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AN AB INITIO STUDY OF CARBOXYLATED GRAPHENE AND BLACK - AND BLUE - PHOSPHORENE[1]

ESTUDO DE PRIMEIROS PRINCÍPIOS DA CARBOXILAÇÃO DE GRAFENO, FOSFORENO NEGRO E FOSFORENO AZUL

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ABSTRACT

This work presents a first-principles study, based on Density Functional Theory calculations, on the structural, electronic and magnetic properties of black and blue phosphorene as well as of graphene functionalized with carboxylic group. The binding distance between phosphorene and carboxyl group assumes a higher value than that on graphene because of phosphorus atomic radius. Carboxyl also pulls slightly closer the graphene and black phosphorene functionalized atom, while blue phosphorene atom is pushed away. Unlike graphene, black and blue phosphorene have not shown relevant spin polarization. These results could help to understand the nanomaterials properties for a new route for the development of biosensors and, regarding to the phosphorenes, interesting properties with many potential applications that can be developed in the sense of the nanobiotechnology field.

Keywords: density functional simulation, functionalization, nanoscience, two dimensional nanostructure.

RESUMO

Este trabalho apresenta cálculos de primeiros princípios baseados na teoria do funcional da densidade, visando a análise das propriedades estruturais, eletrônicas e magnéticas das estruturas de fosforeno negro e azul, bem como da estrutura de grafeno funcionalizados com grupo carboxílico. Com a realização desta pesquisa, foi possível perceber que a distância de ligação entre o fosforeno e o grupo carboxílico assumiu um valor mais elevado que no caso do grafeno devido ao raio atômico do átomo de fósforo ser maior que o do carbono. Os átomos que interagem com a funcionalização, pertencentes às estruturas de fosforeno negro e grafeno, foram ligeiramente atraídos pelo grupo carboxílico, enquanto no fosforeno azul, a carboxila exerceu um leve afastamento. Ao contrário do grafeno, ambos fosforeno azul e negro não demonstraram polarização de spin relevante. Estes resultados emergem a possibilidade de uma nova rota para o desenvolvimento de biosensores e, em virtude das interessantes propriedades que as estruturas de fosforeno apresentam, incluindo potenciais aplicações no campo da nanobiotecnologia.

Palavras-chave: *teoria do funcional da densidade, funcionalização, nanociências, nanomateriais bidimensionais.*

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INTRODUCTION

The two-dimensional (2D) materials display many intriguing physical properties, which are not found in bulk structure because the original electronic structure is substantially altered from its three-dimensional (3D) characteristics (LU et al., 2014). In 2D materials, the electrons are free in two directions and confined in one, and have large surface area, which a variety of possible applications (GAN; HU, 2011).

Lately, black and blue phosphorene - two of the phosphorus (P) allotropes - have been studied. This might be due to their promising spintronics application, as it is already known that both structures are showing edge magnetism in various settings (HASHMI; HONG, 2015; HU; HONG, 2015).

Furthermore, black phosphorene has shown anisotropic electrical (LI et al., 2014) and optical (QIAO et al., 2014) properties. These properties make phosphorene to be quoted as a potential candidate for the next-generation 2D material for many device applications (LIU et al., 2014; ZHANG et al., 2014).

In the same sense, graphene is a 2D nanomaterial, carbon (C) allotrope, which has attracted great interest from the scientific community in recent years due to its electronic and structural characteristics (CASTRO et al., 2009). Being a material one atom thick, it offers a wide range of applications such as in the electronics industry and medicine (ABERGEL et al., 2010; GEIM; NOVOSELOV, 2007; ROBINSON et al., 2008; SCHEDIN et al., 2008).

When atoms or molecules are adsorbed or attached on graphene, they cause changes in its unique properties, making them interesting for applications and new properties of materials (PARK; RUOFF, 2009). The changes caused by covalent functionalizations, such as the addition of chemical groups, -COOH for example, cause significant changes in the electronics and structural properties of graphene (COMPTON; NGUYEN, 2010; YANG et al., 2008).

