Broadband, electrically tunable third-harmonic generation in graphene

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Supplementary Information for
Broadband, electrically tuneable, third harmonic generation in graphene

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S1 THG power dependence
Supplementary Fig.1 plots the experimental power dependence of THG as a function of incident power in double logarithmic scale. The slope is consistent with the cubic relation given by Eq.2 in the main text.

S2 TGHE modeling
$\sigma^{(3)}_{\ell\ell\ell\ell}$ is calculated through a diagrammatic technique, with the light-matter interaction in the scalar potential gauge in order to capture all intra-, inter-band and mixed transitions [1–3]. We evaluate the diagram in Supplementary Fig.2 and denote by $\Pi^{(3)}_\ell$ the response function. $\hat{n}$ and $\hat{j}_\ell$ are the density and paramagnetic current operators. Then, $\sigma^{(3)}_{\ell\ell\ell\ell} = (ie)^3 \lim_{q \to 0} \partial^3 \Pi^{(3)}_\ell / \partial q^3_\ell$, where $e > 0$ is the fundamental charge [2]. The Dirac Hamiltonian of low-energy carriers in SLG is $\mathcal{H}_k = \hbar v_F \vec{k} \cdot \vec{\sigma}$ where $\vec{\sigma} = (\pm \sigma_x, \sigma_y)$ are the Pauli matrices in the sublattice basis. Note that $\pm$ represent the two valleys in the SLG Brillouin zone. We get $\sigma^{(3)}_{xxxx}(\omega, E_F, 0) = i\sigma_0^{(3)} \tilde{\sigma}^{(3)}_{xxxx}(\omega, E_F, 0)$ at $T_e = 0$ [1–3]:

$$\tilde{\sigma}^{(3)}_{xxxx}(\omega, E_F, 0) = \frac{17G(2|E_F|, \hbar \omega_+)}{24(\hbar \omega_+)^4} - \frac{64G(2|E_F|, 2\hbar \omega_+)}{24(\hbar \omega_+)^4} + \frac{45G(2|E_F|, 3\hbar \omega_+)}{24(\hbar \omega_+)^4}$$ (S1)
Supplementary Fig. 1. **THG power dependence.** THG power measured at $3\hbar\omega_0=1.56\text{eV}$ as a function of the fundamental power measured at $\hbar\omega_0=0.52\text{eV}$. The slope $\sim 3$ is typical of the THG process, as for Eq.2 of the main text.

where $G(x, y) = \ln \left| \frac{x+y}{x-y} \right|$, $\sigma_0^{(3)} = N_f e^4 \hbar \omega_F^2 / (32\pi)$ with $N_f = 4$ and $\hbar\omega_+ \equiv \hbar\omega + i0^+$. At finite $T_e$, $\sigma_{t\ell\ell}'$ is evaluated as [4]:

\[
\sigma_{\varrho\varrho}^{(3)}(\omega, E_F, T_e) = \frac{1}{4k_BT_e} \int_{-\infty}^{\infty} dE \frac{\sigma_{\varrho\varrho\varrho}(\omega, E, 0)}{\cosh^2 \left( \frac{E-\mu}{2k_BT_e} \right)}.
\]

(S2)

**S2.1 THGE of SLG as an interface layer**

In order to derive the THGE for SLG on a substrate we consider SLG as an interface layer between air and substrate [5, 6], see Supplementary Fig.3, and implement electromagnetic boundary conditions for the non-harmonic radiations. The Maxwell equations in the nonlinear medium in the $m(\geq 2)$-th order of perturbation are given by [7, 8]:

\[
\nabla \cdot \vec{B}^{(m)} = 0,
\]
\[
\nabla \cdot \vec{E}^{(m)} = \frac{\rho_f^{(m)}}{\epsilon_0} - \frac{1}{\epsilon_0} \nabla \cdot \vec{P}^{(m)},
\]
\[
\nabla \times \vec{E}^{(m)} = i\omega \Sigma \vec{B}^{(m)},
\]
\[
\nabla \times \vec{B}^{(m)} = \mu_0 \vec{J}_f^{(m)} - i\omega \Sigma \vec{E}^{(m)} - i\omega \Sigma \mu_0 \vec{B}^{(m)}.
\]

(S3)  (S4)  (S5)  (S6)
Supplementary Fig. 2. **Feynman diagram for Π_{ℓ}^{(3)} in the scalar potential gauge.** Solid/wavy lines indicate non-interacting Fermionic propagators/external photons. Solid circles and square indicate density and current vertexes.

