Disciplinarum Scientia. Série: Naturais e Tecnológicas, Santa Maria, v. 21, n. 3, p. 89-98, 2020.
Recebido em: 28.10.2020. Aprovado em: 18.12.2020.

ISSN 2176-462X

DOI: 10.37779/nt.v21i3.3570

AB INITIO SIMULATION OF FUNCTIONALIZED β_{12} BOROPHENE

SIMULAÇÃO AB INITIO DE BOROFENO β_{12} FUNCIONALIZADO

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ABSTRACT

In this work we evaluated the structural and electronic properties of C-doped and COOH-functionalized β_{12} borophene through ab initio simulations using the density functional theory (DFT). β_{12} borophene is a stable 2D nanomaterial and composed only by B atoms, with promising applications specially for the electronic industry. The substitutional C-doped β_{12} borophene is chemically favorable with a strong hybridization of carbon-boron energy levels. The COOH-functionalization on β_{12} borophene presents high energy adsorption (around 3.2 eV). The studied functionalizations show metallic electronic properties in the resulting systems, as well as observed for pristine β_{12} borophene.

Keywords: nanomaterials, doping, electronic properties.

RESUMO

Neste trabalho foram avaliadas as propriedades estruturais e eletrônicas do borofeno β_{12} dopado com carbono (C) e com carboxila (COOH) via simulações ab initio fazendo uso da teoria do funcional da densidade (DFT). O borofeno β_{12} é um nanomaterial 2D estável e composto apenas por átomos de boro (B), o qual possui aplicações promissoras, em especial, para a indústria eletrônica. O borofeno β_{12} dopado com C substitucional é quimicamente favorável com uma forte hibridização dos níveis de energia entre os átomos de carbono e boro. A funcionalização com COOH do borofeno β_{12} apresenta também alta energia de adsorção (em torno de 3,2 eV), representando estabilidade química. As funcionalizações analisadas mostram que os sistemas resultantes possuem propriedades eletrônicas metálicas, como observado para o borofeno β_{12} puro.

Palavras-chave: *nanomateriais, dopagem, propriedades eletrônicas.*

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INTRODUCTION

Nanoscience and nanotechnology are based on the ability of materials to exhibit different behaviors and properties when on a nanoscale. These changes depend on the material and the manipulation that will be performed. (PACILÉ *et al.*, 2008; SHEARER *et al.*, 2012; XIAO *et al.*, 2012).

The potential of two-dimensional (2D) materials such as graphene and its derivatives is already recognized in the literature due to their electronic and mechanical properties being dependent on the chemical and structural arrangement of atoms. Such properties make these nanostructured materials promising for application in several fields of science and technology (NOVOSELOV *et al.*, 2004; TERRONES *et al.*, 2010). The graphene like materials open the prospect of studying several other 2D materials such as silicene, phosphorene and borophene (TERRONES *et al.*, 2010; WANG *et al.*, 2019).

Boron has different allotropes and in addition exhibit a semiconductor behavior, it was discovered by Sir Humphry and coworkers in 1808 (RUBAB *et al.*, 2020). One of its main features is the binding ability with other boron atoms resulting in complex clusters (RUBAB *et al.*, 2020; ENTWISTLE, MARDER, 2002).

Another important point that has been observed are the inorganic compounds based on boron, which is fundamental for the development of nanodevices (WANG *et al.*, 2019; RUBAB *et al.*, 2020). Borophene, nanomaterial that is derived from boron, presents a two-dimensional (2D) structure with a thickness of one atom (FENG, *et al.*, 2016). It is a promising candidate to complement graphene variations, due to its metallic behavior and this characteristic helps in the development of electronic nanodevices, sensing, storage, among others (SILVESTRE, 2018; MORTAZAVI *et al.*, 2016). In addition, it has potential applications due to its high surface area for interaction of chemical agents such as functional groups, gases or molecules of biological interest (WANG *et al.*, 2019, MANNIX *et al.*, 2018). This nanomaterial presents bond varieties that can form multicentric interaction, which allows structural variation and covalent bonds (LI *et al.*, 2019; RUBAB *et al.*, 2020).

Borophene was first synthesized in 2015 by Andrew J. Mannix *et al.* (2015), on silver substrate (111) under ultra high vacuum. Over the past few years, three types of boron monolayer, borophene δ_6, β_{12} and χ_3, have been synthesized (LIU *et al.*, 2020; Li *et al.*, 2019). Noble materials such as silver and gold have been used as growth substrates (FENG *et al.*, 2016; KIRALY *et al.*, 2019).

