On the mechanism of gas adsorption for pristine, defective and functionalized graphene

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Defect is no longer deemed an adverse aspect of graphene. Contrarily, it can pave ways of extending applicability of graphene. Here, we discuss the effects of three types of defects on graphene: carbon deficiency, adatom (single Fe) dopant and introduction of functional groups (carboxyl, pyran group) on NO₂ gas adsorption via density functional theory method. We have observed that the unsaturated carbon in defected graphene is highly active to attract NO₂ molecules. Our study suggests that introducing Fe on graphene can enhance the NO₂ adsorption process. Adsorption energy calculations suggest the enhancement in NO₂ adsorption is more profound for Fe-doped mono and tetra vacant graphene than Fe doped bi- and tri-vacant graphene. This study could potentially be useful in developing adsorption-based applications of graphene.

Graphene is regarded as a promising material for many practical applications¹⁻⁷. When used for gas sensing applications, the extremely high active surface area and fast carrier mobility endow graphene the ability to detect a single molecule of target gas⁸⁻¹². Selectivity is an extremely important factor to decide applicability of a particular material for sensors¹³⁻¹⁵. Gas sensing materials can be made selectively for target gas by tuning its characteristics via doping or defect creation¹⁶⁻²⁰. For development of a material as gas sensors, fundamental understanding of mechanisms responsible for gas adsorption is necessary. In this work, we have selected NO₂ as target gas to develop mechanism of gas adsorption on graphene surface. A comprehensive and deep understanding of NO₂ gas adsorption on defected and functionalized graphene can be useful in development of practical graphene-based gas sensors. Previous reports suggest that NO₂ gas adsorption can be enhanced through modifying graphene structure via creation of vacancies²¹,²², doping impurities²²⁻²⁶ and attaching chemical functional groups²⁷⁻³⁰. Using density functional theory (DFT), Lee et al elucidated that the monovacant graphene have strong NO₂ gas adsorption²¹ and Zhou et al proposed that doping of transitional metal atoms (Cu, Ag and Au) can improve the sensing performance of graphene²³. In an experimental study, Zhang et al demonstrated enhanced sensing performance after introducing single carbon vacancy defect into graphene²². Herein, we report an overall view on the effects of vacancies, adatom (Fe atom) and oxygenated groups on NO₂ gas adsorption behaviour of graphene surface using DFT.

The spin-polarized density functional theory calculations are carried out using SIESTA code based on numerical atomic orbitals basis set. The Perdew-Burke-Ernzerhof (PBE) generalized gradient
approximation (GGA) is used as exchange-correlation energy. For all calculations, we have used 300 Ry as the plane wave cut-off energy and 7 x 7 x 1 as Monkhorst-Pack grid of k points. For Partial Density of State (PDOS) calculation, we applied a denser k point value that is 16 x 16 x 1. The structures can only be optimized when the energy difference between each element is less than 10^{-4} eV and the total force is less than 0.05eV/Å. A large 9 x 9 x 1 k points value was tested on pristine graphene structure to ensure that the 7 x 7 x 1 k points value is sufficient for the structure optimization process.

All basic graphene structures interacting with NO$_2$ are shown in Figure 1. In the present study, the modelled systems are based on a supercell of 6 x 5 graphene containing 60 carbon atoms. For a systematic study, we have used three type of structures— 1) Carbon vacancies varying from mono to tetra in graphene as shown in Figure 1a, 2) Single iron doped graphene structures as shown in Figure 1b and 3) Carboxyl and pyran group to understand the role of functional groups in graphene (Figure 1c). The NO$_2$ gas adsorption energy $E_a$ is calculated by following equation: $E_a = E_{\text{substrate+NO}_2} - E_{\text{substrate}} - E_{\text{NO}_2}$ where $E_{\text{substrate+NO}_2}$ and $E_{\text{substrate}}$ represent the energy of pristine or defective graphene after and before NO$_2$ gas adsorption. Here, $E_{\text{NO}_2}$ is the energy of single NO$_2$ gas molecule. The binding energy of Fe doping to graphene structure is calculated by following equation: $E_b = E_{\text{Fe-doped graphene}} - E_{\text{vacant graphene}} - E_{\text{Fe}}$. Where $E_{\text{Fe-doped graphene}}$ and $E_{\text{vacant graphene}}$ are the energy of vacant graphene after and before iron is introduced and $E_{\text{Fe}}$ is the energy of single iron atom.

