Effect of doping with Al/B on the sensitivity of a metallic carbon nanotube to CO₂

Aura Merlano¹*, Andrés M. Garay-Tapia², F. R. Pérez¹ and Ángel Salazar¹

¹Grupo de Óptica y Espectroscopía (GOE), Centro de Ciencia Básica, Universidad Pontificia Bolivariana, A.A. 56006 Medellín, Colombia.
²Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Unidad Mty, Alianza Norte 202, Autopista Monterrey-Aeropuerto Km 10, Apodaca, N.L., México.

*Corresponding author: aura.merlano@upb.edu.co

Abstract. In this work the effect of doping with aluminum (Al) and boron (B) an armchair (6,6) carbon nanotube on its sensitivity to carbon dioxide (CO₂) for possible application in sensors of this gas was studied. Using first-principles calculations within the framework of the density functional theory (DFT), adsorption energies were obtained in the cases when the molecule is initially perpendicular to the surface of the nanotube, near the dopant atom, and located above a carbon atom of the nanotube, above a C-C bond, or directly above the center of a hexagon. It was found that doping with Al does not improve the adsorption of the molecule compared to the pristine nanotube. However, doping with B slightly favors the adsorption for some of the considered positions. The results suggest that B doping might be an acceptable option in the design and construction of nano devices for CO₂ detection.

1. Introduction

Liberation of carbon dioxide (CO₂) into the atmosphere due to the consumption of large amounts of fossil fuels as coal, petroleum and natural gas has become one of the most serious global environment problems, which is focusing attention of the scientific community[1-5]. Global warming concerns have triggered global efforts to reduce the concentration of atmospheric CO₂. Detection, capture and storage of CO₂ gas is considered a crucial strategy for reduction of anthropogenic emission [6].

The adsorption of CO₂ is very important in environmental and industrial applications. In earlier adsorption processes, the choice of an adsorbent was restricted to various types of activated carbons, silica and alumina. Nevertheless, emergence of novel materials has generated new theoretical approaches to adsorption phenomena. The main types of adsorbents of practical environmental importance are presented in Table 1 [7]. Particularly, there is growing interest for metal free carbon-based nanomaterials for gas adsorption. Carbon-based nanomaterials such as fullerene, carbon nanotubes and graphene offer superior thermal and chemical stability as CO₂ adsorbents [8].

Carbon nanotubes (CNTs) have excellent adsorption, catalytic and thermal properties and may be good candidates as CO₂ sensing due to their high conductivity, unique tubular structure, extraordinary chemical stability, and mechanical properties. Furthermore, they also have some advantages such as low power consumption, operation at room temperature, and size and weight reduction [9-14].

Though the adsorption capacity of CNTs remains limited, previous studies have demonstrated that the doping can tailor its electronic and structural properties to increasing its reactivity, enhance the range of molecular species to be detected and further improve the sensing performance [15],[16]. Consequently, the adsorption capability of CNTs can be improved through introducing heteroatom impurities (such as boron, aluminum, nitrogen, silicon, zinc, and titanium) and forming active sites in the nanotube walls [17]. Several researchers have theoretically studied platinum, aluminum,
titanium and gold doped CNTs for detecting gas molecules such as CO, NO, NH₃, N₂, H₂ and C₂H₂ [18-19]. S. Ishii and Y. Takano [20] have reported that doping with alkali metals enhances the conductivity of graphite, resulting in superconductivity. Besides, diamond is superconductor by boron (B) doping. The CNT structure is intermediate between that of 2-dimensional graphite and 3-dimensional diamond. Considering these properties, researchers speculated that elemental B in CNTs would enhance their conductivity.

Now well, materials which simultaneously possess the unique properties of CNTs and high adsorption capability of aluminum (Al), or the unique properties of CNTs and excellent conductivity of B [21] could be useful for the CO₂ sensor technology with superior performance for gas detection.

In the present work, DFT calculations were conducted to investigate the effect of Al and B atoms doping on adsorption of CO₂ onto the surface of an armchair (6,6) CNT. Al possesses the same ns²np¹ valence electric structure of B atom. We explore some possible energetically favorable sites of the nanotube for the adsorption of a CO₂ molecule perpendicular to the CNT surface.

