Adsorption of CO$_2$ on Fe-doped graphene nano-ribbons: Investigation of transport properties

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Abstract. Density functional theory combined with the non-equilibrium Green’s function formalism is used to study the conductance response of Fe-doped graphene nano-ribbons (GNRs) to CO$_2$ gas adsorption. A single Fe atom is either adsorbed on GNR’s surface (aFe-graphene) or it substitutes the carbon atom (sFe-graphene). Metal atom doping reduces the electronic transmission of pristine graphene due to the localization of electronic states near the impurity site. Moreover, the aFe-graphene is found to be less sensitive to the CO$_2$ molecule attachment as compared to the sFe-graphene system. These behaviours are not only consolidated but rather confirmed by calculating the IV characteristics from which both surface resistance and its sensitivity to the gas are estimated. Since the change in the conductivity is one of the main outputs of sensors, our findings will be useful in developing efficient graphene-based solid-state gas sensors.

1. Introduction

Graphene-based sensors have advantages over solid-state gas sensors in terms of sensitivity, response and recovery times, low power consumption and low cost [1]. Moreover, they can operate at room temperature and under ambient conditions. In addition, gas sensing and catalytic properties of graphene can be further enhanced by decorating it with metal and metal-oxide nanoparticles [2,3]. Although the choice of non-noble metal as a dopant is mainly motivated by its low cost, Fe atoms can perform as good as noble metal atoms (such as Pt atom) in terms of improving the sensitivity and selectivity of graphene [4]. Transition metals such as Fe, Co, Ni, and Cu are also known to increase the sensitivity and selectivity of graphene-based sensors for gas detection [4,5]. Since the changes in the resistivity after the gas molecule adsorption is the main output of solid-state sensors, a fundamental understanding of the electronic transport properties of graphene under these conditions enables the utilization of the full potential of functionalized graphene for practical applications.

In the present work, we use density functional theory (DFT) in combination with the non-equilibrium Green’s function formalism to study the electronic transport response of zig-zag graphene nano-ribbons [6] doped with Fe atom and its effect on the adsorption of carbon dioxide (CO$_2$) molecule, which is one of the major greenhouse gases. Capturing, storing and converting CO$_2$ has become a major problem confronting environmental challenges such as the issue of climate change [7,8]. We consider two different cases, either the Fe atom substitutes the carbon atom of graphene...
(sFe-graphene) or it is adsorbed on graphene’s surface (aFe-graphene). The main purpose of this study is to fully explore the effect of the CO$_2$ molecule adsorption on the electronic transport properties of pristine and functionalized graphene. The obtained results are explained in terms of electron localization in the system. Our findings will be useful to design more sensitive graphene-based gas sensors.

2. Computational model and method

Two device geometries are considered. Each contains an active layer of length 22.149 Å and two electrodes each of size 7.383 Å. The active region is long enough to study the effect of a single impurity. Each GNR has a width of 7.10 Å and contains about 64 carbon atoms. Defects and dopants play important role in the electric properties of materials. The adsorption of CO$_2$ on carbon vacancy has already been studied in our group [9]. Here, we wanted to study the adsorption of CO$_2$ on graphene nano-ribbons in assistance of Fe-catalyst. Meanwhile assess the effect of binding of Fe on the adsorption properties. So, we considered two realizations: (a) Fe atom strongly attached to the surface in a substitution of carbon atom, and (b) Fe atom just relaxed on a hollow site above the GNR.

In the computational method, we first optimize the atomic structures using DFT within the general gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation energy [10]. The Brillouin zone sampling/integration was performed using 1x1x100 Monkhorst-Pack technique [11]. The convergence criteria for total energy and Hellman-Feynman forces were 0.001 eV and 0.01 eV/Å, respectively. The transmission and IV curve were calculated along z-direction between the two electrodes. The non-equilibrium Green’s function formalism is used to calculate the transport properties. All simulations were obtained using the first-principles computational package Atomistic toolkit [12].

