Ultrafast Photoluminescence from Graphene

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Since graphene has no band gap, photoluminescence is not expected from relaxed charge carriers. We have, however, observed significant light emission from graphene under excitation by ultrashort (30-fs) laser pulses. Light emission was found to occur across the visible spectral range (1.7–3.5 eV), with emitted photon energies exceeding that of the excitation laser (1.5 eV). The emission exhibits a nonlinear dependence on the laser fluence. In two-pulse correlation measurements, a dominant relaxation time of tens of femtoseconds is observed. A two-temperature model describing the electrons and their interaction with strongly coupled optical phonons can account for the experimental observations.

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The optical properties of graphene have attracted much recent attention. Among the striking results are the universal absorbance of single-layer graphene in the near-infrared-to-visible spectral range [1,2] and the possibility of tuning this absorption in the infrared by Pauli blocking [3,4]. Optical measurements with ultrafast excitation pulses have also provided means of probing electron and phonon dynamics in graphene [5–15]. To date, however, all investigations have been confined to probing the light absorption in graphene. Aside from the weak inelastic scattering associated with the Raman process, there have been no reports of light emission from graphene. The lack of observable emission can be readily understood from the absence of a band gap. Carriers fully relax through rapid electron-electron (*e*-*e*) and electron-phonon (*e*-ph) interactions before the relatively slow process of light emission is possible. Thus, photoluminescence has only been reported in chemically modified graphene [16] where the electronic structure has been modified.

In this Letter, we report the observation of significant broadband light emission from pristine monolayer graphene under excitation by femtosecond laser pulses. This light emission process differs from conventional hot luminescence: it has a nonlinear dependence on the pump excitation and also appears at photon energies well above that of the excitation. In addition, two-pulse correlation measurements reveal a dominant response on the time scale of 10's of fs. These observations can be understood in a model in which the electronic excitations are largely thermalized among themselves, but are only partially equilibrated with strongly coupled optical phonons (SCOPs) and essentially decoupled from other phonons. The ultrafast excitation can thus produce carriers with transient temperatures above 3000 K that give rise to emission in the visible spectral range.

We investigated single-layer graphene samples exfoliated from kish graphite (Toshiba) onto mica substrates [17]. The samples, investigated under ambient conditions, were excited by 30-fs laser pulses at a photon energy of 1.5 eV from an 80-MHz mode-locked Ti:sapphire oscillator. The spatial profile of the laser on the sample was characterized by scanning a sharp edge across the beam. The effective spot size was determined by weighting this profile using the measured nonlinear fluence dependence of luminescence discussed below. The absorbed fluence F was measured directly [2] and includes modest absorption saturation at high fluences [10]. We measured the light emission under excitation by individual pulses and, for the correlation measurements, by pairs of orthogonally polarized pulses. The emission was analyzed by a spectrometer with a cooled charge-coupled device (CCD) array detector. The emission strength is presented in terms of the spectral fluence $\mathcal{F}(\hbar\omega)$, i.e., total radiant energy emitted in all directions per unit area per unit photon energy $\hbar\omega$. There is an estimated uncertainty of a factor of 10 in the calibration of emission strength.

Under excitation by femtosecond laser pulses, the graphene samples produced readily observable light emission from visible to near ultraviolet (1.7–3.5 eV) [Fig. 1(a)]. The emission was unpolarized and angularly broad. Over the observed spectral range, the luminescence quantum efficiency was $\sim 10^{-9}$. In contrast, for continuous-wave excitation of the same photon energy (1.5 eV), we could not detect any graphene light emission (quantum efficiency $< 10^{-12}$). Another distinctive feature of the luminescence is its nonlinear dependence on the pump fluence [Fig. 1(b)]. The integrated emission over the entire observed spectral range varies with the absorbed fluence F as $F^{2.5}$. For narrower spectral windows, a power-law relation is still observed, but with an exponent of 2 for photons near the lower end of our spectral range and of 3.5 for photons at its upper end.

The observations above immediately preclude several possible emission mechanisms. The emission of photons at energies well above the excitation energy implies that we are not observing a conventional hot-luminescence process. Hot luminescence driven by a two-photon absorption process can also be excluded by the strong variation of the