From the structural point of view, unlike in graphene, the phosphorene layers are not perfectly flat; instead, they form a puckered surface due to the sp^3 hybridization (RODIN; CARVALHO; CASTRO NETO, 2014). In this regard, this work presents the electronic and structural properties of the carboxyl chemical group adsorbed in both, black and blue phosphorenes, and compared with a monolayer of carboxylated graphene.

METHODOLOGY

First-principles calculations based on Density Functional Theory (HOHENBERG; KOHN, 1964) with the Local Density Approximation (LDA) of Perdew-Zunger (1981) were performed using the SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms) (SOLER et al., 2002). A double zeta basis set including polarization orbitals was used, and an energy cutoff

of 150 Ry was applied. All calculations are chosen to converge when the residual force on each atom was smaller than 0.05 eV/ Å. In the periodic supercell approach, it was used a vacuum distance normal to the plane of 20 Å (*z* direction) to eliminate interaction between the images.

For calculations describing the interaction of one-carboxyl group with phosphorenes, a (3 × 3) supercell with a total of 32 P atoms and a (4 × 4) supercell with a total of 64 P atoms was used on black and blue phosphorene, respectively. The graphene structure had 144 carbon atoms

The adsorption energy is defined as equation (1)

$$E(ad)= E(phosphorene/gr+carboxyl)-(E(phosphorene/gr)+ E(carboxyl)), \quad (1)$$

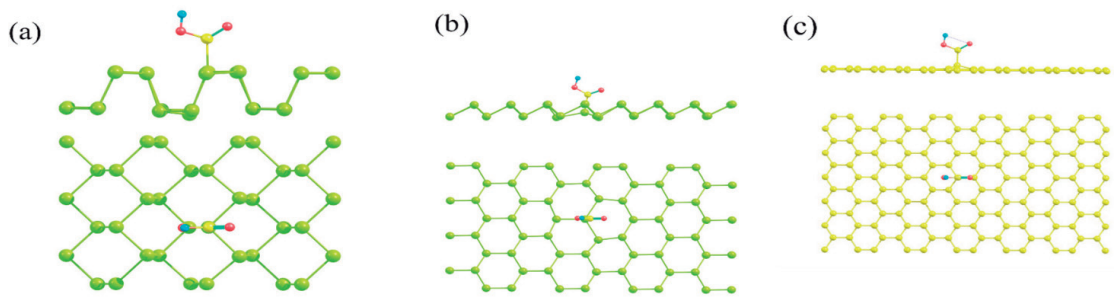
where $E_{(ad)}$ is the energy adsorption and the negative values indicate that the system is attractive. The *E(phosphorene/gr+carboxyl)* corresponds to the total energy of the 2D nanomaterial (phosphorene or graphene) interacting with the carboxyl group and *E((phosphorene/gr)/ E(carboxyl))* is the energy of the isolated 2D nanomaterial/carboxyl group.

RESULTS AND DISCUSSION

The interaction of a single carboxyl group with both phosphorene layers and graphene was investigated. Figure 1 shows the position where a single carboxyl group was set for black and blue phosphorenes and graphene.

Table 1 presents binding distance, adsorption energy and charge transfer values of phosphorene structures and graphene interaction with the carboxyl group. For the relaxed configuration, the binding distances between carboxyl molecule and black and blue phosphorene and graphene are, respectively, 1.93 Å, 1.86 Å and 1.58 Å.

Figure 1 - Side and top view of (a) black and (b) blue carboxylated phosphorenes and (c) carboxylated graphene.



Systems showed binding energy in order of 1.42 eV for black, 2.27 eV for blue phosphorene and 1.16 eV for graphene. Only graphene functionalized with carboxyl group introduced spin polarization, but in an insignificant value.

Table 1 - Adsorption of a carboxyl group on phosphorene and graphene monolayers.

