An *in situ* characterization technique for electron emission behavior under a photo-electric-common-excitation field: study on the vertical few-layer graphene individuals

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Abstract
The *in situ* characterization on the individuals offers an effective way to explore the dynamic behaviors and underlying physics of materials at the nanoscale, and this is of benefit for actual applications. In the field of vacuum micro-nano electronics, the existing *in situ* techniques can obtain the material information such as structure, morphology and composition in the process of electron emission driven by a single source of excitation. However, the relevant process and mechanism become more complicated when two or more excitation sources are commonly acted on the emitters. In this paper, we present an *in situ* nano characterization technique to trigger and record the electron emission behavior under the photo-electric-common-excitation multiple physical fields. Specifically, we probed into the *in situ* electron emission from an individual vertical few-layer graphene (vFLG) emitter under a laser-plus-electrostatic driving field. Electrons were driven out from the vFLG’s emission edge, operated *in situ* under an external electrostatic field coupled with a 785 nm continuous-wave laser-triggered optical field. The incident light has been demonstrated to significantly improve the electron emission properties of graphene, which were recorded as an obvious decrease of the turn-on voltage, a higher emission current by factor of 35, as well as a photo-response on-off ratio as high as 5. More importantly, during their actual electron emission process, a series of *in situ* characterizations such as SEM observation and Raman spectra were used to study the structure, composition and even real-time Raman frequency changes of the emitters. These information can further reveal the key factors for the electron emission properties, such as field enhancement, work function and real-time surface temperature. Thereafter, the emission mechanism of vFLG in this study has been semi-quantitatively demonstrated to be the two concurrent processes of photon-assisted thermal enhanced field emission and photo field emission.

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

1. Introduction

In situ nano characterization study has been widely used in recent three decades since the advent of high-resolution spectroscopy and imaging characterization systems. It gives us an opportunity to probe into the dynamic, time-dependent behaviors and relevant mechanisms at the nanoscale during series of physical processes, such as mechanical deformation [1–3], heating [4, 5], optical focusing [6, 7], electrical biasing [8, 9] and magnetic response [10, 11]. Compared with the traditional methods, the in situ analysis offers more detailed information, especially provides a unique real-time glimpse into the fascinating physics phenomena, which is very important to develop the materials for subsequent applications. For example, in the field of vacuum micro-nano electronics, the electron emission behaviors and the real-time changing natures of materials can be characterized synchronously in modified electron imaging systems (scanning electron microscopy, transmission electron microscopy, atomic force microscopy, etc) [8, 9, 12–14].

Typically, the in situ study for electron emission process is applied under a single excitation source (e.g. an external electrostatic field). The corresponding characterizations for morphology and composition help to reveal the real-time changes in geometrical appearance and surface composition of the cathode materials. According to the typical Fowler–Nordheim (F–N) theory, these two changes are associated with the localized field enhancement factor (β) and the work function (φ), which are the two key factors to the field emission properties [15]. Besides that, the crystallization and defects at atomic-scale inside an emitter also can be examined during the in situ electron emission process, and thus deeper physical mechanisms can be inferred, such as field emission Joule heating breakdown and re-crystallization [16, 17]. For a single driving field variable, it is relatively easy to achieve the above analyses through in situ characterization. However, when two or more excitation fields act on the sample simultaneously, things will get complicated. Specifically, the intrinsic properties of materials can be changed under the influence of multiple physical fields (e.g. an optical-plus-electrostatic driving field), which together affect the final electron emission performance. This means that it will be very difficult to distinguish the actual contribution of each source of excitation, and also very hard to clarify the specific mechanism of the electron emission process.

Along with the development of laser technology, electron emission process can be triggered by high-intensity continuous lasers or laser pulses, i.e. optical field-driven photo-emission. Such a process makes actively controlled ultra-fast electron emission possible [18–21], thus forming a series of applications, such as the state-of-the-art time-resolved electron microscopy and spectroscopy that can access temporal dynamics on a solid surface with high spatial resolution [22–24]. In addition, more importantly, this laser-triggered optical field has been demonstrated to assist in the field electron emission process and improve the performance from a specific emitter by taking advantage of the synergy with the fixed electrostatic field [25–28]. However, the corresponding in situ analysis is insufficient to reveal the essence of such a multi-fields-driven electron emission, although some preliminary results about polarization dependence as well as emitted electron spectrum have been reported on a carbon nanotip sample [29].