Supplementary Fig. 3. **Schematic of SLG on substrate.** The TH radiated waves in the top and bottom medium obey the TH Snell’s law: $n_i(3\omega_0) \sin \theta_i = n_1(\omega_0) \sin \theta$. The red dashed arrows indicate the propagation direction of in-coming and out-going waves.
where $\vec{D}^{(m)} = \epsilon(\omega)\vec{E}^{(m)}$ is the conventional displacement vector. $\rho_{f}^{(m)}$ and $\vec{J}_{f}^{(m)}$ are the $m$-th order Fourier components of free charge and current. Note that $\omega_{\Sigma} = \sum_{i}^{m} \omega_{i}$, with $\omega_{i}$ the incoming photons frequency, with $c$ and $\epsilon_{0}$ the speed of light and vacuum permittivity. For THG, we have $m = 3$, $\omega_{1,2,3} = \omega_{0}$ and $\omega_{\Sigma} = \omega_{THG} = 3\omega_{0}$. $\epsilon(\omega)$ is the isotropic and homogenous linear relative dielectric function. Only electric-dipole contributions are included.

We consider SLG in the $x$-$y$ plane embedded between air and a substrate. SLG is modeled by a dielectric function $\epsilon_{s}(\omega)$, nonlinear polarization, free surface charge and free surface current:

$$\vec{P}^{(m)} = \delta(z)\vec{P}^{(m)}, \quad (S7)$$
$$\rho_{f}^{(m)} = \delta(z)\sigma_{f}^{(m)}, \quad (S8)$$
$$\vec{J}_{f}^{(m)} = \delta(z)\vec{K}_{f}^{(m)}. \quad (S9)$$

Having the Dirac delta, $\delta(z)$, in the above relations implies that SLG only shows up in the electromagnetic boundary conditions. Note that $\vec{P}^{(m)}$ and $\vec{K}_{f}^{(m)}$ are in-plane vectors with zero component along the interface normal, $\hat{z}$.

The interface layer is the only source of nonlinearity. We assume $\sigma_{f}^{(m)} = 0$ and $\vec{K}_{f}^{(m)} = 0$, consistent with our experiments, where there are no free surface charges and currents that oscillate at frequency $m\omega$ with $m = 2, 3, \ldots$.

The boundary conditions for the nonlinear fields at $z=0$ are obtained as:

$$\vec{B}_{1}^{(m)} - \vec{B}_{2}^{(m)} = \mu_{0}(\vec{K}_{f}^{(m)} - i\omega_{\Sigma}\vec{P}^{(m)}) \times \hat{z},$$
$$\left\{ \epsilon_{1}(\omega_{\Sigma})\vec{E}_{1}^{(m)} - \epsilon_{2}(\omega_{\Sigma})\vec{E}_{2}^{(m)} \right\} \cdot \hat{z} = \frac{\sigma_{f}^{(m)} - \vec{\nabla}_{2d} \cdot \vec{P}^{(m)}}{\epsilon_{0}},$$
$$\left( \vec{E}_{1}^{(m)} - \vec{E}_{2}^{(m)} \right) \times \hat{z} = 0. \quad (S10)$$

Where the sub-indexes 1,2 stand for the top(bottom) medium and $\vec{\nabla}_{2d} = \hat{x}\partial/\partial x + \hat{y}\partial/\partial y$. The dielectric function of the interface layer, $\epsilon_{s}(\omega)$, does not emerge in the above boundary conditions.

The wave equation in the top and bottom media, with vanishing nonlinear polarization, follows:

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E}^{(m)} - \frac{\omega_{\Sigma}^{2}}{c^{2}}\epsilon(\omega_{\Sigma})\vec{E}^{(m)} = 0. \quad (S11)$$

which has a plane wave solution [8]:

$$\vec{E}^{(m)} = \hat{\ell}\vec{E}^{(m)} e^{i(\vec{q}_{\Sigma} \cdot \vec{r} - \omega_{\Sigma}t)} + c.c. \quad (S12)$$
\( \hat{\ell} \cdot \vec{q}_\Sigma = 0 \) and the dispersion relation in the top and bottom media is:

\[
q_\Sigma = |\vec{q}_\Sigma| = \frac{\omega_\Sigma}{c} n(\omega_\Sigma) .
\]  
(S13)

where \( n(\omega_\Sigma) = \sqrt{\epsilon(\omega_\Sigma)} \) is the refractive index of the lossless media.

