As a novel and efficient surface analysis technique, graphene-enhanced Raman scattering (GERS) has attracted increasing research attention in recent years. In particular, chemically doped graphene exhibits improved GERS effects when compared with pristine graphene for certain dyes, and it can be used to efficiently detect trace amounts of molecules. However, the GERS mechanism remains an open question. We present a comprehensive study on the GERS effect of pristine graphene and nitrogen-doped graphene. By controlling nitrogen doping, the Fermi level ($E_F$) of graphene shifts, and if this shift aligns with the lowest unoccupied molecular orbital (LUMO) of a molecule, charge transfer is enhanced, thus significantly amplifying the molecule’s vibrational Raman modes. We confirmed these findings using different organic fluorescent molecules: rhodamine B, crystal violet, and methylene blue. The Raman signals from these dye molecules can be detected even for concentrations as low as $10^{-11}$ M, thus providing outstanding molecular sensing capabilities. To explain our results, these nitrogen-doped graphene-molecule systems were modeled using dispersion-corrected density functional theory. Furthermore, we demonstrated that it is possible to determine the gaps between the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO) of different molecules when different laser excitations are used. Our simulated Raman spectra of the molecules also suggest that the measured Raman shifts come from the dyes that have an extra electron. This work demonstrates that nitrogen-doped graphene has enormous potential as a substrate when detecting low concentrations of molecules and could also allow for an effective identification of their HOMO-LUMO gaps.

INTRODUCTION

The surface-enhanced Raman scattering (SERS) effect has become an important technique to detect trace amounts of molecules ($10^{-5}$ to $10^{-10}$ M) (1, 2). The SERS effect comes from two major mechanisms: (i) an intense electromagnetic field (EM) generated by plasmon resonance located close to the metallic structure (3) and (ii) a chemically enhanced mechanism (4) through a charge transfer between the probe molecules and the substrate. Traditionally, SERS substrates are based on a roughened surface of a noble metal (for example, Ag and Au), which provides the plasmons for the EM mechanism to occur. However, this enhancement efficiency varies from metal to metal and largely depends on the SERS substrate fabrication process, which is relatively complex, hard to control, and difficult to keep clean. In addition, metals are usually easily oxidized and are not biologically friendly, which further limits their application in diverse fields. Recently, pristine graphene (PG) has been proven to be an excellent substrate to enhance the Raman signal of molecules (5), giving rise to the expression “graphene-enhanced Raman scattering” (GERS). In addition, it can effectively quench the molecules’ spectral fluorescence background (6). Because of its chemical inertness and good biocompatibility, graphene is very attractive as an efficient metal-free substrate for probing trace amounts of organic molecules. To unveil the GERS mechanism of graphene, several theoretical and experimental studies have been carried out (7, 8). Ling et al. have shown that the enhancement strongly depends on the configuration of the molecule on a graphene substrate, the so-called “first-layer effect.” It implies that the Raman scattering of the first adsorbed layer of the probe molecules on a graphene substrate will be especially enhanced over that of the subsequent layers (9, 10). Later on, Xu et al. further demonstrated that the enhancement of the Raman signal can be modulated by tuning the graphene’s Fermi level ($E_F$) via a graphene-based field effect transistor device (11, 12). Moreover, to explain the GERS mechanism on different neutral molecules, Huang et al. (13) probed molecules with different symmetries and concluded that the enhancement of a molecule’s Raman signal occurs if the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of that given molecule sit on a suitable energy range with respect to the $E_F$ of graphene. In this context, our recent work has demonstrated that, compared with PG, substitutional doping of graphene with heteroatoms (for example, nitrogen and silicon) leads to substrates that can remarkably enhance the GERS effect (14, 15).

Here, large-area monolayer PG and nitrogen-doped graphene (NG) were synthesized on Cu foils using methane (CH$_4$) and ammonia (NH$_3$) as precursors in an ambient pressure chemical vapor deposition (AP-CVD) system (15). We observed that, by tuning the synthesis parameters, the doping levels of NG are also tuned. A striking point lies on the nitrogen doping configuration control within the graphene lattice when varying the synthesis conditions. For example, single substitutional doping (N$_1$) or double substitutional doping (N$_2$) can be controlled...
and identified by Raman spectroscopy and scanning tunneling microscopy (STM). In addition, as-synthesized NG and PG sheets were also used as substrates to probe different fluorescent molecules and to explore the GERS mechanism. For example, we observed a consistent trend that NG leads to a better Raman signal enhancement of the studied fluorescent dye molecules [for example, rhodamine B (RhB), crystal violet (CRV), and methylene blue (MB)] when compared to PG. Through experimental and theoretical studies, we demonstrate here that the LUMO level of NG is closely related to the enhancement of the Raman signal of the studied molecules. We also noted that this enhancement depends strongly on the excitation of the photon energy and the doping level of the graphene. Some signals from these dye molecules can be detected even for concentrations as low as $10^{-11}$ M, which provides excellent molecular sensing capabilities. Ab initio calculations were carried out to investigate a possible chemical mechanism of GERS. The results are consistent with a mechanism involving a charge-transfer excitation, which is described below.

