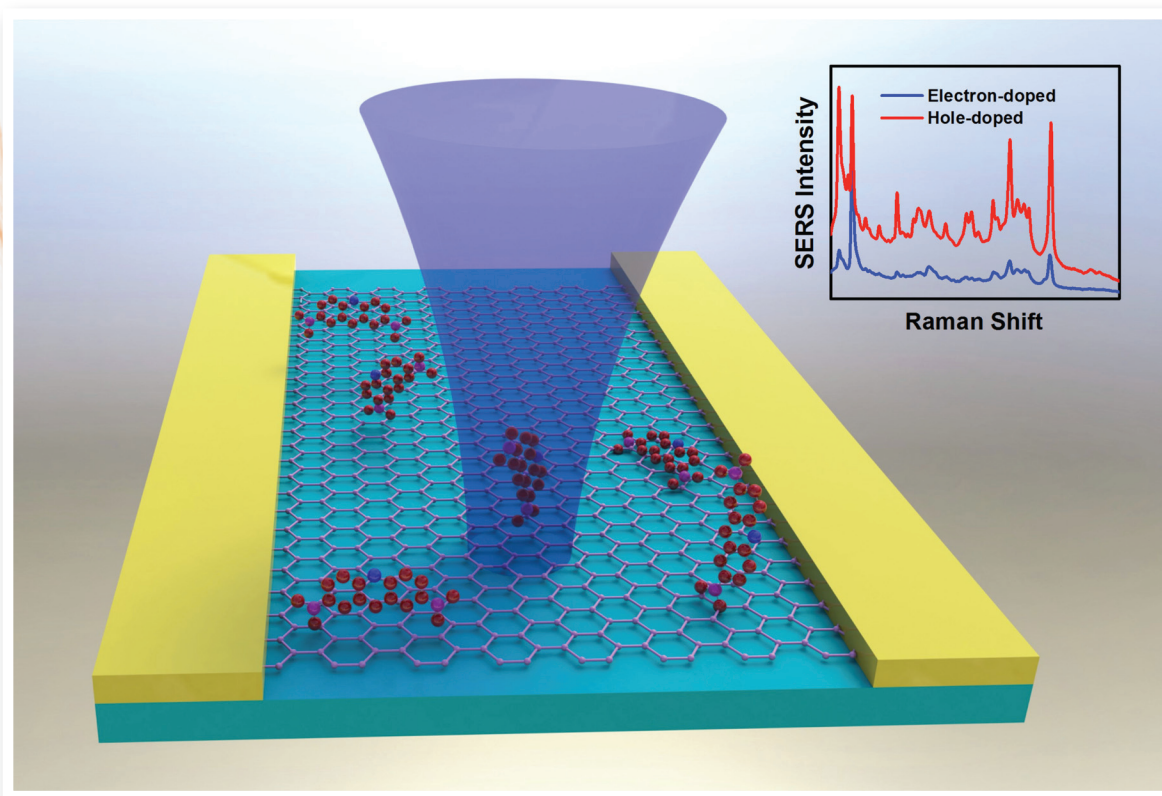## Related Articles

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Tuning surface-enhanced Raman scattering from graphene substrates using the electric field effect and chemical doping

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Graphene recently has been demonstrated to support surface-enhanced Raman scattering. Here, we show that the enhancement of the Raman signal of methylene blue on graphene can be tuned by using either the electric field effect or chemical doping. Both doping experiments show that hole-doped graphene yields a larger enhancement than one which is electron-doped; however, chemical doping leads to a significantly larger modulation of the enhancements. The observed enhancement correlates with the changes in the Fermi level of graphene, indicating that the enhancement is chemical in nature, as electromagnetic enhancement is ruled out by hybrid electrodynamical and quantum mechanical simulations. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4755756]

