

Supporting Information:
**Combining nitrogen substitutional defects and oxygen
intercalation to control the graphene corrugation and doping level**

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INFLUENCE OF THE NITROGEN CONCENTRATION IN THE ELECTRONIC PROPERTIES

As mentioned in the main text, we have employed two different unit cells of the same system to study the influence of the dopant concentration. We have mainly used a rhombic cell of size 16.17 \AA . After analyzing the behavior of the Dirac cone on the N-doped graphene on the $O-(2 \times 1)/\text{Rh}(111)$ substrate, we noticed that the nitrogen concentration may have an important role in the description of electronic properties of the system. For this reason, we made some calculations on a larger unit cell whose size is twice of the original one. It is constructed by joining two identical cells along the x axis, doubling the length of the corresponding Bravais vector to 32.34 \AA . This non-primitive cell preserves the original symmetry but nitrogen concentration is reduced to the half. Since the size of the cell has been considerably increased, the k -point mesh must be adjusted accordingly. Therefore in these calculations we use a $6 \times 11 \times 1$ grid.

Although we briefly commented on the concentration problem in the main text, we would like to give a more detailed explanation about this point based on our computational results. Fig. S1 shows the PDOS of a substitutional nitrogen atom (N) and three other carbon atoms (C1, C2 and C3) for the same system in the two unit cells with different concentrations.

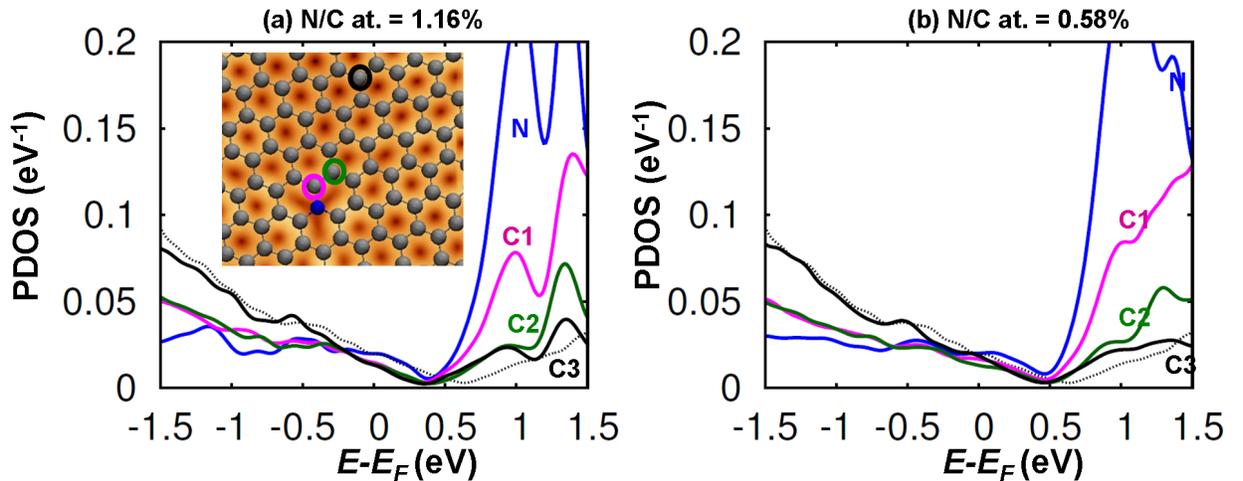


FIG. S1. Comparison between the PDOS of the nitrogen atom (N) and other three carbon atoms in the N-doped graphene on $O-(2 \times 1)/\text{Rh}(111)$ at different defect concentration (a) $N/C = 1.16\%$ and (b) $N/C = 0.58\%$. When the concentration decreases the Dirac cones moves towards p regions.

As we can observe, all the features are essentially the same except for a slight shift of the Dirac cone to the p region. More precisely, the Dirac point moves from $+0.35$ eV for a nitrogen concentration of N/C atoms = 1.16% to $+0.45$ eV for a lower concentration of $N/C=0.58\%$. In the absence of nitrogen defects, the Dirac cone for this system sets on $+0.63$ for the same oxygen coverage at the interface. According to the experimental measurements, carbon atoms near nitrogen defects turn bright for STM bias voltages around $+0.8$ eV. This value indicates that the doping level of the experimental samples must be very close to the limiting value of $+0.63$, what is reasonable taking into account the very low concentration in the samples (N/C at. $\sim 0.1\%$). Unfortunately, this defect concentration would be very hard to simulate with standard computational resources. Therefore, when comparing the doping level of experiments with the results of theoretical calculation this shift in the Dirac cone