**RESULTS**

Large-area monolayer PG and NG sheets were synthesized on copper foils using CH$_4$ and NH$_3$ as precursors in conjunction with an AP-CVD system. Details of the synthesis procedure can be found in our previous report (15). A typical photograph of an NG sheet on copper foil is shown in fig. S1A, which looks like bare copper because of graphene’s high transparency. Synthesized NG can be transferred onto other materials, such as SiO$_2$/Si (fig. S1B) and quartz (fig. S1C) substrates by using polymethyl methacrylate (PMMA)-assisted transfer method (16), and good transparency and homogeneity can be observed from the photographs. Figure 1 (A and B) shows high-resolution transmission electron microscopy (HRTEM) images of monolayer and bilayer NG sheets transferred to TEM grids via PMMA-free methods (17). The inset of Fig. 1A shows the corresponding selected-area electron diffraction pattern of an NG sheet, confirming the hexagonal structure of graphene. Less than 8% of the NG material consists of few layers (for example, bilayer or trilayer), revealing an interlayer spacing of ~0.35 nm (Fig. 1B) (18).

First, control experiments were carried out to study the mechanism of nitrogen doping of graphene by tuning the temperature at which NH$_3$ is introduced during the synthesis reaction (from 950° to 750°C) and its reaction time (from 10 to 60 min) while keeping the CH$_4$ reaction time and temperature constant (that is, 980°C for 30 min). The Raman spectra of NG on SiO$_2$/Si substrates for different synthesis conditions are shown in fig. S1 (D and E). Both the intensity ratio between the 2D and G bands ($I_{2D}/I_G$) and the sharpness of the 2D band confirm the growth of NG (19, 20). When comparing NG to PG, we notice the emergence of a D band in our as-grown NG sheets, which can be attributed to the disorder generated by the introduction of nitrogen atoms within the graphene lattice (20, 21). The average distance between defects in graphene can be obtained by considering the intensity ratio between the D and G bands (22, 23). Note in fig. S1 (D and E) that the intensity ratio of $I_D/I_G$ significantly changes when the NH$_3$ reaction temperature and reaction time are changed, whereas the 2D band remains sharp and symmetric. Therefore, it is possible to tune the experimental conditions and achieve doping control over NG. A detailed Raman characterization analysis also suggests that there might be a competition between the N incorporation into graphene sublattices and the annealing process (fig. S1E) when the NH$_3$ reaction time changes from 10 to 60 min. It is also noteworthy that the $I_D/I_G$ values initially increase, thus suggesting more nitrogen doping, but such values decrease for reaction times beyond 30 min.

Figure 1 (C to E) shows STM results for samples obtained using different synthesis parameters (850°, 800°, and 750°C, respectively). The results confirm the tuning of the doping level. In our previous work, we reported that the NG sample synthesized at 850°C for 10 min in the presence of NH$_3$ shows a unique double substitutional N doping (N$_{AA}$), as can be seen in the triangles shown in Fig. 1C (15). Figure 1F shows a model image of the N$_{AA}$ configuration. It is noteworthy that a lower $I_D/I_G$ intensity ratio is observed for the NG sample synthesized at 800°C compared to that for the NG synthesized at 850°C, whereas the NG sample produced at 750°C exhibits an even lower D band intensity (fig. S1D). Therefore, the NG sample synthesized at 850°C presents a higher level of nitrogen doping, whereas the NG sample grown at 750°C barely shows any N doping. Furthermore, we notice that the NG sample doped at 800°C contains both double substitution (highlighted with circles in Fig. 1D) and single substitution, which is called N$_1$ configuration (pointed out by the arrow in Fig. 1D). Figure 1G shows a model image of the N$_1$ configuration. Therefore, it is possible to correlate the Raman spectroscopy with STM studies and tune the nitrogen atom doping configurations by changing the doping parameters. To confirm the presence of nitrogen in the NG films, x-ray photoelectron spectroscopy (XPS) was carried out (fig. S3). The photoelectron signals were collected from an ellipsoidal area of 300 μm x 700 μm. As a result of this quantification, we have found that the N content is around 2.25 atomic percent (atomic%). By deconvoluting the peak found in the N1s spectrum, we found that most of the nitrogen atoms were in the substitutional configuration (N$_1$ and N$_{AA}$, located at 400.6 eV) rather than in the pyridinic nitrogen configuration (located at 398.6 eV), which is consistent with our STM measurements.

