Gate-tunable third-order nonlinear optical response of massless Dirac fermions in graphene

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Graphene with massless Dirac fermions can have exceptionally strong third-order optical nonlinearities. Yet reported values of nonlinear optical susceptibilities for third-harmonic generation (THG), four-wave mixing (FWM) and self-phase modulation vary over six orders of magnitude. Such variation likely arises from frequency-dependent resonance effects of different processes in graphene under different doping. Here, we report an experimental study of THG and FWM in graphene using gate tuning to adjust the doping level and vary the resonant condition. We find that THG and sum-frequency FWM are strongly enhanced in heavily doped graphene, while the difference-frequency FWM appears just the opposite. Difference-frequency FWM exhibited a novel divergence towards the degenerate case in undoped graphene, leading to a giant enhancement of the nonlinearity. The results are well supported by theory. Our full understanding of the diverse nonlinearity of graphene paves the way towards future design of graphene-based nonlinear optoelectronic devices.

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Shift of chemical potential by gate tuning

For gate tuning of the chemical potential, we adopted the ion-gel gating method using the field-effect transistor structure with graphene supported by fused silica, as depicted in Fig. 1a. This device structure enabled us to measure the linear and nonlinear optical responses of graphene at room temperature and monitor in situ the chemical potential $\mu$ versus the gate voltage $V_g$. Figure 1b plots the graphene resistance as a function of $V_g$. At $V_g \approx 0.9$ V, the resistance is maximum, indicating that graphene is at the charge neutral point (CNP, $\mu = 0$). Away from the CNP, the resistance decreases and $\mu$ shifts to positive or negative values accordingly.

To extract the chemical potential $\mu$ as a function of $V_g$, we measured the transmittance spectra of the gated sample at normal incidence. The spectra at different $V_g$ normalized against the one at $V_g = 0$ are shown in Fig. 1c. As described in Fig. 1d, the interband transitions should be suppressed by Pauli blocking for photon energy $\hbar \omega < 2|\mu|$, where $\omega$ is the angular frequency of light, resulting in a step-like transmission spectrum if the temperature and damping effects are neglected. At finite temperature and with proper damping factors, the spectrum is broadened into a shoulder-like one, as seen in Fig. 1c. We could use the Kubo formula to fit each spectrum and deduce $|\mu|$ from the fitting (described in the Supplementary Information). The deduced $|\mu|$ as a function of $V_g$ is plotted in Fig. 1b. The result agrees well with that (red curve in Fig. 1b) predicted from an ion-gel-gated graphene device with a capacitance of $2.5 \mu$F cm$^{-2}$ (see the Supplementary Information). The uncertainty of $|\mu|$ so obtained was $\pm 10$ meV. Ion-gel gating permitted us to tune $|\mu|$ from 0 to $\sim 0.9$ eV (ref. 3), corresponding to a tuning of the carrier density of graphene from 0 to $-6 \times 10^{13}$ cm$^{-2}$.

Experiment on THG

The linearly polarized femtosecond laser at 1,566 nm ($\hbar \omega_{\text{THG}} = 0.794$ eV) was used to excite THG of ion-gel-gated graphene at normal incidence, as described in the Methods. Two representative output spectra taken in the reflected direction at $\mu = 0$ and $\mu = -0.74$ eV are shown in Fig. 2a. The former shows a THG peak at 2,381 eV superimposed on a broad background, which is absent in the latter. The broad background is known to be due to ultrafast photoluminescence arising from Auger-like scattering of one-photon excited carriers. It disappears when $2|\mu|$ is larger than $\hbar \omega_{\text{THG}}$, so that the one-photon excitation is Pauli blocked. While the THG peak was readily observable at all $\mu$ (Fig. 2b), its intensity exhibits shoulder-like features as $2|\mu|$ moves over $\hbar \omega_{\text{THG}}$ and reaches a maximum strength of $\sim 30$ times that of $\mu = 0$, as seen from the curves plotted in Fig. 2c for four different input wavelengths: 1,300 nm (0.956 eV), 1,400 nm (0.888 eV), 1,566 nm (0.794 eV) and 1,650 nm (0.753 eV). As will be explained more clearly later, these shoulder-like features arise from stepwise switching off of resonant transitions in graphene when $|\mu|$ increases: one-photon, two-photon and three-photon resonant transitions are switched off successively when $2|\mu|$ becomes larger than $\hbar \omega_{\text{THG}}$, $2\hbar \omega_{\text{THG}}$ and $3\hbar \omega_{\text{THG}}$, respectively (unfortunately, the last step could not be reached in our experiment). Note that without graphene on the substrate, THG from the ion-gel-gated fused silica was not observable.