In this paper, we introduce an in situ nano characterization technique for electron emission driven by a photo-electric-common-excitation field. In a modified scanning electron microscope (SEM) equipped with two state-of-art nano-manipulators and a laser scanning arm, the electron emission from an emitter can be in situ excited under an applied external electrostatic field as well as a focused laser-triggered-optical field. At the same time, the real-time sample information about morphology, structure, composition and even the surface temperature can be characterized in situ by SEM and the coupled Raman spectrometer. After analyzing the above in situ measurement results, more detailed and accurate electron emission mechanism under the multiple physical fields will emerge. As an example of the performance of the proposed technique, we present an in situ study of the individual vertical few-layer graphene (vFLG) emitter, which is of great interest for the further development of novel electron emission cold cathode materials. The electrons can be driven out from the vFLG’s top end edge by using an external electrostatic field coupled with an optical field focused by a continuous-wave (CW), 785 nm laser. Improvements of electron emission performance have been demonstrated. More importantly, the in situ SEM observation and Raman spectra reveal the morphology and structure (corresponded to ~β), composition (corresponded to ~φ) and even real-time temperature (~T) changes of the individual vFLGs during their actual electron emission process. Then through Kelvin probe force microscope (KPFM), theoretical simulation and other auxiliary means, the detailed emission mechanisms have been concluded to be the dominant photon-assisted thermal enhanced field emission (PTFE), as well as the subordinate directly photo field emission (PFE), which operated together. With such in situ nano characterization method as an effective technical support, it may be possible to study various mechanisms of electron emission behavior driven by multiple physical fields, such as PFE, PTFE, multi-photon absorbing above-threshold photo field emission (m-PFE), optical field
emission process, including the supply of electrostatic excitation, measurement and data recording of the electron emission process should be divided into two parts. One is the characterization setup under the photo-electric-common-excitation parameters of materials in this process. The real-time characterizations of the key characteristic is the nano characterization technique for the in situ electron emission characterization setup and steps. 2.1. The in situ electron emission characterization setup and steps

The nano characterization technique for the in situ electron emission process should be divided into two parts. One is the excitation, measurement and data recording of the electron emission process, including the supply of electrostatic field and the focusing of the laser-triggered-optical field. The other is the real-time characterizations of the key characteristic parameters of materials in this process.

A schematic drawing of the in situ electron emission characterization setup under the photo-electric-common-excitation field is shown in figure 1(a). The study is performed in situ inside a modified SEM (Quanta 450 FEG, FEI, 10 kV) chamber, which is equipped with two independent state-of-art manipulators (miBot™, Imina Technologies) and a laser scanning arm (Raman-SEM coupling module, Rainshaw inVia). The tungsten (W) microprobe attached with the emitters and another W microprobe are mounted to the manipulators, to act as the cathode and anode, respectively. Both of the microprobes can be moved in three dimensions (xyz) at the step size of nanoscale. Thus, a probe diode electron emission testing structure is achieved, and it is adopted to provide the external electrostatic field for the emitters and extract the current signal. Another optical field triggered by a CW 785 nm laser is then introduced into the chamber through the laser scanning arm, and focused onto the gap between the cathode and anode. Thus, our proposed photo-electric-common-excitation field driven operation mode is constructed. Figure 1(b) shows the typical testing photograph taken from inside of the SEM chamber.

Figure 1. (a) Schematic drawing of the in situ electron emission characterization setup under photo-electric-common-excitation field. (b) A photograph taken inside the chamber of the modified SEM system. (c) Typical SEM image of the tungsten (W) microprobe anode and the vFLGs cathode during the testing process. (d) Optical microscopy image of the laser spot focusing onto the gap between the cathode and anode.

Figure 1(c) displays a low-magnification SEM image of the tungsten (W) microprobe anode and the cathode emitters (vFLGs in this demo) during the testing process. In this case, the W microprobe anode is accurately moved to facing one of the individual FLGs, with a gap spacing of about 50 nm. A driving voltage is then applied to the selected sample to pump up electrons and drive electron emission from it. At the same time, as shown in figure 1(d), the laser beam is focused in the middle of the gap between the cathode and anode. Emission current values are then recorded at different electrostatic voltages as well as laser intensities, respectively.

