Modulating the Charge-Transfer Enhancement in GERS using an Electrical Field under Vacuum and an n/p-Doping Atmosphere

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The modulation of charger-transfer (CT) enhancement in graphene-enhanced Raman scattering (GERS) by an electric field under different atmospheres is reported. The GERS spectra of cobalt phthalocyanine (CoPc) molecules were collected by in situ Raman measurements under ambient air, vacuum, NH_3 atmosphere, and O_2 atmosphere, in which the Fermi level of graphene was modulated by an electrical field effect (EFE). The Raman scattering intensities of adsorbed molecules can be tuned to be stronger or weaker as the graphene Fermi level down-shifts or up-shifts under electrical field modulation. However, the Raman intensity modulation in GERS is seriously influenced by the hysteresis effect in graphene EFE, which makes the modulation ability small and shows strong gate voltage sweep rate dependence in ambient air. Fortunately, the hysteresis effect in graphene EFE can be decreased by performing the measurement under vacuum conditions, and thus the Raman modulation ability in GERS can be increased. Furthermore, compared with the vacuum condition, the Raman modulation ability shows an increase under an NH_3 atmosphere, while it shows a decrease under an O_2 atmosphere, which is due to the different Fermi level modulation region in different atmospheres. More interestingly, this Raman intensity modulation in GERS shows a hysteresis-like behavior that is the same as the graphene Fermi level modulation under the EFE in a different atmosphere. All these observations suggest that the Raman enhancement in GERS occurs through a charge-transfer (CT) enhancement mechanism and the CT process can be modulated by the graphene EFE. This technique will benefit the study of the basic properties of both graphene and chemical enhancement mechanism in surface-enhanced Raman spectroscopy (SERS).

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1. Introduction

Despite the extensive studies of surface-enhanced Raman scattering (SERS) for nearly thirty years, a complete understanding of the mechanism of the enhancement is still an important subject of ongoing research.[1–3] SERS has historically been described in terms of an electromagnetic (EM) enhancement and a chemical enhancement mechanism.[4,5] For the EM mechanism, large amounts of theoretical and experimental studies have advanced our understanding. Compared to the extensive study of the EM mechanism, study of the chemical enhancement mechanism is still lacking.[3,6] Generally, the photoinduced metal–molecule charge transfer (CT) is believed to be the mechanism responsible for chemical enhancement in SERS, yet its microscopic mechanism and relative importance is still hotly debated.[7] A key obstacle of studying the CT mechanism is the fact that the two mechanisms occur simultaneously in the traditional metal-substrate SERS.[4,8] To date no reliable, general experimental strategy appears to have been developed to isolate and quantify these effects.[3,8] In addition, chemical enhancement involves complex interactions among metal nanostructures, molecules, and photons, which add extra difficulties in exploration of the complex CT process.[9]

Recently, we found that graphene can be used as a substrate to suppress the fluorescence[10] and enhance the Raman signals of molecules.[11] We call this Raman enhancement technique graphene-enhanced Raman scattering (GERS). On the basis of the analysis of the properties of graphene, we speculate that the GERS mechanism could not be an EM enhancement and we therefore attribute it to the CT enhancement.[11,12] GERS has several important features, including the fact that it can avoid the complex interactions among metal nanostructures and molecules; in particular, it can separate the CT enhancement from the EM enhancement. All these features will be beneficial for the study of the microscopic mechanism of the CT enhancement.

Although we have proved our speculation by comparing the shift of the Raman G band of graphene before and after adsorption of molecules and studying the "first layer effect" in GERS,[13] which is sometimes used to study the chemical enhancement in SERS,[14] there is still no direct evidence to prove the existence of CT in GERS. According to the characteristics of the chemical enhancement, CT requires the energy matching between the energy levels (highest occupied and lowest occupied molecular orbitals–HOMO, LUMO) of the molecule and the Fermi level of the metal substrate.[6,15] Therefore, tuning the position of the Fermi level of the metal by using an external voltage source can, in principle, drive the entire system in and out of CT resonance.[16] This approach was extensively employed in the past to study the CT resonance contribution by examining the dependence of the SERS of the molecules on the electrochemical potential, and it was proposed as the most reliable method to study CT enhancement experimentally.[1,6,16] However, because these experiments were usually carried out on metal electrodes, many hot spots as well as areas with a large EM enhancement will inevitably contribute to the total Raman signal.[16]

