Physisorption to chemisorption transition of NO2 on graphene induced by the interplay of SiO2 substrate and van der Waals forces: A first principles study

Jiayu Dai, Jianmin Yuan

Department of Physics, College of Science, National University of Defense Technology, Changsha 410073, People’s Republic of China
State key laboratory of high performance computing, National University of Defense Technology, Changsha 410073, People’s Republic of China

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A B S T R A C T
The effect of SiO2 substrate and van der Waals interactions on the adsorption of NO2 molecule on graphene is studied using density functional theory. Contrary to physisorption on suspended graphene, both physisorption and chemisorption phenomena can be found, which are mainly caused by the covalent C–O bonds, the broken symmetry, and the local corrugations induced by SiO2. The electronic structures of the system are significantly influenced after NO2 adsorption, enhancing the detection of NO2. Interestingly, NO2 induces magnetization into graphene, and the spin polarization locates mainly on carbon atoms of graphene. The barrier of the transition from physisorption to chemisorption is about 0.05 eV, and this “pseudo barrier” can be overcome by van der Waals interactions. This work explains the experiments of graphene as gas sensors with high sensitivity, and supports new applications for electronic, spintronic devices.

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1. Introduction

People have been looking for good materials as gas sensors with high sensitivity for a long time. Graphene exhibits potential applications in this field because of its unique properties. After its successful fabrication [1,2], experiments have shown that graphene can be a good sensor for the gases such as NO2 [3,4] and NH3 [5] with high sensitivity. Basically, it is expected that the adsorption of gas molecules on the sensors is stable and the changes of the conductivity should be observable. However, most of gases are found physisorbed on suspended intrinsic graphene [6–8]. Although the physisorption can also change the conductivity of intrinsic graphene, the small adsorption energy and weak coupling between gases and graphene indicate the unstable configuration at room temperature and little change of electronic structure [7]. On the contrary, the dopants and defects in graphene can strongly enhance the adsorption of molecules on graphene [9–14], indicating that doped atoms and defects play important roles in the applications of graphene. Thus, defects, dopants, gases and atoms adsorption or electric field are usually considered as the explanation of the sensitive behaviors of gas molecules on graphene [8,9,11,13,15–20].

We have to notice that in most experiments, graphene is supported on a substrate such as Si/SiO2 or SiC [2,3,5]. There were a lot of researches about the effect of substrate on the electronic structures of graphene. For example, SiC can induce a band gap [21–23] and magnetic moments [24] in graphene, making SiC-graphene a good material for the usage in electronic devices. Also, SiO2 can affect the atomic, electronic and magnetic structures of graphene [25–29]. Furthermore, SiO2 plays a significant role in the adsorption of water on graphene [30], indicating the necessity of the consideration of the environment. According to experiments [31–33], molecules such as NO2 and F4-TCNQ can induce the metal-to-insulator transition in the substrate-graphene system, giving an evidence on the chemisorption of NO2, which was never observed in previous theoretical studies. In particular, the significant charge transfer between graphene and NO2 was observed recently [33], which should not happen in the physisorption process. Until now, there are few studies about the effect of substrate on the adsorption of molecules on graphene, even though it may give some new physics theoretically and discover good materials in the practical applications. Besides, a recent study shows that the van der Waals interaction is important for the molecule adsorption on graphene-SiO2 system [34], spurring us to reconsider the new mechanism for the adsorption.

In this work, by using density functional theory (DFT), we study the atomic and electronic structures of graphene on the oxygen terminated (O-terminated) SiO2 substrate, looking for the most stable configuration. SiO2 induces eight C–O covalent bonds and a small band gap for graphene. Then, one NO2 molecule is put on different sites on the graphene surface. In this way, one chemisorption site is found with a large adsorption energy and a short distance between C atoms and the NO2 molecule, which are caused...
by the break of $\pi$ bonds in graphene and the local corrugations induced by the substrate. Meantime, the electronic and magnetic structures are changed by the NO$_2$ adsorption, in agreement with previous experiments and giving some new and interesting physics. The energy barrier from the physisorption to chemisorption is about 0.05 eV, which can be overcome directly by the consideration of van der Waals interactions. This gives a direct evidence for the substrate-induced transition from physisorption to chemisorption of NO$_2$ on graphene.