The nitrogen doping not only affects the graphene Raman signal (D and D’ bands) but also provides a considerable enhancement factor (EF) in the Raman scattering of the studied organic molecules when compared to PG (15). However, the mechanism for such enhancement remains an open question. Here, we provide an experimental and theoretical study of the GERS mechanism for both PG and NG. To study the GERS effect, different fluorescent dyes, such as RhB, CRV, and MB, were used as probe molecules, the molecular structures of which are depicted in fig. S4A. The dyes were dissolved in ethanol to obtain a solution with a concentration of $5 \times 10^{-5}$ M. Both PG and NG sheets on SiO$_2$/Si were soaked into each solution for 30 min, after which the samples were rinsed with ethanol and then dried under a nitrogen gas flow. Notice that because of the strong fluorescence of the molecules, the organic dye molecules cannot be detected by Raman scattering when they are on a bare SiO$_2$/Si substrate (fig. S5, A, C, and E). However, PG behaves as an efficient fluorescence quencher, and the Raman spectra of the dyes on PG exhibit vibrational modes corresponding to the Raman fingerprints of the molecules (6) (fig. S5, B, D, and F). Raman spectra for both PG and NG samples with RhB, CRV, and MB can be observed in fig. S4 (B to D, respectively).

To better compare the performance of NG and PG as substrates for GERS, we have calculated the EF for different dye molecules. The calculated EF plots are shown in fig. S6 and are calculated using the raw intensity obtained from experimental spectra of molecules onto PG and NG. Because the Raman signal of the studied dyes (RhB, CRV, and MB) on SiO$_2$/Si is barely detected as a result of the strong fluorescence background, the calculated EF is not compared against SiO$_2$/Si. We report an
EF that is 16 times larger for NG than for PG (fig. S6A). It is noteworthy that the EF of a given molecule is not the same for all the Raman modes. For instance, in fig. S6A, the RhB Raman mode located at 1250 cm$^{-1}$ is much more enhanced when compared to that located at 1352 cm$^{-1}$. Such variations in the EF within modes have been previously reported (13). In addition, to compare SERS with GERS, we have also sputtered Au nanoparticles on SiO$_2$/Si substrates, and by using one of the dye molecules (MB), we compared the Raman EF between NG, PG, and Au nanoparticles. We observed (fig. S7) that NG performs around 10 times and PG performs around 5 times better than Au nanoparticles. The performance of Au nanoparticles depends strongly on the size of the particles and, thus, could be improved by tuning the roughness of the Au. However, that falls out of the scope of the present report, and the comparison with Au nanoparticles is useful to show that GERS is a powerful technique.

To confirm the uniformity of the GERS effect within the graphene surfaces (PG and NG), we prepared a $1 \times 10^{-7}$ M RhB solution and soaked both types of graphene into it. Representative Raman mappings of the intensity ratio between the 1650 cm$^{-1}$ peak of RhB and the graphene G band ($I_{1650}/I_G$) are plotted in Fig. 2 (A and B) for PG and NG, respectively. From these mappings, it can be concluded that the average ratio $I_{1650}/I_G$ in PG is ca. 0.7, whereas that in NG is ca. 2. It could also be observed that the GERS effect is quite uniform across the surfaces. For the PG sample (Fig. 2A), around 70% of the area is green-colored, whereas for the NG sample (Fig. 2B), this ratio reaches around 85%, thus demonstrating a very good uniformity of the GERS effect across the samples.

We further studied the GERS mechanism on these systems using several laser lines on freshly prepared NG samples with $5 \times 10^{-5}$ M concentrations of RhB, CRV, and MB. Figure 3 (A to C) shows the Raman spectra of RhB, CRV, and MB, respectively, when using a $5 \times 10^{-5}$ M concentration on NG sheets recorded with excitation laser energies of 2.54 eV (488 nm), 2.41 eV (514.5 nm), 2.18 eV (568.2 nm), and 1.92 eV (647.1 nm) in the 1100 to 2900 cm$^{-1}$ spectral range. The spectra display the main Raman features related to graphene (the D, G, and 2D bands) and a number of other features arising from the dye molecules. The main features of the dye molecules show prominent enhancement when excited with the 2.41 eV laser line for the RhB (marked as solid diamonds) and CRV (marked as solid circles) dye molecules and with the 1.92 eV laser line for the MB (marked as solid stars) molecule. Those Raman features are barely observed for the other laser energies used. It is noteworthy that the remarkable enhancement of the Raman signal of MB, when excited with the 1.92 eV laser line, considerably screens the Raman features are barely observed for the other laser energies used. It is noteworthy that the remarkable enhancement of the Raman signal of MB, when excited with the 1.92 eV laser line, considerably screens the

The laser dependence of the 2D band frequency for various dye molecules on NG (shown in Fig. 4, A to C) displays a linear dispersion relationship. This behavior is explained in Fig. 4D. The 2D band originated from two in-plane transverse optical (iTO) phonons around the K or K’ points in the first Brillouin zone and involves an intervalley double resonance (DR) process. The linear dispersion of electrons in graphene ensures that the incident photon energy will always coincide with the energy separation between the conduction and valence bands near the Dirac point, resulting in a DR process (19). The slope of the 2D band dispersion (Fig. 4, A to C) depicts a slight difference for each dye molecule. By fitting the curve, the slope values for each dye

Fig. 1. HRTEM and STM images of as-transferred NG. (A and B) HRTEM images of monolayer and bilayer NG sheets on TEM grids. The inset of (A) is the corresponding selected-area electron diffraction pattern of NG. (C to E) Typical STM images of NG sheets synthesized using different doping parameters: (C) NH$_3$, 850°C; (D) NH$_3$, 800°C; and (E) NH$_3$, 750°C. (F and G) Models of (F) N$_2$ and (G) N$_4$ nitrogen doping configurations. (H) Model of PG without any nitrogen doping. The triangles in (C) and the circles in (D) indicate the STM double N substitution configuration, and the arrow in (D) indicates the STM single N substitution.
molecule are 89.7, 87.2, and 96.4 cm$^{-1}$/eV for RhB, CRV, and MB, respectively. These results are in agreement with monolayer graphene (19, 24), thus suggesting that the ITO phonon dispersion is not significantly affected by the dye molecules.