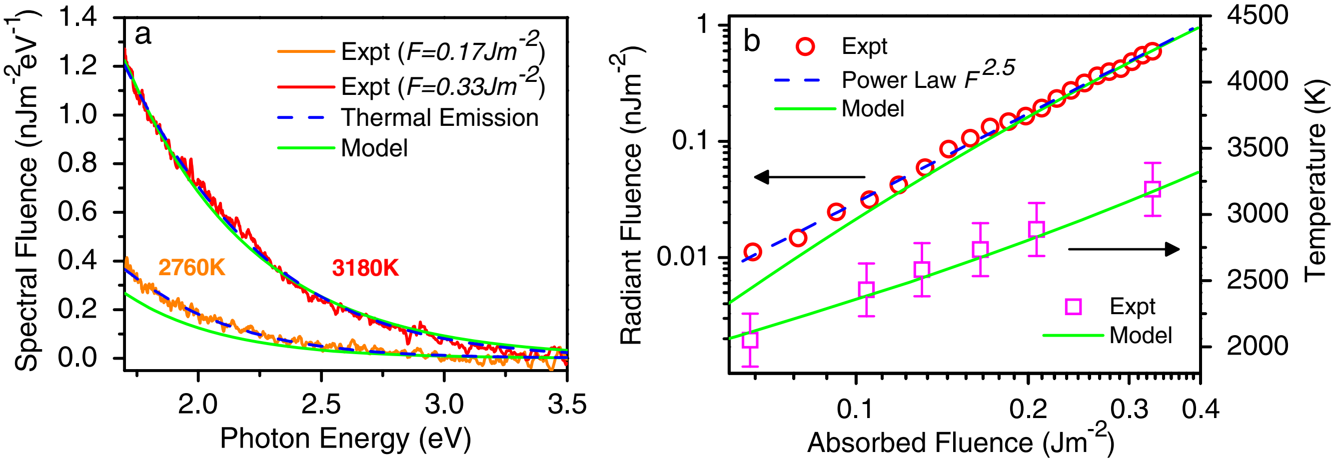

FIG. 1 (color online). (a) Spectral fluence of light emission from graphene for excitation with 30-fs pulses of absorbed fluences of $F = 0.17$ and $0.33\ \mathrm{J\,m^{-2}}$. The spectra are compatible with the predictions for thermal emission (dashed blue lines) for $T_{em} = 2760$ K and 3180 K, respectively. (b) Light emission as a function of absorbed fluence F. The red circles display experimental values for the total radiant fluence for photons from 1.7 to 3.5 eV. The emission can be described phenomenologically by $F^{2.5}$ (dashed blue line). The magenta squares correspond to the experimental emission temperatures T_{em} for different absorbed fluences. The solid green lines in (a) and (b) represent a full calculation using the two-temperature model. The predicted emission fluence has been multiplied by a factor of ~ 0.2 to match the scale of the experimental data.

emission spectrum with pump fluence. A key feature of the experimental data is the steady decrease of light emission with increasing photon energy $\hbar\omega$. This suggests comparison with the spectrum expected for thermal emission. For an effective emission temperature T_{em}, we obtain from Planck's law, a spectral radiant fluence (integrated over all angles and polarizations) of

$$\mathcal{F}(\hbar\omega, T_{em}) = \tau_{em}\varepsilon(\hbar\omega)\frac{\omega^3}{2\pi^2 c^2}\left[\exp\left(\frac{\hbar\omega}{kT_{em}}\right) - 1\right]^{-1}. \quad (1)$$

Here $\varepsilon(\hbar\omega)$ is the emissivity, obtained from the measured absorption spectrum of graphene, and τ_{em} is the effective emission time for each laser excitation pulse. This simple phenomenological description provides an excellent match to the data [Fig. 1(a)]. The inferred values for T_{em} lie in the range of 2000–3200 K and vary sublinearly with pump fluence [Fig. 1(b)]. As for the absolute magnitude of the experimental radiant fluence, our data can be reproduced using Eq. (1) with τ_{em} in the range of 10–100 fs.

The above analysis implies that carriers in graphene are well thermalized among themselves during the period of light emission. This finding suggests very rapid e-e scattering. The electrons and holes are initially created with a nearly monochromatic energy of 0.75 eV. During the period of light emission, which may occur on a time scale of the 30-fs excitation pulse, a largely thermalized energy distribution is apparently established for electrons and holes. This rapid thermalization is compatible with recent theoretical studies, which predict e-e scattering times of 10's of fs for electron densities $\sim 10^{12}\ \mathrm{cm^{-2}}$ [14,18,19]. Still shorter times would be expected under our experimental conditions with electron densities $\sim 10^{14}\ \mathrm{cm^{-2}}$.

The observed emission temperatures give us insight into the emission process. If all of the absorbed laser energy were retained in the electronic system, the low electronic specific heat of graphene would lead to an electronic temperature reaching $T_{el} \sim 9000$ K for $F = 0.33\ \mathrm{J\,m^{-2}}$. This is incompatible with the $T_{em} = 3180$ K extracted from experiment. Therefore, a significant fraction of the deposited energy must leave the electronic system during the emission process. Since lateral diffusion of energy can be ruled out from the time scale, we conclude that energy transfer to other degrees of freedom must occur. In the limit of complete equilibration with all phonon degrees of freedom, i.e., considering the full specific heat of graphene [20], we predict a temperature rise of only 380 K. Thus partial equilibration with the phonons must be considered.