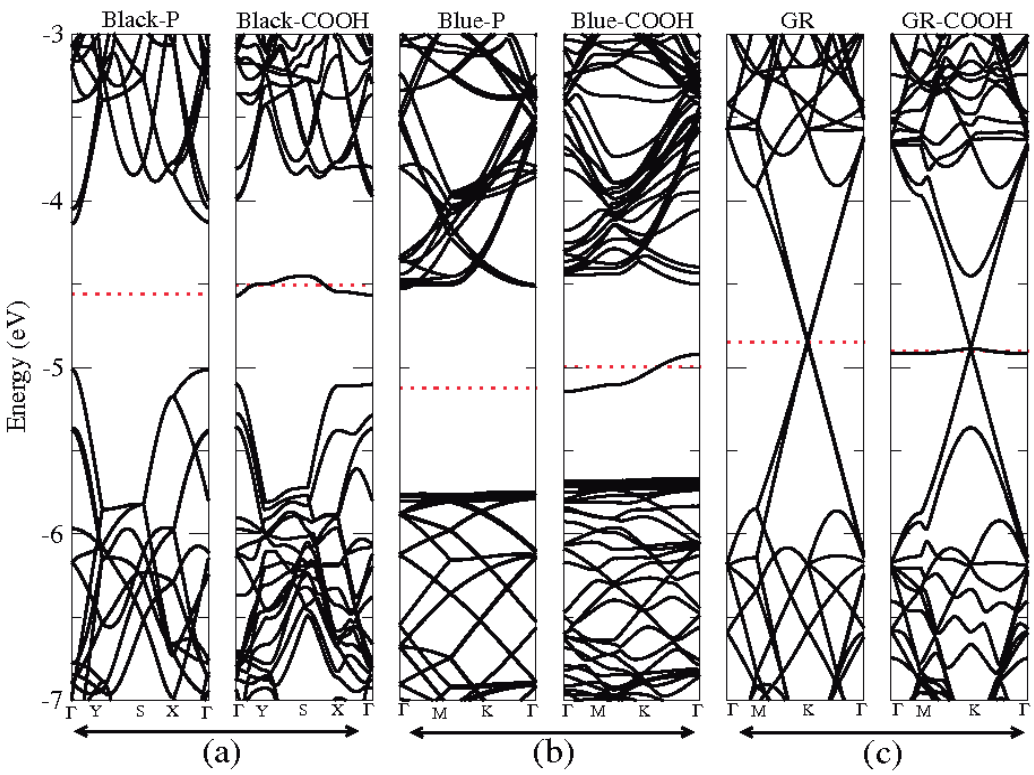
Structure	Binding distance (Å)	Adsorption Energy (eV)	Charge transfer (e^-)*	Spin polarization (μB)
Phosphorene Black-COOH	1.93	-1.42	-0.09	-
Phosphorene Blue-COOH	1.86	-2.27	-0.14	-
Graphene-COOH	1.58	-1.16	+0.11	0.01

*Negative values for charge transfer means that its direction is from the carboxyl group to the monolayer.

As it is possible to see in two phosphorene cases, the larger the binding distance, the smaller the magnitude of adsorption energy and charge transfer values. This may suggest that the adsorption between blue phosphorene and carboxyl molecule is stronger than in the black phosphorene one. In addition, it is interesting to observe that, even though the adsorption energy value for the black phosphorene is reasonably close to the graphene one, for the blue phosphorene, this value is nearly twice of the graphene's adsorption energy. This finding has never been reported before in literature.

The electronic band structures are presented in figure 2. This figure shows the electronic structure of black and blue phosphorenes and graphene, each one followed by its functionalized configuration. The horizontal red dotted line represents the Fermi energy.