We consider a linearly polarized incident laser with arbitrary incident angle exposed to the interface layer:

\[
\vec{E}_{in} = \{ \hat{x} \mathcal{E}_x + \hat{y} \mathcal{E}_y + \hat{z} \mathcal{E}_z \} e^{i(\vec{q} \cdot \vec{r} - \omega_0 t)} + c.c.
\]  
(S14)

where

\[
\vec{q} = \frac{\omega_0}{c} n_1(\omega_0) [-\cos \theta \hat{z} + \sin \theta \hat{x}].
\]  
(S15)

The leading nonlinearity of SLG is encoded in \( \sigma^{(3)} \). Using the SLG symmetry, the third-order nonlinear polarization follows:

\[
\vec{P}^{(3)} = \mathcal{P}^{(3)} \exp \left\{ i \frac{3\omega_0}{c} [n_1(\omega_0) x \sin \theta - ct] \right\} + c.c.
\]  
(S16)

where

\[
\vec{P}^{(3)}_x = i \frac{3\omega_0}{3\omega_0} \sigma^{(3)}_{xxx} \{ \mathcal{E}_x^3 + \mathcal{E}_x^2 \mathcal{E}_y \} ,
\]

\[
\vec{P}^{(3)}_y = i \frac{3\omega_0}{3\omega_0} \sigma^{(3)}_{yxx} \{ \mathcal{E}_y^3 + \mathcal{E}_y^2 \mathcal{E}_x \} ,
\]

\[
\vec{P}^{(3)}_z = 0 .
\]  
(S17)

The wave-vectors of TH radiated waves in the top and bottom media are:

\[
\vec{q}_{3\omega_0,1} = \frac{3\omega_0}{c} n_1(3\omega_0) [\cos \theta_1 \hat{z} + \sin \theta_1 \hat{x}] ,
\]

\[
\vec{q}_{3\omega_0,2} = \frac{3\omega_0}{c} n_2(3\omega_0) [-\cos \theta_2 \hat{z} + \sin \theta_2 \hat{x}] .
\]  
(S18)

According to the boundary condition relations of Eq.S10, we find \( q_{3\omega_0,1,x} = q_{3\omega_0,2,x} = 3q_x \). Therefore, we derive the Snell’s law for THG:

\[
n_2(3\omega_0) \sin \theta_2 = n_1(3\omega_0) \sin \theta_1 = n_1(\omega_0) \sin \theta .
\]  
(S19)

Considering the refractive index frequency dependence, the Snell’s law for THG implies that \( \sin \theta_1 = \frac{n_1(\omega_0)/n_1(3\omega_0)}{\sin \theta} \) is not generally equal to \( \sin \theta \), in contrast with the specular reflection for first harmonic generation [8].
The plane wave nature of the TH radiations implies:

\[
\cos \theta_1 \mathcal{E}_{1,z}^{(3)} + \sin \theta_1 \mathcal{E}_{1,x}^{(3)} = 0, \\
- \cos \theta_2 \mathcal{E}_{2,z}^{(3)} + \sin \theta_2 \mathcal{E}_{2,x}^{(3)} = 0. \tag{S20}
\]

By considering Eqs. S17, S18, the boundary condition relations Eq. S10 become:

\[
n_1(3\omega_0) \left[ \cos \theta_1 \mathcal{E}_{1,x}^{(3)} - \sin \theta_1 \mathcal{E}_{1,z}^{(3)} \right] + \\
n_2(3\omega_0) \left[ \cos \theta_2 \mathcal{E}_{2,x}^{(3)} + \sin \theta_2 \mathcal{E}_{2,z}^{(3)} \right] = i \frac{3\omega_0}{c} \tilde{P}_x, \tag{S21}
\]

\[
n_1(3\omega_0) \cos \theta_1 \mathcal{E}_{1,y}^{(3)} + n_2(3\omega_0) \cos \theta_2 \mathcal{E}_{2,y}^{(3)} = -i \frac{3\omega_0}{c} \tilde{P}_y, \tag{S22}
\]

\[
n_1(3\omega_0) \sin \theta_1 \mathcal{E}_{1,y}^{(3)} - n_2(3\omega_0) \sin \theta_2 \mathcal{E}_{2,y}^{(3)} = 0, \tag{S23}
\]

\[
\mathcal{E}_{1,x}^{(3)} = \mathcal{E}_{2,x}^{(3)}, \quad \mathcal{E}_{1,y}^{(3)} = \mathcal{E}_{2,y}^{(3)}, \quad \mathcal{E}_{1,z}^{(3)} = \mathcal{E}_{2,z}^{(3)}, \tag{S24, S25}
\]

\[
n_1(3\omega_0)^2 \mathcal{E}_{1,z}^{(3)} - n_2(3\omega_0)^2 \mathcal{E}_{2,z}^{(3)} = -i \frac{3\omega_0}{c} \tilde{P}_x n_1(\omega_0) \sin \theta. \tag{S26}
\]