The rest of the article is organized as follows. In Section 2 the details of the computational method based on DFT is presented. Section 3 shows the results related to adsorption energy and optimal positions of CO₂ on the surface of CNTs. Finally, in section 4, conclusions have been drawn on this research.

| Table No. 1 Basic types of adsorbents used for environmental purposes [7]. |
|---------------------------------------------------------------|
| Carbon adsorbents | Mineral adsorbents | Other adsorbents |
|-------------------|-------------------|------------------|
| Active carbons    | Silica gel        | Synthetic polymers |
| Activated carbon fibers | Activated alumina | Metalorganic microporous and mesoporous materials |
| Carbon Molecular sieves | Oxides of metals | Composite adsorbents |
| Carbonaceous nanomaterials | Zeolites        | Mixed adsorbents  |

2. Computational Methods

The study is performed within DFT by using the Vienna ab initio simulation package (VASP) [22] under generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange and correlation. A plane wave basis set with kinetic energy cutoff of 600 eV is used and the Brillouin zone is sampled by adopting (1x1x10) k-points Monkhorst-Pack grid for all structures. Furthermore, a supercell geometry with periodic boundary conditions is used and a sufficiently large vacuum space is inserted between the neighbor nanotubes to avoid their interaction (15.07 Å).

Adsorption properties of CO₂ onto pristine armchair (6,6) CNT and Al and B doped nanotube are investigated. The diameter of the pristine nanotube is 8.19 Å and the length is 9.81 Å, corresponding to four unit cells. To generate an Al-doped CNT, a carbon atom is removed from the perfect hexagonal structure of the CNT and replaced by an Al atom (Fig. 1a). Similarly, we proceeded with the B-doped CNT (Fig. 1b).
Different positions of the CO\textsubscript{2} molecule were considered. For pristine nanotube, three positions on the surface of the nanotube were considered: the molecule above of a carbon atom (Fig. 2a), above the center of the hexagonal ring (Fig. 2b), and above on the central point of a carbon-carbon bond (Fig. 2c). In each one of these positions, the CO\textsubscript{2} molecule was oriented perpendicular to the axis of CNT.

We also considered different sites for the molecule on the Al-doped carbon nanotube: first, directly above the Al atom (Fig. 3a), second, above the center of a carbon atom ring including the aluminum atom (Fig. 3b), and third, above the central point of a carbon-carbon bond (Fig. 3c). The CO\textsubscript{2} molecule was also oriented perpendicular to the Al-doped CNT surface.

Finally, for a B-doped CNT, positions of the gas molecule analogous to those studied in the Al-doped CNT were considered. First, the molecule directly above the B atom (Fig. 4a),
second, the molecule above the center of a carbon atom ring including the boron atom (Fig. 4b), and third, above the central point of a carbon-carbon bond (Fig. 4c). The CO₂ molecule was also oriented perpendicular to the B-doped CNT surface.

![Fig. 4 Positions of the CO₂ molecule on B doped (6,6) CNT.](image)

The adsorption energy $E_{ads}$ of CO₂ onto nanotubes is defined according to Eq. (1), where $E_{tot}(CNT + CO₂)$ denotes the total energy of the nanotube-molecule system, and $E_{tot}(CNT)$ and $E_{tot}(CO₂)$ are the total energies of the isolated nanotube and gas molecule, respectively.

$$E_{ads} = E_{tot}(CNT + CO₂) - E_{tot}(CNT) - E_{tot}(CO₂)$$  \hspace{1cm} (1)

3. Results and Discussion

Individual structural relaxations of pristine, Al- and B-doped CNTs and CO₂ molecule were performed. The optimized structures were obtained by relaxing each structure until the maximum force on any atom was not greater than 0.02 eV/Å. From these optimized structures, the nanotube-molecule systems for the different positions mentioned previously were constructed and new relaxations were performed for each one of the systems. Using Eq. (1), adsorption energies were calculated from the total energy of the respective system, and the isolated nanotube and gas molecule.

3.1. Adsorption of CO₂ on pristine (6,6) CNT

The calculated adsorption energies and final distances between molecule and pristine nanotube are shown in Table 2. In all cases, the adsorption energy is positive. The pristine nanotube and CO₂ above the center of the hexagonal ring and located perpendicular to the axial direction of the nanotube (Fig. 2b) corresponds to the configuration with minimum energy after relaxation (Figs. 5a and 5b). These results are in agreement with previous works where the adsorption of CO₂ on pristine CNTs for other positions was calculated too [9],[23-24].