The viability of graphene as a surface-enhanced Raman spectroscopy (SERS) substrate has been recently demonstrated.[1–4] Due to its simple two-dimensional structure, graphene substrates are more uniform, stable, and reproducible than many commonly used metallic SERS substrates.[5] In SERS, it is widely believed that there are two contributions to its enhancement: an electromagnetic mechanism (EM) through intense enhancement of the localized electromagnetic fields around metallic nanostructures[6–10] and a chemical mechanism (CE) through a combination of metal-molecule chemical interactions.[11–13] Various experimental studies have been carried out to unravel the SERS enhancement mechanism of graphene: Ling *et al.* has shown that the enhancement depends on the orientation of the molecules in its "first-layer" vicinity;[14,15] Xu *et al.* has further shown that SERS enhancement of graphene can be modulated by tuning its Fermi level with a graphene field-effect transistor (GFET) device.[16,17] These studies suggest that SERS enhancement of graphene is a CE effect. However, previously only ∼30% modulations in the enhancement factor were observed with GFET.[16] Moreover, the complexity in GFET fabrication limits its application in engineering the SERS enhancement of graphene effectively on a large scale. Chemical doping, on the other hand, is easier to implement than field-effect doping and could introduce larger change in the doping level of graphene.[18–21]

In this letter, we explore the SERS enhancement mechanism of graphene using both field-effect doping and chemical doping. We find that the enhancement of the Raman signal of methylene blue (MB) on graphene can be tuned using either field-effect or chemical doping. We observe a consistent trend with both doping methods that hole-doped graphene yields a larger enhancement than electron-doped graphene. Compared to field-effect doping, chemical doping yields a significantly larger modulation in graphene enhancement. To study whether changes in the electron density in graphene leads to a modulation of the local electric field, a combined electrodynamics and quantum mechanics model is employed. We find that the local field due to the graphene is largely insensitive to the changes in the electron density and thus unable to explain the observed trend. Our study illustrates that the enhancement in graphene is due to the CE effect.

Graphene was prepared by Scotch tape method on highly hole-doped Si wafers with 300 nm SiO_2. Single-layer graphene was identified from its optical image and double-checked by its Raman spectrum.[22] We fabricated a GFET device, as shown in Figure 1(a). Electrical contacts with graphene are made by electron-beam evaporation of Ti (10 nm) and Au (30 nm). Electrical measurement was done with a lock-in amplifier (Stanford Research System, SR830) at 47 Hz frequency. We deposited probe molecules (methylene blue) on the graphene surface by simply soaking the SiO_2/Si substrate with graphene in the ethanol solution of the molecules (∼5×10^{-5} M). Substrates purposed for comparison were treated in the same way.

Figure 1(b) shows the resistance (R) versus back gate voltage (V_{bg}) curve of the GFET device, with a commonly observed ambipolar behavior.[23] The Dirac point, V_D, is the voltage corresponding to the maximum resistance. We observed that $V_D = 35$ V, signifying that the graphene was initially hole-doped. After coating MB on graphene, the R (V_{bg}) curve shifts left and keeps its shape, indicating that MB molecules pump electrons into graphene and act as an electron donor.[20] The back gate capacitance of SiO_2 in the GFET is $C_{os} = 11.2$ nF/cm^2. From $E_F = \hbar v_F \sqrt{\pi n}$, where $n = C_{os}(V_{bg} - V_D)/e$ and v_F is the Fermi velocity of electrons,[23] we can estimate that $E_F = 120$ meV for electron-doped graphene at $V_{bg} = 50$ V and $E_F = -285$ meV for hole-doped graphene at $V_{bg} = -50$ V (E_F at the Dirac point is defined to be zero).

Raman spectra of MB molecules were obtained at each gate voltage using a Renishaw inVia Micro Raman spectrometer with 647 nm laser. The Raman signal of MB was first measured at two voltages on the same spot: first at 50 V and then at −50 V. Graphene was hole-doped at −50 V and

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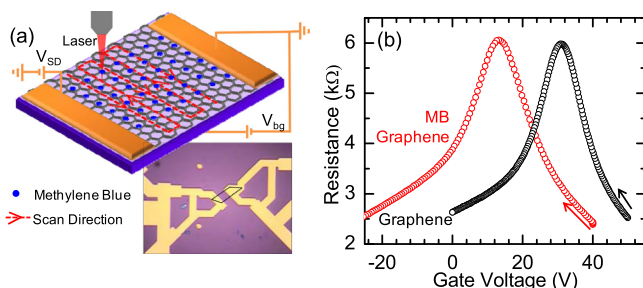
FIG. 1. (a) Schematic and optical image of the GFET device. The dashed line indicates the raster scan direction, while back gate voltage, V_{bg}, is scanned from 50 V to −50 V. Raman signals of methylene blue (MB) are obtained throughout the scanning process. (b) The resistance of graphene at various gate voltages before/after coating MB molecules. The scan direction is indicated by arrows.

