Electroluminescence from graphene excited by electron tunneling

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Abstract
We use low-energy electron tunneling to excite electroluminescence in single layer graphene. Electrons are injected locally using a scanning tunneling microscope and the luminescence is analyzed using a wide-angle optical imaging system. The luminescence can be switched on and off by inverting the tip–sample bias voltage. The observed luminescence is explained in terms of a hot luminescence mechanism.

Keywords: graphene, electron tunneling, photoemission, electroluminescence, scanning tunneling microscopy

(Some figures may appear in colour only in the online journal)

1. Introduction
Graphene-based optoelectronics show considerable promise due to the linear dispersion, tunable Fermi level, and nearly flat absorption profile of graphene \cite{1-3}. Using these properties, graphene photodetectors have been demonstrated by decorating graphene flakes with metal structures \cite{4-6}, quantum dots \cite{7}, and by exciting plasmons in graphene \cite{8, 9}. While graphene optoelectronics has largely concentrated on converting photons into electrons, the reverse process also provides insight into carrier dynamics. For example, electroluminescence (EL) studies of carbon nanotubes (CNTs) have explored thermal, phonon–electron, and electron–electron processes \cite{10-15}. However, very few EL measurements have been performed on graphene. These measurements have either been limited to multilayer flakes \cite{14} or nano-crystal mediated processes \cite{16}.

In this work we use a scanning tunneling microscope (STM) to inject carriers into a graphene flake and study the resulting luminescence in ambient conditions. While STM-based EL has been observed in CNTs \cite{13, 12}, previous attempts on graphite have been unsuccessful \cite{12}. We find that the luminescence depends on the energy of the injected carriers as well as the number of graphene layers. This is consistent with a hot luminescence mechanism. To the best of our knowledge this is the first demonstration of STM-induced EL from single layer graphene.

2. Results and discussion
STM light emission in metals is well-established \cite{17-19}. In noble metals it originates from tunneling electrons exciting a localized plasmon mode in the gap between the tip and metal surface, known as a gap plasmon. The gap plasmon can lead to light emission by either decaying directly into a photon or by coupling to a surface plasmon \cite{19-21}. Plasmons have also been demonstrated in graphene \cite{22-24}. However to excite plasmons in graphene the Fermi level, $E_F$, must be shifted such that $E_F > \hbar\omega$, where $\hbar\omega$ is the energy of the plasmon \cite{25}. Due to this requirement combined with the technical challenges of doping graphene by more than 1 eV, graphene plasmonics has focused on the infrared (IR) spectral range. To generate tunneling-induced light emission at visible wavelengths we therefore have to explore other interaction mechanisms.

The process that we exploit in this work is hot luminescence (HL). For an undoped graphene flake an incident photon can excite an electron–hole pair. Since there are no available states in the valence band the electron will either recombine almost instantaneously with the created electron or will become free and re-emerge as a photon. The energy of the re-emitted photon is typically redshifted due to scattering processes and so the emitted light is visible.
The doping-induced Fermi level must be in the range $\bar{E}_F < \epsilon$, where $\epsilon$ is the required doping level is much lower than for plasmons. This process also requires that a graphene flake is doped, but shown in [26]. Figure 1(a) shows a sketch of the process. Radiative decay channel dominates over Raman processes, as will also be available states for the carriers to recombine non-radiatively. If the flake is doped appropriately, an incident photon ($h\omega_L$) excites an electron–hole pair that can recombine and emit a photon ($h\omega_E$), see right panel. (b) Sketch of the doping mechanisms for the graphene flake due to the tip and the substrate. The case without doping is shown as a reference. (c) Sketch of the experimental setup. The graphene sample is mounted on a piezo-scan-stage on top of an inverted microscope. A STM scan-head incorporating an Au tip is placed on top of the microscope for topographic and luminescence imaging. The resulting luminescence is collected with a 1.4 NA microscope objective and sent to an avalanche photodiode (APD). Figure 1. (a) Diagram of the hot luminescence mechanism (HL). An incident photon ($h\omega_L$) excites an electron–hole pair. If the graphene is undoped (left panel), the electron–hole pair combines non-radiatively and HL is not observed. Under correct doping conditions the electron–hole pair can recombine and emit a photon ($h\omega_E$), see right panel. (b) Sketch of the doping mechanisms for the graphene flake due to the tip and the substrate. The case without doping is shown as a reference. (c) Sketch of the experimental setup. The graphene sample is mounted on a piezo-scan-stage on top of an inverted microscope. A STM scan-head incorporating an Au tip is placed on top of the microscope for topographic and luminescence imaging. The resulting luminescence is collected with a 1.4 NA microscope objective and sent to an avalanche photodiode (APD).

hole, as in the case of Raman and Rayleigh scattering, or recombine non-radiatively. If the flake is doped appropriately, the graphene can still absorb an incident photon and there will also be available states for the carriers to recombine and emit a red-shifted photon [26]. In this case the new radiative decay channel dominates over Raman processes, as shown in [26]. Figure 1(a) shows a sketch of the process. This process also requires that a graphene flake is doped, but the required doping level is much lower than for plasmons. The doping-induced Fermi level must be in the range $h\omega_L > 2|E_F| \geq h\omega_E$, where $h\omega_L$ and $h\omega_E$ are the photon energy of the laser and the emission, respectively [26]. This process can be translated to an STM picture by replacing the incident photon with an injected electron. In this case, the energy of the injected electron (or hole) can be controlled by the bias voltage $V_B$. Figure 1(b) shows a sketch of the experimental setup. A graphene flake was exfoliated onto an indium–tin–oxide (ITO) coated coverslip and placed on an inverted microscope. A home-built STM scan-head incorporating an electrochemically etched gold tip was placed on top of the microscope. The tip was positioned into the focus of a 1.4 NA oil immersion microscope objective, which is used for collecting the EL and sending it to an avalanche photodiode (APD). The sample was placed on a piezo-scan-stage that scanned the sample underneath the STM tip to form simultaneous topographic and luminescence images. For STM measurements the tip was grounded and a bias of $V_B = \pm 2–3$ V was applied to the sample. The tunneling current, $I_t$, was kept constant at 1 nA, corresponding to a tip–sample separation of $\sim 1$ nm.