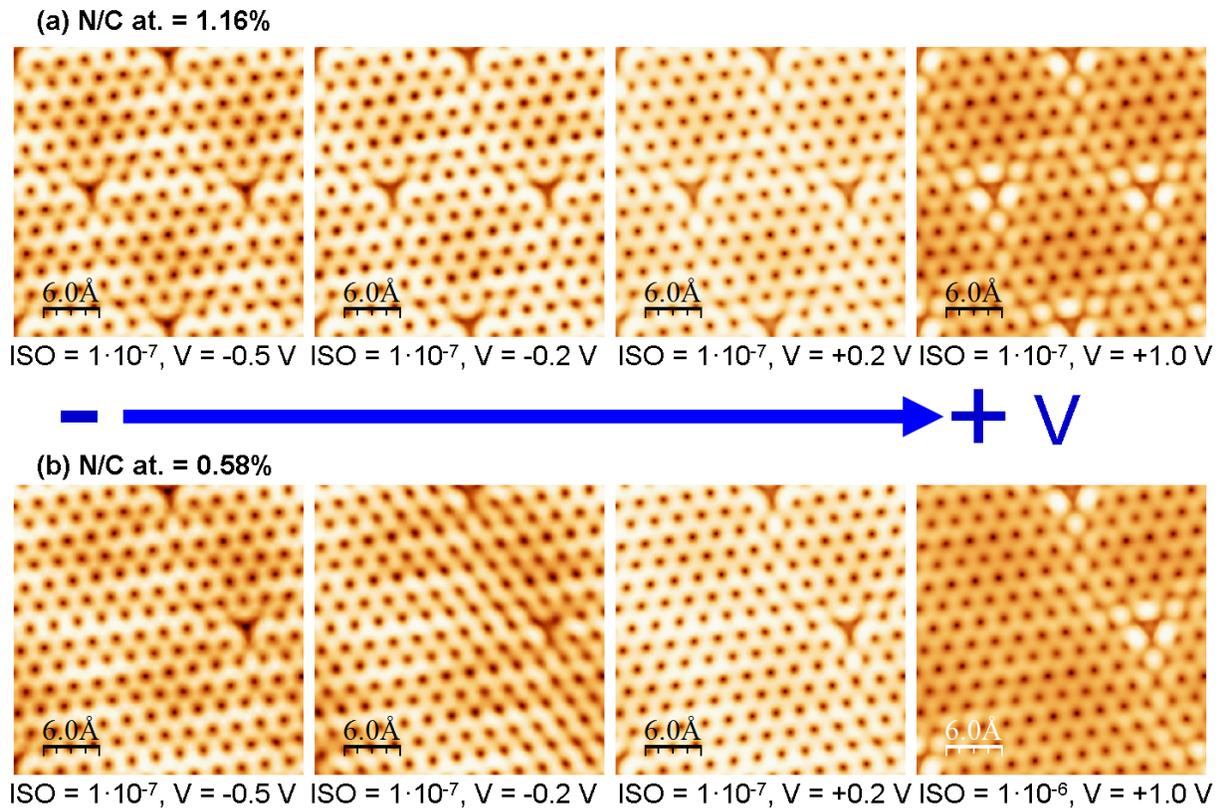


FIG. S2. Comparison between the appearance of a substitutional nitrogen atom on N-doped graphene on $O-(2 \times 1)/Rh(111)$ at different defect concentrations and different STM voltages. The upper (lower) row corresponds to calculations with $N/C=1.16\%$ ($=0.58\%$). Notice how the contrast of the defect varies between each pair of images at the same voltage.

must be considered, especially to compare the voltage in which the fingerprint of nitrogen defects becomes remarkably bright. According to our calculations a constant shift of 0.2 eV in the position of the Dirac cone must be applied when comparing experimental results and theoretical calculations.

To illustrate this effect in a more visual form, Fig. S2 shows a series of Tersoff-Hamann images of the same defect for a selection of STM bias voltages at different concentration. If we compare two images at the same voltage with different concentration, it is clear the change in contrast due to the displacement of the Dirac cone of the system. Notice also how, in the lower concentration case and with negative bias voltages, some darker areas around the defect, which resemble the appearance of real defects in experimental STM images, start to be seen. This fact is more evident along the horizontal direction in the larger cell where the separation between defects is larger.