The optical phonons in graphene serve as the most natural channel for energy relaxation, since electrons interact very efficiently with a set of SCOPs located near the Γ and K points in the Brillouin zone [12,21]. Investigations of phonon dynamics in graphite and carbon nanotubes by time-resolved Raman spectroscopy have directly demonstrated energy transfer from photoexcited electrons to these SCOPs within 200 fs [22,23]. Various studies have also obtained ultrashort (<100 fs) emission times for optical phonons in graphene [18,24], graphite [13,15,25], and carbon nanotubes [26,27].

To analyze the results further, we introduce a model for excitations in the electronic system and in the SCOPs, each characterized by its respective temperature, T_{el} and T_{op}, and linked by the e-ph coupling:

$$\frac{dT_{el}(t)}{dt} = \frac{I(t) - \Gamma(T_{el}, T_{op})}{c_e(T_{el})},$$
$$\frac{dT_{op}(t)}{dt} = \frac{\Gamma(T_{el}, T_{op})}{c_{op}(T_{op})} - \frac{T_{op}(t) - T_0}{\tau_{op}}. \qquad (2)$$

In this description [28], the absorbed laser irradiance $I(t)$ initially excites the electrons. Energy then flows into SCOPs at a rate described by $\Gamma(T_{el}, T_{op})$. This latter quantity reflects the available phase space for electron scattering and includes only one adjustable parameter to describe the overall rate. The specific heat of the electrons (c_e) and the SCOPs (c_{op}) are obtained, respectively, from theory and experimental data using Raman spectroscopy. The slower coupling of the SCOPs to other phonons has also been included using relaxation time τ_{op} estimated from time-resolved Raman measurements [22,23]. We neglect the heating of these more numerous secondary phonons and assume that they remain at the ambient temperature of $T_0 = 300$ K.

Figure 2 displays the predicted temporal evolution for the temperatures of electrons (T_{el}) and SCOPs (T_{op}), as well as the corresponding light emission, for our experimental conditions. We also show T_{el} for the completely decoupled electronic system and for full thermal equilibrium of the graphene sample. These limits, as discussed above, are clearly incompatible with the experimental results. Within the model, rapid energy transfer from electrons to SCOPs occurs during the laser excitation process. This results in a significant decrease in T_{el} compared to the case of uncoupled electrons (from a peak of 9000 K to 3800 K). Equilibration with the SCOPs is almost complete within 50 fs, with the electronic system having lost over 95% of its energy to the SCOPs. Using the temporal evolution of T_{el}, we calculate the expected integrated emission from Eq. (1). We find a good agreement with experiment for the predicted spectral shape, effective emission temperature T_{em}, and emission strength [lines in Figs. 1(a) and 1(b)]. We note that T_{em} approximates the peak value of T_{el} because of the nonlinear dependence of the emission on T_{el} [28].

To probe the dynamics of the light emission process more directly, we performed two-pulse correlation measurements [29] in which the total radiant fluence was measured as a function of the temporal separation between a pair of laser excitation pulses (Fig. 3). The dominant response in the correlation traces occurs in 10's of fs, with a weaker, slower decay extending over 100's of fs. The shape of the correlation trace varied with the spectral range of the detected photons and with pump fluence. For detection of only high-energy photons, we observe a shorter response time than for low-energy photons (Fig. 3). This behavior reflects the more nonlinear dependence of the emission

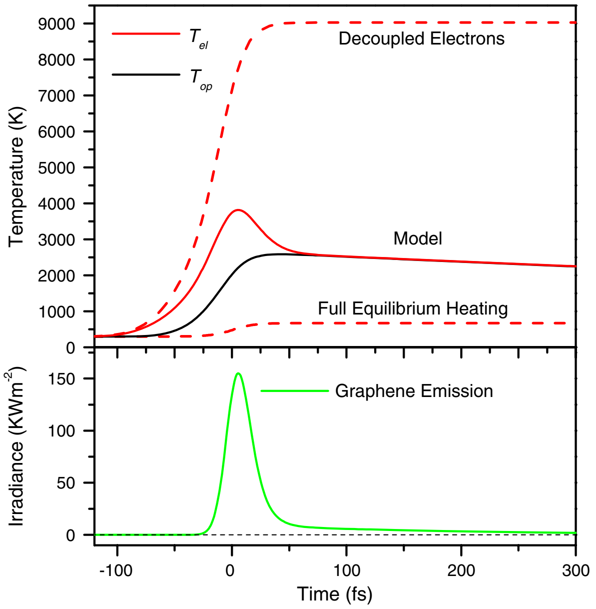

FIG. 2 (color online). Simulations using the two-temperature model of the temporal evolution of the electronic temperature T_{el} (red line), the SCOPs temperature T_{op} (black line), and of the resulting graphene light emission (green line, lower panel) for photon energies from 1.7 to 3.5 eV and absorbed fluence $F = 0.33$ J m^{-2}. For comparison, the upper panel also shows the calculated electronic temperatures for completely decoupled electrons and for full equilibrium of all degrees of freedom of the graphene (dashed red lines).