FIG. 2. (a) Raman spectra of MB molecules on graphene at two gate voltages, 50 V and −50 V. A Raman spectrum of MB on SiO_2 surface (no graphene) is included as a reference. Enhancement from graphene is evident. (b) Intensities of the 1621 cm^{-1} Raman peak of MB at various gate voltages. Error bar of one standard deviation is included in the plot. The laser excitation is ∼0.2 mW/μm^2 and 20 s integration. †: peak from Si. *: G-band of graphene.

electron-doped at +50 V (Fig. 1(b)). We sampled across the graphene substrate and consistently observed that hole-doped graphene gave a larger Raman signal of MB than electron-doped graphene. Typical Raman spectra of MB are shown in Figure 2(a). We then swept the gate voltage gradually from 50 V to −50 V with ∼10 min interval between each voltage, and we measured the Raman intensity of MB following a raster scan with a ∼2 μm step as shown in Figure 1(a). In this way, each Raman spectrum was taken at a different spot. As the Fermi level of graphene shifted down to be more hole-doped, we observed a steady increase in the Raman signal of MB, as shown in Figure 2(b), by plotting the 1621 cm^{-1} Raman peak of MB. Our experimental data clearly show that the SERS enhancement from graphene depends on the position of its Fermi level.

Alternatively, the Fermi level of graphene can be modulated by molecular doping or chemical doping.[18] We hole-doped graphene by extensive O_2 plasma treatment of the Si wafer surface right before graphene transfer. It is believed that O_2 plasma produces hydroxyl group (−OH) molecules as hole-donors on the wafer surface, making graphene hole-doped.[24] Electron-doped graphene is achieved by treating the wafer surface with 3-aminopropyltrimethoxysilane (APTMS). The NH_2 group in APTMS acts as an electron donor, making graphene electron-doped.[20] Graphene on an untreated wafer is slightly hole-doped and considered "normal" graphene. The doping level of graphene (or its Fermi level) is usually confirmed by Raman measurement,[23] as shown in Figure 3(a): for hole-doping, both G-band and 2D-band of graphene upshift; for electron-doping, G-band upshifts and 2D-band downshifts; the intensity ratio of
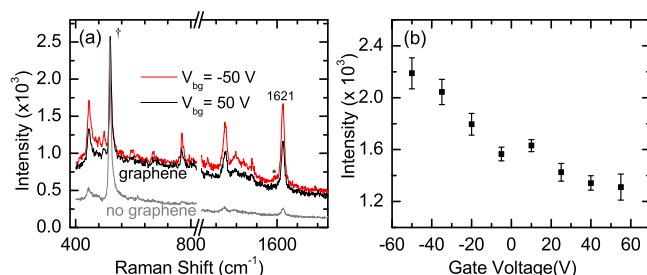
2D-band and G-band, I_{2D}/I_G, decreases with both kinds of doping. From the ratio I_{2D}/I_G, we estimate the Fermi levels to be −290 meV, −40 meV, and 140 meV for hole-doped, normal, and electron-doped graphene, respectively.[23] Following a similar procedure, MB molecules were deposited on the graphene surface and its Raman signal was then measured. The results are consistent with the GFET observations: hole-doped graphene yields larger Raman signal of MB than electron-doped graphene, as shown in Figure 3(b). Since there is no direct interaction between MB molecules and the doping molecular layer beneath graphene, the changes in Raman intensity of MB should solely be contributed by the shifts in the graphene Fermi level induced by the molecular layer.