GERS provides an excellent opportunity to study the CT mechanism because the exclusive CT enhancement in GERS can avoid the interference from EM enhancement in the study of CT enhancement. In our previous work, we had designed an experiment to modulate the Raman signals of molecules in GERS, using the benefit of graphene to easily modulate the Fermi level by an electric field effect (EFE), to prove the CT enhancement in GERS.[12] The results indicated that the GERS intensity indeed showed a modulation with the applied gate voltage variation. However, the Raman intensity modulation only took place when sweeping the gate voltage at a fast rate, while nearly no modulation occurred when sweeping the gate voltage at a slow rate. We simply attributed this modulation difference under different gate voltage sweep rate to the effect of large hysteresis effect because all our measurements were performed in ambient air. As we all know, the hysteresis effect is a common problem in graphene EFE, which hinders the electrical field modulation to the graphene Fermi level, especially under a large range or slow rate gate voltage sweep.[17] In addition, due to the problem that large leak current would arise when applying a gate voltage that was too large, the range of the gate voltage sweep was limited to operate only between –150 and +150 V, which narrowed the window of the graphene Fermi level modulation. For these two reasons, the Raman signals of the molecules in GERS showed only a very small modulation even under a large gate voltage span with a fast sweep rate during our previous work.

In this work, we present a systematic study of the chemical enhancement effect in GERS by investigating the electrical field modulation of the CT enhancement in GERS under different atmospheres, such as ambient air, vacuum, NH_3, and O_2. We performed our measurements under vacuum conditions to suppress the influence of the hysteresis effect in the electrical field modulation of the CT enhancement in GERS. In addition, in order to study the relationship between the hysteresis effect and the modulation of the CT enhancement in GERS, and to enlarge the graphene Fermi level modulation window, we performed the measurements under an NH_3 (n-doping to graphene) atmosphere and under an O_2 (p-doping to graphene) atmosphere. **Figure 1**a shows a schematic diagram of this in situ Raman measurement with the electrical-field-modulated graphene Fermi level variation under different atmospheres. The Raman intensities of molecules in GERS shows a small modulation due to the effect of a large hysteresis effect when measured in ambient air; while it shows an obvious modulation when there is a reduced hysteresis effect due to performing the measurements under vacuum conditions. Furthermore, the Raman modulation ability increases when the measurement is performed under an NH_3 atmosphere, but the modulation ability decreases when the measurement is performed under an O_2 atmosphere compared to that under vacuum conditions. The difference in the Raman modulation behavior under different atmospheres fully proves that CT enhancement is the mechanism responsible for GERS. The exclusive contribution of CT enhancement to GERS can provide an effective approach for studying the CT separately from EM.

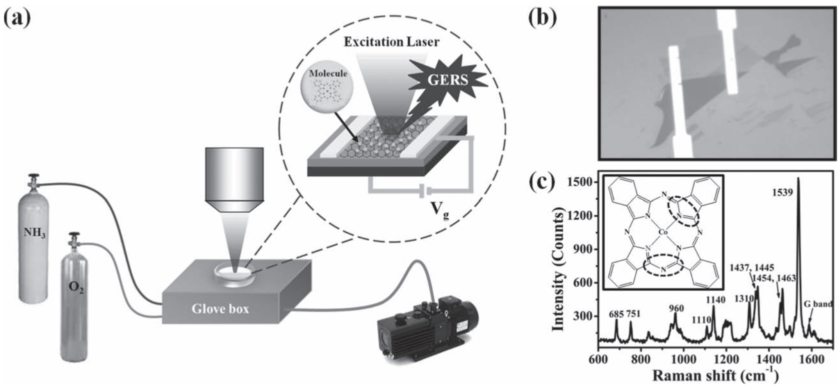

Figure 1. a) Schematic representation for the electrical field modulation of GERS under different atmospheres. b) Optical image of a typical graphene device. c) GERS spectra of CoPc molecules adsorbed on a graphene substrate. The insert in (c) shows the molecular structure of CoPc molecules, and the C–N–C stretching vibration modes in the dash circles are responsible for the peak at 1539 cm^{-1}.

2. Results and Discussion

2.1. Modulating the CT Enhancement in GERS in Ambient Air

A GERS spectrum of cobalt phthalocyanine (CoPc) molecules collected at 632.8 nm laser excitation is shown in Figure 1c. The spectrum is dominated by these signed modes. The strongest peak at 1539 cm^{-1} is assigned to the C–N–C stretching mode of the phthalocyanine macrocycle[18] as shown in the insert of Figure 1c. The Raman intensity of all these modes can be modulated with the gate voltage as shown below. For comparison, we focus only on the 1539 cm^{-1} mode to study the Raman modulation of the CoPc molecules in the following.