During the electron emission measurement, the morphology, structure and composition of the sample can be observed at any time by the imaging function of SEM as well as the spectroscopy analysis (such as EDS) integrated in it. On the other hand, the induced laser can be applied as the excitation source of Raman signals simultaneously, and then the deeper information about crystal structure and defects are collected through the in situ Raman spectrometer [30]. More importantly, taking these obtained Raman spectra as a nanometrology tool [31, 32], the real-time temperature (T) of the emitter during the actual electron emission process can be extracted, and then used for the further emission mechanism analysis.

2.2. Sample preparation and characterizations

We select the vFLG emitters as the demo sample based on the following considerations. Firstly, graphene is a two-dimensional monolayer of carbon atoms showing outstanding intrinsic nature such as ultrahigh electron mobility, high thermal dissipation rate and excellent structural stability [33–36]. In particular, vertically-oriented graphene and its few-layer counterparts show good characteristics in the electron emission behavior, due to their linear sharp emission edge with strongly localized field enhancement [37–41]. Secondly, graphene exhibits extremely wide optical spectral response range determined by the gapless energy dispersion, from deep ultraviolet to terahertz [42–45], and thus a wide range of photo-responsive electron emission characteristic can be realized in combination with their intrinsically fast response rate and high switch ratio [46, 47]. Therefore, it is foreseen that building a photo-electric-common-excitation field driven operation mode should help to achieve better electron emission properties of vFLGs.

The vFLGs sample was prepared directly onto a tungsten (W) microprobe through the inductively coupled plasma chemical vapor deposition (ICPCVD) technique. Tungsten microprobe as the substrate was previously electrochemically sharpened into a cone with tip diameter of less than 100 nm in the sodium hydroxide solution, and then placed into the ICPCVD quartz chamber. During the growth of vFLGs, the substrate was firstly heated to 900°C under 15 sccm Ar and 15 sccm H2 at 0.04 Torr, for cleaning the surface of W tip. And then, a RF power of 1100 W was applied to generate plasma with a DC bias of 200 V, while a flow of 60 sccm CH4 and 10 sccm H2 were introduced into the chamber at 0.058 Torr, thus the vFLGs could be obtained after 5 min of growth time.
boundary phonons of graphene can be observed at around $2D$ peak stemming from the second order of the zone-
for an individual emitter. In addition, in the original Raman
Figure 2.

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A field emission SEM (Zeiss Supra55, 10 kV), a high-
resolution transmission electron microscope (HRTEM) (Titan
G2 60–300, FEI, 80 kV), and a Raman spectrometer (Rain-
shaw inVia Reflex) with an excitation of 785 nm were
employed to study the initial morphology, structure and
composition of the vFLG products, as shown in
figure 2. Typical SEM and TEM images show that the vFLGs sample distributed on the W microprobe.

Figure 2. (a) SEM image of the vFLGs grown on W microprobe, (b) TEM image of the marked area B in (a), (c) High-resolution TEM (HRTEM) image of the marked area C in (b), (d) Typical Raman spectrum of the vFLGs sample distributed on the W microprobe.

Before the formal in situ electron emission measurement, the W anode was firstly moved to contact the top end of the chosen FLG individual to examine its intrinsic electric transport and corresponding photocurrent responsive characteristics. The CW 785 nm laser with different powers (0.09, 3, 7.5, 15 and 30 mW) was focused onto the FLG-W junction. The corresponding laser illumination intensities ($I_{\text{laser}}$) were then calculated as $21$ W cm$^{-2}$, $341$ W cm$^{-2}$, $752$ W cm$^{-2}$, $1442$ W cm$^{-2}$ and $1736$ W cm$^{-2}$, respectively, by measuring the focusing light spots from a coupled optical microscopy images (see the supplementary materials, figure S2). The current versus bias voltage ($I-V$) curves of the FLG-W junction were then recorded (see the supplementary materials, figure S3). It is clear that there exists Schottky contact between the W microprobe anode and the vFLG individual, and thus the $3–5$ layered vFLG sample in this example should be taken as semiconductor, of which the resistivity decreases with the increase of temperature. Those recorded curves for both forward and reverse biases present rising trends as laser intensity increases, which preliminarily indicate that the introduced optical field should work on our sample in such a magnitude of laser energy.