From Eqs. S21-S26, S19, S20 we get:

\[
\mathcal{E}_{i,x}^{(3)} = S_{i,x} \frac{\sigma_{xxx}}{\epsilon_0} \left\{ \mathcal{E}_x^3 + \mathcal{E}_x^2 \mathcal{E}_y^2 \right\}, \tag{S27}
\]

\[
\mathcal{E}_{i,y}^{(3)} = S_{i,y} \frac{\sigma_{xxx}}{\epsilon_0} \left\{ \mathcal{E}_y^3 + \mathcal{E}_y^2 \mathcal{E}_x^2 \right\}, \tag{S28}
\]

\[
\mathcal{E}_{i,z}^{(3)} = S_{i,z} \frac{\sigma_{xxx}}{\epsilon_0} \left\{ \mathcal{E}_x^3 + \mathcal{E}_x^2 \mathcal{E}_y^2 \right\}. \tag{S29}
\]

where

\[
S_{1,x} = S_{2,x} = -\frac{\cos \theta_1 \cos \theta_2}{n_1(3\omega_0) \cos \theta_2 + n_2(3\omega_0) \cos \theta_1}, \tag{S30}
\]

\[
S_{1,y} = S_{2,y} = -\frac{1}{n_1(3\omega_0) \cos \theta_2 + n_2(3\omega_0) \cos \theta_1}, \tag{S31}
\]

\[
S_{1,z} = \frac{\cos \theta_2 \sin \theta_1}{n_1(3\omega_0) \cos \theta_2 + n_2(3\omega_0) \cos \theta_1}, \tag{S32}
\]

\[
S_{2,z} = -\frac{\cos \theta_1 \sin \theta_2}{n_1(3\omega_0) \cos \theta_2 + n_2(3\omega_0) \cos \theta_1}. \tag{S33}
\]
For normal incidence we have \( \theta = 0 \). From Eq. S19 we have \( \theta_1 = \theta_2 = 0 \). Therefore, \( S_{i,z} = 0 \) and \( S_{i,x} = S_{i,y} = -1/[n_1(3\omega_0) + n_2(3\omega_0)] \). The time-average of the incident intensity gives \( I_{\omega_0} = 2n_1(\omega_0)\varepsilon_0c|\vec{E}_{in}|^2 \). The intensity of the transmitted TH signal is \( I_{3\omega_0} = 2n_2(3\omega_0)\varepsilon_0c|\vec{E}^{(3)}|^2 \). From this we get Eq. 2 of the main text for THGE.

### S2.2 Symmetry considerations

The rank-4 tensor of \( \sigma^{(3)} \) transforms as follows under an arbitrary \( \phi \)-rotation:

\[
\sigma_{\alpha'\beta'\gamma'\delta'}^{(3)} = \sum_{\alpha\beta\gamma} R_{\alpha'\alpha}(\phi)R_{\beta'\beta}(\phi)R_{\gamma'\gamma}(\phi)R_{\delta'\delta}(\phi)\sigma_{\alpha\beta\gamma\delta}^{(3)}. \tag{S34}
\]

We take the \( z \)-axis as the rotation-axis, perpendicular to SLG. Therefore, the rotation tensor is:

\[
\vec{R}(\phi) = \begin{pmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{pmatrix}. \tag{S35}
\]

We take \( \hat{\ell} = \vec{R}(\phi) \cdot \hat{x} \). By plugging Eq. S35 in S34, we get:

\[
\sigma_{\hat{\ell}\hat{\ell}\hat{\ell}\hat{\ell}}^{(3)} = \sin \phi \sigma_{yyyy}^{(3)} + \cos \phi \sigma_{xxxx}^{(3)} + \cos \phi \sin \phi \left[ \sigma_{xxyy}^{(3)} + \sigma_{yxyy}^{(3)} + \sigma_{yxyx}^{(3)} + \sigma_{xyxy}^{(3)} \right]
+ \cos \phi \sin \phi \left[ \sigma_{xxxy}^{(3)} + \sigma_{xyxx}^{(3)} + \sigma_{yxxy}^{(3)} + \sigma_{yxxy}^{(3)} \right]
+ \sigma_{xxyy}^{(3)} + \sigma_{yxyy}^{(3)} + \sigma_{xyxy}^{(3)} + \sigma_{yxyx}^{(3)}. \tag{S36}
\]

Because of the \( C_{6v} \) symmetry for SLG on a substrate, there are only 4 independent tensor elements [7]:

\[
\sigma_{xxxx}^{(3)} = \sigma_{yyyy}^{(3)} = \sigma_{xxyy}^{(3)} + \sigma_{yxyy}^{(3)} + \sigma_{xyxy}^{(3)} + \sigma_{yxxy}^{(3)}
\]

\[
\sigma_{xxyy}^{(3)} = \sigma_{yxyx}^{(3)}
\]

\[
\sigma_{xyxy}^{(3)} = \sigma_{yxxy}^{(3)}
\]

\[
\sigma_{yxyx}^{(3)} = \sigma_{yxxy}^{(3)}. \tag{S37}
\]

