorbers for fibre lasers," Nat. Photonics **7**, 842–845 (2013).

Mics, Z., Tielrooij, K.-J., Parvez, K., Jensen, S. A., Ivanov, I., Feng, X., Müllen, K., Bonn, M., and Turchinovich, D., "Thermodynamic picture of ultrafast charge transport in graphene," Nat. Commun. **6**, 7655 (2015).

Mikhailov, S. A., "Quantum theory of the third-order nonlinear electrodynamic effects of graphene," Phys. Rev. B **93**, 085403 (2016).

Mitta, S. B., Choi, M. S., Nipane, A., Ali, F., Kim, C., Teherani, J. T., Hone, J., and Yoo, W. J., "Electrical characterization of 2D materials-based field-effect transistors," 2D Mater. **8**, 012002 (2021).

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A., "Electric field effect in atomically thin carbon films," Science **306**, 666–669 (2004).

Peng, X. and Yan, Y., "Graphene saturable absorbers applications in fiber lasers," J. Eur. Opt. Soc.-Rapid Publ. **17**, 16 (2021).

Rafique, M. Z. E., Basiri, A., Bai, J., Zuo, J., and Yao, Y., "Graphene-plasmonic hybrid metasurface saturable absorber," in *OSA Advanced Photonics Congress 2021* (Optica Publishing Group, 2021), paper No. M5B.3.

Sahoo, A., Marini, A., and Roy, S., "Free-carrier-induced nonlinear dynamics in hybrid graphene-based photonic waveguides," Phys. Rev. A **104**, 063501 (2021).

Soavi, G., Wang, G., Rostami, H., Purdie, D. G., De Fazio, D., Ma, T., Luo, B., Wang, J., Ott, A. K., Yoon, D., Bourelle, S. A., Muench, J. E., Goykhman, I., Dal Conte, S., Celebrano, M., Tomadin, A., Polini, M., Cerullo, G., and Ferrari, A. C., "Broadband, electrically tunable third-harmonic generation in graphene," Nat. Nanotechnol. **13**, 583–588 (2018).

Song, Y.-W., Jang, S.-Y., Han, W.-S., and Bae, M.-K., "Graphene mode-lockers for fiber lasers functioned with evanescent field interaction," Appl. Phys. Lett. **96**, 051122 (2010).

Sun, Z., Hasan, T., Torrisi, F., Popa, D., Privitera, G., Wang, F., Bonaccorso, F., Basko, D. M., and Ferrari, A. C., "Graphene mode-locked ultrafast laser," ACS Nano **4**, 803–810 (2010).

Surya, J. B., Guo, X., Zou, C.-L., and Tang, H. X., "Efficient third-harmonic generation in composite aluminum nitride/silicon nitride microrings," Optica **5**, 103–108 (2018).

Thakur, S., Semnani, B., Safavi-Naeini, S., and Majedi, A. H., "Experimental characterization of the ultrafast, tunable and broadband optical Kerr nonlinearity in graphene," Sci. Rep. **9**, 10540 (2019).

Vanmol, K., Saurav, K., Panapakkam, V., Thienpont, H., Vermeulen, N., Watte, J., and Van Erps, J., "Mode-field matching down-tapers on single-mode optical fibers for edge coupling towards generic photonic integrated circuit platforms," J. Lightwave Technol. **38**, 4834–4842 (2020).

Vasko, F. T., "Saturation of interband absorption in graphene," Phys. Rev. B **82**, 245422 (2010).

Vermeulen, N., Castelló-Lurbe, D., Cheng, J. L., Pasternak, I., Krajewska, A., Ciuk, T., Strupinski, W., Thienpont, H., and Van Erps, J., "Negative Kerr nonlinearity of graphene as seen via chirped-pulse-pumped self-phase modulation," Phys. Rev. Appl. **6**, 044006 (2016).

Vermeulen, N., Castelló-Lurbe, D., Khoder, M., Pasternak, I., Krajewska, A., Ciuk, T., Strupinski, W., Cheng, J. L., Thienpont, H., and Van Erps, J., "Graphene's nonlinear-optical physics revealed through exponentially growing self-phase modulation," Nat. Commun. **9**, 2675 (2018).

Wang, H., Miao, L., Jiang, Y., Lu, S., Li, Z., Li, P., Zhao, C., Zhang, H., and Wen, S., "Enhancing the saturable absorption and carrier dynamics of graphene with plasmonic nanowires," Phys. Status Solidi B **252**, 2159–2166 (2015).

Wong, C. Y., Cheng, Z., Shi, Z., Chen, Y. M., Xu, K., and Tsang, H. K., "Mode-locked fiber laser using graphene on silicon waveguide," in *10th International Conference on Group IV Photonics* (IEEE, 2013), pp. 35–36.

Wu, Y., Yao, B., Cheng, Y., Rao, Y., Gong, Y., Zhou, X., Wu, B., and Chiang, K. S., "Four-wave mixing in a microfiber attached onto a graphene film," IEEE Photonics Technol. Lett. **26**, 249–252 (2014).

Wu, Y., Yao, B. C., Feng, Q. Y., Cao, X. L., Zhou, X. Y., Rao, Y. J., Gong, Y., Zhang, W. L., Wang, Z. G., Chen, Y. F., and Chiang, K. S., "Generation of cascaded four-wave-mixing with graphene-coated microfiber," Photonics Res. **3**, A64–A68 (2015).

Xing, G., Guo, H., Zhang, X., Sum, T. C., and Huan, C. H. A., "The physics of ultrafast saturable absorption in graphene," Opt. Express **18**, 4564–4573 (2010).

Yamashita, S., "Nonlinear optics in carbon nanotube, graphene, and related 2D materials," APL Photonics **4**, 034301 (2019).

You, J. W., Bongu, S. R., Bao, Q., and Panoiu, N. C., "Nonlinear optical properties and applications of 2D materials: Theoretical and experimental aspects," Nanophotonics **8**, 63–97 (2019).

Zapata, J. D., Steinberg, D., Saito, L. A. M., de Oliveira, R. E. P., Cárdenas, A. M., and de Souza, E. A. T., "Efficient graphene saturable absorbers on D-shaped optical fiber for ultrashort pulse generation," Sci. Rep. **6**, 020644 (2016).

Zhang, S., Li, Z., and Xing, F., "Review of polarization optical devices based on graphene materials," Int. J. Mol. Sci. **21**, 1608 (2020).

Zhang, Z. and Voss, P. L., "Full-band quantum-dynamical theory of saturation and four-wave mixing in graphene," Opt. Lett. **36**, 4569 (2011).

Zhu, S.-E., Yuan, S., and Janssen, G. C. A. M., "Optical transmittance of multilayer graphene," Europhys. Lett. **108**, 017007 (2014).