The dependence of THG on input/output polarization is governed by the $D_{6h}$ structural symmetry of graphene. We found that if the normally incident input was linearly polarized and the analyzer for the reflected THG was set at an angle $\theta$ with respect to the input polarization, the observed THG output was proportional to $\cos^2 \theta$. Figure 2d presents two examples of THG versus $\theta$ taken at $\mu = -0.89$ eV with input polarizations along and perpendicular to the source–drain direction (Fig. 1a), respectively. In another measurement, we set the output analyzer parallel to the input polarization and rotated them together with respect to the sample about its surface normal. The observed THG was isotropic, independent of the azimuthal rotation (Fig. 2e). Both results can be understood knowing that the third-order nonlinear susceptibility element,
Fig. 2 | Gate-controlled THG from graphene and its polarization patterns. a. Measured THG spectra by a normally incident femtosecond input pulse at 1,566 nm from graphene gated at μ = 0 (black curve, magnified by 15 times) and μ = −0.74 eV (red curve). The broadband background of the black curve comes from up-converted photoluminescence due to rapid carrier–carrier scattering following one-photon interband excitation. b. Measured spectra versus 2μ and photon energy showing strong dependence of THG at 2.381 eV with μ. The spectra in a correspond to the signal variation following the black and red dashed lines. c. THG signal as a function of 2μ generated by different input wavelengths: 1,300 nm, 1,400 nm, 1,566 nm and 1,650 nm. The corresponding incident laser fluences were 3.14, 3.68, 2.86 and 1.54 J m−2, respectively. Curves are normalized for comparison. Dots are experimental data and curves are guides for the eye. Red and blue arrows mark the shoulder and maximum regions, respectively. d. Illustration that a linearly polarized input generates a linearly co-polarized THG output (with 0.89 eV). In d, THG output through an analyser is plotted as a function of angle θ between the analyser axis and the input polarization and rotating together azimuthally with respect to the sample, the THG output appears isotropic.

χ(3) of graphene is responsible for the THG (see the Supplementary Information).

Experiment on FWM
FWM with two input frequencies ωi and ωj (ωi > ωj) is a more general process than THG, but the effect of shifting μ to switch resonant transitions on and off is similar. Four FWM processes, described in Fig. 3a, are considered here: two-sum-frequency mixings (SFM) with output at 2ωi + ωj and ωi + 2ωj, and two difference-frequency mixings (DFM) with output at 2ωi − ωj and 2ωj − ωi. In our experiment, we chose hωi = 1.195 eV (1,040 nm) and hωj = 0.956 eV (1,300 nm), which generated SFM outputs at 3.346 eV (371 nm) and 3.107 eV (400 nm), and DFM outputs at 1.434 eV (867 nm) and 0.717 eV (1,734 nm). The last DFM output was outside our spectral detection range. To study this process, we slightly shifted hωj to 0.994 eV (1,250 nm) to generate DFM (2ωj − ωi) at 0.794 eV (1,566 nm). The observed spectra taken at μ = 0 and μ = −0.73 eV for the four mixing processes are displayed in Fig. 3b–d, showing the respective spectral peaks.