By implementing Eq. S37 in Eq. S36, we get \( \sigma_{\hat{\ell}\hat{\ell}\hat{\ell}\hat{\ell}}^{(3)} = \sigma_{xxxx}^{(3)} \).
S2.3 Effect of finite relaxation rate

The effect of finite $\tau$ in the TH conductivity can be derived from [3]:

$$\bar{\sigma}_{xxxx}(\omega_0, E_F, 0) \approx \frac{17G(2|E_F|, \hbar\omega_0 + i\Gamma) - 64G(2|E_F|, 2\hbar\omega_0 + i\Gamma) + 45G(2|E_F|, 3\hbar\omega_0 + i\Gamma)}{24(\hbar\omega_0)^4} + \frac{\Gamma}{6(\hbar\omega_0)^4} \left\{ 17 \left[ \frac{1}{2|E_F| + 3\hbar\omega_0 + i\Gamma} + \frac{1}{2|E_F| - 3\hbar\omega_0 - i\Gamma} \right] \right.$$

$$- 8 \left[ \frac{1}{2|E_F| + 2\hbar\omega_0 + i\Gamma} + \frac{1}{2|E_F| - 2\hbar\omega_0 - i\Gamma} \right]$$

$$+ 3\hbar\omega_0 \left[ \frac{1}{(2|E_F| + 3\hbar\omega_0 + i\Gamma)^2} - \frac{1}{(2|E_F| - 3\hbar\omega_0 - i\Gamma)^2} \right] \right\}. \quad (S38)$$

Note that ($\approx$) is because we assume $\Gamma \ll \hbar\omega_0$ [3]. Supplementary Fig.4 shows that a finite $\tau$ has a small effect on THGE for most of SLGs in literature, including the samples used in this paper.

S2.4 $T_e$ and $E_F$ effects on THGE

The $T_e$ and $E_F$ dependence of THGE for SLG on SiO$_2$ at $\hbar\omega_0 = 500$ meV is shown in Supplementary Supplementary Fig.5, where 3 logarithmic singularities at $2|E_F| = \hbar\omega_0, 2\hbar\omega_0, 3\hbar\omega_0$ for $T_e=0$K can be seen. By increasing $T_e$, the first peak at $2|E_F| = \hbar\omega_0$ disappears and the two others merge and form a broad maximum, roughly located at $2|E_F| \sim (2 + 3)\hbar\omega_0/2 = 2.5\hbar\omega_0$. THGE is almost insensitive to $E_F$ for $2|E_F| < \hbar\omega_0$. This can be explained using the asymptotic relation of the TH conductivity for $|E_F| \ll \hbar\omega_0$. For $T_e = 0$:

$$\sigma_{xxxx}^{(3)} \approx e^4\hbar v_F^2 \left( \frac{1}{\hbar\omega_0} + \frac{i}{\pi} \left( \frac{2|E_F|}{3\hbar\omega_0} \right)^3 + \ldots \right) \quad (S39)$$

Eq.S39 and Eq.2 of the main text explain the flat part of the curves in Supplementary Fig.5 in the low-doping regime ($\hbar\omega_0 > 2|E_F|$).

In order to quantify the tunability of THG in SLG by altering $E_F$, we define a parameter:

$$\xi_{THG} \equiv \frac{\eta_{THG}^{max}}{\eta_{THG}^{min}}, \quad (S40)$$

where $\eta_{THG}^{T_e}$ stands for THGE in the nearly undoped regime ($|E_F| \ll \hbar\omega_0$). Supplementary Fig.6 indicates that $\xi_{THG}$ decreases by increasing $T_e$. 

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Supplementary Fig. 4. Effect of momentum relaxation time on THGE. THGE for SLG on Sa as a function of $\omega_0$ for different $\tau = \hbar/\Gamma$ at $T_e=2000K$ and $E_F=200meV$, for incident intensity $\sim 2.4 \times 10^{12}Wm^{-2}$, corresponding to the value used in our experiments.
Supplementary Fig. 5. Doping dependence of THGE at different $T_e$. $E_F$ dependence of THGE for SLG on SiO$_2$ at $\hbar\omega_0 = 500$meV for different $T_e$ between 0K and 1800K. (a) Absolute THGE. (b) THGE normalized to the minimum so that THGE at $E_F = 0$ is equal to 1 for all $T_e$. 
Supplementary Fig. 6. $T_e$ dependence of $\xi^{\text{THG}}$. $T_e$ dependence of doping induced enhancement parameter $\xi^{\text{THG}}$ for $\hbar\omega_0 = 500\text{meV}$.