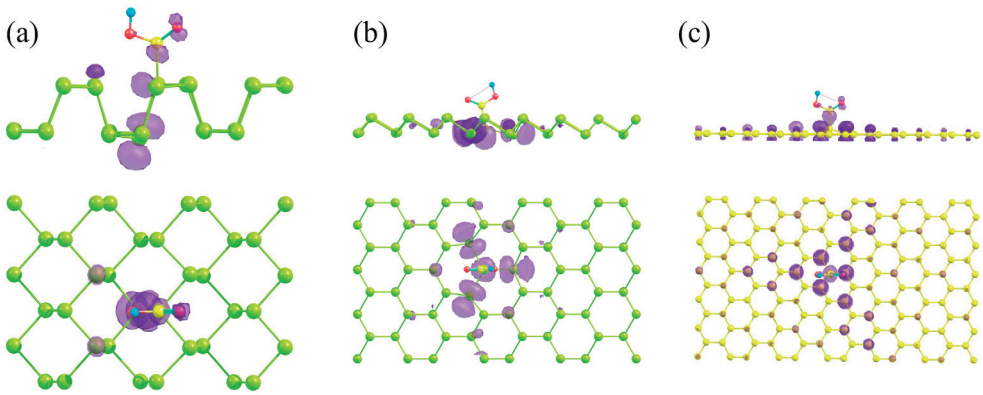
Figure 2 - Electronic band structures for (a) black and (b) blue phosphorenes and graphene (c) followed by their functionalized configuration. The horizontal dotted line corresponds to the Fermi level energy.



As expected, the black and blue phosphorene present semiconductor behavior in its pristine form. From figures 3(a) and (b), it is clear that functionalization causes a modification due to the chemical bond and the symmetry break of the resulting systems. For both, black and blue phosphorene, after functionalization, it is observed a half-filled level around the Fermi energy. This level is characteristic of the sp^3 hybridization through the carbon atom of the carboxyl group and the phosphorous, similar to the observed for the carbon nanotube carboxylation (LARA et al, 2014).

Regarding the structure of graphene bands (Figure 3(c)) functionalized with carboxyl groups, it is observed that, on the Fermi level, there is a characteristic level of the defect generated by sp^3 functionalization (LARA et al, 2014), similar to the behavior of the phosphorene material. In this case, the defect level is more localized than the phosphorenes' ones. This behavior reflects the graphene's lower value for the adsorption energy in comparison to the phosphorus nanostructures, which present more dispersed, and consequently more hybridized, defect levels. In addition, the size of the supercell influences the dispersion of the defective level.

Figure 3 - Electronic charge plot for side and top view of (a) black and (b) blue carboxylated phosphorene and (c) carboxylated graphene. The value of the isosurface plot was 0.00153 e^-/Bohr^3 for all the systems.



The charge plot (Figure 3) was performed around the Fermi level energy. For the black phosphorene (Figure 3(a)), the electronic charge is concentrated on functionalization site. For blue phosphorene (Figure 3(b)) and graphene (Figure 3 (c)), the electronic charge is concentrated in the carboxyl functionalization region, and more localized in the opposite sub lattice where it operates. The behavior observed on the charge plot for all systems confirm the covalent bond and the sp^3-like hybridization between the atoms of the nanomaterial and the C atom of the carboxylic group.

CONCLUSION

The functionalization with carboxyl group in blue and black phosphorene and graphene was evaluated through *ab initio* simulations in order to analyze the electronic and energetic properties. In all systems, the interaction distances between the phosphorus or carbon atom to the carboxyl group

show covalent bonds. The strongest interaction occurred between blue phosphorene and carboxyl, with binding energy about 2.2 eV. In terms of electronic properties, black and blue phosphorene are semiconductors, and adding the carboxyl functional creates a half-filled level near the Fermi energy. In the graphene functionalization, it is also observed a half-filled level, characteristic of the type-sp^3 defect, which is more localized than those presented by the phosphorenes' band structure with the same functionalization. The charge plot shows that the charge was localized at functionalization site for black phosphorene, but blue phosphorene and graphene show, beyond the same black phosphorene effect, a charge concentration at the opposite functionalization sub lattice.

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