The SFM peaks are much stronger at |μ| = 0.73 eV than at μ = 0, but the DFM peaks show the opposite trend. The SFM processes are expected to be quite similar to THG, exhibiting a shoulder-like rise as 2|μ| approaches hωi and hωj (individual shoulders merge into one because of broadening). This is seen for the h(ωi + 2ωj) process in Fig. 3c. The curve shows another rise as 2|μ| approaches 2hωj, 2hωi and h(ωi + ωj). Unfortunately, the top of the rise cannot be seen because it was outside the tuning range of |μ|. The DFM processes behave oppositely: at μ = 0, the output is strong, but as 2|μ| moves towards hωi, hωj, h(2ωi − ωj) or h(2ωi − ωi), it shows a step-like drop, as seen in Fig. 3e for the 2ωi − ωj process and Fig. 3f for both DFM processes.

Theoretical understanding and comparison with experiment
To understand the observed μ-dependences of THG and FWM in graphene in depth, we resort to the theory developed by Cheng et al.39,40. The analytical expression of the third-order nonlinear susceptibility, χ(3), generally has 8 terms for THG and 24 terms for the FWM processes studied here37,38. In our case, χ(3) of graphene is dominated by contributions from interband transitions; with the gapless, linearly dispersed band structure, each term in χ(3) can only have a single resonance at either ωi = 2νi|k| or |ωi ± ωj| = 2νi|k| or |2ωi ± ωj| = 2νi|k| that provides the resonant enhancement. Here, ωi, ωj and νi refer to the input frequencies, which can be either ωi or ωj in practice, νi is the Fermi velocity in graphene and k is the electron wavevector in the first Brillouin zone. The abovementioned resonances can be switched off by Pauli blocking if 2|μ| becomes larger than hωi, hωj ± hωj and [2hωj ± hωj], respectively. It is expected that switch-off of resonances will introduce characteristic changes of χ(3).

Mathematically, we can write a single resonant term in χ(3) in the form of \( \int \frac{A(k)\Delta(n(k, \mu))}{\omega_{ij} - 2v_i |k|} \) dK, where A(k) is the product of transition matrix elements and off-resonance denominators, ωij is the input frequency or frequency combination on interband resonant transition and Δn(k, μ) is the difference of Fermi distributions of electrons between valence and conduction bands. The dependence
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imperfect cancellation of the $H_x(1)$ very small. With 2. The three terms in the brackets describe switching off of one-, two- and three-photon resonant transitions as 2$|\mu>$ moves over $h\omega_o$ and 3$|\mu>$ as illustrated in Fig. 4a. Note that the signs of the first and third terms for one-photon and three-photon resonant transitions are opposite to that of the second term for two-photon resonant transition. When 2$|\mu|$ < $h \omega_o$ all three terms contribute to $x_{xxx}^{(3)}$ but they nearly cancel each other, leaving $x_{xxx}^{(3)}$ very small. With $h\omega_o$ < 2$|\mu|$ < 2$h\omega_o$, one-photon resonant transition is blocked and $G(2h\omega_o/|\mu|) \sim 0$; imperfect cancellation of the $G(2h\omega_o/|\mu|)$ and $G(2h\omega_o/|\mu|)$ terms leads to a significant positive value of $x_{xxx}^{(3)}$. While 2$h\omega_o$ < 2$|\mu|$ < 3$h\omega_o$, the value of $x_{xxx}^{(3)}$ increases further as both one-photon and two-photon resonant transitions are blocked with $G(2h\omega_o/|\mu|) \sim 0$ and $G(2h\omega_o/|\mu|) \sim 0$. Finally, for 2$|\mu|$ > 3$h\omega_o$, all resonant transitions are blocked, leaving again a vanishingly small $x_{xxx}^{(3)}$ from nonresonant contributions. The calculated $\mu$-dependence of $x_{xxx}^{(3)}$ with $h\omega_o$ = 0.956 eV is plotted in Fig. 4b.