S3 Fermi energy, Fermi level, chemical potential and electronic heat capacity in SLG

When a pulsed laser interacts with SLG, after an initial transient of a few tens fs, the electron and hole distributions in the conduction and valence bands are given by the Fermi-Dirac functions $f_{FD}(\varepsilon; \mu, T_e)$ with the same $T_e$ and two chemical potentials $\mu_v$ and $\mu_c$ (see e.g. Refs.9–11). The chemical potential of the electrons and holes in the valence band are, by definition, opposite to each other.

At equilibrium, when $\mu_c = \mu_v$, they are denoted by $\mu$. The term Fermi level ($E_{FL}$) is also sometimes used in literature to denote $\mu$. The Fermi energy ($E_F$) is defined as the value of $\mu$ at $T_e = 0K$ [12]. $E_F$ is thus a function of the electron density only. After recombination of the photoexcited electron-hole pairs, a single Fermi-Dirac distribution is established in both bands and the equilibrium condition $\mu_v = \mu_c$ holds [9–11]. The recombination time depends on carrier density and laser fluence, and can be much longer than the time $\lesssim 20fs$ needed for thermalization (see Ref.9 and references therein).

The electronic heat capacity $c_v$ is defined as the derivative of the electronic energy density $U$ with respect to $T_e$ [12]. It depends on all the variables which affect the electronic energy density, such as $T_e$ and the carrier density or, equivalently, $\mu$ [12]. In a photoexcited system, in general, $c_v$ depends on both the electron and hole densities, i.e. on both $\mu_c$ and $\mu_v$. In this case, $c_v$
can be written as [12]:

\[
c_v(\mu_c, \mu_v, T_e) = \frac{\partial}{\partial T_e} \int_0^\infty d\varepsilon \nu(\varepsilon) \varepsilon f_{FD}(\varepsilon; \mu_c, T_e) \\
+ \frac{\partial}{\partial T_e} \int_0^\infty d\varepsilon \nu(\varepsilon) \varepsilon f_{FD}(\varepsilon; -\mu_v, T_e),
\]

(S41)

where the first integral is the electron and the second the hole contribution. The density of electronic states per unit of area is \(\nu(\varepsilon) = N_f |\varepsilon| / [2\pi(\hbar v_F)^2]\), with \(N_f = 4\) the product of spin and valley degeneracy. The Fermi-Dirac distribution is:

\[
f_{FD}(\varepsilon; \mu, T_e) = \frac{1}{e^{(\varepsilon - \mu)/k_B T_e} + 1},
\]

(S42)

To take the derivative with respect to \(T_e\) in Eq.S41, the dependence of \(c_v\) on \(T_e\) has to be specified. The electron and hole densities are given by:

\[
n_e(\mu_c, T_e) = \int_0^\infty d\varepsilon \nu(\varepsilon) f_{FD}(\varepsilon; \mu_c, T_e),
\]

\[
n_h(-\mu_v, T_e) = \int_0^\infty d\varepsilon \nu(\varepsilon) f_{FD}(\varepsilon; -\mu_v, T_e).
\]

(S43)

Since the total electron density in both bands is constant, the difference between electron and hole densities is constant:

\[
n_e^{(0)} - n_h^{(0)} = n_e(\mu_c, T_e) - n_h(-\mu_v, T_e),
\]

(S44)

where \(n_e^{(0)}\) and \(n_h^{(0)}\) are the intrinsic electron and hole densities before the pump. At equilibrium, when \(\mu_c = \mu_v = \mu\), Eq.S44 can be solved for \(\mu\). A photoexcited density \(\delta n_e\) changes the densities in both bands as follows:

\[
n_e(\mu_c, T_e) = n_e(\mu, T_e) + \delta n_e,
\]

\[
n_h(-\mu_v, T_e) = n_h(-\mu, T_e) + \delta n_e.
\]

(S45)

After finding \(\mu\) with Eq.S44, one can get \(\mu_c\) and \(\mu_v\) with Eq.S45. This defines the dependence of \(c_v\) on \(T_e\) in Eq.S41, and allows us to calculate the derivative with respect to the temperature. The result of Eq.S41 is shown in Supplementary Fig.7 for \(\mu_c = \mu_v = \mu\). In Ref.13 the following expression is given for \(c_v\):

\[
c_v(T_e) = \frac{18\zeta(3)}{\pi(hv_F)^2} k_B^3 T_e^2.
\]

(S46)
Supplementary Fig. 7. $T_e$ dependence of the $c_v$ in equilibrium conditions. Calculations for (a) $E_F=10$ and (b) 300meV. The blue and red dashed lines are Eqs.S46, S47.
Supplementary Fig. 8. \textbf{T}_e \textit{dependence of the electron energy density and c}_v \textit{in out of equilibrium conditions.} (a) Electron energy density and (b) c_v for E_F=200meV. The blue, and red lines correspond to photoexcited densities \(\delta n_e = 10^{12}\) and \(3 \times 10^{12} \text{cm}^{-2}\), while the black line corresponds to a thermalized system with a single \(\mu\).