3. Results and discussion

3.1. Preliminary photo-responsive study of the electrical transport property

The in situ electron emission behavior of the chosen vFLG emitter was then studied under the constructed photo-electric-common-excitation field. The W microprobe anode was drew away about $50$ nm from the FLG’s top end, and was applied a driving electrostatic voltage. Figure 3(a) shows the recorded $I-V$ characteristic curves at various incident laser intensities ($I_{\text{laser}}$). With the applying voltage gradually increased, the emission current was recorded as at least five cycles for each laser intensity condition, until the electron emission reached a repeatable and stable stage. It can be observed that the turn-on
1736 W cm⁻², the on-off ratio can reach as high as 5, which indicates that the intrinsic work function (φ) and the aspect ratio of the sample remained unchanged after exposure, since the morphology, structure, and composition of a sample can be achieved through the coupled SEM and Raman functions. Combined with the above characterizations, the electron emission behavior of an emitter can be firstly analyzed by the F–N theory, which is used for classical field electron emission process and stated as [48]:

$$J = \frac{A(\beta E)^2}{\varphi} \exp \left( -\frac{B_{F}^{3/2}}{\beta E} \right)$$  \hspace{1cm} (1)

where \(A = 1.541 \times 10^{-6}\) is the first F–N constant with the unit of \(A \text{ eV} \text{ V}^{-2}\), \(B = 6.830 \times 890\) is the second F–N constant with the unit of \(e \text{V}^{-3/2} \text{ V} \text{ nm}^{-1}\), \(\varphi\) is work function of the sample, and \(\beta\) is the field enhancement factor, which is closely related to the emitter’s aspect ratio of structure. After a log transformation of equation (1), there should be a linear dependence of the \(\ln(J/(E^2))\) on \(1/E\).

In this case, figure 3(c) gives the corresponding F–N (\(\ln(J/(E^2))–1/E\)) plots for some of the typical \(I–V\) curves (cycles No. 5, No. 7, No. 11, No. 16, No. 21 and No. 30 in figure 3(a)) under various laser intensities. One can observe that these plots usually present nonlinear characters composed of some discrete regions, which can be artificially defined as nearly straight lines within different electrostatic field sections. However, those fitting lines at the higher DC electrostatic field region (inset in figure 3(c)) show obviously different slopes \((k)\) upon various laser intensities. Here, we believe that the intrinsic work function \((\varphi)\) and the aspect ratio of the sample remained unchanged after it is experienced the electron emission process with laser exposure, since the morphology, structure, and composition of

Figure 3. \textit{In situ} electron emission characterizations of the individual vFLG under photo-electric-common-excitation field. (a) The \(I–V\) curves at different incident laser intensities \((I_{\text{laser}})\). The last five cycles were recorded for each laser intensity condition. (b) Time dependent characteristic of the photo-responsed electron emission at a fixed DC electrostatic voltage of 17.0 V. The laser intensity was fixed to about 1736 W cm⁻². (c) The corresponding F–N plots of the selected typical \(I–V\) curves (cycles No. 5, No. 7, No. 11, No. 16, No. 21 and No. 30 in (a)) within the entire electrostatic field and at the high electrostatic field region (inset), respectively. (d) The dependence of the calculated field enhancement factor \((\beta)\) on the \(I_{\text{laser}}\).
the vFLGs have not obviously changed, which was confirmed from the in situ researches of SEM and Raman, as well as the ex post facto KPFM study. However, the actual effective field enhancement factors ($\beta$) calculated from the above slopes present a continuous rise as a function of the increasing incident laser intensity ($I_{laser}$), and these values display an approximate linear distribution, as shown in figure 3(d). It suggests that there should be more complex mechanisms other than pure electrostatic field emission during the electron emission of the vFLGs sample.