While the analytic expression captures the essence of the THG response, the detailed shape of the curve is far from reality because resonant damping and finite electron temperature effects have been neglected. For better comparison with experiment, we include the finite electron temperature ($T_e$) effect on $x_{xxx}^{(3)}$ and proper resonant damping factors ($\Gamma_r = 0.2 \times |\mu|/eV$ (ref. 29) and $\Gamma_r = 0.5 meV$ (ref. 29) for interband and intraband resonances, respectively) in the calculation (Fig. 4c). Both have the effect of smearing out the sharp features, making the calculated spectrum comparable with experiment. As described in detail in the Supplementary Information, the quasi-equilibrium electron temperature $T_e$ can be very high if interband excitations of electrons are strong (4). This happens when the one-photon transition is allowed (2$|\mu| < h\omega_o$); for an incident fluence of 3.14J/m$^2$ from a 200 fs pulse, $T_e$ reaches about 2,100 K. However, if the one-photon transition is blocked (2$|\mu| > h\omega_o$), the electron temperature rise is negligible, and $T_e$ remains essentially at the room temperature (300 K). The temperature effect on THG actually is not very significant because $x_{xxx}^{(3)}$ is small in the range of 2$|\mu|$ < $h\omega_o$ (Supplementary Fig. 1).
Fig. 4 | Theoretical understanding of $\mu$-dependent $\chi^{(3)}$ in THG. a, Schematics showing how increase of $|\mu|$ successively switches off one-photon (magenta), two-photon (green) and three-photon (red) interband transitions by Pauli blocking in graphene. The switch-off is gradual at finite temperature and damping and is described by the reduced brightness of the arrows. Two-photon transition contributes to $\chi^{(3)}$ positively, while one- and three-photon transitions contribute negatively. b, Calculated $\chi^{(3)}$ versus $\mu$ for THG at $3h\omega_0 = 2.868$ eV from graphene at zero temperature with resonant damping neglected, exhibiting singularities at $2|\mu| = h\omega_0$, $2h\omega_0$, and $3h\omega_0$. c, Comparison between experimental data (blue squares) and theoretical simulation (black curve) taking into account the finite temperature and resonant damping effects. $T_f = 300$ K and $2,100$ K for $2|\mu| > h\omega_0$ and $\mu = 0$, respectively, $\Gamma_f = 0.2 \times |\mu|$ eV and $\Gamma_f = 0.5$ meV. The dashed lines mark the positions of $2|\mu| = h\omega_0$ (magenta), $2h\omega_0$ (green) and $3h\omega_0$ (red).

Similar discussion can be applied to FWM. The third-order susceptibility $\chi^{(3)}(\mu)$ for the two-colour SFM (2$\omega_1 + \omega_2$ and $\omega_1 + 2\omega_2$) increases with $|\mu|$ as for THG, but there are five resonant transitions for each SFM process, including: the one-photon transitions at $h\omega_0$ and $h\omega_0$, two-photon transitions at $2h\omega_1$ (or $2h\omega_0$ and $h(\omega_1 + \omega_2)$), and three-photon transition at $h(2\omega_0 + \omega_2)$ (or $h(2\omega_1 + \omega_0)$). Figure 5a shows the calculated $\chi^{(3)}$ versus $\mu$ for $\omega_1 + 2\omega_2$ SFM at zero temperature and without resonant damping. The characteristic features around the five specific values of $\mu$ are clearly seen. The expression of $\chi^{(3)}$ for SFM is given by Supplementary equation (3-4). Again, the terms for two-photon transitions have opposite sign with respect to the terms for one- and three-photon transitions, leading to a much weaker $\chi^{(3)}$ when $2|\mu| < h\omega_0$ and $h\omega_0$. The fine structure of Pauli blocking and resonant damping effects, resonances due to one-photon and two-photon transitions are greatly smeared, as shown in Fig. 5b. Similar to the THG case, the effect of high $T_f$ for $2|\mu| < h\omega_0$, (assuming $\omega_1 > \omega_2$) is not very significant in SFM. The theoretical simulation reasonably agrees with the experimental result plotted in Fig. 5b.