Based on the theory analysis above, the intensity of the GERS spectra should be relevant to the energy alignment between the Fermi level of graphene and the energy level of molecule if the CT enhancement is the mechanism of GERS. Here, we try to modulate the Raman scattering intensities of the molecules in GERS by tuning the graphene Fermi level with an electrical field to prove that CT enhancement exists in GERS. While sweeping the gate voltage from –150 V to +150 V with intervals of 20, 50, 150 and 300 V per step, we recorded the GERS spectra of CoPc at each gate voltage. **Figure 2**a shows the intensity variation of the 1539 cm^{-1} mode under different gate voltage sweep rates extracted from the corresponding spectra. The intensities are normalized to the maximum value observed in the investigated gate voltage range. We can see that the Raman scattering intensities of adsorbed molecules can be tuned to be stronger or weaker as the graphene Fermi level downshifts or up-shifts under electrical field modulation. However, similar to our previous results, the Raman intensities of the molecules show only a small modulation when applying gate voltages with a fast sweep rate, while nearly no modulation is observed when applying gate voltages with a slow sweep rate. We speculate that this modulation difference under different gate voltage sweep rates is due to the effect of a large hysteresis effect because all our sample preparation and measurements were performed in ambient air. The p-doping H_2O and O_2 gas molecules in ambient air will cause a large hysteresis effect to arise in graphene EFE, which will hinder the modulation of the graphene Fermi level variation with EFE, especially under a large range or slow rate gate voltage sweep. In terms of this analysis, the modulation of the CT enhancement in GERS should show gate voltage sweep rate dependence. The Raman modulation ability should decrease as the gate voltage sweep rate is slowing down because the gradually increased hysteresis effect will seriously hinder the variation of the graphene Fermi level measured in ambient air. In order to prove our speculation and eliminate the influence of the hysteresis effect in the modulation of the CT enhancement in GERS, we performed our measurements under vacuum conditions.

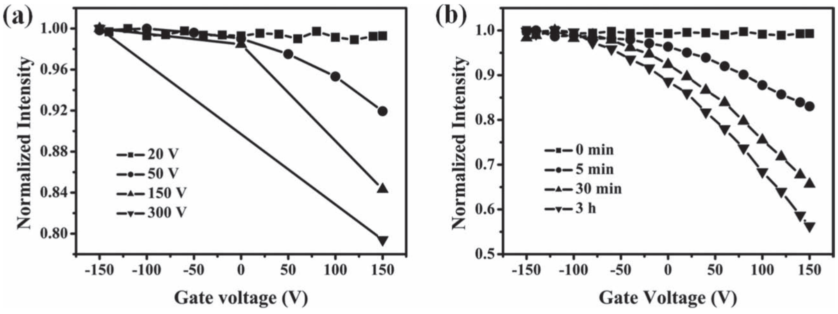

Figure 2. Plot of the GERS intensities of the 1539 cm^{-1} mode of CoPc versus the gate voltage applied on graphene devices, extracted from a) the spectra measured by sweeping the gate voltage from −150 to +150 V at different gate voltage sweep rates in ambient air and b) the spectra measured by sweeping the gate voltage from −150 to +150 V at an interval of 20 V per step at different times under vacuum conditions.

2.2. Modulating the CT Enhancement in GERS under Vacuum Conditions

The vacuum experiment was performed in a home-made vacuum probe station equipped with our Raman setup, and the pressure was maintained at 10^{-1} Pa after evacuation for about 1 min in our probe station. Figure 2b shows the intensity variation of the 1539 cm^{-1} mode modulated by the electrical field, which is measured at different times under vacuum conditions. We can see that an obvious Raman modulation arises when the measurements were performed under vacuum conditions as compared to that in ambient air, and the Raman modulation ability increases gradually with increasing time under vacuum conditions. The result indicates that the Raman modulation is really affected by the

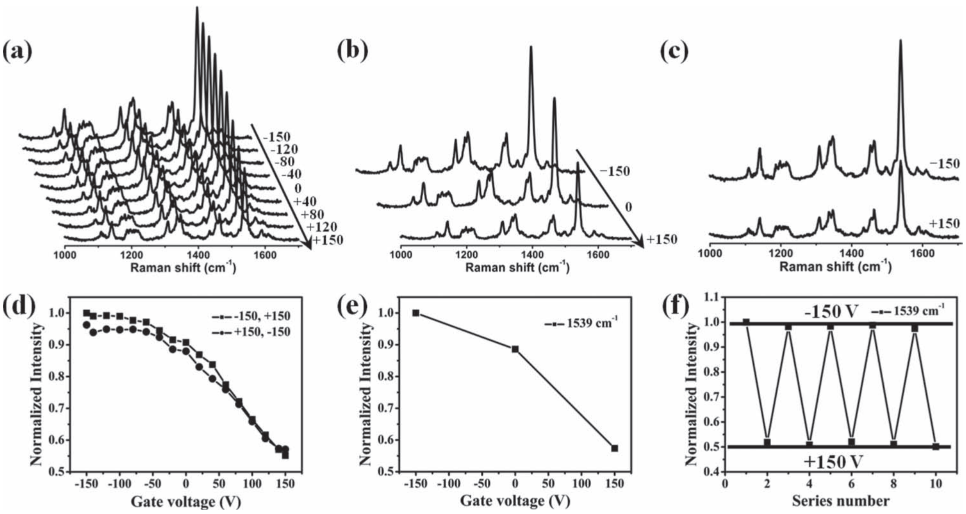

Figure 3. GERS spectra of CoPc modulated by an electrical field measured under vacuum conditions (1×10^{-1} Pa for 3 h). The gate voltage was applied from −150 to +150 V with a slow sweep rate at an interval of a) 20 V per step, and fast sweep rate at intervals of b) 150 and c) 300 V per step. d,e,f) Plots of GERS intensities of the 1539 cm^{-1} mode versus gate voltage extracted from the spectra of (a), (b), and (c), respectively. The corresponding spectra of the reversed gate voltage sweep in Figure 3d are shown in Figure S2 in the SI. In order to get a better look, we show only several spectra in (a) chosen from all spectra of the investigated gate voltage range.