2. Computational details

In order to simulate the adsorption of NO$_2$ on SiO$_2$-graphene surface, density-functional theory (DFT) calculations using the Perdew-Burke-Ernzerhof (PBE) [35] approximation to the exchange–correlation potential [36] are performed. Spin polarization is allowed in all cases so that the magnetic properties can be obtained, as implemented in the Quantum-ESPRESSO package [37]. A plane-wave basis set up to a kinetic energy cutoff of 30 Ry for the wavefunction and of 300 Ry for the charge density is used. Several previous studies have shown that the chemical reactivity and bonds for graphene layer on the O-terminated SiO$_2$ surface are stronger than that on silicon terminated SiO$_2$ surface [29], and O-terminated surface can induce more interesting electronic structures such as a band gap in graphene [25,26]. Thus, we focus on the O-terminated surface of SiO$_2$ in this work. Using a slab configuration, a triclinic supercell of the SiO$_2$-graphene-adsorbate system is modeled using supercell containing 32 carbon atoms ($4 \times 4$ graphene), 72 substrate atoms ($2 \times 2 \times 2$ SiO$_2$(100) surface), and one NO$_2$ molecule. Here, we put C atoms on the top of eight oxygen atoms, which are shown to be the most stable sites [29] and, different from most previous theoretical studies, whose C atoms are a little further away from the oxygen atoms [25,26]. In addition, eight hydrogen atoms are used to passivate the top oxygen atoms when we study the effect of H-passivated oxygen atoms on gas adsorption. The supercell constructed in this work is shown in Fig. 1. The lattice parameters of $a = b = 9.826$ Å, $c = 32$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ are adopted. This supercell makes the lattice mismatch of the interface between graphene and SiO$_2$ less than 0.01%, which has been applied successfully in previous studies [25,26,29]. A $3 \times 3 \times 1$ Monkhorst-Pack [38] grid and Methfessel-Paxton [39] smearing of 0.01 Ry is used for the sample of Brillouin Zone, and a $7 \times 7 \times 2$ Monkhorst-Pack grid (and the tetrahedron method [40]) is used for the calculation of the band structure (density of states (DOS)). Atomic positions are optimized until the maximum force on any atom is less than 0.001 a.u. Larger energy cutoff, more $k$-points were tested but no significant difference was found. In addition, we studied the system of H-passivated bottom Si atoms of SiO$_2$ substrate, and there was no influence on the results of adsorption. The van der Waals interactions, successfully applied in a lot of systems, are implemented by the Dion (vdw-DF) [41,42] and correction (DFT-D) [43,44] scheme. In this work, we used the DFT-D correction for the consideration of van der Waals interactions, which has been shown to perform better with PBE functional.

In analyzing the results, the adsorption energy is defined as

$$E_a = E_t - E_{\text{SiO}_2 + \text{graphene}} - E_{\text{NO}_2},$$

where $E_t$ is the total energy of SiO$_2$ + graphene + NO$_2$ system, $E_{\text{SiO}_2 + \text{graphene}}$ is the energy of the substrate-graphene system, and $E_{\text{NO}_2}$ is the energy of the isolated NO$_2$ molecule. The distance from the adsorbate to the graphene surface is calculated between the atom of the molecule nearest to graphene layer and the carbon atoms of the graphene.

When NO$_2$ is placed on the graphene surface, three adsorbed sites are considered: two close sites (A and B) on top of C atoms, and the center of a carbon hexagon (C). For NO$_2$ molecule, different orientations are also considered, i.e., N atom close to graphene (n), O atom close to graphene (o), and parallel to graphene surface (p). With these initial configurations, the features of NO$_2$ on SiO$_2$–graphene surface can be outlined clearly, and the mechanism of adsorption is expected to be explained in this way.