![Table No. 2 Results of adsorption energy for pristine CNT (6,6) with different positions of the CO₂ molecule.](image)
3.2 Adsorption of CO$_2$ on Al-doped (6,6) CNT

Table 3 shows the results obtained for the Al-doped CNT and the different positions of the CO$_2$ molecule as presented above. The energetically most stable geometry occurs when the CO$_2$ molecule is initially on a C-C bond and located perpendicular to the axial direction of the nanotube (Fig. 6). However, all adsorption energies are higher compared to pristine nanotube. In this way, the interaction between the Al-doped CNT and CO$_2$ molecule is weak and doping with Al does not improve the adsorption of the CO$_2$ molecule.

Previous investigations have reported high adsorption capability of aluminium doped CNT. Wang et al [15] reported that Al-doped SWCNT presents high sensitivity to CO compared to pure SWCNT. Ganji et al [25] found that Pt adsorption ability of Al-CNTs is stronger than that of B and N doped CNTs. However, to the best of our knowledge, there is no report for adsorption of CO$_2$ on the surface of Al-doped (6,6) CNT. Then, it is a preliminary result showing a poor sensing ability of Al-doped (6,6) CNT to carbon dioxide and this motivates us to explore new powerful adsorbent for CO$_2$ molecule.

### Table No. 3 Results of adsorption energy for Al-doped CNT (6,6) with different positions of the CO$_2$ molecule.

| Site             | Orientation with respect to the CNT axis | $E_{\text{ads}}$ (eV) | d (Å)  | Figure |
|------------------|------------------------------------------|------------------------|--------|--------|
| Aluminum atom    | Perpendicular                            | 1.23                   | 1.78   | 3a     |
| hexagonal ring   | Perpendicular                            | 1.51                   | 2.28   | 3b     |
| C-C bond         | Perpendicular                            | 1.32                   | 2.49   | 3c     |
Fig. 6  Al-doped (6,6) CNT and CO₂ above on the central point of a Al-C bond and located perpendicular to the axial direction of the nanotube. (a) Front and (b) side views of optimized structure.

3.3 Adsorption of CO₂ on B-doped (6,6) CNT

Results for the B-doped (6,6) CNT are shown in Table 4. The energetically most favorable situation occurs when CO₂ is above the center of the hexagonal ring (Fig. 7). The B doping slightly favors adsorption of CO₂ compared to pristine and Al doped CNTs. It suggests that B doping may be an acceptable option to improve the CO₂ adsorption in nano devices for gas detection. However, more studies have to be done providing a work direction to experimental scientists developing CNT-based chemical sensors.

Table No. 4 Results of adsorption energy for pristine B doped CNT (6,6) with different positions of the CO₂ molecule.

| Site                  | Orientation with respect to the CNT axis | $E_{\text{ads}}$ (eV) | d (Å) | Figure |
|-----------------------|-----------------------------------------|------------------------|-------|--------|
| boron atom            | Perpendicular                           | 1.07                   | 2.10  | 4a     |
| hexagonal ring        | Perpendicular                           | 1.04                   | 2.55  | 4b     |
| C-C bond              | Perpendicular                           | 1.05                   | 2.42  | 4c     |

Fig. 7  B-doped (6,6) CNT and CO₂ above the center of the hexagonal ring and located perpendicular to the axial direction of the nanotube. (a) Front and (b) side views of optimized structure.

4. Conclusions

A first-principles DFT study on the adsorption of CO₂ gas molecule on pristine, Al and B-doped (6,6) armchair CNTs was performed. Results for pristine (6,6) CNT are consistent with those of other theoretical studies and suggest that adsorption capability for gaseous molecules is limited. Results also show that CO₂ adsorption ability of B-doped CNT is higher than that of an Al-doped CNT. Even so, adsorption is not considerably improved. However, B-doped CNT appears as a good candidate for
detecting CO\textsubscript{2} molecules and more studies must be done. For future work and based on the obtained results, we could think of studying the influence of boron concentration in the adsorption properties of the nanotube to the CO\textsubscript{2}.