In principle, as noted in Ref.14, Eq.S46 is valid at the charge neutrality point \(|\mu| \ll k_B T\) only. For a degenerate system, \(k_B T \ll |\mu|\), we have [4]:

\[
    c_v(\mu, T_e) = \frac{\pi^2}{3} \nu(E_F) k_B^2 T_e ,
\]

as derived \textit{e.g.} in Eqs.8.10 of Ref.4, in Eq.4 of Ref.15 and in Eq.8 in the Supplementary Information of Ref.16. However, the numerical calculation in Supplementary Fig.7 shows that the quadratic approximation (Eq.S46) is much better in the regime where \(T_e \sim 1000K\) and \(\mu \sim 100\text{meV}\). Supplementary Fig.8 shows that, taking into account the difference between \(\mu_{ce}\) and \(\mu_v\), for typical values of the photoexcited density, contributes \(\geq 15\%\) to \(c_v\).
S4 Absorption coefficient and estimate of steady-state $T_e$ under pumping and dissipation

S4.1 SLG absorption coefficient

The average absorbed power per unit area in SLG excited by a pulse of duration $\Delta t$, fluence $F$, and average frequency of the photons $\omega/2\pi$ can be written as:

$$\frac{P}{A} = P[\alpha(\omega, \mu_c, \mu_v, T_e)] \frac{F}{\Delta t} ; \quad (S48)$$

where $\alpha(\omega, \mu_c, \mu_v, T_e)$ is the absorption coefficient and the function $P(x) = x \theta(x)$ equals $x$ for $x > 0$ and $0$ for $x < 0$. For simplicity we omit $P$ in the main text. For frequencies in the optical domain, we consider only the contributions due to direct vertical inter-band electronic transitions. The origin of these transitions is purely quantum and does not depend on disorder. On the other hand, intra-band transitions are mediated by defects [18] and can be described classically. In general, the absorption coefficient is a function of the electron distribution:

$$\alpha(\omega; \mu_c, \mu_v, T_e) = (2.3\%) \frac{2}{1 + n_{\text{sub}}} [1 - f_{\text{FD}}(\hbar\omega/2; \mu_c, T_e) - f_{\text{FD}}(\hbar\omega/2; -\mu_v, T_e)] , \quad (S49)$$

for a sample lying between air and a substrate with refractive index $n_{\text{sub}}$. This expression is obtained using Eq.7.34 in Ref. [19] for the real part of the inter-band conductivity and the relation between absorption and conductivity of thin films discussed in Ref. [20]. This means that the absorption is reduced due to Pauli blocking if the electron or hole distributions at $E_F = \hbar\omega/2$ increase. As $T_e$ increases, the absorption becomes a sizable fraction of its maximum value 2.3%, even in the frequency range $\hbar\omega < 2E_F$ where it vanishes at room temperature.

S4.2 Estimate of steady-state $T_e$ under pumping and dissipation

The number of photoexcited electron-hole pairs per unit area in the time interval $dt$ is given by the number of absorbed photons in the same time interval per unit area, i.e. $(dn_e + dn_h)/2 = (P/A)/(\hbar\omega_0)dt$. In the steady state, the energy delivered by the pump is transferred into the phonon modes. Hence, we identify the electron-hole recombination time with $\tau$. We then get:

$$\frac{1}{2} \left( \frac{dn_e}{dt} + \frac{dn_h}{dt} \right) = \frac{1}{\hbar\omega_0} \frac{P}{A} - \frac{1}{2} \left[ n_e(\mu_c, T_e) + n_h(-\mu_v, T_e) \right] - \frac{(n_e(0) + n_h(0))}{\tau} . \quad (S50)$$
Supplementary Fig. 9. \( \hbar \omega_0 \) dependence of \( T_e \) in photoexcited SLG. \( T_e \) as a function of \( \hbar \omega_0 \) for \( E_F=200 \) meV and \( \tau=100 \) (black), 200 (blue), and 300 fs (red). In (a) we use a constant \( \alpha=0.23\%/[1+n_{\text{sub}}]/2 \) while in (b) we use the full functional dependence of Eq.S49.