3. Results and discussion

3.1. Graphene on SiO$_2$

Firstly, we will discuss the results without van der Waals correction. The monolayer graphene is initially deposited at a distance of 2.0 Å. The optimal configuration is shown in Fig. 2(a). Because the carbon atoms are placed on the top of oxygen atoms of SiO$_2$, eight C–O bonds form and the chemical reactivity is also strong [29] induced by the dangling bonds of oxygen atoms. Local corrugations with a height of 0.53 Å appear in graphene sheet. The structural analysis shows that the lengths of eight C–O bonds are 1.49 Å for shorter bonds and 1.50 Å for longer bonds, which are longer than the C–O bonds calculated using local density approximation (LDA) exchange–correlation functional [25]. This is reasonable because LDA exchange–correlation functional is well known for its overestimated binding energy and underestimated bond length. However, it is worth noting that there are some differences on
the atomic structures of graphene-SiO$_2$ interface here from the previous results [25,26]. For example, eight C–O covalent bonds are found in this work, compared with four C–O bonds in the previous report [25]. Thus, all eight surface oxygen atoms are in the same plane without significant recesses, which is more stable than the other interface structures [29]. Contrarily, the passivation of oxygen atoms at the interface between SiO$_2$ and graphene induces no bond formation, where the graphene layer is further away from the substrate with a distance of 3.91 Å, as shown in Fig. 2(b). Furthermore, the graphene layer is completely planar, and the length of OH bond is about 0.99 Å. Interestingly, the distance of OH···O hydrogen bond is 1.78 Å, which is in agreement with the bond length in water and water clusters [45]. The hydrogen bond network comparable to water indicates the strong structural stability for the configuration of H-passivated substrate.

Since the effect of O-terminated surface with H-passivation on graphene geometry is so different from that of the surface without H-passivated oxygen atoms, their electronic structures should be very different. As shown in Fig. 3, the covalent C–O bonds and local distortion of graphene induce dramatic changes for the electronic band structure, destroying the symmetry and spectrum of $\pi$ bands in graphene and inducing a small band gap with a width of 0.06 eV. The previous results report larger band gaps for graphene-SiO$_2$ system, whose dominant reason is that the different adsorbed sites of graphene on SiO$_2$ surface and the different final interface structures. In the present work, eight C–O bonds are new reported structures, which eliminate all dangling bonds of oxygen. With this configuration, the SiO$_2$ surface exhibits its bulk properties, whose isolated band gap are large. On the other side, the $\pi$ bands of graphene are strongly destroyed and the symmetry is broken. Thus, the cross band at Dirac point is separated with a small band gap shown. That is to say, the bands near Fermi level in Fig. 3 come from carbon in graphene. However, after H-passivated for oxygen atoms, the planar geometry of graphene is kept very well, and its semi-metal electronic structure, linear $\pi$ bands, and Dirac point are also kept well, which are better than the results with LDA calculations [25]. Therefore, the graphene on O-terminated SiO$_2$ surface with H-passivation can be used to substitute the suspended graphene in experiments in order to investigate the properties of the intrinsic ideal graphene.

### 3.2. Adsorption of NO$_2$ without van der Waals

As discussed above, three sites shown in Fig. 1 for the adsorption of NO$_2$ with different molecular orientations are investigated. The results are collected in Table 1, where the adsorption energy, the distance between NO$_2$ and graphene surface (or the C–O, C–N bonds), and the magnetic moment of the system are shown. It is clear that NO$_2$ molecule is stably adsorbed on A site with a large adsorption energy and forming C–N or C–O bonds. For other sites and for all adsorption on H-passivated surface, NO$_2$ is obviously physisorbed with small adsorption energies and large distances from the graphene surface.

In Fig. 4, the charge densities of the typical chemisorption and physisorption are shown. For chemisorption, the charges of the NO$_2$ molecule and carbon atom in graphene are overlapped seriously, indicating the formation of chemical bonds. However, for physisorption, there is not any superposition appearing, showing
the decoupling between the molecule and the graphene surface. Furthermore, the formation of C–O bonds between the SiO2 surface and graphene can be shown clearly in Fig. 4(a), where the charge densities of O atoms and C atoms are overlapped. Besides, in order to detect the NO2 molecules with high sensitivity, the conductivity of the system after adsorption should change significantly. In Fig. 5, the DOSs for typical chemisorption and physisorption are shown. Comparing with the DOS of graphene-SiO2 system without NO2 adsorption, it is obvious that the DOS after chemisorption of NO2 around Fermi level increases for both spin-up and spin-down electrons. Furthermore, it exhibits some characteristics of a half metal, whose DOS of spin-up electrons behaves as a semiconductor and spin-down electrons as a metal. This phenomenon should be stable due to the large adsorption energy. For the adsorption with H-passivated O-terminated surface.