Results and Discussion

Gas adsorption on pristine and carbon vacant graphene. Based on the calculation of absorption energy for this system as depicted in Figure 2a, we can say that the carbon vacancies play an important role in enhancing NO$_2$ gas adsorption on graphene surface. For pristine graphene, the well-distributed charge on the iso-surface (Figure 2b) does not reveal any active sites for the NO$_2$ gas to interact, causing a physical adsorption type process with a small charge transfer of 0.003e$^-$.
from NO2 molecule to pristine graphene. Unsaturated carbon as exposed active sites can be found after introducing some carbon vacancies. These unsaturated carbon atoms in the vicinity of defect in the lattice apply a force to interact with NO2 molecule causing an adsorption mechanism which is similar to a typical chemical adsorption process. Furthermore, the overlap of the charge density between NO2 gas molecule and vacant graphene as shown in Figure 2b illustrates the formation of chemical bonding. This suggests that creation of vacancies causes a transition from physical adsorption to chemical adsorption on graphene. Moreover, we have observed that the structural configuration of NO2 while interacting with graphene surface changes with creation of defects, which is clearly in Figure 2b. When NO2 molecules approach the pristine graphene, it appears that the oxygen atoms prefer to interact with the graphene while in the case of graphene with defects, the excess electrons accumulated on the unsaturated carbon attract the unpaired electron in the nitrogen head of NO2. Our study suggests that vacancies created by odd numbered carbon removal are more favourable for NO2 - graphene surface interaction than the vacancies created by removing the even numbered carbon as shown in Figure 2a. This phenomenon can be attributed to presence of localized sp2 dangling bond of carbon in odd numbered vacant type graphene.

We have studied the Partial Density of States (PDOS) to understand electronic density distribution for carbon atoms near and away from defect sites in carbon vacant graphene (Figure 2c). The monovacancy, bivacancy, trivacancy and tetravacancy are represented as 1vG, 2vG, 3vG and 4vG in this study. For monovacancy (Figure 2c), the carbon atom away from defects (green circle) has steady electronic density suggesting no driving force induced for interacting with NO2 gas molecules. The carbon atom adjacent to the single vacancy (blue circled) shows sharp PDOS peaks (Figure 2c) at far region above Fermi level and red circled carbon gives a peak at -0.74eV. The peak at -0.74eV in Figure 2c associated to red-circled carbon is derived from localized sp2 dangling bonds31 and thus suggesting a strong attraction to NO2 gas molecules with a charge value of 0.029e- that is transferred from 1vG to NO2 molecule. With a observed magnetic moment of 0.88µB which is close to the reported value of 1µB31, the red circled carbon is found to be the main contributor to the induced magnetism of monovacant graphene while interacting with NO2 gas molecule.

In order to understand NO2 adsorption for the trivacancy graphene (3vG) structure (odd numbered vacancy), we specifically focussed on the carbon atom near the defect sites (Figure 2c). Here, unlike the three carbon atoms shown in blue, green and pink circle, the red-circled carbon that shows sharp peaks near Fermi level can be the NO2 adsorption site. Specifically, the peak above the Fermi level at 1.4eV for red-circled carbon reveals a strong force to capture the electrons from NO2 molecules. Therefore, in 3vG the direction of charge transfer is from NO2 gas molecule to the defective graphene surface unlike 1vG. Furthermore, it should be noted that the situations for 2vG and 4vG (even numbered) are quite different from the odd-numbered vacancies (1vG and 3vG) structures. For bivacancy structure (2vG in Figure 2c), the carbon away from the vacant site (pink colour) shows a flat PDOS curve suggesting a low likelihood for NO2 to interact. Atoms near the vacant sites (red, blue and green colour), however provide a low peak at 2.5eV, still generate a weak force for binding NO2 gas molecules. In the case of for 4vG, the PDOS peak at -0.8eV in both red and blue-circled atoms suggest tendency of these atoms to attract NO2 molecules. On comparing the PDOS plots of NO2 adsorption site in 2vG and 4vG structure, a relatively higher peak that is closer to the Fermi level indicates firm binding NO2 molecules to 4vG graphene surface. Furthermore, the value of charge transfer for 2vG and 4vG are 0.017e- and 0.012e- given in Figure 2be pointed out that in the NO2 adsorption process, this red circled carbon atom in 3vG is the main contributor to the induced magnetic moment of 1.01µB, consistent with the reported value of 1.02µB34.
Gas adsorption on Fe doped graphene. Furthermore, the doping effect was studied by introducing single Fe atom into the mono-to-tetra vacant graphene. The Fe doped defected graphene structures are represented as 1v(Fe)G, 2v(Fe)G, 3v(Fe)G, and 4v(Fe)G. The binding energy for the Fe-doped defective graphene system is shown in Figure 3a. Our observations suggest that the Fe
atom binds well in 1ν, 2ν and 3ν graphene due to the availability of space provided for bond formation. As for tetravacancy, the excessive carbon removal makes a capacious room for Fe atom to be accommodated to form two bonds in 4ν(Fe)G structure. The charge density graph shown in Figure 3b verifies the binding energy observation for Fe-graphene complex. The overlap of charge density between Fe and defective graphene reveals the bond formation therefore the number of Fe-C bond for 1ν(Fe)G, 2ν(Fe)G, 3ν(Fe)G and 4ν(Fe)G are 3, 4, 3 and 2 respectively. According to our study, the 2ν(Fe)G shows the most stable structure due to the formation of four Fe-C bonds and with only two Fe-C bonds the 4ν(Fe)G is the least stable structure. The direction of charge transfer from Fe (n-type dopant) to defected graphene is denoted as red and amounts of charge migration are in order of 0.075e⁻, 0.054e⁻, 0.053e⁻ and 0.333e⁻ for 1ν(Fe)G-4(Fe)vG respectively in Figure 3b.