Results from both field-effect doped and chemical doped graphene are summarized in Figure 4, where we plot the SERS enhancement based on the 1621 cm^{-1} peak intensity, normalized to undoped graphene value, versus changes of electron density in graphene. The two methods give a qualitatively consistent trend. However, the absolute value of the slope, representing the modulation strength, appears smaller for field-effect doping than for chemical doping. Our SERS measurements were performed in ambient air conditions, where hole-doping molecules, such as H_2O and O_2, might adsorb or desorb from graphene, cause hysteresis effects, and resist the variation of the graphene Fermi level. As graphene is tuned from electron-doped to hole-doped, Raman measurement might cause those hole-doping molecules to desorb from the graphene surface, making graphene less hole-doped. As a result, the strength of field-effect doping is reduced. The small discrepancy we observe here agrees with
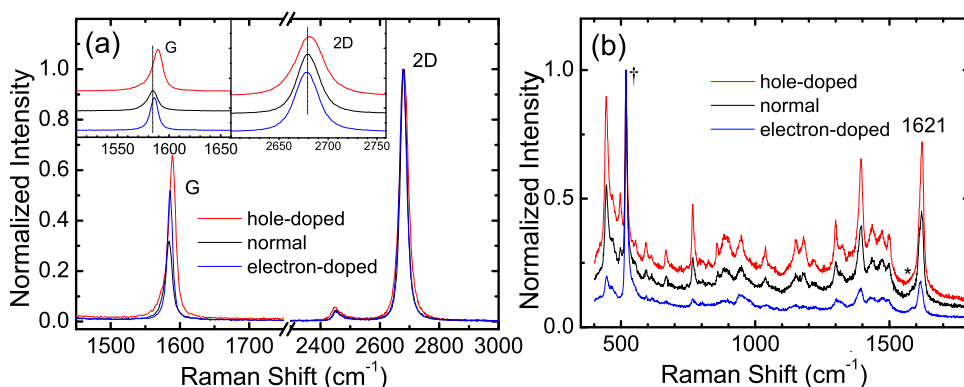
FIG. 3. (a) Raman spectra of hole-doped, electron-doped, and normal graphene. Insets are stack plots to show the shifts. The laser excitation is 514 nm at ∼2 mW/μm^2 and 1 s integration. (b) Raman intensity of MB molecules on the hole-doped, normal and electron-doped graphene with 647 nm excitation. The spectra are normalized according to the 520 cm^{-1} Si Raman peak (labeled by †) among different substrates. G-band from graphene is labeled by *.
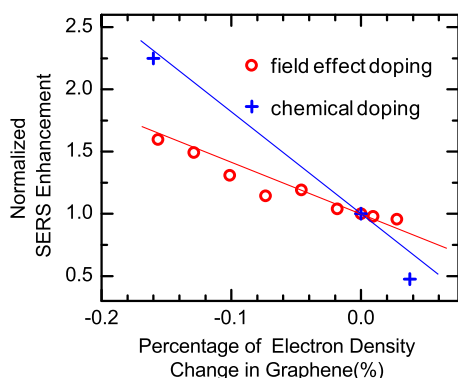
FIG. 4. (a) The combined results from Fig. 2(b) and Fig. 3(b): plot of the SERS enhancement from the intensities of MB at 1621 cm^{-1} for different doping levels of graphene. SERS enhancement is normalized to undoped graphene value. The red and blue lines serve as a visual guide.

FIG. 5. Plot of the normalized SERS enhancement at 1621 cm^{-1} of MB as a function of the change in electron density in the graphene with respect to normal graphene. The enhancement is normalized to the undoped graphene value. The line serves as a visual guide.

the studies from Xu *et al.*, where they also find reduced modulation strength of the graphene Fermi level with electric field in ambient conditions.[1,16]

The experimental measurements find strong characteristics of CE enhancement for graphene. One possible explanation for the observed trend is that the changes in the electron density of graphene due to doping lead to a modulation of the local electric field at the surface. It is well established that charging of metal nanoparticles can lead to a change in their plasmonic properties.[25–28] To examine this, we performed combined electrodynamical and quantum mechanical simulations using the discrete interaction model/quantum mechanics (DIM/QM) method (see supplementary material[33]).[29] DIM/QM combines a time-dependent density functional theory description of MB with an electrodynamics description of graphene. Each atom in graphene is characterized by an atomic polarizability obtained from the experimental dielectric function.[30] Because the two systems are modeled using different levels of theory, there is no possibility of orbital overlap or electronic charge transfer between the two systems; only contributions to the Raman intensity from the local field near graphene (the EM mechanism) are considered in this method. The changes in the electron density of graphene due to the doping can be modeled by changing the plasma frequency of the Drude part of its dielectric function.[25] In this way, we can incorporate the effect of changing the graphene Fermi level as is done experimentally.