To address the efficiency of the GERS mechanism on the PG and NG samples, we have prepared several RhB solutions with concentrations ranging from $5 \times 10^{-7}$ to $5 \times 10^{-11}$ M. Figure 5 (A to G) shows the enhanced Raman scattering effect of each RhB concentration for both NG and PG samples. Once again, notice that the molecules on NG exhibit a higher Raman intensity when compared to the PG substrates. Therefore, the efficiency of the GERS mechanism using NG as a sensing substrate can be noticed for the very low concentration of RhB (5 × 10$^{-11}$ M), whereas the dye molecules cannot be detected on PG for such a low concentration value. Here, the Raman signal remains strongly enhanced, and it is comparable to the 2D band intensity. Figure 5H shows the relative Raman intensity ratio between the strongest Raman peak of RhB (~1650 cm$^{-1}$) and the graphene G band. The black and red curves represent the PG and NG as the sensing substrate, respectively. By comparing the relative Raman intensity of this 1650 cm$^{-1}$ peak with different RhB concentrations, we observe that both the PG and NG samples with $5 \times 10^{-7}$ M RhB show the highest enhancement effect. A possible explanation for this effect could be related to the aggregation of the RhB molecules for high concentrations (for example, $5 \times 10^{-8}$ M) and the cluster formation on top of NG sheets, which decreases the Raman efficiency. In addition, for a low concentration (for example, $5 \times 10^{-11}$ M), only a few RhB molecules will be involved in the Raman process, thus providing a decay of the relative Raman intensity. To better understand the clustering effect, we have performed atomic force microscopy (AFM) studies of NG samples with different concentrations of RhB. AFM images of an NG sample with $1 \times 10^{-3}$ M RhB are shown in Fig. S10A, whereas fig. S10B presents $1 \times 10^{-8}$ M RhB on top of NG. It can be seen that many clusters remain for the high dye concentration ($1 \times 10^{-8}$ M RhB dyes) even after rinsing the sample with ethanol after soaking, but this clustering effect decreases significantly when the concentration drops to $1 \times 10^{-9}$ M. From previous reports (5), it can be concluded that when the concentration is below $10^{-6}$ to $10^{-7}$ M, the layer of adsorbed dye molecule can be regarded as a submonolayer, which could explain that, for an even lower concentration ($1 \times 10^{-8}$ M), very little clustering occurs. Regarding the high-concentration samples (for example, $1 \times 10^{-5}$ M), the adsorbed dyes on top of PG/NG were not considered as monolayers, and clustering could happen on wrinkles, defects, etc. Therefore, rinsing does not remove all the clusters that contribute to the diminishing of the Raman signal of the molecules. Table 1 compares the present work with recent results of the GERS effect reported in the literature (5, 6, 12, 25–29). To the best of our knowledge, it is the first time that such low concentrations of dye molecules are detected when graphene is used as a substrate. Thus, it demonstrates that the NG sample can be effectively used to detect specific organic molecules with ultrahigh sensing capabilities.

Ultraviolet (UV)–visible transmission measurements for RhB, CRV, and MB molecules in solution, as well as those interacting with quartz, PG, and NG, were performed to further study the interactions of the dye molecules with PG and NG (Fig. 6). Previous reports (9, 13, 30) have applied similar methods to study the interaction between dye molecules and PG to better understand the GERS effect. Because of the poor absorption of the dyes on quartz and the lack of interaction between quartz and the molecules, their absorption peaks in the visible range were barely observed on quartz (black curve in Fig. 6, A to C). In contrast, upon contact with PG or NG, RhB, CRV, and MB exhibit absorption peaks, which are denoted by the rose, lavender, and blue boxes, respectively. Thus, the absorption enhancement indicates that electron transition probability between dyes and substrates is increased by PG and NG (30). By comparing the transmission spectra collected from the dye solutions (Fig. 6D), red shifts can be observed when the dye molecules interacted with graphene. For instance, the absorption peak of RhB in solution ranges from 485 to 578 nm (see Fig. 6D, gray curve), and after interacting with graphene (PG or NG), the absorption range red shifts to 541 to 591 nm (Fig. 6A, blue curve). For CRV and MB, red shifts are found when the molecules interacted with NG and PG (Fig. 6, B and C). Besides the changes in HOMO-LUMO gaps, transmission values show significant differences at the $\pi$–$\pi^*$ transition of graphene (13, 30) (ca. 268 nm) before and after interacting with the molecules. For instance, the transmission at the $\pi$–$\pi^*$ transition of PG increases from 89 to 90% after interacting with RhB molecules. Instead, the value of NG decreases from ca. 88 to 84.5% after the interaction with RhB molecules (Fig. 6A). Similar trends can be found for the other molecules (CRV and MB), and more significant absorbance changes can be found for NG when compared to PG substrates. Hence, the interaction between NG and molecules is stronger when compared to PG (9).