Figure 3 a. The binding energy of single Fe-doped graphene complex. b. The charge density isosurface (0, 1) and charge transfer (shown in the direction of red arrow) of single Fe-doped graphene complex.

We have found that the binding energy of 1ν(Fe)G structure is lower than 2ν(Fe)G structure which is not in agreement with the data reported Krasheninnikov et al. However, our relaxed structures and associated characteristics are in well agreement. For example, the elevation height values (distance of Fe atom outward defective graphene plane) of 1.28Å and 0.51Å for 1ν(Fe)G and 2ν(Fe)G respectively are in close match with corresponding value of 1.3Å and 0.55Å by Krasheninnikov et al. Similarly the bond length (Fe-C) value of 1.8Å and 1.96Å for 1ν(Fe)G and 2ν(Fe)G respectively are close to the values 1.82Å and 1.98Å reported by Krasheninnikov et al. NO2 gas adsorption behavior on Fe-doped graphene structure is shown in Figure 4. The value of absorption energy shown in Figure 4a indicates 1ν(Fe)G and 4ν(Fe)G structure are bonded with NO2 molecules more strongly than the 2ν(Fe)G and 3ν(Fe)G structures. According to the charge isosurface distribution shown in Figure 4b, the Fe-doped graphene are prone to interact with the oxygen in NO2 molecule to form Fe-O bonds.
The extended charge distribution along the Fe-O bond for mono and tetra (as shown in blue dash line in Figure 4b) suggest a greater bond strength that provides a higher NO₂ gas adsorption energy than the that of 2v(Fe)G and 3v(Fe)G.

**Figure 4 a.** The NO₂ adsorption energy variation with the number of carbon vacancy dopped by Fe. **b.** The charge density isosurface (0, 1) and charge transfer of NO₂ adsorbed single Fe-doped graphene complex. **c.** Partial Density of States (PDOS) graph of 3d orbital of Fe atom before NO₂ gas adsorbed.
The Fe incorporated defected graphene structure shows better NO2 gas adsorption behavior than the only carbon deficient defected graphene structure; this can be attributed to the excess free d electrons in iron. In order to understand this effect, we conducted PDOS measurements of 3d orbital in Fe atom (Figure 4c). In PDOS plots, a considerably higher peak closely located at the Fermi level in 1v(Fe)G and 4v(Fe)G indicates a significant attraction to capture NO2. The PDOS plots for 2v(Fe)G and 3v(Fe)G structures also have sharp peaks but located away from Fermi level suggesting a relatively low NO2 adsorption energy. Moreover, Figure 4b presents the electrons are shifted from Fe-vacancy complex to NO2 gas molecule with the value of 0.209e-, 0.237e-, 0.192e- and 0.252e- for 1-4 Fe-doped graphene structure.

**Gas adsorption on functionalised graphene.** We have also studied carboxyl and pyran group attached to graphene to understand the role of functional groups in gas adsorption process. Pyran and carbonyl group are two stable structural groups in the reduced graphene oxide which is gas sensing material. According to our calculated values of adsorption energy (Figure 5a), it appears that the pyran group facilitates the NO2 adsorption more effectively than the carbonyl group. For pyran functionalized graphene, the unsaturated carbon atom near pyran group is tightly bonded to NO2. The overlap of charge density between the NO2 and graphene oxide (Figure 5b) as well as the large amount of charge (0.084e-) reveal the formation of the C-N bonding. However, as no active sites can be found in carboxyl group, NO2 gas can only be weakly adsorbed on the graphene oxide surface with a small value of charge (0.01e-) transferred from NO2 gas to graphene surface.

Moreover, the ether group has been reported as an interesting ultrasensitive group for sensing NO2 gas molecules with a reported binding energy value of -0.212eV27. This low NO2 binding energy indicates a good reproducibility for developing the NO2 gas sensor. In contrast, the strong binding of pyran and carbonyl group reported here is not fit for the NO2 gas sensor but can provide the clue for the graphene-based catalyst or capture applications.

It can be concluded that the introduction of defects have an important role in NO2 gas adsorption process. Single Fe dopant is most effective amongst other defected graphene studied for NO2 gas enhancing NO2 gas adsorption. In the case of oxygenated functional group modified graphene surface, the unsaturated carbon defect site near the pyran group is more attractive interaction.
NO₂ than the carboxyl group and thus greatly enhances the gas adsorption characteristic. This study can be useful for future graphene-based adsorption applications as gas capture devices.

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