To explore the electron emission behavior under photo-electric-common-excitation field, it should be clear the interaction relationships between the excited photons, electrons and heat. Theoretically, for a relatively weak optical field, the emitters absorb one or several photons, and result either in PFE (tunneling electron emission) or above-threshold photoemission (m-PFE, over the barrier electron emission). For stronger optical fields, on the other hand, the local electrostatic field together with the laser-induced optical field modifies the tunneling barrier and prompts the OFE. Besides those, some of the plasmonic nanostructures can act as light-trapping components to generate large electromagnetic field enhancements in a specific excitation band, thus generate energetic hot electrons that can directly transit over the surface barrier into a vacuum, which is called the PPE. As an extension of that, the plasmonic nanostructure also can act as a mediator to transit the hot electrons into an electron emitter that the plasmonic nanostructure is adhered to. The injected hot electrons can be released into a vacuum under a small static electric field applied to the emitter. This process was proposed as a PMEE. Moreover, with the increase of the focused laser intensity, the generating heat from light spot can lead to the tunneling thermal enhanced field emission of the emitters, which depends more on the material absorption and lattice vibrations. This will create another determining factor to the electron emission process, i.e. the real-time temperature ($T$), which is of great importance in the Richardson–Schottky equation based on systems at field-thermal equilibrium. Therefore, we need more intuitive in situ experimental data and evidences to distinguish the possible electron emission processes mentioned above.

In our proposed in situ nano characterization study, we firstly consider about the contribution of thermionic emission. Upon the laser excitation, the vFLGs may absorb the laser energy, which leads to an increase of the surface temperature. Here, an in situ Raman spectroscopy was developed to record the different Raman modes of the vFLG sample during the electron emission, whereby the real-time temperature information of the sample could be extracted. To that end, a typical vFLG sample was firstly placed on a thermal stage for measuring its Raman spectra under different temperatures (from room temperature to 550°C). As shown in figure 4(a), the increase of the sample’s temperature leads to a red shift of the G peak (inset in the figure 4(a)). Referring to the special inherent characteristics of graphene, such as very strong covalent bonds and dense lattice structure, the increase of the vFLG’s temperature only lead to a weak red shift of the G peak, which is less than 15 cm$^{-1}$. According to previous studies, the dependence of frequency shift of the G mode under different temperatures can be described as [31]:

$$\omega = \omega_0 + \chi T,$$

where $\omega_0$ presents the frequency of G mode when temperature $T$ is extrapolated to 0°C, and $\chi$ is the first-order temperature coefficient, which defines the slope of the dependence and determines the frequency shift of the G mode when the temperature of the sample increases by 1°C. By fitting the data plots, the extracted negative value $\chi$ is measured as $-(2.22 \pm 0.23) \times 10^{-2} \text{cm}^{-1} \text{°C}^{-1}$, and the extrapolated $\omega_0$ value is 1583.079 cm$^{-1}$ for the vFLGs sample, correspondingly.

Equation (2) was then employed as a calibration for determining the real-time surface temperature of the vFLGs during the electron emission driven by the constructed photo-electric-common-excitation field. Figure 4(b) gives the Raman spectra of the vFLG sample during the electron emission under laser illumination with different intensities, whereby the temperature can be determined. Given the intrinsic properties of graphene discussed above, the G peak’s maximum red shift of the sample was measured as approximately 15 cm$^{-1}$ when laser intensity increased from 21 to 1736 W cm$^{-2}$. Table 1 lists the measured G peak frequencies and calculated temperatures for various $I_{laser}$. The extracted real-time temperature of the vFLG emitter could exceed 200°C when the incident laser power was open to over 10% (with $I_{laser} \sim 341$ W cm$^{-2}$), and even be more than 750°C when it was 100% open (with $I_{laser} \sim 1736$ W cm$^{-2}$). In view of this, the generating heat has been demonstrated to come from the focusing laser, and it leads to the lattice thermal vibration and subsequent tunneling PTFE of the vFLG sample.