To gain further insight into and build a microscopic picture of the physical mechanisms responsible for the observed GERS effect, ab initio calculations were carried out to study the interaction of the dye molecules with PG and NG substrates. The molecular structures shown in Fig. S4A correspond to the ground state of the ions RhB$^+$, CRV$^+$, and MB$^+$, as obtained by the B3LYP/6-31(d,p) calculations. The molecular structure closest to a planar geometry is that of MB$^+$, which is expected to exhibit the strongest $\pi$–$\pi$ interaction with the planar substrates of PG and NG. Although these systems are molecular cations, electron transfer from PG and NG toward the adsorbed molecules (for example, RhB or CRV) corresponds to 0.15 e in PG and 0.28 e in NG (where $e$ is the electron charge). MB adsorbed on PG acquires an extra charge of 0.26 e, but on NG, where the interaction is the strongest, the charge transfer amounts to 0.67 e.

The densities of electronic states (DOS) of the systems are depicted in Fig. 7. The reference energy in these graphs is the $E_F$ of the graphene cluster. The double nitrogen substituted cluster that represents a doping level of 1 atomic % has a Fermi energy raised by 0.22 eV with respect to the

![Fig. 2. Probing the uniformity of GERS effect within the graphene surfaces. (A and B) Raman mapping of the intensity ratio between the 1650 cm$^{-1}$ peak of RhB and the G band ($I_{1650}/I_G$) plotted for (A) PG and for (B) NG. The average ratio of $I_{1650}/I_G$ in PG is ca. 0.7, whereas that in NG is ca. 2. For the PG sample, around 70% of the scanned area is green-colored, whereas for the NG sample, this ratio reaches around 85%, thus demonstrating a very good uniformity across the samples and a signal enhancement for NG when compared to PG.](http://advances.sciencemag.org/Downloaded from http://advances.sciencemag.org/ on September 23, 2017)
Fig. 3. Resonant Raman scattering effect on NG sheets probed for different dye molecules. (A to C) Excitation laser energies of 2.54, 2.41, 2.18, and 1.92 eV are used to test the GERS effect of NG sheets with (A) RhB, (B) CRV, and (C) MB molecules. The probe molecule concentrations are all \(5 \times 10^{-5}\) M. The peaks marked with “◆”, “●”, and “★” are the major Raman signals from RhB, CRV, and MB molecules, respectively. arb., arbitrary.

Fig. 4. Laser dependence of the graphene 2D band frequency for various dye molecules on NG. (A to C) Linear dispersion of the graphene 2D band of NG with (A) RhB, (B) CRV, and (C) MB molecules. (D) Graphene 2D band intervalley DR process, which explains the linear dispersion.
Fig. 5. Comparison of the enhanced Raman scattering effect between NG and PG sheets when probing RhB with different concentrations. (A to G) Raman signals of RhB molecules on PG and NG sheets are shown here with (A) $5 \times 10^{-5}$ M, (B) $5 \times 10^{-6}$ M, (C) $5 \times 10^{-7}$ M, (D) $5 \times 10^{-8}$ M, (E) $5 \times 10^{-9}$ M, (F) $5 \times 10^{-10}$ M, and (G) $5 \times 10^{-11}$ M RhB concentrations. The laser excitation line is 2.41 eV, and the integration time is 10 s for all cases, where the arrows indicate graphene G and D bands. (H) Raman intensity ratio between the strongest RhB peak (1650 cm$^{-1}$) and the graphene G band when NG (red curve) and PG (black curve) are used as a sensing substrate.

