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Electronic transport calculations for CO_2 adsorption on calcium-decorated graphene nanoribbons

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ABSTRACT

Calcium-atom functionalization is considered to be an effective tool of enhancing CO_2 uptake capacity of carbon-based materials (Cazorla et al., 2011). Here we use density functional theory calculations combined with the nonequilibrium Green's function formalism to study electronic transport properties of Ca-decorated zig-zag and armchair graphene nanoribbons after CO_2 adsorption. Sensitivity of the system to CO_2 attachment is considerably increased due to the Ca-decoration: the electronic transmission near the Fermi level increases due to the formation of extended states. In addition, the variations of the electrostatic potential along the transport direction reduces due to CO_2 adsorption. Enhanced electronic transport due to the CO_2 adsorption is also obtained in current-voltage calculations. Since the conductivity change is one of the main properties of gas sensors, our results will be useful in developing graphene-based solid-state gas sensors.

1. Introduction

Sensing and storing carbon dioxide (CO_2) have attracted a lot of interest in recent years in environmental research due to global warming [1–5]. In addition to metal-organic gas adsorbents (see [6] for review), carbon based materials, such as carbon nanotubes and graphene, are considered as potential materials for the capture and sensing greenhouse gases (see Refs. [7–9] for reviews). Surface termination is shown to be an effective tool to increase the gas adsorption properties of such low dimensional materials. For example, calcium (Ca) functionalization increases the CO_2 uptake capacity of carbon-based systems by several times due to the strong interaction between the gas molecule and Ca dopants [10].

Graphene has a potential for gas sensing applications due to its exceptional mechanical, electronic and transport properties such as large surface-to-volume ratio, high charge carrier transport and reduced thermal noise [11–15]. Graphene-based sensors have advantages over the other solid-state devices in terms of low cost, low power consumption, high sensitivity and suitable response/recovery time (see, Refs. [16–22] for reviews). In addition, catalytic and gas sensing properties of graphene can be further increased by metal (metal-oxide) nanoparticle functionalization [23–26] (see,

Refs. [27–30] for review). In this respect, Ca atoms were proposed to be effective in improving the gas sensing properties of graphene [10,31,32].

In this work, we use density functional theory (DFT) combined with the nonequilibrium Green's function formalism to explore the electronic transport properties of zig-zag and armchair graphene nanoribbon [33,34] doped with a single Ca atom. Pristine graphene nanoribbon is less sensitive to CO_2 molecule due to the weak physisorption. Ca-decoration increases the response of the graphene nanoribbon to the gas molecule adsorption. For example, the electron transmission near the Fermi level increases after CO_2 attachment to the Ca atom due to the formation of extended states. The gas adsorption also affects the electrostatic potential profile in the system. Current-voltage calculations also reveal enhanced transport in Ca-decorated graphene nanoribbons due to the CO_2 adsorption.

2. Computational details

Calculations are conducted using DFT within the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation [35]. In geometry optimization calculations, the convergence criteria of 0.001 eV and 0.05 eV/Åwere used for the total energy and Hellman-Feynman forces, respectively. The electrostatic potentials profiles were determined on a real-space

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grid with a mesh cutoff energy of 148 Ry and the double-ζ-polarized basis sets of local numerical orbitals is used in the simulations. Grimme's DFT-D3 empirical dispersion correction [36] to the PBE was used to include van der Waals interactions. All the calculations are conducted using the computational package Atomistix Toolkit [37].

3. Results and discussions

We start with studying the stability of Ca atoms on top of monolayer graphene sheet. It has already been shown by Cazorla et al. that Ca atoms have large binding energies to the surface of graphene and Ca-decorated graphene is thermodynamically stable [10]. Here, we conduct nudged elastic band (NEB) [38] calculations to obtain the energy barrier for the migration of Ca atoms on the surface of graphene. The size of the simulations cell is 8.525 Å × 7.383 Å and the system consists of 24 carbon atoms. We use periodic boundary conditions in all directions and a vacuum spacing of 20 Å is left along perpendicular direction to the graphene layer. The Brillouin zone was sampled using $6 \times 6 \times 1$ Monkhorst k-point sampling [39]. The Ca atom is adsorbed on the hollow site of graphene in both initial and final states with Ca-C distance of 2.66 Å (see left and right insets in Fig. 1). The linear interpolation method is used to calculate the initial path in the NEB simulations. We relaxed all the atoms during the simulations. The residual forces were less than 0.01 eV/Å. The calculated energy barrier for the diffusion of Ca atom is 0.9 eV. This barrier is large enough to prevent the diffusion of the Ca atom on the surface of graphene at room temperature.

Next, we calculate the adsorption energy of CO_2 molecule on the Ca atom using

$$E_{ads} = E_{graphene+Ca+CO_2} - E_{graphene+Ca} - E_{CO_2}, \tag{1}$$

where $E_{graphene+Ca+CO_2}$ is the total energy of graphene + Ca system with CO_2 molecule, $E_{graphene+Ca}$ is the total energy of graphene + Ca sample and E_{CO_2} is the total energy of the isolated CO_2 molecule. We used the same graphene unit cell as in Fig. 1 with the same k-point sampling. However, in order to reduce the numerical error due to the basis set superposition, we calculated the adsorption energy of the CO_2 molecule using the SG-15 basis set [37]. In addition, we have increased the density mesh cutoff (200 Ry) and interaction range (20 Å). The simulations show a strong chemisorption of the CO_2 molecule on the Ca atom. The adsorption energy of the gas molecule is $E_{ads} = -1.6$ eV (or $E_{ads} = -0.067$ eV per C atom in the supercell), which prevents the desorption of the gas molecule at temperatures well above room temperature.

