Research Article

Electronic Structure Calculation of Adsorbate Gas Molecules on an Armchair Graphene Nanoribbon

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By using the first-principle methods, we have investigated the adsorption of the CO, CO₂, NO, and NH₃ molecules on an armchair graphene nanoribbon (AGNR). The optimal adsorption positions and orientations of these molecules on AGNR are determined. The adsorption energies, the charge transfer, and the density of states (DOS) are obtained. The NO, CO, and CO₂ adsorbed molecules act as an acceptor, and the NH₃ adsorbed molecule acts as a donor. The NO and CO molecules contributed with localized states in the center of the original band gap. But the system exhibits *n*-type or *p*-type semiconductor after NH₃ or CO₂ adsorption.

1. Introduction

Recently the study of the sensing property of carbon nanostructures, such as carbon nanotubes (CNTs), graphene, and graphene nanoribbons (GNRs), has attached a lot of research activity [1–3]. Studies show that the graphene and CNTs and GNRs are good gas sensors. Experimental data have shown that the transport properties of nanotube changes upon exposure to gas molecules such as the O₂, NO₂, and NH₃ molecules [2, 4-8]. Experimental and theoretical studies of gas molecule adsorption on the graphene surface have been reported already [9–16] showing that H₂O, NO, CO, NO₂, and NH₃ molecules are physically adsorbed on the graphene. The NH₃, NO, and CO molecules act as donors while H₂O and NO₂ act as acceptors. The conductance of graphene at the Fermi level decreases with adsorbing NO₂ molecules while it increases with adsorbing NO molecules [17]. Due to having flat structure and thus larger accessible surface area, GNRs and graphene may act better than any other carbonbased materials as gas sensors. GNRs' electronic states largely depend on the edge structure (armchair or zigzag). Calculations based on tight bonding approximation predict that zigzag graphene nanoribbons (ZGNRs) are always metallic while armchair graphene nanoribbons (AGNRs) can be either metallic or semiconducting, depending on their

width [18]. However DFT calculations show that AGNRs are semiconducting with a finite band gap and the value of the gap depends on their width [19–21]. Theoretical and ab initio studies of GNRs sensing properties have been reported already, showing that absorption of CO_2 or O_2 molecules changes the AGNR to *p*-type semiconductor, while NH₃ adsorption changes it to a *n*-type semiconductor [22–24].

In this work we performed the first-principle calculations for the adsorption of CO, CO₂, NO, and NH₃ molecules on armchair graphene nanoribbon consisting of 6 dimer lines across the ribbon width (6-AGNR), as shown in Figure 1(a). After geometrical optimization, we obtained the positions and orientations of the adsorbed molecules. We then calculate the adsorption energies (E_a), the density of states (DOS), and the charge transfers between nanoribbon and adsorbate molecules due to bindings between the molecules and carbon in the nanoribbon. By probing the density of states (DOS) of the systems, one can find out the direction of charge transfer (from the molecules to the nanoribbon or vice versa), and from this, one can determine whether the doped molecule acts as a donor or as an acceptor.

In the previous work [22], the exact orientation and position of the adsorbate molecules on the 6-AGNR surface was not calculated. However, we have used the atomic coordinates obtained from simultaneous relaxation in the positions



FIGURE 1: (colour online). (a) The unit cell for 6-AGNR with 36 carbon atoms. (b) The position and orientation of CO molecule on 6-AGNR. (c) The position and orientation of OO_2 molecule on 6-AGNR. (d) The position and orientation of NO molecule on 6-AGNR. (e) The position and orientation of NH_3 molecule on 6-AGNR.

of the adsorbate molecules, 6-AGNR sheet, and their atomic positions.

The organization of this paper is as follows. In Section 2 the computational details are discussed. In Section 3 we investigate the electronic structure of the 6-AGNR with adsorbate molecules, using density functional theory with the local density approximation.

2. Computational Details

Our calculations are based on the use of DFT and the ab initio pseudo-potential plane-wave method using the PWSCF code of the Quantum ESPRESSO [25]. We performed the calculation with LDA and LSDA ultrasoft Vanderbilt pseudopotentials [26]. The Kohn-Sham orbitals are expanded in a plane-wave basis set. The energy cutoff for the wave function and the charge are, respectively, 45 Ry and 300 Ry. The 6-AGNR was simulated by a relatively orthorhombic supercell of 36 carbon atoms, with lattice parameters a = 12.78 Å, b = 13.23 Å in the *xy* planes and c = 10 Å. The sampling of the Brillouin zone was done using a $6 \times 6 \times 1$ grid and tested to give convergent results for the total energy. For calculating the density of states (DOS), we used a $20 \times 20 \times 1$ grid.