Table 1. Ultrasensitive molecular sensor. Comparison of the performance of different graphene samples as GERS substrates for molecular sensing. R6G, rhodamine 6G; PPP, protoporphyrin; CuPc, copper phthalocyanine.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Type of graphene</th>
<th>Detection level</th>
<th>Laser line</th>
<th>Reference</th>
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<td>514 nm</td>
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<tr>
<td>R6G</td>
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<td>PPP</td>
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reference, in accordance with the expected n-type doping behavior of double substitutional nitrogen. When compared to the bare substrates, the DOS of the substrates with adsorbed organic molecules exhibit small modifications because of additional states brought by the molecules. The DOS projected on the adsorbed molecules (PDOS) are also shown (denoted by the filled curves). There is an increasing mixing of states in the order CRV < RhB < MB because of the interaction of the molecules with the PG and NG electronic densities. These molecules are cations and interact electrostatically with the graphene’s electronic density through the induction of image charges (31). The electric field of the image charges shifts the molecular levels and decreases the HOMO-LUMO gap. Figure 7 (C and D) depicts the DOS and PDOS of the CRV over PG and NG systems, respectively; the peaks corresponding to the HOMO (near −2.0 eV) and LUMO (near 0.7 eV) states for the molecule adsorbed on PG shift toward lower energies when adsorbed on NG because of an increased image charge field. For the CRV molecule, the charge transfer is negligible and the electrostatic effect dominates. The other two dyes interacting with NG have the band of states associated with the LUMO level partially filled, and the Coulomb repulsion shifts the HOMO level to a higher energy. The combination of image charge field and Coulomb repulsion does not change the HOMO position of RhB (Fig. 7, A and B). Nevertheless, for MB, where the charge transfer is the highest, the HOMO level is higher in NG (Fig. 7, E and F). In all the studied cases, NG shifts the $E_F$ to a higher energy and brings the LUMO bands of the adsorbates close to that $E_F$. The vertical line indicating the $E_F$ of NG crosses the LUMO bands of all dyes. Figure 7 (B, D, and F) shows the (peak-to-peak) HOMO-LUMO and the HOMO-$E_F$ energy gaps (indicated by the two arrows), which we believe to be the resonance condition needed for outstanding Raman enhancement.

It should be noted that the studied dye molecules are cations that interact more strongly with NG. The highest EF was achieved for RhB on NG (fig. S6A), whose symmetry group is $C_1$, which corresponds to the lowest symmetry among all tested systems ($C_3$ for CRV and $C_{2v}$ for MB). This result is not in agreement with a previous report, where it was concluded that the molecular symmetry has to be close to graphene’s symmetry to achieve high Raman signal enhancement (13). Because the symmetry theory does not explain our findings, we believe that there is no unique explanation for the EFs, and many aspects may contribute to this.

**Fig. 6.** Probing the interaction between various fluorescence molecules with PG and NG through UV-visible transmission measurements. (A to D) UV-visible transmittance spectra of (A) RhB-quartz, PG, NG, RhB-PG, and RhB-NG; (B) CRV-quartz, PG, NG, CRV-PG, and CRV-NG; (C) MB-quartz, PG, NG, MB-PG, and MB-NG; and (D) MB, CRV, and RhB solutions. The absorption valleys related to the HOMO-LUMO gap of the RhB, CRV, and MB are denoted by the rose, lavender, and blue box, respectively.
Table S1 summarizes the value of the calculated HOMO-LUMO gap of each molecule, the experimental absorption peaks for each molecule, and the laser excitation energy when resonant Raman happens with each molecule studied in this work (Fig. 3 and fig. S8). The calculated energy gap values of RhB, CRV, and MB on NG substrates shown in Fig. 7 are 2.20 eV (558.5 nm), 2.41 eV (514.5 nm), and 2.39 eV (518.8 nm), respectively. When comparing those with the experimentally obtained UV-visible transmission data, the theoretical values either fall within the absorption valleys (CRV and MB) or are very close (RhB). Both theoretical and UV-visible transmission experimental data suggest a strong interaction of NG with the dye molecules. From the above calculations, we can conclude that enhanced Raman sensing requires a substrate’s Fermi energy close to the LUMO level of the probe molecule. This feature allows an effective charge-transfer excitation: The photon originally absorbed by the substrate causes an excitation that can be transferred to the molecule through a resonance effect. Other molecules, such as R6G and PPP, were also used to demonstrate this. A comparison of Raman signals between NG GERS and PG GERS is shown in fig. S11. We observed that, for R6G, NG performs six times better than PG, whereas for PPP, NG performs two times better. Because the LUMO alignment with respect to $E_F$ is key to the GERS mechanism, it might be possible that $p$-type doped graphene (not NG) has a better alignment of the LUMO with the $E_F$ for other compounds, but this requires extensive tests on different molecules and $p$-type doped graphene. We also note that Raman sensing is strongest when the laser excitation energy is close to the molecular HOMO-LUMO gap, as shown in Fig. 7 and fig. S8. It is

![Fig. 7. DOS of the clusters representing the adsorbed organic dyes on PG and NG. (A to F) DOS for RhB (A and B), CRV (C and D), and MB (E and F) are shown. The filled areas are the PDOS projected on the dyes. Vertical dashed lines indicate the position of the system’s Fermi energy, $E_F$. Horizontal arrows and values indicate the HOMO-LUMO gaps (in electron volts) and the energy HOMO-$E_F$ (in electron volts).](https://advances.sciencemag.org/)

noteworthy that the HOMO-LUMO gaps of linear carbon chains encapsulated inside carbon nanotubes have also been found using resonant Raman spectroscopy (32, 33). A second conclusion could be drawn by comparing the sensitivity of PG and NG toward the tested dyes: The increasing strength of interaction, that is, CRV < RhB < MB, corresponds to an increased sensitivity, as shown in fig. S4.