hysteresis effect when measured in ambient air. Furthermore, the Raman modulation ability shows a large increase after only 5 min when under vacuum, and then increases slowly over the next 30 min under vacuum, and finally the modulation ability saturates after about 3 h exposure to vacuum. It should be because the graphene has a large surface area, and most of the adsorbed H_2O and O_2 molecules on the graphene device can be easily desorbed at the beginning of the exposure to vacuum, and only a small amount of gas molecules between the substrate and the graphene need a longer time of exposure to vacuum for these residual molecules to be desorbed. In addition, the Raman intensity can be reversibly modulated between –150 and +150 V as shown in Figure S1 (see Supporting Information, SI). And, the superposition of the Raman intensity variations between the forward and back gate voltage sweep gradually becomes better due to the reduction of the hysteresis effect as the vacuum time increases. Therefore, the CT enhancement in GERS can be effectively modulated using an electrical field when suppressing the hysteresis effect by performing the measurement under vacuum conditions.

Figure 3 shows the GERS spectra (Figure 3a–c) and the corresponding Raman intensity variations (Figure 3d–e) of CoPc molecules modulated at different gate voltage sweep rates after exposure to vacuum for about 3 h. It can be seen that the ability of observed Raman modulation with different gate voltage sweep rates is nearly equal, which is different from the results in ambient air as shown above (Figure 2a). It is known that the hysteresis effect is strongly related to the gate voltage sweep rate, and the slower the gate voltage sweeps, the larger the hysteresis effect, and vice versa.[19] In the ambient air, the hysteresis effect arises due to the doping of graphene by H_2O and O_2 molecules, and the effect is more dramatic as the gate voltage sweep rate slow down, so the gate voltage sweep rate will seriously influence the Raman modulation. While under vacuum conditions, the hysteresis effect is nearly eliminated due to the removal of the H_2O and O_2 molecules from the graphene surface, thus the Raman modulation will not be influenced by the gate voltage sweep rate.

2.2.1. Modulating the CT Enhancement in GERS under Different Types of Doping Atmosphere

The n-Doping Effect of NH_3 and the p-doping Effect of O_2 to Graphene: In order to further study the modulation of CT enhancement in GERS, we studied the relationship between the Raman modulation and the hysteresis effect under different types of doping atmosphere. It is known that NH_3 molecules donate electrons to graphene[19] as illustrated in **Figure 4**a; while O_2 molecules accept electrons from graphene[20] as illustrated in **Figure 5**a. As a result, we chose NH_3 as an n-doping atmosphere and O_2 as a p-doping atmosphere for these experiments. Each type of gas molecules was introduced into the probe station after being under vacuum for about 3 h.

Modulating the CT Enhancement in GERS under an NH_3 Atmosphere: Figure 4b sketches the variation of the graphene Fermi level modulated with the gate voltage and its energy alignment with molecular energy level of CoPc in an NH_3 atmosphere. The range of Fermi level modulation will likely be pushed up above the Dirac point due to the stronger n-doping effect of NH_3 to graphene. Figure 4c,d show the intensity variation of the 1539 cm^{-1} mode modulated by an electrical field with slow (Figure 4c) and fast (Figure 4d) gate voltage sweep rates in the beginning of the introduction of NH_3. Compared to the vacuum condition, the Raman modulation ability shows a noticeable increase under both fast and slow gate voltage sweep rates. Although the Raman