The periodic boundary conditions and a supercell approximation were used. The supercell had 36 carbon atoms for a 6-AGNR in a hexagonal lattice. The structural optimizations were performed using a conjugated gradient procedure. Different configurations of gas molecules' adsorption to the 6-AGNR were considered. For each molecule we chosen the position and the orientation in which the hole system has minimum energy. For this position and orientation, the structure are full relaxed until all the force components were smaller than 10^{-1} (*Ry/au*), in order to obtain the exact position and orientation for the molecule.

The amount of charge transfer from 6-AGNR to the molecules can be estimated by projecting the charge density onto the atomic orbitals. We calculated the charge transfer as the difference between the Löwdin charges for pristine 6-AGNR and 6-AGNR with the adsorbate molecules. From this result, one can determine whether the adsorbate molecule acts as an acceptor or as a donor. It is important to note that the size of the charge transfer slightly depends on the method chosen for calculations. The adsorption energy (E_a) is defined as the difference between the energy of the fully relaxed 6-AGNR and the adsorbed molecule on it (E_{total}) and the sum energy of the pristine 6-AGNR (E_{6-AGNR}) and the energy of the isolate molecule ($E_{molecule}$):

$$E_a = E_{\text{total}} - (E_{6-\text{AGNR}} + E_{\text{molecule}}).$$
(1)

3. Molecular Adsorption on 6-AGNR

In this section, after full relaxation, the optimized geometry was obtained, then the charge transfer and the adsorption energy were determined.

As Figure 2 shows, the pristine 6-AGNR is a semiconductor with 1.1 eV band gap. Gas adsorption changes the DOS of 6-AGNR, so it could change 6-AGNR properties.

The CO molecules are adsorbed to the 6-AGNR in the 6-AGNR plane, via its carbon atom as shown in Figure 1(b). The bond length obtained for C–C is 1.35 Å and the angle C–C–O is 165.8° while the bond length of the adsorbed CO is 1.17 Å. The calculated adsorption energy of CO molecules on the 6-AGNR is -2.34 eV. As Figure 2 shows, the lowest unoccupied molecular orbital (LUMO), which appeared as a peak, is located at the center of original band gap slightly above the Fermi level of the pristine 6-AGNR so a charge transfer from the 6-AGNR, to the CO molecule is expected. There is a total charge transfer of 0.02 e from the 6-AGNR to



FIGURE 2: (colour online). Calculated DOS for 6-AGNR with adsorbate CO molecule and pristine 6-AGNR. The red and the black dashed lines show the 6-ANGR with the adsorbate CO molecule Fermi energy and the pristine 6-AGNR Fermi energy, respectively.



FIGURE 3: (colour online). Calculated DOS for 6-AGNR with adsorbate CO_2 molecule and pristine 6-AGNR. The red and the black dashed lines show the 6-ANGR with the adsorbate CO_2 molecule Fermi energy and the pristine 6-AGNR Fermi energy, respectively.

CO molecules; therefore it can be deduced that the CO molecule acts as an acceptor.

The results of CO_2 molecule adsorbed on the ribbon show that in the CO_2 molecule, the C atom is closer to the ribbon surface than the O atoms (Figure 1(c)) and the C–C bond length is 1.50 Å. The bond length and the angle of the adsorbed CO_2 molecule are 1.25 Å and 125.9°, respectively. The angle of the C–O bond with the ribbon plan 116°. The calculated adsorption energy of the CO_2 molecule on the 6-AGNR is –5.23 eV. As can be seen in Figure 3, the LUMO is above Fermi level; it is the orbital that can have an overlap with the 6-AGNR orbitals and thus can cause charge transfer from the ribbon to the molecule. There is a total charge



FIGURE 4: (colour online). Calculated DOS for 6-AGNR with adsorbate NO molecule and pristine 6-AGNR. The red and the black dashed lines show the 6-ANGR with the adsorbate NO molecule Fermi energy and the pristine 6-AGNR Fermi energy, respectively.

transfer of 0.09 e from the 6-AGNR to the CO_2 molecule. Therefore it can be deduced that the CO_2 molecule acts as an acceptor. After adsorbing the CO_2 molecule, the Fermi level shifts toward the valance band (Figure 3), so the system exhibits *p*-type semiconducting behavior.