3. Results and discussions

Figure 2 shows the transmission spectra versus energy for GNR (dotted black line), GNR with Fe atom attached to the surface (green line) and GNR+Fe with adsorption of CO$_2$ on the GNR-Fe composite. Two different cases for the positions of Fe doping are considered: (a) Fe as ad-atom on the hollow site of GNR with a Fe-C distance of about 2.05 Å; and (b) Fe as a substitutional dopant replacing carbon atom. As a reference, the dotted black line in Figure 2 presents the zero-bias T(E) of pristine graphene nano-ribbon without Fe and without CO$_2$ as well. This latter transmission curve shows a step-like behaviour with an enhanced transmission at the Fermi level, which are typical for graphene nano-ribbons. These features originate from the edge-localized electronic states with energies close to the Fermi level. Figure 2a shows that the aFe adsorption results in considerably
reduction when decreasing the electron energy below Fermi level (at about - 0.5 eV). A bit variation occurs when the CO\textsubscript{2} gets adsorbed on aFe as shown by red curve in Figure 2a. In contrast to these features, in the case of sFe shown in Figure 2b the discrepancy between T(E) before the landing of CO\textsubscript{2} molecule and after on sFe is huge. This fact reveals that sFe should play the role of a better gas sensor to CO\textsubscript{2} than aFe does. This will be confirmed with further studies shown below.

In order to get a better insight about the origin of the obtained changes in the transmission spectra due to the doping, we calculated the projected self-consistent Hamiltonian (PSH) eigen-states. These eigen-states are associated with the poles of the green’s function at the given electron energy. In Figure 3, we chose to show the PSH eigenstates of sFe-GNR sample without and with CO\textsubscript{2} adsorbed molecule in order to explain the huge discrepancy in T(E) spectra. The energy is taken to be E-E\textsubscript{F} = -1.0 eV. Figure 3 shows three eigen-states corresponding to: (a) GNR, (b) GNR-sFe, and (c) GNR-sFe with CO\textsubscript{2} molecule. Panel (a) shows the eigen-state to be uniformly-distributed as an extended Bloch-like eigen-function; whereas panel (b) shows a strong localization of electrons around Fe atom; and panel (c) shows also still strong and a bit perturbed but confined near the vicinity of Fe site. Thus, strong electronic localization is the reason causing the huge discrepancy in T(E) behaviours.

Last but not the least, Figure 4 displays the results of IV-curve calculated using DFT with GGA. Figure 4a shows the results of two IV curves for the case of sFe in order to carry on further the preceding analysis. Actually, the IV-curve of GNR-sFe shows higher conductivity than the IV-curve of GNR-sFe with adsorbed CO\textsubscript{2} molecule. From each IV curve, the resistance can be derived, based on it the sensitivity can be estimated using the formula:

\[
S = \frac{|R_e - R_a|}{R_a} \times 100\% \tag{1}
\]

where \(R_e\) and \(R_a\) are the resistances of the sample in exposure and in absence of the gas, respectively. Figure 4b shows the resistance versus bias and Figure 4c shows the sensitivity versus bias.
These latter should be weakly-dependent or independent of bias. Nonetheless, the average value does confirm a higher gas sensitivity (of about 34.5%) corresponding to the case of sFe.

4. Conclusions:
State-of-the-art computational method, based on DFT combined with non-equilibrium Green’s functions formalism, is employed to calculate transmission spectrum and IV-curve of Fe-doped GNRs. Two scenarios are put under the scope: (i) Fe atom used as ad-atom relaxed on hollow site (aFe), and (ii) Fe atom used as a dopant substituting carbon atom (sFe). Tests of adsorption of CO₂ molecule are carried out and the results showed that sFe to have stronger binding to the surface and thus greater effect on the states near Fermi level so it drastically affect the conductivity of the sample. More interestingly is that such behaviours escalated to yield high sensitivity toward the detection of CO₂ molecule.

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Figure 4: (a) IV-curves calculated for GNR-sFe without and with CO₂ molecules, (b) Resistances corresponding to these two cases and (c) Gas sensitivity are shown versus bias.