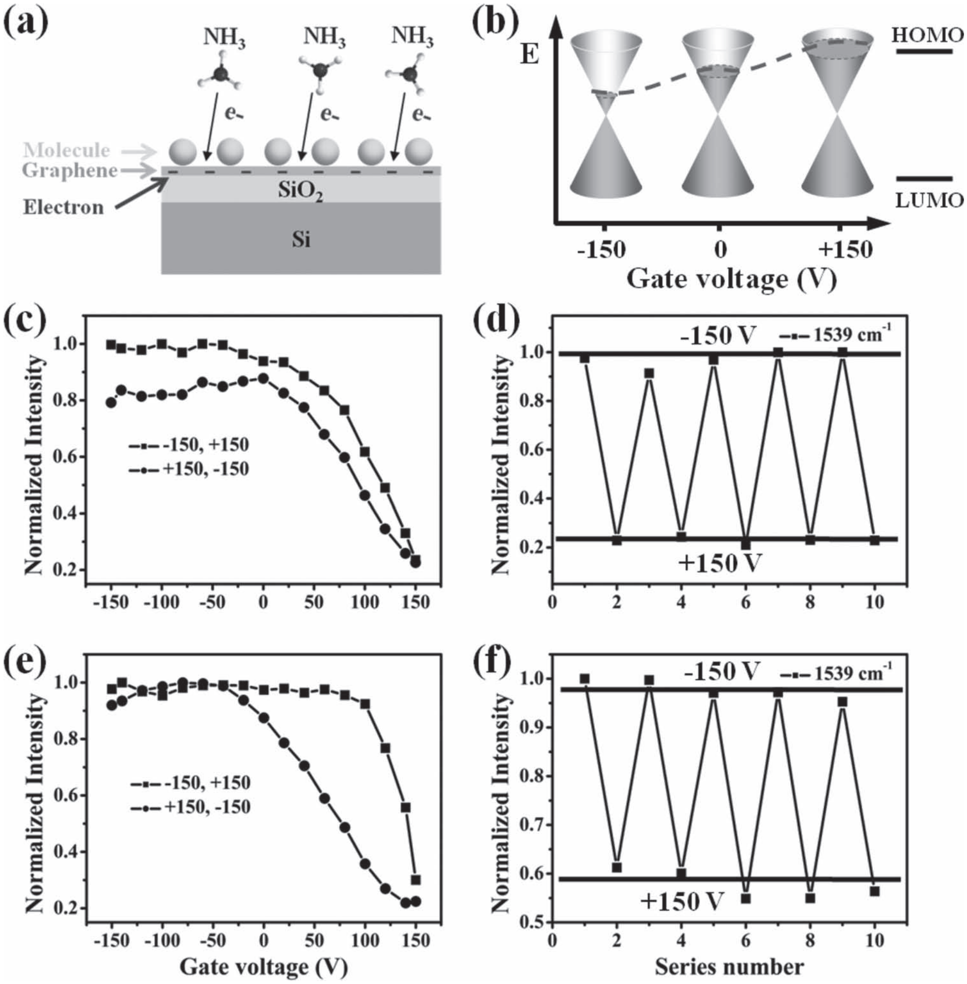

Figure 4. Schematic representation of a) the n-doping effect of NH_3 to graphene and b) the variation of the graphene Fermi level modulated with gate voltage and its energy alignment with molecular energy level of CoPc in an NH_3 atmosphere. Plot of the GERS intensities of the 1539 cm^{-1} mode versus gate voltage, extracted from the spectra measured by sweeping the gate voltage from −150 to +150 V at intervals of c) 20 and d) 300 V per step in the beginning of the introduction of NH_3, and from the spectra measured by sweeping the gate voltage from −150 to +150 V at intervals of e) 20 and f) 300 V per step after exposure to NH_3 for 1 h. The corresponding spectra of Figure 4c are shown in Figure S3 in the SI.

modulation ability is nearly equal for the fast and slow gate voltage sweep rates, there is a small hysteresis behavior exist in the case of slow sweeping, it is likely due to the absorption of few amount of NH_3 on graphene. The Raman intensity starts to decrease when the gate voltage sweeps to about +40 V in this case, while it has been decreased when the gate voltage sweeps to about –80 V under vacuum conditions (see Figure 3d). After exposure of the samples to NH_3 for about 1 h, the Raman modulation ability is still large, but an even larger hysteresis behavior shows up under a slow gate voltage sweep rate (Figure 4e). The Raman intensity begins to decrease until the gate voltage sweeps to about +100 V under the slow gate voltage sweep rate. In the same time, the Raman modulation ability decreases under a fast gate voltage sweep rate (Figure 4f). This is due to a great increase of the amount of NH_3 molecules adsorbed on the graphene device with increasing exposure time, which can bring a large hysteresis effect to hinder the graphene Fermi level modulation, and so hinder the Raman modulation.

Modulating the CT Enhancement in GERS under an O_2 Atmosphere: Figure 5b sketches the variation of the graphene Fermi level modulated with the gate voltage and its energy alignment with molecular energy level of CoPc in an O_2 atmosphere. The range of the Fermi level modulation will likely be pushed below the Dirac point due to the stronger p-doping effect of O_2 to graphene. Figure 5c,d show the intensity variation of the 1539 cm^{-1} mode modulated by an electrical field with slow (Figure 5c) and fast (Figure 5d) gate voltage sweep rates in the beginning of the introduction of O_2. As can be clearly seen, the Raman modulation ability shows a large decrease with both fast and slow gate voltage sweep rates compared to that under vacuum conditions. And, the Raman modulation ability shows a further decrease under both slow (Figure 5e) and fast (Figure 5f) gate voltage sweep rates after exposure of the samples to O_2 for about 1 h, and finally disappears as the exposure time to O_2 increases. Furthermore, a hysteresis behavior also arises due to the doping effect of O_2 to graphene and gradually gets larger as the exposure time to O_2 increases.