In addition to the experimentally obtained real-time temperature information, the contribution from the thermionic emission also can be demonstrated indirectly from a transformation of the electron emission measuring data. The electron emission under field-thermal equilibrium can be described by the Richardson–Schottky equation [15]:

$$J(E_{local}, T) = \frac{4\pi m e k^2 T^2}{h^3} \exp \left( \frac{\beta_2 E_{local}^{1/2} - \phi}{kT} \right),$$

where $m$ and $e$ present the mass and charge of the electron, $k$ is the Boltzmann’s constant, $h$ is the Planck’s constant, and $T$ is the temperature of emitters during the electron emission process. In addition, the constant $\beta_2$ can be expressed as $(e^4/4\pi\varepsilon_0\varepsilon_0)^{1/2}$, in which $\varepsilon$ and $\varepsilon_0$ are permittivity vacuum and relative dielectric constant of the sample, respectively. From equation (3), one can see that at equilibrium temperature the relationship between the emission current density ($J$) and electrostatic field intensity ($E$) can be simplified to:

$$J(E) \propto \exp(E^{3/2}).$$

Figure 4(c) gives the transformational Ln ($J$) versus $E^{3/2}$ curves of the selected testing cycles at different laser intensities. Most of the curves fit in linear distributions, which verifies the existence of field-thermal electron emission behavior (PTFE in this case).
Further, one can ascertain semi-quantitatively the current contribution from the PTFE mechanism, by substituting the obtained temperature values under different laser illumination into equation (3). Figure 5(a) shows the emission current increments integrated from the vFLG's emitting area (∼600 nm² as mentioned above) under the laser intensity of 752 W cm⁻², 1442 W cm⁻² and 1736 W cm⁻², respectively. One can see that the calculated current values are very close to the experimentally measured data, which clearly indicates that for the vFLG sample in this example, the contribution from the PTFE behavior should be dominant. However, on the other hand, it can be observed from figure 5(a) that when the laser intensity is high enough, the actually recorded emission currents typically show a little higher than the theoretical calculation that just considering the PTFE mechanism. Such a result also can be concluded from the Ln(I) versus E¹/² curves in figure 4(c) (see the blue, pink and yellow plots). Specifically, these three fitting curves show bigger slopes at lower electrostatic fields with the increase of the laser intensity. Both of the results mean that with the help of strong laser illuminations, there is other electron emission mechanism which is not associate with the heat generation.

Here, the applied laser-triggered optical field may further affect the electron emission of the vFLG from the following aspects. First of all, according to the Fermi–Golden law, the optical absorption of a specific vFLG sample is determined by the localized electromagnetic field it experiences. The aforementioned applying optical field can consequently increase the electron interband transitions of the graphene, by absorbing one or more photons. These addition electrons can directly tunnel through the graphene edges under the DC electrostatic field, to produce the one-photon absorbing PFE (figure 5(c)) or m-PFE (figure 5(d)). Secondly, the optical enhanced field can be strong enough to reduce the barrier width felt by the electrons within the graphene emitting edges, and thus the electrons can tunnel barrier and form the OFE (figure 5(e)). Thirdly, some plasmon-related electron emission behaviors may happen if the vFLG’s top edges show surface plasmon resonance with the 785 nm excitation wavelength.

In our proposed characterization study, the finite-difference time-domain simulation (Lumerical FDTD solutions) was adopted to calculate the localized electromagnetic field

Table 1. The measured frequencies of the G peak and calculated real-time temperatures of the vFLG sample, for various laser intensities during the in situ electron emission process.

| Laser intensity (I_laser) | G peak frequency (cm⁻¹) | Temperature (°C) |
|---------------------------|------------------------|------------------|
| 21                        | 1581.48                | 72.81            |
| 341                       | 1578.44                | 210.68           |
| 752                       | 1575.41                | 348.65           |
| 1442                      | 1573.38                | 440.66           |
| 1736                      | 1566.29                | 763.11           |