In the steady state this becomes:

\[
n_e^{(0)} + n_h^{(0)} = n_e(\mu_c, T_e) + n_h(-\mu_v, T_e) - \frac{2\tau}{\hbar \omega_0} \frac{P}{A}. \tag{S51}
\]

Combining Eqs.S44, S51, we find:

\[
\delta n_e = \frac{\tau}{\hbar \omega_0} \frac{P}{A}. \tag{S52}
\]

To calculate \( E_F \) (e.g. for a \( n \)-doped sample) one needs to solve Eqs.S42, S43, S44 with \( \mu_c = \mu_v = E_F, T_e = 0 \), and \( n_h^{(0)} = 0 \), finding \( E_F = \hbar v_F \sqrt{\pi n_e} \).

This relation can be used at \( T_e = 300 K \) and electron densities \( n_e^{(0)} \gtrsim 10^{11} \) because the density of thermally excited holes is negligible. In photoexcited SLG, even after recombination of the photoexcited electron-hole pairs, the \( T_e \) dependence of \( \mu \) cannot be ignored. In this case, to calculate \( \mu \), one needs to solve Eqs.S42, S43, S44 with \( \mu_c = \mu_v = \mu \) and \( n_h^{(0)} = 0 \) as a function of \( T_e \). This gives \( \mu = E_F[1 - \pi^2 T_e^2/(6T_F^2)] \) for \( T_e \lesssim T_F \) and \( \mu = E_F T_F/(4\ln 2 \times T_e) \) for \( T_e \gtrsim T_F \) [17], where \( T_F = E_F/K_B \), with \( K_B \) the Boltzmann constant. For a typical case of \( E_F=200 \) meV and \( T_e = 1500 \) K, we have \( \mu \sim 0.3 - 0.5 E_F \). To calculate \( T_e \), we solve the non-linear Eq.4 in the main text, with the \( T_e \) dependence of \( \alpha \) and \( c_v \) discussed above. The values of \( T_e \), as a function of \( \hbar \omega_0 \), for
Supplementary Fig. 10. **$E_F$ dependence of $T_e$ in photoexcited SLG.**

(a) Steady-state $T_e$ as a function of equilibrium $E_F$ for $\tau = 200\text{fs}$ and $\hbar \omega_0 = 0.4$ (red), 0.6 (green) and 0.8eV (blue). (b) $T_e$ as a function of residual (intra-band) absorption for $E_F = 0.6\text{eV}$ and $\hbar \omega_0 = 0.4\text{eV}$.

For $T_e > 300\text{K}$ inter-band transitions can occur also when $\hbar \omega_0 < 2E_F$, as shown in Eq.S49. To apply the theory also to lower temperatures, where intra-band transitions due to disorder play a role in the absorption process, we modify Eq.4 of the main text as follows:

$$T = T_0 + \tau \left[ \frac{\mathcal{P}[\alpha(\omega; \mu_c, \mu_v, T) + \alpha_{\text{res}}] \mathcal{F}}{c_v(\mu_c, \mu_v, T) \Delta t} \right],$$

where a constant $\alpha_{\text{res}}$ is added to $\alpha(\omega, \mu_c, \mu_v, T_e)$ to take into account the contribution of the residual (intra-band) absorption. No modifications are needed in Eq.S51 because the residual absorption, stemming from intra-band transitions, does not directly affect the photoexcited density. We assume that distinct contributions to the absorption are additive because $\alpha$ is much smaller than unity. Supplementary Fig.10a plots $T_e$ as a function of $E_F$ for $\tau = 200\text{fs}$, $\alpha_{\text{res}} = 0.1\%$ and different $\hbar \omega_0$. Supplementary Fig.10b shows $T_e$ for different $\alpha_{\text{res}}$ for $E_F = 0.6\text{eV}$ and $\hbar \omega_0 = 0.4\text{eV}$. Very small values of $\alpha_{\text{res}} \sim 0.1\%$, corresponding to $\alpha \sim 2.3%/20$, lead to $T_e \sim 500-600\text{K}$. $T_e$ rapidly increases to $>1000\text{K}$ for $\alpha_{\text{res}} \sim 1\%$. 
Supplementary Fig. 11. **SLG absorption.** Absorption spectrum on the SLG on Sa sample. The measurement was performed in transmission geometry with a Cary 600 Series FTIR Spectrometer.

Supplementary Fig. 11 reports the experimental absorption for the SLG on Sa sample ($E_F \sim 250\text{meV}$). $\alpha_{res}$ at $\hbar \omega < 2E_F$ is $\sim 1\%$. Since intra-band absorption is mediated by defects [18] and $n_D$ is $\sim 2$-3 times higher in SLG on Sa compared to SLG on Si/SiO$_2$, we use 0.1% for $\alpha_{res}$ in Supplementary Fig. 10a.

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