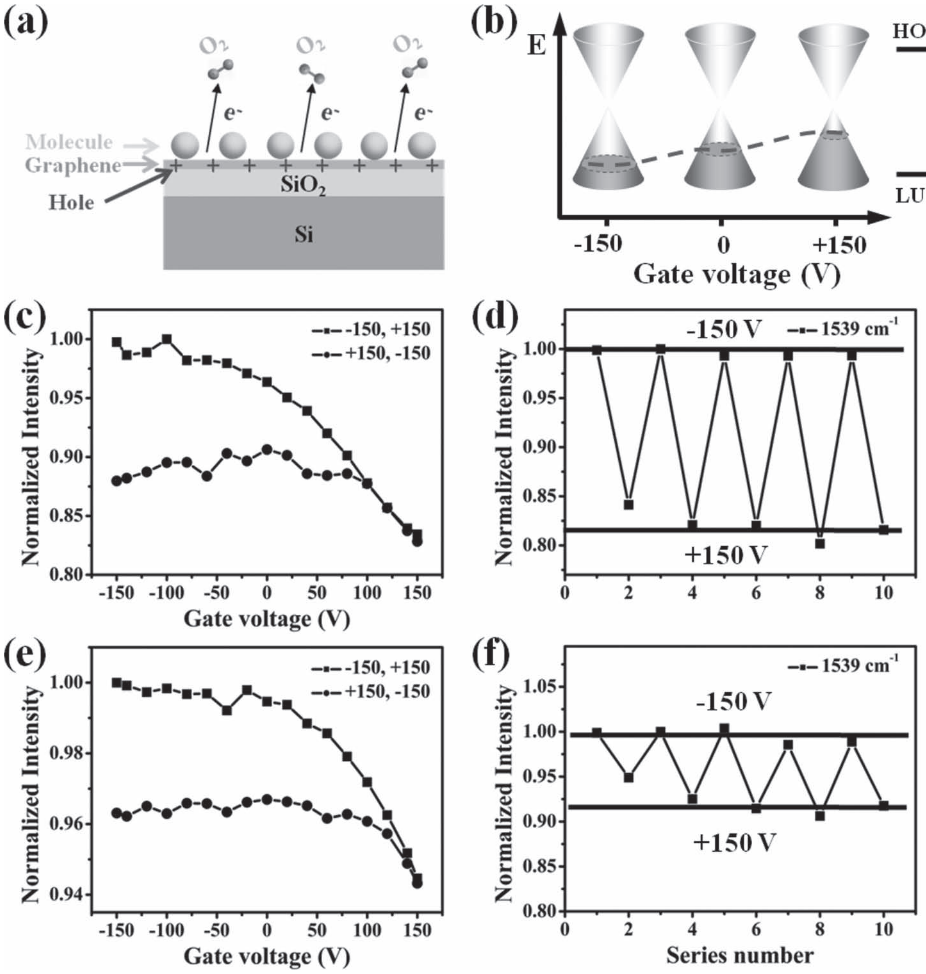

Figure 5. Schematic representation of a) the p-doping effect of O_2 to graphene and b) the variation of the graphene Fermi level modulated with gate voltage and its energy alignment with molecular energy level CoPc in an O_2 atmosphere. Plot of the GERS intensities of the 1539 cm^{-1} mode versus gate voltage, extracted from the spectra measured by sweeping the gate voltage from −150 to +150 V at intervals of c) 20 and d) 300 V per step in the beginning of the introduction of O_2, and from the spectra measured by sweeping the gate voltage from −150 to +150 V at intervals of e) 20 and f) 300 V per step after exposure to O_2 for 1 h.

Relationship between the CT Enhancement Modulation and the Hysteresis Effect under Different Types of Doping Atmosphere: **Figure 6**a shows the Raman intensity variation with the gate voltage modulation after adsorption of large amounts of NH_3 molecules on graphene by exposure of the sample to an NH_3 (n-doping) atmosphere for about 2 h. It can be clearly seen that the Raman intensity does not decrease immediately when up-shifting the graphene Fermi level by switching the gate voltage from 0 to +150 V, while it shows a slow decrease in intensity up to the lowest value with time increasing. Similarly, the Raman intensity increased immediately when the gate voltage returns to 0 V, but that