The results of calculations show that the NO molecule sits in the ribbon plane. NO molecules attached to the ribbon via the N atom, with their N-C bond length 1.43 Å and the O-N–C angle 116.3° (Figure 1(d)). The calculated adsorption energy of the NO molecule on the 6-AGNR is -1.15 eV. As Figure 4 shows, the highest occupied molecular orbital (HOMO), which has appeared as a peak near the Fermi level of pristine 6-AGNR, is half filled and is associated with both $2\pi_x$ and $2\pi_y$ orbitals. Due to these two facts, it can also be ascribed as the lowest unoccupied molecular orbital (LUMO). It causes charge transfer in both directions due to the mixing of the HOMO or the LUMO of NO with the 6-AGNR orbitals below or above the Fermi level. There is a total charge transfer of 0.15 e from the 6-AGNR to the NO molecule. Therefore it can be deduced that the NO molecule acts as an acceptor.

NH₃ molecules attach to the ribbon via the N atom (Figure 1(e)). The N atom sits 0.9 Å away from the edge of the ribbon, the length of N–C bond is 1.48 Å, and the H– N–H angle is 109.1°. The angle that the N–C bond makes with the ribbon plane is 142°. The calculated adsorption energy of the NH₃ molecule on the 6-AGNR is -3.103 eV. There is a total charge transfer of 0.16 e from the NH₃ molecule to the 6-AGNR, so the NH₃ molecule acts as a donor. As Figure 5 shows the band gap decreases after adsorbing the NH₃ molecule and the Fermi level shifts toward the conduction band, so the system exhibits *n*-type semiconducting behavior.



FIGURE 5: (colour online). Calculated DOS for 6-AGNR with adsorbate NH₃ molecule and pristine 6-AGNR. The red and the black dashed lines show the 6-ANGR with the adsorbate NH₃ molecule Fermi energy and the pristine 6-AGNR Fermi energy, respectively.

4. Conclusions

In this work the adsorption of CO, NO, and NH₃ molecules on 6-AGNR was investigated. We optimized the position of the adsorbate molecules on 6-AGNR. After full relaxation, the adsorption energy and the charge transfer properties between the molecules and the 6-AGNR are determined. We showed that the NO, CO₂, and CO molecules act as an acceptor and that the NH₃ molecule acts as a donor which has also been verified in experiment [9]. The NO and CO adsorbed molecules contributed with localized states in the center of original band gap. AGNR semiconductor became *n*-type semiconductor after NH₃ molecule adsorption. The adsorption of NH₃ molecule converts the electronic structure of 6-AGNR as a degenerate semiconductor. These results are consistent with those obtained by Huang et al. [22] and Saffarzadeh [24].

References

- J. Kong, N. R. Franklin, C. Zhou et al., "Nanotube molecular wires as chemical sensors," *Science*, vol. 287, no. 5453, pp. 622– 625, 2000.
- [2] P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, "Extremeoxygen sensitivity of electronic properties of carbon nanotubes," *Science*, vol. 287, no. 5459, pp. 1801–1804, 2000.
- [3] P. Qi, O. Vermesh, M. Grecu et al., "Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection," *Nano Letters*, vol. 3, no. 3, pp. 347–351, 2003.
- [4] S. Chopra, K. McGuire, N. Gothard, A. M. Rao, and A. Pham, "Selective gas detection using a carbon nanotube sensor," *Applied Physics Letters*, vol. 83, no. 11, pp. 2280–2282, 2003.
- [5] L. Valentini, I. Armentano, J. M. Kenny, C. Cantalini, L. Lozzi, and S. Santucci, "Sensors for sub-ppm NO₂ gas detection based on carbon nanotube thin films," *Applied Physics Letters*, vol. 82, no. 6, pp. 961–963, 2003.