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References

[1] International Energy Agency, “CO\textsubscript{2} Emissions From Fuel Combustion Highlights,” 2013.
[2] U. S. EPA, “US Environmental Protection Agency.”
[3] U. S. Epa, “Inventory of U.S. Greenhouse Gas Emissions and Sinks,” 2015.
[4] P. N. Jiří Čejka, Naděžda říklová, Molecular Sieves: From Basic Research to Industrial Applications. Prague, Czech Republic, 2005.
[5] S. U. Pamela A. Matson (Chair), “Advancing the Science of Climate Change,” in NAS - America’s Climate Choices, 2010, p. 2.
[6] D. Y. C. Leung, G. Caramanna, and M. M. Maroto-Valer, “An overview of current status of carbon dioxide capture and storage technologies,” Renew. Sustain. Energy Rev., vol. 39, pp. 426–443, 2014.
[7] I. Dekany, Adsorption and Nanostructures. Springer-Verlag Berlin Heidelberg, 2002.
[8] S. W. de Silva, A. Du, W. Senadeera, and Y. Gu, “Neutral and charged boron-doped fullerenes for CO\textsubscript{2} adsorption,” Beilstein J. Nanotechnol., vol. 5, no. 1, pp. 413–418, Apr. 2014.
[9] A. Srirangarajan and M. U. Kahaly, “Ab Initio Study of Topological Defects in Single Walled Carbon Nanotubes and their Effect on Gas Sensing Mechanism,” Enabling Sci. Nanotechnol., vol. 1341, pp. 379–383, 2011.
[10] E. C. Jesús, J. Li, and C. R. Cabrera, “Latest Advances in Modified / Functionalized Carbon Nanotube-Based Gas Sensors,” 2013, p. 2.
[11] P. Bondavalli, P. Legagneux, and D. Pribat, “Carbon nanotubes based transistors as gas sensors: State of the art and critical review,” Sensors Actuators, B Chem., vol. 140, pp. 304–318, 2009.
[12] N. Peng and Q. Zhang, “Sensing mechanisms of carbon nanotube based NH\textsubscript{3} gas detectors,” pp. 1–15, 2002.
[13] E. Akbari et al., “Analytical calculation of sensing parameters on carbon nanotube based gas sensors,” Sensors (Basel), vol. 14, pp. 5502–15, 2014.
[14] Q. Wang and B. Arash, “A review on applications of carbon nanotubes and graphenes as nanoresonator sensors,” Comput. Mater. Sci., vol. 82, pp. 350–360, 2014.
[15] R. Wang, D. Zhang, W. Sun, Z. Han, and C. Liu, “A novel aluminum-doped carbon nanotubes sensor for carbon monoxide,” J. Mol. Struct. THEOCHEM, vol. 806, no. 1–3, pp. 93–97, 2007.
[16] P. Shao, X. Y. Kuang, L. P. Ding, J. Yang, and M. M. Zhong, “Can CO\textsubscript{2} molecule adsorb effectively on Al-doped boron nitride single walled nanotube?,” Appl. Surf. Sci., vol. 285, no. PARTB, pp. 350–356, 2013.
[17] P. A. Gowri Sankar and K. Udhayakumar, “Electronic properties of boron and silicon doped (10, 0) zigzag single-walled carbon nanotube upon gas molecular adsorption: A DFT comparative study,” J. Nanomater., vol. 2013, no. 2, 2013.
[18] C. S. Yeung, L. V. Liu, and Y. A. Wang, “Adsorption of Small Gas Molecules onto Pt-Doped Single-Walled Carbon Nanotubes,” J. Phys. Chem. C, vol. 112, no. 19, pp. 7401–7411, 2008.
[19] D. R. Kauffman, D. C. Sorescu, D. P. Schofield, B. L. Allen, K. D. Jordan, and A. Star, “Understanding the sensor response of metal-decorated carbon nanotubes,” *Nano Lett.*, vol. 10, no. 3, pp. 958–963, 2010.

[20] S. Ishii and Y. Takano, “High-conductivity boron-doped carbon nanotubes,” *SPIE Newsroom*, p. 2, 2007.

[21] D. Kang, X. Yu, M. Ge, F. Xiao, and H. Xu, “Novel Al-doped carbon nanotubes with adsorption and coagulation promotion for organic pollutant removal,” *J. Environ. Sci.*, pp. 1–12, 2016.

[22] “The VASP site.” [Online]. Available: http://www.vasp.at/. [Accessed: 05-Oct-2016].

[23] J. T. W. Yeow and Y. Wang, “A review of carbon nanotubes-based gas sensors,” *J. Sensors*, vol. 2009, 2009.

[24] A. a. EL-Barbary, G. H. Ismail, and A. M. Babeer, “Effect of Monovacancy Defects on Adsorbing of CO, CO$_2$, NO and NO$_2$ on Carbon Nanotubes: First Principle Calculations,” *J. Surf. Eng. Mater. Adv. Technol.*, vol. 3, no. 2, pp. 287–294, 2013.

[25] M. D. Ganji, M. G. Ahangari, and A. Khoosravi, “Doping of carbon nanotubes with aluminum atom to improve Pt adsorption,” *Appl. Surf. Sci.*, vol. 290, pp. 86–91, 2014.