Figure 4. (a) Dependence of the G mode frequency shift of Raman spectra under different surface temperatures of the vFLG sample. The inset shows the shape of the typical G peaks. The measured data are used to extract the temperature coefficient (χ). (b) The real-time Raman spectra of the vFLG sample during the in situ electron emission process under laser illumination with different I_laser. The inset shows the red shift of the G peak (approximately 15 cm⁻¹) from I_laser of 21 to 1736 W cm⁻². (c) The transformational Ln(I) versus E¹/² curves of the selected curves in figure 3(c).
intensity of an individual vFLG, as a supplementary to the detailed mechanism analysis. Specifically, according to the geometrical structure observed from in situ SEM, the vFLG sample was modeled as a rectangular thin layer with the width and length of 500 nm and 700 nm, respectively. The thickness of single-layer graphene was set to 0.4 nm, while the radius of tungsten microprobe’s tip is 50 nm with its cone angle of 25 degrees. The complex refractive index in the visible range was defined as: $n = 3.0$; the imaginary part of refractive index $k$ is constant for this example, since there exists no obvious resonance peaks at 785 nm in the simulations. It is common knowledge that the undoped graphene does not have any plasmon response at such a waveband. In addition, although the simulations reveal an improvement in electromagnetic field, the calculated localized optical field enhancement (maximum to 1.75) is still not enough to drive the OFE process. By the Poynting Law [51], the calculated effective optical field of the laser illumination in our case is estimated to about 0.08 V $\mu m^{-1}$, and it is below 0.15 V $\mu m^{-1}$ even if we introduce the maximum electromagnetic field enhancement. Compared with the external electrostatic field, such low electromagnetic field intensity should have a negligible effect on the vacuum barrier. On the other hand, the m-PFE mechanism is also not likely responsible because it usually requires a laser intensity stronger than 1 GW cm$^{-2}$. Such a driving intensity is normally generated by a short pulse ultra-fast laser [52], while it is only about 1 kW cm$^{-2}$ in our case. Hence, we believe that

Figure 6(a) shows the simulated model and its corresponding electromagnetic field intensity distributions inspected at the surface of the FLG with incident wavelength of 785 nm, when the W anode is moved to 50 nm from its emission edge. The relative electromagnetic field intensity $E/E_0$ was calculated as high as 1.17 at the center of emission edge, and it exhibits a wave-like distribution along the emission edge orientation of vFLG, with higher values in both endpoints and center location (see the supplementary materials, figure S4(a)). Additionally, considering the dielectric function of tungsten anode obtained from the previous reported values [50], stronger electromagnetic field intensity distribution can be observed onto the tip of W anode probe (see the supplementary materials, figure S4(b)). Moreover, such an effect can be further enhanced by controlling the gap distance between cathode and anode. From figure 6(b), one can see the $E/E_0$ value of vFLG at the center of emitting edge increases with the decrease of the gap, e.g. improving from 1.14 ($\sim$90 nm) to 1.54 ($\sim$10 nm) under the incident wavelength of 785 nm. This suggests that moving closer to the gap between vFLG cathode and W anode helps to synchronously achieve higher levels of electromagnetic and electrostatic field driven intensities. Next, with the gap distance being about 10 nm, we examined the dependence of the relative electromagnetic field intensity on the number of vFLG’s layers. The $E/E_0$ values display to be enhanced when the number of layers is increased (see figure 6(c) and figure S4(c) in the supplementary materials). The calculated relative field intensity of the 7-layers vFLG is approximately 1.26 times higher than the monolayer graphene. It could be understood that the polarization of FLG tended to be stronger as the number of its layers increases, since we have ignored the effect of the number of layers on the graphene’s band in this simulation.

From the above FDTD results, one may continue to determine the possible electron emission mechanisms. The electron emission associated with plasmonics can be ruled out for this example, since there exists no obvious resonance peaks at 785 nm in the simulations. It is common knowledge that the undoped graphene does not have any plasmon response at such a waveband. In addition, although the simulations reveal an improvement in electromagnetic field, the calculated localized optical field enhancement (maximum to 1.75) is still not enough to drive the OFE process. By the Poynting Law [51], the calculated effective optical field of the laser illumination in our case is estimated to about 0.08 V $\mu m^{-1}$, and it is below 0.15 V $\mu m^{-1}$ even if we introduce the maximum electromagnetic field enhancement. Compared with the external electrostatic field, such low electromagnetic field intensity should have a negligible effect on the vacuum barrier. On the other hand, the m-PFE mechanism is also not likely responsible because it usually requires a laser intensity stronger than 1 GW cm$^{-2}$. Such a driving intensity is normally generated by a short pulse ultra-fast laser [52], while it is only about 1 kW cm$^{-2}$ in our case. Hence, we believe that