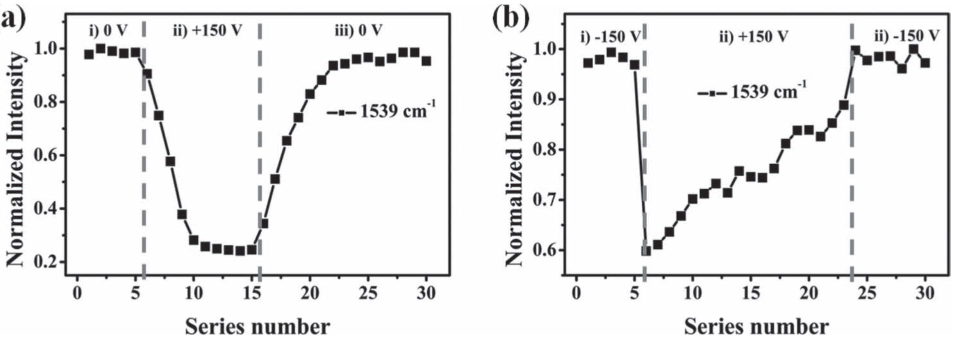

Figure 6. Plot of GERS intensities of the 1539 cm^{-1} mode of CoPc versus the gate voltage applied to graphene devices, extricated from the spectra measured a) after exposure of the samples to NH_3 atmosphere for about 2 h and b) in ambient air.

shows a gradual recovery as time increasing. However, the situation becomes different in ambient air (p-doping) as shown in Figure 6b. The Raman intensity decreases to the lowest value immediately when +150 V is applied to the gate, and then gradually increases as time goes on. The hysteresis-like behavior in the Raman modulation shows obvious differences in the different types of doping atmospheres, which can be attributed to the different hysteresis behaviors of the graphene Fermi level in different doping-type atmospheres. The Fermi level up-shift will be hindered in an n-doping atmosphere, and this means that the Fermi level cannot up-shift immediately, but it can only slowly up-shift to its proper position when applying a positive gate voltage. The situation is different from a p-doping atmosphere; the Fermi level can up-shift to its position immediately when applying a positive gate voltage, but it cannot be maintained at this position, and the Fermi level will slowly down-shift with time increasing. So, that is why the Raman modulation under a slow gate voltage sweep is still large, while it shows a decrease under a fast gate voltage sweep after exposure to NH_3 for a long time; andwhy the Raman modulation under a slow gate voltage sweep shows nearly no modulation in either ambient air or an O_2 atmosphere, while it shows large modulation under a fast gate voltage. In addition, the hysteresis-like behavior in the Raman modulation is the same as that in the graphene Fermi level modulation with EFE, which clearly exhibits a relationship between the Raman intensity and the graphene Fermi level variation, which can further prove that the CT enhancement in GERS is modulated by an electrical field.

2.3. Explanation of the Mechanism of the CT Enhancement Modulation in GERS

In the following parts, we will discuss how the Fermi level variation modulates the CT enhancement in GERS in different types of doping atmospheres. The direction of the CT process should be from graphene to CoPc molecules in the GERS system, which is determined by comparing the frequency shift of the Raman G band and 2D band of graphene before and after molecular adsorption (see Figure S4 in the SI). In addition, the Fermi level of intrinsic graphene is at about –4.6 eV,[21] if we assume the vacuum level is set to be zero here. The HOMO and LUMO energies of the CoPc molecule are at –5.02 and –3.41 eV, respectively.[22,23] The excitation energy of the laser is 1.96 eV (632.8 nm). The electrical-field-induced shift of the Fermi level from the Dirac point can then be approximately calculated according to the following formulas:

$$E_{\mathrm{F}}(n) = -\operatorname{sgn}(n)\hbar v_{\mathrm{F}}\sqrt{(\pi|n|)}$$

$$n = \alpha V_{\mathrm{g}} = C_{\mathrm{g}}(V_{\mathrm{g}} - V_{\mathrm{Dirac}})/e$$

where $v_{\mathrm{F}} = 10^6$ m/s, $n, C_{\mathrm{g}}, e, V_{\mathrm{Dirac}}, V_{\mathrm{g}}$, and $\hbar$ the Fermi velocity, charge density, gate capacitance, electron charge, the gate voltage corresponding to the charge-neutral Dirac point, the gate voltage, and the Dirac constant (reduced planck constant), respectively.[24,25] Therefore, the picture illustrates the relationship between the CT enhancement and the energy alignment in different atmospheres as shown in **Figure 7**. Under vacuum conditions, the Fermi level variation ranges from –4.98 to –4.22 eV when modulated under a gate voltage sweep from –150 to +150 V (middle, Figure 7) based on these formulas. That means the variation range of the energy gap between the graphene Fermi level and the LUMO of molecule is from about 1.57 to 0.81 eV under a gate voltage ranging from –150 to +150 V. So, the Raman intensity gets stronger as the energy gap becomes closer to the excitation energy of the laser (1.96 eV) by down-shifting the graphene Fermi level with a negative gate voltage, while the intensity gets weaker as the energy gap moves away from the excitation energy of the laser by up-shifting the graphene Fermi level with a positive gate voltage.