In Figure 5, we show a plot of the normalized SERS enhancement from the MB peak at 1621 cm^{-1} as a function of the electron density of graphene. The values are normalized to the intensity when the Fermi level of graphene is at its Dirac point, i.e., undoped graphene. We immediately see that enhancement from graphene changes when we adjust its electron density from −30% to 30%. Even though the change in the electron density in the simulation is very large as compared to that in the experiments (∼0.3%), the magnitude of the change in Raman intensity is very small (∼2%) when compared to that seen experimentally in Figure 4 (several folds). The simulations clearly indicate that the EM enhancement of graphene is insensitive to the modulation of the Fermi level. Hence, the changes in Raman intensity of MB observed experimentally must be caused by a chemical
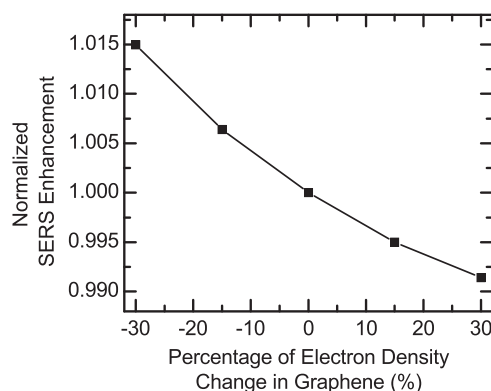
mechanism. This is in strong agreement with the expectations that graphene cannot support a plasmon excitation in the visible region and thus do not generate a significantly large electric field near the surface.

The CE is usually classified into three parts:[12] (a) enhancement due to non-resonance chemical interactions between molecule and nanostructure (graphene in this case), (b) charge-transfer (CT) resonance Raman enhancement with the excitation wavelength being resonant with nanostructure–molecule CT transitions, and (c) resonance Raman effect with incident laser energy resonant with a molecular transition. Xu *et al.* attributed the effect of modulating the Fermi level as evidence of the CT resonance mechanism.[16] The decrease in the Fermi level of graphene due to hole doping leads to a closer energy level alignment between the LUMO of the molecule and Fermi level of graphene. If this is the case, we would expect that signatures of a CT resonance between MB and graphene should be present in the Raman spectrum as the Fermi level is decreased. However, our experimental spectra of MB for both electron- and hole-doped appear to be similar. Another possibility is that the modulations of the Fermi level could rise to increase Raman scattering through the non-resonance chemical mechanism.[11] This mechanism does not require the CT resonance to be excited but shows a similar strong dependence on the Fermi level. Finally, the molecular resonance in MB could be modulated by doping the graphene. Trall *et al.* have recently shown that the absorption maxima of rhodamine 6 G on graphene is detuned from that in solution leading to smaller Raman cross-sections.[3] The doping of graphene could lead to a tuning of the molecular resonance relative to the laser wavelength, which results in modulation of the resonance Raman effect and gives rise to the observed changes in graphene enhancement. Further experiments combined with theoretical simulations are required to determine the exact mechanism of the enhancement in the Raman scattering of molecules on graphene.

In conclusion, we have demonstrated that both field-effect and chemical doping can lead to modulation of the Raman scattering from MB adsorbed on graphene. Both methods show that hole-doped graphene yields a larger enhancement than electron-doped and that the enhancement correlates with changes in the Fermi level. The chemical

doping shows significantly larger modulation of the enhancements and thus provides a simpler method for tuning the Raman signal of molecules that can be conveniently upscaled. A hybrid electrodynamical and quantum mechanical model was then employed to exclude the electromagnetic enhancement mechanism. This illustrates that the enhancement in graphene is chemical in nature; however, further experiments are needed to determine the exact origin of the enhancement. Thus, doping of graphene provides a potentially simple way of optimizing the SERS signal,[31,32] especially if graphene is combined with a traditional noble metal SERS substrate.[4,5]

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