Ling et al. (34) carried out wavelength-scanned Raman measurements of the CuPc molecules deposited onto mechanically exfoliated PG, obtaining the Raman excitation profile of different vibrational modes of the CuPc molecule on PG. These authors concluded that the profiles obtained using PG are completely different from those recorded without graphene, and a charge-transfer resonance peak located at ~1.9 eV occurs when the PG $E_F$ aligns with the molecular HOMO-LUMO gap. These results are similar to ours, in which a charge-transfer mechanism takes place; graphene can influence the Raman signal of the dye molecules, and a clear resonant effect is observed when the laser excitation energy is close to the molecular HOMO-LUMO gap. However, a clear advantage of our technique is that, by using NG as substrate, it is possible to tune the $E_F$ of graphene and elucidate the alignment of the LUMO of the molecules with the $E_F$ in doped graphene.

As the last test of the charge-transfer excitation model, we performed a vibrational analysis of the isolated dyes and calculated the intensities of the Raman active modes. We considered that the charge-transfer excitation is much faster than the molecular geometric relaxation because fluorescence is suppressed. For these calculations, we adopted the conformation of the cationic ground state and two charge states, the positively charged state and a neutral state obtained by adding one electron to the molecules without allowing molecular relaxation. The resulting simulated Raman spectra are shown in Fig. 8 (B to D). The frequencies of the neutral molecules do not change much from the values obtained for the cations; however, the relative intensities change because of the charge redistribution in the neutral systems. When compared to the experimental spectra shown in Fig. 3 and fig. S4, the simulated Raman spectra agree remarkably well with the measured frequencies and intensities. (The peaks marked with “◆,” “●,” and “★” are the major experimental Raman signals from RhB, CRV, and MB molecules, respectively.) We note that the features in the experimental spectra seem to be a combination of the neutral molecule (stronger) and the cation (weaker) spectra, thus suggesting that GERS comes from a charge-transfer excitation.

**Fig. 8.** Simulated Raman spectra of the dye molecules. (A) Simulated configuration when RhB, CRV, and MB molecules lay on top of NG sheets. (B to D) Simulated Raman spectrum when (B) RhB, (C) CRV, and (D) MB are on top of NG sheets. Black curves are the spectra of the cations, and colored curves are the spectra of neutral molecules in the same geometry of the cations.
DISCUSSION
We have demonstrated that it is possible to control the nitrogen content and configuration within the graphene lattice (either as a single or as a double substitution) by changing the synthesis conditions (for example, temperature when introducing NH3 and reaction time). These NG monolayers were then further used as GERS substrates to probe various dye molecules, and we observed extraordinary sensing properties when compared to PG sheets. For example, the Raman signals of these particular dye molecules can be detected for concentrations as low as $10^{-14}$ M, which is the lowest ever reported value to date when graphene is used as a substrate. Electronic structure calculations and the simulation of the Raman spectra by density functional theory (DFT) suggest that a charge-transfer excitation is the mechanism for GERS. The enhancement of the studied molecules’ Raman signal is more significant for NG than it is for PG because the LUMO levels of the dyes are closer to the $E_F$ of NG. There is no correlation between the dye molecule symmetry and the enhancement of the Raman signal, according to the analysis of the obtained data. Furthermore, when using different laser excitations, it is possible to determine the HOMO-LUMO gap of a molecule simply by performing resonant Raman measurements. Our findings indicate that doped graphene could be tuned for an effective sensing of fluorescent molecules via GERS when the appropriate laser excitation is used, and HOMO-LUMO gaps of the molecules could also be extracted via resonant Raman. These results open up new avenues for developing emerging molecular-sensing techniques. This work on NG complements other research carried out using PG, and we have explored the effects of N doping in conjunction with different dye concentrations, UV-visible transmission data, and theoretical simulations. On the basis of these results and other published work on PG, we propose a model for the Raman enhancement induced by doped graphene.

MATERIALS AND METHODS

Sample growth
Large-area monolayer PG and NG sheets were synthesized on copper foils (99.8% purity, 25 μm thick; Alfa Aesar) using CH4 and NH3 as precursors in our AP-CVD system (15). In a typical procedure, a copper foil was cleaned and put in the center of the CVD reactor, whereas Ar and H2 were introduced into the furnace and then heated up to 980°C. At 980°C, the copper foil was annealed for 10 min, after which CH4 was introduced into the furnace for 5 min and graphene would grow on the copper foil. If the furnace was cooled down to room temperature, PG was obtained. If the furnace was cooled down to a certain temperature (for example, 800°C) and NH3 was introduced for a certain period of time (for example, 10 min), NG was grown. For more experimental details regarding the synthesis conditions, please refer to our previous work (15).

TEM characterization
TEM images were acquired with a JEOL JEM-2100F electron microscope with an accelerating voltage of 200 kV, a field-emission source, and an ultrahigh-resolution pole piece (Cs = 0.5 nm) with a 1.9 Å Scherzer limit.

STM measurement
STM measurements were conducted with a home-built variable-temperature scanning tunneling microscope in an ultrahigh vacuum (UHV) system with a base pressure lower than $1 \times 10^{-10}$ mbar. The NG/Si samples were loaded into the low-temperature scanning tunneling microscope. The samples were degassed in UHV at 200°C to 300°C for several hours before performing the STM/scanning tunneling spectroscopy measurements. Here, all the STM data were acquired at 85 K if not otherwise stated. A commercial Pt-Ir tip was prepared by gentle field emission at a clean Au(111) sample. The bias voltage was applied on the sample during the STM observations. The STM images were analyzed using WSxM (30).