To see the effect of Ca-adatom and CO_2 molecule on the electronic structure of graphene, we have calculated the band structure of hexagonal graphene supercell consisting of 98 C atoms (see the insets in Fig. 2(a–c)). For pristine graphene, we obtained a linear
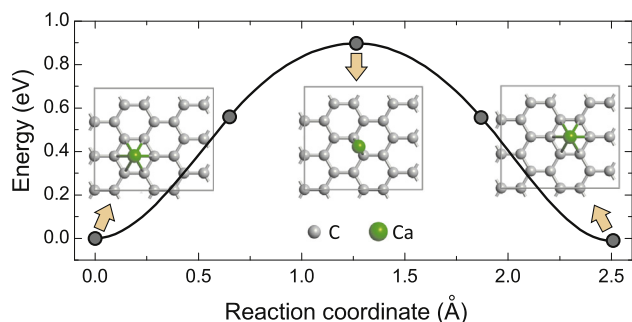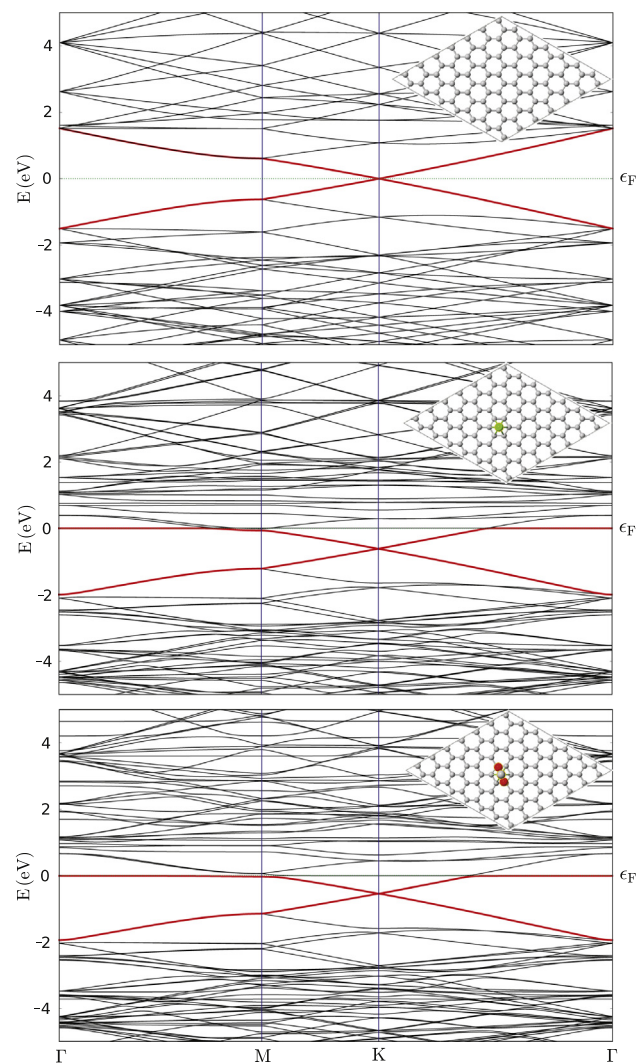

Fig. 2. Band structure of pristine graphene (a), graphene with Ca atom (b) and graphene with CO_2 molecule absorbed on Ca atom. Insets show the simulation cells.

dispersion relation at the K-point, where the Fermi level crosses the Dirac point (Fig. 2(a)). The adsorption of Ca atom results in a shift of the Fermi level above the Dirac point (Fig. 2(b)), which is typical for metal atom adsorption on graphene [40]. Ca atom also locally changes the carbon-carbon bonds, affecting the electronic properties of graphene. Fig. 2(c) shows the band structure of graphene after CO_2 adsorption on the Ca atom. The system still shows the metallic behavior, where the Dirac point is shifted below the Fermi level. Such a change in the band structure of graphene is due to the charge transfer from the metal atoms to graphene (see, e.g., Ref. [41]). To study the charge distribution in the considered systems, we have conducted partial charge calculations using the density derived electrostatic and chemical charges method [42,43]. This charge partitioning method is shown to be the most suitable method for systems consisting of both organic and inorganic components [44]. The hollow-site attachment of the Ca atom changes the partial charge of the C atoms in the underlying benzene ring from neutral to $-0.063|e|$. The partial charge of the Ca atom becomes $0.611|e|$, indicating significant charge transfer from the Ca atom to graphene. The partial charges of C and O atoms of an isolated CO_2 molecule are $0.71|e|$ and $-0.355|e|$, respectively. A significant charge transfer is obtained from the Ca atom to the CO_2 molecule after the adsorption. Now the partial charges of the Ca atom and C atom of the molecule becomes $1.313|e|$ and $0.28|e|$,

Fig. 1. Energy profile for the migration of a Ca atom on the top of monolayer graphene. Insets show the migration pathway.