In sharp contrast to SFM, the DFM processes (2$\omega_1 - \omega_2$ and 2$\omega_3 - \omega_1$) show opposite $\mu$-dependence with the output strongest at $\mu \sim 0$. The expression of $\chi^{(3)}$ for DFM is the same as that for SFM except for a flip of sign on $\omega_1$ or $\omega_2$ (see the Supplementary Information). Pauli blocking occurs at $2|\mu| > h\omega_1$ and $h\omega_1$ for one-photon transitions, $2|\mu| > 2h\omega_0$ (or $2h\omega_0$ and $h(\omega_1 + \omega_2)$) for two-photon transitions, and $2|\mu| > h(2\omega_0 + \omega_1)$ (or $h(2\omega_1 + \omega_0)$) for three-photon transition. The corresponding characteristic features can again be seen in the calculated $\chi^{(3)}$ versus $\mu$ (Fig. 5c for the 2$\omega_1 - \omega_2$ DFM process). Note that the feature at $2|\mu| = h|\omega_1 - \omega_2|$ is present, but is very weak and hardly visible in Fig. 5c, because it is described by a $G\left(\frac{2|\mu|}{h|\omega_1 - \omega_2|}\right)$ term with a coefficient proportional to $(\omega_1 - \omega_2)^3$. Increase or decrease at each step of the change depends on the sign of the frequency factor associated with each type of transition. It is seen that for the 2$\omega_1 - \omega_2$ DFM process, there are three terms in the equation for $\chi^{(3)}$ that have the frequency factor $(\omega_1 - \omega_2)^3$ in the denominator. They contribute dominantly to $\chi^{(3)}$ when $2|\mu| < h\omega_0$, especially if $\omega_1$ is close to $\omega_0$, and yield a large step change when each term drops off at a specific value of $|\mu|$ because of Pauli blocking of the specific type of resonant transitions. The exceptionally large $\chi^{(3)}$ for DFM is in strong contrast to the very weak $\chi^{(3)}$ for SFM. Inclusion of the finite electron temperature and resonant damping effects in the calculation of $\chi^{(3)}$, as a function of $\mu$ again smears out the peaks and spreads out the curve. In this case, the effect of high $T_f$ for $2|\mu| < h\omega_0$ (assuming $\omega_1 > \omega_2$) is more significant; as $|\mu|$ decreases towards zero, it causes $\chi^{(3)}$ to increase less and spread out more (Supplementary Fig. 2). The calculated curve of $\chi^{(3)}$ versus $\mu$ agrees fairly well with the experimental results, as shown in Fig. 5d and Supplementary Fig. 2.

We note that as long as $2|\mu| < h\omega_0$ or $h\omega_0$, the 2$\omega_3 - \omega_1$ and 2$\omega_2 - \omega_1$ DFM would appear divergent through the frequency factor $(\omega_1 - \omega_2)^2$ as $\omega_1$ approaches $\omega_2$ (Supplementary equation (3-6) or (3-7)). One therefore expects that degenerate FWM including self-phase modulation would be extraordinarily strong in undoped graphene ($\mu = 0$). This was not noticed in the early pioneering work of Hendry et al. We experimentally verify such a behaviour, we measured DFM of 2$\omega_1 - \omega_2$, with $\mu$ close to zero, $\omega_1$ fixed at 1.195 eV (1,040 nm), and $\omega_1$ tuned from 0.956 eV (1,300 nm) to 1.11 eV (1,120 nm). As shown in Fig. 5e, $\chi^{(3)}$ for DFM increased by approximately three times as $\Delta \omega = \omega_1 - \omega_2$ decreased and agrees fairly well with the theoretical calculation. We expect a more rapid rise of DFM if DFM at smaller $\omega_1$ could be measured.
was satisfied in their experiments. For DFM, our experimental value of $|\chi^{(3)}_\text{xxxx}|$ is also close to the theoretical one as seen in Fig. 5c. It is seen that the measured values of $|\chi^{(3)}_\text{xxxx}|$ for THG and FWM in undoped graphene varies by about three orders of magnitude, and it could be further enhanced by another few orders if FWM moves towards degeneracy.