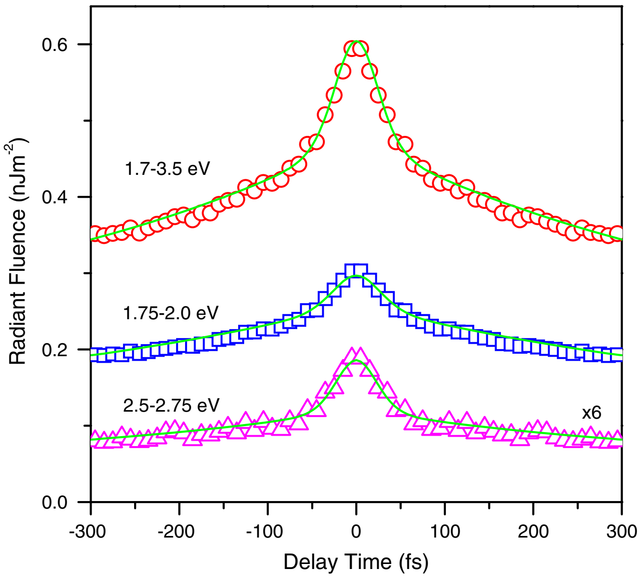

FIG. 3 (color online). Total radiant fluence emitted by graphene over photon energies of 1.7–3.5 eV (red circles), 1.75–2.0 eV (blue squares) and 2.5–2.75 eV (magenta triangles) as a function of temporal separation between two excitation pulses, each with absorbed fluence $F = 0.17$ J m^{-2}. The data for positive and negative delays were averaged to increase the signal-to-noise ratio. The symbols are experimental data; the green lines are the predictions of the two-temperature model, multiplied by ~0.2 to match the scale of the experimental data.

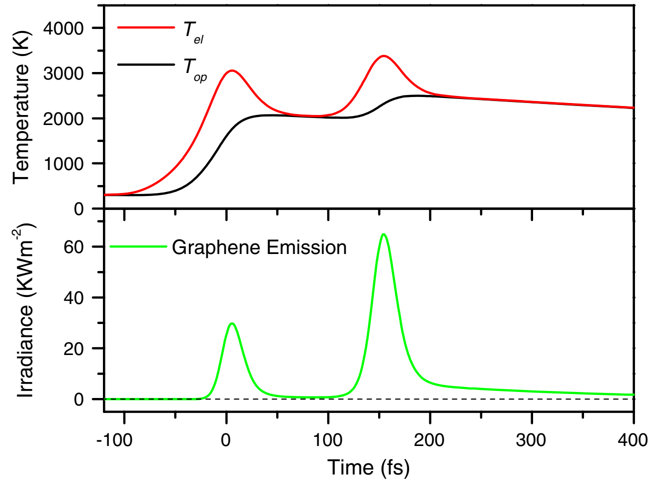

FIG. 4 (color online). Simulations as in Fig. 2, but with excitation by a pair of laser pulses separated in time by 150 fs. Each pulse has absorbed fluence $F = 0.17\ \mathrm{J\,m^{-2}}$.

strength on T_{el} for higher photon energies than for lower ones.

The origin of the correlation feature can be understood from the calculation of T_{el} under two-pulse excitation within the two-temperature model (Fig. 4). When the two pulses are sufficiently close to one another, the peak value of T_{el} achieved by the second pulse exceeds that from one pulse alone. Since the light emission process is strongly nonlinear in temperature, we then observe a greater signal than for the two fully separated pulses. The enhancement is strongest at very short pulse separations, where electrons remain partially out of equilibrium with the SCOPs. A weaker enhancement of the emission persists during the slower decay of the subsystems of equilibrated electrons and SCOPs. The model is found to yield good agreement with the measured two-pulse correlation functions for all three spectral ranges (lines in Fig. 3).

In conclusion, the observed spectrally broad light emission from graphene can be understood as a direct consequence of a transient regime in which the electron distribution is driven strongly out of equilibrium by ultrafast laser excitation. The results further indicate that *e-e* scattering under our experimental conditions is efficient on the 10-fs time scale, that energy loss to the SCOPs is significant on a time scale below 100 fs, and that equilibration with other phonons occurs on the time scale of 1 ps.

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