![Figure 5](image-url)
the one photon absorbing PFE should be another mechanism which worked with the PTFE mechanism (see figure 5(c)), acting on the electron emission from the individual vFLGs. Although the energy of single photon $\sim 1.5836$ eV (corresponding to the $\sim 785$ nm laser) is not high enough to enable the electrons directly throw over the emitter’s vacuum barrier, it is sufficient to assist in improving the tunneling electron emission current under a known external electrostatic field. The simulated absorption spectra for vFLGs with different layers also demonstrate that no matter how thick the graphene is, the emitter always has a certain degree of light absorption, which is about 2.6% at 785 nm wavelength condition (figure 6(d)). In general, such an absorption property is enough to get considerable photon-assisted thermal energy, as well as a certain amount of photons absorbing energy, to enhance the intrinsic electron emission performance from the vFLG sample.

As a result, the emission mechanism of vFLG in this study has been semi-quantitatively demonstrated to be the two concurrent processes of PTFE and PFE. Although the Richardson–Schottky field-thermal emission equation has been carried out in this case for a preliminary verification, we believe that a universal electron emission equation applicable to vFLGs under photo-electric-common-excitation multiple physical fields should be re-proposed and modified in our subsequent studies. Basically, due to the introduce of the laser light field, the tunneling emission ability of electrons in graphene can be influenced by the following two aspects: the first one is the electron supply function, in which the temperature is not just controlled by the lattice vibrations, but also controlled by the actual electron energy. It may be high enough under a fast light field, and does not have to wait for the lattice thermal vibrations. The second one should be the electron transmittance coefficient, in which the near field intensity generated by a strong light also may play an important role.

3.4. The method's versatility

The high versatility of the in situ nano characterization technique has been proven by characterizing and analyzing another PMEE process from a gold-on-graphene (Au-on-Gr) nanostructure. In fact, the proposed method should be applicable to the in situ electron emission excitation and corresponding characterization of any emitter (either pure or composite) or micro-region. On the other hand, our proposed setup can be extended to vacuum chambers of other characterization devices, such as TEM and STM. Other measurement devices (e.g. KPFM, AFM, SNOM, HRTEM and EELS) can be further coupled to enrich the in situ analysis means for the electron emission process. In this way, it is possible to give a quantitatively physical image description of the complex electron emission process driven by multiple physical fields.

4. Conclusions

We have proposed, and experimentally demonstrated, the in situ nano characterization technique of electron emission behavior driven by a photo-electric-common-excitation field. In a modified SEM chamber, the electron emission from a single emitter can be excited in situ under a laser-plus-electrostatic field,
through appropriate devices such as nano-manipulators and laser scanning arm. Synchronously, the sample information about morphology, structure, composition and even the surface temperature can be characterized in situ by a series of coupled devices. All of the above help to understand the deep physical mechanisms of the electron emission behavior. We have applied this technique to investigate the electron emission of individual vFLG. The turn-on voltage of the vFLG decreased obviously with the increase of the laser intensity, and the recorded maximum emission current could be higher by a factor of 35 compared to the single electrostatic field condition, with a high photo-response on-off ratio of approximately 5. Moreover, by using the in situ SEM and Raman characterizations, the morphology, composition and even temperature changes of the vFLG have been observed in real-time, and thus the electron emission mechanisms have been analyzed as the concurrent two mechanisms of dominant PTFE and a fraction of directly PFE, which were verified by the FDTD results. The strategy and method presented here are quite general and should be applicable to the semi-quantitative research of complex electron emission processes under multiple physical field driving conditions.

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Author contributions

DSZ and XNS proposed the investigation of using a photo-electric-common-excitation field in the electron emission of nanostructures. DSZ, XNS, SY, and CHJ conceived and initiated the present study. SY performed the in situ measurements and analyzed the results. XY, GL and ZRZ performed the FLG growth and characterization. WH performed the FDTD simulations. WJX, CXX and LF assisted in the measurement. ZY, CJ and SJC assisted in the data analysis. SY, DSZ and XNS wrote the paper. WH and CHJ contributed to the discussions.

Conflicts of interest

The authors declare no competing financial interest.

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