Observing the structural stability and the electronic properties, the most stable borophene present the β_{12} arrangement (ZHANG *et al.*, 2015). It is a material with great sensitivity to gas, and has been applied in studies for small molecules and chemical groups adsorption such as CO, NO, CO_2, NH_3, among others (HUANG *et al.*, 2018; TAN; TAHINI; SMITH, 2017; LIU *et al.*, 2020).

Thus, this work evaluates the functionalization of β_{12} borophene with one substitutional carbon atom (C) and with one adsorbed carboxyl chemical group (COOH). The study was based on ab initio computational simulation using the SIESTA code to evaluate the electronic and structural properties of the isolated and functionalized β_{12} borophene. The aim of this work is to understand the nature of single borophene functionalization for future studies for atomic and molecular adsorption.

METHODOLOGY

For the C-doping and COOH-functionalization on β_{12} borophene were performed first-principles calculations based on Density Functional Theory (HOHENBERG; KOHN, 1964) implemented on SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms) (SOLER, *et al.*, 2002). The exchange and correlation potential were described using the Generalized Gradient Approximation (GGA) term (PERDEW; BURKE; ERNZERHOF, 1996). A double zeta basis set including polarization orbitals (DZP) was used, with an energy shift of 0.05 eV and energy cutoff of 200 Ry.

All calculations were done in order to converge when the residual forces on each atom was smaller than 0.05 eV/Å. We first performed a few tests to achieve the appropriate unit cell size (5 atoms) and after we assumed a 3x3 supercell on *x* and *z* directions for all the systems.

The calculations to describe the substitutional C-doped systems were performed using three different configurations on the supercell. The formation energy ($E_{form}(C)$) for these systems were calculated according to Equation 1:

$$E_{form}(C) = -\{E(\text{borophene+carbon}) - [E(\text{borophene}) - E(\text{boron}) + E(\text{carbon})]\} \quad (1)$$

where E(borophene+carbon) refers to the substitutional C-doped β_{12} borophene structure's energy, E(borophene) corresponds to the energy of pristine β_{12} borophene structure, E(boron) is the energy of a single boron atom and E(carbon) represents the energy of a single carbon atom.

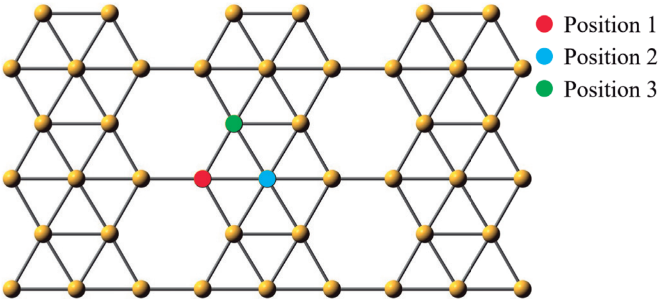
The carboxyl group functionalization also has been performed in three different configurations, assuming the same arrangements as the C-doping systems. The adsorption energy ($E_{ad}(COOH)$) for these systems was calculated according to Equation 2:

$$E_{ad}(COOH) = -\{E(\text{borophene+COOH}) - [E(\text{borophene}) + E(\text{COOH})]\} \quad (2)$$

where E(borophene+COOH) refers to the COOH functionalized β_{12} borophene structure's energy, E(borophene) corresponds to the energy of pristine β_{12} borophene structure and E(COOH) is the energy of a single COOH chemical group. Positive values for the $E_{form}(C)$ and $E_{ad}(COOH)$ indicate that the interaction is favorable.

Figure 1 represents the β_{12} borophene structure's top view with its doping/functionalization sites.

Figure 1 - β_{12} borophene structure with its doping/functionalization sites (1 to 3).



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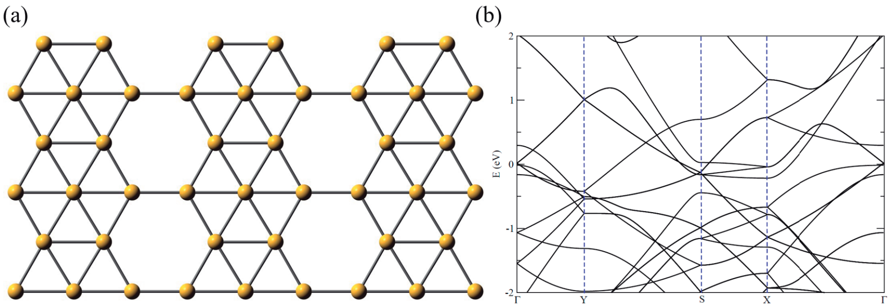
RESULTS

Initially we simulate the β_{12} borophene supercell in the pristine form. The Figure 2 represents the structural arrangements in (a) and the corresponding electronic band structures in (b). The structural configuration shows a flat surface composed by B atoms presenting binding distances from 1.65 to 1.79 Å.