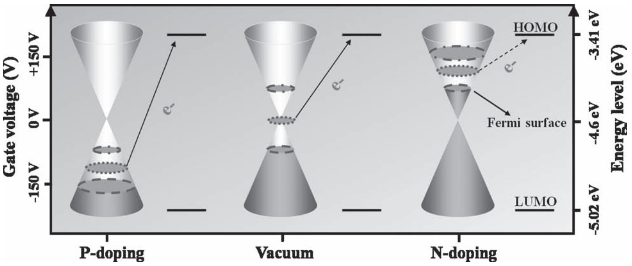

Figure 7. Schematic of the possible mechanism for the modulation of the charge-transfer enhancement in GERS by using an electrical field measured under different types of doping conditions. The Fermi surface of graphene under −150, 0, and +150 V are represented by the dash, dot, and dash dot cycles, respectively.

Under NH_3 atmosphere, the Fermi level variation range should be greatly up-shifted due to the n-doping effect of NH_3 (right, Figure 7). Although the positions of the graphene Fermi level under gate voltage modulation cannot be determined accurately, we can make sure that the entire Fermi level variation range can be pushed above the Dirac point. This means that the variation range of the graphene Fermi level is closer to the LUMO of the molecule, which makes the energy gap between the graphene Fermi level and the LUMO of molecule far smaller than the excitation energy of the laser. Under this condition, the CT process should be most sensitive to the graphene Fermi level variation, so the Raman modulation ability has the largest value under an NH_3 atmosphere.

While, under an O_2 atmosphere, the Fermi level variation range should be greatly down-shifted due to the p-doping effect of O_2 (left, Figure 7). Similarly, the entire Fermi level variation range can be drawn below the Dirac point, the variation range of the Fermi level is far from the LUMO of the molecule, which makes the energy gap between the graphene Fermi level and the LUMO of molecule closer to the excitation energy of the laser. Under this condition, the CT process should be insensitive to the graphene Fermi level variation, so the Raman modulation ability should have the smallest value under an O_2 atmosphere.

3. Conclusion

In summary, we have studied the CT enhancement separated from the EM enhancement by modulating the charge-transfer enhancement in GERS using an electrical field. The

Raman modulation in GERS by the EFE is strongly influenced by the hysteresis effect. The Raman scattering intensities of the molecules show an obvious modulation with the Fermi level variation modulated by an electrical field when measured under vacuum conditions to suppress the hysteresis effect. In addition, the relationship between the Raman modulation and the hysteresis effect under vacuum and in n-/p-doping atmospheres reveals strong dependence of the Raman intensity on the graphene Fermi level variation. Furthermore, the Raman modulation ability shows a difference under different types of doping atmospheres due to the different energy alignment range between the Fermi level of graphene and the LUMO of molecule. Therefore, the dependence of the GERS intensity on the graphene Fermi level variation fully proves that the CT is the mechanism of GERS. This approach will benefit the study of CT enhancement separated from EM enhancement, as well as the study of the CT between graphene and adsorbed molecules.

4. Experimental Section

Fabrication of Graphene Devices: Graphene devices were fabricated as described in our previous work.[12] Briefly, graphene sheets were produced by mechanical exfoliation of kish graphite using scotch tape and then deposited onto a p-doped Si substrate with a layer of SiO_2 300 nm thick. The graphene sheets were identified as monolayers by optical microscopy (OM) and Raman spectroscopy. Standard electron-beam lithography and lift-off techniques with poly(methyl methacrylate) (PMMA) as resist were finally used to fabricate the contact electrodes to the graphene layer. The electrodes were made of Cr/Au (5 nm/50 nm). Figure 1b shows the OM image of the graphene device.

Deposition of Probe Molecules on Graphene Devices: CoPc molecules were dissolved in ***N*,*N***-dimethylformamide (DMF) with a concentration of 1×10^{-6} M. The CoPc molecules were adsorbed on the graphene substrates by simply soaking the graphene devices into the solution for about 1 h. After soaking, the sample with molecules was washed with DMF to remove the free molecules and then dried under the flowing N_2.

Conditions of Raman Collection: A Raman spectrum was obtained in situ at each gate voltage by using a Horiba HR800 Raman system with a 600 lines/mm grating and using a 632.8 nm laser (E_{laser} = 1.96 eV) excitation. The incident laser beam was focused by a 50× objective and the laser power on the samples was kept below 0.5 mW to avoid laser-induced heating. The spectra integration time was 10 s per spectrum. The intensities and frequencies of the peaks are obtained by fitting them with a Lorentzian function.

Vacuum and Controlled Atmosphere Experiments: For vacuum and controlled atmosphere experiments, a home-made vacuum probe station was used. The pressure could be down to 10^{-1} Pa in the vacuum probe station by pumping for about 1 min. Overall 8 graphene devices were extensively tested with different gas exposure, all of them were first tested in ambient air and vacuum conditions, and then 4 samples were tested under an O_2 atmosphere, and the other 4 samples were tested under an NH_3 atmosphere. The same general behavior was observed for the different batches of samples tested under different atmospheres.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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