X-ray photoelectron spectroscopy
Elemental and chemical state analyses were carried out on NG samples transferred onto SiO2/Si substrates by means of XPS (Axis Ultra DLD, Shimadzu) using a monochromatic Al-Kα line (1486.7 eV) with 12 kV/12 mA. The photoelectron signals were collected from a 700 μm × 300 μm ellipsoidal area, and an electron flood gun was used to eliminate the charging effect.

Raman characterization
Raman spectra were acquired under ambient conditions using a micro-Raman spectrometer (Renishaw inVia) and a triple monochromator Horiba T64000 operating in single mode. In both spectrometers, a grating of 1800 lines/mm was used in the backscattering geometry, and a 100× objective lens was used to focus a laser spot size of ~1 μm onto the sample. The laser wavelengths used for exciting the samples were 647.1 nm (1.92 eV), 514.5 nm (2.41 eV), and 488 nm (2.54 eV) in the Renishaw inVia and 568.2 nm (2.18 eV) in the T64000 spectrometer from an Ar-Kr laser.

Atomic force microscope
The AFM characterization was performed in an MFP-3D AFM by Asylum Research using the noncontact tapping mode.

UV-visible transmittance
For UV-visible measurements, monolayers of NG and PG, which were synthesized by CVD, were transferred onto quartz substrates. As discussed in Fig. 5H, the dye solutions with low concentrations (for example, $10^{-7}$ M) show the highest enhancement effect. Thus, herein, $10^{-7}$ M MB, CRV, and RhB solutions were used to soak the substrates (quartz, NG on quartz, and BG on quartz). The UV-visible transmittance measurements were performed using a LAMBDA 950 UV/Vis/NIR spectrophotometer, and the wavelength ranged from 240 to 800 nm with a 0.2-nm data interval. A blank quartz substrate was used as the background.

Theoretical modeling
Graphene was studied in the framework of DFT with the hybrid B3LYP functional (35), as implemented in the Gaussian 09 (36) computational package. The 6-31G(d,p) basis set has been adopted in all calculations. PG was modeled as a 10 × 10 graphene flake (200 carbon atoms), with hydrogen atoms saturating the edges. NG was built by substituting two carbons with nitrogen atoms at the center of the flake to represent a double substitution in the same sublattice and attain a doping level of 1%. The dye molecules were considered in their cationic forms, RhB+, CRV+, and MB+. The lowest energy conformation was obtained for the five isolated molecules (dyes, PG, and NG). The interaction of the dyes with PG and NG was studied with a dispersion-corrected version of the B3LYP functional as proposed by Grimme (37). Geometries were re-optimized to account for the interaction of dyes with the substrates. Total DOS and PDOS were calculated by adopting a Gaussian broadening
Simulated Raman spectra of the dye molecules were obtained. Vibrational analysis was performed for the ground state conformation of the cations RhB\(^+\), CrV\(^+\), and MB\(^+\), as well as for the neutral molecules RhB\(^0\), CrV\(^0\), and MB\(^0\) that have the same molecular geometry as the cations but with an added electron. These calculations used the same DFT functional used for ground state conformation and electronic structure, B3LYP/6-31(d,p) within Gaussian 09. The Raman spectrum was obtained using the frequency/intensity data from the B3LYP vibrational analysis as a sum of Lorentzian line shapes of 4 cm\(^{-1}\) half-width. The vibrational spectrum (frequencies) was compressed by a constant factor of 0.97 to align the Raman features with experimental results.

**Vibrational spectrum calculations**

**Supplementary Materials**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/7/e1600322/DC1

**Supplementary material and Methods**

fig. S1. NG sheets on different substrates and their typical Raman spectra with different synthesis conditions.

fig. S2. Raman mapping of PG and NG showing monolayer coverage.

fig. S3. XPS spectra (C1s and N1s) of NG synthesized at 850°C.

fig. S4. Probing-enhanced Raman scattering effect between NG and PG sheets for different synthesis conditions.

fig. S5. Comparison of Raman spectra with bare SiO\(_x\)/Si substrates and NG for probing different dye molecules at their resonant condition.

fig. S6. Enhancement factors for three different dye molecules between NG and PG.

fig. S7. Comparison of GERS and SERS by applying sputtered Au nanoparticles as SERS substrates for comparison.

fig. S8. Testing the molecular sensitivity of the NG with different laser energies.

fig. S9. Photos of RhB in ethanol solution with different concentrations.

fig. S10. AFM images of NG samples with different concentrations of RhB.

fig. S11. Raman spectrum of S \times 10^{-12} M RhB on NG.

fig. S12. Probing GERS effect between NG and PG for additional molecules such as R6G and PPP.

Refer to the references and notes section for a list of publications and data that support the findings presented in this article.


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Ultrasensitive molecular sensor using N-doped graphene through enhanced Raman scattering

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