- [6] T. Ueda, M. M. H. Bhuiyana, H. Norimatsua, S. Katsukia, T. Ikegamia, and F. Mitsugi, "Development of carbon nanotube-based gas sensors for NO_x gas detection working at low temperature," *Physica E*, vol. 40, no. 7, pp. 2272–2277, 2008.
- [7] P. Qi, O. Vermesh, M. Grecu et al., "Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection," *Nano Letters*, vol. 3, no. 3, pp. 347–351, 2003.
- [8] D. Zhang, Z. Liu, C. Li et al., "Detection of NO₂ down to ppb levels using individual and multiple In₂O₃ nanowire devices," *Nano Letters*, vol. 4, no. 10, pp. 1919–1924, 2004.
- [9] F. Schedin, A. K. Geim, S. V. Morozov et al., "Detection of individual gas molecules adsorbed on graphene," *Nature Materials*, vol. 6, no. 9, pp. 652–655, 2007.
- [10] J. P. Novak, E. S. Snow, E. J. Houser, D. Park, J. L. Stepnowski, and R. A. McGill, "Nerve agent detection using networks of single-walled carbon nanotubes," *Applied Physics Letters*, vol. 83, no. 19, pp. 4026–4028, 2003.
- [11] T. O. Wehling, K. S. Novoselov, S. V. Morozov et al., "Molecular doping of graphene," *Nano Letters*, vol. 8, no. 1, pp. 173– 177, 2008.
- [12] J. Dai, P. Giannozzi, and J. Yuan, "Adsorption of pairs of NO_x molecules on single-walled carbon nanotubes and formation of NO + NO₃ from NO₂," *Surface Science*, vol. 603, no. 21, pp. 3234–3238, 2009.
- [13] J. D. Fowler, M. J. Allen, V. C. Tung, Y. Yang, R. B. Kaner, and B. H. Weiller, "Practical chemical sensors from chemically derived graphene," ACS Nano, vol. 3, no. 2, pp. 301–306, 2009.
- [14] O. Leenaerts, B. Partoens, and F. M. Peeters, "Adsorption of H₂O, NH₃, CO, NO₂, and NO on graphene: a first-principles study," *Physical Review B*, vol. 77, no. 12, Article ID 125416, 6 pages, 2008.
- [15] R. M. Ribeiro, N. M. R. Peres, J. Continho, and P. R. Briddon, "Inducing energy gaps in monolayer and bilayer graphene: local density approximation calculations," *Physical Review B*, vol. 78, no. 7, Article ID 075442, 7 pages, 1990.
- [16] Y. H. Zhang, Y. B. Chen, K. G. Zhou et al., "Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study," *Nanotechnology*, vol. 20, no. 18, Article ID 185504, 2009.
- [17] K. Imani, M. R. Abolhassani, and A. A. Sabouri-Dodaran, "Electronic transport calculation of adsorbate NO₂ and NO molecules on graphene using maximally localized wannier functions," *The European Physical Journal B*, vol. 74, no. 1, pp. 135–138, 2010.
- [18] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, "Edge state in graphene ribbons: nanometer size effect and edge shape dependence," *Physical Review B*, vol. 54, no. 24, pp. 17954–17961, 1996.
- [19] V. Barone, O. Hod, and G. E. Scuseria, "Electronic structure and stability of semiconducting graphene nanoribbons," *Nano Letters*, vol. 6, no. 12, pp. 2748–2754, 2006.
- [20] M. Y. Han, B. Özyilmaz, Y. Zhang, and P. Kim, "Energy bandgap engineering of graphene nanoribbons," *Physical Review Letters*, vol. 98, no. 20, Article ID 206805, 4 pages, 2007.
- [21] L. Tapasztó, G. Dobrik, P. Lambin, and L. P. Biró, "Tailoring the atomic structure of graphene nanoribbons by scanning tunnelling microscope lithography," *Nature Nanotechnology*, vol. 3, no. 7, pp. 397–401, 2008.
- [22] B. Huang, Z. Li, Z. Liu et al., "Adsorption of gas molecules on graphene nanoribbons and its implication for nanoscale molecule sensor," *Journal of Physical Chemistry C*, vol. 112, no. 35, pp. 13442–13446, 2008.

- [23] H. E. Romero, P. Joshi, A. K. Gupta et al., "Adsorption of ammonia on graphene," *Nanotechnology*, vol. 20, no. 24, Article ID 245501, 2009.
- [24] A. Saffarzadeh, "Modeling of gas adsorption on graphene nanoribbons," *Journal of Applied Physics*, vol. 107, no. 11, Article ID 114309, 7 pages, 2010.
- [25] P. Giannozzi, S. Baroni, N. Bonini et al., "Quantum espresso: a modular and open-source software project for quantum simulations of materials," *Journal of Physics*, vol. 21, no. 39, Article ID 395502, 2009.
- [26] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," *Physical Review B*, vol. 41, no. 11, pp. 7892–7895, 1990, The Pseudopotential generation.







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