Figure 2 - (a) Structural configuration and (b) electronic band structures for the pristine β_{12} borophene. The Fermi energy corresponds to 0 eV.



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We can observe that the β_{12} borophene structure has a metallic characteristic that agrees with previous studies available in the literature (PENG *et al.*, 2017). This characteristic is relevant for electronic applications associated with the control of charge injection on the nanometric systems.

In the next step, we evaluate the impact of the C- and COOH-functionalization on the β_{12} borophene using three different positions on the surface that represent all possible configurations for adsorption sites due to the symmetry of the nanostructure.

i) C-Doping in the β_{12} borophene structure

The B atoms of positions 1, 2, and 3 of the β_{12} borophene structure were substituted, separately, by a C atom in order to evaluate the structural and electronic properties of the resulting nanomaterial. The Table 1 shows the configurations and their respective values of formation energies.

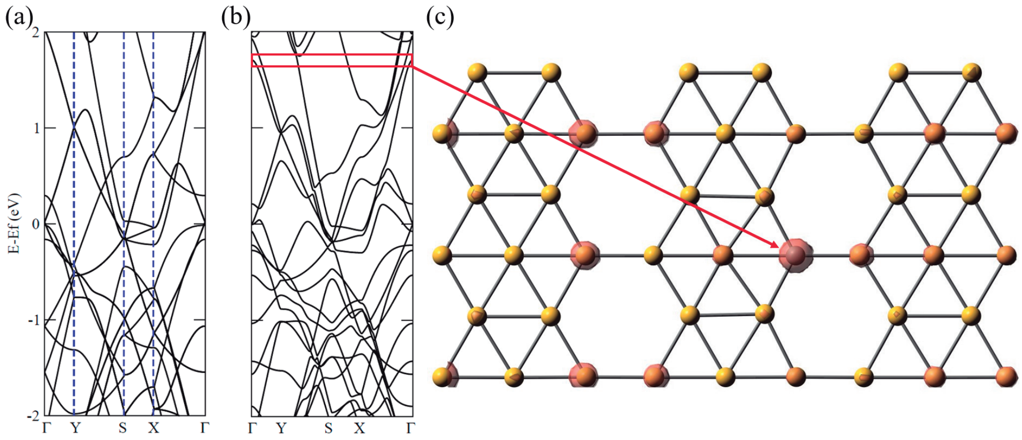
Table 1 - Formation energy ($E_{form}(C)$) of C-doped borophene nanostructures.

Configuration	$E_{form}(C)$ (eV)
1	3.68
2	1.16
3	3.09

Source: Made by the authors.

From the evaluated C-doped systems, configuration 1 was shown to be more stable, with a formation energy of 3.68 eV and a 1.57 Å to 1.75 Å binding distance between C and B neighborhood atoms. Figure 3 shows the electronic band structure for pristine and C-doped β_{12} borophene where the Fermi energy corresponds to 0 eV. Also, is highlighted the electronic Local Density of States (LDOS) plot of the C-doped β_{12} borophene system for the selected energy range. This energy range has been chosen due to the presence of new energy states when compared to pristine β_{12} borophene.

Figure 3 - Electronic band structures for the (a) pristine and (b) C-doped β_{12} borophene, and (c) the LDOS for the selected energy range (the C atom is highlighted by the arrow). The Fermi energy corresponds to 0 eV. The contour plot for the LDOS is 0.000422 $e^{-}/Å^{3}$.



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Analyzing the Figure 3, we noticed that the electronic properties of the more stable system remain metallic after the C-doping, as observed in the pristine β_{12} borophene nanostructure. We also performed the LDOS plot for the C-doped system. We verified, in the selected energy range, which presents a new dispersed electronic level, that there is a contribution from the C atom, indicating a high C-B hybridization. In addition, the results show no spin polarization of the pristine or C-doped systems.

ii) COOH-functionalization of β_{12} borophene

The B atoms of positions 1, 2, and 3 of the β_{12} borophene structure were functionalized, separately, by a -COOH chemical group in order to evaluate the structural and electronic properties of the resulting nanomaterial. Table 2 presents the studied configurations, their respective bonding distances and adsorption energy values.

For COOH-functionalized systems, configuration 1 was the one with the highest adsorption energy with a value of 3.18 eV and a binding distance of 1.62 Å among the B atom of position 1 and the C atom from -COOH group. It is important to mention that these three configurations represent all the possibilities of functionalization due to the symmetry properties of the borophene nanomaterial.