The observation of HL in graphene requires doping. Figure 1(c) shows three different regimes of doping, corresponding to no doping, substrate doping, and tip doping [29]. The Fermi level of the graphene flake can also be altered by placing the graphene flake on a substrate with a different work function. In our case we used an oxygen-plasma cleaned ITO coated glass substrate, which leads to a p-doped graphene flake [27, 28]. Based on the work functions, this type of contact doping can be as large as $\sim 0.5$ eV. Additionally, the STM tip gives rise to band-bending in the graphene due to two mechanisms. First, the work function difference between the tip material and the graphene leads to local doping of the graphene flake. For example, an Au tip in combination with graphene gives rise to a p-doping due to the higher work function of the Au tip [29]. Second, the bias voltage $V_B$ gives rise to a capacitive effect. For the bias voltages used in our measurements, these two mechanisms lead to graphene doping of $\sim 0.5–0.65$ eV [29], which is sufficient to observe HL at visible or near-IR wavelengths.

Since the graphene flake is p-doped it should be possible to observe HL when electrons are injected, as illustrated in figure 2(a). The resulting image is shown in figure 2(b) and it clearly shows EL from the graphene flake. However, when $V_B$ is changed to inject holes instead of electrons (figure 2(c)) the luminescence disappears as shown in figure 2(d). This measurement is in agreement with the proposed HL mechanism. Count rates of $\sim 2$ kHz were recorded, corresponding to an electron-to-photon conversion efficiency of $\sim 10^{-6}$. The background in figure 2(d) originates from the radiative decay of plasmons in the Au tip that were excited by electrons tunneling from the substrate into the tip. To verify that the sample was not altered by injecting holes, an additional electron injection image was acquired, which turned out to be in agreement with figure 2(b). Additionally Raman spectra were acquired before and after the STM measurements and no disorder-induced D band scattering was observed indicating that the process is not related to defects and it is not damaging the flake [30, 31]. We note that [12] and [10] observed STM light emission from multi-wall carbon nanotubes using $I_t = 10–50$ nA, compared to $I_t = 1$ nA used in the present work. The authors argued that the emission was related to Van Hove singularities or local defects; neither of these effects can explain the observed luminescence in graphene.

The HL mechanism in graphene is different from the plasmon-induced mechanism observed in noble metals. Unlike metals, HL in graphene does not require an intermediate plasmon mode, such as a gap plasmon, for momentum conservation. To illustrate this, similar HL images were taken using a tungsten tip, which does not support...
Figure 2. Sketch of the HL mechanism and the measurements. The graphene flake is p-doped due to the tip and substrate. (a) Electrons are injected and inter-band transitions are allowed. (b) HL image of the flake when electrons are injected. (c) Holes are injected, but inter-band transitions are forbidden. (d) HL image of the flake when holes are injected.

IR, which qualitatively agrees with the optically excited HL presented in [26]. Since this sample was prepared on ITO both the substrate and tip doping are present, which is sufficient to lead to the observed HL.

HL is an inter-band process and as such the strength of the signal should scale with the number of layers. The most prevalent example of this is the 2.3% absorption per layer in graphene [2]. To determine the scaling of the HL signal with the number of layers an additional sample was prepared. In this case the flake was exfoliated onto a glass coverslip and a platinum electrode was evaporated onto one side of the flake. The doping from the electrode is negligible because
of the large separation distance between the electrode and the measurement location [36, 29]. As before, the sample was p-doped due to the Au tip and electrons were injected via tunneling. Figure 4(a) shows the topographic image of a flake with different numbers of layers. The entire image was acquired on the flake and the single layer graphene (SLG) area is labeled. The HL image is shown in figure 4(b). Interestingly, the number of layers shown in the topography is also visible in the HL image. Horizontal dashed lines from the topography and HL are shown in figures 4(c) and (d). Since the signal-to-noise ratio was low the top parts of the images were binned vertically. The horizontal dashed lines are spaced by 0.5 nm and 50 c s−1 in figure 4(c) and figure 4(d), respectively. The topographic step height is slightly larger than expected for graphene and is likely due to calibration errors of the scan-head. These profiles illustrate that the HL signal scales linearly with the number of layers and provides strong evidence that the EL mechanism is an inter-band process, as expected.

3. Summary

In conclusion, we have demonstrated high-resolution graphene luminescence excited by electron tunneling. The luminescence signal depends on the bias voltage $V_B$ and scales with the number of graphene layers. Our observations are in tune with a hot luminescence mechanism, which can be controlled by local doping. Because tunneling-induced hot luminescence depends on doping, our technique can be employed for recording spatial maps of the relative Fermi level. In comparison to Kelvin probe microscopy, this technique would allow for the local photon properties to be correlated with the relative Fermi level at that location. This technique would provide insight into the radiative decay pathways of graphene-based devices. By using mid-infrared detectors, our technique can also be used to electrically excite plasmons in graphene.

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