In the end, we investigate the possibility of the transition of configurations from physisorption to chemisorption reported above. After a Climbing-Image Nudged Elastic Band (CI-NEB) calculation, the minimum path from physisorption on B site to chemisorption on A site with "n" orientation is shown in Fig. 7, where five images are chosen in the calculation. It is shown that the barrier is about 0.05 eV. For other sites and other orientations, the barriers from physisorption to chemisorption are also below 0.1 eV, indicating the feasibility of the migration of molecules to stable chemisorption on graphene.

### 3.3. Van der Waals effect

In a lot of experiments, significant changes in conductivity and charge transfer are observed after the molecular adsorption even at room temperature [8,33], indicating the chemisorption should be dominant in the process. Since there is a barrier from physisorption to chemisorption here, we should ask what is the mechanism of inducing the final transition? The above results show that the barrier of 0.05 eV can be overcome by some external forces such as temperature of 580 K. However, it is well known that it cannot treat van der Waals interactions in DFT with GGA and LDA functional, which are also not included in the above calculations. Therefore, it is worthy understanding the van der Waals effect on the system. We firstly study the configurations of NO2 on the pristine suspended graphene with van der Waals correction, resulting in similar physisorption except getting a little larger adsorption energies and smaller distances. Interestingly, after adding the correction term of DFT-D [43,44], the feature of physisorption on the graphene-SiO2 system is totally changed. Within van der Waals correction, the chemisorption of NO2 on A site does not change. However, using the physisorption on B site as the initial configuration, the NO2 molecule will diffuse without any barrier to chemisorption. That is to say, the energy barrier from GGA calculation is a "pseudo barrier", and NO2 on B site is not a stable configuration, which will transit to the stable one on A site. In other words, the van der Waals interactions between NO2 and graphene “overcome” the barrier calculated from GGA functional. Thus, the mechanism of the experiments of graphene-SiO2 system for the usage of gas
sensors with high sensitivity can be explained more clearly, leading to a good material for NO2 sensors. In particular, the van der Waals attractions should be more important for the doping of molecules on multilayer graphene [33], which can induce significant charge transfer between the graphene and the molecules.

3.4. Conclusion

In conclusion, the SiO2 substrate and van der Waals interactions can enhance the detection of NO2 molecule on graphene. The C–O covalent bonds and the local corrugations may be key reasons for this chemisorption. Furthermore, the chemisorption of NO2 induces the visible change for the DOS around the Fermi level, which can be used as gas sensors with high sensitivity. Without van der Waals correction, the physisorption seems metastable with very small adsorption energy, and the change of DOS comes from the isolated-like NO2 molecule. Interestingly, chemisorption of NO2 on A site introduces spin polarization into graphene, and the intrinsic magnetization in NO2 molecule disappears. Contrary to this, the magnetization of NO2 retains its isolated characteristic for physisorption. Importantly, the “pseudo barrier” from physisorption to chemisorption transition with GGA calculation is only 0.05 eV and can be “overcome” by the consideration of the van der Waals attraction.

Fig. 5. (a) DOS of graphene-SiO2 system with O-terminated surface, (b) DOS of adsorption of NO2 on A site with “n” orientation, (c) LDOS of NO2 (solid line) and carbon atoms in graphene (dotted line); (d)–(f) are the same as (a)–(c) with H-passivated surface. The orientation of arrows represents the direction of spin polarization. Dashed lines represent the Fermi level.

Fig. 6. (a) Spin density of “n” orientated NO2 adsorption on A site; (b) Spin density of “n” orientated NO2 adsorption on B site. Isosurface value is 0.01 a.u.

Fig. 7. Minimum energy pathways from B site to A site for NO2 on graphene induced by SiO2 substrate.
der Waals attraction. In fact, our further study shows that NH\textsubscript{3} on graphene-SiO\textsubscript{2} system has similar phenomena reported here, but the chemisorption is only the metastable configuration. This study explains well for the experiments of detecting NO\textsubscript{2} on graphene, and the system of graphene on SiO\textsubscript{2} surface with O-termination can also be used in the field of gas sensors and electronics.

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