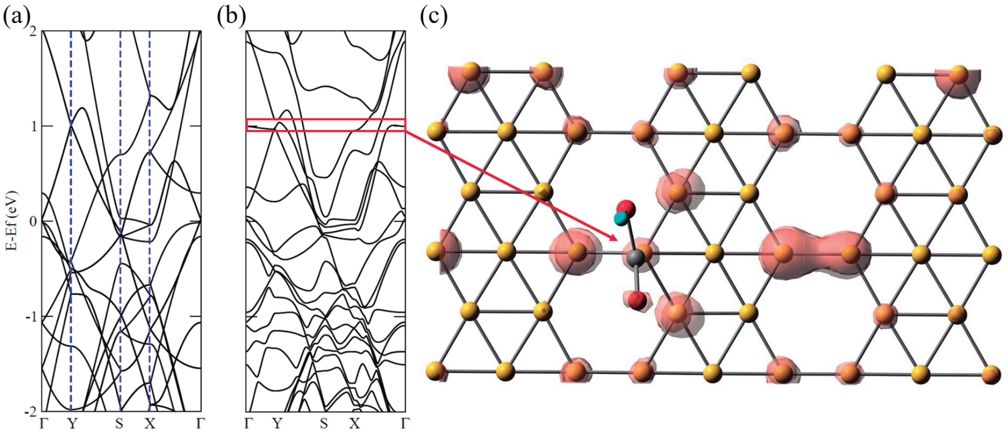
Tabela 2 - Binding distance and adsorption energy for the COOH-functionalized β_{12} borophene.

Configuration	Binding distance (Å)	Adsorption energy (eV)
1	1.62	3.18
2	1.62	2.31
3	1.60	3.16

Source: Made by the authors.

Figure 4 shows the electronic band structures for the pristine and COOH-functionalized β_{12} borophene, where the Fermi level is located at 0 eV. The LDOS of the β_{12} COOH-functionalized borophene system is also presented in the energy range highlighted.

Figure 4 - Electronic band structures for the (a) pristine and (b) COOH-functionalized β_{12} borophene. On the right is shown the (c) LDOS for the COOH-functionalized β_{12} borophene. The Fermi energy corresponds to 0 eV. The contour plot for the LDOS is 0.001048 $e^-/Å^3$.



Source: Made by the authors.

Analyzing Figure 4, it is observed that the electronic band structure for the more stable COOH-functionalized borophene system presents the same metallic behavior present in the pristine system. Likewise, spin polarization is not observed in pristine or functionalized systems. This behavior is similar to that observed with C-doping in the borophene structure.

We also performed the LDOS analysis, which shows us that for the selected energy range, where we can observe a new state dispersed in the band structure, there is a contribution from the -COOH group, leading to the conclusion that we can find a chemical interaction among -COOH's

C atom and β_{12} borophene's B atom from position 1. Another interesting fact is that the respective electronic charge transfer is not considerable, presenting a value of 0.004 e^- from the carboxyl to the β_{12} borophene.

In general, we observed that the functionalization of borophene by C-doping or by the insertion of the -COOH group does not alter the metallic electronic properties compared to the pristine system. On the other hand, there is a strong incorporation of these functionalization's on the structural arrangements with formation energies favorable to chemical interaction and with high hybridization of the orbitals and, consequently, of the electronic levels. Similar study of Tonel *et al.* (2013) for graphene functionalized with one -COOH presents a small energy adsorption (around 1.10 eV, also representing an attractive interaction), these results can be understood in terms of the high chemical stability of the graphene structure when compared to borophene's.

FINAL REMARKS

This work was based on the study of the structure of C-doped and COOH-functionalized β_{12} borophene via ab initio simulations using the Density Functional Theory implemented on the SIESTA code.

The formation energy of the C-doped β_{12} borophene systems show that the more stable configuration presents a value of 3.68 eV, demonstrating that this doping is highly favorable. In this same system, is observed a strong hybridization of carbon-boron energy levels, demonstrating the stability and incorporation of this atom in the system and remaining with metallic electronic properties.

In the case of functionalization via COOH on the β_{12} borophene, the most stable configuration presents a bonding distance of 1.62 Å and a binding energy of 3.18 eV, which can be considered a favorable configuration for the functionalization process of carboxylic groups. This system also has metallic electronic properties, as well as the others evaluated.

Therefore, the simulations demonstrate the chemical stability of functionalized borophene, highlighting the potential of the borophene properties for technological applications such as gas adsoption/detection (SHUKLA *et al.*, 2017) and the possibility of anchoring atoms or molecules in these studied interaction sites.

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