**Conclusions**

We have demonstrated that the third-order nonlinearity of graphene is exceptionally large and can be varied by orders of magnitude with the help of gate-controlled doping or shift of the chemical potential. The results can be understood from a unified theory on FWM in graphene. It is now possible to well predict the dependence of the third-order nonlinear responses of graphene on input frequencies and doping level. The understanding can be extended to other nonlinear optical processes in graphene, such as effective second-order processes\(^42-44\), and even high-order harmonic generation\(^45\). In general, the optical nonlinearity of linear-band materials with the chemical potential close to the Dirac or Weyl point tends to diverge in cases where input frequency combination approaches zero. The resulting giant nonlinearity of such materials, particularly graphene, can be of great use in future optoelectronic devices\(^4\).
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Author contributions

S.W. and W.-T.L. conceived and supervised the project. T.J., D.H., Y.S. and Y.Y. prepared the devices and performed the experiments, with assistance from Y.D., L.S. and J.Z. on gate-dependent optical transmittance measurement. X.F., Z.Z., K.L. and C.Z. provided the chemical vapour deposition-grown graphene samples. T.J., D.H., J.C., I.E.S., Y.-R.S., W.-T.L. and S.W. analysed the data. T.J., D.H., I.E.S., Y.-R.S., W.-T.L. and S.W. wrote the paper with contributions from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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Methods

Device fabrication. Single crystalline\textsuperscript{45} or polycrystalline\textsuperscript{47} graphene monolayers used in the experiment were grown by chemical vapour deposition and transferred onto fused silica substrates. Source, drain and gate electrodes (50 nm Au and 5 nm Cr) were patterned through a dry stencil mask by electron beam deposition. All the electrodes were wire-bonded to a chip carrier for electrical control. Ion-gel gating was achieved by uniformly applying freshly prepared ion-gel solution onto the graphene devices, and further drying in a glove box filled with high-purity argon gas. The ion-gel solution was prepared by dissolving 16.7 mg of poly(styrene-b-ethylene oxide-b-styrene) (PS-PEO-PS) and 0.5 g of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) into 1.82 ml of dry dichloromethane. PS-PEO-PS, [EMIM][TFSI] and dry dichloromethane were purchased from J&K Scientific. Experimental results of THG and FWM from single crystalline and polycrystalline graphene, as well as exfoliated monolayer, were found to be very much the same.

Characterization and measurement. The device characterization and experimental measurement were conducted in sample scanning optical microscopes that combined with femtosecond laser systems and an electrical transport setup. During the whole measurement, the graphene device was maintained in a dry nitrogen environment at room temperature. The CNP of graphene was determined by its maximum resistance in response to $V_g$ as shown in Fig. 1b. A Fourier transform infrared spectrometer (VERTEX 70) was used to measure the transmittance spectra of gated graphene, from which $\mu$ was deduced as described in the main text and in the Supplementary Information.

For THG measurements, a linearly polarized femtosecond laser beam (MaiTai HP and Inspire Auto, Spectra Physics) tunable from 345 to 2,500 nm was focused and normally incident on graphene through a microscopic objective (100x, numerical aperture 0.95, Nikon), and the reflected THG signal was collected. The sample sitting on a nano-positioning stage enabled us to locate defect-free areas on the sample. A single-photon counting silicon avalanche photodetector (Perkin-Elmer) or a fibre-coupled spectrograph equipped with a liquid-nitrogen-cooled silicon charge-coupled device (Princeton Instruments) was used to detect the THG signal after proper filtering. The detailed optical arrangement is depicted in Supplementary Fig. 3a. For measurement of the polarization-dependent azimuthal pattern of THG measurement (displayed in Fig. 2d,e), the transmitted THG geometry was adopted with the setup sketched in Supplementary Fig. 3b. For FWM measurements, a different femtosecond laser system (Insight Deepsee, Spectra Physics) was used, which could simultaneously produce two beams of different wavelengths at a repetition rate of 80 MHz, one tunable from 700 to 1,300 nm and the other fixed at 1,040 nm. The two beams were sent collinearly on the sample at normal incidence through a scanning optical microscope and the reflected FWM signal was detected. For the DFM signals in Fig. 3d (blue dots), the spectra were recorded by a fibre-coupled spectrograph equipped with a liquid-nitrogen-cooled InGaAs array detector (PyLoN-IR, Princeton Instruments).

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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